

Electrochemistry and Energy Storage Device (2018- Scheme)

Electrochemistry

Electrochemistry is a branch of chemistry which deals with the transformation of chemical energy into electrical energy or vice versa.

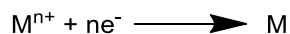
Electrolyte: Substances which are capable of conducting electricity either in molten state or in aqueous state are known as electrolyte. **Example:** acid, base etc.

Electrolysis: The process of decomposition of an electrolyte by the passage of electric current is known as electrolysis.

Oxidation is a process, which involves loss of electrons by a substance.



Reduction is a process, which involves gain of electrons by a substance.

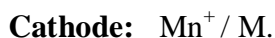


Redox reaction: Reaction which involves both oxidation and reduction process are called Redox reaction.

Electrochemical cell is a device which converts chemical energy into electrical energy or vice-versa by redox reaction. Electrochemical cell are classified into two types

- 1. Galvanic or voltaic cells:** In galvanic cell the free energy change (chemical energy) of electrode redox reaction are converted into electrical energy.
- 2. Electrolytic cell:** It is a device in which electrical energy from an external source can be used to bring about chemical reactions.

Single Electrode or half cell: When a metal rod is dipped in a solution containing its own ions, equilibrium is established at the interface between metal atom and its solution (ions). This arrangement is called as single electrode or half-cell. It is represented as:



Anode: Electrode where oxidation reaction takes place is called Anode.

Cathode: Electrode where reduction reaction takes place is called cathode.

Electrode potential is defined as the potential developed at the interface between the metal and the solution, when it is in contact with a solution of its ions.

OR

Electrode potential is a measure of tendency of a metal to lose or gain electrons, when it is in contact with a solution containing its own ions.

The tendency of a metal to lose electrons is called as **oxidation potential** and the tendency of a metal to gain electrons is called **reduction potential**.

Oxidation potential = - Reduction potential.

Standard electrode potential (E°): Standard electrode potential is defined as potential difference that exists at the interface when a metal is in contact with its own ions at 298K and 1 atm pressure, where in the active concentration of the ion is exactly unity or 1 mole per liter.

Electrochemistry and Energy Storage Device (2018- Scheme)

Example: Standard electrode potential of Zn ($E^\circ_{\text{Zn}} = -0.76 \text{ V}$)
Standard electrode potential of Cu ($E^\circ_{\text{Cu}} = +0.34 \text{ V}$)

Standard oxidation potential of an electrode is equal to the standard reduction potential of same electrode but with opposite sign.

Free Energy

Free energy is a thermodynamic quantity equivalent to the capacity of a system to do work. The change in the free energy is the maximum amount of work that a thermodynamic system can perform in a process at constant temperature, and its sign indicates whether a process is thermodynamically favorable or forbidden.

Entropy

Entropy is a thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system. Entropy denoted by S.

Cell Potential

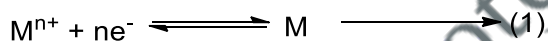
The cell potential is the way in which we can measure how much voltage exists between the two half cells of a battery.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}} \quad \text{and} \quad E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{Anode}}$$

Electrochemical series: The arrangement of elements in the increasing order of their standard reduction potential is referred as electrochemical series.

Nernst's Equation

Consider a general redox reaction of the type



Equilibrium constant, K_c for the above reaction is,

$$K_c = \frac{[\text{M}]}{[\text{M}^{n+}]}$$

According to thermodynamics, for a reversible process, equilibrium constant K_c is related to change in free energy ΔG as,

$$\Delta G = \Delta G^\circ + RT \ln K_c \quad \text{---} \rightarrow (2)$$

Where ΔG° is the standard free energy change and is measured at unit concentration of reactants and products, R = Gas constant, T = absolute temperature, K_c = Equilibrium constant. The decrease in free energy for any reversible process is equal to the maximum work (W_{max}) done by the system.

That is,

$$-\Delta G = W_{\text{max}}$$

In case of galvanic cell,

$$W_{\text{max}} = \text{Electrical energy supplied by the cell}$$

$$W_{\text{max}} = nFE$$

Hence,

$$-\Delta G = nFE \quad \text{---} \rightarrow (3)$$

Under standard conditions,

$$-\Delta G^\circ = nFE^\circ \quad \text{---} \rightarrow (4)$$

Electrochemistry and Energy Storage Device (2018- Scheme)

Substituting equation (3) and (4) in equation (2), we get

$$-nFE = -nFE^0 + RT \ln K_c$$

Divide throughout by $-nF$ and Substituting the value of K_c

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

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

Where, E = Electrode potential

E^0 = Standard Electrode potential

n = no of electrons involved in reaction

F = Faraday constant = 96500 C

In case of metal – metal ion electrode, as M is solid metal, $[M] = 1$,

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

Changing \ln to \log , we get Nernst equation at any temperature

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

This Expression is known as Nernst equation.

Substituting the values of $R = 8.314 \text{ J/K/mol}$, $T = 298 \text{ K}$ and $F = 96500 \text{ C}$, We get

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

This is the reduced form of Nernst equation for single electrode potential at 298 K.

Reference electrodes

The electrode with a known potential used to determine the potential of other electrode is called as reference electrodes. Reference electrodes are classified as primary reference electrode and secondary reference electrode.

Primary reference electrode

Standard hydrogen electrode (SHE) is considered as primary reference electrode as the electrode potentials of other electrodes are assigned with respect to it and its electrode potential at all temperature is taken as zero.

Secondary reference electrode

An electrode whose potential is measured with respect to SHE and then can be used as reference electrode for measuring potentials of other electrodes is referred to as **Secondary reference electrode**.

Electrochemistry and Energy Storage Device (2018- Scheme)

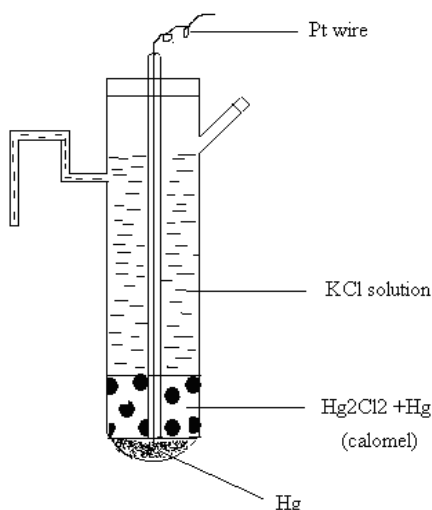
Two such electrodes which are in common use are

1. Calomel Electrode
2. Silver-Silver chloride electrode.

Calomel electrode (CE)

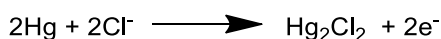
The calomel electrode consists of a glass tube in which liquid mercury is placed at the bottom. It is covered by a paste of Hg and Hg₂Cl₂ (mercurous chloride) called as calomel which is further in contact with a saturated or normal or decinormal potassium chloride solution. A platinum wire sealed in a glass tube is dipped into mercury and used to provide the external electrical contact.

The calomel electrode is represented as, Pt, Hg_(l) | Hg₂Cl₂(s) | KCl

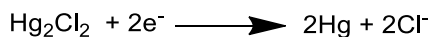


Depending upon the nature of the other electrode of the cell, the calomel electrode can act as anode or cathode.

When it acts as anode the electrode reaction is



When it acts as cathode, the electrode reaction is



Nernst equation for calomel electrode is,

$$E_{\text{CE}} = E_{\text{CE}}^0 - \frac{2.303 RT}{nF} \log [\text{Cl}^-]^2$$

The electrode potential depends on the concentration of the chloride ions. At 298K, the electrode potentials are as follows

Electrochemistry and Energy Storage Device (2018- Scheme)

Name	Decinormal CE	Normal CE	Saturated CE
Concentration of KCl	0.1 N	1.0 N	Saturated
Potential of CE in V	0.333	0.281	0.242

Uses

- It is used for the measurement of single electrode potential.
- It is used as reference electrode in all potential determination.

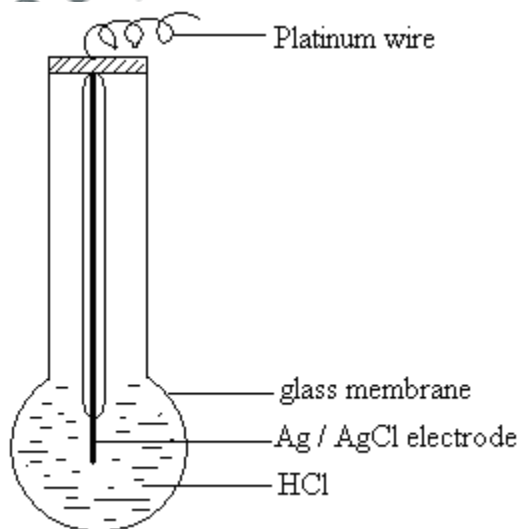
Advantages of calomel electrode

1. It is simple to construct.
2. The cell potential is reproducible and constant over a long period.
3. The cell potential does not vary with temperature.
4. Not poisoned by impurities.

Ion selective electrode

Ion selective electrode is the one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution. This electrode consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact. Therefore these electrodes are also referred as membrane electrode.

Glass electrode



Electrochemistry and Energy Storage Device (2018- Scheme)

The glass pH electrode is a long glass tube with glass membrane at the bottom. Glass membrane made up of corning glass with composition 72% SiO₂, 22% Na₂O, 6% CaO. Its thickness varies from 0.03 – 0.1 mm. The glass bulb is filled with solution of constant pH (0.1 M HCl), and is inserted with Ag-AgCl electrode, which is internal reference electrode and also serves for the external contact. The electrode is dipped in a solution containing H⁺ ions.

