UNIT – 1

POLYMER CHEMISTRY

Definition:

Polymer is a macromolecule built up by the combination of large number of smaller repeating units called monomers through covalent bonding.

Example: Polythene, PVC, Bakelite etc.

Polymerization:

The process of synthesis of polymers from monomers having more than two reactive sites is known as polymerization.

Degree of polymerization:

The number of repeating units in a polymer is known as degree of polymerization.

$$\text{Degree of polymerization} = \frac{\textit{Total molecular weight of polymer}}{\textit{molecular weight of monomer}}$$

Functionality:

Number of reactive sites present in a monomer is called functionality of monomer. The monomer must have at least 2 reactive sites.

$$n\,CH_2{=}CH_2 \longrightarrow \left[CH_2{-}CH_2 \right]_n$$

Thus ethylene is bi-functional. Functionality determines structure and property of a polymer. Linear, branched and cross linked polymers are formed by bi-functional and poly-functional monomers respectively.

Classification of polymers:

Polymers may be classified according to the following ways;

1. Based on the origin
   a) Natural polymers
   b) Synthetic polymers

a) Natural polymers:

Polymers from natural materials or biological origin are called natural polymers. Example: cotton, cellulose and proteins.

b) Synthetic polymers:

Polymers that are synthesized in the laboratory. Eg: Polyethylene, PVC and PS

2) Based on monomeric units:

a) Homo polymers.
b) Co polymers.

a) **Homo polymers**: A polymer having identical monomer.
Ex: A-A-A-A

b) **Co polymers**: A polymer having different monomeric units.
Ex: -A-X-A-X

3) Based on chain structure:

Polymer may exist as linear chain, branched chain or cross linked chains.

a) Linear polymers
b) Branched polymers
c) Cross linked polymers

a) **Linear polymers**:

Polymers in which the monomeric units are connected to each other in the form of long straight chain are called linear polymers.

It is due to close packing as well as high magnitude of intermolecular forces of attraction in linear polymers which possess high melting point, density and tensile strength. Ex: HDPE, P.S and Nylon.

b) **Branched polymer**:

If a small amount of tri functional monomer is mixed with a bi functional monomer it results in the formation of branched polymer.

Ex: LDPE and Starch

c) **Cross linked polymer**:

These are polymers in which monomeric units are cross linked together by only covalent bonds to form a cross liked polymer. Increase in amount of tri functional or tetra functional monomer results in formation of highly cross linked polymer. Ex: Bakelite.

4) Based on intermolecular interaction:

Properties of polymers depend upon the intermolecular forces present in the molecule. Based on the magnitude of these forces present, polymers are classified as:

a) Thermo plastics
b) Thermo setting plastics
c) Fibers
d) Elastomers

a) **Thermo Plastics**:

Thermo plastic is reversible polymers. On cooling they become a hard mass and on heating they get softened without change in polymer structure. Ex: Polythene.

b) **Thermo setting plastics**:

These polymers undergo permanent change on heating. Once they have solidified, they cannot be softened during moulding process. Thermo setting plastic are irreversible. Ex: Bakelite.

c) **Fibers**:

Fibers have strong intermolecular forces between the chains due to 'H' bonding; hence they have high tensile strength. Ex: Nylon.

d) **Elastomers**:

In elastomer the magnitude of intermolecular forces is very weak and hence such polymers can be easily stretched. Rigidity in elastomer can be introduced by adding cross linking agent. Ex: Rubber.

Types of Polymerization:

There are 2 types of polymerization reactions:

1) Addition (or) Chain growth polymerization.
2) Condensation (or) Step growth polymerization.
3) Co-polymerization.

Addition (or) Chain growth polymerization:

In this mechanism the monomeric units are linked together through a covalent bond to form a large molecule without any loss of simple molecules like water, NH_3 etc.

Ex: Polythene, PVC.

Polythene:

$$\begin{array}{ccc} nCH_2=CH_2 & \xrightarrow[High Pressure]{>300^0} & -(CH_2-CH_2)_n- \\ Ethylene & & Poly\ ethylene \end{array}$$

PVC:

$$\begin{array}{ccc} nCH_2=CHCl & \xrightarrow[H_2O_2]{<80^0 C} & -(CH_2-CHCl)_n- \\ Vinyl\ Chloride & & Poly\ Vinyl\ Chloride \end{array}$$

Addition polymerization is carried out in three steps:

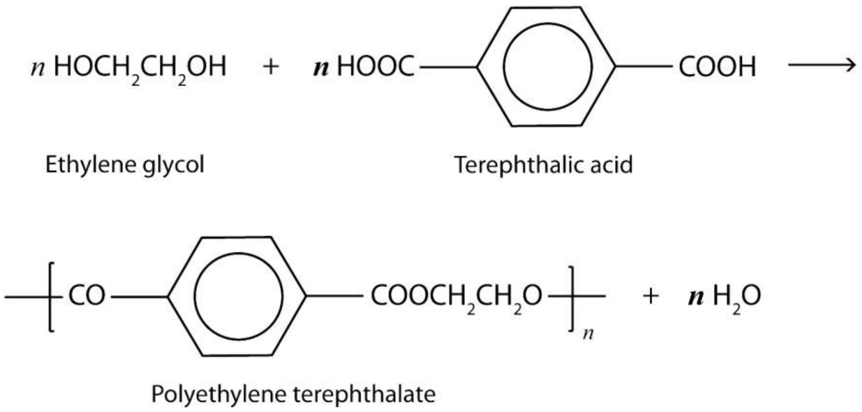
1) Free radical mechanism.
2) Ionic addition mechanism (Cationic & Anionic)
3) Coordination mechanism.

Condensation (or) Step growth polymerization:

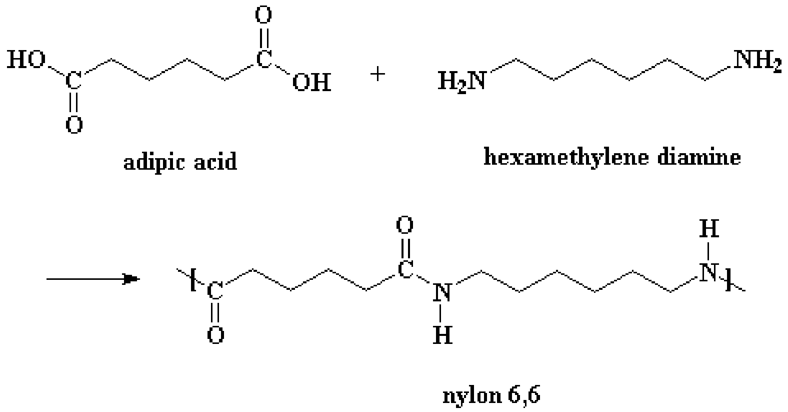
In this mechanism the monomeric units are linked together through a covalent bond to form a large molecule followed by the elimination of simple molecules like H_2O, NH_3, CH_3OH etc.

Ex: Polyester, Nylon 6:6 etc.

Polyester (polyethylene terephthalate):



Nylon 6, 6 :



Co-polymerization: Polymerization involving two or more than two species of monomers is called Copolymerization.

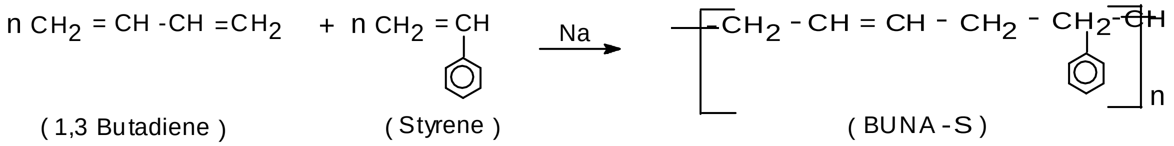
Eg: BUNA-N, BUNA-S etc.

BUNA-N:

$$n(CH_2=CH-CH=CH_2)+n(CH_2=CHCN)\xrightarrow[Catalyst]{Na}-(CH_2-CH=CH-CH_2-CHCN-CH_2)_n-$$

(1,3 Butadiene) (Acrylonitrile) (Nitrile Butadiene Rubber)

BUNA-S:



PROPERTIES OF POLYMERS:

Physical properties:

1. Crystallinity
2. Molecular weight
3. Solubility
4. Effect of heat
5. Diffusion & Permeability

Mechanical properties:

1. Toughness.
2. Strength.
3. Elasticity

Physical properties:

Crystallinity:

As the polymer molecules are long chains, the degree to which the molecules of a polymer are arranged in orderly pattern with respect to each other is a measure of crystallinity. Crystallite is defined as a small region of a macromolecular material in which portions of large molecules are linked to each other in some regular way. Usually a polymer is a mixture of 60% crystalline, 40% amorphous etc. As the crystallinity increases, the brittleness, strength and chemical resistance of a polymer increases. Eg: HDPE possess 80-85% crystallinity.

Molecular weight:

When polymerization takes place, the growing polymer chains are terminated at different sizes of molecules, as a result the polymer molecules have different number of monomeric units, hence different molecular weights. As a result the molecular weight of the polymer should be expressed as average molecular weight ($\overline{M}$).

Solubility:

When a polymer is dissolved in a suitable solvent, it absorbs water and swells in size and forms a viscous heterogeneous solution unlike NaCl when added to water.

Effect of heat on polymer:

At room temperature polymers are solids existing in visco elastic state. As the temperature increases the polymer melts and this is called the melting point of polymer (T_f) where the polymer exists in visco fluid state. As the temperature further increases to boiling (T_b) the polymer decomposes to its monomers which are in vapor phase. On the other hand when the temperature is lowered below zero degree the polymer becomes hard, brittle and glassy. This temperature is called as glass transition temperature (T_g). Eg: T_g of rubber = -73˚C

Diffusion and permeability:

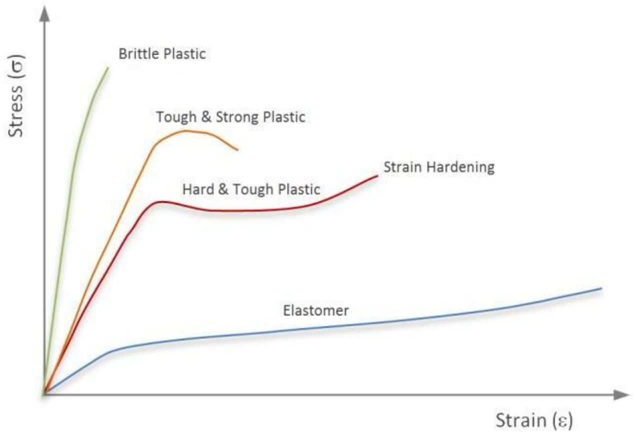
Crystalline polymers resist diffusion of molecules through voids or other gaps and tend to resist diffusion because of much greater degree of molecular packing.

Mechanical Properties:

1. Toughness:

The impact strength is measured as toughness. Below glass transition temperature (T_g) the polymers break with a brittle fracture and they become tougher when they proceed from room temperature to T_g. The size of the crystalline structure also determines the toughness.

2. Strength:



The strength of a polymer depends on length of polymer chain, branching, cross linking, molecular weight. Even the intermolecular forces of attraction, presence of polar groups increases the strength of the polymer. The strength of a polymer is determined by stress-strain test.

3. Elastic character:

Elasticity is the property of recovering original shape after removal of deforming stress. Natural rubber possesses high elasticity due to the coiled helix structure of polyisoprene.

PLASTICS:

Plastics are higher molecular weight organic polymers which show the property of plasticity and can be moulded into desired shape by applying heat and pressure in presence of catalyst.

Advantages of Plastics:

They show good thermal and electrical insulation
High corrosion resistance
Light in weight
Low maintence cost

Types of Plastics:

Based on type or resin plastic are classified into 2 types:

1. Thermo plastics. 2. Thermo setting plastics.

1. Thermo plastics:

i) These are linear long chained polymer, which can be softened on heating and hardened on cooling.
ii) These are formed by addition/chain polymerization.
iii) They possess weak van der Walls forces in between two polymeric chains.
iv) These resins are usually soluble in organic solvents.
v) These plastic can be reclaimed from waste.
vi) They can be reshaped, remoulded and reshaped.
vii) These plastic are softer and flexible

Eg: PE, PVC, PS & PTFE etc.

2. Thermo setting plastic

i) These plastics are 3D, cross linked polymers. Which cannot be softened on heating and hardened on cooling.
ii) Once they are solidified they cannot be softened.
iii) They are formed by condensation/step polymerization.
iv) They cannot be reused and reshaped.
v) They cannot be reclaimed from waste.

vi) They are hard, strong and more brittle.
vii) These are insoluble in almost all organic solvents.
Eg: Bakelite, Urea-formaldehyde etc.

Compounding of plastics:

The polymer resin is mixed with various ingredients during fabrication to improve useful properties. This process is called "*Compounding of plastics*".

1) **Resins**: These resins act as binders which hold the different constituents together. Example: PVC, Bakelite etc.

2) **Plasticizers**: These are added to the plastic to increase plasticity and flexibility of polymer. Example: vegetable oils, camphor etc.

3) **Fillers**: These are added to the plastic to improve hardness, tensile strength, opacity to plastics. They also reduce cost of polymer. Example: metallic oxides, quartz etc.

4) **Lubricants**: These are added to give good finishing to the plastic. Example: waxes, soaps etc.

5) **Catalysts**: These are added to accelerate the polymerization reaction. Example: CuO, lead oxide, peroxides etc.

6) **Stabilizers**: These are added to improve thermal stability during polymerization. Example: white lead, red lead etc.

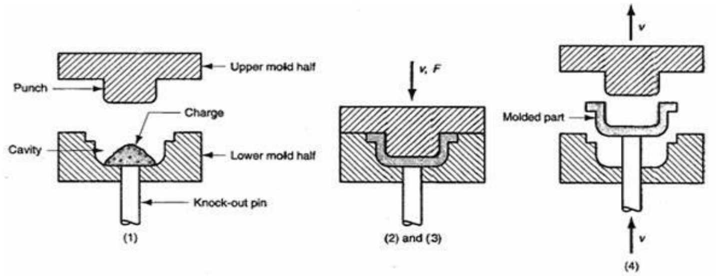
7) **Colouring agents**: They give desire colour to plastic. Example: FeO, Ultramarine, organic dyes etc.

Fabrication/Molding Techniques of plastics:

Depending on type of resin, fabrication techniques are: 5 types

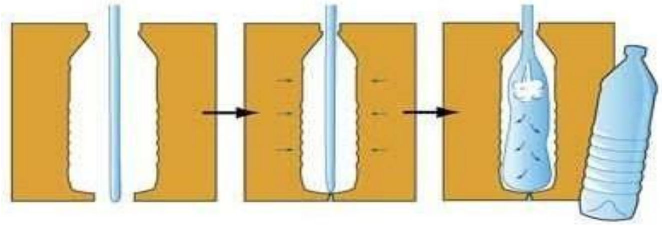
1. **Compression moulding.**
2. Injection moulding.
3. Transfer moulding.
4. Extrusion moulding.
5. **Blow moulding.**

1. Compression moulding: This method is used for both thermo plastics and thermo setting plastics. A desired quantity of plastic resin is filled in cavity present in bottom mould. Top and bottom mould are capable of being moved relative to each other. Curing is done either by heating in case of thermo setting plastic. After curing article is commonly used for the manufacturing of cylinders, handle less articles etc.



Compression molding for thermoplastics: (1) charge is loaded, (2) and (3) charge is compressed and cured, and (4) opening the mold halves and removing the part from the cavity.

2. Blow molding: This method is also called as "*Bubble Casting Method*". It is used for molding of hallow type plastics. Compounding powder plastic are melted and forced through a gate into the blow pin. The plastic substance is expanded and cooled by being made to flow around an air bubble. After few seconds the article is ready.



Some Important Plastics Preparations:

Poly Vinyl Chloride (P.V.C):

Preparation: It is prepared by free radical chain polymerization of vinyl chloride monomer in presence of H_2O_2.

$$\underset{Vinyl\ Chloride}{nCH_2 = CHCl} \xrightarrow[H_2O_2]{<80^0 C} \underset{Poly\ Vinyl\ Chloride}{-(CH_2 - CHCl)_n -}$$

Properties:

1. It is colourless, chemical inert nature.
2. It is strong and brittle.
3. It is not stable to heat.
4. It has excellent insulating nature.

Applications:

1. ***Plasticized* PVC** is used for electrical insulations, radio and telephone components, chemical containers, cameras and aircrafts.
2. ***Unplasticized* PVC** is rigid and brittle. This PVC is used for making safety helmets, tyres, cycle and motor cycle mudguards.

Bakelite:

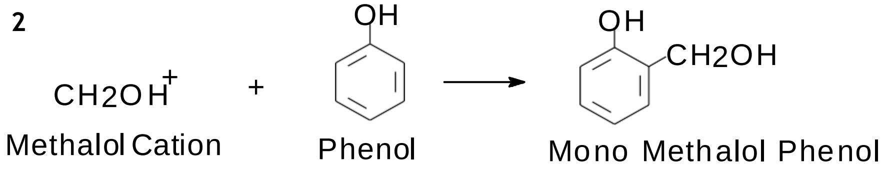
1. Formaldehyde reacts with acetic acid to form methyl cation.

Step: 1 $HCHO + H^+ \longrightarrow CH_2OH^+$

Methalol Cation

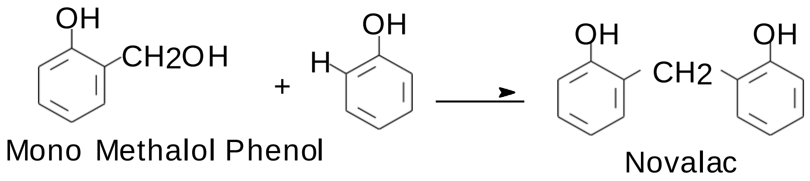
2. Methlol cation reacts with phenol to give mono, di, tri Methlol phenol.

