CHEMISTRY (EEE,ECE & CSE)
UNIT-1
STRUCTURE AND BONDING MODELS

1. Derive Schrodinger's wave equation for particle present in one dimensional box?

Schrödinger Equation is a mathematical expression which describes the change of a physical quantity over time in which the quantum effects like wave-particle duality are significant. The Schrödinger Equation has two forms: the time-dependent Schrödinger Equation and the time-independent Schrödinger Equation. The time-dependent Schrödinger Wave Equation derivation is provided here so that students can learn the concept more effectively.

The time-independent Schrödinger wave equation for a single non-relativistic particle, such as an electron, is as follows:

$H\Psi = E\Psi$

Where:

H is the Hamiltonian operator, representing the total energy of the system.

Ψ (Psi) is the wave function, which is a mathematical function that describes the quantum state of the particle.

E is the energy eigenvalue associated with the wave function Ψ.

The Hamiltonian operator (H) is defined as the sum of the kinetic energy operator (T) and the potential energy operator (V):

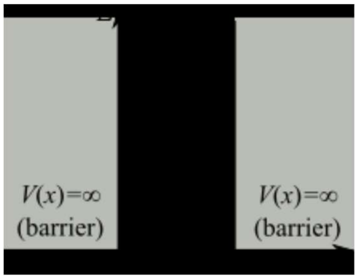
$H = T + V$

Where,

T represents the kinetic energy of the particle and is usually expressed in terms of the momentum operator (p).

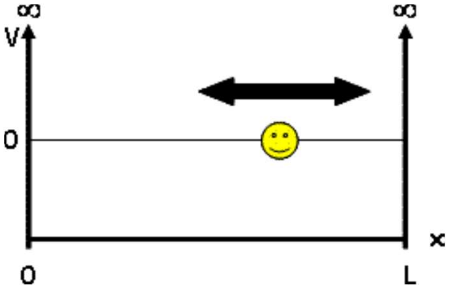
V represents the potential energy of the particle, which depends on its interaction with external forces and other particles.

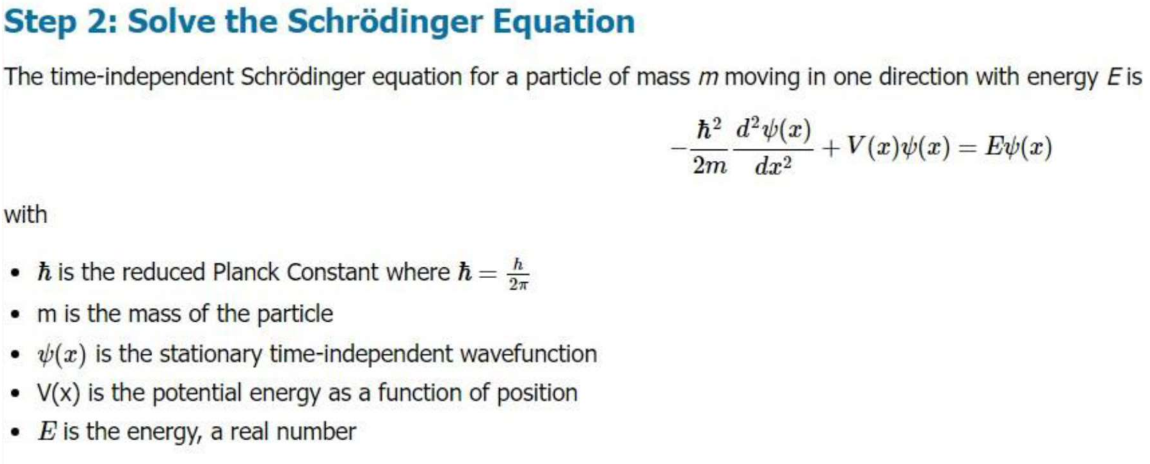
Particle in one dimensional box:



Step 1: Define the Potential Energy V:

The potential energy is *0 inside the box* (V=0 for 0<x<L) and *goes to infinity at the walls of the box* (V=∞ for x<0 or x>L). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these boundary conditions when solving the Schrödinger Equation.





Step 2: Solve the Schrödinger Equation

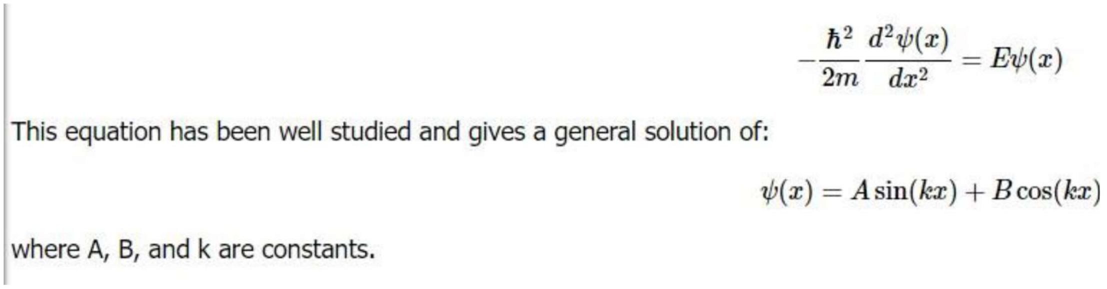
The time-independent Schrödinger equation for a particle of mass *m* moving in one direction with energy *E* is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

with

- $\hbar$ is the reduced Planck Constant where $\hbar=\frac{h}{2\pi}$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- V(x) is the potential energy as a function of position
- E is the energy, a real number

This equation can be modified for a particle of mass *m* free to move parallel to the x-axis with zero potential energy (V = 0 everywhere) resulting in the quantum mechanical description of free motion in one dimension:



$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

This equation has been well studied and gives a general solution of:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

where A, B, and k are constants.

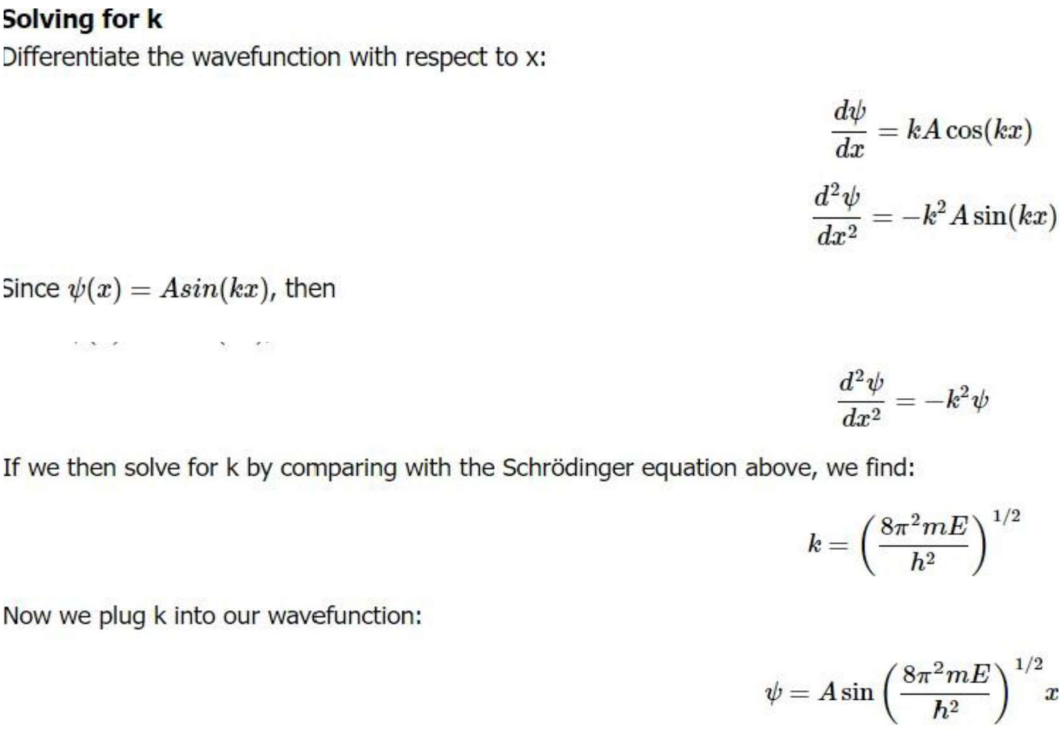
Step 3: Define the wave function

The solution to the Schrödinger equation we found above is the general solution for a 1- dimensional system. We now need to apply our boundary conditions to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at x=0

or x=L is zero. When x=0, sin(0)=0 and cos(0)=1; therefore, B must equal 0 to fulfil this boundary condition giving:

ψ(x)=A sin(kx)

We can now solve for our constants (A and k) systematically to define the wave function.



Solving for k

Differentiate the wavefunction with respect to x:

$$\frac{d\psi}{dx} = kA\cos(kx)$$

$$\frac{d^2\psi}{dx^2} = -k^2 A\sin(kx)$$

Since $\psi(x) = Asin(kx)$, then

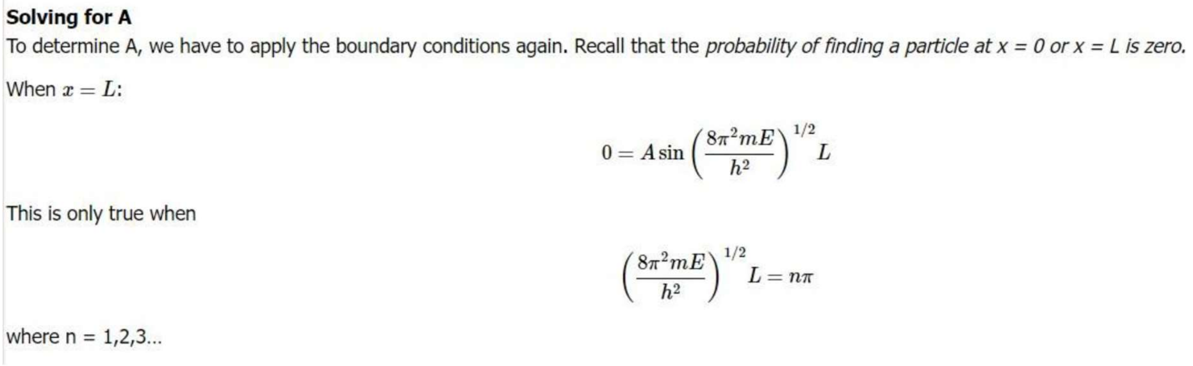
$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k = \left(\frac{8\pi^2 mE}{h^2}\right)^{1/2}$$

Now we plug k into our wavefunction:

$$\psi = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x$$



Solving for A

To determine A, we have to apply the boundary conditions again. Recall that the *probability of finding a particle at x = 0 or x = L is zero.*

When $x = L$:

$$0 = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} L$$

This is only true when

$$\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} L = n\pi$$

where n = 1,2,3...

Plugging this back in gives us:

$$\psi = A\sin\frac{n\pi}{L}x:$$

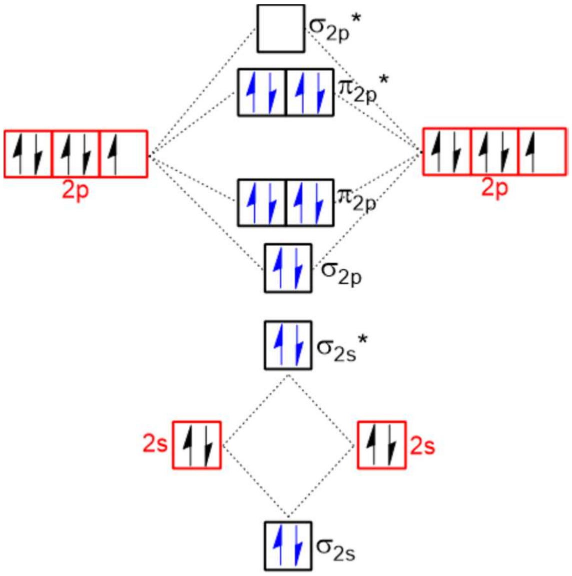
To determine A, recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are normalizing the wave function.

2. **Explain the Homo Molecular Orbital Theory (MO Theory) with suitable example?**

Molecular Orbital Theory (MO Theory):

a. MO Theory provides a powerful framework for understanding the electronic structure and bonding in molecules.
b. It can explain a wide range of molecular properties, including bond strengths, bond lengths, and magnetic behaviour.
c. It has been instrumental in explaining the bonding in complex molecules and in predicting the reactivity of chemical compounds.
d. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called ant bonding molecular orbital.
e. The bonding molecular orbital has lower energy and hence greater stability than the corresponding ant bonding molecular orbital.
f. The bonding molecular orbital has lower energy and hence greater stability than the corresponding ant bonding molecular orbital.
g. A molecular orbital is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, a molecular orbital is polycentric.
h. The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers. According to this principle, electrons are filled in the following order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p…
i. The molecular orbitals like atomic orbitals are filled in accordance with Hund's rule.