The glass electrode is represented as, Ag_(s) | AgCl_(s) | HCl_(0.1M) | Glass membrane

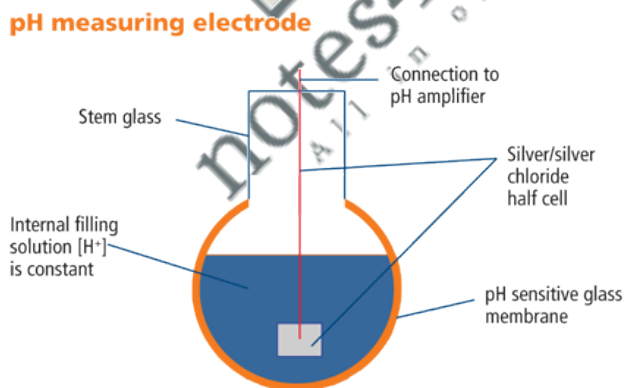
Working

Glass pH electrode, when dipped in a solution the membrane undergoes an ion exchange reaction.

The membrane undergoes an ion exchange reaction. The Na⁺ ions on the glass are exchanged for H⁺ ions.



The exchange of ions by the inner and outer membrane gives to a boundary potential (E_b). This boundary potential depends upon concentration of H⁺ ion in two solution (C₁ and C₂, where C₁= 0.1 M).



Therefore

$$E_b = E_2 - E_1$$

$$E_b = 0.0591 \log C_2/C_1 \quad (n=1 \text{ for } \text{H}^+ \text{ ions})$$

$$E_b = 0.0591 \log C_2 - 0.0591 \log C_1$$

Since the concentration of the inner solution is constant (C₁=0.1 M). The above equation becomes,

$$E_b = L + 0.0591 \log C_2 \quad (\text{where } L \text{ is constant, } C_1=0.1 \text{ M, \& } L = -0.0591 \log C_1)$$

$$E_b = L - 0.0591 \text{ pH} \quad (\text{pH} = -\log [\text{H}^+])$$

The potential of the glass electrode has three components

1. The boundary potential

Electrochemistry and Energy Storage Device (2018- Scheme)

2. The potential of internal Ag-AgCl reference electrode
3. Small asymmetry potential

$$E_G = E_b + E_{Ag/AgCl} + E_{asy}$$

$$E_G = L - 0.0591 \text{ pH} + E_{Ag/AgCl} + E_{asy}$$

$$E_G = L^1 - 0.0591 \text{ pH}$$

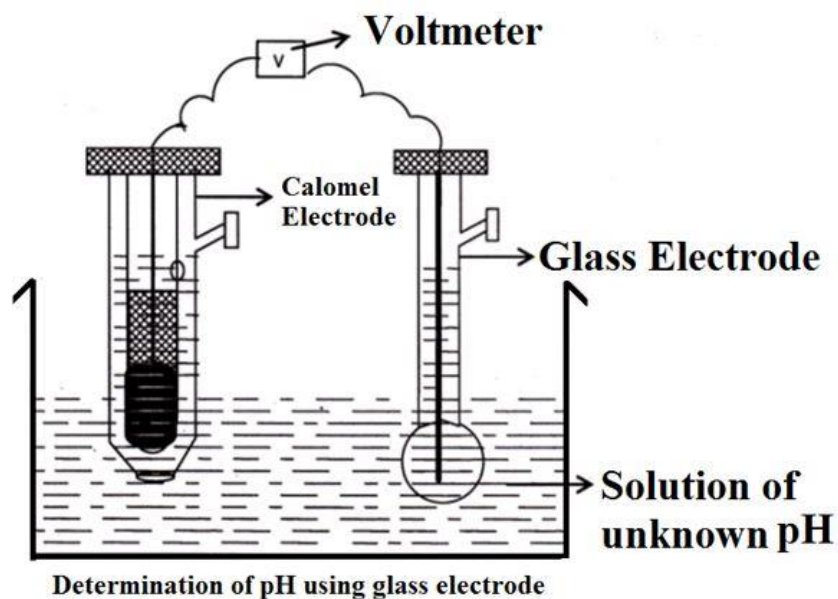
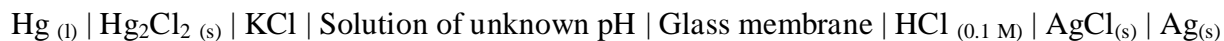
$$\text{(Where } L^1 = L + E_{Ag/AgCl} + E_{asy}\text{)}$$

$$E_G = L^1 - 0.0591 \text{ pH}$$

Determination of pH using glass electrode

To determine the pH of a given solution the glass electrode is dipped in a solution whose pH need to be determined. It is combined with a saturated calomel electrode which is a reference electrode.

The cell is represented as



The emf of the so formed cell is determined potentiometrically.

$$E_{\text{cell}} = E_G - E_{\text{CE}}$$

$$E_{\text{cell}} = L^1 - 0.0591 \text{ pH} - E_{\text{CE}}$$

$$0.0591 \text{ pH} = L^1 - E_{\text{CE}} - E_{\text{cell}}$$

$$\text{pH} = \frac{L^1 - E_{\text{CE}} - E_{\text{cell}}}{0.0591}$$

Electrochemistry and Energy Storage Device (2018- Scheme)

Advantages of glass electrode

1. It is portable and compact.
2. Even in very dilute solutions, it gives accurate results.
3. The electrode can be used in the presence of oxidizing & reducing substances & metal ions.
4. It is not poisoned easily.
5. It is simple to operate. It can be used in portable instruments and therefore extensively used in chemical, industrial, agricultural and biological laboratories.

Limitations of glass electrode

1. The electrode can be used up to a pH of 13. But becomes sensitive to Na^+ ions above pH of 9 resulting in an alkaline error. (because relationship between pH and glass electrode potential will be slightly altered beyond a pH 9)
2. It does not function properly in pure alcohol and some organic solvents.
3. Because of the high resistance of glass, simple potentiometers cannot be used. It requires sensitive electronic potentiometers for emf measurement.

Concentration cell

A concentration cell is an electrochemical device in which electrode and electrolyte present in both half cells are same but the concentration of metal or electrolyte is different.

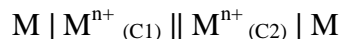
There are two types of concentration cells depending on whether the difference is in concentration of metal or concentration of metal ion solution.

1. Electrolyte concentration cells
2. Electrode concentration cells

Electrolyte concentration cells

Electrolyte concentration cell is a galvanic cell in which electrode and electrolyte present in both half cells are same but the concentration of electrolyte is different.

Example: Consider a concentration cell consisting of two metal rod dipped in its own ionic solution of different concentration C_1 and C_2 . If $C_2 > C_1$ then it is represented as



Emf of the cell is given by, $E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$

$$E_{\text{cell}} = \left(E^{\circ} + \frac{0.0591}{n} \log[C_2] \right) - \left(E^{\circ} + \frac{0.0591}{n} \log[C_1] \right)$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1} \quad (\text{Where, } C_2 > C_1)$$

Hence by knowing the concentration of the electrolyte the EMF of the cell can be determined.

Batteries

Cell is a device which converts chemical energy into electrical energy. A cell forms a single unit and generates less energy. Higher voltage can be achieved by coupling number of cells.

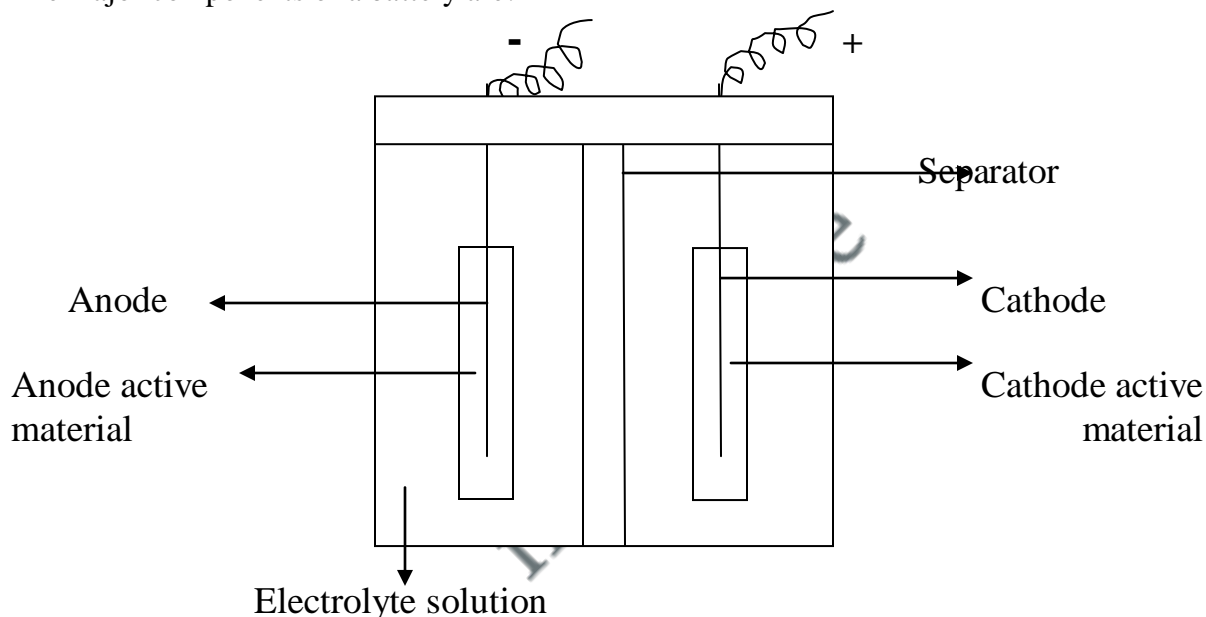
Battery can store Chemical energy in the form of active material and on demand convert it into electrical energy through electrochemical redox reaction.