Step: 2



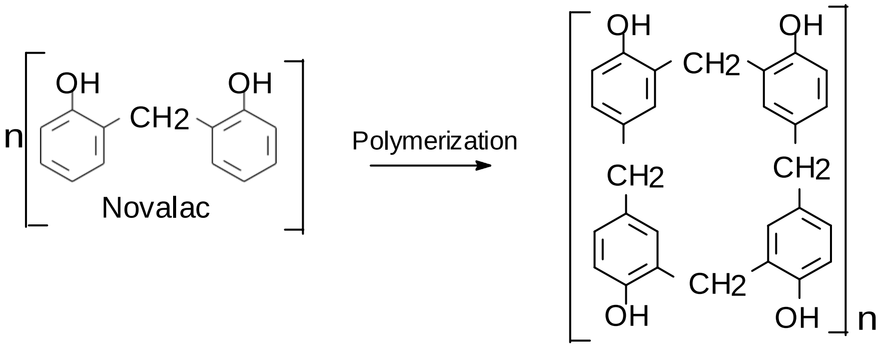
3. Mono Methlol phenol reacts with phenol to give Novalac compound. To lose water molecules this is an evidence of condensation polymer reaction.

Step: 3



4. Novalac under goes polymerization to give Bakelite.

Step: 4



BAKELITE

Properties:

It is hard and strong and colour less. It is excellent insulation property.

It is highly resistant to chemicals and atmospheric conditions like O_2, CO_2, UV etc.

Applications:

It is used to prepare telephone cabinets and panels. It is used to making electrical insulator parts like switches and switch boards. As an anion exchanger in water purification by ion exchange method.

Unit – 2

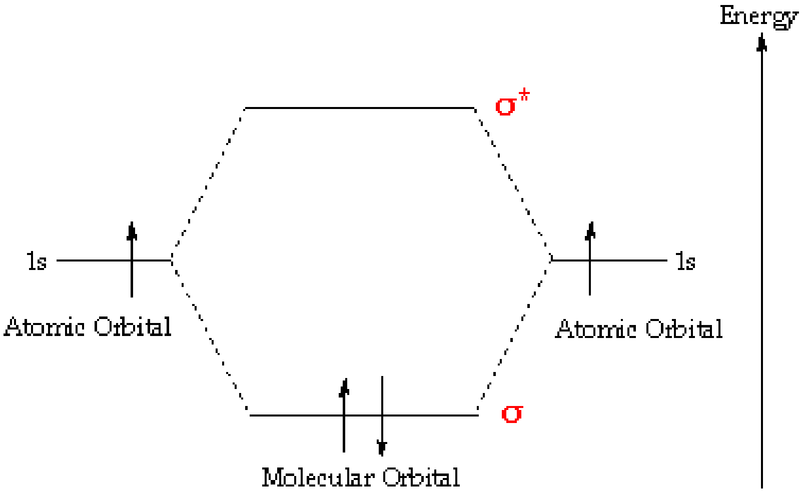
Structure and Bonding Models

Molecular Orbital Theory

The Valence Bond Theory failed to answer certain questions like why He_2 molecule does not exist and why O_2 is paramagnetic. Therefore in 1932 F. Hood and R.S. Mulliken came up with Molecular Orbital Theory to explain questions like the ones above.

Salient features of Molecular Orbital theory:

- According to the Molecular Orbital Theory, a molecule is different from its constituent atoms. Thus the atoms constituting the molecule are considered to be moving along the entire molecule under the influence of all the nuclei.
- Molecular orbitals are obtained through the combination of atomic orbitals of comparable energies.
- The number of molecular orbitals is always same as that of the number of atomic orbitals from which they are formed.



- Electrons can be considered as having either particle or wave nature. Therefore, we can describe an electron in an atom as occupying an atomic orbital, or by a wave function Ψ. These are solutions to the Schrodinger wave equation. Electrons in a molecule occupy molecular orbitals. We can obtain the wave function of a molecular orbital by LCAO method.

Linear Combination of Atomic Orbitals (LCAO)

- As per this method, the formation of orbitals is because of Linear Combination (addition or subtraction) of atomic orbitals which combine to form the molecule. Consider two atoms A and B which have atomic orbitals described by the wave functions Ψ_A and Ψ_B.
- If the electron cloud of these two atoms overlaps, then we can obtain the wave function for the molecule by a linear combination of the atomic orbitals Ψ_A and Ψ_B. The below equation forms two molecular orbitals.

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

Bonding Molecular Orbitals

When the addition of wave function takes place, the type of molecular orbitals formed are Bonding Molecular Orbitals. We can represent them by $\Psi_{MO} = \Psi_A + \Psi_B$. They have lower energy than atomic orbitals involved.

Anti-Bonding Molecular Orbitals

When molecular orbital forms by the subtraction of wave function, the type of molecular orbitals formed are antibonding Molecular Orbitals. We can represent them as $\Psi_{MO} = \Psi_A - \Psi_B$. They have higher energy than atomic orbitals. Therefore, the combination of two atomic orbitals results in the formation of two molecular orbitals. They are the bonding molecular orbital (BMO) and the anti-bonding molecular orbital (ABMO).

Relative Energies of Molecular Orbitals:

- **Bonding Molecular Orbitals (BMO)** – Energy of Bonding Molecular Orbitals is less than that of Anti Bonding Molecular Orbitals. This is because of the increase in the attraction of both the nuclei for both the electron (of the combining atom).
- **Anti-Bonding Molecular Orbitals (ABMO)** – Energy of Anti Bonding Molecular Orbitals is higher than Bonding Molecular Orbitals. This is because the electron tries to move away from the nuclei and is in a repulsive state.
- The bonding molecular orbitals are represented as σ (Sigma), π (pi), δ (delta) and the corresponding anti-bonding orbitals are denoted as σ*, π* and δ*.

Rules for Filling of Molecular Orbitals

We have to follow certain rules while filling up molecular orbitals with electrons in order to write correct molecular configurations. They are

- **Aufbau Principle** – This principle states that those molecular orbitals which have the lowest energy are filled first.
- **Pauli's Exclusion Principle** – According to this principle, each molecular orbital can accommodate a maximum of two electrons having opposite spins.
- **Hund's Rule** - The Hund's rule states that in two molecular orbitals of the same energy, the pairing of electrons will occur when each orbital of same energy consist of one electron.
- **Bond Order:** Bond order gives the number of covalent bonds between the two combining atoms. The bond order of a molecule can be calculated using the following equation

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

Where, N_b = Total number of electrons present in the bonding molecular orbitals

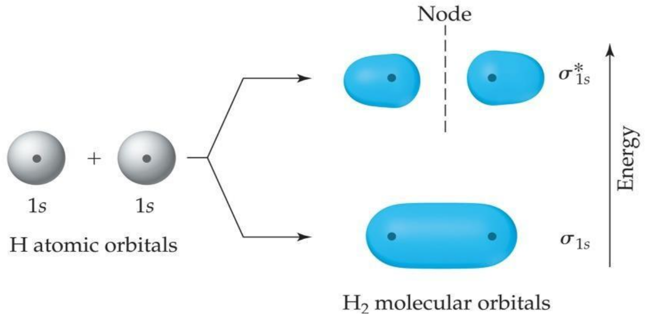
N_a = Total number of electrons present in the anti-bonding molecular orbitals and

A bond order of zero value indicates that the molecule doesn't exist.

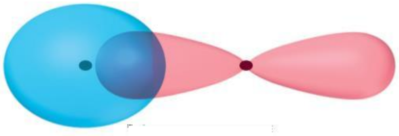
Sigma (σ) and Pi (π) Molecular orbitals:

Molecular orbitals formed by overlapping of *s* atomic orbitals or head to head overlap of *s* and *p* atomic orbitals or head to head overlap of *p*-atomic orbitals are known as "**Sigma Molecular Orbitals**" where as molecular orbitals which are formed through sideway or lateral overlap of two p=orbitals are known as "**Pi Molecular Orbitals**".

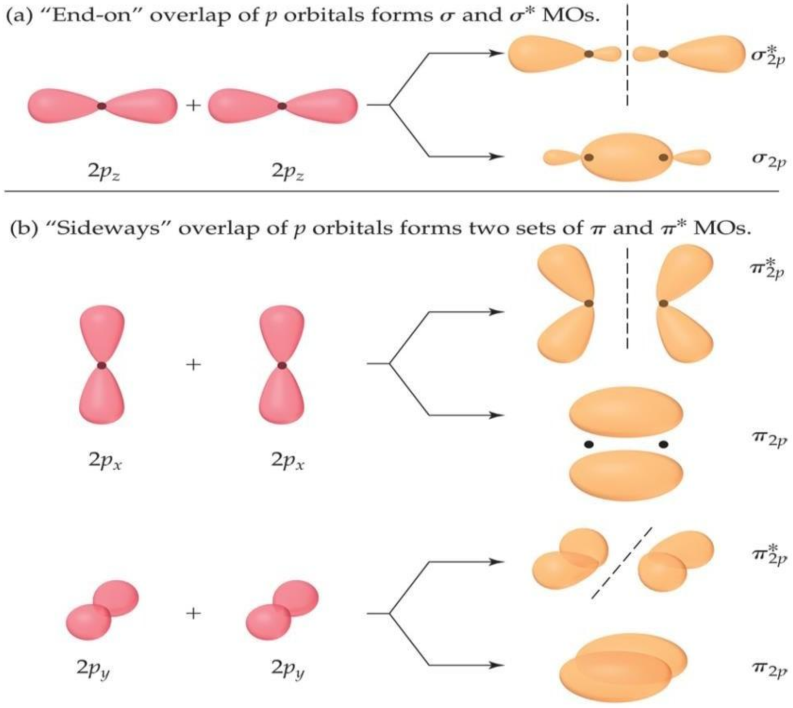
s-s mixing:



s-p **mixing:**



p-p mixing:



Bonding in Homo nuclear & Hetero nuclear di-atomic molecules:

The nature and behavior of a molecule depends upon how the atoms are bonded based on their electronic configurations. The information obtained is as follows:

➢ Stability of a molecule:

If N_b and N_a are the number of electrons in bonding and antibonding MOs, then

- When $N_b > N_a$; the molecule is stable
- When $N_b < N_a$; the molecule is unstable
- When $N_b = N_a$; the molecule is unstable

Thus, even when N_b is equal to N_a, the atoms do not combine to form molecules. This is because the effect of antibonding electrons is slightly more than the bonding electrons.

Bond Order:

- If bond order is positive, then the molecule is stable.
- If bond order is negative or zero, the molecule is unstable.
- Greater the bond order, more is the bond dissociation energy and greater is the stability of the molecule.
- Higher the bond order, shorter is the bond length and more stable is the molecule.

Magnetic Character:

If all the electrons in the molecule of a substance are paired, the substance is diamagnetic. Conversely, the presence of one or more unpaired electrons is the cause of paramagnetism of the molecule.

Energy Level Diagrams:

H_2 molecule: The molecule is stable (bond order is positive) and diamagnetic.

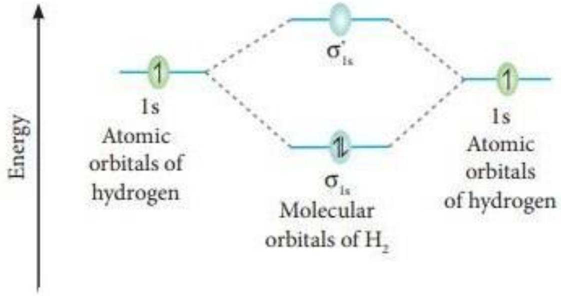
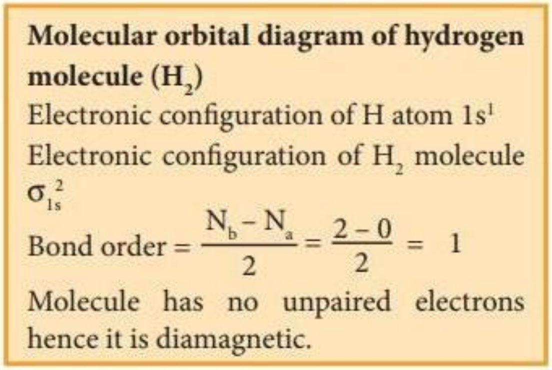


Fig 10.30 MO Diagram for H_2 molecule



Molecular orbital diagram of hydrogen molecule (H_2)

Electronic configuration of H atom $1s^1$

Electronic configuration of H_2 molecule σ_{1s}^2

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

Molecule has no unpaired electrons hence it is diamagnetic.

C_2 molecule: The molecule is stable (bond order is positive) and diamagnetic.

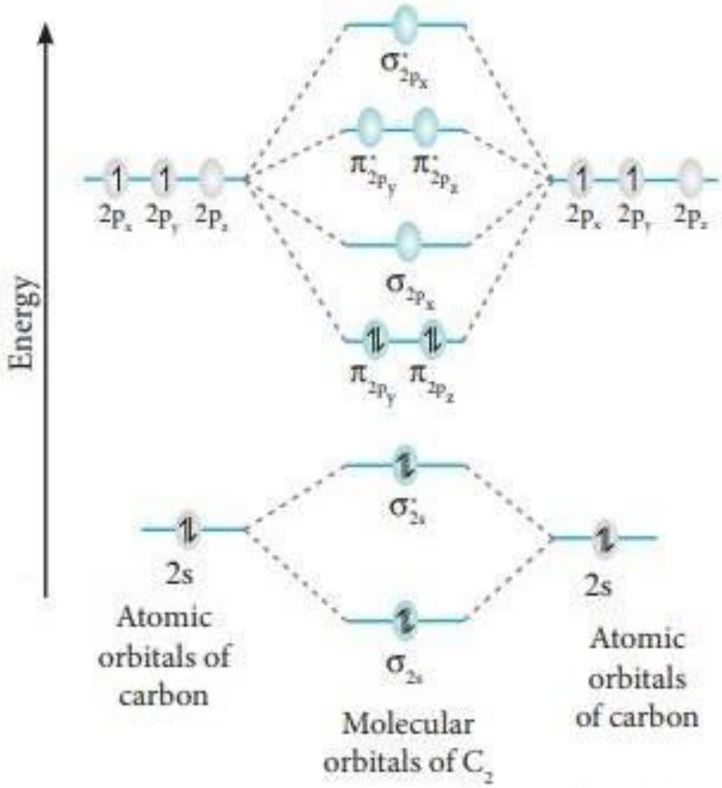
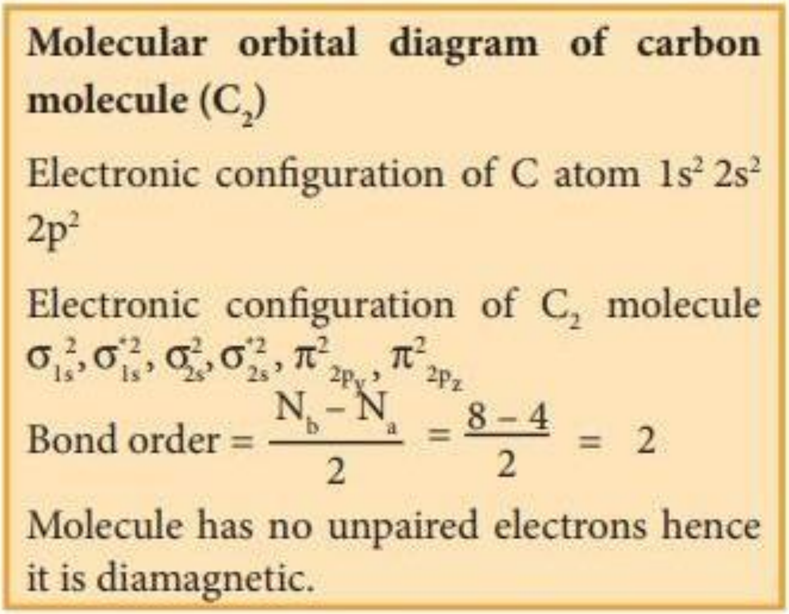


Fig 10.33 MO Diagram for C_2 molecule



Molecular orbital diagram of carbon molecule (C_2)

Electronic configuration of C atom $1s^2\,2s^2\,2p^2$

Electronic configuration of C_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$$

Molecule has no unpaired electrons hence it is diamagnetic.

N_2 molecule: The molecule is stable (bond order is positive) and diamagnetic.

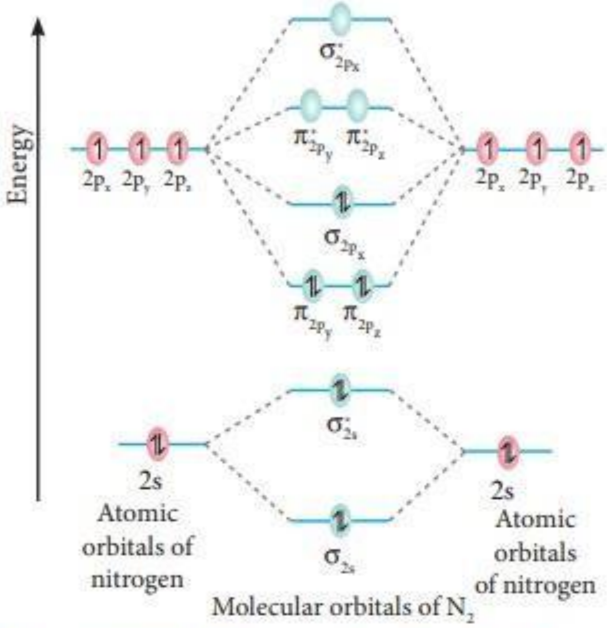


Fig 10.34 MO Diagram for N_2 molecule

Molecular orbital diagram of nitrogen molecule (N_2)

Electronic configuration of N atom $1s^2\, 2s^2\, 2p^3$

Electronic configuration of N_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}\, \sigma_2{}^2px$

Bond order $= \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

O_2 molecule: The molecule is stable (bond order is positive) and paramagnetic.

