DEPARTMENT OF CHEMISTRY

MODULE-1

Free energy

Definition:- Free energy refers to the amount of internal **energy** of a thermodynamic system that is available to perform work.

The sum of its enthalpy (H) and the product of the temperature and the entropy (S) of the system.

This quantity is defined as follows:

$$G = H - TS$$

In chemical reactions involving the changes in thermodynamic quantities, a variation on this equation is often encountered:

$$\Delta G = \Delta H - T\Delta S$$

ENTROPY

A thermodynamic state or property that measures the degree of disorder or randomness of a system.

It is represented by S

SI unit of entropy is Joules per Kelvin (JK^{-1})

Entropy can also be related to the states of matter: **solid, liquids,** and **gases**. Entropy increases as it goes from **solid** to **liquid** to **gas,** such that. $S_{solid} < S_{liquid} < S_{gas}$.

ELECTROCHEMISTRY and BATTERY TECHNOLOGY

Electrochemistry: It is a branch of chemistry which deals with the study of transformation of chemical energy into electrical energy and vice versa".

Electrochemical cells: "An electrochemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy".

SINGLE ELECTRODE POTENTIAL (E):

It can be defined as "the potential developed at the interface between the metal and solution, when it is in contact with a solution of its own ions"

OR

"Single electrode potential is a measure of tendency of a given half cell reaction to occur as reduction, when it is in equilibrium with the other half cell"

STANDARD ELECTRODE POTENTIAL (E^o):

"Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration; at 298K.If the elctrode involves a gas then the gas at one atmosphere pressure".

n

*EMF OF THE CELL***:**

"Emf is the potential difference between the two electrodes of a galvanic cell which causes the flow of current from one electrode to other",

$$EMF = E_{Cathode} - E_{Anode}$$

Nernst equation for single electrode potential:

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature.

The decrease free energy (-ΔG) represents the maximum amount of work that can be obtained from a chemical cell reaction.

-ΔG=W max……………………………1

W max = nFE…………………………….2

Where, n= No of electrons, E=Electrode potential & F= Faraday constant.

.' . -ΔG= nFE…………………………….3

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Under standard condition

$-\Delta G^o = nFE^o$……………………………….4.

Where, $-\Delta G^o$=Decrease free energy under standard condition, E^o=Standard electrode potential

Consider a reversible electrode reaction

$$M^{n+} + ne^- \rightleftharpoons M$$ ………………………5

According to Vanthoff's reaction isotherm

$$\Delta G = \Delta G^0 + RT.\ln K_c$$ …………6

Where, K_c=Equilibrium constant

Substitute the value of K_c, we have

$$\Delta G = \Delta G^0 + RT.\ln \frac{[M]}{[M^{n+}]}$$ …………7

Divide the equation (6) by -nF

From equation (3) and (4)

$$E = E^0 - \frac{RT}{nF}.\ln \frac{[M]}{[M^{n+}]}$$ ……………8

For a solid metal concentration is unity, so that [M] = 1

Then, we have

$$E = E^0 - \frac{RT}{nF}.\ln \frac{1}{[M^{n+}]}$$ ……………9

$$E = E^0 + \frac{RT}{nF}.\ln [M^{n+}]$$…………….10

$$E = E^0 + \frac{2.303RT}{nF}.\log [M^{n+}]$$………11

3

Substitute the value of R=8.314J/K/mol, T=298K, F=96500C/mol to the eqn. (11)

$$E = E^0 + \frac{0.0591}{n}.\log[M^{n+}] \ldots\ldots 12$$

Equation 12 is the Nernst equation for single electrode.

Nernst equation for emf of cells:

$$E_{cell} = E^0{}_{cell} + \frac{0.0591}{n}.\log\left[\frac{Species.at.Cathode}{Species.at.Anode}\right]$$

Reference electrodes:

"Reference electrodes are the electrode with reference to those, the electrode potential of any electrode can be measured".

There are two types of Reference electrodes

1) Primary reference electrode

2) Secondary reference electrode

Primary reference electrode –Standard hydrogen electrode, SHE whose potential is arbitrarily taken as Zero at all temperature.

Limitations of Primary Reference Electrode:

1. It is difficult to maintain H^+ ion concentration as 1M.
2. It is difficult to maintain a flow of one atm of hydrogen at the interface of Pt electrode.
3. Impurities present in hydrogen flow may poison the Pt electrode which alters the potential value.
4. It can't be used in presence of oxidizing agents.

Secondary reference electrode -Are the reference electrodes whose potential with respect to SHE are known and these are used to determine the electrode potential of other electrodes.

EX;- Calomel Electrode, Ag-AgCl Electrode etc

Advantages of Secondary Reference Electrodes:-

1. They have a constant and stable potential values at a particular temperature.
2. They are calibrated with respect to SHE.
3. They have the least potential gradient with temperature.
4. The potential values are reliable and measurements can be made with great accuracy.

Calomel electrode:

Calomel electrode is a metal-metal salt ion electrode. It consists of mercury, mercurous Chloride and a solution of KCl. Mercury is placed at the bottom of a glass tube.
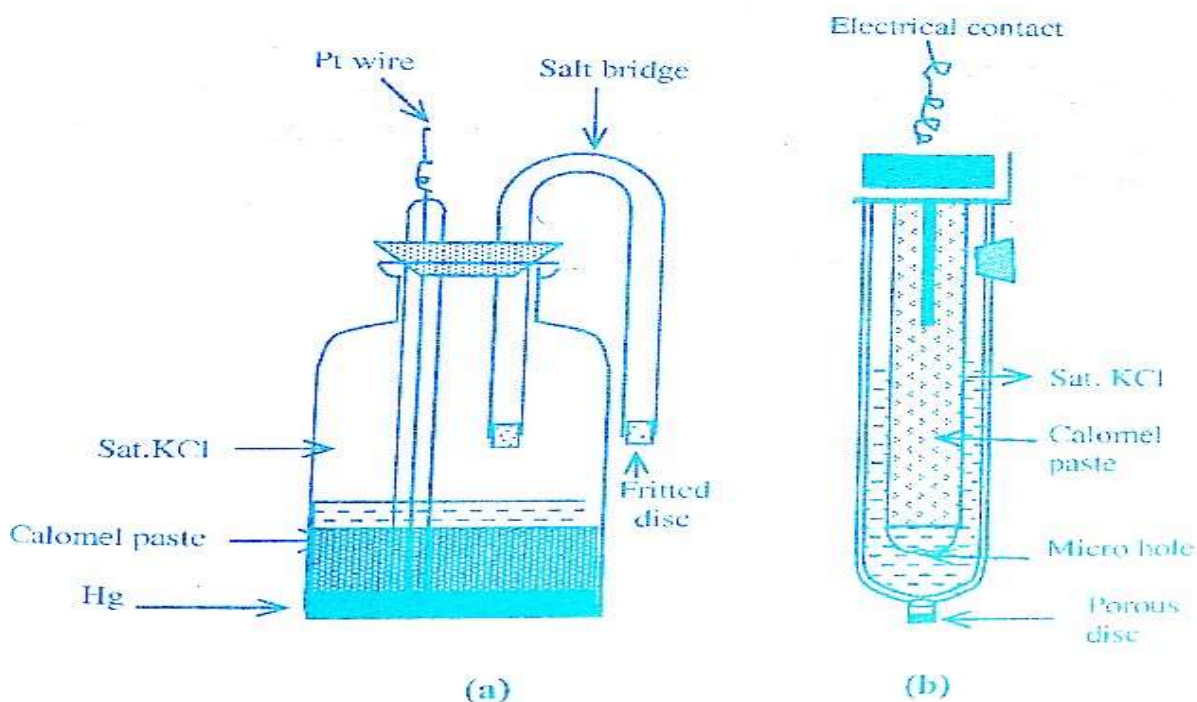
A paste of mercury and mercurous chloride Is placed above the mercury. The space above the paste is filled with a KCl solution of known concentration. A platinum wire is kept immersed into the mercury to obtain electrical contact. Calomel electrode can be represented as, **Hg| Hg₂Cl₂|Cl⁻.**

The calomel electrode can acts as anode or cathode depending on the nature of the other electrode of the cell.

The net cell reversible electrode reaction is,

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$
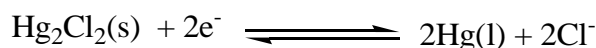
The Nernst equation is given by,

$$E = E^0 - \frac{2.303RT}{2F}\log[Cl^-]^2$$

$$E = E^0 - \frac{2.303RT}{F}\log[Cl^-]$$

$$E = E^0 - 0.0591\log[Cl^-] \text{ at } 298 \text{ K}$$

The electrode potential of calomel electrode is depending upon the concentration of KCl used, 0.1N KCL→ 0.334V, 1N KCL→0.281V, Sat.KCL→0.2422V.

Advantages:-

1. Simple to Construct.

 2. Cell potential does not vary with temperature.

3. The cell potential is reproducible and constant over a long period.

Applications:

1. It is used as secondary reference electrode in the measurement of single electrode.

2. It is used as reference electrode in all potentiometer determinations.

3) The SCE is used in pH measurement

Ion-selective electrode: "Ion selective electrode is one which selectively responds to specific ions in a mixture and the potential developed at the electrode is a function of the concentration of those ions in the solution".

Uses:- To determine the concentration of a number of cations and anions such as H^+, Li^+, Na^+, K^+, Pb^{2+}, Cu^{2+}, Mg^{2+}, CN^-, NO^{3-}, F^- etc.

There are Four types of membranes, They are

1) Glass membranes   3) Solid State membranes
2) Heterogeneous membranes   4) Liquid membranes

Glass electrode:

Principle: - A thin walled glass bulb containing an acid is immersed in another solution a potential is developed across the glass membrane. The potential difference, E_b at the interface is referred to as boundary potential is the difference in potential (E_1-E_2) developed across the layer of the glass membrane b/w the two liquids.
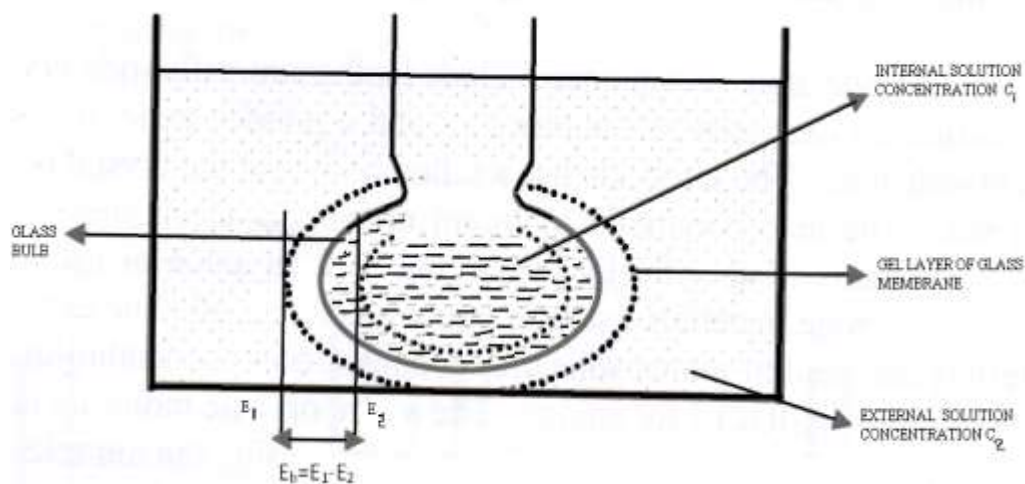
The potential of glass electrode E_G is given by

$E_G=E_1-E_2$ 1   Where, E_1&E_2 are the electrode potential of outer & inner membrane

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E_G= [E^o+0.0591 log [C_2]] - [E^o+0.0591 log [C_1]] 2   Where C_1 & C_2 are the concentration inner & outer acid solutions.

$$E_G = 0.0591.\log \frac{[C_2]}{[C_1]} \quad \text{...............3} \quad \textbf{Or} \quad E_G = 0.0591.\log \frac{[C_2]}{[C_1]}$$
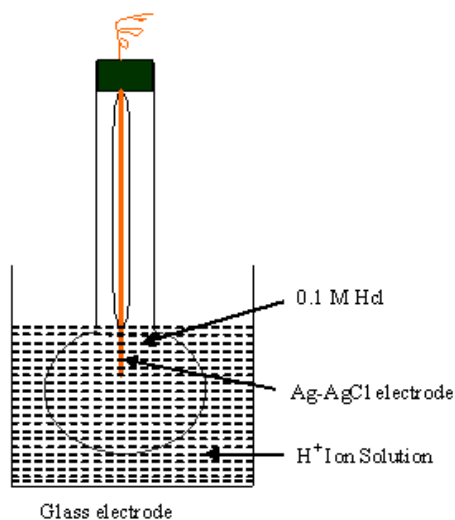
$$E_G = -0.0591.\log[C_1] + 0.0591.\log[C_2] \text{......4}$$

Since the H^+ concentration inside the glass bulb is a constant. The first term on RHS of the above equation becomes a constant.

$$E_G = Constant + 0.0591.\ log[C_2] \text{.............5}$$

$$E_G = Constant + 0.0591.\ log[H^+] \text{.........6} \qquad \text{Since, } C_2 = [H^+]$$

$$E_G = Constant - 0.0591.\ pH \text{............7} \qquad \text{Where pH = -log } [H^+]$$

0.1 M HCl

Ag-AgCl electrode

H^+Ion Solution

Glass electrode

A glass electrode is an ion selective electrode where potential depends upon the pH of the medium. The glass electrode consists of a glass bulb made up of special type of glass (22%Na_2O, 6%CaO, and 72%SiO_2) which has low melting point and relatively high electrical conductivity. The glass bulb is filled with a solution of constant pH (0.1MHCl) and insert with a Ag-AgCl electrode, which is the Internal reference electrode and also serves for the external electrical contact. The electrode dipped in a solution containing H^+ ions. The electrode representation is,

Glass | 0.1M HCl | Ag-AgCl.

Advantages

1. This electrode can be used to determine pH in the range 0-9, with special type of glass even up to 12 can be calculated.

2. It can be used even in the case of strong oxidizing agents.

3. The equilibrium is reached quickly.

4. It is simple to operate, hence extensively used in various laboratories.

Limitations

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.

2. This electrode cannot be used to determine the pH above 12.

Determination of pH using glass electrode:

Principle: When a thin glass membrane is placed between two solutions of different pH values, a potential difference arises across the membrane. The potential difference varies as the pH of these solutions varies. In practice, pH of one of these solutions is kept constant and therefore the electrode potential depends on pH of the other solution ie. Experimental solution.
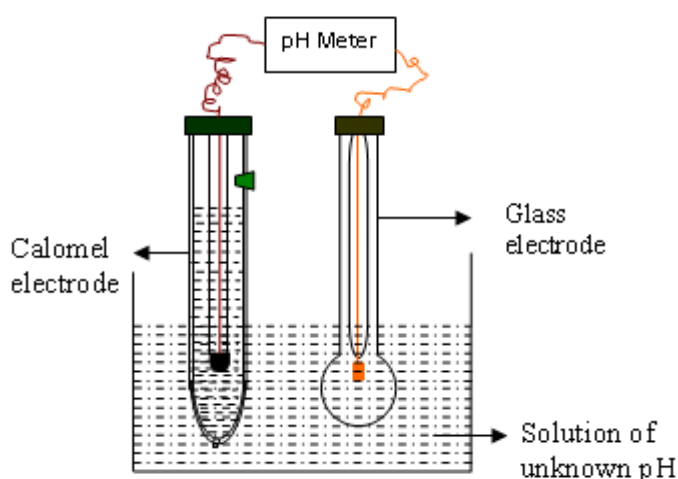
Procedure: glass electrode is immersed in the solution; the pH is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge. The cell assembly is represented as,

Hg| Hg$_2$Cl$_2$|Cl$^-$||Solution of unknown pH|glass|0.1M HCl|Ag$^+$|AgCl

The emf of the above cell, E$_{cell}$ is measured using an electronic voltmeter with a pH meter.

The emf of the cell is given by

E$_{cell}$ = E$_{cathode}$ - E$_{anode}$ 1

E$_{cell}$ = E$_{glass}$ - E$_{SCE}$ 2

Since E$_{SCE}$ is knowing EMF of the cell,

Substitute the value of E$_G$ to equation (2)

$$E_{cell} = Cons\tan t - 0.0591.pH - E_{sce} \quad ....3$$

$$pH = \frac{Cons\tan t - E_{cell} - E_{sce}}{0.0591} \quad ....4$$

Concentration cells:

Electrolyte Concentration cell;- "Concentration cell is an electrochemical cell in which the electrode material and the solution in both the electrodes are composed of the same substances but only the concentrations of the two solutions are different".

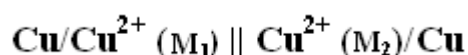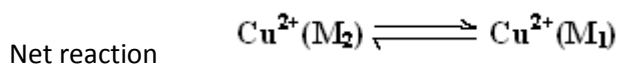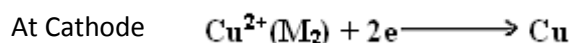A typical example of Copper concentration cell is shown below.
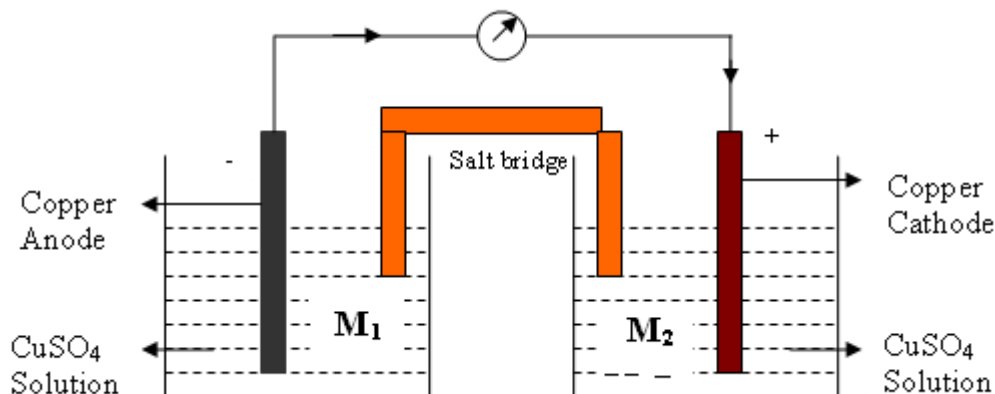
It consists of two Copper electrodes are immersed in two different concentration of $CuSO_4$ solutions .These two electrodes are externally connected by metallic wire and internally by a salt bridge. The cell can be represented as,

$$Cu/Cu^{2+} (M_1) \parallel Cu^{2+} (M_2)/Cu$$

By convention left hand electrode is the anode and right hand electrode is cathode.

At Anode $\qquad Cu \longrightarrow Cu^{2+}(M_1) + 2e$

At Cathode $\qquad Cu^{2+}(M_2) + 2e \longrightarrow Cu$

Net reaction $\qquad Cu^{2+}(M_2) \rightleftharpoons Cu^{2+}(M_1)$
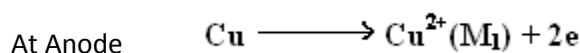
The net cell reaction is merely the change in concentration as a result of current flow.

Emf of concentration cell:

We know that electrode potential depends upon the concentration of the electrolyte. By convention, the potential of the cell is

$\qquad E_{cell} = E_{cathode} - E_{anode}$ 1

$$E_{cell} = \frac{0.0591}{n}.\log[M_2] - \frac{0.0591}{n}.\log[M_1] \qquad ....2$$

$$E_{cell} = \frac{0.0591}{n}\log\frac{[M_2]}{[M_1]} \qquad \text{at 298K} \qquad ....3$$

From equation (3) following conclusions may be drawn.

1. When the two solutions are of the same concentrations, $\log\frac{[M_2]}{[M_1]} = 0$ and no electricity flows.

Hence, Ecell=0

2. When $M_2/M_1>1$ i.e $M_2>M_1$, log M_2/M_1 is positive & electrode potential is positive.

3. Higher the ratio of M_2/M_1, higher is the value of cell potential.

BATTERY TECHNOLOGY

Battery: It is a device consisting of two or more galvanic cells connected in series or parallel or both.

Principle components of a battery are:

1. An anode where oxidation occurs.
2. A cathode where reduction occurs.
3. An electrolyte, which is ionically conducting.
4. A separator to separate anode and cathode compartments.
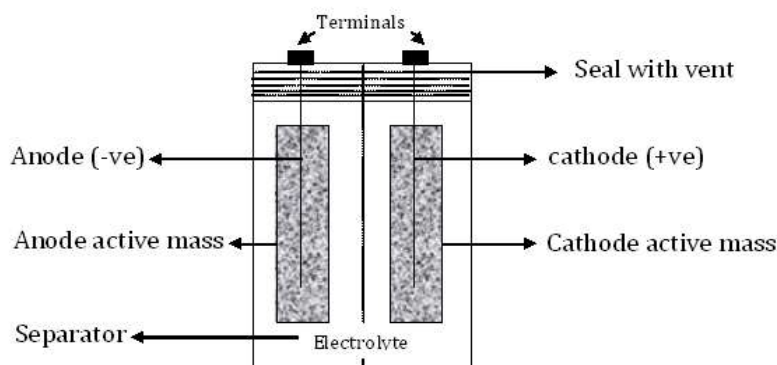
Classification of batteries:

1. Primary batteries: In these batteries the cell reaction is not reversible, after discharging cannot be rechargeable.

Ex. Zn-MnO$_2$ dry cell.

2. <u>Secondary batteries</u>: In these battery the cell reaction is completely reversible, after discharging can easily rechargeable.

 Ex. Lead-acid battery, Ni-MH battery.

3. <u>Reserve batteries</u>: In these batteries, one of the active components (e.g. electrolyte) of the battery is separated from the rest of the components. It is assembled just before the use.
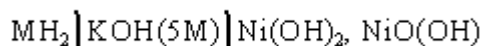
 Ex. Mg-water activated battery.
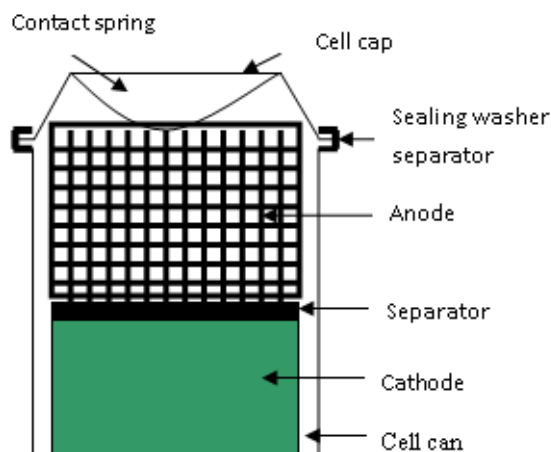
Nickel-metal hydride battery:

Construction: In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed. The active material for the anode is a mixture of a metal hydride (such as TiH_2, VH_2, or ZrH_2) and a hydrogen storage alloy (such as $LaNi_5$ or $TiNi$). The active material for cathode is nickel oxy hydroxide, $NiO(OH)$. An aqueous solution of KOH acts as the electrolyte. Polypropylene is used as the separator.

The anode material has (i) a good hydrogen storage capacity capable of adsorbing and desorbing hydrogen as the battery is discharged and charged. (ii) High resistance to chemical oxidation and corrosion and (iii) high electrochemical reactivity.

Cell representation:
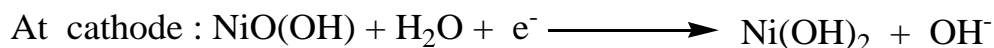
$$MH_2 \big| KOH(5M) \big| Ni(OH)_2, NiO(OH)$$

Cell reactions:

At anode : $MH + OH^- \longrightarrow M + H_2O + e^-$

At cathode : $NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$

 Over all reaction: $MH + NiO(OH) \longrightarrow M + Ni(OH)_2$

Uses: Used in cellular phones, camcorders and laptop computers.

Figure 3.3 Transport Diagram
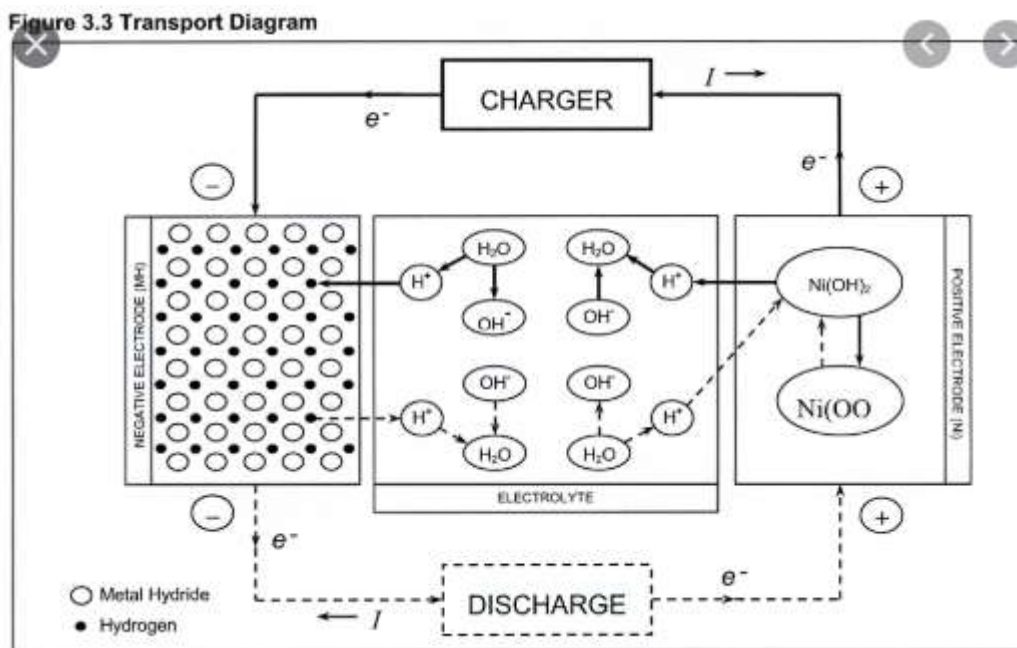
Advantages:

- Less sensitive to high temperatures than Li-ion and Lead-acid
- Handle abuse (overcharge or over-discharge better than Li-ion bat

Disadvantages:

- More cells in series are need to achieve some given voltage.
- Cost

Lithium batteries: These batteries with high energy density, high energy efficiency, high voltage and long life cycle.

There are two types of lithium-based batteries available.

- 1. Lithium batteries
- 2. Lithium-ion batteries

In lithium batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable.