Definition: A Battery is a device that consists of two or more galvanic cells connected in series or parallel or both, which converts chemical energy into electrical energy through redox reactions.

Components of the batteries:

Basic electrochemical unit in a battery is a galvanic cell. A galvanic cell is a device that generates electrical energy at the expense of decrease of free energy of electrode reaction of a cell.

The major components of a battery are:



(1)Anode or negative electrode: It releases electrons to the external circuit by undergoing oxidation.

(2)Cathode or positive electrode: It accepts electrons from the external circuit and the active material undergo reduction reaction.

(3)Electrolyte: A solution of an acid, alkali or salt having higher ionic conductivity is commonly used as electrolyte. Electrolyte provides medium for transfer of ions between the anode and cathode.

(4)Separator: The material used to separate anode and cathode in a battery to prevent internal short circuiting. It is permeable to the electrolyte and maintains the desired ionic conductivity.

Example: cellulose, vinyl polymers, cellophane etc.

Classification of batteries: Batteries are classified as

1. Primary batteries
2. Secondary batteries
3. Reserve batteries

Electrochemistry and Energy Storage Device (2018- Scheme)

1. Primary batteries: Batteries in which chemical energy is converted into electrical energy. In this type of batteries the cell reaction are not reversible. They are not rechargeable and once discharged they have no further electrical use.

Example: Zn-MnO₂ Battery, Li-MnO₂ batteries, etc.

2. Secondary batteries: In secondary batteries the cell reactions are reversible. They are also called as storage batteries. The discharged cell can be recharged by passing current through it in the direction opposite to that of discharge current. Example: Lead storage batteries, Nickel – Cadmium battery, etc.

During discharge chemical energy is converted into electrical energy and during charging electrical energy is converted into chemical energy.

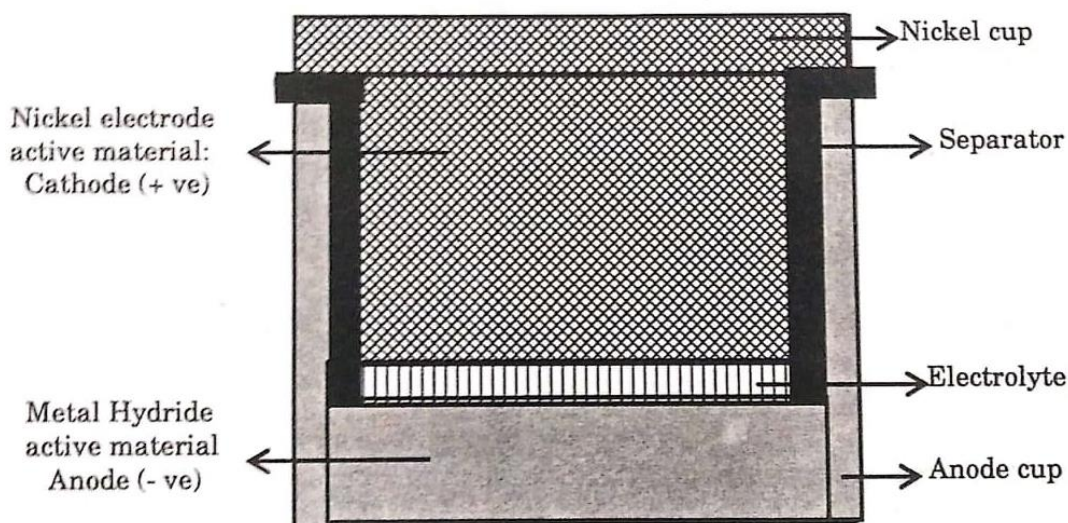
3. Reserve batteries: One of the components in the reserve batteries is stored separately and is incorporated into the battery when required. Usually electrolyte is stored separately. The advantages of reserve batteries are long shelf life and high performance reliability.

These batteries are used to deliver high power for relatively short period of time in weapons system like missiles.

Example: Mg-AgCl and Mg-CuCl batteries; both can be activate whenever required just by adding water, Zn-Ag₂O batteries, etc.

Nickel - Metal Hydride (Ni-MH) battery

It is alkaline rechargeable battery

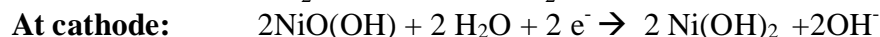
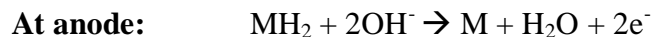


Nickel metal hydride consists of

- **Anode:** Porous nickel grid pasted with hydrides of metals like VH₂, ZrH₂ and TiH₂ with hydrogen storage metal alloy such as TiNi₂ or LaNi₅.
- **Cathode:** Porous nickel grid pasted with nickel oxy hydroxide (NiO(OH)) and Ni(OH)₂
- **Electrolyte:** Aqueous solution of KOH (28%)
- **Separator:** Anode and cathode are separated by polypropylene which acts as a medium for absorbing electrolyte and insulator between two electrodes.
- **Voltage:** 1.3V
- **Cell representation:** MH₂, M / KOH (28%) /, NiO(OH), Ni(OH)₂

Electrochemistry and Energy Storage Device (2018- Scheme)

Reactions:



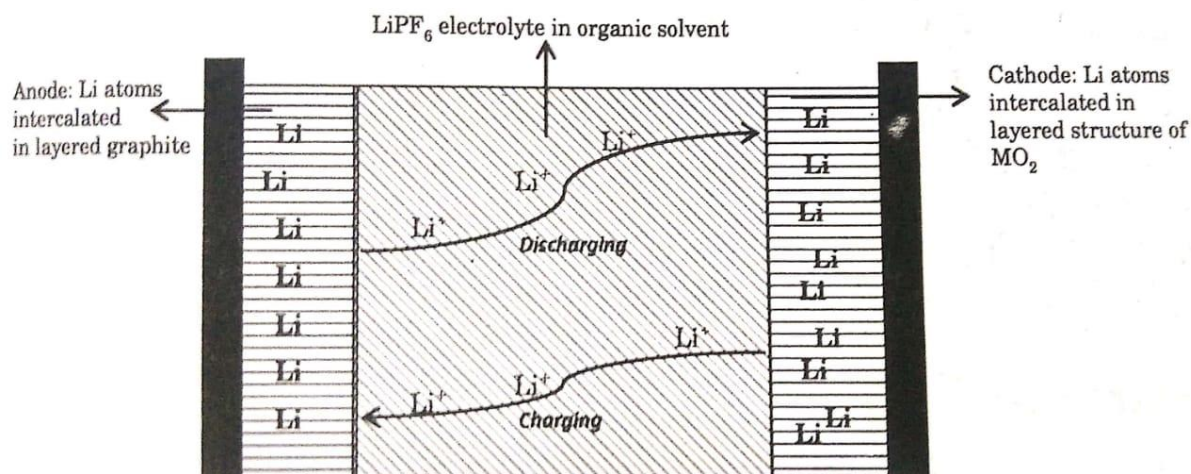
During charging cell reactions will be reversed. The potential of the cell is 1.3 V having high capacity, long life and rapid recharge capacity

Applications

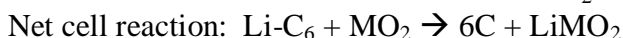
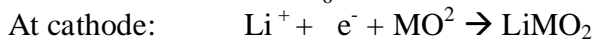
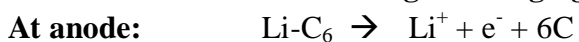
- In consumer electronic devices such as cellular phones, computers etc.
- In electric vehicles and space crafts.

Lithium ion battery

Rechargeable, Lithium ion batteries possesses many advantages over traditional batteries such as lead acid and Ni-Cd batteries. They include high voltage, high energy density (240 Whr/kg), high cycle life and very low self-discharge when not in use. It provides maximum voltage of 3.7V



- **Anode:** Graphite carbon.
- **Cathode:** Lithium-metal oxide (Li-MO₂), where M is Co or Mn.
- **Electrolyte:** LiPF₆ (Lithium hexafluorophosphate) in a mixture of organic solvent like ethylene carbonate and dimethyl carbonate.
- **Separator:** Microporous polyethylene or polypropylene
- **Voltage:** 3.6V
- **Cell representation:** $\text{Li} \mid \text{Li}^+, \text{C} \mid \text{LiPF}_6 \text{ in ethylene carbonate} \mid \text{Li-MO}_2$
- **Electrode reaction during discharging**



During charging cell reactions will be reversed.

Electrochemistry and Energy Storage Device (2018- Scheme)

Advantages

1. High energy density
2. Long life
3. High cell voltage
4. Low self-discharge
5. Wide range of operating temperature

Uses

1. In cell phones, laptops and also in defense, electrical vehicles, power tools and aerospace applications,
2. Portable LCD TV
3. Portable CD player etc.



Corrosion is defined as **“the destruction or deterioration of metals or alloys by the surrounding environment through chemical or electrochemical changes.**

The familiar examples of corrosion are

- i. Rusting of iron – A reddish brown scale formation on iron and steel objects. It is due to the formation of hydrated ferric oxide.
- ii. Green scales formed on copper vessels. It is due to the formation of basic cupric carbonate $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$.