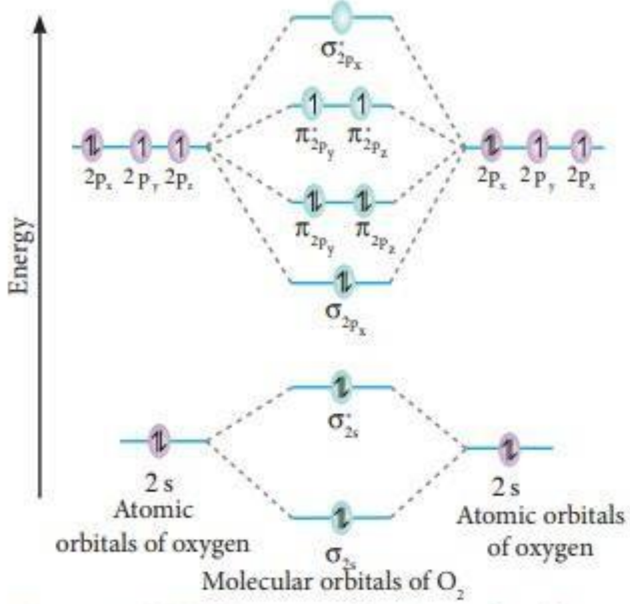


Fig 10.35 MO Diagram for O_2 molecule

Molecular orbital diagram of oxygen molecule (O_2)

Electronic configuration of O atom $1s^2\,2s^2\,2p^4$

Electronic configuration of O_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi^2_{2p_y}, \pi^2_{2p_z}, \pi^{*1}_{2p_y}, \pi^{*1}_{2p_z}$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-6}{2} = 2$$

Molecule has two unpaired electrons hence it is paramagnetic.

Bonding in Hetero nuclear di-atomic molecule:

CO molecule: The molecule is stable (bond order is positive) and diamagnetic.

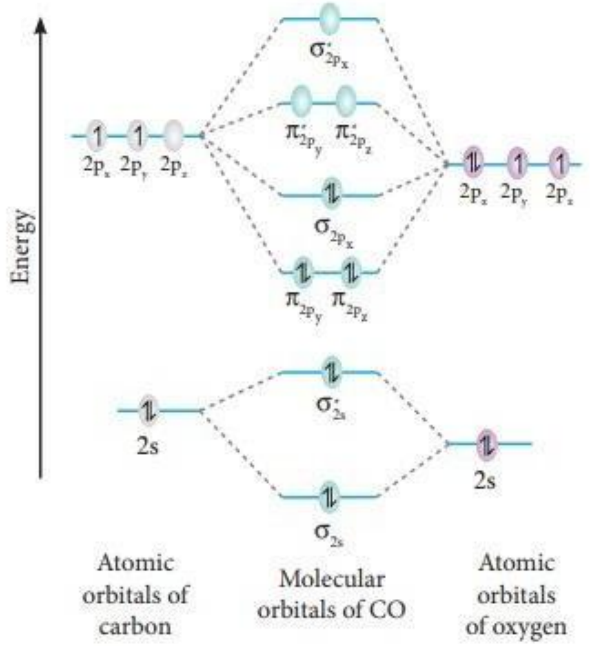
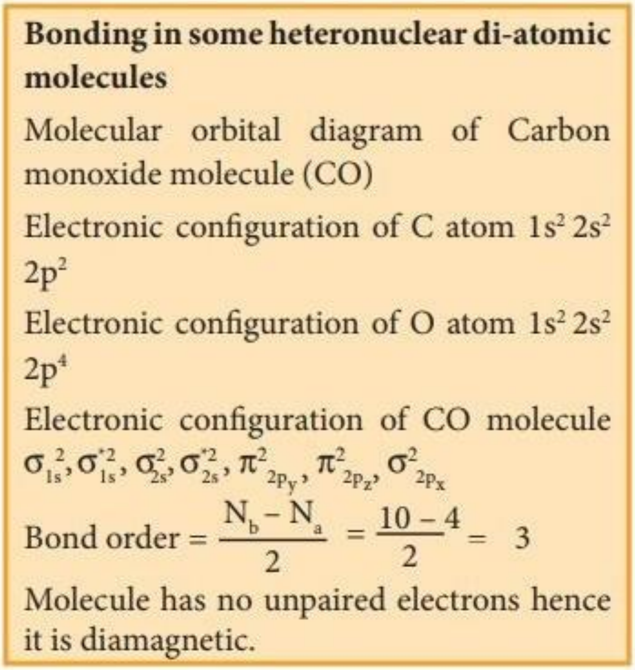


Fig 10.36 MO Diagram for CO molecule



Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom $1s^2\ 2s^2\ 2p^2$

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

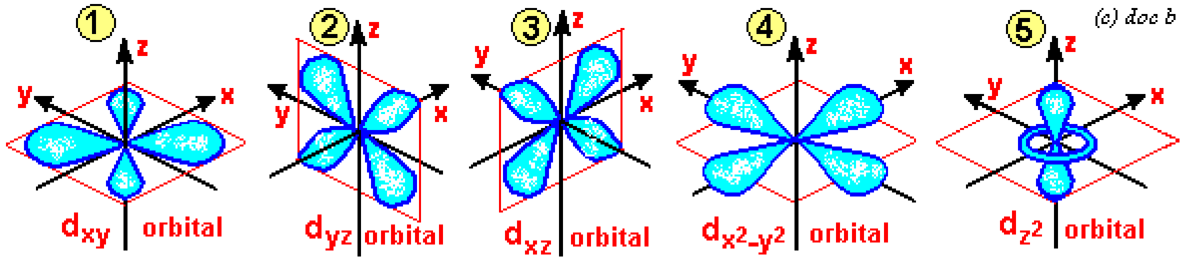
Electronic configuration of CO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}, \sigma^2_{2p_x}$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{10 - 4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

Shapes of *d*-orbitals:

For *d*-subshell, *l* = 2, there are five values of m namely -2, -1, 0, 1, 2. It means d- orbitals can have five orientations. These are represented by d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}; for example, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$. The d_{xy}, d_{yz} and d_{zx} orbitals have same shape i.e., clover leaf shape but they lie in XY, YZ and ZX planes respectively.



The d_{z2} orbital is symmetrical about Z-axis and has a dumb - bell shape with a doughnut shaped electron cloud in the centre. The d_{x2-y2} orbital is also clover leaf shaped but its leaves are directed along the X and Y- axis.

Based on the orientations of the lobes of the five *d* orbitals with respect to the coordinate axes, five *d* orbitals have been grouped into the following two sets.

(i) **t_{2g} set of orbitals**: this set consists of the orbitals whose lobes lie between the axes and are called ***non-axial orbitals***. These are dxy, dxz, dyz orbitals. The letter t in t2g refers to triply degenerate set. The subscript g, stands for 'gerade' or even.

(ii) **e_g set of orbitals:** Orbitals of this set have their lobes along the axes and hence, are called ***axial orbitals.*** These are d_{x2-y2} and d_{z2} orbitals. The term 'e' in eg refers to doubly degenerate set.

Crystal Field Theory:

Crystal field theory (CFT) is a model developed by **Hans Bethe** and **John Von Vlech.** It explained the bonding in complex compounds and the stability of these compounds. It was based on the degeneracies of d-orbitals. According to it the d-orbitals splits when the ligands approach the central metal ion.

Salient features of CFT:

- CFT considers the bonds to be *ionic* arising purely due to ***electrostatic interaction*** between the metal ions and the ligands. Since these interactions are similar to that present in crystals, the theory is called as C*rystal field theory*.
- If the ligand is anion (negatively charged) then the metal ion has to be a cation (positively charged) and the force of attraction is due to opposite charges.
- If the ligand is a neutral molecule like H_2O, NH_3, etc then the negative end of their dipoles are attracted towards the central metal ion.
- The energy level of the *d*-orbitals of the metal atom (or ion) is affected by the field produced by the ligands.
- In case of free transition metal ions, all the five *d*-orbitals have equal energies (*i.e.*, they are degenerate). This degeneracy is maintained if the negative charges are present around the central metal ion in a spherical symmetrical field.
- However if the negative field is due to the ligands which may be negative ion or polar molecules with their negative ends towards the central metal ion, then the field no longer remains symmetrical and the degeneracy is split.
- The *d*-orbitals split into two parts (named as t_{2g} and e_g orbitals) depending on the number of ligands approaching the metal ion which is known as *"**Crystal field splitting**"*.
- For a given metal ion, the pattern of crystal field splitting depends on the number of ligands and their arrangement surrounding the metal ion.

Crystal field splitting in Octahedral Complexes:

- In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels. The bottom three energy levels are named d_{xy}, d_{xz}, and d_{yz} (collectively referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (collectively referred to as e_g).
- In case of octahedral complexes, splitting energy separation is denoted by Δ_o (where subscript 'o' is for octahedral).

- The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral field, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} are lower ($0.4\Delta_o$).

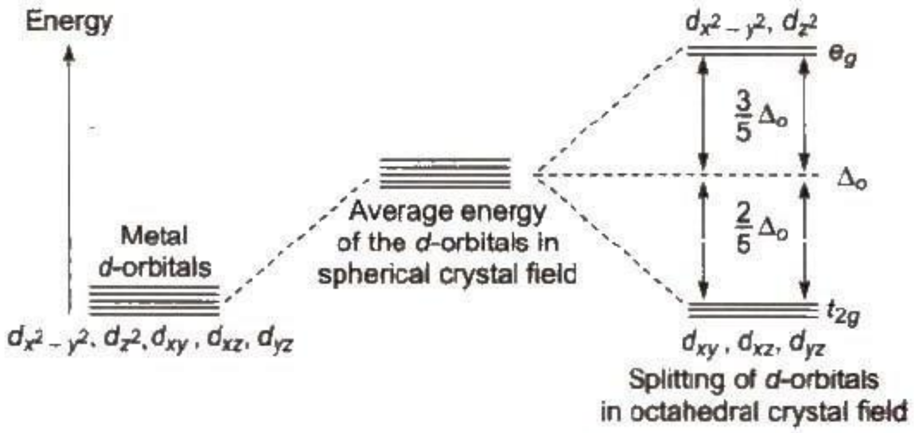
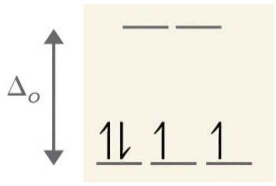


***Figure** : Splitting of the degenerate d-orbitals due to an octahedral ligand field*

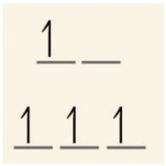
- Crystal field splitting occurs in such a way that the average energy of d-orbitals before and after splitting remains unaltered. This is known as ***barycentre*** (the energy level that corresponds to the hypothetical spherically symmetrical environment) ***rule.***
- Filling of electrons in orbitals takes place by following Aufbau, Hund and Pauli's exclusion principles.

For example, if one had a d^3 complex, there would be three unpaired electrons. If one were to add an electron, however, it has the ability to fill a higher energy orbital (d_{z^2} or $d_{x^2-y^2}$) or pair with an electron residing in the d_{xy}, d_{xz}, or d_{yz} orbitals. This pairing of the electrons requires energy (spin pairing energy).



$t^4_{2g}\ e^o_g$.

Low Spin, StrongField (Δ_o>P)



$t^3_{2g}\ e^1_g$

High Spin, Weak Field (Δ_o<P)

- If the pairing energy is less than the crystal field splitting energy, Δ_0 , then the next electron will go into the d_{xy}, d_{xz}, or d_{yz} orbitals due to stability.
- This situation allows for the least amount of unpaired electrons, and is known as ***low spin***. If the pairing energy is greater than Δ_0 , then the next electron will go into the d_{z^2} or $d_{x^2-y^2}$ orbitals as an unpaired electron. This situation allows for the most number of unpaired electrons, and is known as ***high spin***.
- Ligands that cause a transition metal to have a small crystal field splitting, which leads to high spin, are called ***weak-field ligands***. Ligands that produce a large crystal field splitting, which leads to low spin, are called ***strong field ligands***.

Note: The oxidation state and the strength of the ligands determine splitting; the higher the oxidation state or the stronger the ligand, the larger the splitting. Ligands are classified as strong or weak based on the spectrochemical series:

$I^- < Br^- < Cl^- < SCN^- < F^- < OH^- < ox^{2-} < ONO^- < H_2O < SCN^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^-$

Crystal Field Stabilization Energy:

A consequence of Crystal Field Theory is that the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand field geometry and metal d-electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration and knowledge of the splitting patterns.

"The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field."

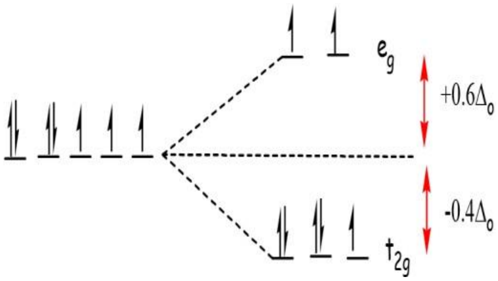
$$\mathrm{CFSE} = \Delta E = \mathrm{E}_{\text{ligand field}} - \mathrm{E}_{\text{isotropic field}} \text{--} \textbf{Eq. 1}$$

For an octahedral complex, an electron in the more stable t_{2g} *subset* is treated as contributing $-0.4\Delta_o$ whereas an electron in the higher energy e_g *subset* contributes to a destabilization of $+0.6\Delta_o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δ_o. If any electrons are paired within a single orbital, then the term P is used to represent the spin pairing energy.

Example 1: CFSE for a high spin d^7 complex

What is the Crystal Field Stabilization Energy for a high spin d^7 octahedral complex?

Solution: The splitting pattern and electron configuration for both isotropic and octahedral fields are shown below.



The energy of the isotropic field ($E_{\text{isotropic field}}$) is

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (5 \times -2/5\Delta_o) + (2 \times 3/5\Delta_o) + 2P = -4/5\Delta_o + 2P$$

Therefore, CFSE is

$$CFSE = E_{\text{ligand field}} - E_{\text{isotropic field}}$$

$$= (-4/5\Delta_o + 2P) - 2P$$

$$= -4/5\Delta_o$$

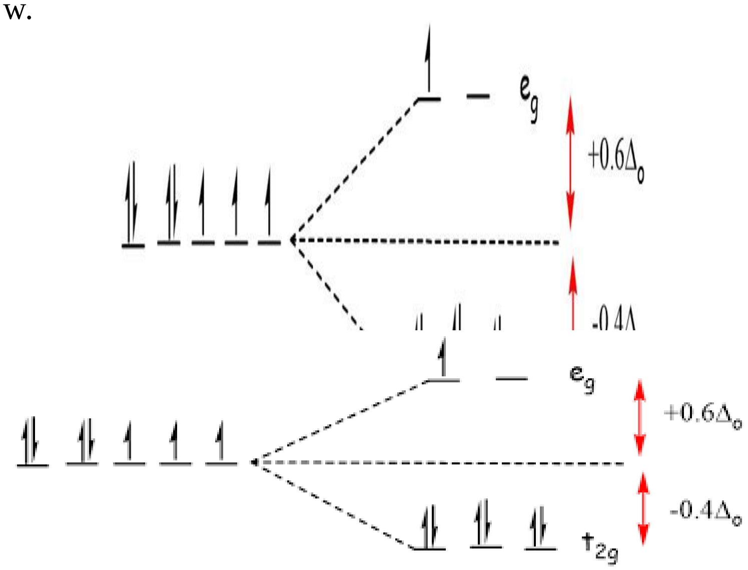
Notice that the Spin pairing Energy falls out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the ligand field is the same as that in isotropic field of the free metal ion.

Example 2: CFSE for a low spin d^7 complex

What is the Crystal Field Stabilization Energy for a low spin d^7 octahedral complex?

Solution:

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (6 \times -2/5\Delta_o) + (1 \times 3/5\Delta_o) + 3P$$

$$= -9/5\Delta_o + 3P$$

So *via* Equation 1, the CFSE is

$$CFSE = E_{\text{ligand field}} - E_{\text{isotropic field}}$$

$$= (-9/5\Delta_o + 3P) - 2P$$

$$= -9/5\Delta_o + P$$

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more a more stable configuration than the high spin d^7 configuration in Example 1, but we have then to take into consideration the Pairing energy P to know definitely, which varies between $200 - 4$

Unit 3
Electrochemistry & Applications

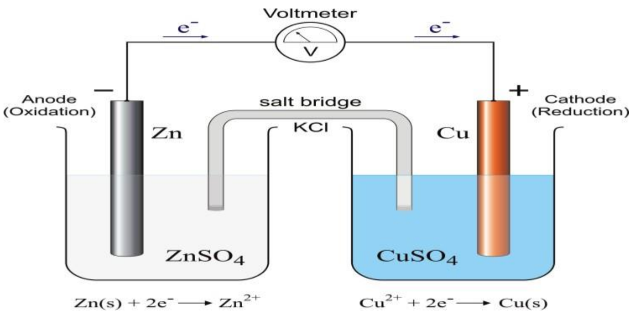
Electrochemistry deals with the interaction between electrical energy and chemical change. When a chemical reaction is caused by an externally supplied current, it is called electrolysis, on the other hand if an electric current is produced by a spontaneous chemical reaction as in a battery, it is called an *electrochemical* reaction.