In lithium-ion batteries, lithium compounds are used as anode.

These batteries are known as re-chargeable batteries.

Lithium has the following characteristics.
(i)   It is light weight.
(ii)   It has high electrochemical equivalence (3.86 Ah g^{-1}).
(iii)   It has good electrical conductivity.
(iv)   It has high standard electrode potential (-3.05V).

Li- ion battery:

A conventional lithium ion battery consists of Li ion and a metal oxide such as lithium cobalt oxide ($LiCoO_2$) forms the anode and carbon (graphite) as cathode. The electrolyte consists of a lithium salt in an organic solvent. The

salts include lithium hexafluorophosphate $LiPF_6$, lithium tetrafluoroborate $LiBF_4$ and lithium perchlorate $LiClO_4$. The solvents used are ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The cell delivers an emf of 4V.

Anode reaction: $LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + xLi^+ + x\,e$

Cathode reaction: $x\,Li^+ + xe + Graphite \longrightarrow xLi\text{-}Graphite$

Net reaction: $LiCoO_2 + Graphite \rightleftharpoons Li_{1-x}CoO_2 + xLi\text{-}Graphite$
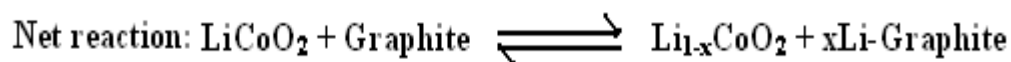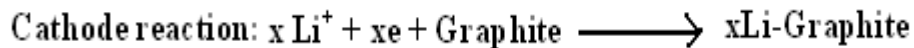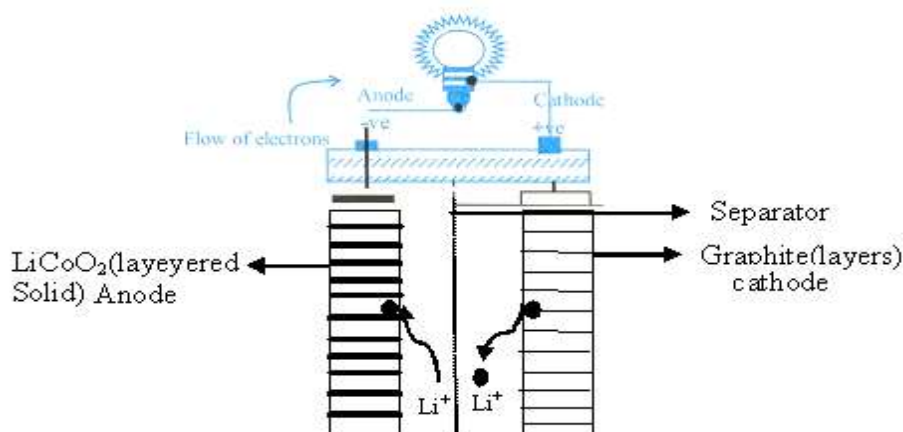
With discharge the Co is oxidized from Co^{3+} to Co^{4+}. The reverse process (reduction) occurs when the battery is being charged.

Applications: Used in laptops, cell phones and airspace applications.

Schematic representation of a Lithium-ion cell
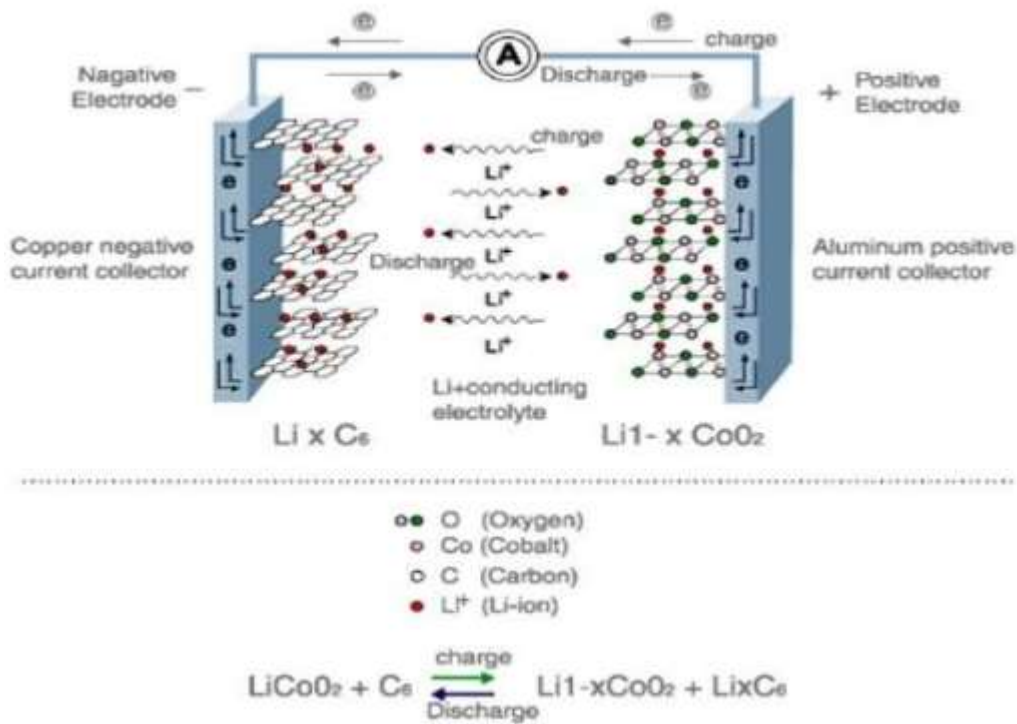
- ●○ O (Oxygen)
- ○ Co (Cobalt)
- ○ C (Carbon)
- ● Li^+ (Li-ion)

$$LiCoO_2 + C_6 \underset{Discharge}{\overset{charge}{\rightleftarrows}} Li_{1-x}CoO_2 + Li_xC_6$$

Upon charging, Li^+ ions are released by the cathode and intercalated at the anode. When the cell is discharged, Li^+ ions are extracted by the cathode and inserted into the anode.

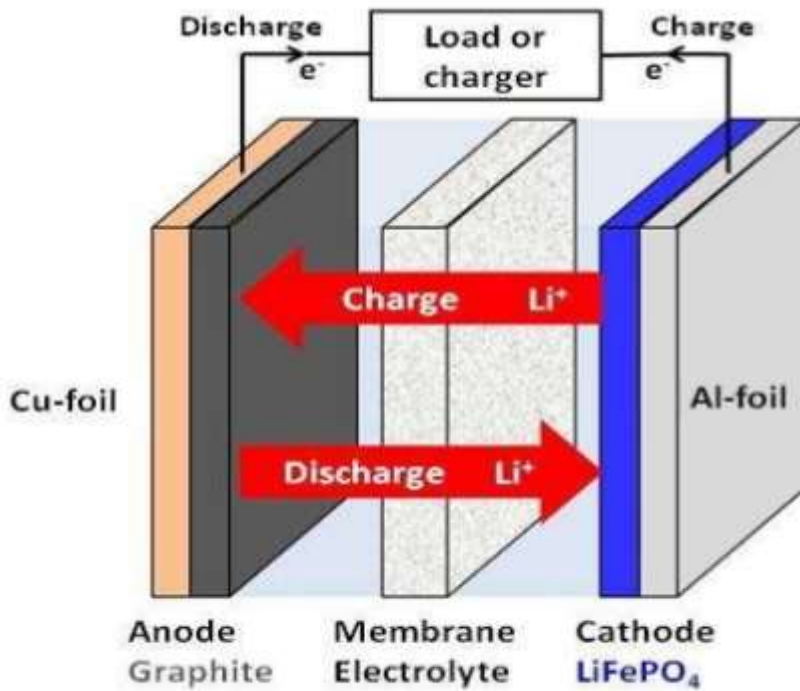- During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery.

- Simply, the Li-ion is transfers between anode and cathode through lithium Electrolyte.

- Since neither the anode nor the cathode materials essentially change, the operation is safer than that of a Lithium metal battery.

- Advantages with respect to lead-acid batteries:
  - Less sensitive to high temperatures (specially with solid electrolytes)
  - Lighter (compare Li and C with Pb)
  - They do not have deposits every charge/discharge cycle (that's why the efficiency is 99%)
  - Less cells in series are need to achieve some given voltage.
- Disadvantages:
  - Cost

MODULE-2

CORROSION and METAL FINISHING

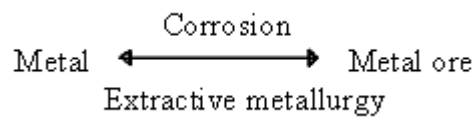**Definition:** Corrosion is a destruction reaction taking place spontaneously by chemical or electrochemical reaction of the metal by the surrounding environment on the surface of the metal.

Corrosion

Metal ⟷ Metal ore

Extractive metallurgy

A slow and continuous process of destruction of metallic substance through spontaneous chemical and electrochemical attack by its environment starting at its surface is called corrosion.

Reason: Pure isolated metals will have higher energy content than their corresponding ores and their compounds hence they have a natural tendency to revert back to combined form by combining with the contents of the environment such as gases, liquids, moisture etc. when exposed. This is the basic reason for corrosion.

Electrochemical theory of corrosion:-

According to electrochemical theory, corrosion of metals occurs due to the following changes, when they are exposed to the environment.

1) A large number of minute galvanic cells are formed which acts as anodic and cathodic areas.

2) At anode the metal undergoes oxidation and electrons are liberated which migrates towards cathodic region

3) Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxyl ions at the cathode

Air

Moisture

Anodic area e^- Cathodic area   Iron metal
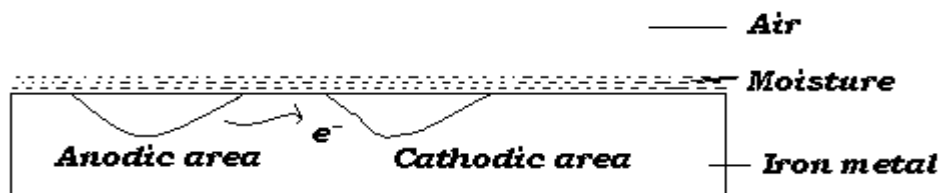
Anodic reactions: At anode the metal undergoes oxidation-liberating electrons

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

Metal   Metal ions
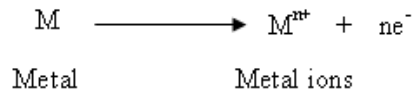
Ex: when iron is exposed to the environment it undergoes oxidation as

$$Fe \longrightarrow Fe^{2+} + 2e^-$$
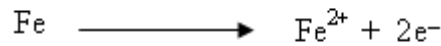
Cathodic reactions: The electrons released at anode migrate to the cathodic area and reduces oxygen to hydroxyl ions.

The different cathodic reactions are,

a) In acidic medium: In acidic medium and in the absence of oxygen, hydrogen ions are reduced to hydrogen gas

$$2H^+ + 2e^- \longrightarrow H_2$$
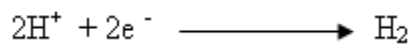
b) In alkaline and in the absence of O_2. If the solution is alkaline and in the absence of oxygen the cathodic reaction is,

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$
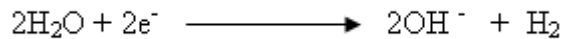
c) In neutral and aerated medium: when the solution is neutral and aerated, hydroxyl ions are formed as follows.

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$
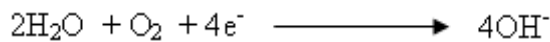
d) Formation of corrosion product: The hydroxyl ions migrate towards anode and react with metal ions (M^{n+} ions) and forms corrosion product. In the case of iron OH- reacts with Fe^{2+} ions and forms an insoluble hydrated ferric oxide known as brown rust.

$$2Fe^{++} + 4OH^- \longrightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2(Fe_2O_3. 3H_2O) \text{ rust}.$$
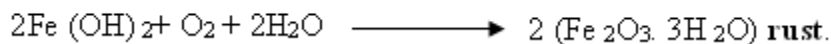
If i_{corr} (corrosion current) is the current flowing,

Then Rate of corrosion = $\mathbf{i_{corr}/nF}$ grams per second. n=charge on the ions, F=Faraday constant

The total current due to the cathodic reaction ($\sum i_c$) must be equal but opposite in sign, to the total current flowing out due to the anodic reaction ($-\sum i_a$).

$$\mathbf{i_{corr} = -\sum i_a = \sum i_c}$$

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__Galvanic Series__: The arrangement of elements in the order of their standard reduction potential is referred to as emf or electrochemical series. Such an arrangement of few elements given in the table.

M^{n+}/M_n	E°(V)	M^{n+}/M_n	E°(V)
Li^+/Li	-0.305	Sn^{2+}/Sn	-0.14
K^+/K	-2.93	Pb^{2+}/Pb	-0.126
Ca^+/Ca	-2.87	H^+/H_2	0.000
Na^+/Na	-2.71	Cu^{2+}/Cu	0.34
Zn^{2+}/Zn	-0.76	Ag^+/Ag	0.80
Fe^{2+}/Fe	-0.44	Hg^{2+}/Hg	0.85
Cd^{2+}/Cd	-0.40	Pt^{2+}/Pt	1.20
Ni^{2+}/Ni	-0.236	Au^{3+}/Au	1.38

1). A negative value indicates oxidation tendency and a positive value indicates reduction tendency with respect to hydrogen.

2).The metal with lower electrode potential is more reactive and as the electrode potential increases, the reactivity decreases and metals with higher electrode potentials are more noble.

3).Metals with lower electrode potentials has the tendency to replace metals with higher electrode potential from their solutions for example, Zn displaces Cu, Cu displaces Ag.

4).Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

Factors affecting rate of corrosion

1. Primary Factors
- Ratio of anodic to cathodic area
- Nature of Metal
- Nature of Corrosion product

2. Secondary Factors
- pH
- Conductivity
- Temperature
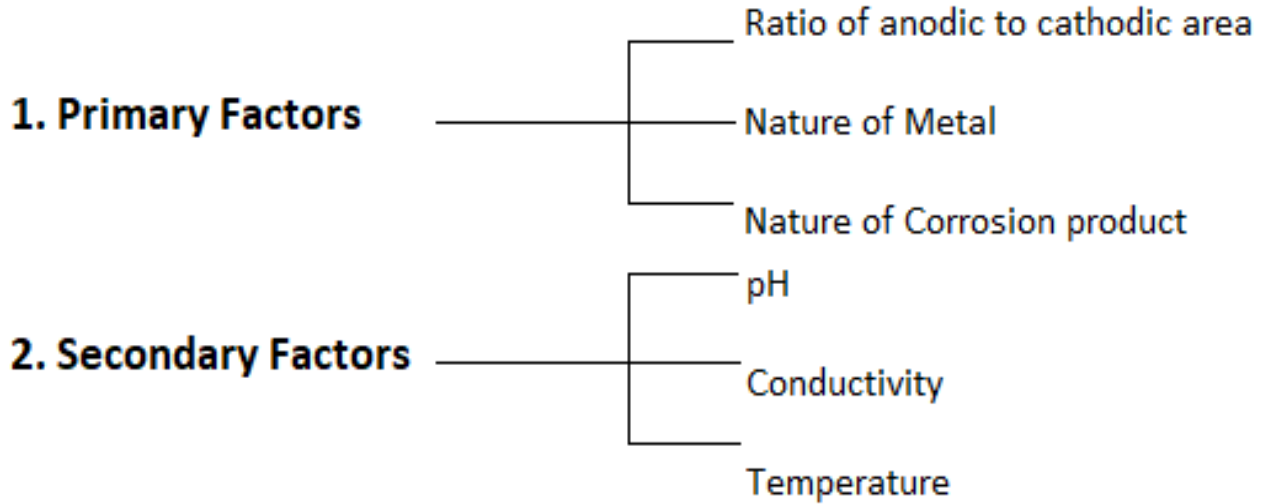
Primary Factors **(Related to metal)**

1. **Ratio of Anodic to Cathodic areas:-**The Rate of corrosion is highly influenced by the relative sizes of anodic and cathodic areas.

    Smaller the anodic area and larger the cathodic area then the rate of corrosion is more (Because the rate of consumption of electrons at the cathode is more therefore anode under undergoes more oxidation and increases the rate of corrosion at anode.)

    If the cathode is smaller than the anode, the rate of electrons consumption at the cathodic area decreases and the rate of corrosion also decreases.
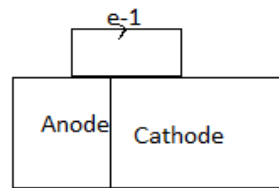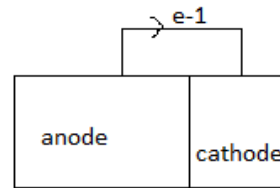
a) Rate of corrosion is more   b) Rate of corrosion is less

Ex.

2. **Nature of the metal;-**

1. Corrosion is a surface phenomenon smaller the size more will be the area exposed & more will be the rate of corrosion.
2. Rough surface will suffer more corrosion compared to smooth surface.
3. Impure metal is more corrosive.
4. Metals with lower electrode potential are more reactive(rate of corrosion is more) than with higher electrode potential

3. **Nature of corrosion product:**

Corrosion of the metal the product is usually its oxide which forms a layer on its surface. The oxide layer determines the corrosion rate. If the corrosion product is adherent, insoluble, stable, uniform, nonporous with low ionic & electronic conductivities then the layer will form a barrier for further corrosion, hence prevents corrosion and vice versa.

Secondary factor (Related to Environment)

1. **pH of the medium:**

Acidic medium i.e. lower pH is more corrosive than the alkaline medium (i.e. higher pH) however some metals like Zn, Al etc. undergo corrosion in alkaline medium also hence a pH range around 7 i.e. (6-8) gives least corrosion.

2. **Conductivity:-**

Higher the conductance more will be the flow of corrosion current, hence corrosion of metal buried in clay and mineralized soils will be more than those under dry sandy soils. The rate of corrosion in a dry atmosphere is less than that in a wet atmosphere

Ex. A metal immersed in sea water corrodes rapidly than a metal immersed in river water.

3. Temperature;-

Rate of corrosion reaction always increase with increase in temperature, increase in temperature increases the conductance of the medium which contributes the rate of corrosion.
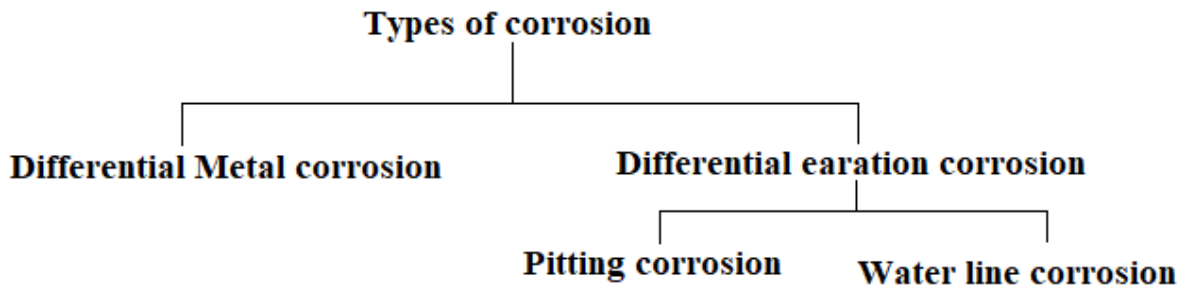
1). *Differential metal corrosion:*

When two dissimilar metals are in direct contact with one another and exposed to a corrosive conducting medium, the metal higher up in the electrochemical series behaves as anode and suffers from corrosion, whereas the metal lower in the electrochemical series become cathode with respect to the other metal and is protected from corrosion. This type of
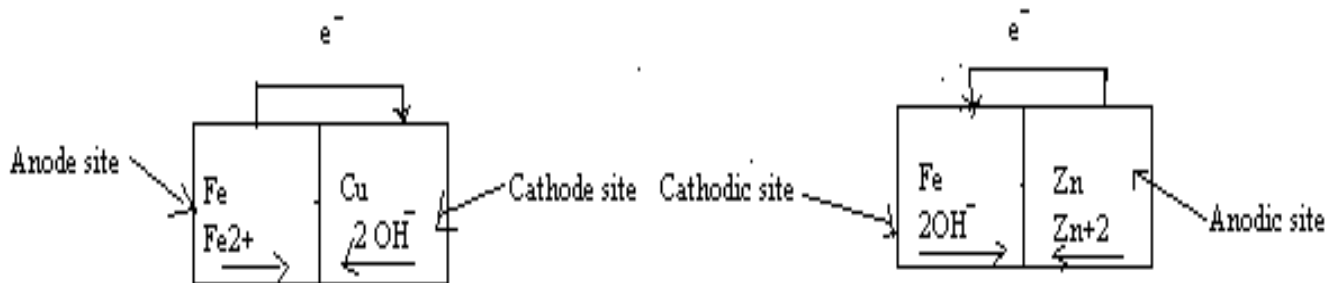
corrosion is also known as *galvanic corrosion*.

When Zn & Cu metals are electrically connected and exposed to an electrolyte, Zn metal higher in galvanic series forms anode and suffers from corrosion whereas Cu lower in

electrochemical series forms cathode hence protected from corrosion. The extent of corrosion depends on the difference in the electrode potential of the two metals and also their relative areas exposed, if the potential difference between the electrodes is high, greater the extent of corrosion. **Eg:** 1). Brass taps fixed to an iron pipe. 2). Steel screws in a brass marine hard ware.

2). *Differential Aeration Corrosion:*

When a metal surface is exposed to differential air or oxygen concentrations forms differential aeration cell. The more oxygenated part of the metal behaves as cathode and the less oxygenated part become anode .Differential aeration of metal causes a flow of current called the differential current & the corrosion is called as differential aeration corrosion.

This phenomenon can be explained by two types of differential aeration corrosion. They are.
   a. Pitting Corrosion   b. Water line corrosion

a. *Pitting Corrosion:*
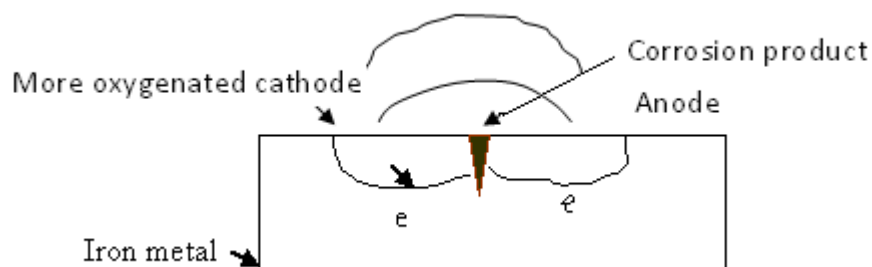
● **Pitting corrosion** is a localized accelerated attack in which only small areas of the metal surface are attacked whilst the remainder is largely unaffected. This localized attack results in pitting. The pits may initiate and propagate to a certain depth resulting in the formation of cavities and becomes inactive.
●   Pitting is very destructive and frequently ruins the tubes, pipes etc.
●   Pitting is due to breakdown or cracking of the protective film on a metal at specific points.
●   The presence of impurities like sand, dust, scale, etc., on the surface of metal leads to pitting.
●   Pitting corrosion is due to the formation of differential aeration cell.
●   This attack becomes more intensified with time.

b. *Water line corrosion:*

Poor oxygenated Area (anode) — more oxygenated area (cathode)
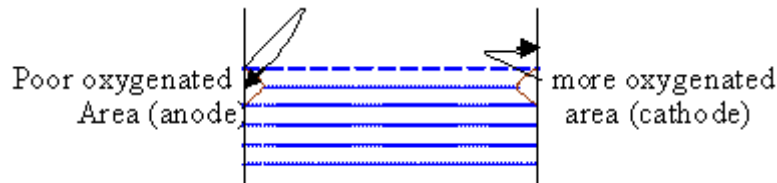
- Differential aeration accounts for the corrosion of metals partially immersed in a solution, just below the water line. This type of differential aeration corrosion is also known as **water line corrosion.**
- Consider a steel tank containing water. The maximum corrosion takes place along a line just beneath the level of water meniscus. The area above the waterline is highly oxygenated and acts as the cathodic and completely unaffected by corrosion. (Eg. Marine plants attacking themselves in the sides).

Corrosion control:

Corrosion can be controlled by preventing the formation of galvanic cells the common methods used to control corrosion of metals are as follows.

1. **Anodizing:- Anodizing of Aluminium**
2. **Cathodic protection: - 1. Sacrificial Anodic Method**
   2. Impressed current Method
3. **Metal coatings:-Galvanization**

Anodization of Al:

Def^n: - 'A process in which a protective active oxide is formed chemically on metals is called anodization'.

Anodization of Al consists of the following steps.

Step 1: - Preparation of Al base metal surface.

The metal surface is degreased using organic solvents & rust is removed by sand blasting, grinding, acid pickling etc.

Step 2: - Al base metal is placed in an oxidizing bath like chromic acid (Cr_2O_3) or boric acid (H_2BO_3) or H_2SO_4.

Step 3: - The base metal is made anode and connected to a battery while lead is used as cathode. A current of $150mA/Cm^3$ at 10-28v at 25-40°C is passed Al_2O_3 gets deposited. Then it is washed with water.

Step 4:- The base metal with the oxide layer is boiled with water using colouring agent to get desired colour.

$$Al_2O_3 + H_2O \longrightarrow Al_2O_3.H_2O$$

Step 5:- The base metal is further treated with nickel acetate to increase its resistance to corrosion.

Application:
- It is used to make soapbox, Tiffin carriers, window frames etc.

Covering the metal (substrate or base metal) with a layer of another metal in order to control the corrosion of the base metal by the environment is called as metal coating.

Cathodic protection:

The principle of this method is to convert the corrosive base metal into a cathode. This is done by
1. Sacrificial anodic protection. 2. Impressed current technique.

1. *Sacrificial anode method:*

The metallic structure to be protected is made relatively a cathode by using another anodic metal contact with it. So that the corrosion is now concentrated on more anodic metal protecting the base metal from corrosion. The sacrificial anodes to be replaced by fresh ones as and when it is required. Commonly used sacrificial anodes are: Mg, Zn, Al etc.

This method is generally employed for the structures buried in water or streamers anchored in the sea, buried pipelines, ship hulls etc.