The metals undergo corrosion due to the oxidation by losing electron and the resulting product is called as rust, which mainly contains oxides, sulphates, carbonates and bicarbonates of the metals. Due to corrosion, metals lose their valuable properties such as conductivity, strength, shining, malleability, ductility etc.

Cause for corrosion: Each metal tries to get original state such as ore form (oxides, sulphates, carbonates and bicarbonates of the metals) which are more stable and low energetic. Therefore corrosion is the reverse process of metallurgy.

Classification of corrosion

Chemical corrosion (Dry corrosion)

Chemical corrosion occurs due to the direct chemical reaction between the metal and the gases present in the corrosion environment. This type of corrosion is generally observed in the absence of moisture. Therefore it is also known as dry corrosion.

Example: Oxidation of metals or alloys on exposure to oxygen in air.

Electrochemical corrosion (Wet corrosion)

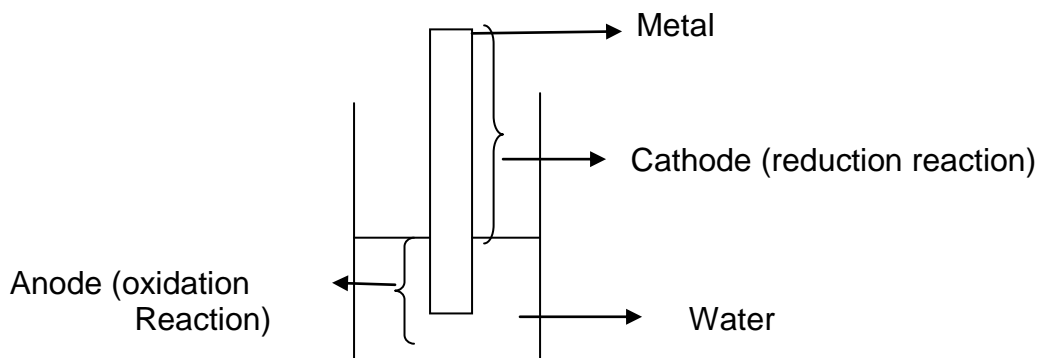
Electrochemical corrosion involves reactions in aqueous medium and moist-air. The conducting surface of the metal undergoes an electrochemical reaction with the moisture and oxygen present in the atmosphere. This process can be explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion

Electrochemical theory of corrosion explains the corrosion on the basis of galvanic cell formation. According to this theory, corrosion of metal takes place due to the formation of anodic and cathodic region on the same metal surface or when two different metals are in contact with each other in the presence of a conducting medium. At anodic region metal undergo oxidation by losing its valance electron and gets corroded. While at cathodic region reduction reaction takes place. Thus cathodic region is unaffected by the cathodic reaction.

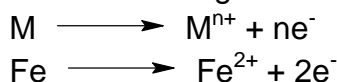
The electrons liberated at the anodic region migrate to the cathodic region constituting corrosion current. The metal ions liberated at the anode and the anions formed at the cathode diffuse towards each other through the conducting medium and forms a corrosion product.

When a part of the metal is dipped in an aqueous solution, the part which is exposed to lower concentration of air (or oxygen) acts as anode, while the part which is exposed to higher concentration of air (or oxygen) acts as cathode. (Because oxygen as greater tendency to absorb electrons)



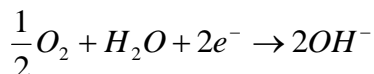
Corrosion reaction

At **anode** region metal undergo oxidation liberating electron.

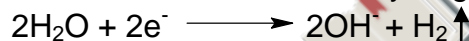


Cathodic reaction depends on the nature of the corrosion environment.

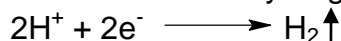
- a) If the surrounding environment is aerated and almost neutral, oxygen and water are reduced to OH^{-} ions.



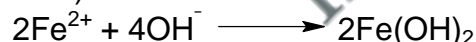
- b) If the surrounding environment is de-aerated and almost neutral the cathodic reaction involves the liberation of hydrogen gas and hydroxyl ions.



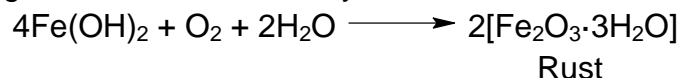
- c) If the surrounding environment is deaerated and acidic the cathodic reaction involves the evolution of hydrogen gas.



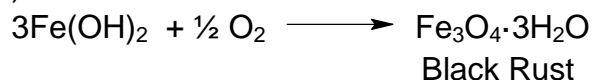
Corrosion of iron produces Fe^{2+} ions and OH^{-} ions at the anodic and cathodic region respectively. These ions diffuse towards each other forming insoluble product $Fe(OH)_2$ (ferrous hydroxide)



In an oxidizing environment ferrous hydroxide is oxidized to ferric oxide.



In the presence of limited oxygen, ferrous hydroxide is converted into magnetic oxide of iron (Fe_3O_4) and is known as black rust.



Note: 1

- (i) The cathodic and anodic process occurs at the same rate.
- (ii) The formation of galvanic cells on the metal surface is due to the following reasons.
 - (a) Contact with other metal
 - (b) Difference in the concentration of air or oxygen.
 - (c) Stress and strain on the material.
 - (d) Precipitation at the grain boundaries.

Note: 2

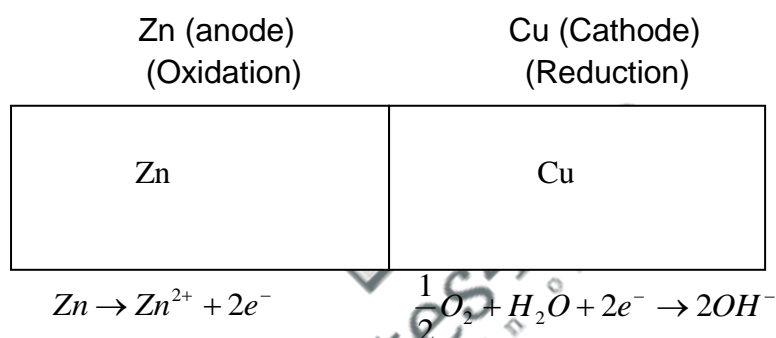
An arrangement of metals in the order of their corrosion resistance in the given environment is referred to as galvanic series.

Types of Corrosion

Differential metal Corrosion or Galvanic Corrosion:

When two dissimilar metals are in contact with each other in a corrosion conducting medium, the metal with lower electrode potential becomes anodic and undergoes corrosion, whereas, the metal with higher electrode potential becomes cathodic and remains unaffected. This kind of corrosion is called as **differential metal corrosion**. The rate of corrosion depends on the difference in electrode potential. Higher the difference faster is the rate of corrosion

Example: When Zinc is in contact with Copper, Zinc metal being placed higher up in the electrochemical series acts as anodic and gets corroded, whereas Copper metal which is placed below Zn in electrochemical series is protected from corrosion.



This type of corrosion can be observed in the following

- (i) Steel pipe connected to copper plumbing
- (ii) Lead antimony solder around copper wires

Differential aeration corrosion

Differential aeration corrosion occurs when one part of the metal is exposed to lower concentration of air when compared to other part. When a metal is exposed to different concentration of air (O₂), part of the metal exposed to lower concentration of O₂ will having lower potential becomes anodic and undergoes corrosion. Other part of the metal which is exposed to higher concentration of O₂ becomes cathodic and remains unaffected. Thus a differential aeration of metal causes a flow of current called as differential current.

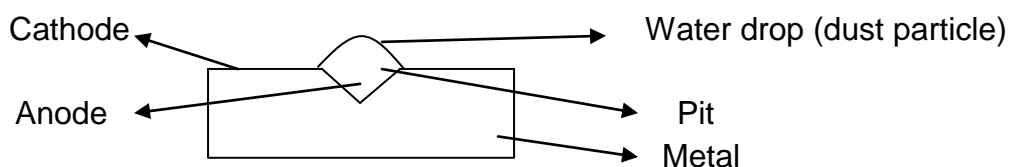
Example: When an iron rod is partially immersed in water, the part exposed to atmosphere is more oxygenated and forms cathode and the part immersed in water which is less oxygenated forms anode.

There are two types of differential aeration corrosion.

- i. Pitting corrosion
- ii. Water line corrosion

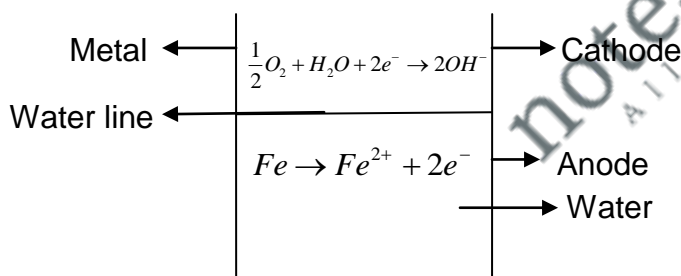
i. Pitting corrosion

Pitting corrosion results when small particle of dust particle or oil drop or moisture (water drop) gets deposited on the surface of the metal. The portion covered is less aerated compared to the large exposed area and thus acts as anode with respect to the surface exposed. Corrosion takes place below the deposit resulting in the formation of pit. Once a pit is formed corrosion rate accelerated due to further decrease in concentration of O_2 within the pit.



ii. Water line corrosion

Water line corrosion can be observed in steel tanks partially filled with water. The area above the water line, which is more oxygenated acts as cathode and is unaffected by corrosion, whereas corrosion takes place along a line just beneath the level of water meniscus because it is exposed to lower oxygen concentration. Most intense corrosion is observed just below the water line, hence it is called as **water line corrosion**.