Differences between electrolytic cell and electrochemical cell

S. No	Electrolytic Cell	Electrochemical Cell
1.	An electrolytic cell is a type of electrochemical cell where electrical energy can be used to create a chemical reaction.	An electrochemical cell is a system that can produce electrical energy through spontaneous chemical reactions.
2.	In electrolytic cell, electrical energy is converted into chemical energy.	In electrochemical cell, chemical energy is converted into electrical energy.
3.	Electrolytic cells need external electrical energy sources.	Electrochemical cells do not need external electrical energy sources.
4.	In electrolytic cells, non-spontaneous chemical reactions take place.	In electrochemical cells, spontaneous chemical reactions take place.
5.	In an electrolytic cell, the anode is positive and the cathode is negative.	In an electrochemical cell, the anode is negative and the cathode is positive.
6.	Electrons are passed from the battery to cathode and then the electrons enter the anode through the electrolytic solution in electrolytic cells.	Electrons are passed from anode to cathode in electrochemical cells.

Galvanic (or) Voltaic Cells

- A Galvanic cell or Voltaic cell is an electrochemical cell that converts chemical energy to electrical energy by spontaneous redox reaction within the cell.



- It generally consists of two different metals connected by a salt bridge, or individual half cells separated by a porous membrane.
- A common electrochemical or voltaic cell is Daniel cell.
- It consists of two half cells as shown in the figure. The half-cell on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution (1M), another half cell on the right contains a copper metal electrode dipped in $CuSO_4$ solution (1M).
- The two half cells are joined by a salt bridge, which prevents mechanical mixing of the solution.
- When the zinc and copper electrodes are joined by a metallic wire.

The electrode reactions are:

At anode (-ve) : $Zn \longrightarrow Zn^{2+} + 2e^-$ E = -0.77 volt (Oxidation half reaction)

At cathode (+ve) : $Cu^{2+} + 2e^- \longrightarrow Cu$ E = +0.37 volt (reduction half reaction)

$$\boxed{\text{Net reaction : } Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu \text{ (e.m.f of the cell = 1.1 volts.)}}$$

The following observations are made:

a) Electrical current flows through ‘Zn’ electrode to ‘Cu’ electrode through external circuit.

b) Zinc rod losses its mass while copper rod gains mass.

c) Concentration of $ZnSO_4$ solution increases while concentration of copper sulphate solution decreases.

d) Solutions in both the compartments remain electrically neutral.

Representation of Galvanic cell: ***$Zn/Zn^{2+}(1\ M)\ ||\ Cu^{2+}(1\ M)/Cu$***

Reversible and Irreversible cells:

The e.m.f. of the Daniel cell is 1.1 volt and the cell reaction is,

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

To such a cell an external e.m.f. which is exactly equal to 1.1 volt is applied, the cell reaction stops. But if the external e.m.f. is increased infinitesimally by small amount, then the cell reaction is reversed as given below.

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

If the external e.m.f. applied is less than 1.1 volt, then no change in the cell reaction takes place. This type of cell is called **reversible cells**. Any cell which does not satisfy the above condition is called **Irreversible cells**

Electrode Potential:

Electrode potential is defined as the potential of a cell consisting of the electrode in question acting as a cathode and the standard hydrogen electrode acting as an anode. Reduction always takes place at the cathode, and oxidation at the anode. According to the IUPAC convention, the term electrode potential is reserved exclusively to describe half-reactions written as reductions.

Electromotive Force (emf):

- The flow of electrons from one electrode to another electrode is due to the difference in electrode potentials. "The difference in electrode potentials which causes the flow of current from one electrode to another electrode is called Electromotive Force (EMF) of the electro chemical cell"

$$E_{(cell)} = E_{(ox)} + E_{(red)}$$

(or)

$$E_{(cell)} = E_{(Right)} - E_{(Left)}$$

where $E_{(Cell)}$ = e. m. f.

$E_{(Right)}$ = electrode potential of right hand side electrode

$E_{(left)}$ = electrode potential of left side electrode

Single electrode potential

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

Ex: Galvanic cell

Representation of Galvanic cell:

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

[single electrode (anode)] [single electrode (cathode)]

The half cell reaction corresponds oxidation: $Zn \longrightarrow Zn^{2+} + 2e^{-}$ ($E_{(ox)}$ = -0.77 volt)

The electrode is called oxidation electrode and the potential is oxidation potential which represents as $E_{(Ox)}/E_{(L)}/E_{(Anode)}$.

The half cell reaction corresponds reduction: $Cu^{2+} + 2e^{-} \longrightarrow Cu$ ($E_{(red)}$ = +0.34 volt)

The electrode is called reduction electrode and the potential is reduction potential which represents as $E_{(Red)}/E_{(R)}/E_{(Cathode)}$.

e.m.f of the cell is equal to the sum of oxidation potential and reduction potential. It is also expressed as the reduction potential of the right hand side minus reduction potential of the left hand side electrode. Electrode potentials generally refers to the reduction potential. $E_{(cell)} = E_{(R)} - E_{(L)}$

Example:

E(R) of Cu^{2+}/Cu = 0.34V

E(L) of Zn/Zn^{2+} = -0.77V

$E_{(cell)} = E_{(R)} - E_{(L)}$

= 0.34 – (-0.77)

= 1.10V

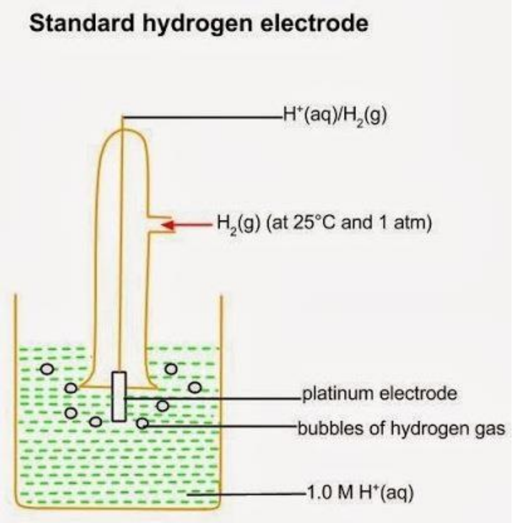
Standard Electrodes (Reference Electrode):

A Standard electrode is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials.

Standard Hydrogen Electrode (Glass electrode):

Construction:

i. It consists of a small platinum foil coated with platinum black which absorbs hydrogen gas.
ii. A platinum wire welded to the electrode. The electrode is sealed with a glass tube.
iii. The platinum foil is surrounded by an outer glass tube having an inlet at the top to H_2 gas is passed at one atmospheric pressure through the inlet of the glass tube.
iv. A small amount of gas is absorbed by the platinum electrode, while the remaining escapes through the lower holes provided at the base of the glass tube.



Working:

- Hydrogen gas is converted into H^+ ions and discharged into the solution, this electrode acts as anode following reaction takes place:

$$H_2 \rightarrow 2H^+ + 2e^- \text{ (Oxidation)}$$

- H^+ ions from the solution are converted into H_2 gas, hydrogen electrode acts as cathode following reaction takes place:

$$2H^+ + 2e^- \rightarrow H_2 \text{ (reduction)}$$

Thus hydrogen electrode is reversible with respect to H^+ ions. This electrode is represented as

$$Pt, H_2 \text{ (1 atm)} / H^+ \text{ (1M)}$$

Limitations:

1. It cannot be used in the presence of ions of many metals.
2. It cannot be used in solutions containing redox systems.
3. It is difficult to setup hydrogen electrode.
4. Maintenance of the pressure of the gas is difficult.

Electrochemical Series (Galvanic Series)

Arrangement of metals and nonmetals in increasing order of their standard reduction potentials or decreasing oxidation potentials is known as ***electrochemical (or) galvanic series***.

Standard Electrode Potentials of metals and nonmetals at 25^{0}C:

Electrode	***Half cell reaction***	***E^0 / V***
Li/Li^+	$Li \rightarrow Li^+ + e^-$	-3.05
Mg/Mg^{2+}	$Mg \rightarrow Mg^{2+} + 2e^-$	-2.37
Al/Al^{3+}	$Al \rightarrow Al^{3+} + 3e^-$	-1.66
Zn/Zn^{2+}	$Zn \rightarrow Zn^{2+} + 2e^-$	-0.76
Fe/Fe^{2+}	$Fe \rightarrow Fe^{2+} + 2e^-$	-0.44
Ni/Ni^{2+}	$Ni \rightarrow Ni^{2+} + 2e^-$	-0.25
H_2/H^+	**$H_2 \rightarrow 2H^+ + 2e^-$**	**0.00**
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+0.80
F_2/F^-	$2F^- + 2e^- \rightarrow F_2$	+2.87

Applications of Electrochemical series:

1. Comparison of relative reducing (or) oxidizing power of elements.
   Example, $E^0_{(Zn/Zn2+)}$ = -0.76 V, $E^0_{(Ni/Ni2+)}$ = -0.25 V.

From the values Zinc occupies a position higher in the series as compare to Nickel. So Zinc is a strong reducing agent than Nickel.

2. Predicting the feasibility of a redox reaction.
   Example,

1. $Fe + Ni^{2+} \longrightarrow Fe^{2+} + Ni$ (Reaction is feasible)
2. $2Ag + Cu^{2+} \longrightarrow 2Ag^+ + Cu$ (Reaction is not feasible)

3. Predicting whether a metal can evolve hydrogen from an acid (or) not.
   i) Those metals lying above hydrogen in the series are act as stronger reducing agents than hydrogen and they can lose electrons, so hydrogen gas will be evolved. Ex: Na, K, Zn, Mg and Al

ii) Those metals lying below hydrogen are weaker reducing agents than hydrogen they cannot lose electron, so hydrogen gas will not be liberated. Ex: Cu, Ag and Hg

4. Calculation of equilibrium constant:

- To known the standard potential value of a cell reaction its equilibrium constant easily calculated.

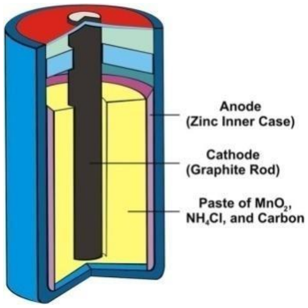
BATTERIES

Battery is a device consisting of one or more electrochemical cells (galvanic cell) that convert stored chemical energy into electrical energy. These batteries are used as source of D.C power.

Batteries Are Three Types: 1) Primary cells (or) Dry cell.
2) Secondary cells (or) rechargeable cells.
3) Fuel cells.

1) Primary Cells (or) Dry cells:

- These are disposable batteries, which are designed to use once and discard.
- The cell reaction is not reversible; hence when all the reactants are converted into products, no more electricity is produced.



Example: Leclanche cell

Leclanche Cell (Dry Cell):

- This is a primary cell without fluid component.
- The anode of the cell is a mixture of ammonium chloride, zinc chloride and manganese oxide to which starch is added to make a thick paste.
- The graphite rod which is immersed in the center of the cell acts as cathode.

Cell Reactions:

Anode: $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$

Cathode: $2MnO_{2(s)} + NH_4^+ + H_2O_{(l)} + 2e^- \longrightarrow Mn_2O_{3(s)} + NH_3 + 2OH^-_{(aq)}$

Net reaction: $Zn_{(S)} + 2MnO_{2(s)} + NH_4^+ + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + Mn_2O_{3(S)} + NH_3 + 2OH^-$

- Reaction between NH_4^+(from NH_4Cl) and OH^- formed at cathode evolves NH_3 gas which disrupts the current flow.
- This is prevented by the reaction of NH_3 with Zn^{+2} (from $ZnCl_2$) to form complex $[Zn(NH_3)_2 Cl_2]$.
- The reactions involved in the dry cell cannot be reversed by passing electricity back through the cell. Hence dry cell is a **primary cell**.

Advantages:

- Low price; gives voltage of about 1.5V; normally works without leaking (leak proof cells); possess high energy density; non-toxic; contains no liquid electrolytes.

Applications:

- Dry cell is used in consumer electronic devices like calculators, transistor radios, flash lights, quartz wall clocks, walkman etc. and in small portable appliances where small amount of current is needed.

Secondary cells:

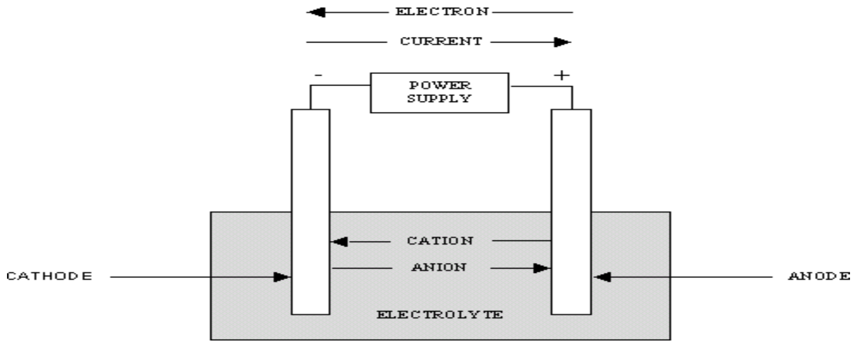
Secondary cell is an electrical battery which can be charged and discharged any number of times.

Eg. Lead acid, Ni-Cd batteries

Lead acid battery:

Construction:

In a electrolytic cell a huge number of lead plates are placed which act as negative electrode or anode and lead oxide plates are placed which acts as positive terminal or cathode. This apparatus is placed in electrolytic solution of H_2SO_4.



Negative plate reaction:

$$Pb(s) + H_2SO_4\,(aq) \rightarrow PbSO_4(s) + 2\,H^+\,(aq) + 2e^-$$

Positive plate reaction:

$$PbO_2(s) + H_2SO_4\,(aq) + 2H^+\,(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$

The total reaction can be written as

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

When the secondary cell is charging it acts like an electrolytic cell, when it is discharging it acts like a voltaic cell.

Applications of lead acid battery:

- Most of the world's lead–acid batteries are automobile starting, lighting and ignition.
- Lead–acid batteries are used in emergency lighting.
- Large lead–acid batteries are also used to power the electric motors in diesel electric submarines when submerged, and are used as emergency power on nuclear submarines as well.

Advantages of lead acid battery:

- Inexpensive and simple to manufacture.
- When used correctly, it is durable and provides dependable service.
- The self-discharge rate is the lowest in rechargeable battery systems.
- Low maintenance requirements, Capable of high discharge rates.

Disadvantages of lead acid battery:

- Cannot be stored in a discharged condition.
- Allows only a limited number of full discharge cycles.
- Low energy density.
- Environmentally unfriendly — the electrolyte and the lead content can cause environmental damage.
- Transportation restrictions on flooded lead acid — there are environmental concerns regarding spillage in case of an accident.

pH metry

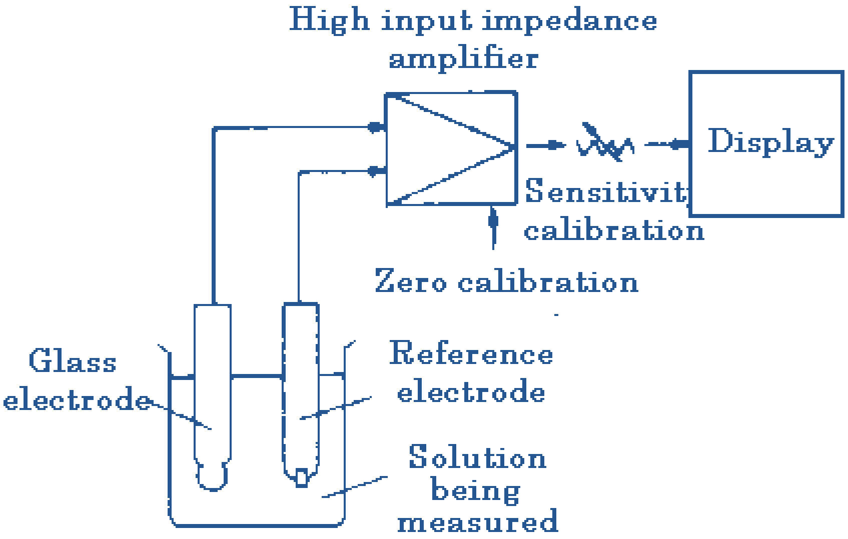
Concept of pH:

It is defined as the measure of acidity or alkalinity of a solution on a logarithmic scale on which 7 is neutral, lower values are more acidic and higher values are more alkaline. The pH is equal to $-\log_{10}[H^+]$, where $[H^+]$ is the hydrogen ion concentration in moles per litre.

pH meter:

A **pH meter** is a scientific instrument used to determine the acidity or alkalinity of a solution. It generally measures the difference in electrical potential between a pH electrode and a reference electrode. The difference in the magnitude of the electrical potential is linearly related to the pH according to the Nernst equation.

A pH meter contains a pH probe that passes the electrical signals to the pH meter and pH meter displays the pH value of the solution. The glass pH probe contains two electrodes, a sensor electrode and a reference electrode. These electrodes are in the form of glass tubes one contains pH 7 buffer and other contains saturated potassium chloride solution. The sensor electrode bulb is made up of porous glass or permeable glass membrane coated with silica and metal salts.