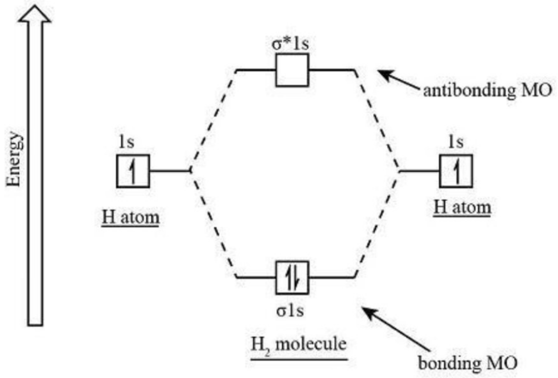


Homo Nuclear Diatomic Molecules:

a. Molecules formed upon the bonding of two same elements are known as homo nuclear diatomic molecules.

b. For example di hydrogen (H_2), Di nitrogen (N_2), etc. In this article, we will study the formation of these diatomic molecules, their stability, and other characteristics.

Molecular orbital diagram of H_2:



a. Molecular orbital and then pairing takes place. So both the electrons are in sigma 1s orbitals.

b. Anti-bonding molecular orbitals are empty. So as all the electrons in hydrogen molecule are paired up, it is diamagnetic. Filling of these two electrons takes place from the bonding.

Bond order:

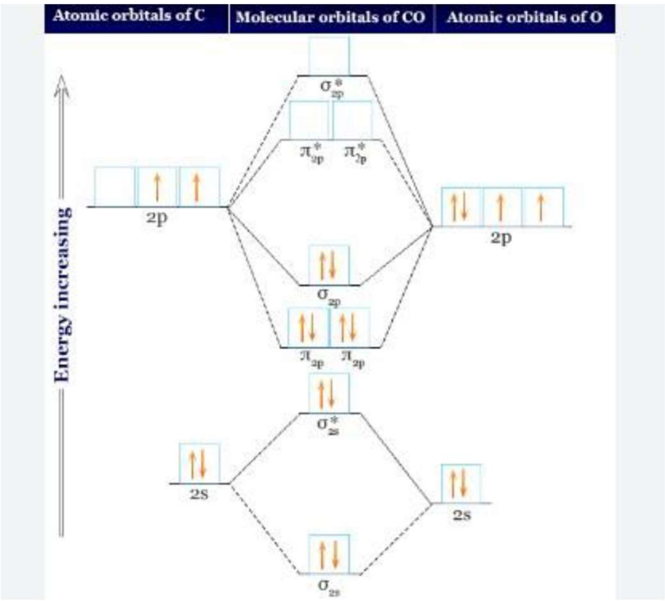
Hydrogen has two electrons in a bonding orbital and zero electrons in anti-bonding orbitals. Therefore the bond order is one.

[B .O = 0.5(2-0) = 1].

3. Explain the Hetero Molecular Orbital Theory (MO Theory) with suitable example and its applications?

Hetero nuclear diatomic molecules:

a. Diatomic molecules with two non-identical atoms are called hetero nuclear diatomic molecules.
b. When atoms are not identical, the molecule forms by combining atomic orbitals of unequal energies.
c. The result is a polar bond in which atomic orbitals contribute unevenly to each molecular orbital.
Molecular orbital diagram of CO:



Molecular orbital diagram of CO:

Electronic configuration of C atom: 1s2 2s2 2p2 Electronic configuration of O atom: $1s^2$ $2s^2$ $2p^4$

Electronic configuration of CO molecule:

σ1s2, σ1s*2, σ2s2, σ2s*2, π2py2, π2pz2 σ2px2

Bond order:

Bond order = (N b − N a) / 2 = 10 – 4/ 2= 3

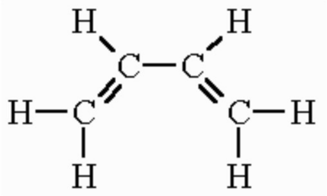
The molecule has no unpaired electrons hence it is diamagnetic.

Applications of MO Theory:

1. There are two major uses of the orbital pictures and energies generated from MO theory. One is to predict reactivity, and the other is to predict properties like UV spectra.

2. It is used to describe molecular structure and bonding. This theory is useful because it describes the electrons better than valence bond theory (VBT). MO theory begins by looking at atomic orbitals (AOs) on each atom in a molecule.

3. Write about Molecular Orbital Diagram of Butadiene ($C4H6$)?



Butadiene is a conjugated dyne consisting of two adjacent pi-bonds and comprised of 4 p-orbitals and 4 pi-electrons.□

To draw the molecular orbital diagram of butadiene, start by drawing 4 p-orbitals all aligned with the same phase. This has zero nodes and is the lowest energy pi-orbital ($\pi 1$).

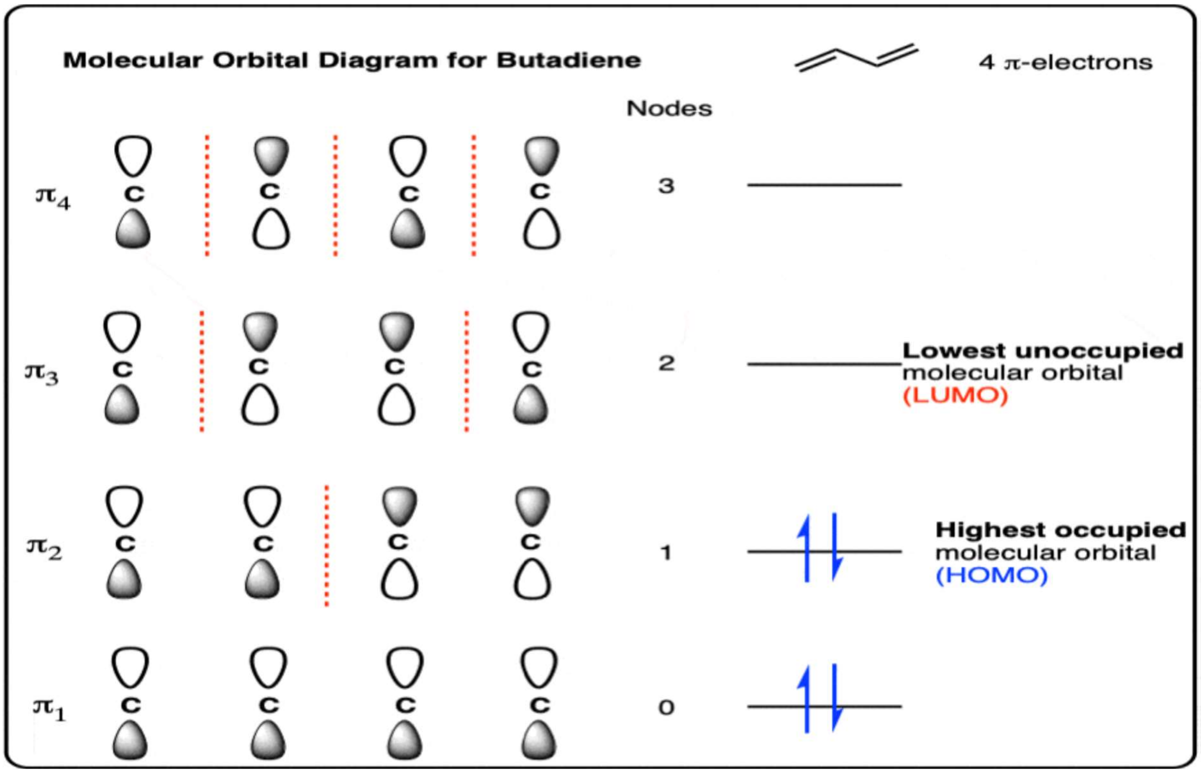
As the number of nodes in an orbital increase, so does its energy. The highest-energy molecular orbital has three nodes and has all p-orbitals with opposite phases ($\pi 4$).

Intermediate orbitals ($\pi 2$) and ($\pi 3$) have one and two nodes, respectively.

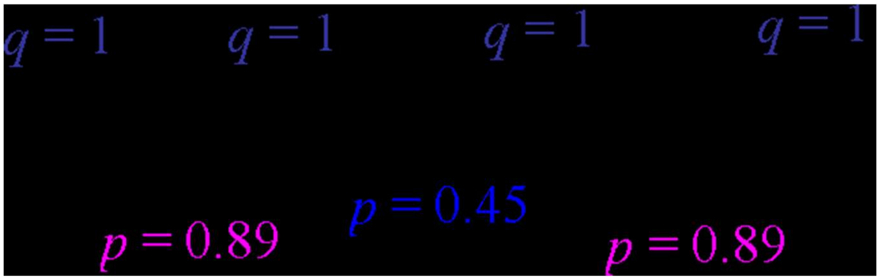
Once the molecular orbital diagram is built, the next step is to add the 4 pi-electrons. This will fill up the lowest-energy orbital ($\pi 1$) and the second-lowest-energy orbital ($\pi 2$)

The highest-occupied molecular orbital (HOMO) of butadiene is the highest-energy orbital that contains pi-electrons. This is $\pi 2$.

The lowest-unoccupied molecular orbital (LUMO) of butadiene is the lowest-energy orbital that has zero pi-electrons. This is $\pi 3$.

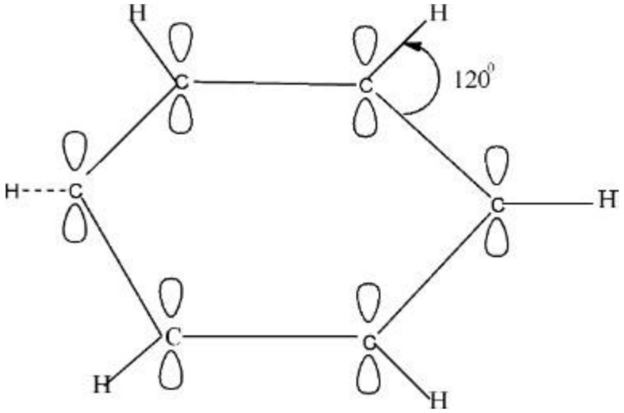


Bond Order:



4. Write about Molecular Orbital Diagram of BENZENE?
Molecular Orbital Diagram of Benzene:

1. Benzene is an organic compound that has the formula of C6H6.
2. It is an aromatic compound and consists of a single ring structure.
3. The carbon atoms are sp2 hybridised in benzene and all of them lie in the same plane.
4. They have a 120 angle orientation. Perpendicular to the plane of the hybrid orbital, there exists an hybridized p orbital which contains two lobes.
5. There are three sp2 hybrid orbitals of each carbon and from these, two of the orbitals overlap interracially, with neighbouring orbitals so that σ–carbon bonds are formed.
6. The leftover third hybrid orbital of each carbon undergoes overlapping with the hydrogen's half-filled 1s orbital and forms σ C–σ H bond. So, in total there are 12 sigma bonds, where 6 of them are carbon-carbon and the other six are carbon- hydrogen. However, in each carbon atom there exist one hybridized 2pz2 orbital.



7. The 2pz2 orbital which is un hybridized overlaps with the adjacent carbon atoms 2pz2 orbital and forms a continuous π molecular network, and incorporates the six π electrons. Finally, as a result of this, we get the formation of two clouds of electrons shaped in form of rings, one above and one below the plane of atoms.

Bond Order:

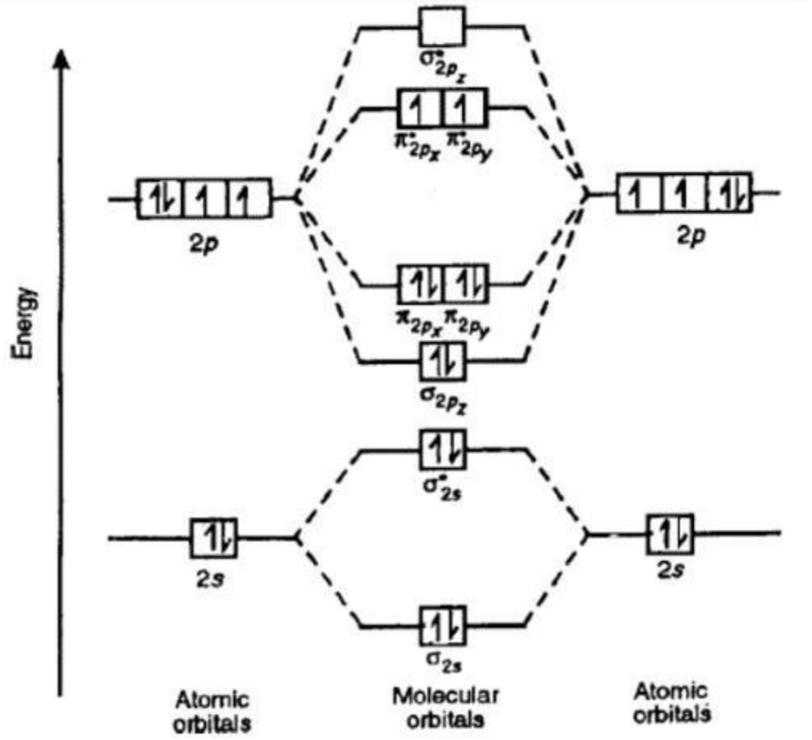
The six π electrons go into the three bonding orbitals. This is the π bond order for 6 C-C bonds.