Examples for differential aeration corrosion:

- i. Part of the nail inside the wall being exposed to lower oxygen concentration than the exposed part undergoes corrosion.
- ii. Window rods inside the frame suffer corrosion but not the exposed parts.
- iii. Metal surface under dirt, dust, scale or water undergoes corrosion.
- iv. Paper pins inside the paper get corroded and the exposed part is free from corrosion.
- v. Partially buried pipe line in soil or water undergoes corrosion below the soil or water. Whereas the exposed part is free from corrosion.

Factors affecting the rate of corrosion

There are two type of factor affecting rate of corrosion

- (i) **Primary factor (Related to Metal)**
- (ii) **Secondary factor (Related to Environment)**

i. **Primary factor**

a) **Nature of corrosion product**

The nature of the corrosion product decides the rate of further corrosion. If the corrosion product deposited is insoluble, stable, uniform and nonporous, it acts as a protective film preventing the further corrosion of metal. A thin continuous film formed on the surface acts as a barrier between the fresh metal surface and the corrosion environment.

On the other hand if the corrosion product is soluble, unstable, non uniform and porous, the corrosion continues. In such cases, the fresh metal surface is continuously exposed to the corrosion environment and corrosion of the metal surface takes place continuously.

Metals like Al, Cr, Ti, Zr, etc., are highly passive because of the formation of protective films on the metal surface, which prevents further corrosion.

Metals such as Fe, Zn, Mg, etc., do not form any protective film and undergoes corrosion when exposed to oxidizing environment.

b) **Ratio of Anodic to Cathodic areas**

The rate of corrosion is greatly influenced by the relative sizes of anodic and cathodic areas. If a metal has a small anodic area and large cathodic area, corrosion rate is faster. This is because at anode, oxidation takes place and electrons are liberated. At the cathode, these electrons are consumed. When the anode is smaller and cathode region is large, all the electrons liberated at the anode are rapidly consumed at the cathode region. This process makes the anodic reaction to take place at its maximum rate, thus increasing the corrosion rate. If the cathode is smaller, the consumption of electrons will be slower and corrosion rate decreases. If the ratio of anodic to cathodic area is small, corrosion rate is very high. For the same reason iron bolts and nuts are not used in copper boilers.

$$\text{Rate of corrosion} \propto \frac{\text{Cathodic area}}{\text{Anodic area}}$$

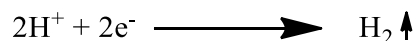
ii. **Secondary factor (related to environment)**

a. **Temperature**

In general, the rate of a chemical reaction increases with rise in temperature. Corrosion process is one such chemical reaction (redox reaction). Thus rate of corrosion increases as the temperature increases. (Increase in temperature increases the kinetic energy of reactant molecule, which increases the velocity of reactant molecules. Due to the increases the velocity, number of collision between the reactant molecules increases there by increasing the rate of reaction.)

b. pH

Acidic media are more corrosive compared to alkaline and neutral media. Thus lower the pH of the corrosion medium, higher is the corrosion rate. Cathodic reaction involves consumption of electrons by H^+ ions.



As the pH decreases, H^+ ions concentration increases, thereby increasing the consumption of electrons. Therefore anodic region loses more electrons and increases the rate of corrosion.

c. Conductivity

The rate of corrosion increases with increase in conductance of the medium. As the conductance of the medium increases, ions can move easily through the medium. This decreases the polarization potential and due to this the rate of corrosion increases.

Example: Metal immersed in sea water (more conducting) corrodes faster than metal immersed in river water (less conducting).

Corrosion Control

Corrosion of metal is a natural spontaneous process, by which a metal is converted in to more stable compound state. Therefore corrosion control is more realistic than corrosion prevention. The corrosion types are so numerous, the mechanism of corrosion are so different and conditions under which corrosion takes place are so varied that no single method can be used to control all possible corrosion cases. Some of the important methods used in controlling corrosion of metals are,

1. Protective Coating

The Protective coating protects the metal from corrosion by acting as a barrier between the metal and the corrosive environment. The principle types of coating applied on the metal surface are,

Metal Coating: The process of covering the base metal with a layer of another metal is known as metal coating. By this method the base metal can be protected. Metal coating can be anodic metal coating or cathodic metal coating.

Anodic Coating: Anodic coatings are produced by coating a base metal with more active metals which are anodic to the base metal such as Zn, Al, Mg, etc.,

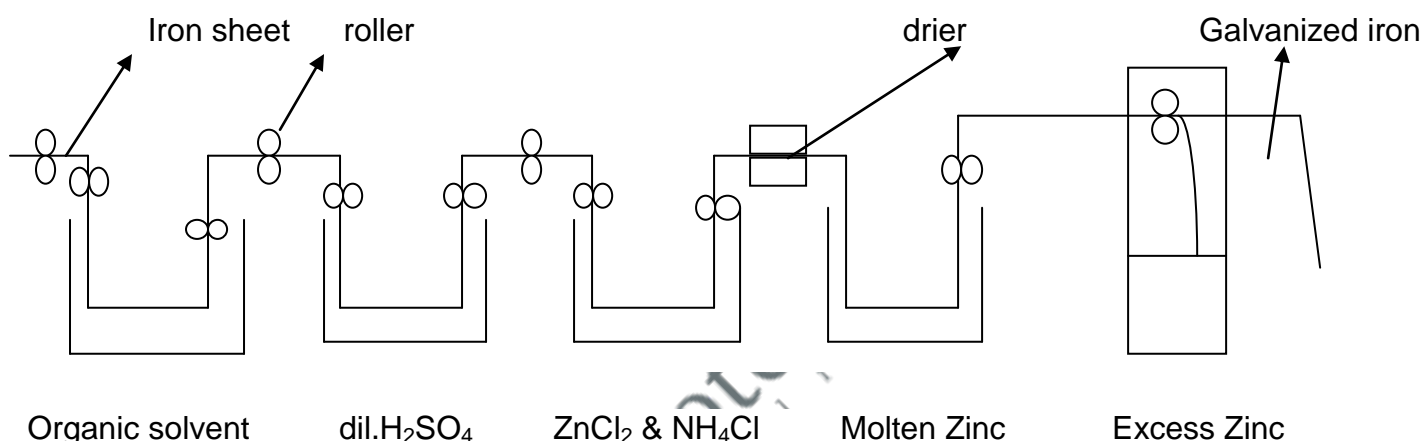
The important characteristics of anodic coating are that, even if the coating is ruptured, the base metal does not undergo corrosion. The exposed surface of the base metal is cathodic w.r.t. the coating metal and the coating metal preferentially undergoes corrosion. The protection is ensured as long as the anodic coating metal is still present on the surface. Therefore anodic metal coating is also known as sacrificial coating.

Example: Galvanizing is familiar anodic coating and is extensively used to protect iron and steel objects.

Galvanization: It is a process of Coating a base metal with zinc metal. It is carried out by hot dipping method.

Hot dipping method: It involves the dipping of base metal in molten anodic metal (Zn). The coating metal should melt at a relatively low temperature and the base metal must with standing this temperature without undergoing any changes in its properties. The galvanization process involves the following steps.

- The metal surface is washed with organic solvent to remove oil or grease present on the surface.
- Rust and other deposit are removed by washing with dilute H_2SO_4 .
- The clean and dry sheet is passed through aqueous solution of zinc chloride and ammonium chloride flux and dried. The flux helps the molten metal to adhere (adsorb) on the metal surface.
- The article is then dipped in a bath of molten Zinc maintained at $425-430^\circ C$.
- The excess Zn on the surface is removed by passing through a pair of hot rollers which wipes out excess of coating and produces a thin coating.



Galvanization is used extensively to protect iron from corrosion in the form of roofing sheets, fencing wire, buckets, bolts, nuts, nails, screws, pipes, tubes etc. Galvanized steel are used in construction where high degree of corrosion resistance is required. Galvanized articles are not used for preparing and storing food stuffs since zinc dissolve in dilute acids producing toxic Zinc compound.

Surface conversion Coating

Inorganic coatings are generally chemical conversion coatings. A surface layer of metal is converted into a compound, by chemical or electrochemical reactions, which forms barrier between the underlying metal surface and the corrosion environment. The chemical conversion coatings are different from other types of coatings in the sense that, they are the integral part of the metal itself. This types of coatings formed on the metal surface by electrolytic method. In addition to the corrosion resistance, also provide increased electrical insulation and enhanced adherence for paints and other similar organic coatings.

Anodization

Anodization is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as protective layer. A protective oxide film generally produced on nonferrous metals like Al, Mg, Cr, Zn, Ni, and their alloys by anodic oxidation process, in which the base metal is made as anode in electrolytic bath of suitable composition (Chromic acid, H_2SO_4 , H_3PO_4 , H_2CrO_4) and by passing direct current. Lead is generally used as cathode.

The anodic oxide film formed on Al in the electrolyte bath tends to be porous and provides good adherence for paints and dyes. The strength and corrosion resistance of the anodized film can be increased by the so called sealing, which involves heating in boiling water or steam or metal salt solution. The treatment changes porous alumina at the surface of coating in to its mono hydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), which occupies more volume, thereby pores are sealed.