A silver wire coated with silver chloride is immersed in pH 7 buffer in the bulb. On the other hand calomel electrode is used as reference electrode

When the probe is placed in a solution to measure the pH, hydrogen ions accumulate around the bulb and replace the metal ions from the bulb. This exchange of ions generates some electric flow that is captured by the silver wire. The voltage of this electric flow is measured by the pH meter by converting it into pH value by comparing the generated voltage with the reference electrode.

- Increase in acidity of the solution has a greater concentration of hydrogen ions that increases the voltage. This increased voltage decreases the pH reading in pH meter.

- In the same manner, an increase in alkalinity decreases the hydrogen ions or increases in hydroxyl ions concentration also decrease the voltage and increase the pH value in pH meter.

Applications of pH metry:

Acid-Base titrations:

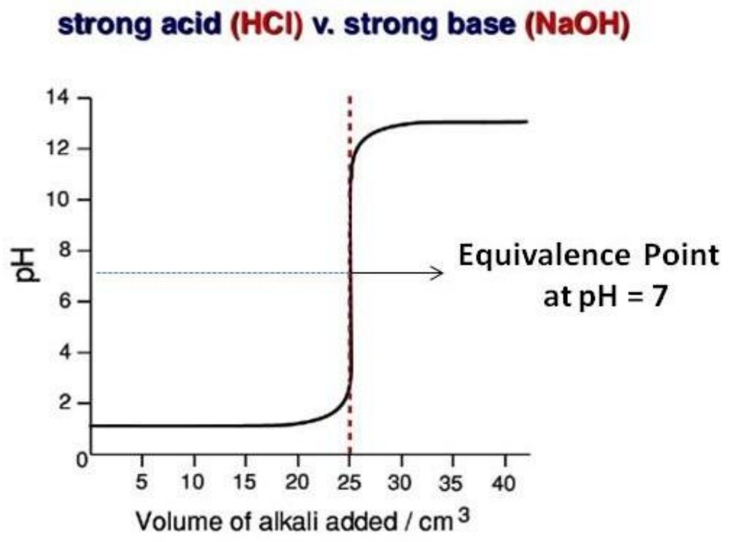
An **acid-base titration** is a method of quantitative analysis for determining the concentration of an **acid** or **base** by exactly neutralizing it with a standard solution of **base** or **acid** having known concentration.

Titration curve:

A titration curve is the plot of the pH of the analyte solution versus the volume of the titrant added as the titration progresses.

1) Titration of a strong acid with a strong base

Consider analyte is hydrochloric acid HCl (strong acid) and the titrant is sodium hydroxide NaOH (strong base). If we start plotting the pH of the analyte against the volume of NaOH that we are adding from the burette, we will get a titration curve as shown below.



- Initially no NaOH was added yet, so the pH of the analyte is low (it predominantly contains H_3O^+ from dissociation of HCl).

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

- As NaOH is added dropwise, H_3O^+ slowly starts getting consumed by OH^- produced by dissociation of NaOH. Analyte is still acidic due to predominance of H_3O^+ ions.

- At equivalence point (halfway up the steep curve), the number of moles of NaOH added = number of moles of HCl in the analyte. At this point, H_3O^+ ions are completely neutralized by OH^- ions. The solution only has salt (NaCl) and water and therefore the pH is neutral i.e. pH = 7.

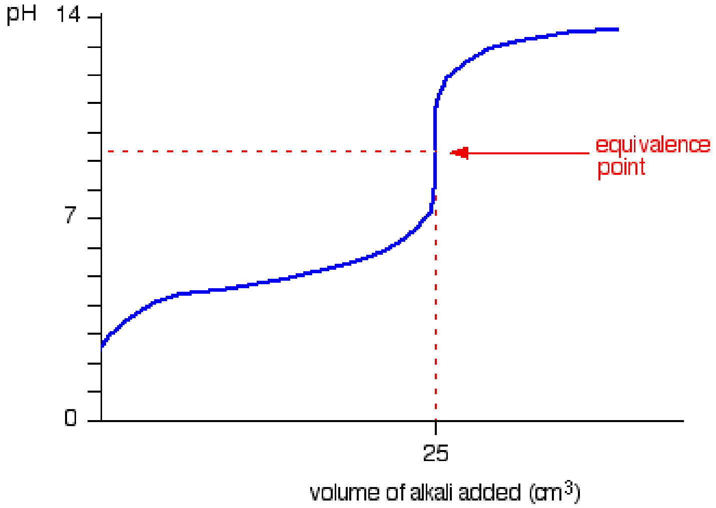
$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NaOH} \xrightarrow{\text{at equivalence point}} \underset{\text{salt}}{NaCl} + H_2O$$

- As the addition of NaOH continues, pH starts becoming basic because HCl has been completely neutralized and now excess of OH^- ions are present in the solution (from dissociation of NaOH).

$$NaOH \xrightarrow{\text{after equivalence point}} Na^+ + OH^-$$

2) Titration of a weak acid with a strong base

Assume our analyte is acetic acid CH_3COOH (weak acid) and the titrant is sodium hydroxide NaOH (strong base). If we start plotting the pH of the analyte against the volume of NaOH that we are adding from the burette, we will get a titration curve as shown below.

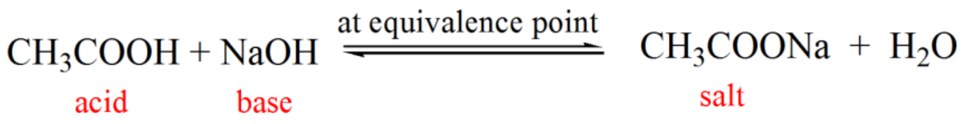


- Initially no NaOH was added yet, so the pH of the analyte is low (it predominantly contains H_3O^+ from dissociation of CH_3COOH). But acetic acid is a weak acid, so the starting pH is higher than what we noticed in the case of a strong acid (HCl).

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

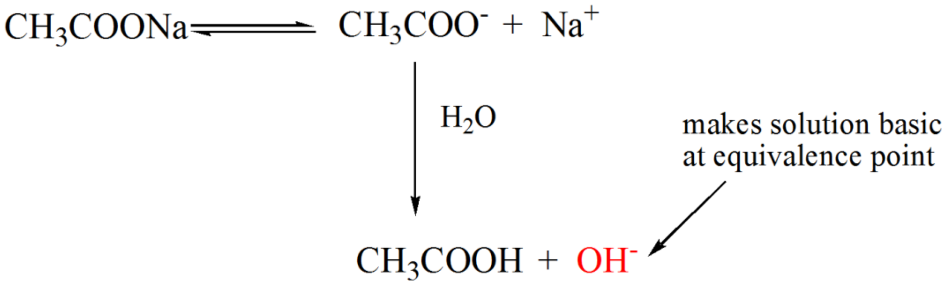
- As NaOH is added dropwise, H_3O^+ slowly starts getting consumed by OH^- (produced by dissociation of NaOH). But analyte is still acidic due to predominance of H_3O^+ ions.

- At equivalence point (halfway up the steep curve), the number of moles of NaOH added = number of moles of CH_3COOH in the analyte. The H_3O^+ ions are completely neutralized by OH^- ions. The solution contains only CH_3COONa salt and H_2O.



$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{NaOH} \xrightleftharpoons{\text{at equivalence point}} \underset{\text{salt}}{CH_3COONa} + H_2O$$

- It is observed that in the case of a weak acid versus strong base, *the pH is not neutral at the equivalence point*. The solution is basic (pH ~ 9) at the equivalence point. It is because at the equivalence point the solution contains CH_3COONa salt which dissociates into acetate ions CH_3COO^- and sodium ions Na^+. As we know that CH_3COO^- is the conjugate base of the weak acid CH_3COOH and so it is relatively a strong base (weak acid CH_3COOH has a strong conjugate base), and will thus react with H_2O to produce hydroxide ions OH- thus increasing the pH to ~ 9 at the equivalence point.



$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$$CH_3COO^- \xrightarrow{H_2O} CH_3COOH + OH^-$$

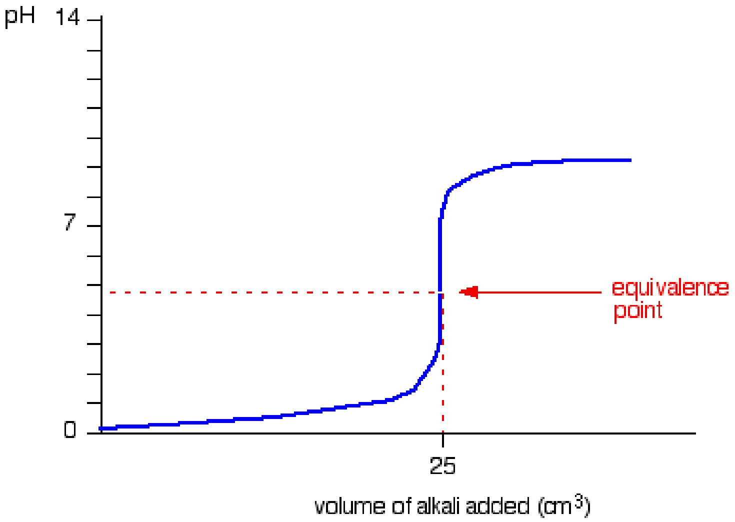
- Beyond the equivalence point (when sodium hydroxide is in excess) the curve is identical as in the case of stong acid-strong base.

3) Titration of a strong acid with a weak base

Suppose our analyte is hydrochloric acid HCl (strong acid) and the titrant is ammonia NH_3 (weak base). If we start plotting the pH of the analyte against the volume of NH_3 that we are adding from the burette we will get a titration curve as shown below.

- Initially no NH_3 was added yet, so the pH of the analyte is low (it predominantly contains H_3O+ from dissociation of HCl).

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$



- As NH_3 is added dropwise, H_3O^+ slowly starts getting consumed by NH_3. Analyte is still acidic due to predominance of H_3O^+ ions.

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

- At the equivalence point (halfway up the steep curve), the number of moles of NH_3 added = number of moles of HCl in the analyte. The H_3O^+ ions are completely neutralized by NH_3.
- It is observed that,in the case of a weak base versus a strong acid, *the* pH *is not neutral at the equivalence point*. The solution is infact acidic (pH ~ 5.5) at the equivalence point. This is because at the equivalence point, the solution only has ammonium ions NH_4^+ and chloride ions Cl^-. But again if you recall, the ammonium ion NH_4^+ is the conjugate acid of the weak base NH_3. So NH_4^+ is a relatively strong acid (weak base NH_3 has a strong conjugate acid), and thus NH_4^+ will react with H_2O to produce hydronium ions making the solution acidic.

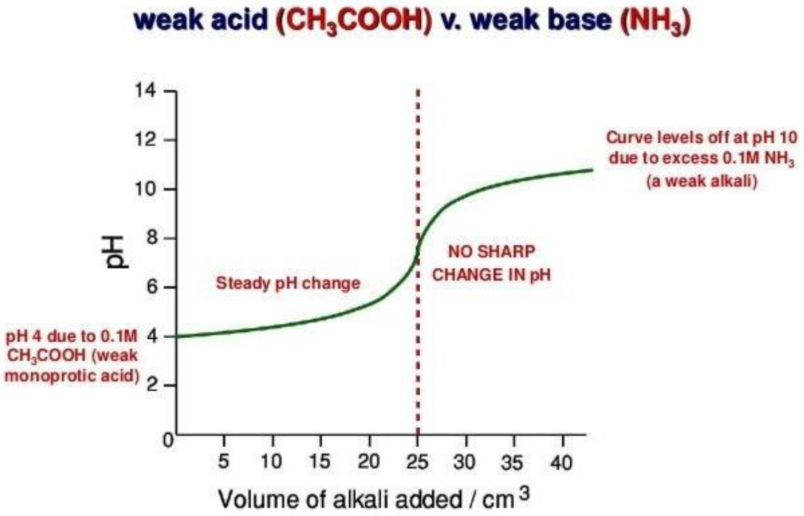
makes solution acidic
at equivalence point

$$NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$$

- After the equivalence point, NH_3 addition continues and is in excess, so the pH increases. NH_3 is a weak base so the pH is above 7, but is lower than what we saw with a strong base NaOH.

4) Titration of a weak base with a weak acid

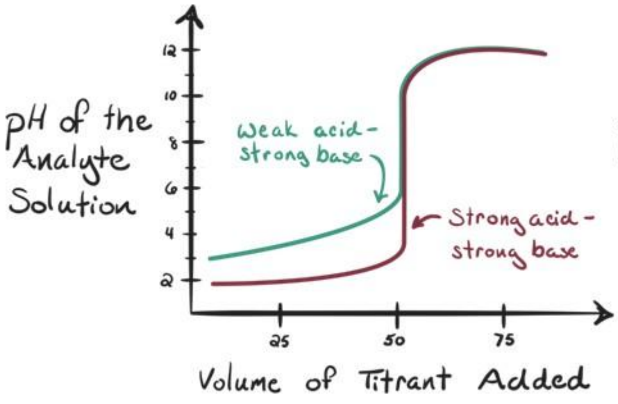
Assume our analyte is NH_3 (weak base) and the titrant is acetic acid CH_3COOH (weak acid). If we start plotting the pH of the analyte against the volume of acetic acid that we are adding from the burette, we will get a titration curve as shown below.



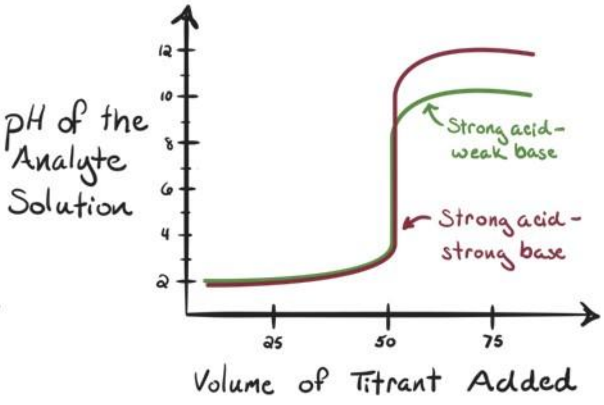
It is noticed that there isn't any steep bit in this plot. There is just what we call a 'point of inflexion' at the equivalence point. Lack of any steep change in pH throughout the titration renders titration of a weak base versus a weak acid difficult, and not much information can be extracted from such a curve.

Comparative Study:

The comparative variations in the pH plots in the case of weak acid or weak base influence with strong acid or strong base is shown below.



Comparative study of
SA-SB vs WA-SB



Comparative study of
SA-SB vs SA-WB

Conductometry

Conductivity:

It is the ability of a metal to conduct electricity when a potential difference (Voltage) is applied. A substance which offers very less resistance to the flow of current allows more current to pass through it and hence the power to conduct electricity is the inverse of resistance.

Resistance is measured in Ohms and Conductivity is measured in ohm^{-1} or Mhos. Internationally recommended unit is *Siemen.*

Conducting Solution:

A solution conducts electricity if there are mobile ions in solution. This solution is referred to as an electrolytic solution. Some ions are more mobile in solution than others:

For eg. $H^+_{(aq)}$ is more mobile than other cations.

$OH^-_{(aq)}$ is more mobile than other anions.

For dilute aqueous solutions at the same concentration and temperature:

- A strong acid conducts electricity well because of the higher concentration of very mobile $H^+_{(aq)}$.
- A weak acid conducts electricity less well because of the lower concentration of very mobile $H^+_{(aq)}$.
- A strong base conducts electricity well because of the higher concentration of very mobile $OH^-_{(aq)}$.
- A weak base conducts electricity less well because of the lower concentration of very mobile $OH^-_{(aq)}$

Acid-Base Conductometric Titrations:

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

We will consider the following types of acid-base conductometric titrations:

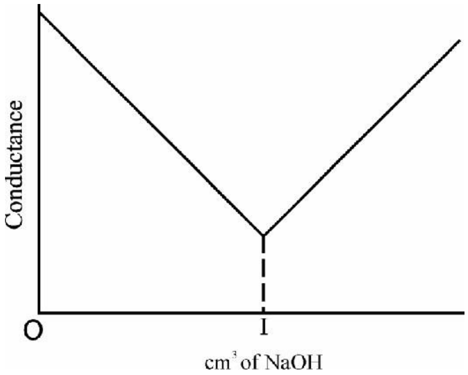
- Strong acid and strong base conductometric titration

- Strong acid and weak base conducotmetric titration
- Weak acid and strong base conductometric titration
- Weak acid and weak base conductometric titration

Some Typical Conductometric Titration Curves are:

1) Strong Acid vs Strong Base, e.g. HCl with NaOH:

- Initially, when NaOH is not added, the conductance is high due to the presence of highly mobile hydrogen ions.
- When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water.
- This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl.
- After the equivalence point, the conductance increases due to the large conductivity of OH^- ions.

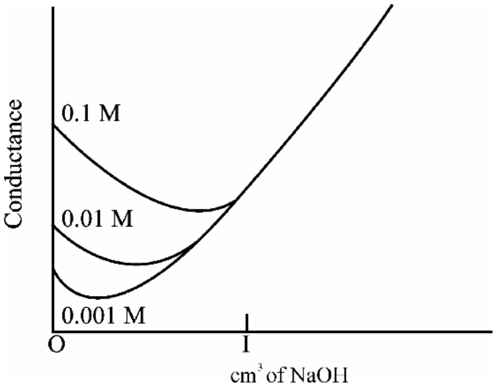


Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

2) Weak Acid vs Strong Base, e.g. acetic acid with NaOH:

- Initially the conductance is low due to the feeble ionization of acetic acid.
- On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate.