For one C-C π bond, BO = 3/6 = 0.5. For a single C-C bond in benzene, the total BO = σ + π

= 1 + 0.5 = 1.5.

5. **Draw the MOT diagrams of O_2 and N_2?**

Molecular orbital diagram of O2:



a. A molecular orbital (or MO) is an orbital in the atomic structure of molecules. It is a molecule’s electron wave function that is used to calculate its chemical and physical properties.

b. Electronic configuration of oxygen molecule;

ó1s^{2} < *ó1s^{2} < ó2s^{2} < *ó2s^{2} , [π 2px^{2} = π2py^{2}] < ó 2pz^{2} < [*π2px^{1} =*π2py^{1}] < *ó2pz Bond order:

Given element – Oxygen

Atomic number of oxygen – 8 Electronic configuration – 1s^{2}2s^{2}2p4

Total number of electrons in nitrogen molecule – 16 Electronic configuration of oxygen molecule;

Let’s calculate the bond order of Oxygen:

Bond order = Bonding electrons – Anti bonding electrons / 2

= 10 – 6 / 2 = 2

Therefore, the order of O2 is 2. O2 have unpaired electrons, Hence it is Paramagnetic.

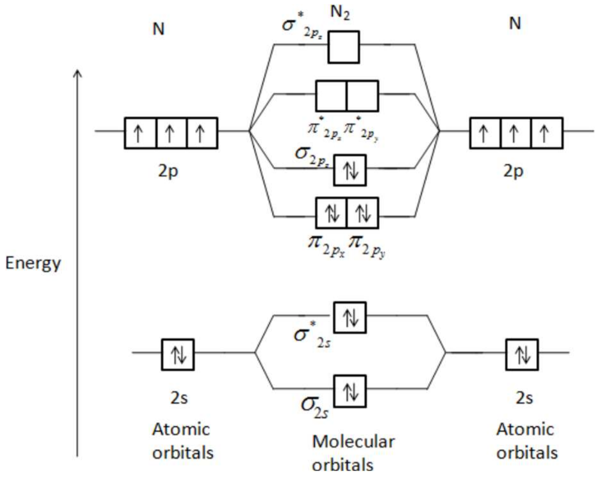
Molecular orbital diagram of N2:

A molecular orbital (or MO) is an orbital in the atomic structure of molecules. It is a molecule's electron wave function that is used to calculate its chemical and physical properties.

Given element – Nitrogen Atomic number of nitrogen – 7

Electronic configuration – $1s^2 2s^2 2p^3$

Total number of electrons in nitrogen molecule – 14



Electronic configuration:

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2$, $[\pi 2p_x^2 = \pi 2p_y^2] < \sigma 2p_z^2 < [\pi^* 2p_x = \pi^* 2p_y] < \sigma^* 2p_z$

Let's calculate the bond order of N_2;

$$Bond\ order = \frac{Bonding\ electrons - Anti\ bonding\ electrons}{2}$$

$$= \frac{10-4}{2} = 3$$

Therefore, the order of N_2 is 3.

: N≡N :

N_2 does not have unpaired electrons, hence it is diamagnetic.

UNIT-2

MODERN ENGINEERING MATERIALS

1.Write about the preparation of semiconductors?

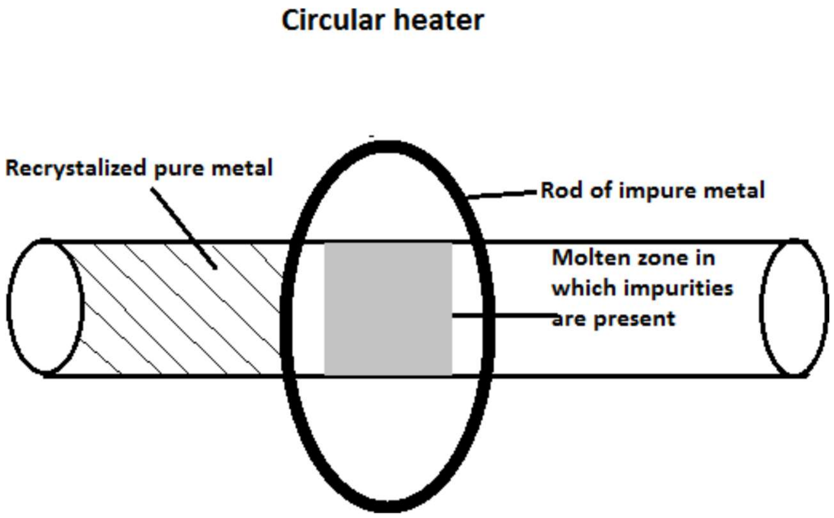
Zone refining or Fractional crystallisation:

i. Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method.

ii. This process is known as ultra-purification because it results in impurity level decreasing to ppm level.

iii. Zone refining is used to produce semiconductors

iv. A circular heater is fitted around a rod of impure metal and is slowly moved down the rod. At the heated zone, the rod melts and as the heater passes on, pure metal crystallizes while impurities pass into the adjacent molten part.



Czochraiski Crystal Pulling Technique:

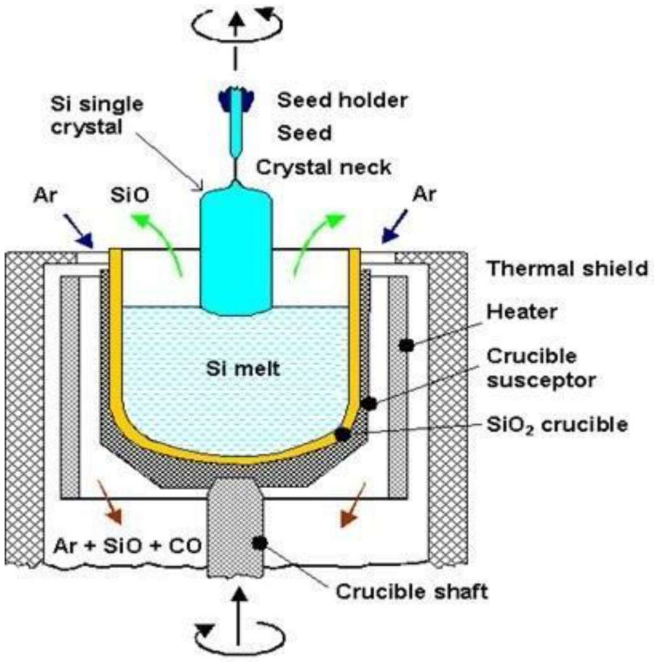
i. The Czochralski (CZ) method is a crystal growth technology that starts with insertion of a small seed crystal into a melt in a crucible, pulling the seed upwards to obtain a single crystal.

ii. The method is named after the Polish scientist Jan Czochralski, who developed it in 1916.

iii. The Czochralski process (Cz) is also known as —crystal pulling‖ or —pulling from the melt‖. In this process, Silicon (Si) is first melted and then allowed to freeze into a crystalline state in a controlled manner.

iv. The advantage of this method is that it is fast and highly controllable.

v. It is widely used for growing large-size single crystals. a wide range of commercial and the relatively high growth rate.



2. Describe about super conductors?

A superconductor is defined as a substance that offers no resistance to the electric current when it becomes colder than a critical temperature.

Prominent examples of superconductors include aluminium, niobium, magnesium diboride, cuprates such as yttrium barium copper oxide and iron pnictides

Superconductivity occurs at a specific material's critical temperature (Tc). As temperature decreases, a superconducting material's resistance gradually decreases until it reaches critical temperature. At this point resistance drops off, often to zero.

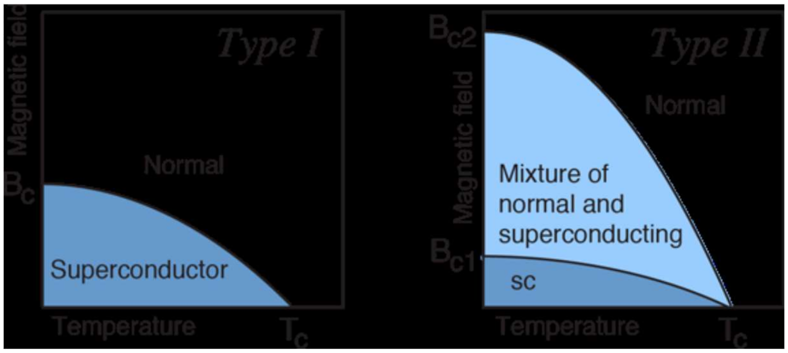
TYPES OF SUPERCONDUCTORS:

There are two types of superconductors. :

They are called Type I and Type II superconductors.

TYPE I SUPERCONDUCTOR	**TYPE II SUPERCONDUCTOR**
1. They exhibit complete Meissnereffect .	1. They exhibit partial Meissner effect.
2. These are perfect diamagnetic.	2. These are not perfect diamagnetic.
3. These are known as soft superconductors	3. These are known as hard superconductors.

4. They have only one critical magnetic field.	4. They have two critical magnetic fields.
5. This material undergoes a sharp transition from the superconducting state of the normal state at the critical magnetic field.	5. These materials undergo a gradual transition from the superconducting state to the normal state between the two critical magnetic fields.
6. The highest value of critical magnetic field is 0.1 wb /.	6. The upper critical field can be of the order of 50 wb/.
7. Applications are very limited.	7. They are used to generate very high magnetic field.
8. Examples:- lead, tin, mercury , etc.	8. Examples:- alloys like Nb-Sn, Nb-Ti, Nb-Zr, etc.



SUPERCONDUCTOR APPLICATIONS:

Semiconductors are extensively used in the manufacturing of electronic devices like transistors, diodes, ICs, etc.

Superconductors are used in manufacturing high-speed connections in computer ICs, making superconducting coils, MRIs, etc.

Superconductors are used in particle accelerators, generators, transportation, computing, electric motors, medical, power transmission, etc.

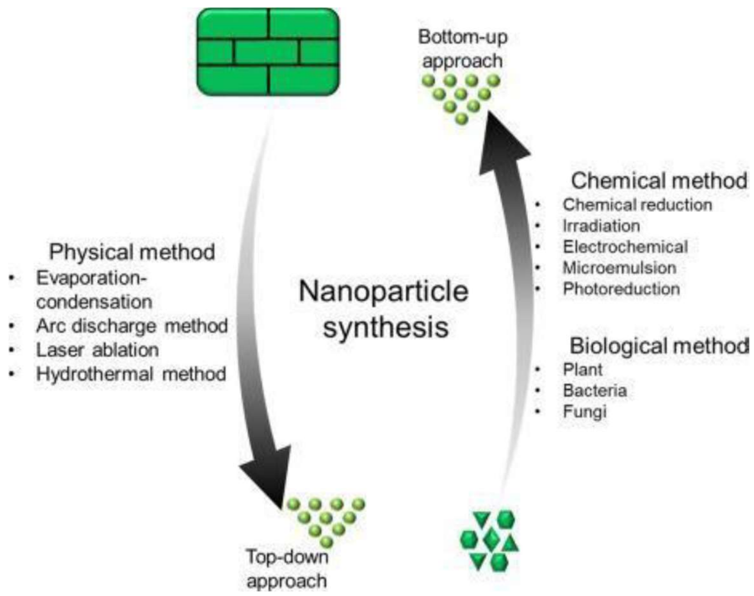
Superconductors are primarily employed for creating powerful electromagnets in MRI scanners.

These conductors are used to transmit power for long distances.

They are used in memory or storage elements.

3. Explain the preparation of Nano materials?

General Methods for the Preparation of Nanomaterial:



Top-Down Approach:

Top-down approach involves the breaking down of the bulk material into Nano sized structures or particles.

Top-down synthesis techniques are extension of those that have been used for producing micron sized particles.

Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties.

The biggest problem with the top-down approach is the imperfection of surface structure.

Examples of such techniques are high-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, and aerosol.

Bottom-Up Approach:

The alternative approach, which has the potential of creating less waste and hence the more economical, is the _bottom- up‘.

Bottom-up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by cluster.

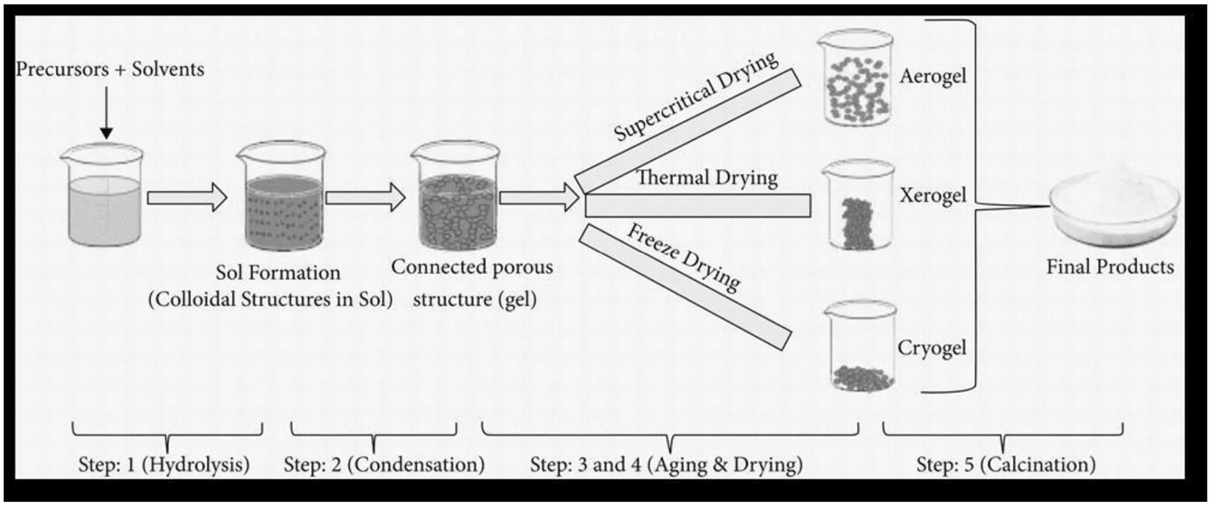
Many of these techniques are still under development or are just beginning to be used for commercial production of Nano powders.