Sacrificial anode
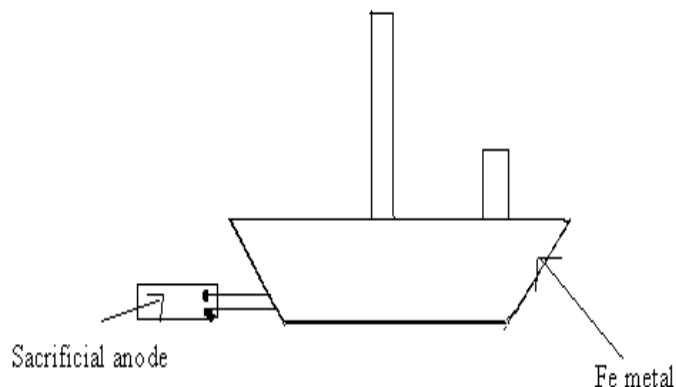
Fe metal

2. *Impressed current technique*:

In this method the anodic base metal which is oxidizable in corrosion reaction is supplied with electrons the current is applied in the opposite direction to nullify the corrosion current i.e. through a small current flow by means of a battery so that oxidation is suppressed and corrosion of the base metal is reduced. An insoluble anode (ex: graphite, high silicon content iron, etc.) is buried in the soil, and connected to the structure to be protected. The anode is usually placed in a backfill, to provide a better electrical contact with the surroundings. This is employed to large metal structures buried in soil.
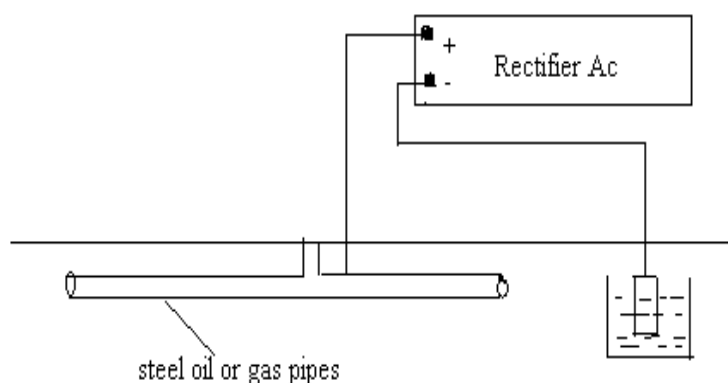
Galvanizing:

Coating of Zn on Fe is commonly called as galvanization. It is an anodic metal coating process; this is done using hot dipping method which involves several steps.

Step 1: Preparation of base metal surface.

  a. Cleaning with organic solvents like trichloroethylene.
  b. Sand blasting to remove scale.
  c. Grinding and polishing to remove rust.
  d. Acid pickling to remove traces of oxide layer.
  e. Washing with water and drying.

Step 2: Hot dipping.

The base metal is dipped in molten Zn at 425-432°C with ammonium chloride or $ZnCl_2$ as flux.

Step 3: Removal of excess coating of Zn.

This is done by centrifuging in case of small article or by calendaring in case of a sheet.

Step 4: Annealing

The substrate is heated above the melting point of Zn & cooled slowly.
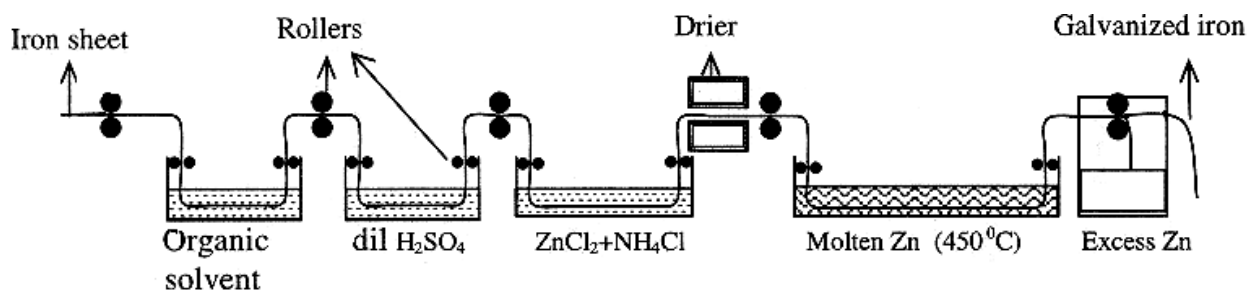
Galvanization of iron

Advantages:

Since the coating is anodic in nature the exposure of base metal will not cause corrosion.

Disadvantages:

Since Zn salts are poisonous food materials cannot be stored in container.

Uses:

To make galvanized articles.

In making of roofing sheets, buckets, wires, pipes.

To manufacture automobile parts, bolts & nuts, nails etc.

METAL FINISHING:

Def^n: Metal finishing is the process of deposition of a layer of one metal on the surface of substrate (metal, plastic etc) or the process of conversion of a surface layer of atoms on a metal into an oxide film. (Note: Metal finishing is the process of surface modification of a metal)

Electroplating and Electroless plating are two important techniques of metal finishing.

Technological importance of metal finishing: Metal finishing is carried out to obtain technologically important surface properties. These properties are:

1.   A decorative appearance.
2.   An improved corrosion resistance.
3.   An improved heat resistance.
4.   An improved surface hardness. (An improved resistance to wear and tear. An improved resistance to abrasion.)
5.   Improved solder ability.
6.   Good thermal conductivity.
7.   Good electrical conductivity.
8.   Good thermal reflectivity.
9.   Good optical reflectivity.

Principles of Metal Finishing:
a) Polarization:

Def^n: - Polarization is defined as a process where there is a variation of electrode potential due to inadequate supply of ionic species from the bulk of the solution to the electrode surface.

Consider an electrolytic cell under operation. When current is being passed, positive ions are produced at the anode and are consumed at the cathode. If the diffusion of ions in the electrolyte is slow, there will be an accumulation of positive ions in the vicinity of anode. Similarly, there will be a depletion of ions in the vicinity of cathode. Under these conditions, the anode and cathode are said to be polarized. This type of polarization is known as concentration polarization. **(Note: In galvanic cells, polarization leads to a variation of electrode potential).**

In electrolytic cells, polarization leads to use of higher potentials than required theoretically.

Factors affecting the electrode polarization:

1. Nature of the electrode: Electrodes with rough surface have low polarization.
2. Nature of products formed at the electrode: If the products form a film on the surface, polarization increases.
3. Nature of the electrolyte: Lower the concentration of the electrolyte, lower is the polarization.
4. Temperature: Higher the temperature, lower is the polarization, because, at higher temperatures rate of diffusion of ions is higher.
5. Rate of stirring of the electrolyte: Stirring helps in minimizing the polarization effects.

b) *Decomposition potential*:

"**When an electric current is passed through an electrolyte, electrolysis takes place only when applied voltage is above a certain value called a decomposition Voltage**" below this value no electrolysis occurs since the current passing through the cell is very low. Consider the electrolysis of a dilute acid, only when the applied voltage exceeds 1.7 V there is an evolution of oxygen & hydrogen, below this value no electrolysis occurs.

The decomposition voltage may be defined as "**The minimum external voltage that must be applied in order to bring about continuous electrolysis of an electrolyte**" Electrolysis of salt solution also occurs above a certain minimum voltage.

A plot of current v/s applied voltage is as shown in the figure

When the applied voltage is small the increase in current is very slight however, beyond the decomposition potential there is a sharp increase in the current. The decomposition voltage of an electrolyte is due to emf of the cell set by the products of electrolysis. The product formed accumulate on the electrode and a cell is set up which exerts a back emf which resist the flow of current until the applied voltage exceeds this emf. The magnitude of the back emf is same as the decomposition potential.
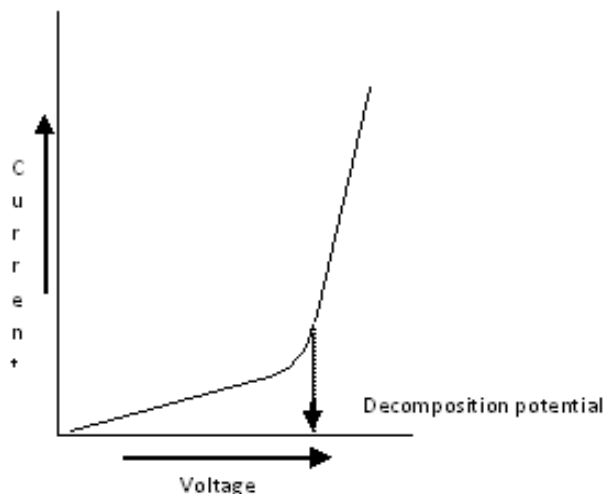
c) *Over voltage (over potential) (η):*

Def^n:- Over voltage is defined as the excess voltage that has to be applied above the theoretical decomposition potential to start the electrolysis.

η = Experimental decomposition potential - Theoretical decomposition potential.

<u>Example</u>: For electrolysis of water using smooth platinum electrodes, the theoretical decomposition potential is 1.23 V. The experimental decomposition potential is 1.7 V. The difference, 0.47 V, is the over voltage.

It was observed that during electrolysis back emf arises and a minimum voltage is to be applied for continuous electrolysis. If the back emf is overcome, electrolysis must proceed. This back emf may be calculated by considering the cell set up by the products of electrolysis and it is equal to the emf of the reversible cell at one atmosphere. When this emf is compared with the decomposition potential, it is found that the value is higher than the required emf value. ***The difference between the observed voltage and the theoretical voltage is known as over voltage.*** Over voltage depends on nature of electrode, physical state of the substances deposited, current density and temperature. It is due to surface phenomenon. It depends on how ions are discharged and the rate at which they are discharged. Hydrogen over voltage is of particular significance in many electrolytic reactions and especially in electroplating and corrosion.

Electroplating:

Definition: Electroplating is the process of electrolytic deposition of a metal on the surface of another metal; the substrate may be another metal, a polymer, a ceramic or a composite.

Principal components of an electroplating process: The principal components are shown in the following figure.

The main components are:

1. Electroplating bath: It contains a suitable salt solution of the metal being plated. It also contains other additives.
2. Anode: It may be a rod or pellets of the metal being plated. It may be an inert electrode. It should be electrically conducting.
3. Cathode: It is the article to be plated. It should have an electrically conducting surface.
4. Inert vessel: It contains above mentioned materials. It may be a vessel made of rubber lined steel, plastic concrete or wood.
5. D.C. power supply: The positive terminal of the power supply is connected to the anode and the negative terminal is connected to the cathode.
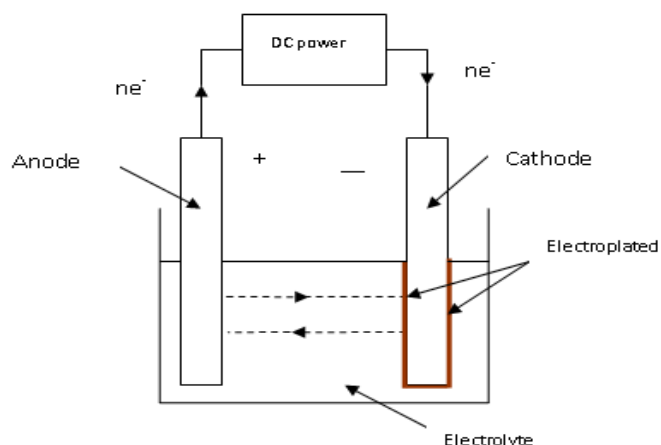
Reactions at anode and cathode during electroplating:

At anode oxidation takes place

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

When the anode used is an insoluble (inert) anode, oxygen evolution occurs at the anode:

$$H_2O \longrightarrow 1/2\ O_2 + 2H^+ + 2e^-$$
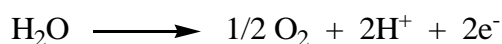
At cathode, reduction occurs. The metal gets deposited on the cathode surface. For example:

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
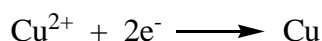
Surface preparation (Pretreatment):

Importance of surface preparation before electroplating: A good adherent deposit is obtained only if the substrate surface is free from dirt, grease, oxide scale and rust. Therefore it is necessary to clean the surface thoroughly before electrodeposition. If bright deposits are required, the surface must be smooth.

Surface cleaning involves following steps:

1. Removal of organic substances – solvent cleaning, alkali cleaning.
2. Removal of inorganic substances – mechanical cleaning, pickling.
3. Rinsing with water.

1. Removal of organic substances – degreasing process:

a) *Organic solvent cleaning*: It is used to remove oils, greases etc. from the surface. For cleaning, organic solvents such as trichloro ethylene ($CCl_2 = CHCl$), methylene chloride (CH_2Cl_2), carbon tetra chloride (CCl_4)etc. are used.

   In vapour phase degreasing method, vapours of the solvent (trichloro ethylene) are allowed to condense on the metal surface. The condensed liquid washes away the oil, grease and other organic matter from the surface.

b) *Alkali cleaning*: Residual oil and grease from the surface is removed by treatment with alkaline solutions (NaOH, Na_2CO_3 etc.) Alkali cleaning is made more effective by making the metal cathodic in a hot alkali solution. The hydrogen gas liberated at the cathode helps to dislodge the greasy matter.

2. Removal of inorganic substances – descaling process:

a) *Mechanical cleaning*: It is used to remove oxide scales and rust from the metal surface. Simple mechanical cleaning involves hand cleaning using sand paper, bristle brush etc. Other methods involve polishing the surface i) using grinding wheels, ii) by sand blasting and iii) by electropolishing.

b) *Pickling:* It is used to remove oxide scales and rust present on the metal surface by dissolution. Pickling involves dipping the object in dilute acids (HCl, HNO_3, H_2SO_4 or a mixture) for considerable period of time.

*Rinsing with water***:** The object is finally rinsed with deionized water.

Electroplating of chromium:-

The surface of the object is cleaned thoroughly. Organic substances are removed by solvent cleaning and alkali cleaning. Inorganic substances are removed by mechanical cleaning and pickling. Finally, the surface is washed with deionized water. Then, chromium plating is done under the following conditions.

1. Plating bath composition	Chromic acid (H_2CrO_4) + H_2SO_4 in the weight ratio 100 : 1
2. Operating temperature	45-60 ^{o}C
3. Current density	100 – 200 mA cm^{-2}
4. Current efficiency	8 – 12 %
5. Anode	Insoluble anode: Pb-Sb or Pb-Sn alloy coated with PbO_2.
6. Cathode	Object to be plated
7. Anodic reaction	Liberation of oxygen: $$H_2O \longrightarrow 1/2\ O_2\ +\ 2H^+\ +\ 2e^-$$
8. Cathodic reaction	$$Cr^{3+}\ +\ 3e^- \longrightarrow Cr$$
9. Applications	1. Used in decorative coating. 2. Used in corrosion resistant coating.

In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3+ state by a complex anodic reaction in the presence of sulphate ions. The Cr^{3+} then gets reduced to Cr on the substrate surface. For a good deposit, the Cr^{3+} concentration must be low. The PbO_2 oxidizes a part of Cr^{3+} to Cr^{6+}, thus reducing the concentration of Cr^{3+}.   In chromium plating we do not use chromium metal as anode due to the following reasons.

1. If chromium dissolves at anode, there will be a high concentration of Cr^{3+} in solution. In such cases, a <u>black</u> deposit is obtained.
2. In acidic solutions, chromium may undergo passivation.

ELECTROLESS PLATING:

Defⁿ:- Electroless plating is a method of depositing a metal over a substrate by controlled chemical reduction of metal ions by a suitable reducing agent **without** using electrical energy.

Metal ions + reducing agent → Metal + oxidized product.

Advantages of electroless plating:

1. Electrical equipment is not required.
2. Semiconductors and insulators can also be plated.
3. Electroless plating baths have better throwing power.
4. Electroless coatings are harder than the electrodeposited coatings.
5. Electroless deposits posses' unique chemical, mechanical & magnetic properties.

Distinction between electroplating and electroless plating:

Property	Electroplating	Electroless plating
Source	Electrical energy is obtained from external source.	No electrical energy is required
Site of anodic reaction.	Anodic reaction takes place at separate anode used in the electrolytic cell.	The site of anode reaction is the article to be plated.
Site of cathodic reaction.	Article to be plated acts as cathode No	Catalytic surface on the article to be plated
Anode	metal	Reducing agent in solution
Type of deposit obtained	Pure	Contaminated
Type of cathode used for plating	Plating is carried out on metals.	Plating may be carried out on insulators (ex: plastics) and semiconductors.
Anode reaction	$M \longrightarrow M^{n+} + ne^-$ OR $H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$	Reducing agent $\square$ Oxidized product $+ n\ e^-$

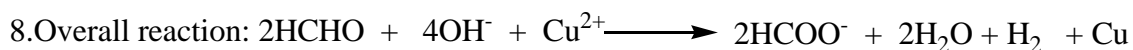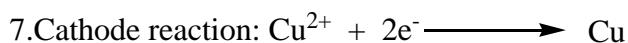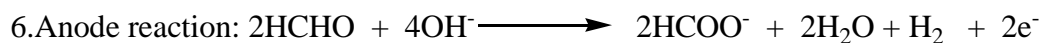|		
Cathode reaction	$M^{n+} + ne^- \longrightarrow M$	$M^{n+} + ne^- \longrightarrow M$

Electroless plating of Copper (PCB- Printed Circuit Board):

Before electroless plating, the surface is cleaned thoroughly. Insulators such as plastics and printed circuit boards are activated by dipping first in stannous chloride ($SnCl_2$) and then in palladium chloride ($PdCl_2$). Then, the electroless plating is done under the following conditions:

1. Plating bath solution : $CuSO_4$
2. Reducing agent : Formaldehyde (HCHO)
3. Complexing agent and exaltant : EDTA
4. Buffer (pH = 11) : Sodium hydroxide and Rochelle salt (Na-K-tartrate)
5. Temperature : 25 ^{o}C

6. Anode reaction: $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

7. Cathode reaction: $Cu^{2+} + 2e^- \longrightarrow Cu$

8. Overall reaction: $2HCHO + 4OH^- + Cu^{2+} \longrightarrow 2HCOO^- + 2H_2O + H_2 + Cu$

Formaldehyde and copper sulphate are added to the plating bath periodically.

Applications:

1. Widely used for moralizing (PCB's) printed circuit boards.
2. For producing through hole connections.
3. For plating on non-conductors.
4. As an undercoat for electroplating.
5. For decorative plating on plastics.

Electroless Plating of Nickel

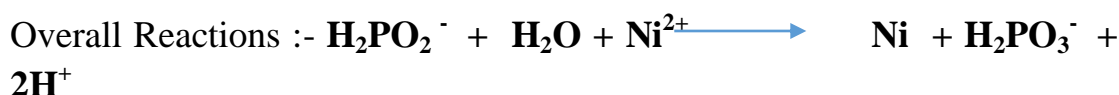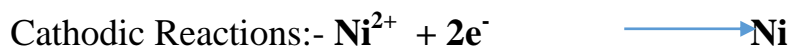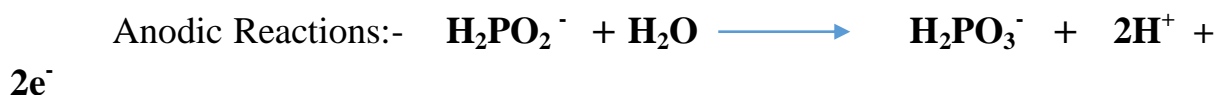It consists of the following steps

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1. **Preparation of the substrate surface**:- The metal substrate is first degreased using organic solvents or by alkali treatment followed by treatment with sulfuric acid.

Non-metallic objects are activated by dipping in SnCl2 and then PdCl2

2. Plating bath solution;-

    i)   Electrolyte:-   Nickel Chloride Solution i.e $20g/dm^3$

    ii)   Reducing agent:-   Hypophosphite ($20g/dm^3$)

    iii)   pH:-   4-5

    iv)   Complexing agent:- Sodium Succinate($15g/dm^3$)

    v)   Temperature:- $73\text{-}75^oC$

Reactions involved during electroless plating

Anodic Reactions:- $H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^-$

Cathodic Reactions:- $Ni^{2+} + 2e^- \longrightarrow Ni$

Overall Reactions :- $H_2PO_2^- + H_2O + Ni^{2+} \longrightarrow Ni + H_2PO_3^- + 2H^+$

Both Oxidation and reduction takes place on the same substrate

Expected questions:

1) What is corrosion? Discuss the electrochemical theory of corrosion.
2) Discuss the various factors that influence the rate of corrosion.
3) What is sacrificial anodic protection?
4) What is meant by differential aeration corrosion? How can it be prevented?
5) Explain the impressed current cathodic protection.
6) Write a note on:
    a). Galvanic corrosion b). Pitting corrosion c). Waterline corrosion

    d). Stress corrosion   e). Anodizing of Aluminium   f). Phosphating

    g). Galvanizing. h). Tinning

7) Mention the Technological importance of metal finishing.
8) Explain the polarization, decomposition potential and over voltage.
9) Write a note on Electroplating of Chromium.
10) Give an account on Electroplating of nickel.
11) Distinguish between electroplating and electroless plating
12) Explain Electroless plating of Cu on PCB.

MODULE-3

Energy system

Chemical Fuels:-

Fuels:

Def^n: - Fuel is a carbonaceous combustible substance which on combustion liberates a large amount of energy in the form of heat.

Classification of fuels: Fuels are classified based on occurrence & State of aggregation or state of phase.

Based on occurrence fuels are classified as.

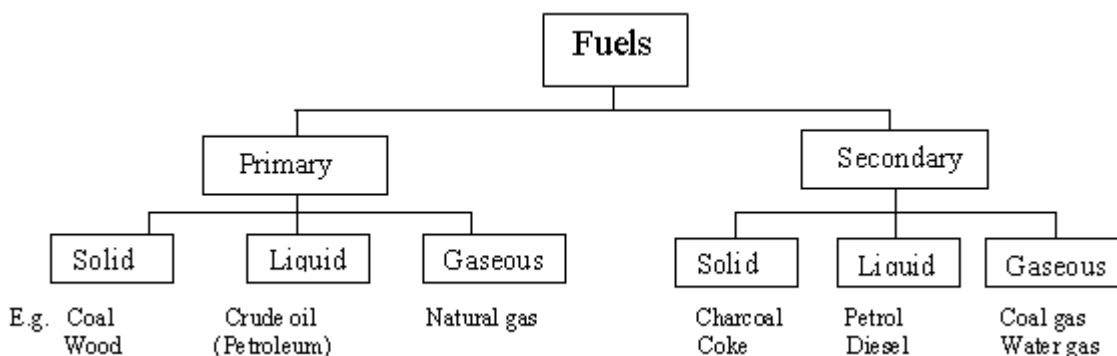1) *Primary fuels or Natural fuels*

Primary fuels are carbonaceous fuels which are occurring in nature.
Eg. Wood, coal, petroleum, natural gas etc.

2) *Secondary fuels or Artificial fuels*.
Secondary fuels are those which are derived from primary fuels.
Eg. Coke, charcoal, diesel, producer gas etc.

Characteristics of a good fuel:

1. High calorific value
2. Moderate ignition temperature

3. Low ash content
4. Low moisture content
5. No harmful combustion products
6. Combustion control
7. Ease of availability
8. Ease of storage and transport

Calorific value:

It's defined as the "Total quantity of heat liberated when a unit weight (or unit volume in gaseous fuel) is burnt completely in air or oxygen".

E.g.   C + O$_2$ → CO$_2$ + heat
    12g   32g   97,644 calories
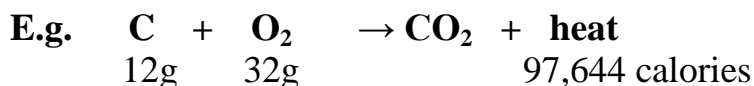
i.e 12g of carbon on burning liberates 97,644 calories of heat energy on complete combustion . Therefore 1g of carbon on complete combustion liberates 8137 calories of heat energy.
 Calorific value is expressed in 'Kilojoules/Kg' for solids & liquids types of fuels & 'Kilojoules /m^3' for gaseous fuels. It's also expressed as calorie/gm or Kilocalories / Kg.

Types of calorific value:
1. Gross calorific value(GCV) / Higher calorific value(HCV)
2. Net calorific value (NCV)   / Lower calorific value (NCV)

Gross calorific value(GCV): *It is the amount of heat liberated when a unit mass or a unit volume of the fuel is burnt completely in air or oxygen and the products of combustion are cooled to ambient temperature(288K).*

Fuels generally contain some amount of hydrogen during combustion the hydrogen is converted into steam. When the products are cooled to the room temperature the latent heat of condensation of steam gets included in the experimentally measured calorific value therefore the experimentally measured calorific value is usually little higher than normal value & hence called HCV.

GCV = NCV + Latent heat of condensation

Net calorific value (NCV): *'It is defined as the total amount of heat energy liberated when one unit of fuel undergoes complete combustion and the products of combustion are allowed to escape'.* Here water vapour, moisture & hot combustible gases are allowed to escape therefore lesser amount of heat energy is available and hence the calorific value will be little less than the normal value hence called lower calorific value.

NCV = GCV – Latent heat of condensation

Determination of calorific value of solid & liquid fuel using Bomb Calorimeter:
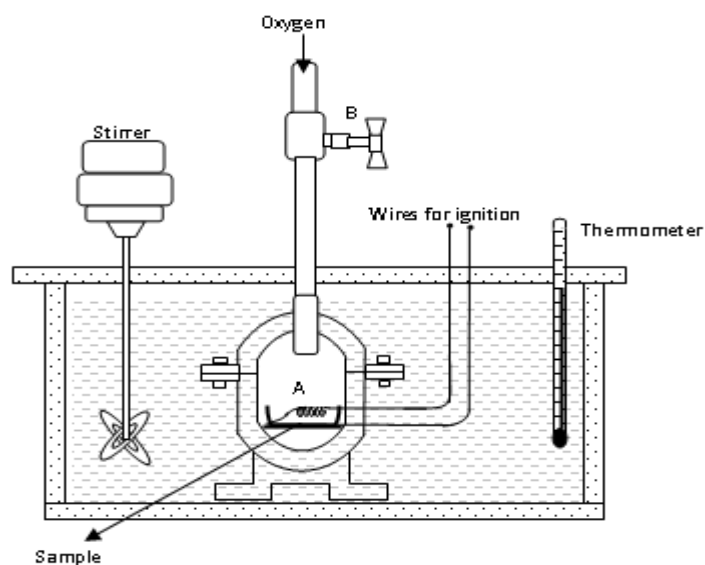
Principle: A known weight of the sample is burnt completely in excess of oxygen. The liberated heat is absorbed by the surrounding water & calorimeter. Thus the heat liberated during the combustion of fuel is equal to the heat absorbed by water and calorimeter.

Construction:

- The bomb calorimeter (shown in the fig.) consists of an outer cylindrical steel vessel (bomb) with an airtight screw and an inlet for oxygen.

- The bomb has a platinum crucible with a loop of wire. The ends of the wire project out and can be connected to a source of electric current.
- The bomb is immersed in rectangular vessel (calorimeter) containing water, which is continuously stirred.
- A Beckmann thermometer is introduced into the calorimeter.