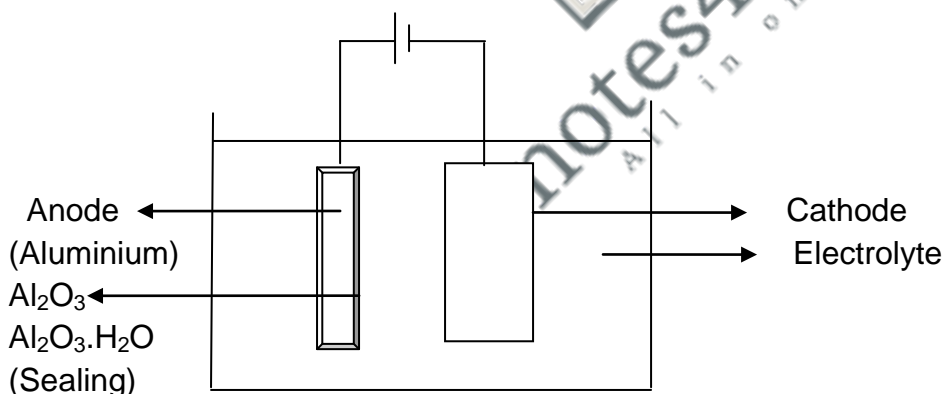
Anode : Aluminium article
Cathode : Steel or Copper
Temperature : 35°C
Electrolyte : 10% sulphuric acid or 5-10% chromic acid or oxalic acid
Current density: $10\text{-}20 \text{ mA/cm}^2$

Electrode reaction

At anode : $2\text{Al}_{(s)} + 3\text{H}_2\text{O}_{(l)} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$

At cathode : $6\text{H}^+_{(aq)} + 6\text{e}^- \rightarrow 3\text{H}_{2(g)}$

Net cell reaction : $2\text{Al}_{(s)} + 3\text{H}_2\text{O}_{(l)} \rightarrow \text{Al}_2\text{O}_3_{(s)} + 3\text{H}_{2(g)}$



Anodized articles are used as exterior for roofs, walls, and window frames, soap boxes, Tiffin carriers etc.

2. Cathodic protection

Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode.

Principle: Corrosion can be prevented by eliminating the anodic sites and converting the entire metal into cathodic area.

Cathodic protection can be achieved by following methods

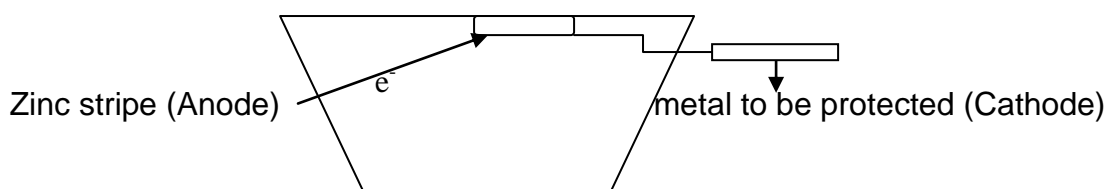
- a. Sacrificial anodic method.
- b. Impressed current method.

a. Sacrificial anodic method.

In this method the base metal to be protected from corrosion is brought in contact with more anodic metals like Zn, Mg, Al, etc., (i.e. metal having lower standard electrode potential compared to the base metal). These metals are called as sacrificial metals. The sacrificial metals acts as anode and hence it undergo corrosion, while the base metal acts as cathode and so it is protected. Anode is periodically replaced by fresh block of sacrificial metals.

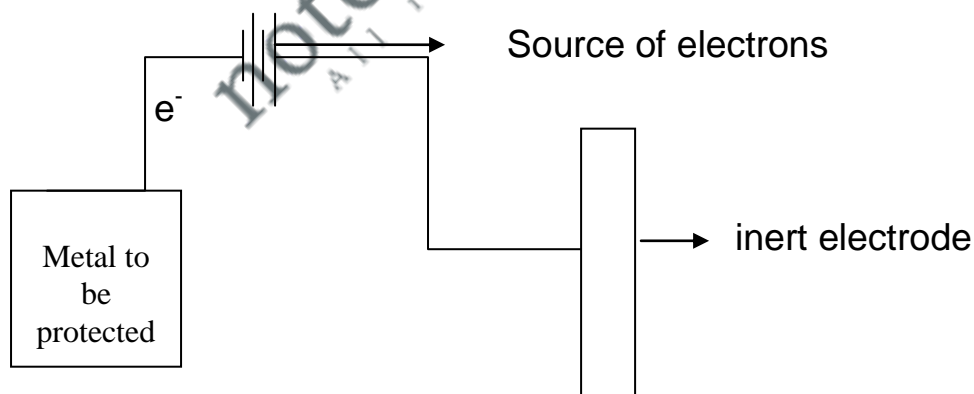
This type of cathodic protection is used to protect buried pipe line, underground cables, water tanks, boilers, ships etc., from corrosion.

Example: To protect Cu from corrosion, it is brought in contact with Zn. Zn having lower standard electrode potential acts anode and get corroded, while Cu having higher standard electrode potential acts as cathode and get protected from corrosion.



b. Impressed current method.

In impressed current method, an impressed current is applied in opposite direction to the metal to nullify the corrosion current i.e. the base metal to be protected from corrosion is made as cathode by connecting it to the -ve terminal of the battery. While +ve terminal is connected to the inert anode like resin, bonded graphite rod, Si-Fe alloy or platinized titanium



Metal Finishing

The term metal finishing covers a wide range of processes carried out to modify the surface properties of a metal. The name given to all those processes employed to modify the surface properties of conducting or non-conducting materials by deposition of a layer of metal over them.

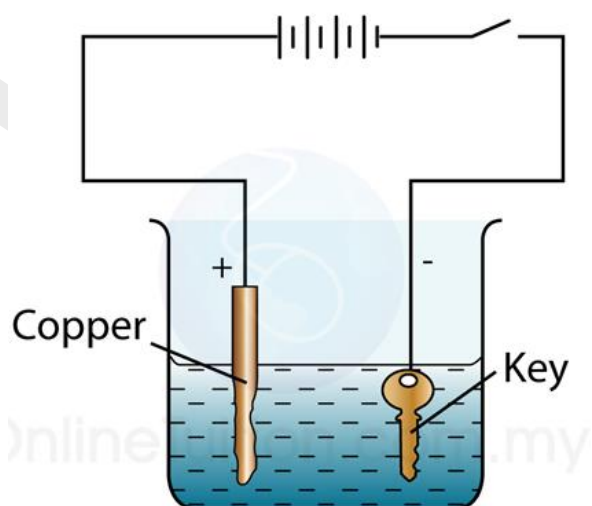
Definition: Metal finishing is the process of deposition of a layer of the metal on the surface of substrate.

A thin coating of metal can be developed on the surface of any material either by using **electric current** or a **suitable reducing agent**. Correspondingly two techniques mostly used for metal finishing namely **Electroplating** & **Electroless plating**.

Technological Importance of Metal Finishing: Metal Finishing is carried out to obtain technologically important surface properties, these properties are;

- A decorative appearance
- An improved corrosion
- An improved surface hardness
- To provide good electrical and thermal conducting surface
- To increase thermal resistance
- To increase optical reflectivity (Brightness)
- To improve chemical resistance
- To improve tarnish resistance
- Abrasion and wear resistance
- In the manufacturing of electrical and electronic components

Electroplating: Coating a layer of metal over the surface of another metal, alloy or any other conducting material by applying an electric current” is called as Electroplating. By this method any conducting material can be coated with thin and uniform layer of another metal.



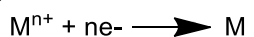
Electroplating is carried out in a device called electrolytic cell. It consists of two electrodes; material to be coated with metal is taken as cathode & is connected to –ve terminal of the battery. An anode is connected to +ve terminal of the battery. Both electrodes are dipped in an electrolyte solution containing ionic solution of the metal.

Metal Finishing

When a direct current is passed through an electrolyte solution,

- Cations (metal ions) move towards cathode. At the cathodic surface, metal ions are reduced to metal atoms & get deposited over it. This process of deposition of metal on the cathodic material is called electroplating. Thus, concentration of cations decreases in the bulk of the solution.

At cathode,



- Anions move towards anode, where they get oxidized. Anode can be dissolvable anode or inert anode. In case of dissolvable anode, anode reaction is oxidation of metal atoms to metal ions. In such case, thickness of anode gradually decreases & hence it has to be replaced periodically to continue the electrolysis.

At anode,



In case of inert anode, only chemicals present on the electrode surface are oxidized and anode itself will not react. Here, electrolyte should be added from outside to maintain the cationic concentration & thereby to continue the electrolysis. By the act of electric current, an electrolyte is decomposed at the surface of electrodes. This process of decomposition of an electrolyte by passing electric current is called electrolysis.

Principles governing electroplating: The fundamental principles governing electroplating are;

- a. Decomposition potential (E_D)
- b. Overvoltage (η)
- c. Polarization

a. Decomposition Potential (E_D): In an electrolytic cell the following processes occur during electroplating of metal;

- Cations (metal ions) are attracted towards cathode.
- Anions are attracted towards anode.
- Metal ions are reduced to metal atoms at the surface of cathode.
- Anions are oxidized at the surface of anode.

Each of these steps has its own potential. If the externally applied potential is less than potential of these processes, then electroplating of metal does not occur. In other words, electroplating of metal occurs smoothly and continuously when the applied potential is greater than the potential of all these steps.