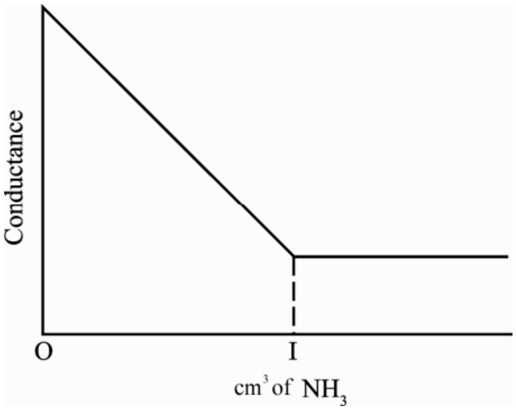
- But very soon, the conductance increases on adding NaOH as NaOH neutralizes the undissociated CH_3COOH to CH_3COONa which is the strong electrolyte.
- This increase in conductance continues raise up to the equivalence point.
- Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions.



Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

3) **Strong Acid vs Weak Base, e.g. sulphuric acid with dilute ammonia**:

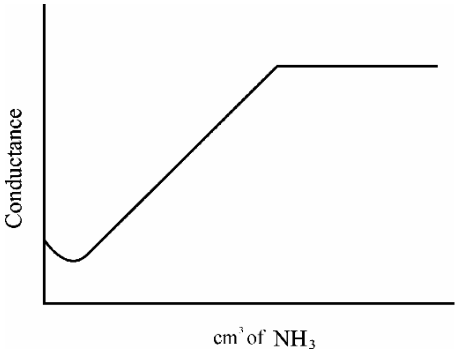
- Initially the conductance is high and then it decreases due to the replacement of H^+.
- But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate



Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_3)

4) Weak Acid vs Weak Base, e.g. acetic acid with dilute ammonia:

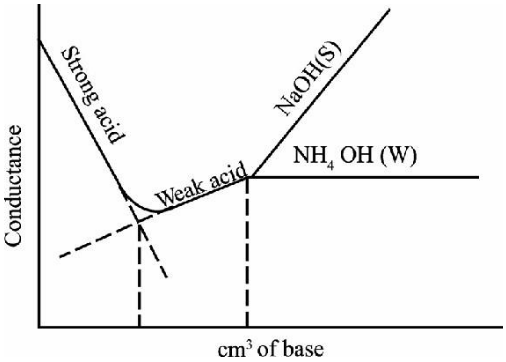
- The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base.
- After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting.



Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH)

5) **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base**:

- In this curve there are two break points.
- The first break point corresponds to the neutralization of strong acid.
- When the strong acid has been completely neutralized only then the weak acid starts neutralizing.
- The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH^- ions in case of a strong base as the titrant.
- However, when the titrant is a weak base, it remains almost constant after the end point.



Conductometric titration of a mixture of a strong acid (HCl) + weak acid (CH_3COOH) vs. a strong base (NaOH) + weak base (NH_4OH)

UNIT – 4 CORROSION

Corrosion is defined as the deterioration of a metal or alloy by chemical or electro chemical reactions with its surrounding environment. Due to corrosion the useful properties of metal like malleability, ductility, electrical conductivity and also the surface appearance are lost. Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulfides, etc. Examples: Rusting of Iron [$Fe_2O_3.xH_2O$].

Causes of corrosion:

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

$$\textbf{Metallic compound} + \textbf{Energy} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \textbf{Metal}$$

Types of corrosion:

1) **Dry corrosion** (or) Chemical corrosion.
2) **Wet corrosion** (or) Electro chemical corrosion.

DRY or CHEMICAL CORROSION

- The deterioration or destruction of the metal in presence of dry atmospheric gases like O_2, CO_2, and H_2S etc in absence of moisture is known as chemical/Dry corrosion.
- Oxygen is the mainly responsible for the corrosion of most metallic substance when compared to other gases and liquid metals.

Dry Corrosion is mainly of three types:

1. Oxidation Corrosion.
2. Corrosion by other gases.
3. Liquid Metal Corrosion.

1. Oxidation Corrosion

Some of the metals directly react with oxygen in the absence of moisture at low or high temperature. All metals react with oxygen at higher temperature except Ag, Au and Pt.

Eg. Rusting of iron.

2. **Corrosion By Other Gases**

If the corrosion of metal is due to other gases like Cl_2, SO_2, H_2S, and NO_2 in dry atmosphere, it is called corrosion by other gases.

Eg. $4Ag + 2H_2S + O_2 \longrightarrow 2Ag_2S + 2H_2O$ (black film)

3. **Liquid Metal Corrosion**

When liquid metal is allowed to flow over solid metal at high temperature. The solid metal is weakened either due to its dissolution into liquid metal into it.

Eg. Liquid sodium used as a coolant in nuclear reactors cause the corrosion of cadmium rods.

Mechanism of Dry Corrosion

- In this corrosion, the metal then gets oxidized to metal ions and the electrons are released reduce oxygen to form oxide ion.
- The metal ion and oxide ion finally combine to form metal oxide (M_2O_n) on the metal surface.

Chemical equation:

$$\begin{array}{lcll} 2M & \longrightarrow & 2M^{n+} + 2\,ne^- & \text{(oxidation)} \\ (n/2)O_2 + 2\,ne^- & \longrightarrow & n\,O^{2-} & \text{(reduction)} \\ \hline 2M + (n/2)O_2 & \longrightarrow & M_2O_n & \text{(metal oxide)} \\ \hline \end{array}$$

The nature of the metal oxide layer plays an important role in determining further corrosion process.

1. **Stable, protective and non-porous oxide:**

   - The formation of oxide film on the metal surface acts as physical barrier between the metal and the environment and prevents further corrosion of metal. E.g. Al, Cr, Cu and W.

2. **Porous and non-protective oxide film:**

   - The formation of a loose, non-homogeneous and porous oxide film permits the oxygen on to metal surface through pores or cracks further corrosion takes place. E.g. Alkali and Alkaline earth metals.

Pilling-Bed worth Rule:

- The protective or non-protective oxide film is determined by the ratio of the volume of metal oxide layer to the volume of the metal consumed. This ratio is known as Pilling-Bedworth ratio.

$$\text{Pilling-Bed worth Ratio} = \frac{\text{Volume of metal oxide formed}}{\text{Volume of metal consumed}}$$

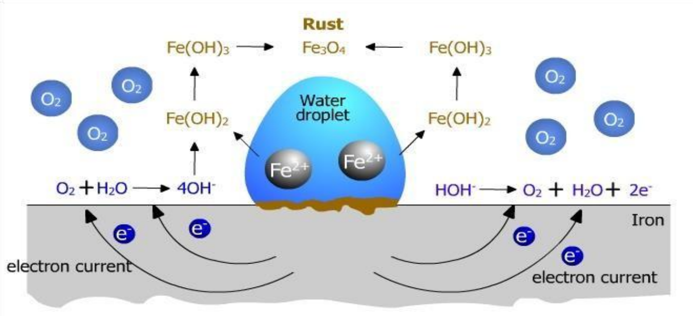
According to Pilling-Bed worth rule,

- If the ratio is less than one the metal oxide layer will be porous and non-protective. E.g. oxide layers of alkali and alkaline earth metals.

- If the ratio is equal or greater than one then the metal oxide layer will be non-porous and protective. E.g. oxide layers of Al, Cr, Cu, and W.

Wet (or) Electro Chemical Corrosion:

- When the metal is in contact with moisture or solution, anode and cathode area will be formed on the metal surface.
- The solution or moisture provide electrolytic medium. At anode metal atom undergo oxidation to produce metal ions.
- The electrons migrate towards the cathode on the metal surface. The reduction reaction takes place at cathode.
- The corrosion product is formed near cathode. The anode suffers metal loss due to continuous dissolution of metal.



Formation of Rust.

Mechanism of Wet Corrosion:

This mechanism is explained two ways: 1. Evolution of Hydrogen gas (H_2)
2. Absorption of Oxygen (O_2).

1. Evolution of Hydrogen gas (H_2).

In the absence of oxygen and acidic medium metal oxidation takes place at anodic area and evolution of hydrogen gas takes place at Cathodic area.

Chemical reaction:

$$\text{Anode:} \quad Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{(oxidation)}$$

$$\text{Cathode:} \quad 2H^+ + 2e^- \longrightarrow H_2 \quad \text{(reduction)}$$

$$\text{Net reaction:} \quad Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$$

1. Absorption of Oxygen (O_2)

This is type of corrosion takes place in neutral or alkaline medium in the presence of oxygen. The Fe^{2+} ions produced at anode migrate towards the cathode through moisture and react with OH^- to form $Fe(OH)_2$. Further oxidation $Fe_2O_3.H_2O$ is formed.

Chemical reaction:

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

Cathode: $H_2O + O_2 + 2e^- \longrightarrow 2OH^-$ (reduction)

Net reaction: $Fe + H_2O + O_2 \longrightarrow Fe(OH)_2$

Differences between Dry and Wet Corrosion:

Dry or Chemical corrosion	Wet or Electrochemical corrosion.
1. It takes place at dry conditions.	1. It takes place in wet condition.
2. It involves direct chemical attack of environment on the metal.	2. It involves the formation of large number of galvanic cells.
3. It can take place on homo and heterogeneous surfaces.	3. It can takes place only on heterogeneous surface
4. Corrosion product accumulated at the same spot where corrosion has occurred.	4. corrosion product accumulated at cathode where corrosion occurs at anode.
5. Uniform corrosion takes place.	5. Non uniform corrosion takes place.

Note:

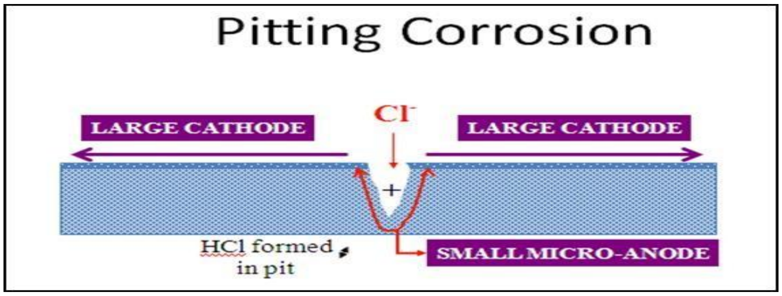
- The corrosion of the metal at anode is directly proportional to the ratio of areas of the cathodic to anodic parts.
- When a larger cathode area and a smaller anode area, severe corrosion is takes place.
- When a smaller cathode area and a larger anode area less corrosion takes place.

TYPES OF CORROSION

1. PITTING CORROSION

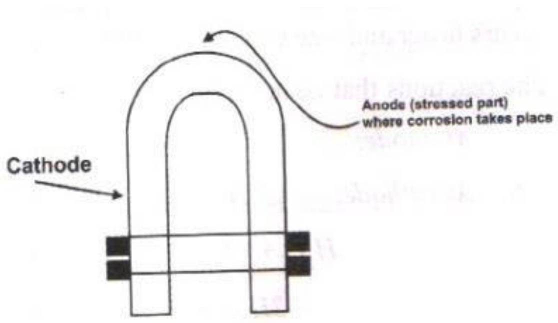
- Pitting corrosion is a localised form of corrosion due to breakdown of a protective layer or dirt on the metal surface.
- The portion of a metal covered by water or other particles is less aerated and acts as anode.
- The other portion of metal exposed to more oxygen of the environment acts as a cathode.

- Corrosion takes place at a portion below dust and a small pit is formed. Then the rate of corrosion increases due to small anodic area and large cathodic area.



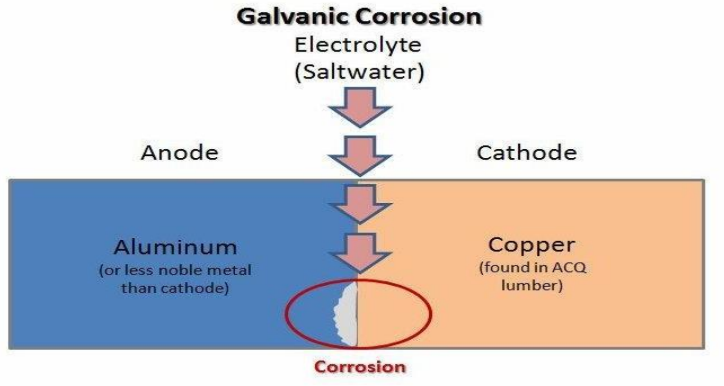
2. STRESS CORROSION

- Stress Corrosion is seen in metals suffering from stress which may result from mechanical operations such as design reverting, cold working, welding , bending, pressing, quenching etc.
- In a corrosive environment the stressed portion acts as anode and undergoes corrosion. The other unstressed part of the metal acts a cathode. *Ex***:** caustic embrittlement in boilers.



3. GALVANIC CORROSION

- This type of corrosion occurs when two different metals are in contact with each other due to the formation of galvanic cell.
- The metal having less standard reduction potential value act as anode it undergoes oxidation and liberates electrons, which migrates to cathode.



- The other metal having high standard reduction potential value acts as cathode and reduction reaction takes place on its surface forming OH^- ions.
- The rate of corrosion depends on potential difference between two metals.
- If the difference is more, corrosion occurs faster and vice versa.
- The anodic metal undergoes corrosion and cathodic metal is unaffected.

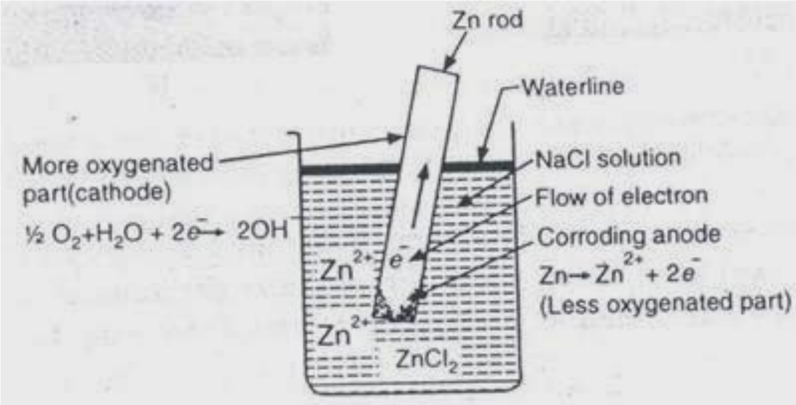
At anode: $M \longrightarrow M^+ + ne^-$ (oxidation reaction)

At cathode: $2H^+ + 2e^- \longrightarrow H_2$ (reduction reaction)

Example: zinc metal in contact with copper metal, brass tap in contact with iron pipe etc.

4. DIFFERENTIAL AERATION CORROSION (WATER LINE CORROSION)

- This type of corrosion occurs when a metal is exposed to different concentration of oxygen.
- The part of metal which is more exposed to air acts as cathode.
- The other part of the metal, which is less exposed to air acts as anode and undergoes corrosion.



Differential aeration corrosion

- It is differential aeration type of corrosion observed in water storage tanks, ships etc.
- During water line corrosion, the part of the metal below water line is exposed to less oxygen concentration acts as anode and undergoes corrosion.
- The other part which is more exposed to atmospheric oxygen acts as cathode.

Cathodic protection:

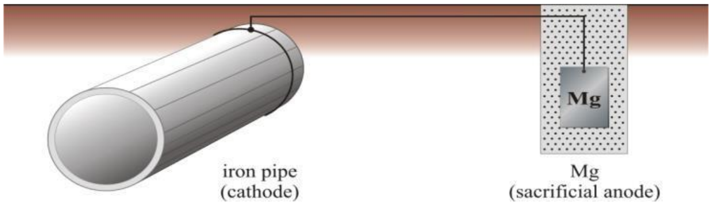
In this method the metal to be protected is forced to act as cathode and corrosion is controlled.

This is two ways

a) Sacrificial anodic protection.
b) Impressed current method.

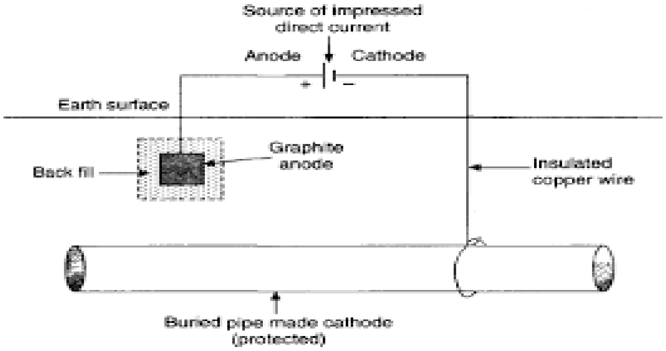
a) Sacrificial anodic protection:

- In this method the metal to be protected is connected by a wire to a more anodic or reactive metal.
- During corrosion more anodic metal gets corroded while the base metal (cathode) is protected.
- The more active metal used is known as sacrificial anode. This metal replaces time to time by fresh one.
- The most active metals commonly used Mg and Zn.



b) Impressed current method:

- In this method, the metallic object to be protected is made cathode by connecting it with the negative terminal of the D.C source.
- The positive terminal is connected to an anode like graphite or platinum.
- The impressed current nullifies the corrosion current.
- The electrons flow to the metallic object as a result it act as cathode and is protected.



Corrosion inhibitors:

Corrosion inhibitors are the chemical substances which reduce the corrosion rate when added in small amounts to the corrosive environment.

These are of two types

a) Anodic inhibitors

b) Cathodic inhibitors

a) Anodic inhibitors

These substances when added in small amounts suppress the anodic reactions and protect against corrosion.