Organometallic chemical route, revere-micelle route, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, template assisted sol-gel, electrode position etc, are some of the well- known bottom–up techniques reported for the preparation of luminescent nanoparticles.

Sol-gel process:

Thesol gel process is a more chemical method (wet chemical method) for the synthesis of various nano structures, especially metal oxide nanoparticles.

In this method, the molecular metal alkoxide is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis /alcoholysis.



Hydrolysis:

The molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis.

Since silicon tetraethyl orthosilicate [TEOS; $Si(OC2H5)4$] is the most common alkoxide, it undergoes partial or complete hydrolysis forming silanol.

$Si(OR)4+H2O \rightarrow Si(OR)3(OH)+ROH$

Since silicon alkoxides hydrolyse relatively slowly, adding acid or base catalysts speeds up the process of turning metal precursor molecules into tri alkoxy silanol, $Si(OR)3(OH)$.

The amount of water and catalyst present will determine whether hydrolysis proceed partially, converting metal alkoxides into $Si (OR)_{4n}(OH)_n$, or proceeds fully, converting all OR groups in alkoxides to OH:

$Si(OR)_4+4H_2O \rightarrow Si(OH)_4+4ROH$

Poly Condensation:

Further condensation yields cluster species Si-O-Si (Siloxane)

$(OR)_3Si - OH + HO - Si(OR)_3 \rightarrow (OR)_3Si - O - Si(OR)_3 + H_2O$ $(OR)_3 Si - OR + HO - Si (OR)_3 \rightarrow (OR)_3Si - O - Si(OR)_3 + ROH$

Applications:

- The materials obtained from the sol-gel method are used in various optical, electronic, energy, surface engineering, biosensors, and pharmaceutical and separation technologies (such as chromatography).

- Sol-gel has several advantages as a matrix for inhibitors, which are cheap to produce, low processing temperature, environmentally friendly, high purity, fairly good adhesion, production of organic-inorganic hybrids and coat complex substrate.

4. How to characterize the nano materials by BET and TEM method?

Brunauer-Emmett-Teller (BET) analysis:

- Brunauer-Emmett-Teller (BET) analys is a physical characterization technique that provides quantitative data on the specific surface area and porosity distribution of solid materials.

- The method is suitable for a wide range of solid matrices from catalyst powders to monolithic materials.

- The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area of fly ash and coated fly ash.

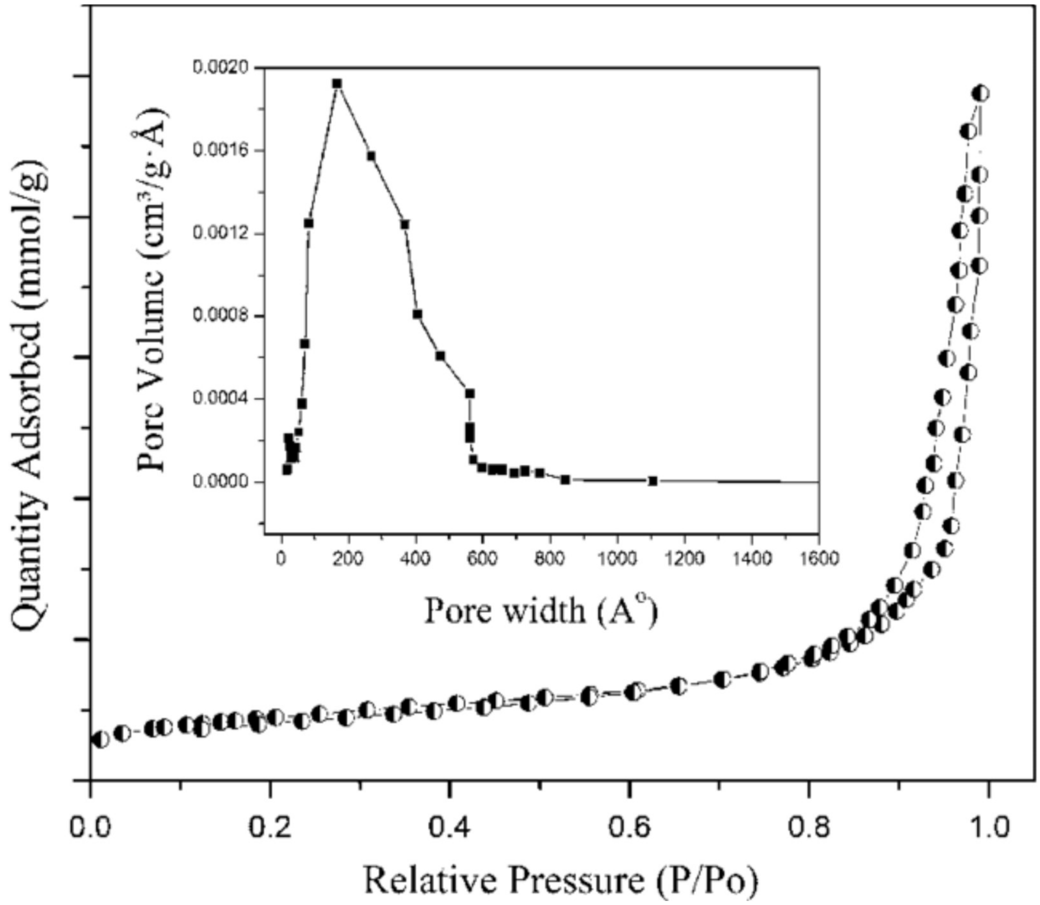
- The amount of gas adsorbed depends on the exposed surface are but also on the temperature, gas pressure and strength of interaction between the gas and solid.

- In BET surface area analysis, nitrogen is usually used because of its availability in high purity and its strong interaction with most solids. Because the interaction between gaseous and solid phases is usually weak, the surface is cooled using liquid N_2 to obtain detectable amounts of adsorption. Known amounts of nitrogen gas are then released stepwise into the sample cell.

- Relative pressures less than atmospheric pressure is achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure.

- After the adsorption layers are formed, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified.

- The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure.



Nitrogen Sorption (BET) isotherms of the ZnO nanoparticles:

BET Method Applications:

- Brunauer–Emmett–Teller (BET) theory is used to measure the surface area of solid or porous materials. It gives important information on their physical structure as the area of a material's surface affects how that solid will interact with its environment.

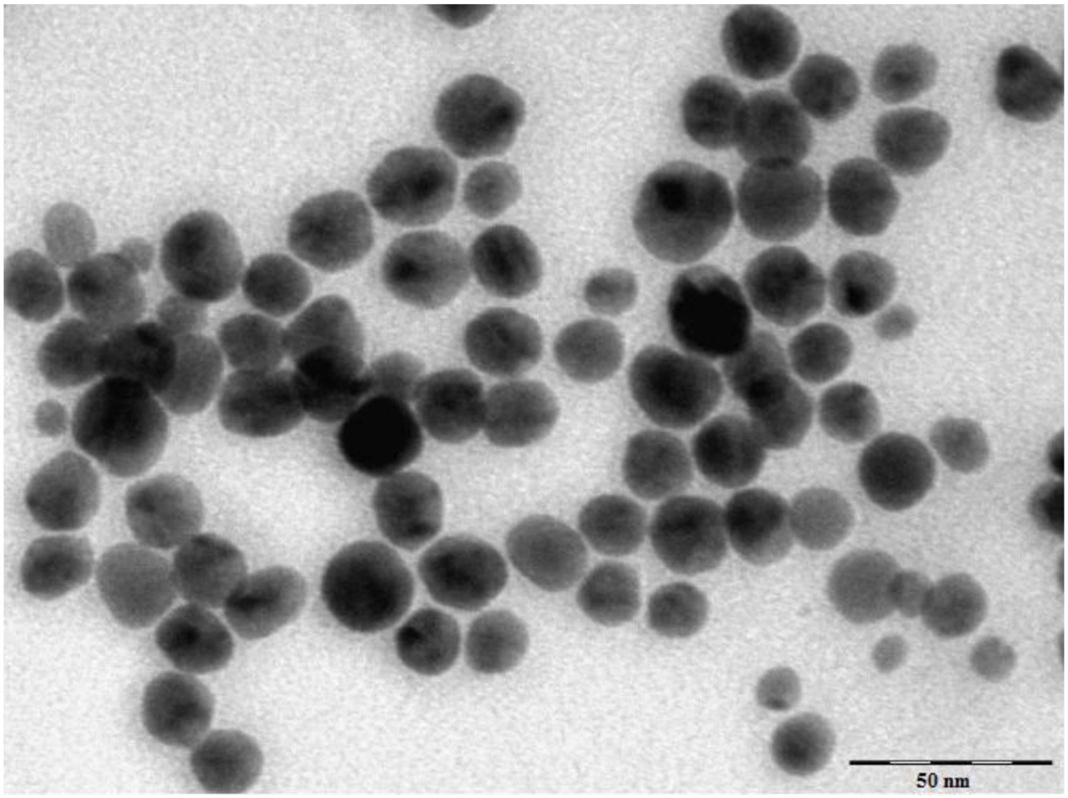
Transmission Electron Microscopy (TEM):

- Transmission Electron Microscopy (TEM) is a technique that uses an electron beam to image a nanoparticle sample, providing much higher resolution than is possible with light- based imaging techniques.

- TEM is the preferred method to directly measure nanoparticle size, grain size, size distribution, and morphology.

- TEM has been considered the golden standard for general nanoparticle characterization.

- TEM is a flexible technique that generates images in the range size from 1 to 100 nm allowing to determine the physical properties of nanoparticles (size, shape, surface topology, crystal structure, and general morphology), and also give insights into the morphology of aggregation and chemical composition of a great variety of samples.



5 Write about fullerenes and Graphite?

Fullerenes:

- The fullerenes (allotropes of carbon) are graphene sheets rolled into tubes or spheres.

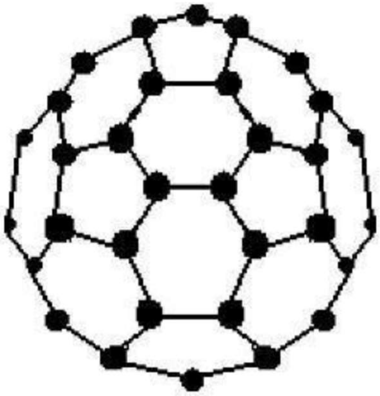
- It is a cage like molecule composed of 60 carbon atoms (C60) joined together by single and double bonds to form a hollow sphere with 20 hexagonal and 12 pentagonal faces (a design that resembles a football).

- It was named as buckminsterfullerene or buck ball after the name of American architect Buckminster Fuller.

- The fullerene receives its name from the architect Buckminster Fuller, who designed homes in the shape of a geodesic dome based on pentagons and hexagons, sometimes even referred to as "buck ball". There are three important types of Fullerenes: C60, C70, and Fullerenes

Buckminsterfullerene's:

- Buckminsterfullerene's (C60) are spherical carbon allotropes where 60 atoms are assembled in pentagons and hexagons, in geometry similar to a soccer ball. Their cage structure and polyaromaticity cause the formation of a displaced electron cloud that allows these molecules to act as charge transfer complexes.