The minimum external voltage (potential) that must be applied in order to carry out continuous electrolysis in an electrolytic cell is called as decomposition potential (E_D).

$$\text{Decomposition potential } (E_D) = E_{\text{Back}} + \eta$$

Where, η is the over potential and E_{Back} is the back potential. E_{Back} is the difference in potential of anodic & cathodic reactions occurring in the cell during electrolysis. This

Metal Finishing

potential opposes the externally applied potential and hence it is called as back potential. E_{Back} can be calculated theoretically.

$$E_{\text{Back}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

For any system, knowing the salt being electrolyzed, back EMF can be theoretically calculated. Therefore it is also called as theoretical decomposition potential.

b. Over Voltage (η): Normally Decomposition potential (E_D) required to carry out continuous electrolysis is greater than theoretical decomposition potential.

This difference between decomposition potential (E_D) and theoretical decomposition potential (E_{Back}) is called over potential (η). **Over voltage is defined as “the excess voltage that has to be applied above the theoretical potential for continuous electrolysis”.**

$$\text{Over Voltage } (\eta) = \text{Experimental } E_D - \text{Theoretical } E_D$$

$$\eta = E_D - E_{\text{Back}}$$

Over potential depends upon several factors such as

- ✓ Conductivity of the solution.
- ✓ Nature of metal electrodes.
- ✓ Current density applied.
- ✓ Temperature.
- ✓ Rate of stirring of the electrolyte solution.

Over potential is mainly due to polarization of electrodes and other side reactions that occur at the electrode surface during electroplating. One of the main side reaction is liberation of hydrogen at the cathode.

c. Polarization: During electrolysis, metal ions present at the vicinity of cathode get reduced to metal atoms. Therefore concentration of metal ions at the vicinity of the cathode decreases. To maintain the same concentration, metal ions must be supplied from the bulk of the solution to vicinity of the electrode. If the metal ions are not supplied sufficiently, then the concentration of metal ions decreases. This leads to decrease in potential of electrode according to Nernst equation.

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

The decrease in Electrode Potential due to insufficient supply of ions from bulk of the solution to surface of the electrode is called polarization.

Polarization depends on

- Nature of the electrode
- Nature of Electrolyte
- Temperature
- Rate of stirring of the electrolyte

Electroplating of Chromium:

Decorative Chromium Coatings: Decorative Chromium deposit is coating a thin layer of chromium with thickness of 0.25 to 0.75 μm . Decorative Chromium coatings exhibit excellent tarnish, corrosion resistance with appealing colour and high optical

Metal Finishing

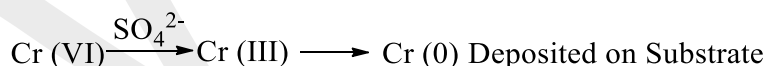
reflectivity. This technique used to impart bright & decorative look to materials like automotive bumps, wheel rims, taps, handle bars etc.

Hard Chromium Coatings: Deposition of chromium with a thickness of 5 to 750µm. Exhibits good surface hardness, excellent tarnish, corrosion, wear and scratch resistance. This technique used in hand guns, aircraft parts, axels, piston rings etc.

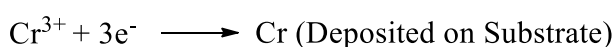
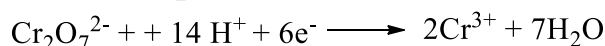
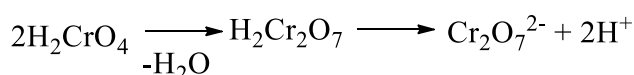
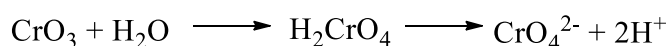
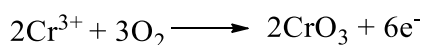
The surface of the object is cleaned thoroughly; organic substances are removed by solvent cleaning and alkali cleaning. Inorganic substances are removed by mechanical cleaning and picking. Finally the surface is washed with deionized water. Then chroming plating is done under the following conditions.

Sl. NO.	Plating conditions	Decorative chromium plating	Hard chromium plating
1	Plating bath composition	Chromic acid (H ₂ CrO ₄) + H ₂ SO ₄ in the weight ratio 100 : 1	Chromic acid (H ₂ CrO ₄) + H ₂ SO ₄ in the weight ratio 100 : 1
2	Operating temperature.	45-55°C	45-55°C
3	Current density	145 – 430 A/ft ²	290 – 580 A/ft ²
4	Current efficiency	10 – 15 %	17 – 21 %
5	Anode	Insoluble anode: Pb-Sb or Pb-Sn alloy coated with PbO ₂	Insoluble anode: Pb-Sb or Pb-Sn alloy coated with PbO ₂
6	Cathode	Object to be plated	Object to be plated
7	Anodic reaction	H ₂ O → 1/2 O ₂ + 2H ⁺ + 2e ⁻	H ₂ O → 1/2 O ₂ + 2H ⁺ + 2e ⁻
8	Cathodic reaction	Cr ³⁺ + 3e ⁻ → Cr	Cr ³⁺ + 3e ⁻ → Cr

The plating bath contains chromic acid, during electroplating of chromium; Cr (VI) is reduced to Cr (III) in the presence of SO₄²⁻ catalyst. Cr (III) is reduced to Cr (0), which gets deposited on the substrate.



For a good deposit, the Cr³⁺ concentration must be low. The PbO₂ oxidizes a part of Cr³⁺ to Cr⁶⁺ thus reducing the concentration of Cr³⁺.

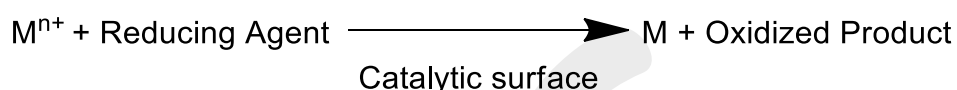


Chromium anodes are not used in Cr-plating, because;

- ❖ If chromium dissolves at anode, there will be a high concentration of Cr³⁺ in solution; in such case a black deposit is obtained.

Electroless Plating: It is defined as “the process in which metal is depositing over a substrate by controlled chemical reduction of metal ions by a suitable reducing agent without using electrical energy”.

A layer of metal is coated over the material by chemical reduction method without using an electric current. Material to be coated is immersed in ionic solution of the metal & then a reducing agent is added. Reducing agent reduces metal ions into metal atoms, which get deposited over the material and in the process reducing agent itself is oxidized. Material surface should be catalytically activated to catalyze the redox reaction.



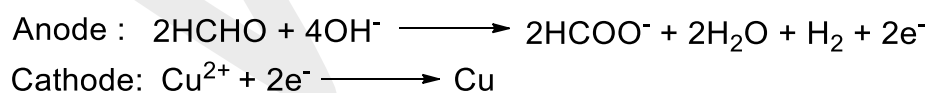
Electroless Plating of Copper: Before Electroless plating the plastic board is degreased and etched in acid. It is activated by dipping in $\text{SnCl}_2 / \text{HCl}$ at 25°C followed by dipping in PdCl_2 .

Electroless plating is done under the following conditions,

- ❖ Plating bath solution - Copper Sulphate,
- ❖ Reducing agent - Formaldehyde
- ❖ Complexing agent – EDTA,
- ❖ Buffer - Sodium Hydroxide [$\text{p}^{\text{H}}=11$]
- ❖ Temperature - 25°C .

The plating is carried out at room temperature by dipping the activated plastic board in the bath solution. The metallic copper obtained as a reduced product in the bath deposit on the metal surface.

Reactions:



Application: Typical application of Electroless copper plating is printed circuit boards, particularly double sided boards in which plating through holes is required.

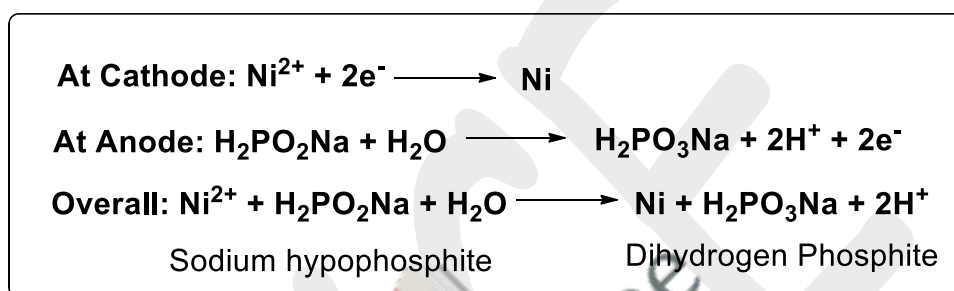
Electroless plating of Nickel: Before Electroless plating the plastic board is degreased and etched by organic solvents and dilute H_2SO_4 . Electroless nickel is deposited directly on Iron, Al and brass without any pretreatment in presence of reducing agents. However nonmetallic materials like plastics, glass etc. are catalytically activated by dipping in $\text{SnCl}_2 / \text{HCl}$ at 25°C followed by dipping in PdCl_2 . SnCl_2 reduces palladium ions on the surface of the object to palladium which catalyzes the deposition reaction.

Metal Finishing

Electroless plating is done under the following conditions,

Sl. No.	Plating Condition	
1	Metal Ion Solution	Nickel Chloride (20g/L)
2	Reducing agent	Sodium Hypophosphite (20g/L)
3	Temperature	93°C
4	pH	4 – 4.5
5	Complexing agents & exhalant	Sodium succinate (15g/L)
6	Buffer	Sodium acetate (10g/L)

Reactions:



Applications: In automotive industry to coat on bumpers, rims and exhaust pipes.

Distinctions b/w Electroplating and Electroless plating:

Sl. No.	Property	Electroplating	Electroless plating
1.	Driving Force	Electric Current	Autocatalytic Redox Reaction
2.	Anode	Separate Anode	Catalytic surface of substrate
3.	Cathode	Article to be plated	Catalytically active surface
4.	Reducing agent	Electrons	Chemical reagent
5.	Anode reactant	Metal (or) H_2O	Chemical reagent
6.	Applicability	Only to conductors	Conductors and non-conductors.
7.	Throwing Power	Low	High.