Working:

- A known mass of the fuel is made into a pellet and taken in the crucible.
- Oxygen is passed through the bomb.
- A known mass of water is taken in the calorimeter and is closed with the lid.
- The initial temperature of water is noted.
- The ends of the wire are connected to an electric source so as to ignite the fuel.
- The heat released is absorbed by water. The temperature of water rises.
- The final temperature is noted.

Observation & calculations:

Mass of the fuel $= m$ kg
Mass of the water $= W$ kg
Water equivalent of calorimeter $= w$ kg
Initial temp. of water $= t_1$ ℃
Final temp. of water $= t_2$ ℃
Specific heat of water $= S$ KJ/kg/ ℃

$$GCV = \frac{(W+w) \times (t_2-t_1) \times S}{m}$$

Let the fuel contain H percentage of hydrogen

2H + ½ O$_2$ →H$_2$O
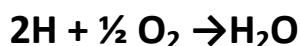
2 atoms of hydrogen produce   one molecule of water
2g of hydrogen produce   ---   18 g of water
x g of hydrogen produce   ----   9 g of water
x % hydrogen $\equiv$ $\frac{9}{100} \times$ x   g of water $= 0.09 \times$ x g of water

NCV   =   GCV   -   latent heat of steam formed
        =   GCV   - $0.09 \times$ x $\times$ latent heat of steam
        Latent heat of steam = 2454 kJ kg^{-1}

1 calorie $= 4.187$ kJ kg^{-1}

$$NCV = GCV - 0.09 \times H \times 2454$$

Knocking:

"The production of shock waves in an IC engine as a result of an explosive combustion of fuel-air mixture consequent to an increase in the compression ratio, beyond a certain value leading to a rattling sound".

Compression ratio = Volume of cylinder at the end of suction stroke

Volume of cylinder at the end of compression stroke

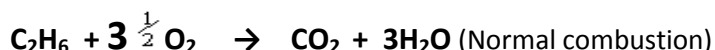Under ideal conditions, in an IC engine the petrol-air mixture drawn into the cylinder of the engine undergoes compression and then ignited. The hydrocarbons in the petrol undergo complete combustion and the flame propagates smoothly. But sometimes due to deposits of carbon on the walls of the cylinder the hydrocarbons in the petrol form peroxy compounds. The accumulated peroxides decompose suddenly and burst into flames producing shock waves. These wave hits the walls of the engine and the piston with a rattling sound.

The reactions that take place in an IC engine are given below

Under ideal conditions:

$C_2H_6 + 3\frac{1}{2} O_2 \rightarrow CO_2 + 3H_2O$ (Normal combustion)

Under Knocking conditions: (Explosive combustion)

$C_2H_6 + O_2 \rightarrow CH_3-O-O-CH_3$

$CH_3-O-O-CH_3 \rightarrow CH_3CHO + H_2O$

$CH_3CHO + 3/2 O_2 \rightarrow HCHO + CO_2 + H_2O$

$HCHO + O_2 \rightarrow H_2O + CO_2$

Effects of knocking: 1. Decreases life of engine. 2. Causes noise pollution. 3. Consumption of fuel is more.4) Driving becomes unpleasant

Anti knocking agents

Leaded Petrol(TEL):

The octane no of the petrol can be increased by reducing the tendency of knocking by addition of small amounts of compounds called anti knocking agents. The extensively used anti knock agent is tetraethyl lead (TEL). It decomposes the peroxides formed prevents knocking. In the process lead gets deposited on the inner walls of the engines and at spark plugs. Hence dichloroethane and dibromoethane are added along with tetraethyl lead these convert the lead into lead halides which are volatile and escape with exhaust gases.

Demerits of the use of leaded petrol (TEL)

- The release of lead compounds pollutes the atmosphere.
- Catalytic converters (Rd catalyst) are used in IC engines to convert CO in the exhaust to CO_2. TEL used as anti knocking agent poisons the catalyst.

Unleaded Petrol(MTBE):

It does not contain lead composition instead Methyl tertiary butyl ether (MTBE) is added to petrol (unleaded) to boost its octane number. The oxygen of MTBE brings about complete combustion of petrol preventing peroxide formation and hence knocking is prevented.

- It can be used in IC engine with catalytic converter.

Power Alcohol:

Power alcohol is a gasoline blend containing ethanol which can be used as a fuel in internal combustion engine.

Gasohol is a blend of 10-85% of absolute ethanol and 90-15% of petrol by volume and is used as a fuel in the United States.

Alcohol contains higher percentage of oxygen than MTBE and hence brings about complete oxidation of petrol more effectively. It has better antiknocking characteristics than unleaded petrol.

Advantages of power alcohol.

1). Power output is high. 2). Doesn't release CO, causes less pollution. 3). Alcohol is obtained from molasses, an agricultural product and hence renewable. 4). Biodegradable.

Biodiesel:

It's a clean burning fuel obtained from the renewable resources such as vegetable oils like palm, soya bean, peanut etc. which are all triglycerides. triglycerides subjected to trans esterification reaction with excess methanol in presence of NaOH catalyst. The product mixture is monomethyl ester of long chain fatty acids & glycerin. The mixture is allowed to settle & the bottom glycerin layer is drawn off. This mixture of methyl esters is called as biodiesel & has the desired characteristics of diesel fuel.

$$
\begin{array}{c}
CH_2OCOR_1 \\
| \\
CHOCOR_2 \\
| \\
CH_2OCOR_3 \\
\text{Triglycerides}
\end{array}
+ 3CH_3OH \xrightarrow{\text{NaOH}}
\begin{array}{c}
CH_3OCOR_1 \\
+ \\
CH_3OCOR_2 \\
+ \\
CH_3OCOR_3 \\
\text{biodiesel}
\end{array}
+
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH \\
\text{glycerol}
\end{array}
$$
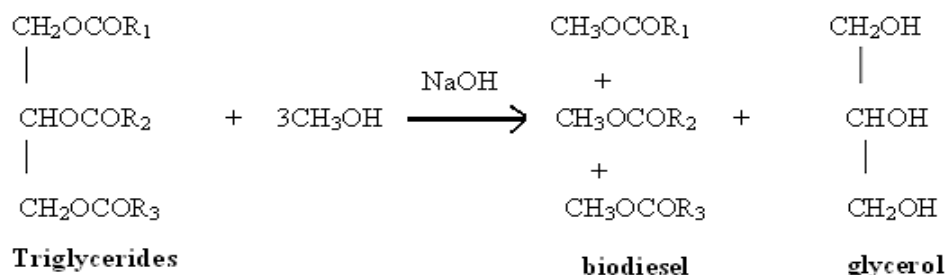
Advantages

1. Its biodegradable, nontoxic hence environment friendly.
2. It can be used as an alternative fuel for compression ignition engine or can be blended with petroleum diesel & used.
3. It is free from sulphur compounds.

FUEL CELLS:

Definition of a fuel cell: Fuel cell can be defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.

Differences between a battery and a fuel cell

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Battery	Fuel cell
1. It is a device consisting of two or more galvanic cells connected in series or parallel or both.	1. It is a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.
2. Store chemical energy. 3. Reactants are within the cell. 4. Products remain within the cell.	2. Do not store chemical energy. 3. Reactants are supplied continuously. 4. Products are continuously removed from the cell.
5. Efficiency is less Ex: Lead-acid battery, Ni-MH battery.	5. Efficiency is more Ex: H_2-O_2, Methanol-Oxygen Fuel cell.

Limitations of fuel cells:
1. Fuel cells produce energy only as long as fuels and oxidants are supplied
2. They cannot be recharged because either the raw materials or the products are gases.

Advantages of fuel cells:
1. Theoretically, the efficiency can be 100%. In practice, the efficiency is 50-80% which is high compared to conventional methods.
2. Harmful products are absent. Hence fuel cells are environment friendly.
3. No need of charging.
4. Silent operation.
5. No moving parts. Hence wear and tear is eliminated.

Methanol – Oxygen fuel cell: Methanol is an efficient electroactive organic fuel at low temperature.

The advantages of methanol are

i) It has low carbon content.

(ii) It has a readily oxidizable OH group.
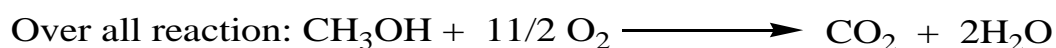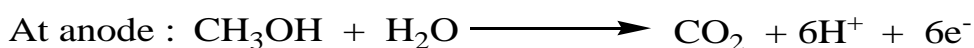
(iii) It has high solubility in aqueous electrolytes.
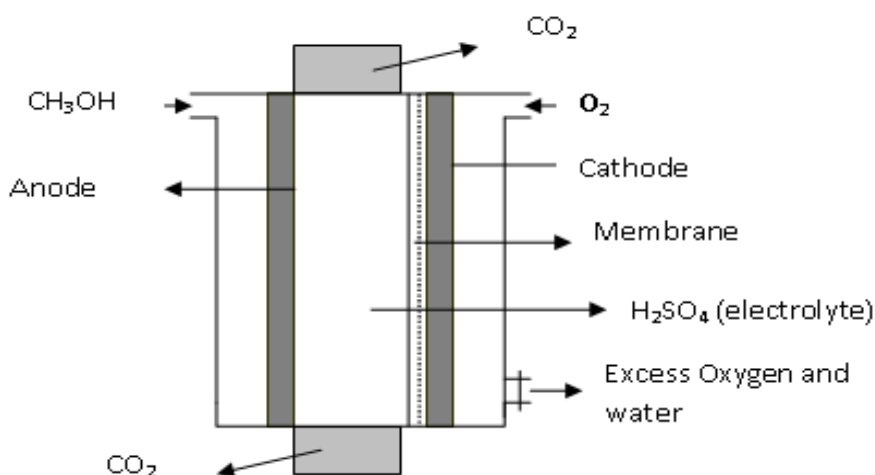
Construction: It consists of anode and cathode electrodes both are made of platinum. Sulphuric acid acts as the electrolyte. A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode. Methanol – H_2SO_4 mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.

Cell reactions:

At anode : $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

At cathode : $11/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Over all reaction: $CH_3OH + 11/2\ O_2 \longrightarrow CO_2 + 2H_2O$

Uses: 1) Used in Military applications.

2) Used for large scale power production stations.

Solid oxide fuel cell(SOFC):

SOFCs operate at higher temperature (1100 -1800 Fahrenheat).
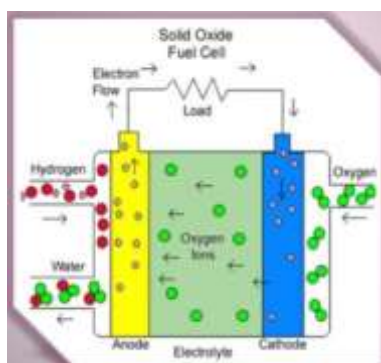
Construction: SOFC is made up of three ceramic materials which form three layers, the anode, cathode and electrolyte. The electrolyte is Yattria stabilized Zirconia material which has permeability to allow O^{2-} ions from cathode to anode. The Anode material is made up of

Nickel doped yatria stabilized zirconia cermets. The cathode is made up of Lanthanum Manganite.
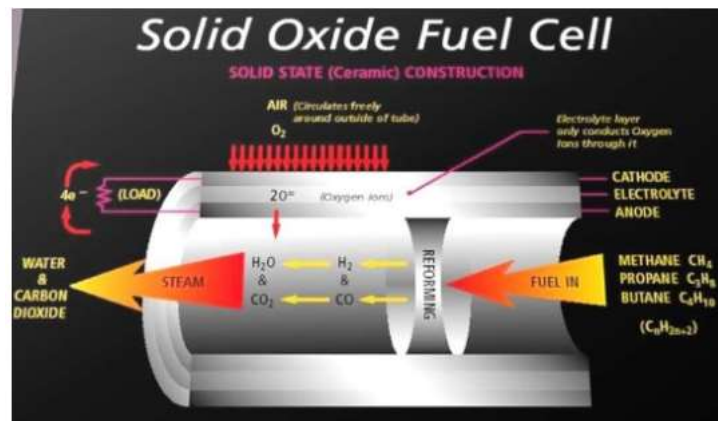
Working:
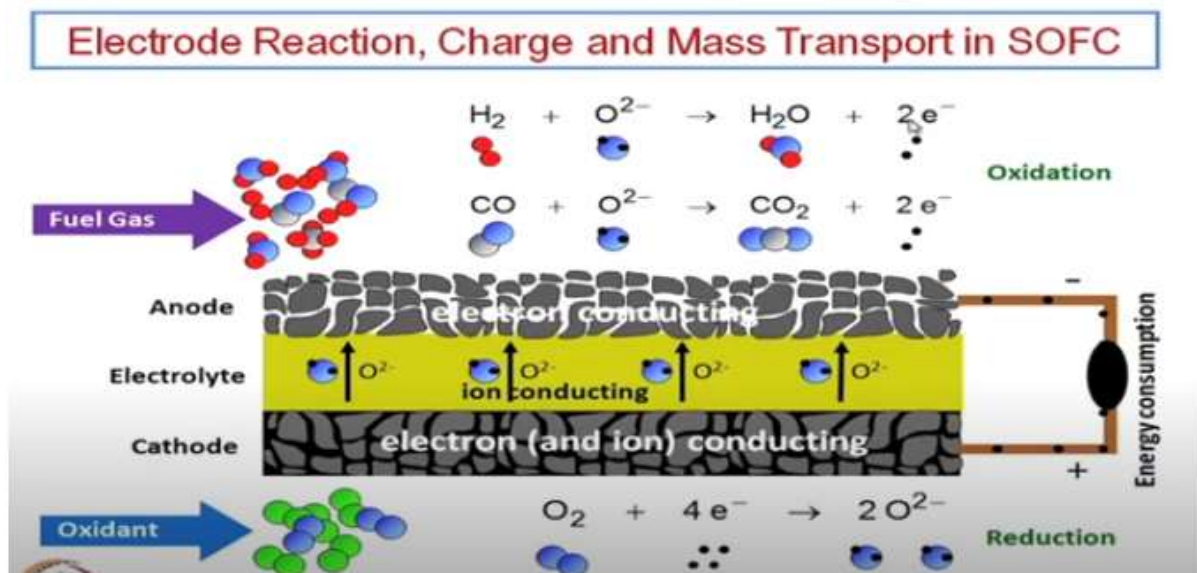
Cathode reaction:

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

Anode reaction :

$$2H_2 + 2O^{2-} \longrightarrow 2H_2O + 42e^-$$

$$CO + O^{2-} \longrightarrow CO_2 + 2e^-$$

Overall reaction

$$H_2 + CO + O_2 \longrightarrow H_2O + CO_2$$

Applications of SOFC:

- Used in power and heat generators in houses

- Auxiliary power units of electrical systems in vehicles

- Used in stationary power generating systems

- Used to spin turbines for electricity generation

SOLAR ENERGY:

The radiations reaching earth from the sun and converting them in to different useful forms of energy is called solar energy. The utilization of solar energy is of two types – Direct solar power and indirect solar power.

Photovoltaic cells

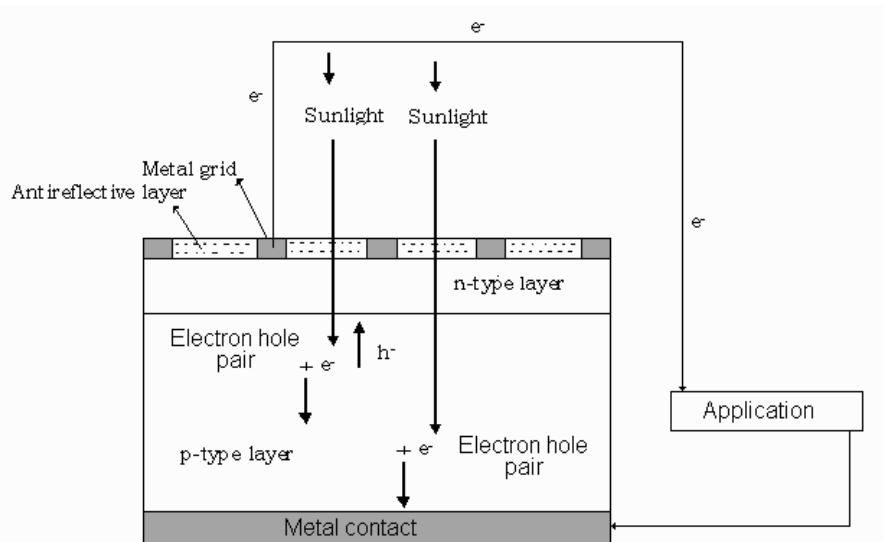Photovoltaic cells or solar cells are the Semiconducting devices which converts solar energy into electrical energy.

Eg. When semiconductor such as silicon is illuminated by photons (from sunlight) electricity is generated.

Photovoltaic cell consist of a p-n junction formed from a semiconductor diodes of p-type and n- type brought together to form a metallurgical junction. n- Type is formed by doping Silicon with Phosphorous and p-type is formed by doping boron with silicon. The diode has two electrical contacts, one of which is in the form of a metallic grid and the other is a layer of noble metal on the back of the solar cell. A thin layer of an antireflective layer is coated on the surface. When the light radiation consisting of photon particles incident on the metallic grid of the semiconductor normal to the plane .the photons carry a certain amount of energy given by $E= hc/\lambda$ Where h is planck's constant c is the velocity of light and λ is the wavelength of the radiation . Those photons which possess the energy greater than Eg are absorbed .The electrons acquire this energy & are removed which leads to the formation of electron hole pair. These electrons are driven out into the external circuit and could be stored and used for various applications such as spinning of fan, working of a motor etc.

Advantages:

1. The Solar power is pollution free.

2. It can operated with little maintenance or intervention after initial setup.

3. The Solar power is becoming more and more economical as costs associated with production decreases, and the technology becomes more effective in energy conversion.

4. The Solar power can be viewed as a local resource because of original climatic variances.
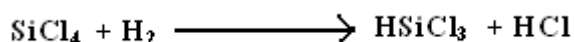
Disadvantages:

1. The Solar power is only practical in certain areas with a favorable climate and latitude.   That is, areas near the tropics and which are relatively cloud free.

2. The Solar power is not available at night.

3. The Solar power decreases during cloudy.

4. The Solar power must be converted into some other form of energy to be stored.

5. Solar cell technologies produce DC power which must be converted to the AC power.

Production of solar grade silicon:

The metallurgical grade silicon is treated with dry HCl gas about 300ºC to form trichlorosilane and a small amount of tetrachlorosilane. The mixture is distilled to get pure trichlorosilane.

$$Si + 3HCl \longrightarrow HSiCl_3 + H_2 \uparrow$$
$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2 \uparrow$$
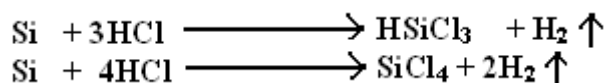
Silicon tetrachloride is reduced with hydrogen at 1000 ºC in a reactor.

$$SiCl_4 + H_2 \longrightarrow HSiCl_3 + HCl$$

The trichlorosilanes is then passed through fixed bed columns filled with quaternary ammonium ion exchange resin acting as catalyst.

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$
$$2H_2SiCl_2 \longrightarrow SiH_4 + 2HSiCl_3$$
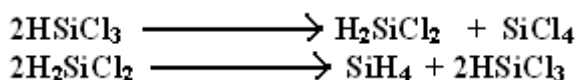
The products are distilled & separated tetrachlorosilane & trichlorosilane are recycled to the hydrogenation reactor and the exchange resin respectively.

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Silicon hydride or silane is further purified by distillation & passed into a reactor containing heated silicon seed rods. Silane gets pyrolysed to form polysilicon (semiconductor grade silicon).

$$SiH_4 \longrightarrow Si + 2H_2$$

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MODULE-4

ENVIRONMENTAL POLLUTION AND WASTE MANAGEMENT

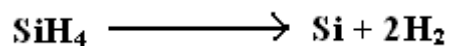**AIR POLLUTION**: The excessive discharge of undesirable foreign substances into the atmosphere air, thereby adversely affecting the quality of air, and causing damage to human, plants and animal lives.

PRIMARY AIR POLLUTANTS

Primary air pollutants that are directly emitted into the atmosphere through natural or human activity. These are emitted from identifiable sources. Examples of primary air pollutants: SO_2, NO, NO_2, CO.

I. **Oxides of Sulphur**
   Sulphur dioxide (SO_2) and Sulphur trioxide (SO_3) are referred together as Oxides of Sulphur (SOx).
   Sources:
   - **Natural:** Volcanic activity releases SO_2, SO_3, H_2S, S and particulate matter in to atmosphere.
   - **Anthropogenic:**
   a) Thermal power plants, in which sulphur – containing coal and fossil fuels are burnt.
   $$S + O_2 \longrightarrow SO_2$$
   b) Petroleum industries , oil refineries, sulphuric acid plants, and sulphide ore-roasting plants.
   c) Smelting of sulphide ores contribute to increase in SO_2 concentration in atmosphere.
   d) Oxygen formed by thermal decomposition of ozone oxidizes H_2S in the atmosphere to SO_2. $H_2S + 3[O] \longrightarrow SO_2 + H_2O$
   e) SO_3 is a secondary air pollutant and is formed by the oxidation of SO_2 in the atmosphere by atomic oxygen or molecular oxygen or ozone.
   $$SO_2 + [O] \longrightarrow SO_3$$
   $$SO_2 + 1/2O_2 \longrightarrow SO_3$$
   $$SO_2 + O_3 \longrightarrow SO_3 + O_2$$
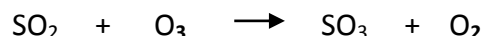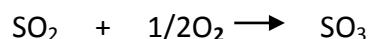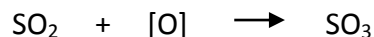
   Effects:
   a) Cardiac, respiratory and pulmonary diseases.
   b) Eye irritation, throat troubles and digestive tract.

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c) Corrosion of metals.
d) Damages plant cells and membranes, chlorophyll, metabolism leading to growth yield reduction.
e) H_2SO_4 mist can damage natural and synthetic fibres.
f) SO_2 in the atmosphere can react with marble leaving behind pitted and discoloured surface and this is called stone leprocy.

$$2CaCO_3 + 2SO_2 + O_2 \longrightarrow 2CaSO_4 + 2CO_2$$
$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$
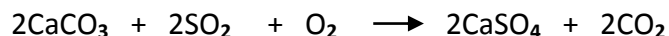
g) Acid rain: $SO_2 + H_2O \longrightarrow H_2SO_3$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

It can harm aquatic life, leach metal from soil and destroys fertility of the soil.

Control:

Largest amount of sulphur is removed by crushing and washing the coal before combustion

a) Removal of SO_2 from flue gas
   i) Adsorb SO_2 on a suitable adsorbent (sodium aluminate) to form stable sulphates in fluidized bed at 315^OC, with subsequent regeneration, example:
   $$Na_2O.\ Al_2O_3 + SO_2 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 + Al_2SO_3$$
   ii) Adsorb SO_2 from flue gases on activated carbon followed by regeneration and conversion to sulphuric acid or elemental sulphur.
b) Natural dispersion
   Natural dispersion of SO_x at high elevation, so that ground level concentration are acceptable. In india, minimum stack height recommended is 30m.
c) Switch to Natural gas from the conventional high sulphur fuels like coal and petroleum, reduces SO_x emissions.
d) Use clean sulphur free nuclear power to generate electricity.
e) The flue gases are passed through slurry of limestone, 90% of SO_2 is removed.
   $$CaCO_3 \longrightarrow CaO + CO_2$$
   $$2CaO + SO_2 \longrightarrow CaSO_3$$
   $$2CaO + 2SO_2 + O_2 \longrightarrow 2CaSO_4$$
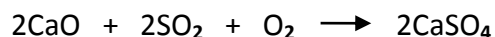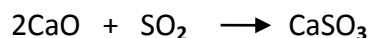
II. **Oxides of Nitrogen**

Nitric oxide (NO), nitrous oxide (N_2O) and nitrogen dioxide (NO_2) are the common oxides of nitrogen (NO_x).

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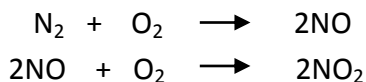a) The reaction of oxygen with nitrogen compounds in the fuel – this is termed Fuel NO_x.

b) The reaction of nitrogen with oxygen in the combustion air – this is termed Thermal NO_x. The basic reaction leading to formation NO and NO_2 are:

$$N_2 + O_2 \longrightarrow 2NO$$
$$2NO + O_2 \longrightarrow 2NO_2$$

Sources:

- **Natural:** Lightning, volcano and bacterial decay of nitrogenous compounds.
- **Anthropogenic:**

a) The major man made source of oxides of nitrogen is combustion of coal, oil, natural gas and gasoline.

b) Automobile exhaust contributes to 40.8% of oxides of nitrogen.

c) Other sources are acid manufacture, explosive industry, nitrogenous fertilizers and acid - pickling plants.

Effects

a) In high NO_2 areas, respiratory illness, inflammation of lung tissue, damage to lungs.

b) It causes eye irritation and difficulty in breathing thereby leading to asthma and bronchitis.

c) NO_X can result in the formation of secondary pollutants by reacting with hydrocarbon and air through complex reactions. The secondary pollutants combine with fog creating photochemical smog which has harmful effects on human health, plants, photosynthetic activity and cause chlorosis.

d) N_2O is a greenhouse gas which is 300 times more damaging than CO_2.

e) Acid rain:

$$N_2O + H_2O + O_3 \longrightarrow HNO_3 + N_2O_5$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$
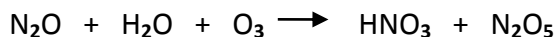
Control

a) **Removal of oxides of nitrogen during combustion**

Low NO_x burners ensure that initial fuel combustion occurs within fuel rich conditions that is with low oxygen concentrations, such that any gaseous nitrogen produced is reduced to N_2 without oxygen.

Once initial combustion has taken place, further air is added to the combustion chamber to ensure complete combustion of the fuel. This greatly reduces the opportunities for NO_x production.

b) **Removal of oxides of nitrogen after combustion**

Treating the flue gases can reduce the emissions of NOx generated during combustion. This can be done by:

(i) **Selective Catalytic Reduction:** Ammonia is injected into the flue gas. The oxides present in the flue gas react with the ammonia in presence of catalyst usually vanadium or tungsten oxide at 300 ^{O}C – 400 ^{O}C and are converted to nitrogen and water.

$$4NO + 4NH_3 + O2 \longrightarrow 4N_2 + 6H_2O$$
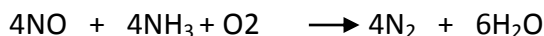
(ii) **Sorption:** Treatment of flue gas by injection of sorbents (such as ammonia, powdered limestone, or carbon) can remove NOx and other pollutants like sulphur.