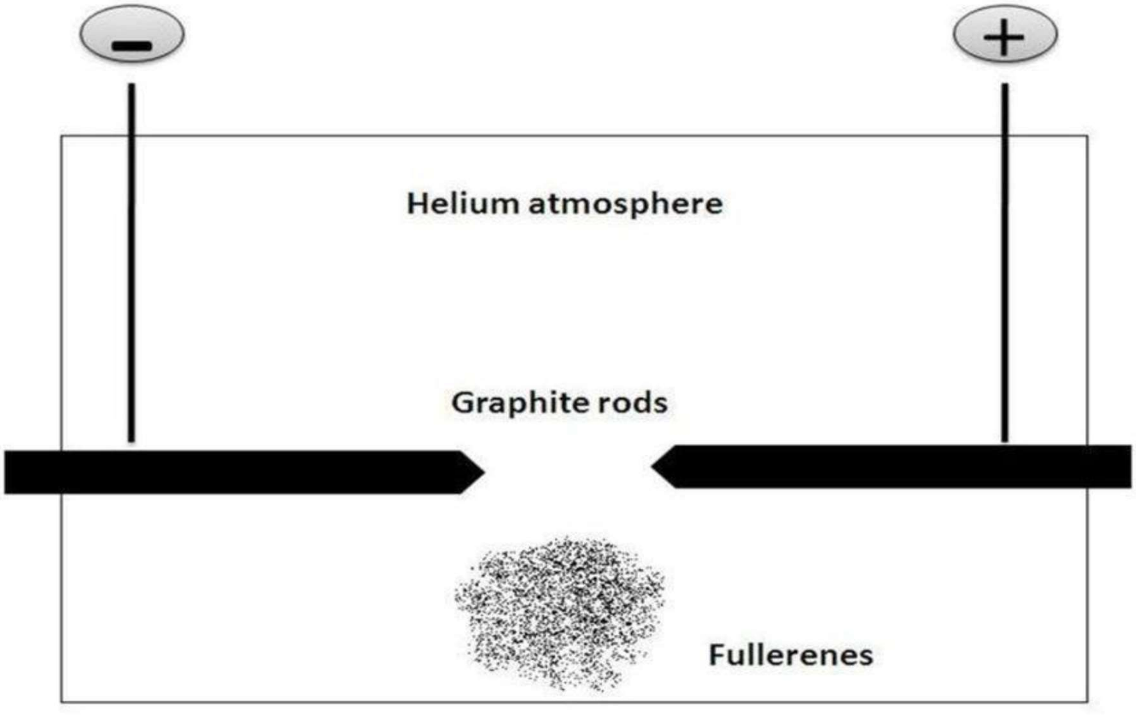


The C_{60} molecule used in smart materials

Preparation:

Arc discharge method:

- This method of producing Fullerenes utilizes carbon arc method in which graphite electrodes are vaporized in a low pressure helium atmosphere by passing an electrical current through the electrodes, thus generating an arc which produces carbon soot containing fullerenes



Properties:

- Its behaviour and structure depend on the temperature. As the temperature is increased fullerene gets converted into the C70.

- The structure of fullerenes can change under different pressures.

- Fullerene has an ionization enthalpy of 7.61 electron volts.

- Its electron affinity is 2.6 to 2.8 electrons volts.

- Fullerenes are stable, but not totally unreactive.

- In chemical reactions, fullerene can act as an electrophile.

- It acts as an electron-accepting group and is characterised as an oxidizing agent.

Applications:

- Fullerenes (C60) and their derivatives have potential antiviral activity, and may be used for the treatment of HIV-infection.

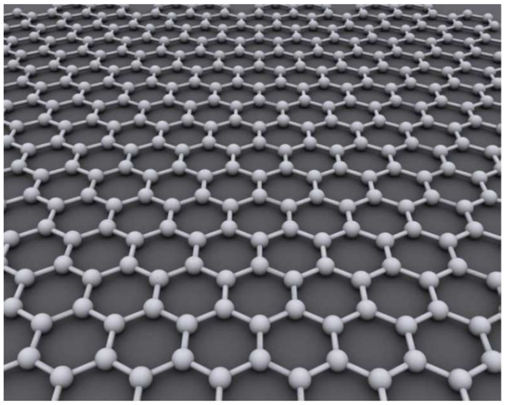
- They have potential medicinal applications as they can bind specific antibiotics and target certain types of cancer cells such as melanoma.

- They are used as biological antioxidants.

- They are also used as potential photosensitizers in photodynamic therapy and catalysts for hydrogenation.

Graphene:

- Graphene is a crystalline allotrope of carbon with two-dimensional, atomic scale, hexagonal pattern. Here each carbon atom forms four bonds, three s bonds (sp2 hybridized) with its three neighbours and one p bond oriented out of plane. It is the basic structural element of other allotropes like graphite, fullerene, nanotubes, Nano cones, etc. hence called mother of all carbon nanomaterial‘s.



Preparation:

- There are two key graphene synthesis routes, and they can be categorized as (i) top-down and (ii) bottom-up techniques and are schematically represented.

- In top-down methods, bulk material such as graphite is transformed into its smallest constituents to produce graphene.

- In the bottom-up synthesis route, graphene is produced through the decomposition of carbon-containing precursors (both gaseous and liquid) followed by the formation of a hexagonal structure of graphene.

Chemical Reduction Process:

- Chemical oxidation of graphite to graphene oxide followed by the reduction process is the commonly used method for mass scale production of graphene or reduced graphene oxide (RGO).

- Among the large number of chemical reducing agents used to prepare RGO or graphene, the most efficient reductant is hydrazine.

- It is toxic in nature and harmful to the environment, thus it is in high demand to use green reductants for RGO synthesis.

- We understand that due to high demand of graphene/graphene oxide/reduced graphene oxide recently and which is expected to be more in future, green synthesis methods are extremely important.

Properties:

- It is nearly transparent.
- It is 200 times stronger than steel by weight due to its tightly packed carbon atoms.
- It conducts heat and electricity with great efficiency due to presence of p electrons. Nowadays.
- It is commonly used in semiconductors, batteries, electronics, composite industries, and many more.

Applications:

- Biological Engineering: Bioengineering will certainly be a field in which graphene will become a vital part of in the future; though some obstacles need to be overcome before it can be used.
- Optical Electronics.
- Ultra-filtration.
- Composite Materials.
- Photovoltaic Cells.
- Energy Storage.

ENGINEERING CHEMISTRY (MECHANICAL)
Unit-1
WATER TECHNOLOGY

1. Explain in detail about Boiler corrosion?

Water is mainly used in boilers for the generation of steam and as coolant. A boiler water should correspond with following composition

(i) Its hardness should be less than 0.2 ppm.

(ii) Its caustic alkalinity (due to OH^-) should be between 0.15 and 0.45 ppm.

(iii) Its soda alkalinity (due to Na_2CO_3) should be between 0.45 - 1 ppm.

But due to use of hard water some operational troubles in boiler are created known as ill effects. There are main four factors affecting boiler;

- Priming and foaming
- Scale and sludge formation
- Boiler Corrosion
- Caustic embrittlement

1. Priming and foaming

Priming: “Violent and vigorous boiling of boiler water which leads to “Wet” steam formation is called priming.” Wet steam is steam contaminated with droplets of dissolved salts. This phenomenon is called as ‘carry over’

Priming is caused by

1. Presence of considerable amount of dissolved salts
2. Very high level of boiler feed water
3. Presence of excessive foam
4. High speed of steam generation
5. Faulty boiler design

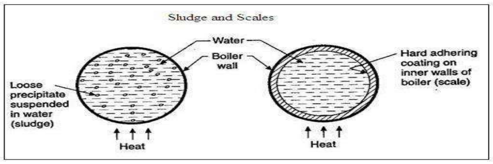
Foaming: “It is the formation of continuous foam or bubbles on the surface of water.”

Causes:

1. High concentration of dissolved salts in boiler feed water
2. Presence of oil droplets and alkalies
3. Presence of finely dispersed suspended material
4. Violent agitation of boiler feed water

Disadvantages of priming and foaming:

1. Due to foaming actual height of water column cannot be judged well.
2. Due to priming, the salts present in the droplets enter in the part of machineries



where steam is being used, thereby decreasing life of machineries.

3. Dissolved salts in droplet of wet steam get deposited on evaporation of water, which reduces efficiency of machine parts.
4. Foaming causes wet steam formation.

Prevention of Priming and foaming:

1. Foaming can be prevented by adding antifoaming agents like castor oil or by adding chemical like sodium aluminate and followed by blow down operation.
2. Priming can be prevented by use of well softened or filtered water
3. Maintaining low water level in boiler can prevent priming.
4. Rapid changes in steam rate should be avoided.
5. Steam purifier can be used.

2. Sludge and scale formation

   Sludge: Sludge is a soft, loose and slimy deposit of precipitated salts in boiler tube. It gets deposited at the bends and valves, affecting free flow of water.

   Sludge formation:

   In boiler water evaporate continuously and the concentration of salt goes on increasing. After the saturation point dissolved get precipitated. If the precipitate remains in boiler tubes as loose and slimy matter, they are called as sludge. They are generally formed at cooler parts of boiler and the parts of boiler where flow rate is slow.

   Disadvantages:-

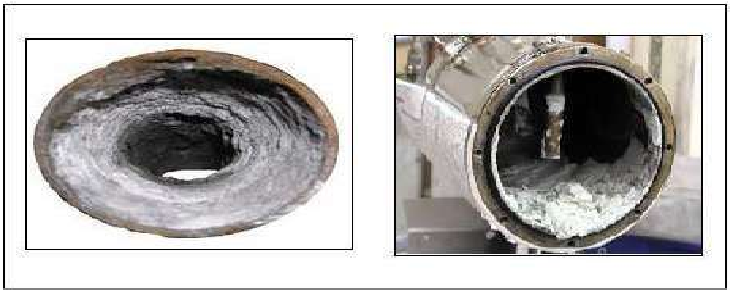
   1. They waste some portion of heat.
   2. It disturbs working of boiler and sometimes may choke up the pipe
   3. It reduces the flow rate of water in boiler.

Prevention:-

1. Use of water containing very low quantity of total dissolved solids
2. Frequently making blow down operation.
3. They can be removed by using mechanical scrappers.

Scale formation:-

Definition: The hard and strong deposits formed inside boiler tube is called as scale.



In boiler water evaporate continuously and the concentration of salt goes on increasing. After the saturation point dissolved salts get precipitated. If the precipitate remains in boiler tubes as hard, strong, adherent matter, they are called as scales. They are generally formed at hotter parts of boiler and are bad conductors of heat.

Causes-

i) Decomposition of bicarbonates:

At high temp, bicarbonates decompose into sticky water insoluble material.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2 \uparrow$$

ii) Hydrolysis of magnesium salts: at higher temperature, magnesium salt undergoes hydrolysis, to form sticky.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 \downarrow + 2HCl \uparrow$$

iii) Presence of silica: Silica in the form of colloidal particles can deposit as calcium silicate or magnesium silicate as strong adhering material.

iv) Decreased solubility of $CaSO_4$:

$CaSO_4$ has lesser solubility at higher temperature .Hence at high temp. $CaSO_4$ present in boiler will precipitate as hard scale forming material.

Disadvantage of Scales:

- Wastage of Fuel: Scales are bad conductors of heat and result in the reduction of heat transfer to the boil.
- Over heating of boiler: Scale reduces transfer of heat from boiler to boiler water, hence overheating is required to keep the required steam pressure.
- Boiler Safety:

  Overheating of boiler is done due to scale formation. To maintain constant steam supply with required pressure boilers are overheated. Overheating makes boiler metal soft and weak which causes distortion of boiler tube & becomes dangerous in high pressure boiler.
- Danger of explosion:

  When thick scale cracks due to uneven expansion, the water comes in contact with overheated boiler metal which causes large amount of steam formation & develops sudden high pressure. Due to this boiler metal may burst with explosion.

Removal of scales:

- The scale can be dissolved by use of suitable chemicals like EDTA, sodium phosphate, calgon etc and removed by blow down operation.
- Thin scales can be removed by use of scrapper or wire brush.
- Thick scales can be removed by hammer and chisel.
- To remove hard & brittle scale thermal shocks techniques is used.

Prevention of scales:

- Use of softened water.
- Adding sodium phosphate to the water. (Phosphate conditioning).
- Frequent blow down operations to remove the scales
- Adding sodium aluminates, which can trap the scale forming particles.
- Adding organic chemicals like tannin which forms coating on the scale forming particles. This matter becomes easily removable by blow down operation.

Differentiate between sludge and scale in boiler

Sr. No	Sludge	Scale
1.	Sludge is a loose deposit or slimy matter	Scale is hard coating
2	Sludge is soft, less adherent on boiler metal and can be removed easily by brushes, detergents.	Scale is strongly adhered to boiler metal and difficult to remove.
3	Sludge is formed at the cooler parts & where flow rate is slow.	Scale is form at the hotter parts.
4	Sludge may lead to chocking	Scale may lead to bulging of metal tube
5	Sludge formation is due to an increase in concentration of salts in boiler water.	Scales are formed due to $CaSO_4$, $CaCO_3$,$Mg(OH)_2$, $MgSiO_3$, $CaSiO_3$

3. *Boiler Corrosion:*

Boiler corrosion is decay or destruction of boiler metal either due to chemical or electrochemical reaction with its environment.

Disadvantages of corrosion are:

- Shortening of boiler life
- Leakage of the joints and rivets
- Increased cost of repairs &maintenance

Corrosion in boiler is due to following

reasons A] Dissolved Gases B]

Dissolved Salts

A] Dissolved Gases – 1. Dissolved O_2 2. Dissolved CO_2

(1) Dissolved Oxygen – Water usually contains dissolved oxygen at room temperature. As the water is heated dissolved oxygen is set free and boiler metal starts corroding. Dissolved oxygen reacts with iron of boiler in the presence of

water to form rust as follows-

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

$4Fe(OH)_2 \longrightarrow + O_2 \quad 2\{Fe_2O_3 . 2H_2O\}$

Ferrous hydroxide

Removal of dissolved oxygen –

(i)By adding some quantity of Na_2SO_3(SodiumSulphite), Na_2S (SodiumSulphide), hydrazine(N_2H_4). $Na_2SO_3 + 1/2O_2 \longrightarrow Na_2SO_4$

$Na_2S + 2O_2 \longrightarrow Na_2SO_4$

$N_2H_4 + O_2 \longrightarrow 2H_2O + N_2$

(ii) Dissolved oxygen can also be removed by mechanical deaerators.