E.g. molybdates, phosphates and chromates.

b) Cathodic inhibitors

These substances when added in small amounts get absorbed on to the cathodic surface and prevent the reduction reactions there by prevent corrosion.

E.g. organic inhibitors like amines and mercaptans.

Protective coatings:

The coating on the metal surface acts as a physical barrier between the metal and corrosive environment and prevent the corrosion to protect the metal. The protective coating can be of two types:

a) **Metallic coating**
b) **Organic coating**

Metallic coating:

Metallic coatings are produced by coating one metal on the surface of another metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Metallic coatings broadly classified into two types.

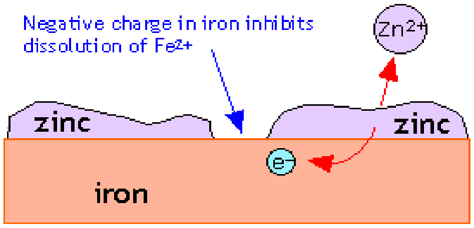
1. Anodic coatings
2. Cathodic coatings

Anodic coating:

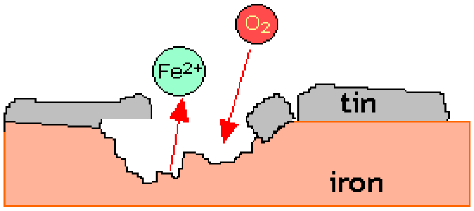
This type of coatings is produced by coating metal used as anodic metal on the surface of the base metal. Ex: coating of Zn, Al and Cd on Fe are anodic, because their reduction potentials are lower than that of base metal iron. If any pores or breaks in metallic coating, exposing the base metal, a galvanic cell is formed between coating metal and base metal, where the coating metal dissolves anodically and the base metal is protected.

Cathodic coating:

Cathodic coatings are obtained by coating a more noble metal (higher reduction potential) than the base metal. The coating metal has higher reduction potential than the base metal and protects the base metal due to their higher corrosion resistance than the base metal. Ex: Coating of tin (Sn) on the surface of iron. Cathodic coating provides effective protection to the base metal. If any pores or cracks formed in the cathodic coating more corrosion takes place to the base metal, because of small anode and large cathode area.



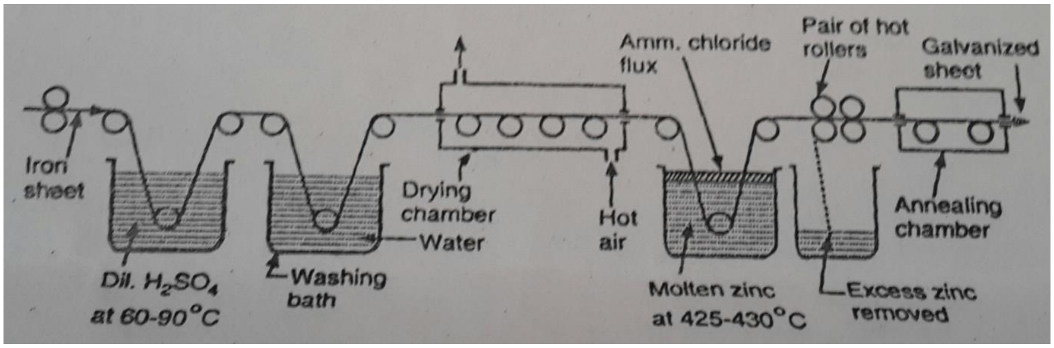
Sacrificial coating



Noble coating

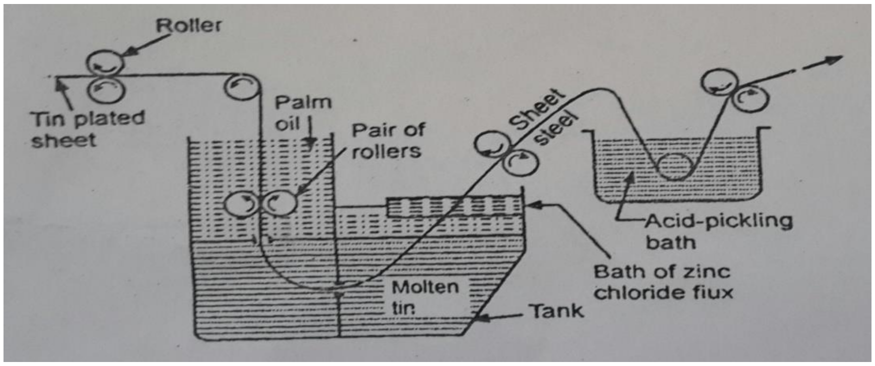
Galvanising:

- It is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting.
- The process is carried out as follows:
- The iron or steel article is first cleaned by pickling with dilute sulphuric acid solution for 15-20 minutes at 60 - 90^0C.
- This treatment also removes any scale, rust and impurities. The article is then washed well and dried.
- It is then dipped in bath of molten zinc, maintained at $425\text{-}430^0$C. The surface of the bath is kept covered with a flux (NH_4Cl) to prevent oxide formation.
- When the article is taken out, it is found to have been coated with a thin layer of zinc. It is then passed through a pair of hot rollers.
- This process removes excess of zinc and produces a thin film of uniform thickness.
- Then it is annealed at a temperature of 650^0C and finally cooled slowly.



Tinning:

- The process of coating tin over the iron or steel articles.
- The process consists in first treating steel sheet in dilute sulphuric acid to remove any oxide film. After this it is passed through a bath of zinc chloride flux.
- The flux helps the molten metal to adhere to the metal sheet. Next, the sheet passes through a tank of molten tin and finally through a series of rollers from underneath the surface of a layer of palm oil which protects the hot tin coated surface against oxidation.
- The rollers remove any excess of tin and produce a thin film of uniform thickness on the steel sheet.



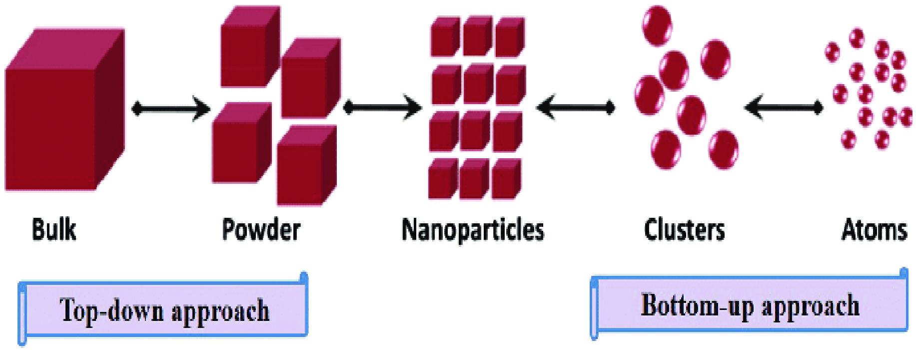
UNIT - 5

Chemistry of Advanced Engineering Materials Nanomaterials

Nanomaterials are the materials having components within the size less than 100nm at least in one dimension. They may be in the form of particles, tubes, rods or fibers. These are developed to exhibit novel characteristics compared to the same material with bulk features, such as increased strength, chemical reactivity or conductivity, catalytic activity, magnetic properties etc.

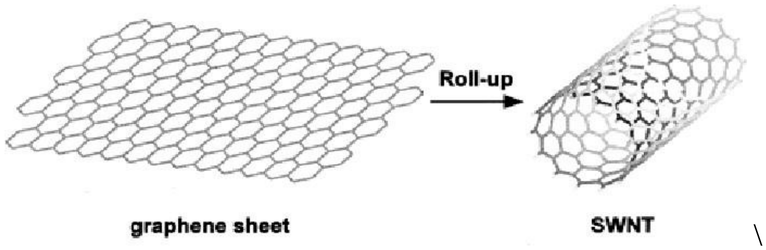
General Methods of Preparation: There are basically two major types of approach for the preparation of nanomaterials.

1. **Top – down approach:** In this method bulk materials are converted to powder and then to nanoparticles by making use of lithographic methods. This method is used in the microelectronic industry.
2. **Bottom – up approach:** In this method very small particles like individual molecules or atoms are assembled to get clusters which in turn are aggregated to get nanoparticles. This method is used to prepare a new class of nanomaterials.



CARBON NANOTUBES (CNTs)

- Carbon nano tubes are long, thin cylinders of carbon and were discovered in 1991 by **S. Iijima**.
- These are large macro molecules that are unique for their size, shape and remarkable physical properties.
- Carbon nanotubes are allotrope of carbon with nano structure.



- They are considered as a sheet of graphite rolled into a cylinder thus carbon tubes are extended tubes of rolled graphite sheets.
- Nano tubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nano tubes.

TYPES OF CARBON NANO TUBES (CNTs):

- Carbon nanotubes are lattice of carbon atoms, having each carbon is covalently bonded to three other carbon atoms.
- Depending upon the way of arrangement, they are two types of CNTs.
  1. Single Walled Nano Tubes (SWNT).

  2. Multi Walled Nano Tubes (MWNT).

SINGLE WALLED NANOTUBES: Single walled nanotubes have a diameter of close to 1nm and length is many million times of longer. The structure of single walled nano tubes obtained by wrapping a one atom thick layer of graphite called graphene into a seamless cylinder.

- There are three types of SWNTS based on the way the graphene sheet is wrapped. Graphene sheet is represented by a pair of indices (n, m) called the chiral vector.
- If m=0, the nano tubes are called "**zig-zag**". The lines of carbon bonds are down the centre.
- If n=m, the nanotubes are called "**armchair**". The lines of hexagons are parallel to the axis of the nanotubes.
- Other than two functions they are called **chiral**. It has a twist or spiral around the nanotubes.

MULTI-WALLED NANOTUBES (MWNT): Multi walled nano tubes consist of multiple rolled layers of graphite. The interlayer distance in multi walled nanotubes is close to the distance between graphene layers in graphite is 3.3A^{o}.

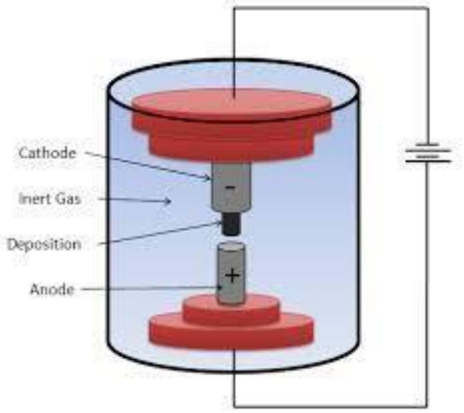
- It exhibit both metallic and semi conducting properties. There are two models which can be used to describe the structures of multi walled nano tube.
- In the Russian doll model, sheets of graphite are arranged in concentric cylinders.
- In the parchment model looks like a rolled news paper.

SYNTHESIS OF CARBON NANO TUBES: The following are methods to produce carbon nano tubes.

- Arc discharge method.
- Laser ablation method.
- Chemical vapour deposition (CVD).

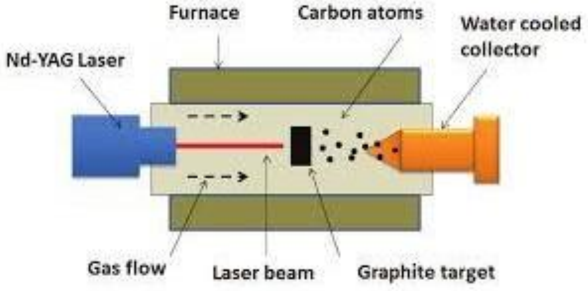
ARC DISCHARGE:-

- This method creates carbon nano tubes through arc vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas at low pressure.
- A direct current of 50 to 100A driven by approximately 20v creates a high temperature discharge between the two electrodes this discharge vaporizes one of carbon rods and forms a small rod shaped deposit on the other rod.



LASER ABLATION:-

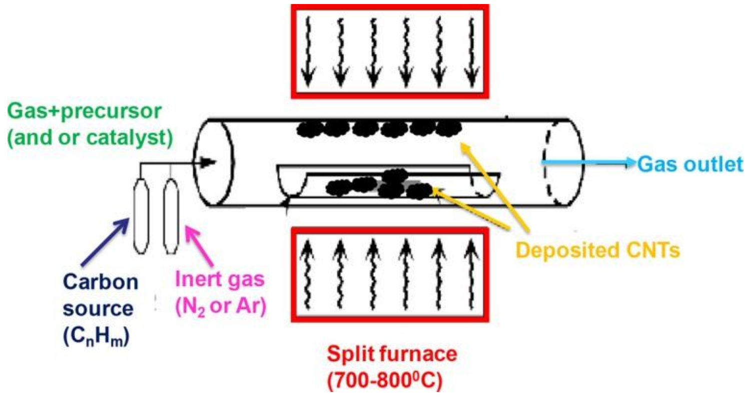
- A pulsed or continuous laser is used to vaporise graphite target in oven at 1200^{o}C.



- The oven filled with inert gas in order to keep pressure and also contains graphite target.
- When high intense laser beam strikes the graphite target, vaporization of graphite takes place.
- A very hot fume of graphite formed then expands, and cools rapidly. As the vaporized species cool, small carbon molecules and atoms quickly condense to form larger clusters like fullerenes and SWNT etc.

CHEMICAL VAPOUR DEPOSITION (CVD):-

- In this method a carbon source like methane and acetylene used as in the gas phase and an energy source need to transfer energy to a gaseous carbon molecule.
- The energy source is used to crack the molecule into reactive atomic carbon.



- It is two step processes in 1st step catalyst preparation step generally transitions metals used as supported catalyst in second step chemical etching or thermal annealing takes place, in case of chemical etching NH_3 used as etchant or 650-900^{O}C temperature should maintain in thermal annealing process.

PROPERTIES OF CARBON NANOTUBES (NANO MATERIALS)

Mechanical Properties:

1. **Strength:**

- The strength of the sp^2 carbon-carbon bond gives carbon nanotubes amazing mechanical properties.
- Carbon nano tubes are the strongest and stiffest materials in terms of tensile strength and elastic modulus respectively.
- This type of strength results from the covalent sp^2 bonds formed between the individual atoms.

2. **Hardness:**

- During synthesis of carbon nano tube of super hard material by compressing above 24 GPa at room temperature.

- The hardness of this material was measured with a nano-indenter.

3. **Electrical Properties:** Carbon nano tube can be metallic or semi conducting depending on their structure.

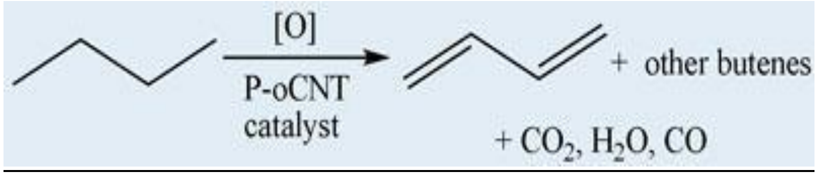
Engineering Application of Carbon Nano Tubes

1. In Fuel Cells:

- Hydrogen can be stored in the carbon nano tubes, which is turn used for the fuel cells. SWNT more effective in this case.
- Carbon nano tubes replace platinum as the catalyst in the fuel cells. They are resistant to corrosion

2. In Catalysis:

- A catalyst having CNTs makes a reaction milder, safer and more selective.
- Oxidized CNTs with phosphorous added are selective catalysts for the oxidative dehydrogenation of butane to butadiene.



3. In Medicine:

- Carbon nano tubes are being highly used in the fields of efficient drug delivery.

Used as drug delivery of cancer cells. It attacks only at cancer spots does not harm healthy cells and significantly reduces side effects.

FULLERENES:

Fullerenes are a family of carbon allotropes, molecules entirely composed of carbon, in the form of hollow, sphere, ellipsoid, tube or plane.

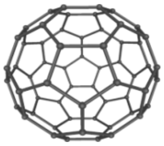
Fullerenes are following types

1. Spherical Fullerenes.
2. Cylindrical Fullerenes.
3. Planar Fullerenes.

Spherical Fullerenes: They look like a soccer ball, often called Bucky balls.
Cylindrical Fullerenes: These are called carbon nanotubes.
Planar Fullerenes: Graphene is an example of planar fullerene sheet.

Structure:

- Fullerenes are a class of closed-cage carbon molecule containing 12 pentagons and variable number of hexagons.
- C_{60} is a spherical crystal of carbon atoms with an arrangement of even number of sp^2 atoms over the surface of closed hollow cage.



Structure of C_{60}

- The C_{60} molecule has truncated icosahedrons structure.
- An icosahedrons is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal.
- A carbon atom is present at each vertex the valences of each carbon atom satisfied by two single and one double bond.

Properties:

- It is mustard colored solid.
- C_{60} is poor conductor of electricity. When fullerenes reacts with good electron donors like alkali metals, its conductivity increases.
- It is moderately soluble in the common organic solvents, especially in aromatic hydrocarbons.
- It is very tough and high tensile strength.
- It can be compressed to lose 30% of its volume without destroying its cage structure.
- It is thermally stable up to 600°C.

Super Conducting Fullerenes:

- C_{60} is poor conductor of electricity. When fullerenes reacts with good electron donors like alkali metals, its conductivity increases. Alkali fullerenes are such as **K_3 C_{60}** are super conducting.

Engineering Application of Fullerenes:

- Fullerenes can easily accept electrons; therefore they may be used as charge carrier in batteries.
- Alkali metal fullerides are superconductors. Eg. K_3C_{60}
- Its spherical structure makes it suitable for the use as lubricant.
- Researchers have found that water soluble derivatives of fullerenes inhibit the HIV-I protease and therefore useful in fighting the HIV that leads to AIDS.
- Fullerenes are powerful oxidants.