III. **Carbon Monoxide**

Carbon Monoxide (CO) is one of the serious air pollutants and is 96.5% as heavy as air. The atmospheric residence time of CO is 4 months, it is poisonous, colourless, odourless, non-corrosive, asphyxiant gas.

Sources

a) Natural: Natural processes such as forest fires, natural gas emission, marsh gas production and volcanic actions produces carbon monoxide in the atmosphere.

b) Anthropogenic:

(i) Incomplete combustion of fuel or carbonaceous compounds from automobiles, industries and oil – refineries.

$$2C + O_2 \longrightarrow 2CO$$

(ii) Reaction between CO_2 and carbonaceous material at high temperature gives CO.

$$CO_2 + C \longrightarrow 2CO$$
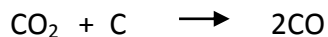
(iii) Dissociation of CO_2 at very high temperature gives CO

$$CO_2 \longrightarrow CO + O$$
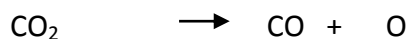
c) Cigarette smoke and domestic heat appliances are the other sources of CO.

Effects

a) Carbon monoxides causes headache, visual difficulty, paralysis and even death in the human beings.

b) The haemoglobin in blood has 200 times more affinity towards CO than for oxygen. When air contaminated with CO is inhaled, CO reacts with the haemoglobin of RBC to form carboxy-haemoglobin,hence impairing the transfer of oxygen to the tissues reducing the oxygen – carrying capacity of blood.

$$Hb \ + \ O_2 \ \longrightarrow \ Hb\text{-}O_2$$

$$Hb\text{-}O_2 + \ CO \ \longrightarrow \ COHb \ + \ O_2$$

CO can also displace oxygen in oxyhaemoglobin forming carboxy-haemoglobin

c) This can also lead to serious effects on the cardio-vascular system.

d) High CO concentration (100 – 1000 ppm) can affect leaf drop, leaf curling, reduction in the leaf size and chlorophyll with premature aging.

Control

a) Modification of internal combustion engines.

b) Development of exhaust system reactors which will complete the combustion process and change the potential pollutant into more acceptable materials.
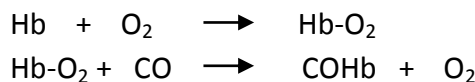
c) Development of substitute fuels for gasoline.

d) Development of pollution free power sources such as fuel cells.

IV. **Hydrocarbons**

Hydrocarbon is an organic compound consisting entirely of hydrogen and oxygen.

Sources

a) Natural

- Trees emit large quantities of hydrocarbons into the atmosphere.
- Considerable quantities of hydrocarbons are formed by the bacterial decomposition of organic matter in water, sediments and soil.
- Domestic animals contribute to about 85 million tones of methane into atmosphere each day.

b) Anthropogenic

- Automobile exhaust consisting of unburnt petrol is the major manmade source of hydrocarbon in the atmosphere.

c) Methane is a naturally occurring hydrocarbon emitted into the atmosphere in large quantities. It is produced by bacteria through anaerobic decomposition of organic matter.

$$2(CH_2O) \ \longrightarrow \ CO_2 \ + \ CH_4$$

Effects

a) Hydrocarbons at high concentration (> 500 ppm) have carcinogenic effects on lungs.

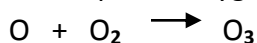b) Inhalation of vapours of benzene, toluene, etc causes much irritation to the mucous membrane.
c) Cyclic hydrocarbons affect nervous system and cause loss of coordination.
d) Methane and benzopyrene creates narcotic effect in human being.
e) Methane is a green house gas and can cause in global warming.
f) Hydrocarbons and oxides of nitrogen are the major culprits in the formation of photochemical oxidants (Peroxy acetyl nitrate, Peroxy benzoyl nitrate and O_3, etc) which are harmful secondary pollutants.

Formation of photochemical oxidants (Photochemical smog):
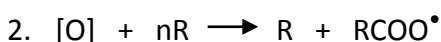
1. $NO_2 \longrightarrow NO + [O]$
2. $[O] + nR \longrightarrow R + RCOO^\bullet$
3. Atmospheric oxygen quickly combines with molecular oxygen to give ozone.
   $O + O_2 \longrightarrow O_3$
4. The peroxy free radical oxidizes NO to NO_2 thus building up a higher concentration of NO_2 in the atmosphere.
   $RCOO^\bullet + NO \longrightarrow RCO^\bullet + NO_2$
   $RCO^\bullet + O_2 \longrightarrow RCO^\bullet_3$
5. The peroxy free radical may react with NO_2 forming Peroxy acetyl nitrate (PAN) and Peroxy benzoyl nitrae (PBzN) which are powerful eye irritants.
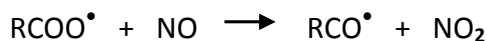
$$RCO^\bullet_3 + NO_2 \longrightarrow \overset{\overset{\displaystyle O}{\|}}{R}COONO_2$$
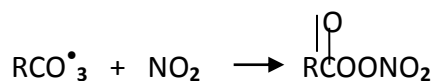
PAN and O_3 forms small droplets with water vapour and is referred to as photochemical smog. Photochemical smog is characterized by irritating fumes and irritates eyes, lungs and leads to cracking of rubber and extensive damage to plant life.

Control

a) Hydrocarbons from auto exhaust can be controlled by processes such as incineration, adsorption, absorption, etc.

$$\text{Hydrocarbons} \longrightarrow CO_2 + H_2O$$
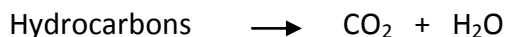
CATALYTIC CONVERTER

It is a device used to reduce the toxicity of emissions from an IC engine.

Catalytic converters represent the best technology available which are capable of bringing the exhaust emissions to the negligible levels.

The catalysts used in the converters are classified into: a) Oxidizing   b) Reducing   c) 3 way Catalysts

a) **Oxidizing Catalytic system**:   accelerates the completion of the oxidation of CO & hydrocarbons into CO_2 & H_2O vapour respectively.

$$2\,CO + O_2 \longrightarrow 2CO_2$$
$$C_nH_{2n+2} + 2n\,O_2 \longrightarrow nCO_2 + 2n\,H_2O$$
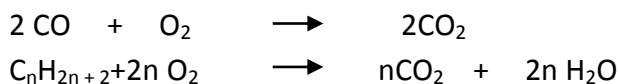
In this system, metals such as Pt & Pd are used as catalysts. Since these catalysts can be poisoned by Pb, S & P, only unleaded petrol should be used in automobiles equipped with Catalytic Converter.

b) **Reducing Catalytic systems**: Generally used catalysts are Rhodium& Ruthenium. They accelerate the reduction of $NO_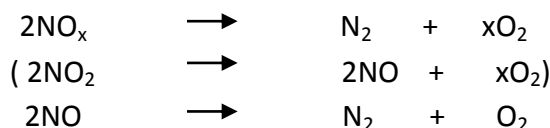x$ to N_2. Conversion of NH_3 is undesirable because the subsequent use of an oxidizing (agent) catalyst could recreate NO_x from NH_3

$$2NO_x \longrightarrow N_2 + xO_2$$
$$(\,2NO_2 \longrightarrow 2NO + xO_2)$$
$$2NO \longrightarrow N_2 + O_2$$

Mechanism

(i)   Reducing stage: The oxides of nitrogen are reduced to N_2 and some amount of NH_3 in the presence of reducing catalyst and the reducing gases (CO & Hydrocarbons).

(ii)   Oxidizing stage: Air is introduced to provide an oxidizing atmosphere for complete oxidation of CO and hydrocarbons into CO_2 and water in the presence of finely divided oxidizing catalyst.

c) **The three way catalytic converter system** (operating at 800 $^{\circ}$C) is more efficient than two-stage converter system. The three- way catalyst is composed of platinum and Rhodium. This system is capable of promoting reactions among the air contaminants. The unit oxidizes hydrocarbons and carbon monoxide simultaneously to CO_2 and water while reducing NO_x to N_2 at the same time. Here, the hydrocarbons and carbon monoxide react with the oxygen in the NO_x to form CO_2, H_2O, N_2 and O_2.

$$HC + CO + NO_x \longrightarrow CO_2 + H_2O + N_2 + O_2$$

This system is quite effective in reducing the exhaust emissions to negligible levels.
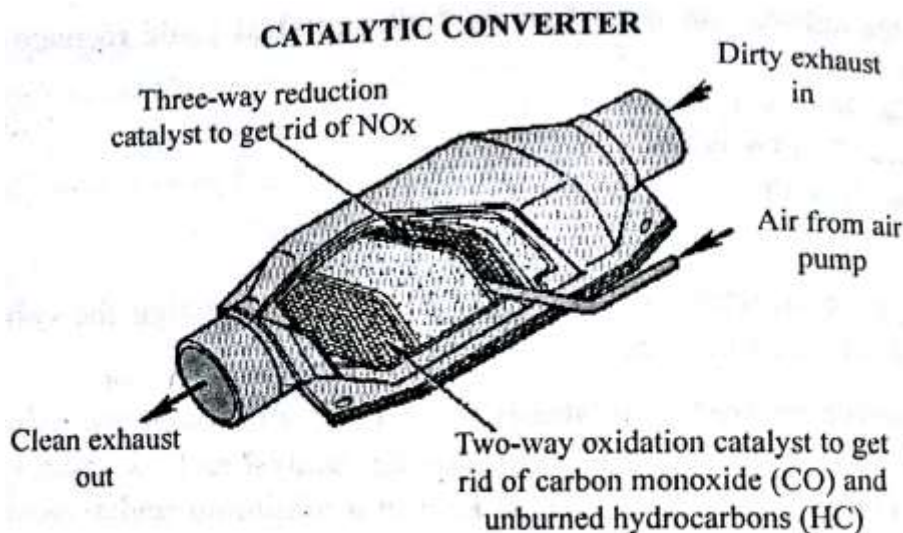
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Fig 4.3 Three-way catalytic converter

PARTICULATE MATTERS

Particulate matter or aerosols are finely divided solid particles or liquid droplets suspended in air. They include smoke, dust, fumes, flyash, mist and spray. The size of particulate matter may vary from 0.002 to 500 μm. The name dust and soot are used for solids and mist and for fog refer to liquids. Particulate matter with less than 2.5 μm in size is called fine particulates. These remain suspended in air for a considerable period of time. Those with sizes greater than 2.5 μm are called coarse particulates. These coarse particulates settle rapidly.

The concentration of particulates in air is expressed in terms of the total suspended particulates (TSP). It is the unit of mass of particles per unit volume of air in $\mu g/m^3$.

Sources of Particulate Matter
1) Natural : Biological particulate matter are pollen, fungi, bacteria, protozoa, algae & viruses.
2) Anthropogenic: The following industrial operations such as
   a) Crushing, grinding and blasting of solid materials (dust).
   b) Processing of materials like coal, cement & asbestos (dust).
   c) Incomplete combustion of carbonaceous materials (smoke).
   d) Condensation of vapours of metallic oxides formed during sublimation, distillation or calcinations (fumes).
   e) Burning of coal which leaves behind a mixture of non-combustible inorganic oxides (ash).

f) Condensation of vapors, dispersion of liquids and chemical reactions forming liquid droplets (mist).

g) Atomization of liquid droplets (spray).

Types of Particulate Matter

S No.	Type	Source	Size
1	Smoke	Incomplete combustion of fuel or carbonaceous material	Solid or liquid, 0.05 to 0.1 μm
2	Dust	Crushing, grinding, blasting of solid	Solid, 1 to 100 μm
3	Mist	Condensation of vapour	Liquid, < 10 μm
4	Spray	Atomization	Liquid, 10 - 100 μm
5	Fumes	Condensation of vapour by sublimation, distillation, boiling, calcination	Solid or liquid, 0.1 to 1 μm
6	Fly ash	Burning of coal forming non-combustible inorganic oxides	Solid, 1-100 μm

Effects

1) **On Plants:**
   a) Deposition of toxic metals on soil make it unsuitable for plant growth.
   b) Absorption of CO_2 is restricted.

2) **On Human beings:**
   a) They cause respiratory problems.
   b) Causes sneezing, coughing, nose blocking and heavy breathing.
   c) Asbestos exposure causes mesothelioma.
   d) Lead as particulate affects children brain, interferes with the development of maturation of RBCs.
   e) Develops symptoms of asthma.
   f) Acid and aldehyde particulates cause eye, nose and throat irritation.

3) **On Property:**
   a) They damage metals, buildings and painted surfaces.

Control of particulate matter:

Many techniques for the control of particulates have been developed, techniques include:

a) **Gravity settling chambers:**

Fig: 4.1.1: Gravity settling chamber
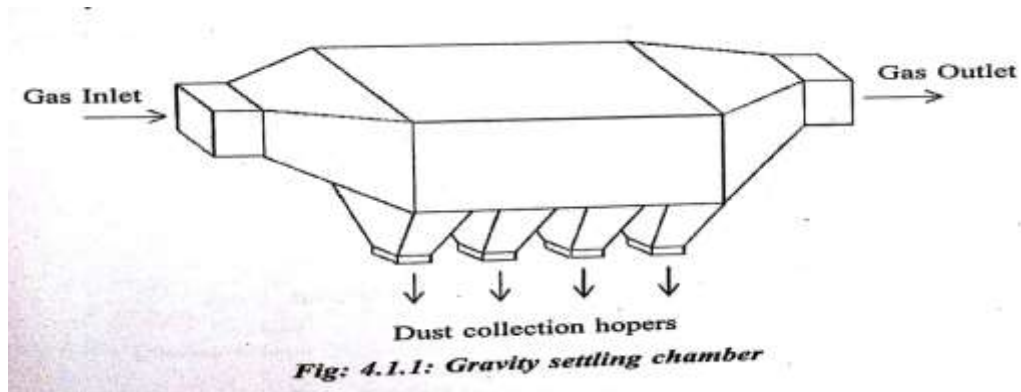
The principle of this method is the gravity deposition of the particulates present in a gas. The gas is led into a dust chamber which is a rectangular tank at a slow rate in one direction. As the gas flows, the suspended particles get deposited. The degree of purification is about 40-50% and therefore is usually used for preliminary purification.

b) **Wet scrubbers:** The simplest type of wet scrubber is the spray tower. When a particulate laden gas is passed into a chamber, it comes in contact with water spray. Water droplets capture particulate and settle down at the bottom of the chamber and the degree of gas purification is about 80%.

Fig: 4.1.4: Wet scrubber
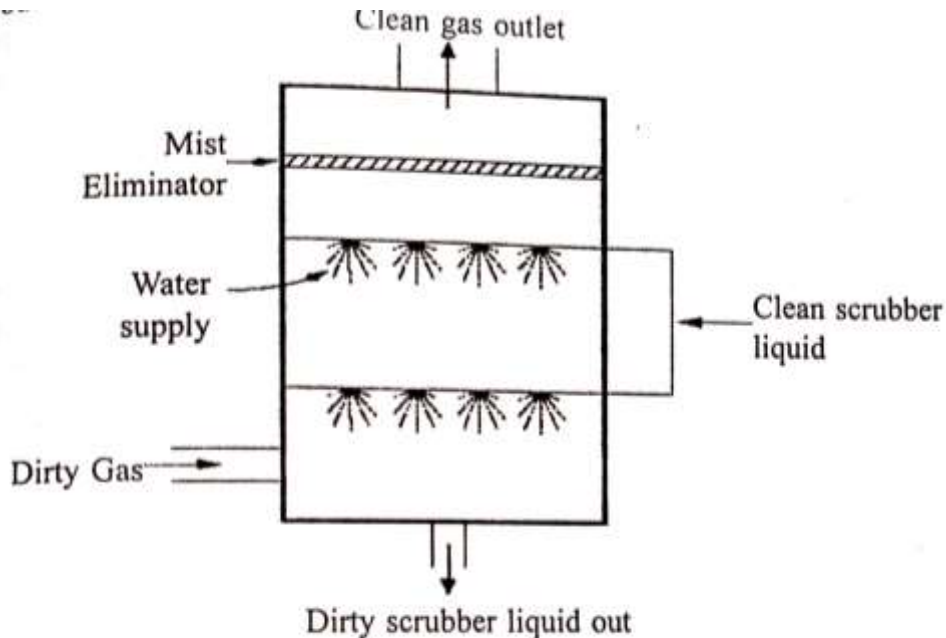
c) **Fabric filters:** Filteration involves passing the effluent gas through fabric filters which use cotton, wool, artificial fibers and glass fibers for filteration or through granular materials like

ceramics, cement and plastics. By choosing appropriate filters, it is possible to remove very fine particulate associated with gases.
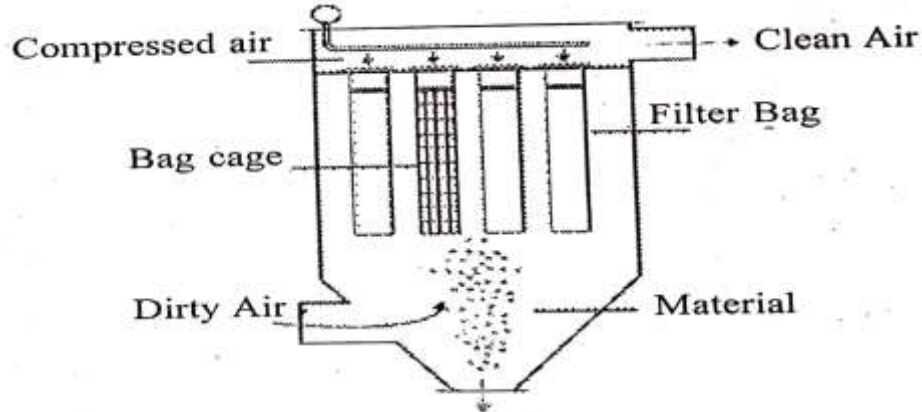
Fig: 4.1.3: Fabric filter

d) **Centrifugal collector:** This method depends on centrifugal force to separate particles from gas. The dust laden gas is allowed to spiral down the outer cylinder in the chamber and reaches the bottom. Then it moves upwards in the inner spiral concentric with the outer and leaves through the outlet. When gas spirals, the particulate are projected outward due to centrifugal force and slide down through the wall into the hopper.
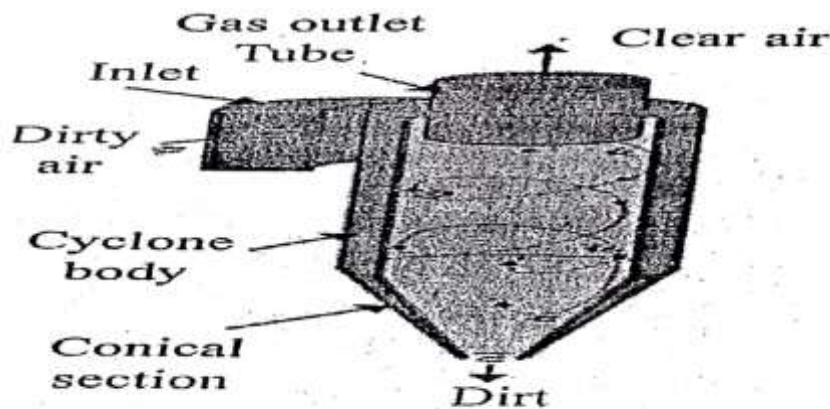
Fig: 4.1.2: Centrifugal separator

e) **Cottrell's Electrostatic precipitator:** When dust laden gas is passed into a chamber under the influence of electric field of 5000-40000V, the particulates gain static charge on collision with the ions of the gas and get deposited on the oppositely charged electrodes. The particulate free gas is allowed to go out through the outlet.
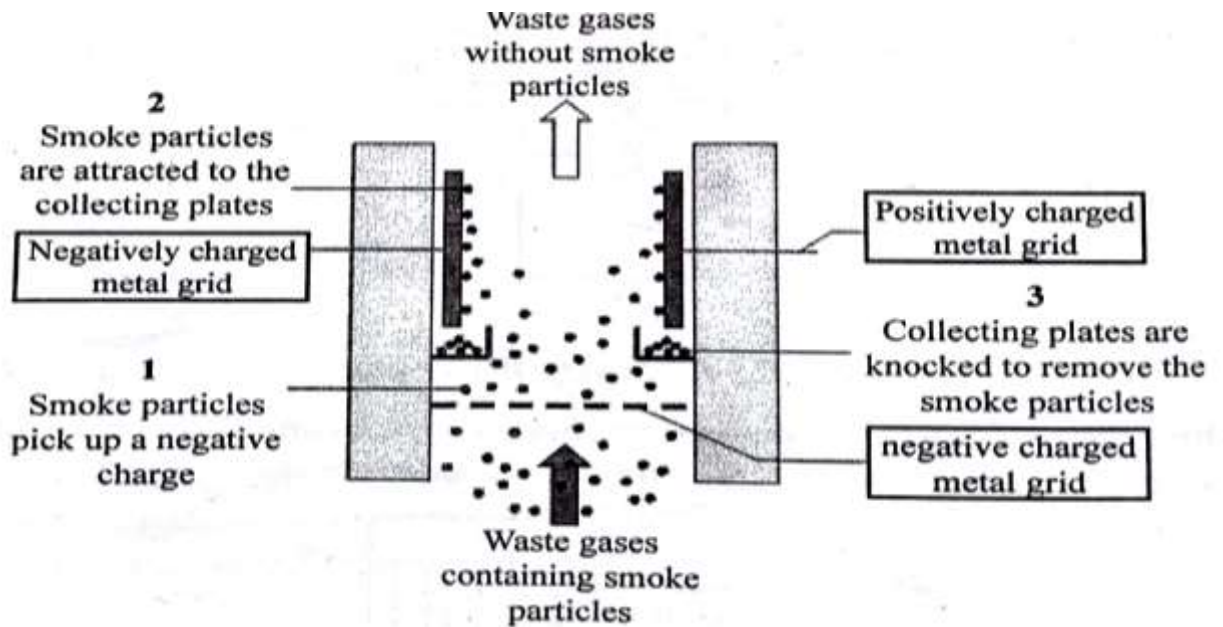
LEAD AS AIR POLLUTANT:

Sources of Lead

- The most important anthropogenic source of lead is the automobile exhaust gases and lead based paints. Organolead compounds such as TEL & TML are used as additives to petrol to give leaded petrol. They function as antiknock agents. At the engine temperatures, these compounds decompose to atomic lead & alkyl free radicals. The elemental lead thus formed is converted to volatile compounds and escapes into the atmosphere along with other automobile exhaust gases. However, lead is eliminated from gasoline, and there is a significant decrease in human exposure to lead. That lead still remain in soil even today.
- Lead also comes from metal smelting, lead-acid battery manufacturing and other factories that use lead.
- Lead enters water through contact with plumbing, lead based pipes or solder that leaches lead into water through corrosion.

Effects

a) Air borne lead enters the body, it distributes throughout the blood and accumulates in the bones because of the similarity in size of Ca^{2+} & Pb^{2+}. Depending on the level of exposure, lead can adversely affect the nervous system, kidney function, immune system, developmental systems & the cardiovascular systems.

b) It is known that lead ions inhibit atleast two enzymes that catalyse the bio-synthesis of haemoglobin resulting in anaemia.

c) Infants & young children are especially sensitive to even low levels of lead, which may contribute to behavioral problems and learning deficits.

d) Elevated levels of lead in the environment can lead to decreased growth & reproductive rates in plants and animals.

Control

a) Replacement of conventional lead based products by lead free products.

b) Eliminate lead contamination in drinking water by processes such as RO, distillation & filtration using carbon filters specifically manufactured for lead removal.

c) Lead smelting plants should design their storage piles in such a way that the movements of lead materials are minimized to lessen exposure to wind & air.

MERCURY AS AIR POLLUTANT:

Sources: Natural sources of mercury include volcanoes, natural mercury deposits and release from the ocean. Manmade sources include coal combustion, waste incineration, metal processing industries. Other sources include mercury containing products, for example: batteries, thermometers and barometers, electric switches, lamps, dental amalgam, cosmetics etc.

Effects: The three most common forms of mercury are elemental, inorganic and methyl mercury. Methyl mercury is among organic mercury compounds and is present in sea foods such as fish and shell fishes. It is a poison for the nervous system. It causes "Minamata" disease Exposure during pregnancy may harm the unborn baby's brain. It also affects heart and circulatory system.

Elemental mercury is also poisonous to the nervous system. Humans are mainly exposed by inhaling vapors. These are absorbed into the body via the lungs and moves easily from the bloodstream into the brain. The inhalation of elemental mercury vapors can cause neurological and behavioral disorders, such as tremors, emotional instability, insomnia, memory loss, neuromuscular changes and headaches. They can also harm the kidneys and thyroid. High exposures have also led to deaths.

Inorganic mercury compounds primarily causes burning chest pain, darkened discoloration of the oral mucous membrane and severe gastrointestinal symptoms, impaired kidney function. The target organ toxicity of inorganic mercury is kidney damage, mainly in the proximal convoluted tubules.

Control:

a) Promote the use of clean energy sources that do not burn coal: Burning coal for power and heat is the major source of mercury.

b) Eliminate mercury mining and use of mercury in gold extraction: Mercury is present in sufficient quantities, it can be recycled and reused, no further need for mercury mining. Non- mercury gold extraction must be promoted.

c) Discontinue the usage of non- essential mercury containing products, such as batteries, thermometers, lamps, skin lightening cosmetics, etc and implement safe disposal of remaining mercury containing products.

d) Mercury emission is controlled at the source by using fabric filters, wet scrubbers or electrostatic precipitators. Installation of traps and filters in the industries using mercury can be effective in controlling release of mercury into the environment.

SECONDARY AIR POLLUTANTS

Secondary pollutants are air pollutants that are not directly released into the atmosphere but forms when primary pollutants react in the atmosphere.
Examples of secondary air pollutants: Ozone, Nitric acids, Sulphuric acids

Ozone

Ozone or trioxygen, is an inorganic molecule with the chemical formula O_3. Ozone forms a protective layer in the stratosphere which absorbs potentially harmful UV radiations from sun. The thickness of the ozone layer is about 3 mm and is called ozonosphere/ chapman layer.

Ozone when present in troposphere is ahealth hazard as it is one of the constituents of photochemical smog. Ozone is a powerful oxidant produced and used many industrial and consumer applications related to oxidation.

Formation of Ozone

- Ground level ozone forms when primary pollutants such as oxides of nitrogen (NOx) and volatile organic compounds (VOCs) react with sunlight.