(2) Dissolved CO_2

There are two main sources CO_2 in boiler water, dissolved CO_2 in raw water and CO_2 formed by decomposition of bicarbonates.

$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$

$CO_2 + H_2O \longrightarrow H_2CO_3$

Removal of CO_2

(i) CO_2 from water can be removed by using addition of suitable amount of NH_3

$CO_2 + 2 NH_3 + H_2O \rightarrow (NH_4)_2CO_3$.

To avoid corrosion due to NH_3, its concentration restricted below 1 ppm.

(ii) CO_2 can be removed by by mechanical de-aeration along with O_2

B) Hydrolysis of salts:

If water contains weak base- strong acid salts like $MgCl_2$, $CaSO_4$ etc, then they are hydrolysed at high temperature form strong acid .This acid corrodes boiler metal

$MgCl_2 + 2 H_2O \rightarrow Mg(OH)_2 \downarrow + 2 HCl \uparrow$

To prevent corrosion due to acid formation in boiler ‘the pH of water is adjusted to 8.5-9.0.

4.Caustic embrittlement:

It is the phenomenon during which the boiler material becomes highly brittle due to the accumulation and reaction of caustic substances with boiler metal.

OR

It is the phenomenon of embrittlement of boiler metal due to the accumulation and reaction of caustic soda with boiler metal.

Definition: It is the fast corrosion of boiler caused by presence of highly alkaline water in high pressure boiler.

Causes of Caustic embrittlement:

- During softening of boiler water by lime-soda process Na_2CO_3 is added to boiler water to reduce the hardness but if the amount of Na_2CO_3 exceeds, then it gets hydrolysed to form hydroxide.
- Hydroxide makes the water caustic.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The caustic water flows into the minute-hair cracks, present in the inner side of the boiler by capillary action and react with boiler metal.

Disadvantages:

- The hydroxide formed, comes in contact with boiler metal thereby boiler metal as sodium ferrite it decreases the strength of boiler metal.

$$Fe + NaOH + \frac{1}{2} O_2 \longrightarrow \underset{\text{Sodium Ferrate}}{NaFeO_2} + H_2$$

- Sodium ferrate is brittle in nature; if attack of NaOH is continuous then whole boiler becomes brittle causing failure of boiler.

Prevention:

- By using Sodium phosphate for water softening instead of Na_2CO_3.
- By adding tannin or lignin to boiler water which blocks the cracks.
- By adjusting pH 8-9 of boiler water.
- By adding to boiler water to keep the ratio of Na_2SO_4 to NaOH as 1:1, 2:1, 3:1 at pressure 10,20 and above 20 atmospheres respectively.

2 Write about Zeolite and Ion exchange process?

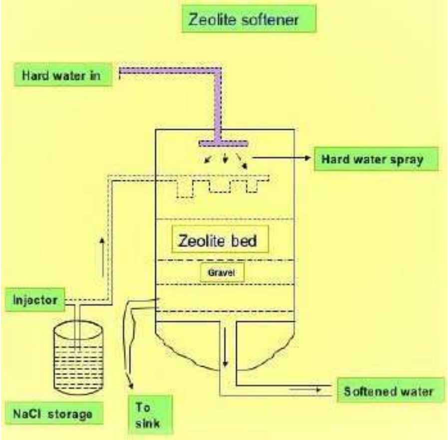
Principle - Zeolites are naturally occurring hydrated sodium alumina silicate minerals (like Na_2O. Al_2O_3. $xSiO_2$. yH_2O) where x= 2-10, y=2-6. Zeolites are capable of exchanging reversibly its loosely held sodium ions for hardness producing ions like Ca^{2+}, Mg^{2+} in water.

Zeolites are also known as permutits and in Greek it means "boiling stone".
Zeolite holds sodium ions
loosely and can be simply represented as Na_2Ze where Ze represents insoluble radical frame work.

Zeolites are two types,

(i) Natural zeolites are non porous for Ex; Natrolite $Na_2Al_3O_3.4SiO_22H_2O$

(ii) Synthetic zeolites posses gel structure. Synthetic Zeolites posses higher exchange capacity than natural Zeolites.



Process –

1. For Softening of water by Zeolite process, hard water is paased through a bed of zeolite at a specified rate; kept in a cylindrical unit.
2. The hardness causing ions (Ca^{+2}, Mg^{+2} etc.) are retained by the zeolite as CaZe and MgZe; while the outgoing water contains sodium salts.
3. Reactions taking place during the softening process are $Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$ $Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$

   $Na_2Ze + CaCl_2$ (or $CaSO_4$) $\rightarrow CaZe + 2NaCl$ (or Na_2SO_4) $Na_2Ze + MgCl_2$ (or $MgSO_4$) $\rightarrow MgZe + 2NaCl$ (or Na_2SO_4)

Regeneration:

1.After some time the zeolite is completely converted into calcium and magnesium Zeolites. Eventually, the bed stops to soften water i.e.; it gets exhausted. At this stage the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated 10%NaCl solution(brine).

$CaZe$ (or $MgZe$) + $2NaCl \rightarrow Na_2Ze + CaCl_2$ (or $MgCl_2$)

Limitations:

(i) If the supply of water is turbid in will clog the pores of zeolite led thereby making it inactive.

(ii) Water contains large quantities of colored ions such as Mn^{+2} and Fe^{+2} they may be removed first because these ions produce Mn and Fe Zeolites , which are difficult to regenerate.

(iii) Mineral acids destroy the zeolite bed.

(iv) Hot water should not be used as it Zeolite tends to dissolve in it.

Advantages:

(i) Hardness is almost completely removed and water of 5-10ppm hardness is produced.

(ii) Equipment used is compact and occupies small space

(iii) It is quite clean process.

(iv) It is rapid process which requires less time.

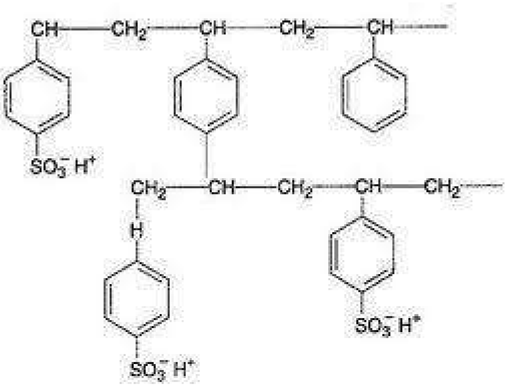
(v) The process automatically adjusts itself to water of different hardness.

2.Demineralization or Deionisation by Ion-exchange process

Ion exchange resins are insoluble, cross linked, long chain, high molecular weight organic polymers with micro porous structure, and the functional groups attached to the chains are responsible for the ion – exchanging properties.

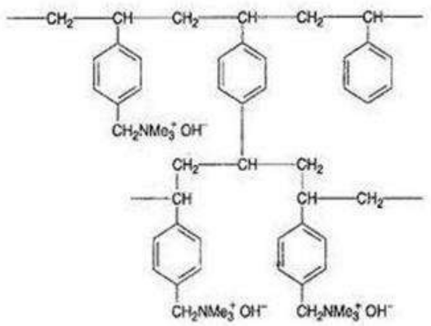
Ion exchange resins are of two types

1. Cation exchange resins(R-H+): - These are the resins containing acidic functional groups (-COOH, SO_3H etc,) are capable of exchanging their H^+ ions with other cations, which comes in their contact.



Cation exchange resin($R^{-}H^{+}$) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in water.

2. Anion Exchanger resins($R^{+}OH^{-}$):-These are the resins containing basic functional groups (-NH2=NH, hydrochloride, hydroxyl) are capable of exchanging their anions with other anions which comes in their contact.



Anions exchange resins ($R^{+}OH^{-}$) are styrene-divinyl benzene or amine-formaldehyde, copolymers, which contains basic functional group such as amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium, groups as an integral part of the resin matrix. These after treatment with dilute NaOH solution become capable to exchange their OH- anions with anions in water.

Principle: When water containing cations and anions is passed through the ion exchange resins, cation exchange resin captures all the cations and anion exchanger resin captures all the anions to give pure water free from all the ions. Hard water is passed first through cation exchange column, where all the cations like Ca^{+2} etc present in water are removed and equivalent amount of H^{+} ions released from this column to water, thus

$RH^{+} + Ca^{2+} \rightarrow \quad RCa^{2+} +$

$2H^{+}\ RH^{+} + Mg^{2+} \rightarrow$

$RMg^{2+} + 2H^{+}$

After cation exchange column, the hard water is passed through anion exchange column where all the anions like $SO4^{2-}$, Cl^{-} etc present in the water are removed and equivalent amount of OH^{-} ions are released from this column to water thus,

$R(OH)2 + Cl^{-} \rightarrow RCl^{-} + 2OH^{-}$

$R(OH)2 \quad +_{4} SO^{2-} \rightarrow {}_{4}R'SO^{2-}$

$+ \ 2OH^{-} \ R(OH)2 \quad + \quad {}_{3} CO^{2-}$

$\rightarrow R' \ CO^{2-} + 2OH^{-}$

H^{+} and OH^{-} ions released from cation and anion exchange columns get combined to produce water molecule.

$H^{+} + OH^{-} \longrightarrow H2O$

The water coming out from the exchanger is deionized or demeneralised water.

Regeneration:

When capacities of cation and anion exchangers to exchange H^{+} and OH^{-} respectively are lost they are said to be exhausted.

(i) The exhausted cation exchanger is regenerated by washing with dil. HCl solution.

$$R\ Na2 + 2\ HCl \longrightarrow R\ H2 + 2NaCl$$

$$R\ Ca + 2\ HCl \longrightarrow R\ H2 + CaCl2$$

(ii) Cation exhausted anion exchanger resin is generated by washing with NaOH solution. $RCl2 \quad + \quad 2NaOH \longrightarrow$

$R(OH)2 + 2NaCl$

$RSO4 \quad +2NaOH \longrightarrow R'\ (OH)2 + Na2SO4$

Thus the water coming out from exchanger is free from cations as well as anions. Such ion-free water is called as deionised or demineralised water. This method is also called as deionization or demineralization process.

Advantages:

1. This method gives water of very low hardness between 0-2ppm.
2. The process can be used to soften highly acidic or alkaline water.

Disadvantages:

1. Capital cost is high since equipment and chemicals both are costly.
2. If water contains turbidity then the efficiency of the process is reduced.

3 Write about Desalination of brackish water?

Water containing high concentration of dissolved salts with a peculiar salty or brackish taste is called brackish water. Sea water is an example of brackish water as it contains about 3.5% of dissolved salts. Removal of dissolved salts (NaCl) from water is called as desalination process.Commonly used techniques for desalination.

1. Distillation
2. Freezing
3. Electro-dialysis
4. Reverse osmosis

1. Distillation – Huge evaporators are used for boiling the brackish water and vapours collected are condensed to get pure water. It is an expensive method for common practice.

2. Freezing – When brackish water is cooled salt is left in the mother liquor and ice crystals are formed. These crystals can be easily separated, washed and melted to get pure water.

3. Electro-dialysis – Electro-dialysis is based on the fact that the ions present in the saline water migrate towards their respective electrodes, through ion-selective membranes (natural or synthetic) under the influence of applied emf.

4. Reverse Osmosis-The flow of solvent from higher concentration to lower concentration solution through a semi permeable membrane by applying slightly higher external pressure than osmotic pressure of higher concentration solution.

Electro-dialysis

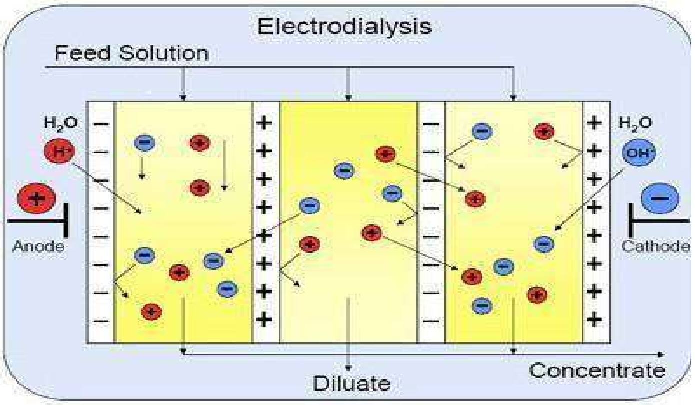
Principle - Electro-dialysis is based on the fact that the ions present in the saline water migrate towards their respective electrodes, through ion-selective membranes (natural or synthetic) under the influence of applied emf.

Construction and working:-

- Electro-dialysis unit consist of electrodes (cathode and anode) and thin rigid ion selective membranes. The anode is placed near the anion selective membrane. Cathode is placed near the cation selective membrane.