Composite Materials:

Composites may be defined as multiphase materials consisting of two/more distinct phases with an interface separating them. The properties of composites are different from those of the parent materials such as higher specific strength and stiffness, higher tensile strength, thermal expansion and electrical conductivity, low-cost easy fabrication, better corrosion resistance, toughness, impact and thermal shock resistance, etc.

Composites in general consist of two phases: Matrix phase and Dispersed phase.

Matrix phase: It is the continuous body constituent that encloses the composite and gives it its bulk form.

Dispersed phase: It is the structural constituent that determines the internal structure of a composite.

The surface forming the common boundary between these two phases is known as ***interphase***.

These materials find their applications in automobile industries, turbine engines, valves, pump parts, spray nozzles, wire drawing dies, fabrication of roof and floors, furniture, sport goods, high speed machinery, components of rockets, aircrafts, electronic circuit boards, etc.

Fiber Reinforced Polymeric composites (FRP):

- The combination of polymeric substances with the solid fillers is called Reinforced plastics.
- The fillers act as reinforcing materials.
- The polymer links the filler particles through a binding agent.
- The fibers are used in the form of continuous lengths, staples or whiskers.
- The reinforced fiber may be natural or synthetic, organic/inorganic polymers such as jute, asbestos, nylon, glass, carbon and aramid.
- The two components are fiber and resin combined in a suitable manner by two processes.
    1. Laminating processing
    2. Moulding processing.

Properties:

- They are light weight and highly strong.
- They have high impact strength and not easily corroded.
- They have good thermal stability.

Applications:

- These are used in electrical and electronic industries for making exhaust fans, computer tapes, insulators, and switch gear parts.
- These are used in automobiles for making door handles, battery cases and engine cooling fans.
- These are also used in air craft, space vehicles and military goods.

Carbon fiber reinforced polymeric composites (CFRP):

- The combination of polymeric (matrix) substance with carbon fiber is called **CFRP**.
- They have high stiffness and good strength.
- Many polymeric substances like thermoplastics and thermo settings are suitable for combination with carbon fibers.
- In thermo setting resins, polyester, phenolic and vinyl resins are used.
- In case of thermo plastics polyamine, polycarbonate and poly sulfonates are used.

Properties:

- They have high stiffness and good strength.
- They have good mechanical properties.
- They have low thermal expansions.

Uses:

- These are used in structural constructions.
- These are used in space vehicles and satellites.
- These are also used as sports equipments.

Glass fiber reinforced polymeric composites (GFRP):

- The combinations of polymeric (matrix) substance with glass fibers are called **GFRP.**
- The glass is drawn into threads in the foam of filaments fine than cotton or silk thread.
- The filaments are woven in the foam of mat, the fiber materials is suitable bonded with plastic materials to be rein forced.
- The common plastics are polyester, vinyl derivatives, polyamines and epoxy resins.

Properties:

- They have high tensile strength, excellent chemical and corrosion resistance.

Uses:

- These are used to prepare automotive parts and storage tanks.
- It is used for making industrial floorings and plastic pipes.
- It is used for making transport vehicles to reduce vehicle weight and boost fuel efficiency.

Aramid Plastic:

The combinations of polymeric (matrix) substance with aramid fibers are called **Aramid plastics.**

Bio degradable polymers

- Polymers that undergo degradation by the enzymatic action of microorganisms and bacteria are called as bio degradable polymers.
- These agents lead to breaking of chemical structures of polymers resulting changes in the properties of polymers and structural modifications.
- Biodegradation is chemical breakdown of materials by physiological environment (exposure to moisture, heat, oxygen, ozone).
  Eg: Polyhydroxy alkanoates (PHA) **BIPOL**, polylactic acid **PLA**, polyvinylacetate **PVA**, **MATER BI**

Biodegradable plastics are two types.

1. Hydro Biodegradable Plastics (H.B.P)
2. Oxygen Biodegradable Plastics (O.B.P)

Hydro Biodegradable Plastics (H.B.P):

- These plastics undergo chemical degradation by hydrolysis.
- These tend to degrade more than O.B.P can be made from agriculture resources such as sugar cane and wheat etc.
- These plastics can be converted in to CO_2, H_2O and bio mass.

Oxygen Biodegradable Plastics (O.B.P):

- These plastics undergo chemical degradation by oxidation.
- These can be made from products of oil or natural gas and also converted into CO_2, H_2O and bio mass.

Basic requirements of biodegradable polymers:

- production of non toxic products.
- capable of maintaining good mechanical integrity until degradation
- controlled rates of degradation.

Factors controlling the rate of degradation:

- percentage of the crystallinity of the polymer
- molecular weight of the polymer
- hydrophobicity of the polymer
- environment surrounding the polymer

Applications:

- These are used in the field of medicine for making capsules and orthopedic devices.
- Polyesters compounds are used as safety belts and tents.

- PET bottles are used in cool drinks and fruit juices.

Green Chemistry

One of the most important new aspects of chemistry is the development of Green Chemistry. Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
Green Chemistry is based on **Twelve Principles**.

1. **Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy:** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals:** Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency:** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstock's:** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives:** Unnecessary derivatization should be minimized.
9. **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into safe degradation.
11. **Real-time analysis for Pollution Prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

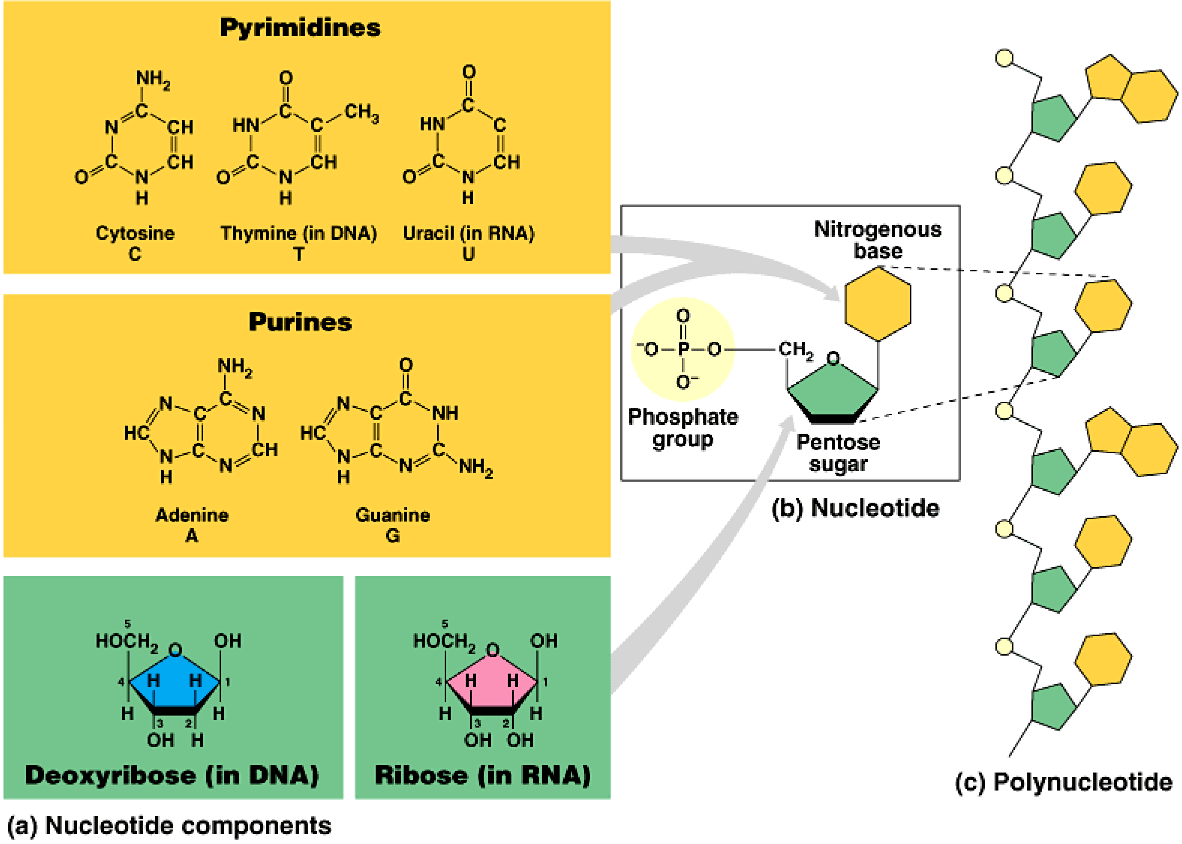
"The chemist can choose the reaction with proper foresight and planning that are economically sound, environmentally compatible and socially acceptable, which makes it a green reaction."

Nucleic Acids

The particles in nucleus of a cell which are responsible for heredity, are called as Chromosomes. These are made up of proteins and another type of biomolecules called ***Nucleic Acids***. Nucleic acids are mainly of two types, the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Since nucleic acids are long chain polymers of nucleotides, they are also called polynucleotides.

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecule, it is β-D-ribose.

DNA contains two sets (family of pyrimidines & purines) of four bases *viz.,* adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases; the first three bases are same as in DNA but the fourth one is uracil (U).



(a) Nucleotide components

(b) Nucleotide

(c) Polynucleotide

Structure of Nucleic Acids:

A unit formed by the attachment of a base to 1′ position of sugar is known as nucleoside. In nucleosides, the sugar carbons are numbered as 1′, 2′, 3′, etc. in order to distinguish these from the bases. When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide. These are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.

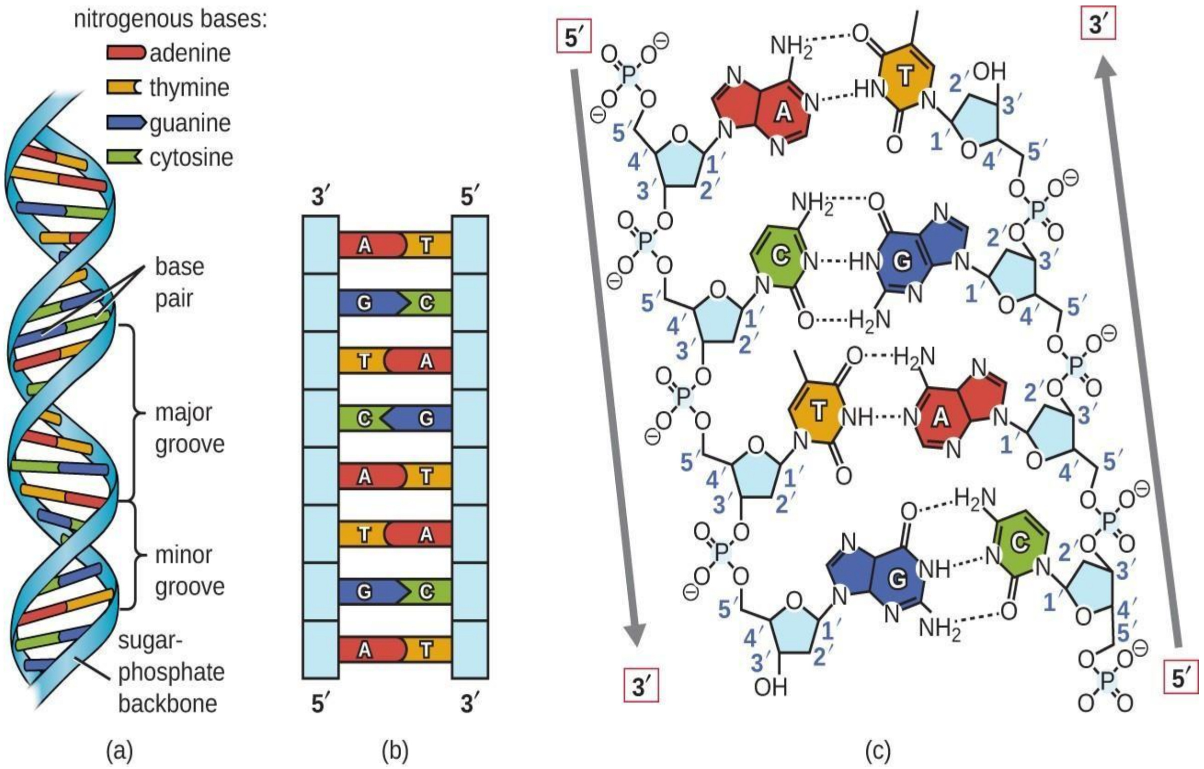
Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA single stranded helix is present which sometimes folds back on itself.

Structure of DNA (Deoxyribonucleic acid):

DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. It is exclusively responsible for maintaining the identity of different species of organisms over millions of years.

DNA is made up of nucleotides which contain nitrogenous group, a phosphate group, and a sugar group.



The order of the nitrogenous bases – thymine(T), guanine(G), cytosine(C), and adenine(A), is crucial in determining the genetic code.

The nucleotides are linked together *via* phosphodiester linkages resulting in the formation of two long strands which spiral to produce a structure known as the double-helix which resembles that of a ladder wherein the sugar and phosphate molecules form the sides while the rungs are formed by the bases.

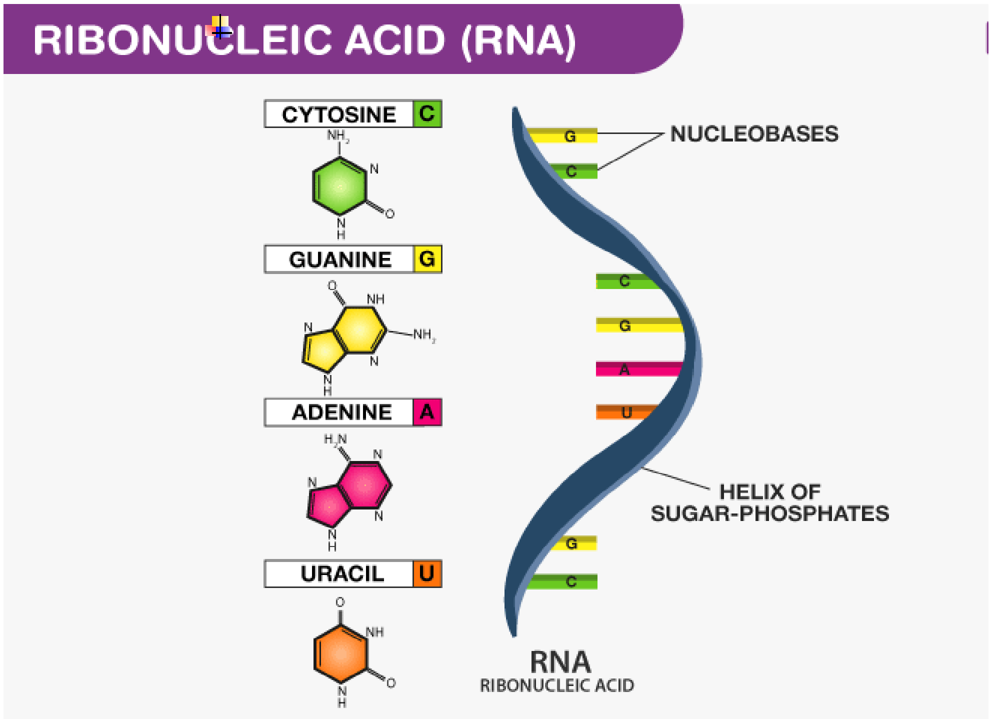
- The bases located on one strand pair up with the bases on the other strand, like **guanine** bases pair up with **cytosine (G-C)** bases and **adenine** bases pair up with **thymine (A-T)** bases following Complementary base pair theory.

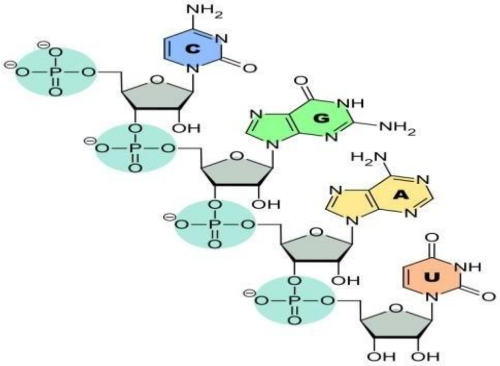
Based upon the salt concentration and humidity levels, these DNA moieties are classified into **A-DNA, B-DNA, C-DNA, D-DNA, Z-DNA** having variations in the number of base pairs and specifications.

Structure of RNA (Ribonucleic acid):

Ribonucleic acid (RNA) is a nucleic acid which is directly involved in protein synthesis. Ribonucleic acid is an important nucleotide with long chains of nucleic acid present in all living cells. Its main role is to act as a messenger conveying instructions from DNA for controlling the proteins synthesis.

RNA connects the sugar ribose, phosphates, and the nitrogenous bases adenine (A), guanine (G), cytosine (C), and uracil (U) through phosphodiester linkages.





- DNA and RNA share the nitrogenous bases A, G, and C. Thymine is usually only present in DNA and uracil is usually only present in RNA.

- Based on the type of genes, the RNA moieties are classified into **tRNA, mRNA, rRNA**

  and **snRNA**.

- Unlike DNA, RNA in biological cells is predominantly a single-stranded molecule. While DNA contains *deoxyribose,* RNA contains *ribose*, characterized by the presence of the 2′-hydroxyl group on the pentose ring. This hydroxyl group make RNA less stable than DNA because it is more susceptible to hydrolysis.

- Only 1 strand of DNA is transcribed which is why RNA is single stranded. DNA has a template strand and a coding strand. RNA is transcribed from the template strand and is complementary to this strand. The RNA transcript is identical to the coding strand except the RNA transcript has uracil bases where the DNA coding strand has thymine bases.