  NO_x + VOC_s + Sunlight = Ozone
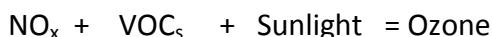
- Ozone is formed in the stratosphere by the photo dissociation of ozone molecule by absorbing UV radiation of 240 nm wavelength.
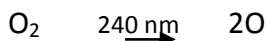
  $O_2 \xrightarrow{240 \text{ nm}} 2O$

DEPARTMENT OF CHEMISTRY

- The atomic oxygen combines with molecularoxygen producing ozone.

$$O + O_2 \longrightarrow O_3$$
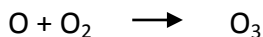
- Ozone dissociates by absorbing UV radiation in the range 200-300 nm

$$O_3 \longrightarrow O + O_2$$
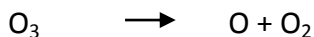
Ozone is formed again by the reaction between the products and thus there exists a dynamic equilibrium between the formation and dissociation of ozone maintaining ozone concentration in the atmosphere at a constant level.

Effects of UV radiation

For the ecosystem, the ozone layer is more significant since it absorbs the harmful UV radiation of sun and prevents it from reaching the earth's surface. UV radiation causes skin cancer eye disorders and suppresses the immune system, decrease in long range agricultural productivity, albumin coagulation, change in global rain.

Effects of Ozone

a) **Positive effects at upper atmosphere:** The ozone layer is beneficial, preventing damaging UV light from reaching the earth's surface, to the benefit of both plants and animals.

b) **Negative effects at upper atmosphere:** ozone has very high oxidizing potential, can damage mucous and respiratory tissues in animals, and also tissues in plants, above concentration of about 100 ppl near ground level.

Ozone Depletion: The wearing out (reduction) of the amount of ozone in the stratosphere is called ozone depletion.

Compounds emitted from anthropogenic source dissociate ozone into ordinary oxygen and are called ozone depleting substances (ODS). Substances like Chlorofluoro Carbons (CFCs or freons) used as coolants in refrigeration and air conditioning are very stable on the earth and slowly drift into stratosphere,Halons found in cleaning agents, aerosols, insulating foams.They react with UV radiation to form chlorine free radical which is a potential ozone depleting species.

$$CF_2Cl_2 \xrightarrow{\text{UV radiation}} CF_2Cl + Cl^{\bullet}$$
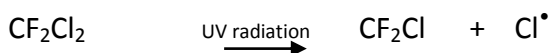
$Cl^{\bullet}$ catalyzes the degradation of ozone
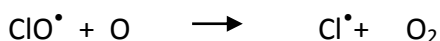
$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$$

$Cl^\bullet$ radical is regenerated in this reaction. The free $Cl^\bullet$ again react with O_3 and the process continues resulting in depletion of ozone layer.

The combined effect is $O_3 \longrightarrow O + O_2$

$Cl^\bullet$ can repeat the process and one CFC molecule can destroy several thousands of ozone. The thinning is most pronounced in the polar regions, ozone hole was detected over Antarctica during 1985.

Effects of ozone layer depletion

As ozone depletes in the stratosphere, it forms a 'hole' in the layer. This hole enables harmful UV rays to enter the Earth's atmosphere. UV rays of the sun are associated with a no. of health related and environmental issues.

a) **On humans**: Higher risk of the skin cancer, eye cataracts, immune system damage, accelerated aging of skin, damage to DNA and leads to mutation & blindness, ozone chemically can cause difficulty in breathing, chest pain, throat irritation and hampers lung functioning.

b) **Marine life:** Phytoplankton & zooplankton are very sensitive to the amount of light in their environment and increase in UV rays would greatly affect them. Because these organisms are the base of the food chain, declines in their number would likely have wide reaching effects for all marine life.

c) **Plants:** Increase in UV rays can cause decreased plant growth, and lower quality crops for humans. Plants form the basis for most food chains, thus negative effects would likely cascade to those organisms relying on them.

Control

a) Alternatives for CFCs include HCFC (hydrochloro-fluoro carbons) and HFA(Hydrofluoro alkanes). These substances contain hydrogen atoms in the molecule and they are susceptible for oxidation and have short atmospheric resident time. They undergo degradation before reaching the stratosphere. The ozone depletion potential of HFA is zero since it has no Chlorine atoms.

b) Usage of eco-friendly household cleaning products is encouraged.

c) Usage of public transport is encouraged with limited private driving to control vehicular emissions.

d) Declared on 1996 by UNEP (United Nations Environment Programme), 16th September is celebrated as ' International day for the preservation of ozone layer. It's main aim is to create awareness on ill effects caused by ozone layer depletion.

e) Montreal protocol was formed in the year 1987 with an aim of stopping the usage of CFCs. It also strengthens the order that ozone depleting substances should not be produced and consumed.

f) Encourage growth of plants that produce oxygen, discourage deforestation.

WASTE MANAGEMENT

" Waste is any substance which is discarded after primary use, or is worthless, defective and of no use."

The collection, transportation and disposal of garbage, sewage and other waste products is called waste management.

Waste management encompasses management of all processes and resources for proper handling of waste materials, from maintenance of waste transport trucks and dumping facilities to compliance with health codes and environmental regulations.

It includes the following initial steps:

(i)   Identifying the type of waste.
(ii) Identifying the source of waste.
(iii) Determination of the potential health hazard.
(iv) Determination of the volume of waste generated.
(v)   Identifying the safe collection method.
(vi) Identifying the safe transportation method.
(vii) Identifying the safe disposal method.

Harmful effects of Waste

(i) It can create a breeding ground for pathogenic microorganisms and vectors of disease.
(ii) It cause a public nuisance due to unsightliness and bad smell.

(iii)   It can cause contamination of surrounding soil, groundwater and surface water.

(iv)   It can also create fire hazards, physical hazards and have poisoning effects.

(v)   It can pollute the surrounding air and can seriously affect the health of humans, wildlife and our environment.

Simple tips to reduce waste

(i)   Reduce or minimize use of plastic bags and polystyrene foam.

(ii)   Compost yard waste which also helps enrich the soil and reduces water run – off.

(iii)   Take reusable bags to the store when shopping.

(iv)   Donate unwanted, slightly used clothing, furniture and other household items to local non- profit organization.

(v)   Store leftover foods in reusable containers instead of single use plastic bags or polystyrene foam containers.

PRINCIPLES OF WASTE MANAGEMENT

Integrated Waste Management Hierarchy

Most Preferred

1) **REDUCE:** cleaner production, sustainable consumption & prevention
2) **REUSE:** Reusing waste in its current form
3) **RECYCLING & COMPOSTING:** Processing waste to recovercommercially valuable products
4) **RECOVER:** Recover energy from waste
5) **RESIDUALS:** Safe disposal in a landfill

Least Preferred

The aim of the waste hierarchy is to extract the maximum practical benefits from the products & to generate the minimum amount of end waste.

a) **Reduce:** The basic step is that policies should promote measures to prevent the generation of waste.

b) **Reuse:** The next step or preferred action is to seek alternative uses for the waste that has been generated.
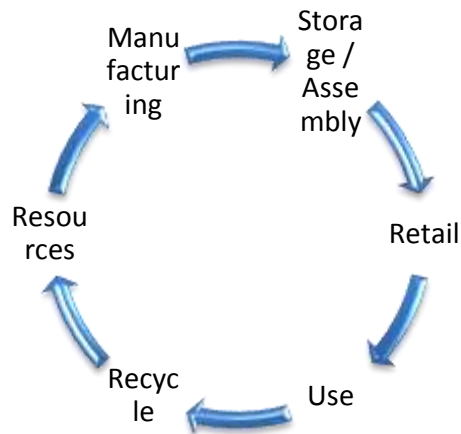
c) **Recycling:** It includes composting.

d) **Recovery:** Material recovery conversion of waste to energy.

e) **Residuals:** Includes safe disposals in landfills or through incineration without energy recovery. It is used for waste which has not been prevented diverted or recovered.

PRODUCT DESIGN: LIFE CYCLE

Product life – cycle analysis is a way to optimize the use of the world's limited resources by avoiding the unnecessary generation of waste.

Here each stage in the life – cycle offers opportunities to rethink the need for the product, to redesign, to minimize waste potential, to extent its use.

SOLID WASTE

Solid waste refers to all non – liquid waste or garbage arising from animal and human activities that are discarded as unwanted and useless.

Solid waste can be classified into different types depending on their sources:

a) Municipal Solid wastes (MSW)   b) Hazardous wastes
c) Industrial wastes   d) Agricultural wastes

e) Bio-medical wastes

Sources: Residential areas and homes, Industries, Commercial establishments, Institutions, Municipal services, Manufacturing plants and sites, Construction & demolition areas, Agriculture.

The Solid Waste management system:

The solid waste management includes:

(i) **Generation**: The materials which can no longer be used and want to get rid of them becomes a waste.

(ii) **Storage**: This involves keeping the waste prior to disposal and it is not necessary for all type of waste.

(iii) **Collection**: Waste collected for transportation to the disposal site. The volume of waste collected should be estimated.

(iv) **Transportation**: Depending on the availability and volume of waste different modes of transportation can be adopted for final disposal of the waste.

(v) **Disposal**: This involve the safe disposal to minimize pollution.

Characteristics of Solid wastes:

Information and data on characteristics of solid waste are important for selecting a suitable disposal technique.

- **Physical Characteristics:**
    - **Density of waste** (mass per unit volume): The design of sanitary landfills, storage, types of collection and transport vehicles etc. The efficient operation of a landfill demands compaction of wastes to optimum density.
    - **Moisture Content**: Moisture increases the weight of solid wastes and thereby, the cost of collection and transport. Moisture content determines the economic feasibility of waste treatment by incineration because wet waste consumes energy for evaporation of water. The typical range of moisture content is 20% to 40%.
    - **Size distribution**: It helps in the recovery of materials especially with mechanical means such as trommel screens and magnetic separators.
- **Chemical Characteristics:** If solid wastes are to be used as fuel, or are used for any other purpose, we must know the chemical nature of the waste, including the following:
    - Lipids (found in variety of wastes, suitable for energy recovery)
    - Carbohydrates content (found in food and yard wastes)

- Proteins (found in food and garden wastes)
- Natural fibres (found in paper products, food and yard wastes, suitable for energy recovery)
- Synthetic organic material (Plastics, suitable for pyrolysis and energy conversion)
- Non-combustibles (glass and other materials)
- Heating value of waste (or calorific value of waste)

Disposal techniques:

a. **Scientific landfilling/ burial:** Waste is directly disposed into a large pit or trench, and waste should be covered with a thin layer of soil. It has a liner at the bottom to prevent the groundwater from contaminating with the mix of the liquid that oozes from the waste that is buried called the leachate. When the landfill is completed, it is capped with a layer of clay or a synthetic liner in order to prevent water from entering. A final topsoil cover is placed, compacted and graded, and various forms of vegetation may be planted in order to reclaim the area otherwise it will be useless land. Vertical wells installed in scientific landfills help extract methane regularly, and the gas can then be used for electricity and heat generation purposes.

b. **Composting:** Vegetable and organic waste can be dug into the soil to add humus and fibre. Aerobic composting is the creation of fertilizing compost using bacteria that thrive in an oxygen-rich environment. Aerobic composting is considered the fastest method of composting but involves more work in terms of rotating the organic material periodically.

   Anaerobic composting is the creation of fertilizing compost using bacteria that cannot thrive in the presence of oxygen. Anaerobic composting is known to work slowly, but also requires lesser work.

c. **Burning or incineration:** Controlled burning of organic and combustible waste to ash, reduces volume and weight for safe disposal in outer land fields. In some cases, the heat generated by incineration can be used to generate electric power.

d. **Autoclave:** Autoclaves are closed chambers that apply both heat and pressure, and sometimes steam, over a period of time to sterilize medical equipment. Autoclaves are used to destroy microorganisms that may be present in medical waste before disposal in a traditional landfill.

e. **Recycling:** Some waste like plastic bags, containers and glass can be recycled. Recycling or recovery of resources is taking maximum benefits from discarded items. The process aims at reducing energy loss, consumption of new material and reduction of landfills.

Electronic waster or e-waste management: Electronic waste or e-waste is a term refers to electronic and electrical goods that have become unwanted, non-working or obsolete, and have

essentially reached the end of their useful life. Because technology advances at such a high rate, many electronic devices become "trash" after a few short years of use. They contain hazardous and toxic materials which cannot be disposed off with other solid waste.

Sources of e-waste:

- Waste generated from the products used for data processing such as computer devices like monitor, speakers, keyboards, printers, laptops, mouse, circuit boards, scanners, cables.
- Electronic devices used for entertainment like TV, DVDs and CD players, MP3, radio.
- Equipment or devices used for communication like mobiles, landline phones, fax.
- Kitchen equipment such as toasters, coffee makers, microwave ovens.
- Other equipments such as lamps, clocks, calculators, camera, flashlights, lab equipments (hot plates, microscopes, calorimeters).

Characteristics:

1. **Hazardous Components in e-waste:** Electronic waste consists of a large number of components of various sizes and shapes, some of which contain hazardous components that need to be removed for separate treatment. Eg: Brominated flame retardants like HBCD (Hexabromocyclododecane) and heavy metals such as lead, mercury, cadmium and beryllium.
2. **Material Composition of e-waste:** The copper, aluminium and precious metals (Pt, Ag) makes up more than 80% of the value of the e-waste. Recovery and recycling of these precious metals and copper remain as the major economic drive from a long time.

Effects:

1. Informal processing of e-waste in developing countries can lead to adverse human health effects and environmental pollution.
2. Electronic scrap components, contain potentially harmful components such as lead, cadmium, beryllium or brominated flame retardants, polychlorinated biphenyls (PCBs), dioxins are carcinogenic in nature.

Disposal methods of E-waste:

1. **Acid Bath:** Acid bath involves soaking of the electronic circuits in the powerful sulphuric, hydrochloric or nitric acid solutions that free the metals from the electronic pathways. The recovered metal is used in the manufacturing of other products.

2. **Recycling of E-waste**: Mobile phones, monitors, CPUs, floppy drives, laptops, keyboards, cables and connecting wires can be re-utilized with the help of the recycling process. It involves dismantling of the electronic device, separation of the parts having hazardous substances like CRT, printed circuit boards etc and then recovery of the precious metals like copper, gold or lead can be done.

3. **Reuse of electronic devices**: This is most preferred process where with slight modifications the mobile phones, computers, laptops, printers can be reused or given as second hand product to the other person. The old electronic equipment can also be donated as charity to the person in need as well as can be solded to others.

4. **Incineration**: It involves combustion of electronic waste at high temperature in specially designed incinerators. In this way the waste volume is extremely reduced and the energy obtained can also be utilized separately.

5. **Landfilling**: Soil is excavated and trenches are made for burying the e-waste in it. An impervious liner is made of clay or plastic with a leachate basin for collection and transferring the e-waste to the treatment plant.

Bio-medical waste (BMW): Bio-medical waste, also known as infectious waste or medical waste, and is defined as solid waste generated during the diagnosis, testing, treatment, research or production of biological products for humans or animals.

Sources: Hospitals, clinics, dispensaries, blood banks, animal house, mortuaries, animal research, labs and veterinary institutions. According to WHO 85% of BMW is non-hazardous, 10% is infectious and 5% is non-infectious.

Types:

1. **Infectious waste (including sharp objects and pathological waste)**: Waste that may transmit infection from virus, bacteria, parasites to human, i.e. lab cultures, tissues, body parts, blood and other body fluids, swabs, excreta, needles, knives, etc.

2. **Radioactive waste**: Unused liquid in radiotherapy or lab research, contaminated glassware, etc.

3. **Chemical waste:** Expired lab reagents, film developer, disinfectant.

4. **Pharmaceutical waste:** Expired and contaminated medicines.

5. **Non-risk waste:** No risk to human health because no blood or any related bodily fluid, i.e. office paper, wrapper, kitchen waste, general waste.

Characteristics:

- Heating value (or calorific value) of waste should be more than 8370 KJ/Kg.

- Percentage of combustible matter should be above 60%.
- Moisture content should be below 30%.

Disposal Methods:

1) **Chemical disinfection:**Certain chemicals are added to waste to kill or inactivate the pathogens. Solid and even highly hazardous health-care wastes, including microbiological cultures, sharp objects etc, may also be disinfected chemically. Non-liquid infectious wastes need to be shredded first to ensure that all portions of the waste are exposed to the chemicals. The most common effective disinfectants commonly used are formaldehyde, glutaraldehyde, sodium hypochlorite, chlorine dioxide.

2) **Microwave irradiation**: Most micro-organisms in bio-medical waste are destroyed by the action of microwaves of a frequency of 2450 MHz and a wavelength of 12.24 cm. The water contained in the waste is rapidly heated by the microwaves and the infectious components are destroyed by heat conduction.

3) **Autoclaving**: Thermal treatment is typically used for sharp objects and certain other types of infectious waste. An autoclave is essentially a large pressure cooker that uses high temperatures and steam to deeply penetrate all materials and kill any microorganisms.

4) **Incineration** :Incineration is a high temperature dry oxidation process that reduces organic and combustible waste to inorganic , incombustible matter and results in a very significant reduction of waste volume and weight. This process is usually selected to treat wastes that cannot be recycled, reused or disposed of in a landfill site.

5) **Sanitary landfills**: The use of landfills for bio-medical waste has to be regarded as last option. It should not be dumped in open spaces, as this leads to acute pollution problems, fires, higher risks of disease transmission. Sanitary landfills are safer due to the geological isolation of wastes from the environment and appropriate engineering preparations to control site operations.

<u>**DEPARTMENT OF CHEMISTRY**</u>

Water Technology

Impurities in water:

1) *Dissolved impurities:*

Dissolved impurities are mainly bicarbonate, chloride and sulphate salts of calcium, magnesium, iron, sodium and potassium. In addition, small amounts of nitrates, nitrites, silicates, ammonia and ferrous salts are also present. The presence of these salts imparts hardness to water.

Ex: - When water is in contact with soil (or rock), limestone present in rock combines with water along with CO_2 of water to give $Ca(HCO_3)_2$. This impurity dissolves in water. Hence it acts as a dissolved impurity.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

In general underground water contains more dissolved salts than surface water.

2). *Suspended impurities*:

Suspended impurities are the dispersion of solid particles, which can be removed by filtration or settling. They are of two types: Inorganic and Organic

Sand, clay, silica oxides of iron and aluminum etc are inorganic type of suspended impurities. Wood pieces, Leaf, decaying vegetable matter, microorganisms etc are organic impurities. These impurities impart turbidity, bad colour, bad odour and bad taste to water.

3). *Dissolved gases:*

The water contains mainly CO_2, O_2 as dissolved gases. Some water may contain ammonia and sulphur compounds such as hydrogen sulphide (H_2S) as dissolved gas. Presence of these gases imparts foul smell to water.

4). <u>Organic matter (microscopic matter):</u>

Organic compound derived from decay of vegetable and animal matter including many pathogenic bacteria and microorganisms are also present in water. They are the main cause for water borne diseases. These can be removed from water by boiling and chlorination.

Boiler feed water:

A boiler is a closed vessel which operates at different pressure and temperature. Water heated in boiler under pressure is transformed to steam.
The water used in these types of boiler is called as boiler feed water.

(The steam generated in these boilers is being used for various purposes like power generation, space heating, drying, sterilization etc.)

Boiler troubles

1. Scale and Sludge formation
2. Priming and Foaming
3. Boiler corrosion

1. **Scale and Sludge formation:-**Water is heated under higher pressure at higher temperature inside the boilers which makes the water to get evaporated in the form of steam. As the boiling point of water is much less than that of many impurities gets progressively deposited inside the boiler.

   The hard deposite adhered to the inner surface of boilers which are difficult to remove are called as scales.
   Ex. Scales formed due to presence of impurities like $Mg(HCO_3)$, $Ca(HCO_3)$, $CaSO_4$ etc
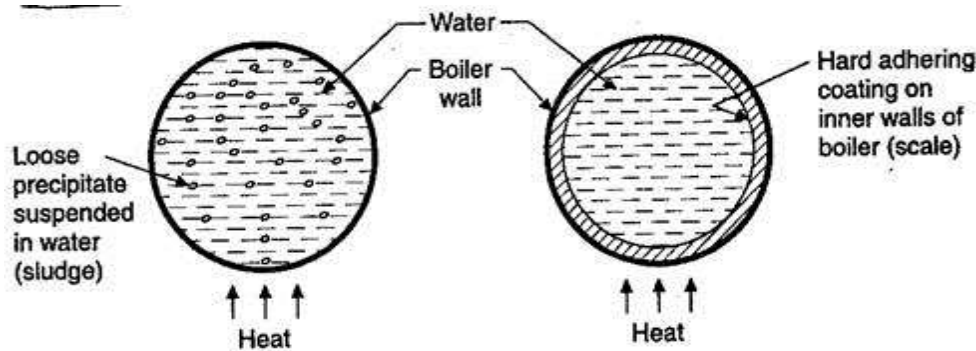
Problems caused by scales

1. Loss of fuels
2. Reduction of Boiler efficiency
3. Boiler explosion
4. Expense of cleaning.

Methods to Remove Scales

1. Blow down operation for loose scales
2. By giving thermal shocks, which involves alternate heating and cooling that makes the scales brittle.
3. Chemical treatment with HCl for Carbonates and EDTA for Ca/Mg Salts

Loose collection of suspended solids in the cooler, less turbulent parts of the boiler and in the distribution of pipes is called sludge.

Sludge formation may be due to presence of $MgCO_3$, $CaCl_2$, $MgCl_2$

Problems caused by sludge

1. Loss of fuels
2. Reduction of Boiler efficiency
3. Expense of cleaning.

Prevention of Sludge

1. By using soft water for the boiler operation
2. Removal of concentrated salty water from time to time so that deposition of sludge is prevented

Boiler corrosion

The process of degradation of the boiler surface by the attack of boiler feed water is called as boiler corrosion

Corrosion in boiler is due to the following reasons

1. Presence of dissolved oxygen: The Dissolved oxygen present in the boiler feed water can attack boiler surface and produce rust as follows
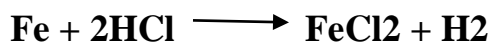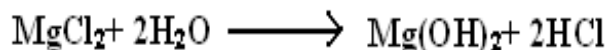
$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3.2H_2O] \text{ rust}$$
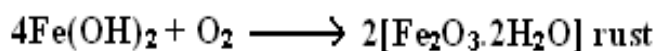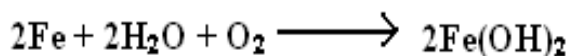
2. Presence of carbon dioxide: carbon dioxide forms carbonic acid in presence of water which is slightly acidic in nature and hence cause corrosion

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

3. Presence of Dissolved salts ($MgCl_2$)
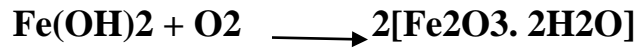   Magnesium chloride forms hydrochloric acid in presence of water which has slow effect on boiler materials.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

$$Fe + 2HCl \longrightarrow FeCl2 + H2$$

$$FeCl2 + H20 \longrightarrow Fe(OH)2 + 2HCl$$

$$Fe(OH)2 + O2 \longrightarrow 2[Fe2O3. 2H2O]$$
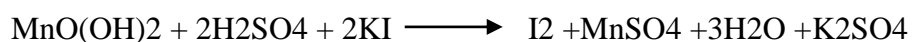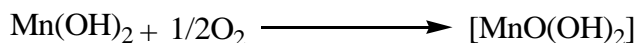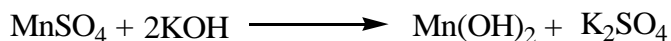
Disadvantages of boiler corrosion

1. Shortening of boiler life.
2. Leakages of joints and riverts.
3. Increased cost of repairs and maintenance.

1. Biological Oxygen Demand

Def ^{n}:-The amount of Dissolved oxygen consumed by the microorganism to oxidise the biologically oxidisable impurities present in 1 liter of water sample over the period of 5 days at 20^oC

Winkler's method BOD measurement: In this method BOD is determined by measuring the dissolved oxygen contents before and after 5 days incubation by indirect iodometric method.

Principle:- This method is based on the indirect iodometric titration. Manganese sulphate reacts with alkaline solution to give manganese hydroxide. Manganese hydroxide reacts with DO to give basic manganese oxide and precipitated. Precipitation is dissolved by addition of con. H_2SO_4. Manganese oxides Oxidise potassium iodide to iodine. The liberated iodine is titrated against standard $Na_2S_2O_3$.

$$MnSO_4 + 2KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

$$Mn(OH)_2 + 1/2O_2 \longrightarrow [MnO(OH)_2]$$

$$MnO(OH)2 + 2H2SO4 + 2KI \longrightarrow I2 + MnSO4 + 3H2O + K2SO4$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

(Note: 300 ml of waste water is diluted to 600 ml, and dived in two iodine bottles (300 ml each)

Blank titration: DO content of the one bottle determined immediately add 2ml of $MnSO_4$ and 3 ml of alkaline KI to the reagent bottle containing a known volume of water. Obtained Basic manganese hydroxide Precipitation is dissolved using con H_2SO_4. Take a 50 cm^3 of the above reaction mixture into 250 cm^3 conical flask. Add 4-5 drop of starch indicator and titrate the liberated iodine against standard sodium thiosulphate, till the colour changes from blue to colour less.

Sample titration:= The second bottle is incubated for 5 days at 20°C, After 5 days unconsumed DO is determined as above procedure.

Observation and calculation

D_1 is the DO of the sample in mg/ml at the start of the experiment

D_2 is the DO of the sample in mg/ml after 5 days.

A is ml of the sample before dilution

B is ml of the sample after dilution

$$BOD=\frac{(DO1-DO2)B}{A}$$

Importance of BOD: BOD is most important in sewage treatment, as it indicates the amount of decomposable organic matter in the sewage or extent of pollution or amount of dissolved oxygen. On the basics, environments design the treatment.

Greater the concentration of organic matter in the sewage, greater the BOD.

Chemical oxygen demand

It is the amount of oxygen in milligrams required to oxidize organic and inorganic Impurities present in one liter of waste water using strong oxidizing agent like $K_2Cr_2O_7$ under acidic medium.

Principle: A Known amount of water is refluxed with a known excess acidified $K_2Cr_2O_7$ and a small amount of Ag_2SO_4 and $HgSO_4$ are added. $K_2Cr_2O_7$ oxidizes all oxidisable impurities.

The amount of unconsumed $K_2Cr_2O_7$ is determined by titration with std. FAS (ferrous ammonium sulphate) solution using ferroin indicator. The amount of $K_2Cr_2O_7$ solution consumed corresponds to the COD of the sewage sample.