- Cation selective membrane will allow only cation to pass throug it, as this membrane consists of negatively charged fixed functional groups which repel anions.
- Anion selective membrane will allow only anions to pass through it, as this membrane consists of positively charged fixed groups which repel cations.
- When an electric field is applied, perpendicular to the direction of flow of water the cations move towards the cathode through cation selective membrane and anions move towards the anode through the anion selective membrane.
- The net result is depletion of ions in the central compartment while it increases in the two side compartments. Desalined water is periodically drawn out from the central compartment.

Diagram:



Applications:-

1. The process is economical as per the capital cost.
2. Removal of salt from tree water, to get pure water.
3. The unit is compact and method is best suited.
4. Removal of ionic pollutants from treated industrial waste.
5. Removal of limited quantity of salts from sea water to get drinking (mineral) water.

Limitations:-

1. Electro-dialysis process does not remove dissolved organic matter.
2. It does not remove colloidal impurities.
3. Replacement of membranes is required which add cost in its use.

4 Define Hard water and explain alkalinity of water?

Hardness in water is the characteristic which prevents the lathering of soap. The water which does not produce lather with soap, but forms insoluble white scum or precipitate is called as hard water. On the other hand, water which forms lather easily with soap is called as soft water. Hardness is due to presence of dissolved salts of carbonates, bicarbonates, chlorides, sulphates, nitrates of calcium & magnesium, and other heavy metals.

On the basis of these salts, hardness is divided in to two main types –

A. Temporary Hardness/Carbonate Hardness
B. Permanent/Non carbonates Hardness

1. Temporary hardness is caused by presence of dissolved bicarbonates and carbonates of calcium, magnesium and other heavy metals.
2.
e.g. $CaCO3$, $MgCO3$, $Ca (HCO3)2$, $Mg (HCO3)2$, $Fe2CO3$ etc
Temporary hardness can be largely removed by simple boiling of water. Temporary hardness is also called as carbonate hardness or alkaline hardness.

$Mg(HCO_3)_2 \xrightarrow{boiling} Mg(OH)_2 + 2CO_2$

$Ca(HCO3)2 \xrightarrow{boiling} CaCO3 + CO2 +$
$H2O\ MgCO3 \xrightarrow{boiling} Mg(OH)2 + CO2$

3. Permanent/Non carbonate Hardness:

Permanent Hardness is caused by presence of dissolved chlorides, sulphates of calcium, magnesium, iron and other heavy metals. e.g. $CaCl2$, $MgCl2$, $CaSO4$, $MgSO4$ etc. Unlike temporary hardness permanent hardness is not destroyed on simple boiling but can be removed by chemical treatment method. Permanent hardness is also called as non - carbonate hardness or non - alkaline hardness.

Total Hardness: It is the hardness due to the presence of all hardness causing salts.
i.e. Total hardness = Temporary Hardness + Permanent Hardness

Unit of Hardness: The hardness of water is always expressed in terms of calcium carbonate equivalent because calcium carbonate is most insoluble salt that can be precipitated in water treatment moreover; its molecular weight is 100.

$CaCO_3$ Equivalence of hardness causing salt
= Mass of hardness causing salt X Equivalent Wt. Or Molecular Wt. of $CaCO_3$

Equivalent Wt. Or Molecular Wt. of hardness causing salt

i) mg CaCO3 eq. per lit (mg/L) – It is defined as the number of milligrams of calcium carbonate (CaCO3) present in one litre of water.
i.e., 1 mg/L = 1 mg of CaCO3 eq. hardness of 1L
of water. But 1 L of water weighs
= 1 Kg = 1000 g = 1000 × 1000 mg = 10^6 mg.
Thus 1 mg/L = 1 mg of CaCO3 eq. per 10^6 mg of water
= 1 part of CaCO3 eq. per 10^6 parts of water = 1 ppm

ii) ppm CaCO3 eq. per lit – It is defined as the number of parts by weight of calcium carbonate (CaCO3) present per million (10^6) parts by weight of water,
i.e., 1 ppm = 1 part of CaCO3 eq. hardness in 10^6 parts of water.

iii) degree clerk (^{0}Cl) & degree French (^{0}Fr) –
1 ^{0}Fr = 1 part per 10^5 parts of water
1 ^{0}Cl = 1 part per 70000 parts of water

Alkalinity in water sample is due to presence of OH^-, $CO3^{2-,}$ $HCO^{3-.}$

These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange indicators.

The determination is based on the following reactions.

ii) $OH^- + H^+ \longrightarrow H2O$

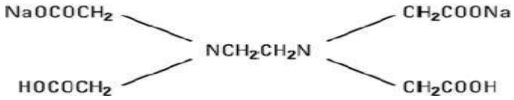
iii) $CO3^{2-} + H^+ \longrightarrow HCO3^-$

iv) $HCO3^- + H^+ \longrightarrow H2O + CO2$

The titration of the water sample against a standard acid upto phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to hydroxide and one half of the normal carbonate.
On the other hand, titration of the water sample against a standard acid methyl orange end point
(M) marks the completion of reactions (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions).

Thus, P = Neutralization of OH^- *and* $CO3^{2-}$

M = Neutralization of OH^-, $CO3^{2-}$, $HCO3^-$



Procedure –

- Take V ml of alkaline water sample in a conical flask and add 1-2 drops of phenolphthalein indicator in it.
- Titrate this sample against std. strong acid solution from burette, till pink colour changes to colourless. Let the burette reading be V1 ml.
- Add few drops of methyl orange indicator into the same titrating mixture and continue the titration till the yellow colour of mixture changes to orange. Note the burette reading as V2 ml.

Phenolphthalein alkalinity (P):
= (V1 × Z × 50 × 1000) / V ppm of CaCO3 equivalents.

Methyl orange alkalinity OR Total alkalinity (M):
= (V2 × Z × 50 × 1000) / V ppm of CaCO3 equivalents

The amount of alkalinities due to OH^-, $CO3^{-2}$, HCO^{3-} types are calculated from the relation between value of P & M.

Alkalinity	Quantity of OH^-	Quantity of $CO3^{2-}$	Quantity of HCO^{3-}
P =0	0	0	M
P =1/2M	0	2P	0
P = M	P	0	0
P < 1/2M	0	2P	M-2P
P > 1/2M	(2P-M)	2(M-P)	0

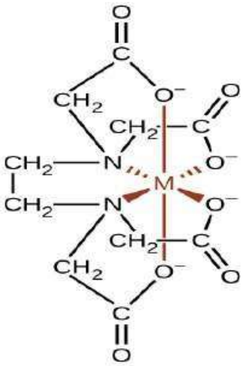
5 How to determine the hardness of water by using EDTA method?

Determination of hardness of water by EDTA method

- It is a complexometric titration using standard EDTA reagent and EBT is used as an indicator.
- EDTA is Ethylene diammine tetra acetic acid. It is a good complexing agent.

Di-Sodium EDTA

EDTA is a hexadentate ligand. It forms stable, cyclic co-ordination complexes with large number heavy metal ions in hard water. Due to this it is possible to determine the total hardness of water using EDTA reagents.



Principle – EDTA forms stable complexes easily with heavy metal ions present in hard water

Theory – Hardness of water is due to presence of dissolved salts of calcium, magnesium, iron and other heavy metals. The hard water is buffered to pH – 10 by adding buffer solution with pH – 10 and few drops of EBT indicator. EBT forms a week complex with metal ions which has wine red colour [M-EBT]complex. During the course of reaction H^+ ions are released which decrease the pH of the reaction mixture. Thus buffer solution of pH – 10 is necessary during the reaction.

$$M^{2+} \quad + \quad EBT \xrightarrow{pH - 10} [M\text{-}EBT] + \quad 2H^+$$

(Metal Ions) *Blue* *Wine Red*

In the course of titration of water sample against EDTA, EDTA first combines with metal ions to give very stable and colourless [M-EDTA]complex. .

$$[M\text{-}EBT] \quad + \quad EDTA \xrightarrow{pH - 10} [M\text{- }EDTA] \quad + \quad EBT$$

(Metal Ions) Colourless Blue

Thus, at the equivalence point, there is change in the colour from wine red (due to metal-EBT) to blue (due to free EBT) and total hardness can be determined.

Procedure -

Titration part-I Standardization of EDTA solution:

Fill a burette with di-sodium EDTA solution and pipette out 10 ml std. $MgSO_4$ Sol^n in a conical flask. Add about 5 ml buffer solution of pH-10 and 41-2 drops of EBT indicator. Titrate the wine red coloured mixture against the EDTA solution till colour changes to blue. Let the titration reading be V_1 ml.

Part II: Hardness of water sample

Take 10 ml water sample in a conical flask. Add 5 ml of buffer solution of pH 10 and 1-2 drops of EBT indicator. Titrate this wine red mixture against the standard EDTA solution till the colour change to blue. Let the titration reading be Y ml.

Calculations:

Part II: Total hardness of water sample:

Total hardness of a water sample is determined, by using formula

Hardness of water sample = $(Y \times Z \times 100 \times 1000) / V$

ppm $CaCO_3$ equivalent. Where Y= Volume of EDTA
Z= Molarity of EDTA
V= Volume of Water sample

Temporary and permanent hardness by EDTA:

Hardness of the boiled and filtered water sample is further determined. The boiled and filtered water sample contains only permanent hardness.Permanent hardness is subtracted from total hardness to get temporary hardness

Advanantages:

2. In EDTA titration method suitable indicators available for accurate reading.
3. Sharp colour change at the end point of titration can be observed.
4. The EDTA titration method is convenient have greater accuracy, rapid, and easy.

UNIT-2

ELECTRO CHEMISTRY AND APPLICATIONS

1. **Define corrosion? Discuss in detail about chemical or dry 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 mainly 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

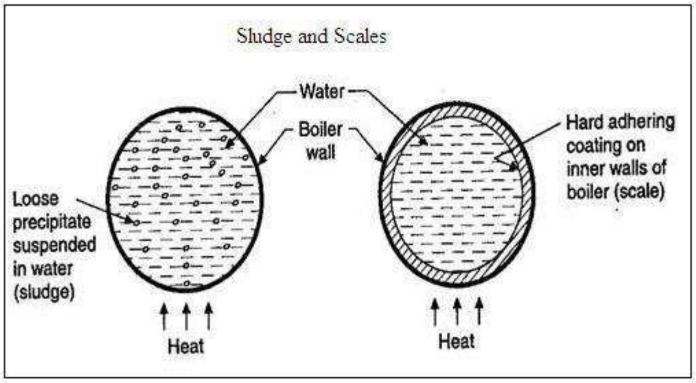
If the corrosion of metal is due to other gases like Cl_2, SO_2, H_2S, and NO_2 in dry atmosphere, it is called corrosion by other gases.

Eg. $2Ag + Cl_2 \longrightarrow 2AgCl$ (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:

$$2M \longrightarrow 2M^{n+} + 2\,ne^- \quad \text{(oxidation)}$$

$$nO_2 + 2\,ne^- \longrightarrow 2n\,O^{2-} \quad \text{(reduction)}$$

$$2M + nO_2 \longrightarrow M_2O_{2n} \quad \text{(metal oxide)}$$

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,

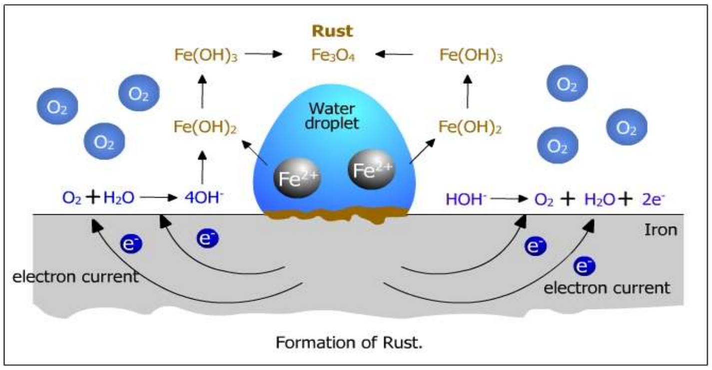
- If the ratio is less than one the metal oxide layer will be porous and non-protective. E.g. oxide layers of alkali and alkaline earth metals.

- 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.

2 Discuss in detail about electrochemical or wet corrosion?

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.



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:

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

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

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

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: $\longrightarrow Fe$ $Fe^{2+} + 2e-$

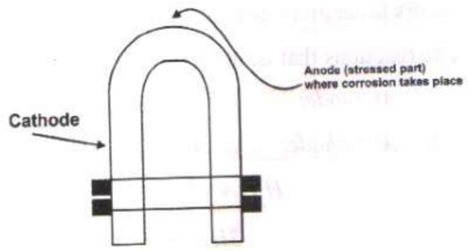
Cathode: $H_2O + O_2 + 2e \longrightarrow 2OH^-$ (reduction)

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

TYPES OF WET CORROSION

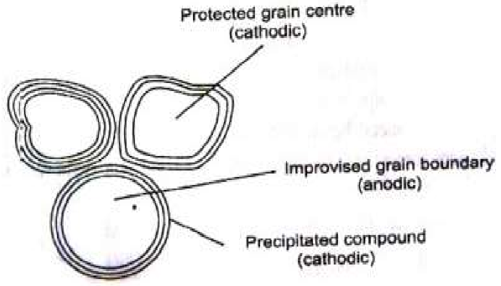
1. STRESS CORROSION

- 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.