Procedure:-

Sample or Back titration:-

 Pipette 25 ml of waste water into a clean conical flask add 2 test tube of 2N H_2SO_4 solution and pipette out 10 ml of $K_2Cr_2O_7$ solution to the same conical flask. Add 1g of $HgSO_4$ followed by 1g Ag_2SO_4. Attach a reflux condenser and reflux contents for 2 hours. Cool and titrate the unconsumed $K_2Cr_2O_7$ against FAS using ferroin indicator till the color of the solution changes from bluish green color to reddish brown.

Blank titration:- The above procedure is repeated without adding Waste water sample.

Observation and calculation:-

Volume of water sample taken= V cm^3

Volume of standard FAS used in sample titration= Y cm^3

Volume of standard FAS in the blank titration= X cm^3

Normality of FAS solution= N

Amount of K2Cr2O7 consumed in satisfying the COD in terms of FAS solution=(X-Y)cm^3

$$N_1 \times V = N \times (X-Y)$$

Normality of COD of the sample $N = \dfrac{N*(X-Y)}{V}$

1000cm^3 of waste water sample = $\dfrac{8*(X-Y)*N*1000}{25}$ mg of O2/ltr

Importance:

1) The COD test is widely used for measuring the pollutional strength of domestic and industrial wastes.
2) Management and design of treatment plant.
3) The major advantages of COD test are that the determination is completed in three hours as compared to the 5 days required for BOD determination.

Determination of sulphates in water by gravimetric method

Principle: When water contains sulphate ions is treated with Barium chloride solution. The sulphate is converted into sparingly soluble barium Sulphate. The ppt. is separated and weighed.

$MgSO_4$ or $CaSO_4$ + $BaCl_2$ $\longrightarrow$ $CaCl_2$ or $MgCl_2$ + $BaSO_4\downarrow$

From the weight of ppt., the amount of sulphate in water sample can be calculated.

Procedure: 1. 100 cm^3 of water sample into a clean beaker+ 2drops of methyl red indicator + con. HCl drop by drop till to get pink colour +2drop con. HCl is in excess.

2. The above solution is heat nearly to boiling + 10% hot $BaCl_2$ + stir well till to get white ppt. + 2drops of $BaCl_2$ is in excess.

3. The ppt is digested for two hours and then filter through No. 4 Whatman grade filter paper. Wash the ppt. with cold water many times to remove chloride contents if any.

4. The filter paper along with ppt. is transferred to previously weighed crucible and heat up to 900^oC.

5. The ppt. is cool in decicator and then finds out its weight.

Calculation: Refer notes

233.4g of $BaSO_4$ contains 96.06g of sulphate

Wg of $BaSO_4$ contains $= \dfrac{96.06 \times W}{233.4}$ A g of SO_4^{2-}

100 cm^3 water sample contains Ag of SO_4^{2-}

10cm^3 of solution contains $= \dfrac{A \times 10^6}{g \text{ of } SO4^{2-}}$

## Determination of Fluorides in water by colorimetric method

Principle: Fluorides contents in water are determined by colorimetric method. When the water sample contains fluorides ions is treated with Z- SPADNS in acidic medium, F⁻ bleaches the Z-SPADNS reagent and the amount of bleaching depends on the concentration of F⁻ according to Beer's Lambert law .

Procedure:

1. Draw 1, 2, 3, ---------8 ml of standard NaF solution in eight different 50 ml volumetric flask. Add 2 drops of 0.5% $NaAsO_3$ to remove residual chlorine if any and $10cm^3$ Z-SPADNS reagent. Dilute the solution up to the mark and shake well.
2. Prepare test solution by taking analytic sample in similar way
3. Prepare blank solution by taking 2drops of 0.5% $NaAsO_3$ and $10cm^3$ Z- SPADANS with out taking NaF solution.
4. Measure the absorbance of each solution with respect to blank at 570nm wave length.
5. Draw the calibration curve by plotting concentration verses absorbance and find out the concentration of F⁻ in test solution with the help of graph.
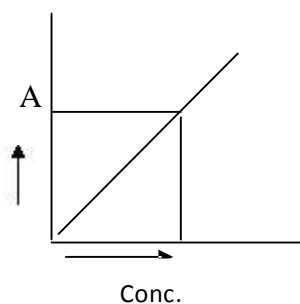
Sewage treatment:- Sewage water is a waste from kitchen, laundries, bathroom, laboratories and industries. The domestic sewage contains heavy load of BOD, pathogens bacteria, colour, odour and bad smell etc. Sewage water is

discharged into water bodies, leads to deficiency of dissolved oxygen and leads to the death of the oxygen. Pathogen bacteria are causing water borne diseases.

1. **Primary treatments:-** In these treatment suspended solids, gases, oil and grease are removed as follows

   a) **Screening:-**Suspended and floating substances are removed in this process by passing waste water through metal bar screens or mesh screens.

   b) **Slit and Grit removal:-**In this method the Waste water is passed through channels in a grit chamber. Water flows slowly in this chamber as a result of this silt and grit particles(Heavy pieces, pebbles, sand) Being heavy, settles down at the bottom of the chamber

   c) **Oil and grease removal:-** Oil and grease is removed by passing air under high pressure into the sewage water. As the solubility of air in water decreases during this process, air comes out of water in the form of bubbles, these bubbles carry oil with them to the top which can be removed by skimming

   d) **Sedimentation**:- it is to remove finer suspended impurities. The particles which do not settle down by gravity are coagulated by the addition of coagulants such as alum, ferrous sulphate etc. the sediment particles are filtered off.

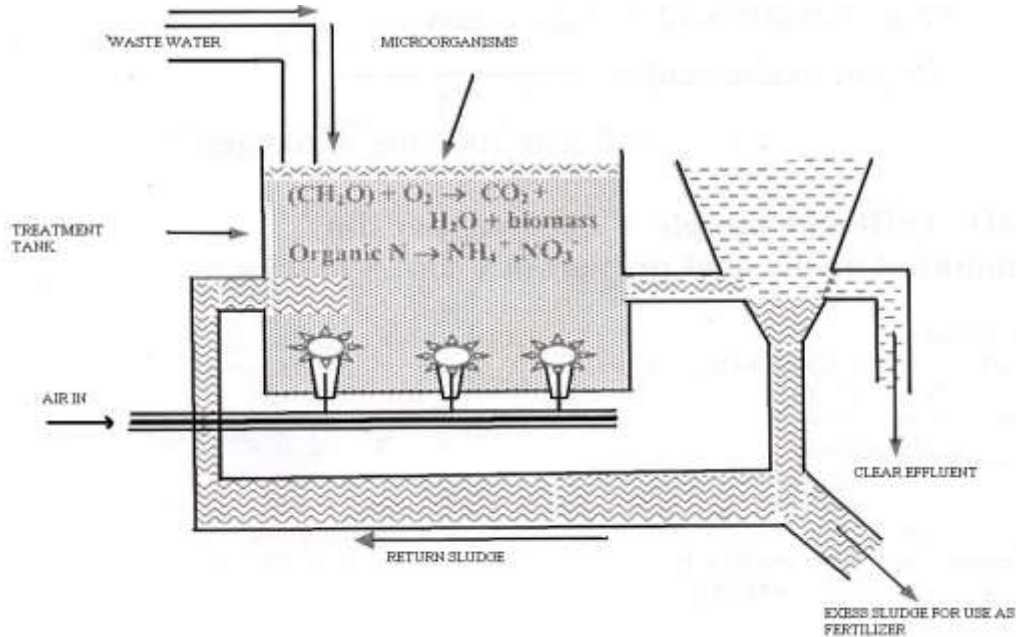2. **Secondary treatment**: Secondary process involves an aerobic oxidation of organic matter.

Activated sludge process: This processis to remove biologically Oxidizable impurities present in polluted water. Here Waste water sample after primary treatment is mixed with activated sludge (Water sample containing higher concentration of microorganisms like Azobacter, Bacillus, Zoophagus etc) and taken into the large tank. Air is passed into the tank to maintain aerobic conditions. Under aerobic condition, Microorganisms oxidize Biological oxidizable impurities into CO2 and H2O.

c) <u>Tertiary treatment</u>:

i. Treatment with lime for the removal of phosphates as insoluble calcium phosphates.

$$Ca(OH)_2 + PO_4^{3-} \longrightarrow Ca_3(PO4)_2^{-}$$
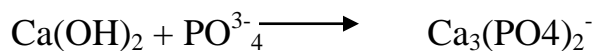
ii. Treatment with S^{2-} ions for the removal of metal ions as insoluble metal sulphides.

iii. Treatment with activated charcoal to adsorb remaining organic compounds.

iv. Treatment with alum to remove the colloidal impurities not removed in the previous treatments.

v.   Filtration

Softening of water by ion exchange process:

In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin. Ion exchange resins are high molecular weight, cross linked polymers with a porous structure. The functional groups which are attached to the chains are responsible for ion exchange properties.

The resins containing acidic groups which are capable exchanging H^+ (or Na^+) ions for cations (Ca^{2+} or $Mg^{2+)}$) present in water are known as cation exchange resins(RH^+).

The resins containing basic groups which are capable exchanging OH^- for anions (Cl^-, SO_4^{2-}) present in water are known as anion exchange resins ($R\,OH^-$).
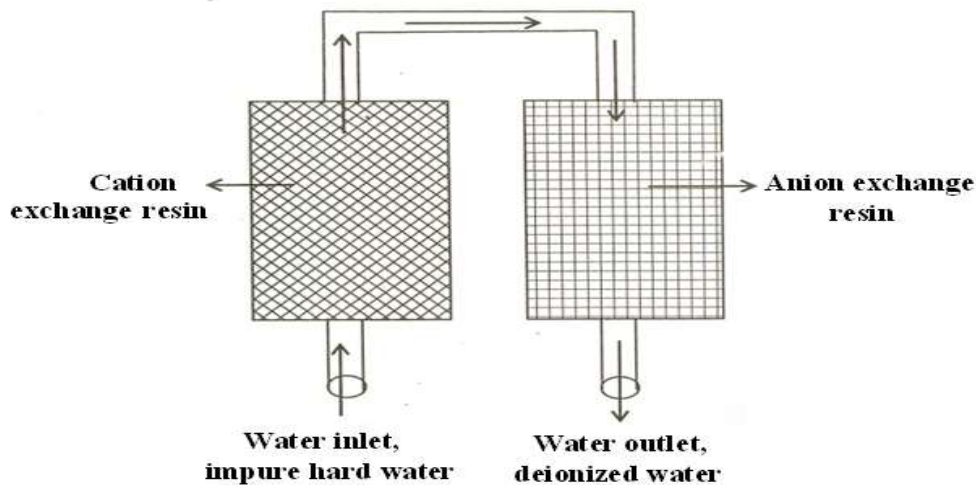
Process: In this process, cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cation like Ca^{2+}, Mg^{2+} are removed from hard water by exchanging with H^+ ions as follows

$$Ca^{2+} + 2R^- - H^+ \longrightarrow R_2^{2-} - Ca^{2+} + 2H^+$$
$$Mg^{2+} + 2R^- - H^+ \longrightarrow R_2^{2-} - Mg^{2+} + 2H^+$$

Hard water is then passed through anion exchange resin where ions like Cl^- , SO_4^{2-}
are exchanged with OH^- ions as follows;

$$R^+ - OH^- + Cl^- \longrightarrow R^+ - Cl^- + OH^-$$

These H^+ and OH^- ions released combine to form water molecule. Thus water coming out of two resins is ions free and called as ion-exchanged or demineralize water.

Desalination or Desalting:

Desalination is a process of partial or complete demineralization of highly saline water (sea water). The important methods of desalination are

1) **Reverse osmosis:-** If pure water and salt water are separated by a semipermeable membrane , the water molecules flows from pure water to salt water. This process of movement of solvent (water) molecules from dilute solutions into concentrated solution through a semipermeable membrane is called osmosis. Pressure excerted due to osmosis is called osmotic pressure.
   Water can be made to flow in reverse direction (Salt water to pure water) by applying pressure on the water greater than osmotic pressure. This process is called reverse osmosis.
   A reverse osmosis unit consists of a steel vessel, a membrane and a high pressure pump. The membrane are generally made of cellulose acetate or Nylon.
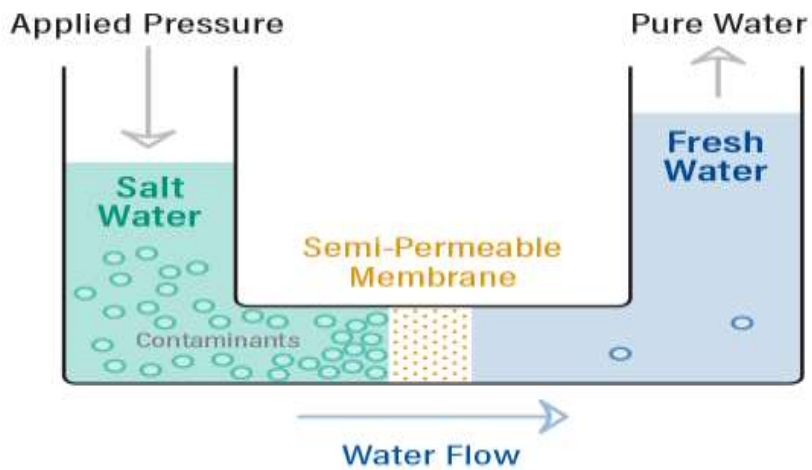
Osmosis   Reverse osmosis

OR

Reverse Osmosis

MODULE-5

Instrumental Method of Analysis

Types of Instrumental Method of Analysis

Instrumental Method of Analysis can be classified into two types

1.   **Electrochemical methods** : It involves the measurement of current ,voltage or resistance in relation to the concentration of a certain specie in solution EX: Potentiometer method, Conductometric method etc

2.   **Optical methods:** The optical methods are based on how the sample acts towards the electromagnetic radiation.

Colorimetry

Instrumentation

The essential parts of colorimeter are

1. **Source** – Light

2. **Filter**   - To filter undesired radiations , it allows radiations of a definite wave length

          range to pass through it and reach the sample

3. **Cuvette** - Sample Holder

4. **Photocell** - To receive the transmitted light

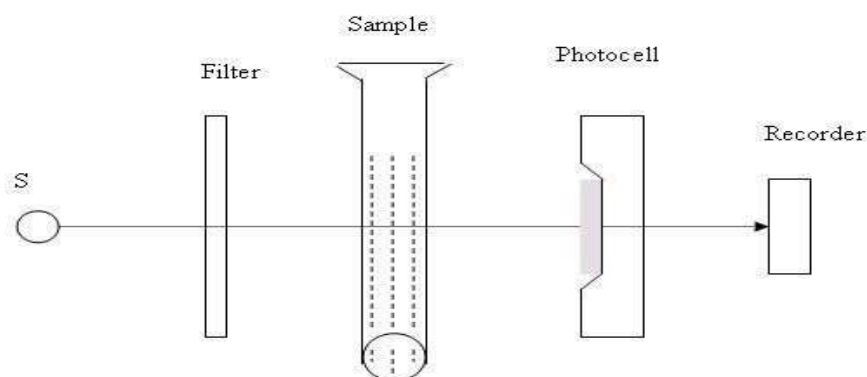5. **Recorder** – to record the absorbance in nm.

Theory: Colorimetric analysis depends upon the measurement of quantity of light absorbed by a colored solution. Quantitative analysis by colorimetric is based on beer –Lambert

Law, which can be expressed by the relation

Lambert's law: This law states that "When monochromatic light passes through a transparent medium, the rate of decrease in intensity with thickness of the medium is proportional to the intensity of the light"

Beer's law- This law states that "When monochromatic light passes through a transparent medium, the rate of decrease in intensity with concentration of the medium is proportional to the intensity of the light

Therefore absorbance of the colored solution changes with both concentration and thickness of the solution, if thickness kept constant, absorbance of the solution increases with increase in the concentration. On measuring the Absorbance of know and unknown concentrate solutions with respect blank. Concentration of unknown solution can be determined from the graph

Application

Quantitative Analysis: Colorimetric determination of copper in copper sulphate solution. From a burette, take 5, 10, 15, 20 cm^3 of given copper sulphate solution into four separate 50cm^3 volumetric flask. From another burette, add 5 cm^3 of ammonia to each one of them, to the unknown solution and blank solution flask. To the entire six flasks, add water up to the mark.
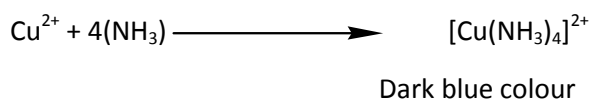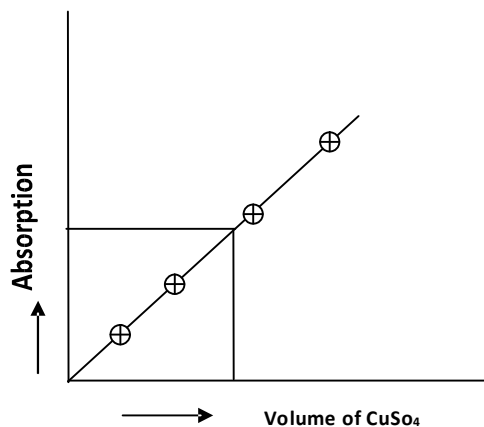
DEPARTMENT OF CHEMISTRY

Mix well. Wait for 10 minutes. In the colorimeter set the wavelength of light to 620 nm. For the blank solution, set absorbance to zero. Then, measure the absorbance of other five solutions.

Plot a graph of **absorbance** against volume of $CuSO_4$. Determine the volume of $CuSO_4$ in **unknown solution from**

the graph

$$Cu^{2+} + 4(NH_3) \longrightarrow [Cu(NH_3)_4]^{2+}$$

Dark blue colour

Calculate the mass of Cu in the given solution.

Flame photometry

Theory: Emission of characteristic radiation by element and the correlation of the emission intensity with the concentration of the element is the basis of flame photometry.

When a solution containing the sample element or the ion is aspirated into the flame, a series of changes take place at the flame.

First, the solvent gets evaporated leaving behind the salt in the flame

1. The salt then gets evaporated into vapours of the salt, which further undergo disassociation into the constituent atoms

2. Metal atoms formed in the flame absorb heat energy from the flame and get electronically excited into their higher energy level

3. Excited metal atoms fall back to their ground state by emitting the energy in the form of radiations

4.The intensity of the light radiation emitted is proportional to the no. of atoms in the excited state which in turn is proportional to the no. of atoms in the flame are the concentration of the solution fed into the flame

5. Thus the concentration of the solution is related to the intensity of emitted radiation

6. By measuring the intensity of the emitted radiation by a flame photometer concentration can be determined

Instrumentation

A flame photometer is consists of the pressure regulator, flow meter, burner optical system photo sensitive detector and output recorder. A filter of the element whose concentration is to be determined is inserted between the flame and the detector. Propane gas is used as fuel and air is used as oxidant. The whole analysis depends on the flow rate of the fuel, oxidant, and the rate of introduction of the sample and droplet size.
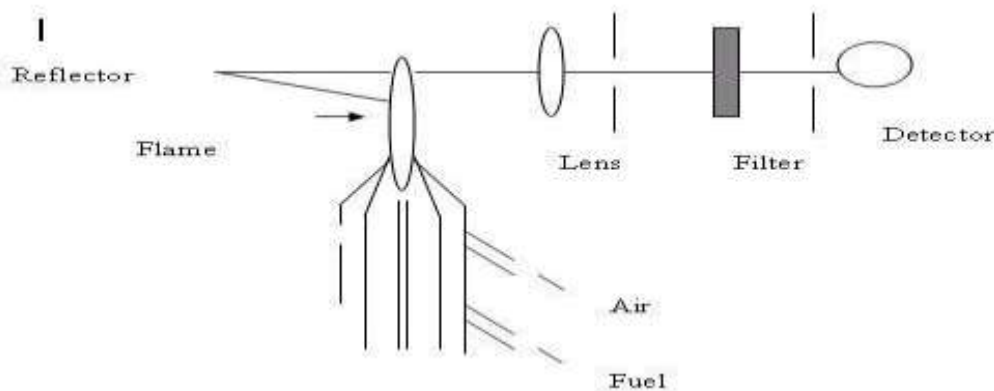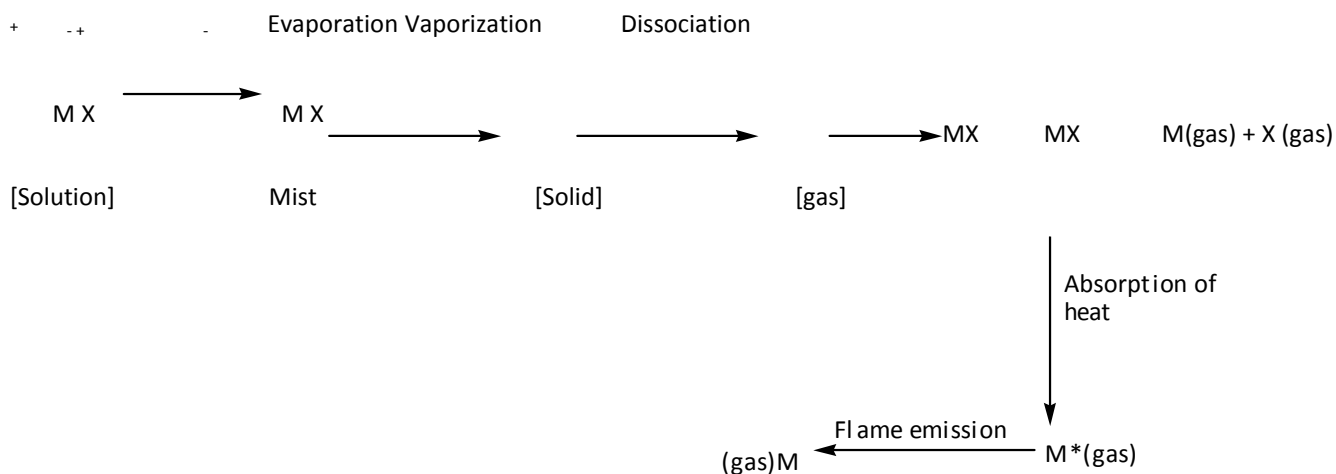
Evaporation Vaporization   Dissociation

+   - +   -

M X   M X   MX   MX   M(gas) + X (gas)

[Solution]   Mist   [Solid]   [gas]

Absorption of heat

Flame emission

(gas)M   M*(gas)

Reflector

Flame

Lens   Filter

Detector

Air

Fuel

Application:

Estimation of sodium content in the given sample of water

1.   The given sodium chloride solution (stock solution) is taken in burette and 2, 4, 6, 8 and 10 cm^3 of solution are drawn into different 50 cm^3 volumetric flasks and diluted up to the mark with distilled water. A
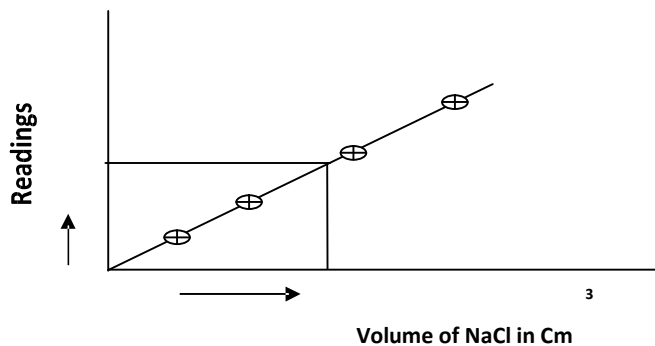
blank solution is also be prepared by collecting 50 cm^3 of pure distilled water in a separate 50 cm^3 volumetric flask.

2.   The filter of wavelength 589 nm is brought into position and the fuel ignited. The fuel supply is regulated to obtain a steady blue flame. The blank solution is aspirated into the flame and the reading set to zero.

Volume of NaCl in Cm^3

3.   Each of the standard solutions is separately aspirated into the flame and the readings are recorded. The reading for the test solution is also noted. A calibration line obtained by plotting readings against volume of NaCl solution. From the graph the volume of test solution and the amount of sodium in the test solution in terms of ppm is calculated.

Potentiometry

Theory: A Potentiometric titration may be defined as a titration in which the end point is detected by measuring the change in potential of a suitable electrode during the titration. The electrode which responds to the change in concentration of the ion in the solution is called the indicator electrode. The indicator electrode is combined with the reference electrode to form the cell and the e.m.f of the so formed cell is measured during the titration The e.m.f of the cell changes gradually till the end point and changes rapidly at very close to the end point and again the change is gradual after the end point. When e.m.f., is plotted as

ordinate and the volume of titrant added as abscissa, the point of inflection of the curve corresponds to the equivalence point or end point of the titration

Instrumentation Potentiometric method consist of Potentiometer and two electrodes in which one electrode is indicator electrode (eg Platinum electrode) and reference electrode

Instrument used: Potentiometer or pH meter

Electrodes: Indicator electrode eg – platinum

Reference electrode: calomel for potentiometer, glass electrode for pH meter.

1.   The solution to be titrated is taken in the beaker and titrant is taken in the

micro burette.

2.   Immerse the electrodes in the beaker along with stirrer

3.   The electrodes are connected to the potentiometer which gives the emf values

Applications

Oxidation Reduction reactions;

Estimation of amount FAS in FAS solution (FAS vs. $K_2Cr_2O_7$)

1. The FAS solution is taken in the beaker and $K_2Cr_2O_7$ is taken in the micro burette.

2. Immerse the electrodes in the beaker along with stirrer The electrodes are connected to the

potentiometer which gives the emf values

3. Go on adding the titrating reagent with an in travel of 0.5 ml

4. There will be sudden jump in the emf value after adding some amount of reagent

5. carry out the experiment for five more readings

6. plot first derivative curve ΔE/ ΔV Vs volume of reagent added

7. The volume correspond to the maximum peak in the graph is called equivalence point or end point of the reaction

8. Using formula normality and amount can be calculated.

$\Delta pH \backslash \Delta v$

Volume of $K_2Cr_2O_7$ in cm^3
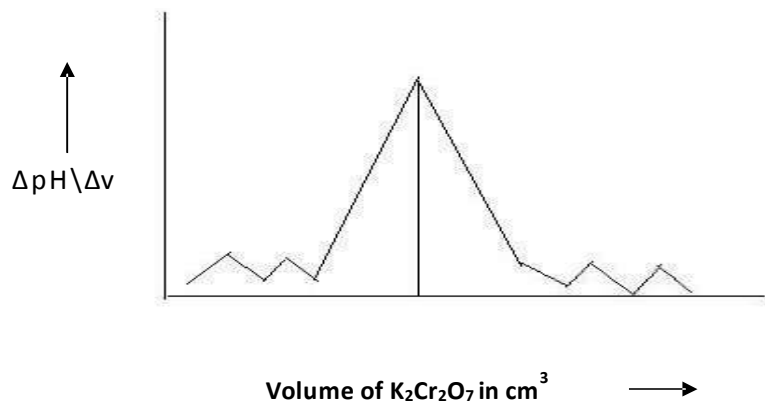
Conductometric titrations:-

1. Strong acid vs strong Base:-

Let us consider the titration of HCl v/s. NaOH which proceeds according to the neutralisation reaction,

NaOH + HCl $\longrightarrow$ NaCl + H2O

$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H2O$

When a solution of HCl is titrated with NaOH, the conductance of the solution gradually decreases due to the removal of H+ ions of highly ionised HCl to form unionised water (Highly mobile H+ ions are replaced by less mobile Na+ ions) . After the equivalence point, the conductance increases appreciably due to the added OH- ion.

(a) strong acid vs strong base
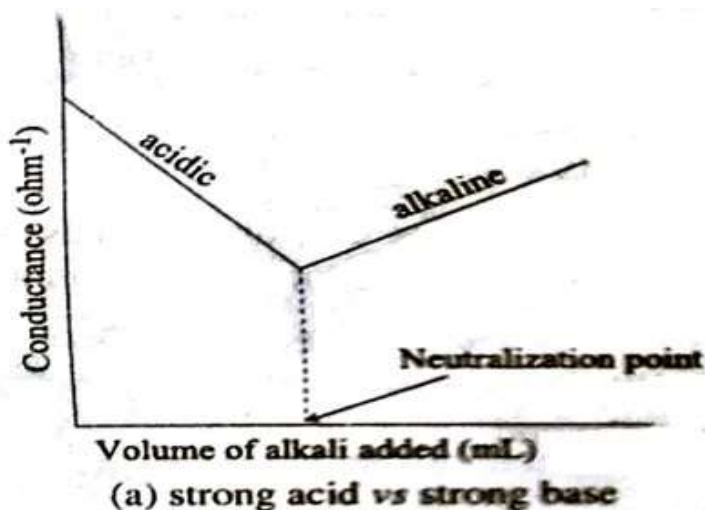
2. Weak acid v/s strong base

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 un-dissociated CH3COOH to CH3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH – ions.
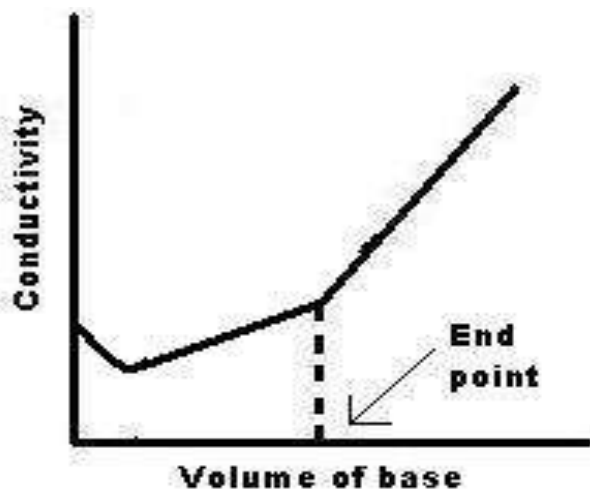
CH_3COOH **+** $NaOH$ $\longrightarrow$ CH_3COONa **+** H_2O

3. Mixture of Acid v/s Strong base or Weak Base.

Mixture of a Strong Acid and a Weak Acid vs. a Strong 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. Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH3COOH) vs. a strong base (NaOH) or a weak base (NH4OH)
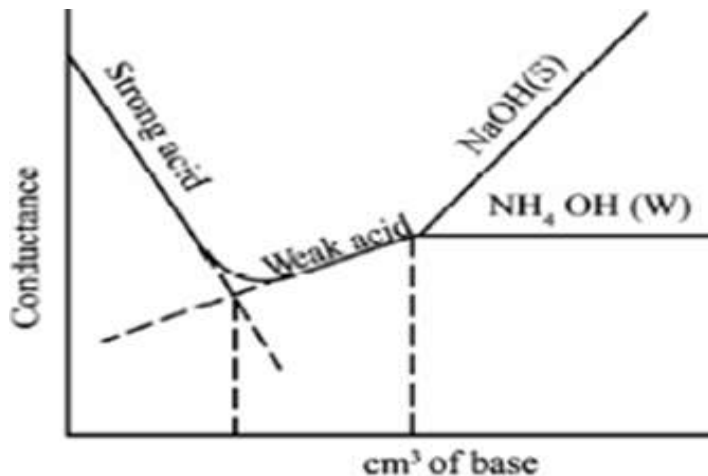
Atomic Absorption spectroscopy

Atomic absorption spectroscopy is the measurement of an absoption of optical radiation by atoms in the gaseous phase.

Principles:- An electrically heated surface is used to vapourise through aspiration of solution of the analyte sample into free atoms of a particular element in the atomic absorption spectroscopy. When a beam of light is passed through the free atoms in the analyte, the atoms will absorb in the visible and ultraviolet region resulting in changes in electronic structure (Excited state). Only a particular wavelength of light is absorbed by the electrons of the atom to go to excited state, which is a measure of the characteristics of the sample. The degree of absorption will vary with concentration of the analyte.
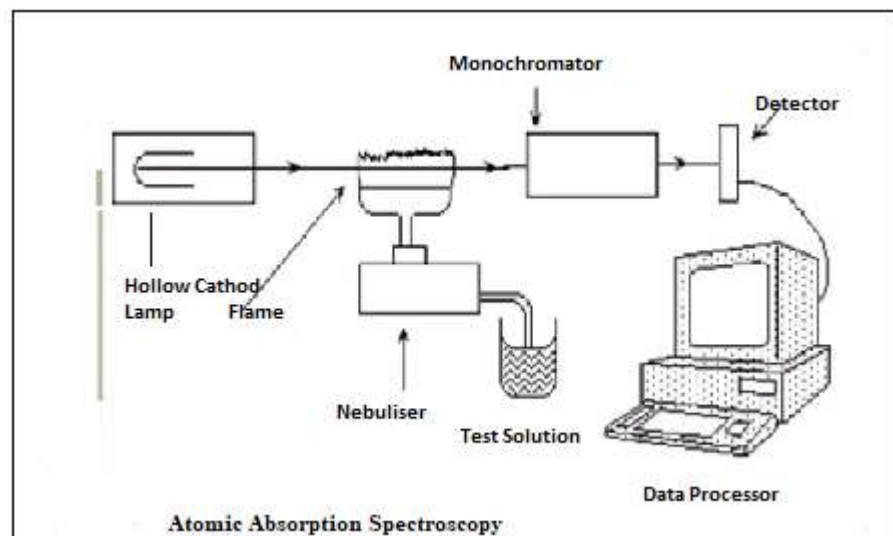
Atomic Absorption Spectroscopy

Instrumentation:-

1. **Light source**:- The light source emits the atomic spectrum of a particular element.
   To detect a particular element specific lamps are used in each case.
   The hollow cathode lamp (HCL) or electrodeless lamps (EDL) are widely used.

2. **Sample cell**:- An atomic sample vapour is generated in the sample in the light beam from the cell by introducing the sample into a burner system(Flame AAS) or electrically heated furnace or platform aligned in the optical path of the spectrophotometer

3. **Nebuliser**:- Suck up liquid sample at controlled rate
   Creates a fine aerosol spray for the introduction of into flame
   Mix the Aerosol, Fuel and Oxidant thoroughly for introduction
   Into flame

4. **Specific light Measurement**:- It includes several components
   a) A monochromator to disperse several wavelength of light that are emitted from the light source to isolate a particular line of interest
   b) A detector to produce an electric current that is dependent on the light intensity. This electrical current is amplified and processed by the instrumental electronics to produce a signal which is a measure of light attenuation occurring in the sample cell
   c) The signal is processed to generate an instrument readout in concentration units

Applications:-

1. This is the most widely used technique for the quantitative determination of metals at trace level which present in various material.

Disadvantages:-

1. The sample must be in solution at least volatile.

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Nano Technology

Definition: Nano materials can b defined as those materials, whose characteristics length scale lies within the nano range (1-100nm).

OR

A nano materials refers to a materials with at least one of its dimension in nano scale (ie 10^{-9}m)

Size defendent properties of Nanomaterials

1. **Surface Area:-** If a bulk material is sub divided into individual nano materials, the total surface area greatly increased. This will make materials more chemically reactive in some cases materials that are inert in bulk form are more reactive when converted into nano scale and affect their properties like Catallytic activity, gas adsorption chemical reactivity significantly.

   Ex. Bulk gold is catalytically inactive. But Gold nano particles are catalytically very active for selective redox reaction.

2. **Electrical properties:-** The electronic bands in bulk materials are continuous due to overlapping of orbitals of billions of atoms. But, in the nano size materials, very few atoms or molecules are present so the electronics bands becomes separate. And the separation between different electronic state varies with size of nano materials.
   Hence, some metals which are good conductors in bulk becomes semiconductors and insulators as their size is decreased to nano scale.

3. **Optical properties:-** The descrete electronic states of nano materials allows absoption and emission of light of specific wavelength. Hence nano materials exhibit unique colours different from bulk materials
   Colour of few colloidal solution is due to the scattering of radiation by nano particles of different size.

4. **Magnetic Properties:-** Magnetic properties of nano structured materials are different from that of bulk materials. The large surface to volume ratio results in a substantial proportion

of atoms having different magnetic coupling with neighboring atoms leading to different magnetic properties

> **EX.** Bulk gold and Platinum are non magnetic but at the nano size they act as magnetic particals.

5. **Mechanical Properties:-** Mechanical properties like tensile strength, malleability of nano materials are stronger than bulk materials.
   Ex. Copper nano particles smaller than 50nm are considered as super hard materials that do not exhibit the same malleability and ductility as bulk copper.

Synthesis of Nano materials

There are many techniques available to synthesise nano materials which can be generally grouped into top-down and bottom-up approach.

In top-down approaches, bigger materials are broken down into small nano size materials by means of various physical methods, they are sputtering, pulsed laser deposition, laser ablation, electric arc method ion beam implantation etc.

Top down

i. Bigger materials broken down into small nano materials using various physical methods

ii. Require expensive apparatus

iii. uncontrolled with respect to composition, size, microstructure and aspect ratio of nano materials

iv. Cause crystallographic damage, surface defects, internal stress

In bottom-up approach desired nano materials is built from the bottom; by orderly assemble of of growth species like atoms or ions or molecules. These are simple chemical methods.

Bottom up

i. Small materials are assembled to build desired nano materials

ii.   Simple, versatile and economically viable

iii. Better control over chemical composition, size, microstructure and aspect ratio of nano materials

iv.   Nano structures with less defect and purity can be synthesized

Top-Down   Bottom-Up

Bulk Material   Powdered Material   Nanoparticles   Clusters   Atoms
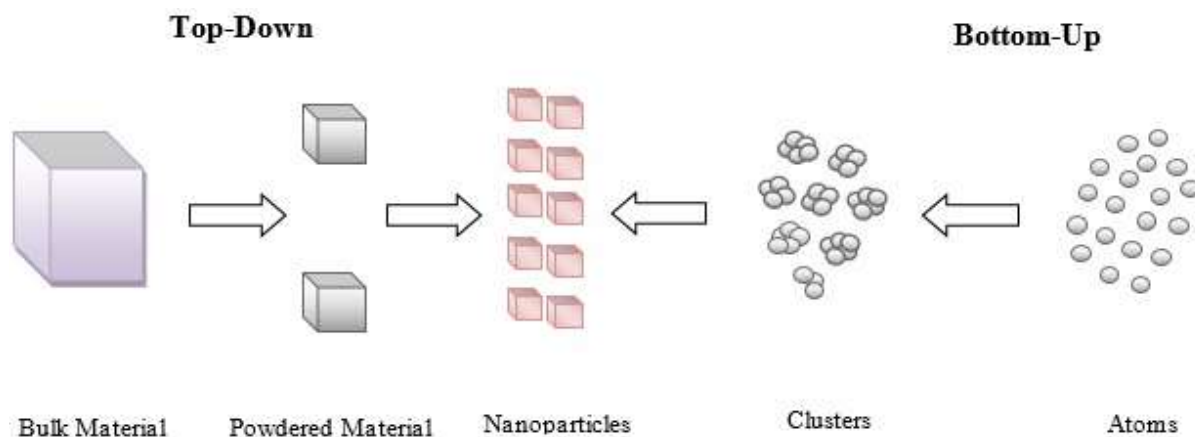
Synthesis of nano materials by

1.   Sol-gel process
2.   Gas condensation process
3.   Chemical vapour condensation method
4.   Precipitation method

1. SOL-GEL PROCESS

In sol-gel synthesis, either a metal salt or metal alkoxide is used as precursor

✓ First Sol is prepared by dispersing precursors in solvent
(in alcohol or water) in acid or basic conditions.

$$MOR + H_2O \longrightarrow MOH + ROH \quad \text{(Hydrolysis)}$$
                                    Sol
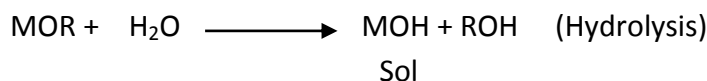
✓   Conversion of sol to gel: Sol is further converted in to gel by poly condensation results in the formation of oxide bridge network is called gel

$$MOH + ROH \longrightarrow M\text{-}O\text{-}M + R\text{-}OH \quad \text{(Condensation)}$$

- ✓ Aging of the gel: Gel on aging for a known period of time, finally condenses to to nanoscale clusters of metal hydroxides.
- ✓ Drying of gel; If the solvent is removed by thermal evoparation, resulting product is termed as Xerogel. If the solvent is extracted under super critical conditions, the product is an Aerogel.
- ✓ Calcination; The sample thus obtained is thus heat treated at higher temperature to obtain nano particles.
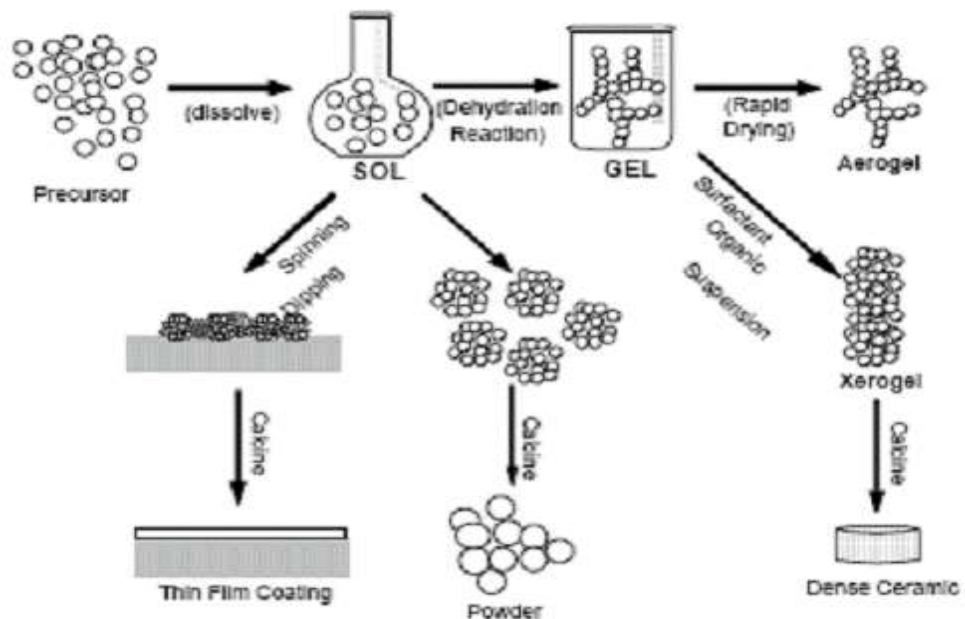
Advantages

- ✓ Nano materials of high purity with good homogeneity can be   obtained
- ✓ Easy to control the size and shape of nano materials
- ✓ Simple and inexpensive equipment

2. Precipitation Method

Step 1:- In this techniques the precursors (inorganic metal salts such as nitrates, chlorides or acetates) is dissolved in water

Step 2:- metal cations exists in the form of hydrated species, for example $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$etc.

**Step 3**:- The metal hydrated species are added to precipitating agent like $NaOH$ or NH_4OH, it causes condensation of metal hydrated species

Step 4:- Thus concentration of solution increases and reaches a critical level called super saturation. At this concentration nucleation formation is initiated. Thus nucleus further grows into particles, which gets precipitated.

Step 5:- The precipitate is filtrated, washed with water and finally calcined at high temperature to get crystalline metal oxide.

3. Chemical vapour Deposition (CVD)

By CVD method is possible to produce almost any metals and non metallic materials , also oxides, carbides , hydrides of metals

Chemical vapour deposition
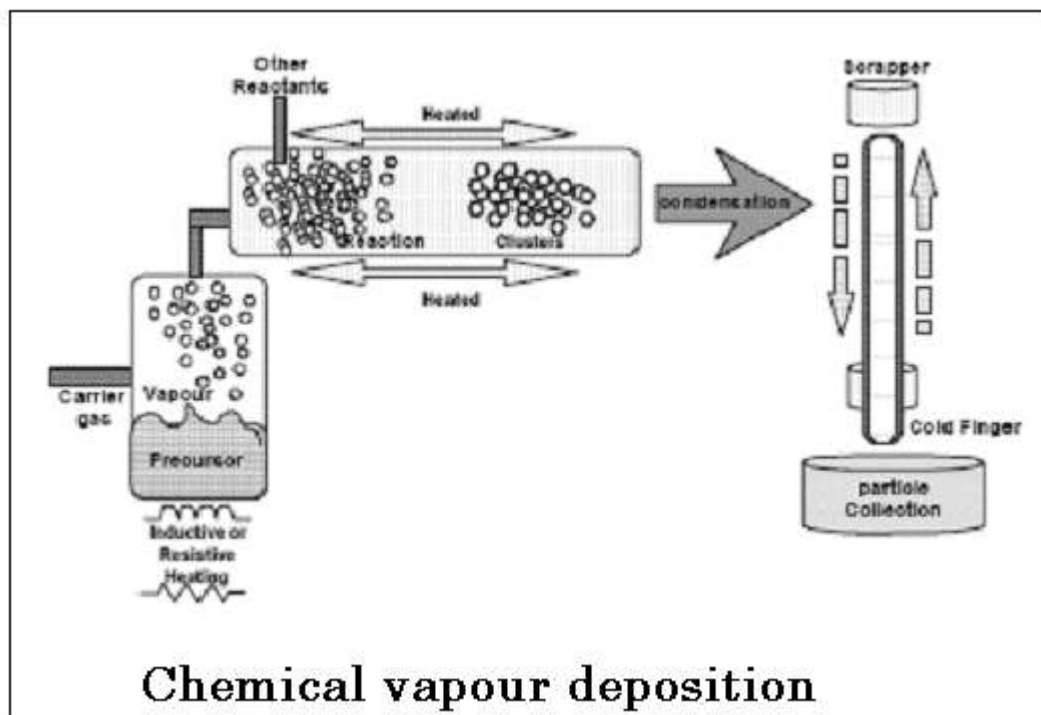
➢ Nano particles synthesised from the gaseous phase by a chemical or decomposition of precursors at high temperature.

➢ In this method the precursors are vaporised and mixed with an inert carrier gas like N_2 and the mixture is fed into the reactor.

➢ The precursors undergo reaction, producing a product which is condensed and deposited on the cold finger (Liquid nitrogen), which can collected using scrapper.

Nano scale materials

1. Carbon nanotubes (CNTs)

Carbon nanotubes are allotropes of graphitic carbon with a cylindrical structure And diameter less than 100nm and length can go up to few microns. CNTs are cylindrical tubes with a central hollow core, formed by rolling up of graphite sheets.

There are two types of CNTs. They are

1. Single walled carbon nanotubes (SWCNTs):- They are formed by rolling up of single graphite layer. Diameter of SWCNTs is 1-4nm and length can go upto few micrometers.

2. Multi walled carbon nanotubes (MWCNTs):- They consists of two or more concentric graphene cylinders with van der waals forces between adjacent tubes. Diameter of MWCNTs varies from 30-50nm, length can go up to few micrometers.
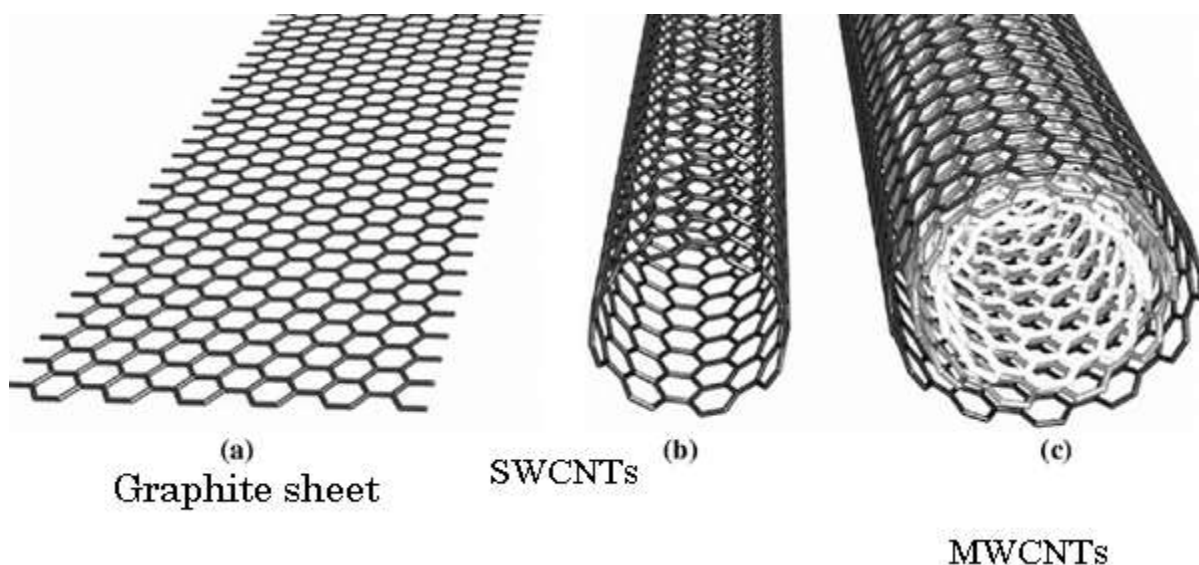
(a) Graphite sheet   (b) SWCNTs   (c) MWCNTs

Properties:

- ✓ CNTs are about 20 times stronger and 6 times lighter than steel
- ✓ CNTs as hard as Diamond and thermal capacity is twice that of pure diamond
- ✓ CNTs have high tensile strength
- ✓ It is thermally stable to upto 4000K
- ✓ CNTs have high electrical conductivity.

Applications:-

- ✓ They are used as electrode materials in Li-ion rechargeable batteries
- ✓ CNTs finds applications in nano electronics and optics
- ✓ SWCNTs are used in cancer thermotheraphy to selectively kill cancer cells without harming healthy tissues.
- ✓ Electricals cables are fabricated with CNTs as they posses excellent electrical conductivity and thermal resistance.

2.Fullerenes

Fullerenes are allotropic forms of carbon. made of only carbon atoms having closed cage structure. Many number of molecules with different carbon atoms like C60, C70, C74, C76, C78 etc have been prepared and investigated. But the most common is the C60 fullerene called Buckminster fullerene (Richard Buckminster fuller built geodesic dome with spherical shape) or Bucky ball.

Structure

- Fullerenes consists of fused Penatagons and Hexagons.
- C60 fullerene consists of 12 pentagons and 20 hexagones, 90 edges and 60 vertices
- All 60 carbon atoms are located at the vertices of a truncated icosohedron .
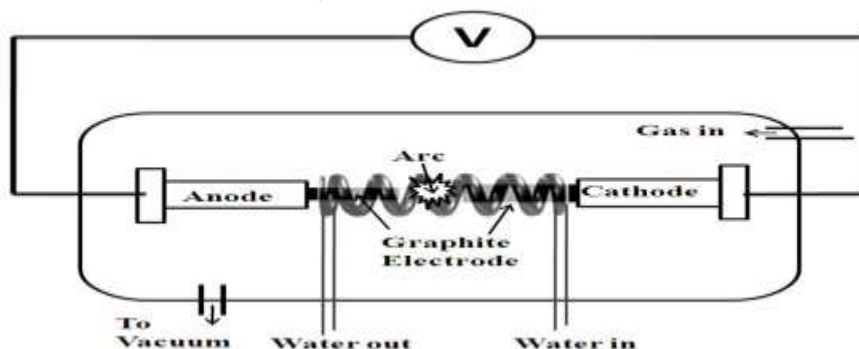- All carbon atoms are sp2 hybridised and trigonally bonded.
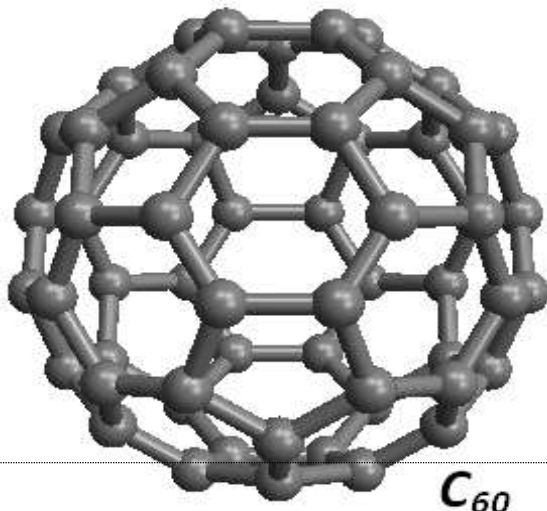
C_{60}

Synthesis

Fullerenes are best produced by creating an electric arc between carbon or graphite electrodes in an inert gas atmosphere. Electric arc liberates a black powder in the form of a soot. 10% of the soot is made up of C_{60} this is extracted by salvation in a small amount of toluene.

Properties

➤ It is a black powder.
➤ It has density 1.65 gcm^{-3}, sublimes at 800K
➤ Refractive index 2.2 at 600nm
➤ Resistivity 1014ohm/m
➤ It can be dissolved in common solvents at room temperature for example trichloro benzene, CS_2 and benzene.

Application: Used in
✓ Super conductor

- ✓ Microelectronic device
- ✓ Nonlinear optic device
- ✓ It is catalytically active for few organic reactions like hydrocarbon coupling, hydrogenation and dehydrogenations.

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