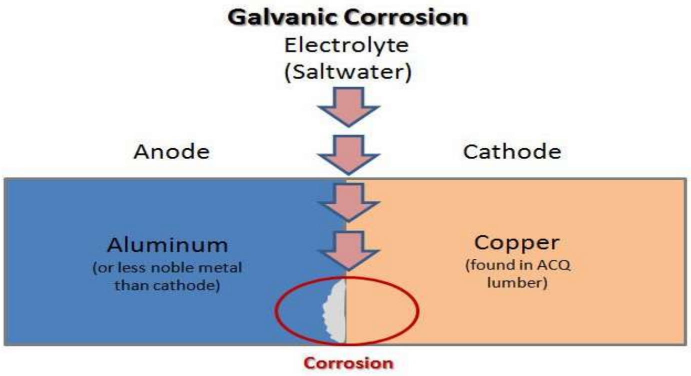
2. INTERGRANULAR CORROSION

- This corrosion is observed in case of alloys.
- The corrosion product is observed at the boundaries of grains. Externally, it is not seen.
- There is a sudden failure of material due to this corrosion.



- For example, during the welding of stainless steel (an alloy of Fe, C, Cr), chromium carbide is precipitated at the grain boundaries and the region adjacent to grain boundaries becomes depleted of chromium composition and is made anodic with respect to solid solution within the grains richer in chromium.
- Rapid quenching after heat treatment of a metal is the remedy of inter-granular corrosion.

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.

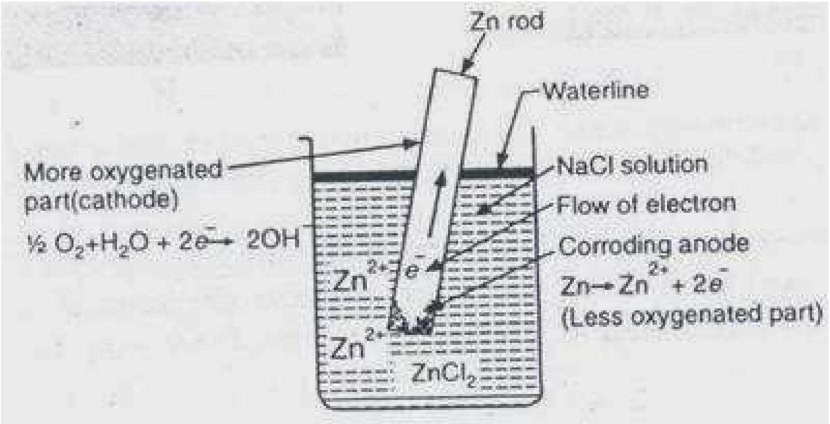
  At anode: $M \longrightarrow M^+ + ne^-$ (oxidation reaction)

  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. WATER LINE CORROSION (OR) DIFFERENTIAL AERATION 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.

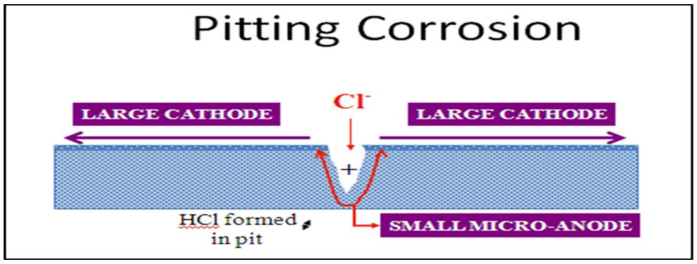


Differential aeration corrosion

- 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.

5. 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.



3 Explain various factors influencing the rate of corrosion and surface protection?

FACTORS AFFECTING CORROSION:

Important factors effect on the rate of corrosion are:

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

1. Nature of the metal:

I) Position of metal in galvanic series:

- When two metals or alloys are in electrical contact in presence of electrolyte, the metal which higher oxidation potential suffers corrosion.

The extent of corrosion is determined by the difference in the position of the metals. The greater is difference, the faster and higher is the corrosion.

Examples: 1. when iron electrical contact with Cu (or) Sn, iron undergoes corrosion since iron is higher oxidation potential than Cu and Sn.

2. When iron is coupled with Zn, Zinc undergoes corrosion due to zinc is higher oxidation potential than iron.

II) Purity of metal:

- Generally pure metal does not corrodes, impurities are present in a metal anodic part get cored. The extent of corrosion increases with the increasing impurities.

III) Surface of metal:

- A rough surface metal readily corrodes as it collects more dirt and provides more cathode spot for corrosion. A polished surface does not corrode easily.

IV) Relative areas of the anodic and cathodic parts:

- When two dissimilar metals are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and 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.

2. Nature of corrosive environment

i) Presence of impurities in atmosphere:

- The impurities like industrial gases and particulate matter, which is responsible for electrical conductivity of the surrounding environment, causes the corrosion of metal.

ii) Temperature:

- Corrosion rate is proportional to temperature. Increase in temperature results in an increase in the conductance of the aqueous medium and rate of corrosion also increases and vice versa.

iii) pH:

- Corrosion rate is more in acidic media than basic media. Low pH increase corrosion rate.

iv) Moisture in the atmosphere:

- Moisture containing atmosphere acts as an electrolyte and causes electrochemical type of corrosion.

PROTECTION OF METAL SURFACE:

1. Proper selection and Designing of materials:

- Corrosion is controlled by using Proper selection and Designing of materials.

- A pure metal should be selected over an impure metal as it is more resistant to corrosion than the latter.
- Metals occupying lower position in electrochemical series should be preferred over those in higher position.
- Alloys should be selected over the pure metal.
- Avoid the galvanic couplings in constructions.
- Avoid a combination of small anodic and large cathodic areas.

2. Cathodic protection:

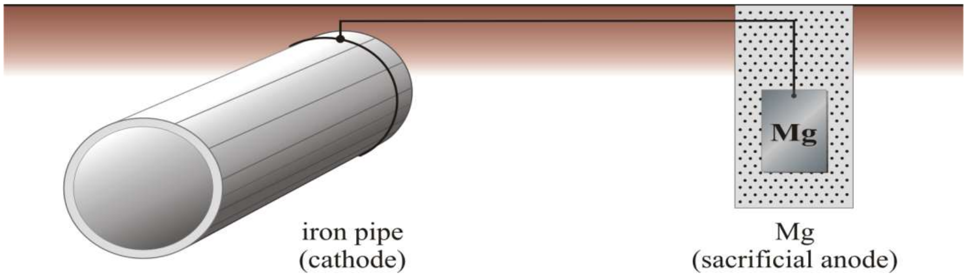
In this method the metal to be protected is forced to act as cathode and corrosion is controlled.

This is two ways

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

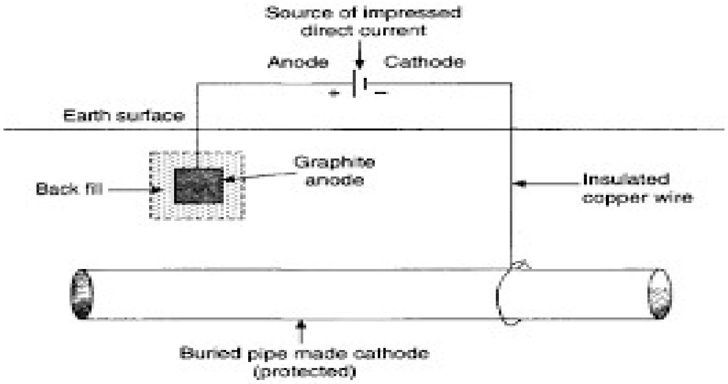
a) Sacrificial anodic protection:

- 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.



Application of 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

a) 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

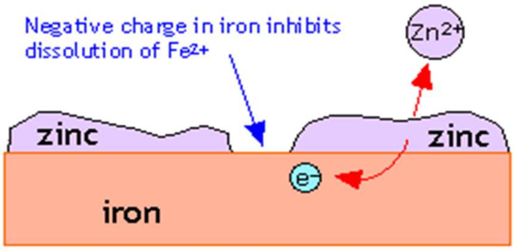
1. Anodic coatings:
   This type of coatings is produced by coating metal used as anodic metal on the surface of the base metal. Ex: coating of Zn, Al and Cd on Fe are anodic, because their reduction potentials are lower than that of base metal iron. If any pores or breaks in metallic coating, exposing 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.
2. Cathodic coating:

Cathodic coatings are obtained by coating a more noble metal (higher reduction potential)

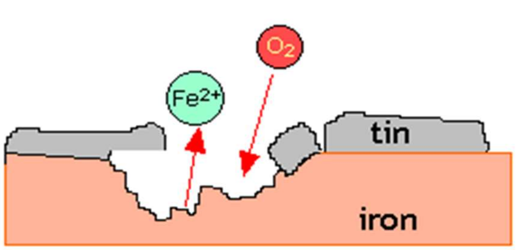
than the base metal. The coating metal has higher reduction potential than the base metal and

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



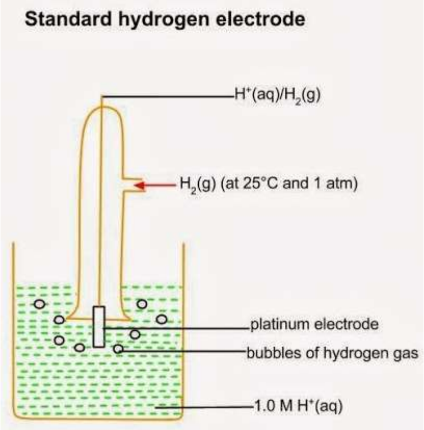
Noble coating

4 Explain any two of standard electrodes?

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 platinised electrode, while the remain escapes through the lower holes provided at the base of The glass tube.


Standard hydrogen electrode

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

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

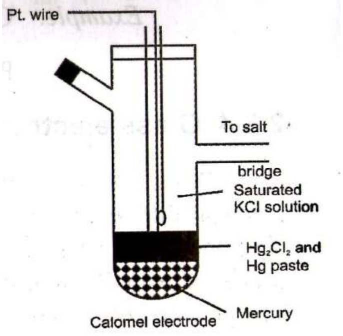
Limitations:

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.

Calomel electrode (Metal-metal salt ion electrode):

Construction:

- It consists of mercury, solid mercurous chloride and potassium chloride solution.
- Mercury is placed at the bottom of a glass tube with a side tube on both the sides.
- It is connected to the outer circuit by means of a platinum wire sealed in a glass tube.
- The surface of mercury is covered with a paste of mercurous chloride (calomel).
- A saturated, normal and deci normal potassium chloride solution is introduced through the side tube present in the right side.



Calomel electrode

Working:

When this electrode acts as anode the following reaction takes place:

At Anode: $2Hg(l) \leftrightarrows Hg_2^{2+} + 2e^-$ (Oxidation)

At Cathode: $Hg_2Cl_2 + 2e^- \leftrightarrows 2Hg + 2Cl^-$ (Reduction)

Thus calomel electrode is reversible with respect to ions. This electrode is represented as

$$Hg, Hg_2Cl_2(S); KCl \text{ (Solution)}$$

- The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. It can be determined accurately by connecting the electrode to a standard hydrogen electrode.
- Electrode potentials of calomel electrode at different concentrations of potassium chloride at 25°C are:

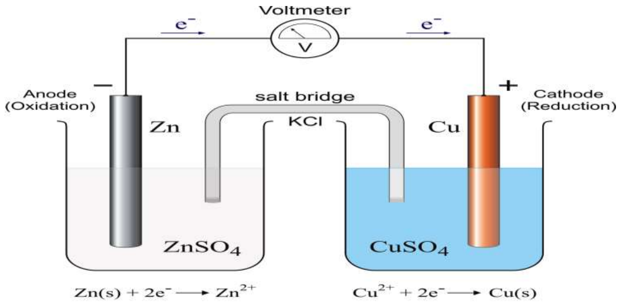
For saturated KCl solution, E = 0.24 *volts*
For 1 N KCl Solution, E = -0.28 *volts*
For 0.1 N KCl Solution, E = -0.34 *volts*

5 What is Electrochemical cell? Give an example and explain reversible and irreversible cells?

- electrochemical cell that converts chemical energy to electrical energy by spontaneous redox reaction within the cell.

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 CuSO4 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)

Net reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (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,

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

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.

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

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. The free energy (ΔG) of these cells are decreases.

Any cell which does not satisfy the above condition is called Irreversible cells.

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)

$$E_{(cell)} = E_{(Cathode)} - E_{(Anode)}$$

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 gain. 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 $Zn^{2+} + 2e^-$ ($E_{(ox)}$ = -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+}→ + $2e^-$ 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 Cu2+/Cu = 0.34V
E(L) of Zn/Zn2+ = -0.77V
$E_{(cell)} = E_{(R)} - E_{(L)}$
$= 0.34 - (-0.77)$
$= 1.10V$