CHEMICAL FUELS AND PHOTOVOLTAIC CELLS

Chemical fuels:

A chemical fuel is a substance which on combustion in air or oxygen produces significant amount of heat, which can be used for domestic and other purposes. They contain Carbon & Hydrogen as major constituents. During combustion, these are oxidized to Carbon dioxide and water.

Eg: wood, coal, petroleum, natural gas, etc.

Definition:

A fuel is defined as a naturally occurring or an artificially manufactured combustible carbonaceous material, which serves particularly as a source of heat and light and also in a few cases as a source of raw material.

Importance of Hydrocarbon fuels:

Petroleum coal & natural gas are the hydrocarbon fuels. These are also called fossil fuels or non-renewable energy sources, formed from dead plants and animals, buried deeply under high pressure, about 345 million years ago. These fuels are excellent hydrocarbon fuels as they contain carbon and hydrogen as major elements. When they are burnt in sufficient supply of air, they are oxidized to CO_2 and H_2O and release significant amount of energy in the form of heat which can be converted into a suitable form to perform useful work.

Among fossil fuels natural gas is superior fuel and has many advantages over coal and petroleum. It burns cleanly, leaves no residue and produces less CO_2 per unit energy than the other two fossil fuels. Further unlike coal, it does not produce any NO_x , SO_x , CO etc. It is therefore the safest and excellent fuel. These fossil fuels are used for transportation, industrial processes, heating, cooling buildings and generating electric power.

The reserves of these fuels are fast depleting because of high rate of consumption.

Classification of chemical fuels:

Based on their physical state, chemical fuels are classified into solid, liquid and gaseous fuels.

Solid: Wood, coal, charcoal, coke etc.

Liquid: Petroleum oil, petrol, kerosene, diesel oil etc.

Gases: Natural gas, coal gas, biogas, LPG etc.

Based on their occurrence, chemical fuels are classified into primary and secondary fuels. Fuels that occur in nature are called primary fuels. Eg: Wood, coal, petroleum, natural gas. Fuels that are derived from primary fuels are called secondary fuels. Eg: charcoal, petrol, kerosene, diesel, biogas, LPG etc.

Calorific value:

Calorific value of a fuel is defined as the amount of heat released when a unit quantity (mass or volume) of a fuel is burnt completely in air or oxygen. Calorific value is expressed in Joule per kg (J/kg) for solid fuels and joules per cubic meter (J/cm³) for gaseous fuels in SI units.

Calorific value is of two types, Gross and Net calorific value.

Gross (Higher) calorific value [GCV]:

It is defined as the amount of heat released when unit quantity of a fuel is burnt completely in air and the combustion products are cooled to room temperature.

On combustion carbon and hydrogen present in fuels are converted into carbon dioxide and steam respectively. On cooling steam gets condensed to water and liberates its latent heat. Hence gross calorific value includes the latent heat of steam. Therefore it is always higher than the net calorific value.

Net (lower) calorific value [NCV]:

It is defined as the amount of heat released when a unit quantity of a fuel is burnt completely in air, and the products of combustion are let off into the atmosphere.

The combustion products are not cooled. Therefore net calorific value does not include the latent heat of steam. Net calorific value is always lower than gross calorific value.

Therefore, Net calorific value = Gross calorific value – latent heat of steam

$$\text{i.e., NCV} = \text{GCV} - (\text{Mass of H}_2 \times 9 \times \text{latent heat of steam})$$

[Since H₂O contains 2g of H, on combustion it gives 18g of water.

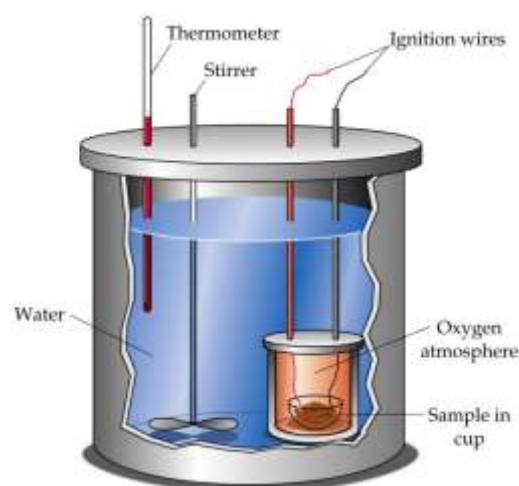
Therefore, 1g of H gives 9g of water, releases 587 KCal/Kg or 2454KJ / Kg of energy.]

$$\text{Therefore, NCV} = \text{GCV} - \frac{9 \times \%H}{100} \times 587 \text{ KCal / Kg}$$

Determination of calorific value of a solid and liquid fuel using Bomb calorimeter:

Principle: A known weight of solid or liquid fuel is burnt completely in excess of oxygen. The liberated heat is absorbed by the surrounding water and calorimeter. Thus, the heat liberated during combustion of a fuel = heat absorbed by water and copper calorimeter.

Construction: The apparatus consists of a stainless steel air tight cylindrical bomb. The bomb has an inlet valve for providing oxygen inside the bomb & an electrical ignition coil for initiation of combustion of fuel. The Cu calorimeter is equipped with a stirrer for dissipation of heat & a thermometer for measuring rise in temperature.



Working: A known mass of solid or liquid fuel is placed in a stainless steel crucible. The crucible containing the fuel is placed in the bomb. The bomb is sealed air tight with lid. The sealed bomb is then placed in a large insulated Cu calorimeter. It is filled with accurately measured quantity of water. The water is kept in constant agitation by mechanical stirrer. The initial temperature of water is noted. The bomb is filled with oxygen & combustion of fuel is initiated by passing electric current through the ignition coil.

As the fuel is burnt, heat is liberated & is absorbed by surrounding water & Cu calorimeter. The temperature of water gradually increases & attains a maximum value. This maximum temperature is noted. The water equivalent of the calorimeter is determined by burning a fuel of known calorific value.

Observation and calculation:

Mass of fuel = m kg

Mass of water taken in calorimeter = w_1 kg

Water equivalent of calorimeter = w_2 kg

Initial temperature of water = t_1 °C

Maximum temperature of water = t_2 °C

Rise in temperature of water = $(t_2 - t_1)$ °C = Δt °C

Specific heat of water = $S = 4.187 \text{ kJ/kg/}^\circ\text{C}$

Heat released by $m \text{ g}$ of fuel = heat gained by water + heat gained by calorimeter

$$\text{i.e., } m \times \text{GCV} = (w_1 + w_2) (t_2 - t_1) \times S$$

$$\text{GCV} = \frac{(w_1 + w_2) (t_2 - t_1) \times S}{m} \text{ kJ / kg}$$

Therefore, Net calorific value = GCV – latent heat of steam

$$\text{i.e., } \text{NCV} = \text{GCV} - (0.09 \times \text{H\%} \times \text{latent heat of steam})$$

Problems:

1. Calculate the gross calorific value and net calorific value of a sample of coal. 0.5g of which when burnt in a bomb calorimeter raised the temperature of water from 293K to 296.4K. The mass of water is 1000g and water equivalent of calorimeter is 350g. The specific heat of water is 4.187 kJ/kg/K, latent heat of steam is 2454 kJ/kg. The coal sample contains 93% carbon, 5% hydrogen and 2% ash.

Solution:

Mass of the fuel, $m = 0.5 \text{ g} = 0.5 \times 10^{-3} \text{ kg}$

Mass of water, $w_1 = 1000 \text{ g} = 1000 \times 10^{-3} \text{ kg}$

Water equivalent of calorimeter = $w_2 = 350 \text{ g} = 350 \times 10^{-3} \text{ kg}$

Initial temperature of water = $t_1 \text{ }^\circ\text{C} = 293 \text{ K}$

Final temperature of water = $t_2 \text{ }^\circ\text{C} = 296.4 \text{ K}$

Specific heat of water = $S = 4.187 \text{ kJ / kg / }^\circ\text{C}$

Latent heat of steam = $L = 2454 \text{ kJ / kg / }^\circ\text{C}$

$$\text{GCV} = \frac{(w_1 + w_2) (t_2 - t_1) \times S}{m} \text{ kJ / kg}$$

$$\text{GCV} = 38436.66 \text{ kJ / kg}$$

$$\text{NCV} = \text{GCV} - \text{Heat of condensation of H}_2\text{O}$$

(Heat of condensation of H_2O = Mass of H_2O formed during combustion - Latent heat of H_2O)

$$\text{NCV} = \text{GCV} - (0.09 \times \text{H\%} \times \text{latent heat of steam})$$

$$\text{NCV} = 37332.36 \text{ kJ / kg}$$

2. A 0.6g coal sample with 92% C, 5% H_2 and 3% ash caused a rise in the temperature of 2000g of water by 3.2°C in a bomb calorimeter experiment.

Calculate the gross and net calorific value of coal, given water equivalent = 200g.

Specific heat of water = 4.187 kJ/kg/°C

Latent heat of steam = 580 calories/g (1 calorie = 4.18 Joules)

3. Calculate the gross calorific value of a coal sample from the following data:

Weight of coal sample taken = 5.5×10^{-3} kg

Weight of water taken in the calorimeter = 2.5 kg

Water equivalent of calorimeter = 0.5 kg

Initial temperature of water = 24 °C

Final temperature of water = 28 °C

4. Calculate the gross and net calorific value of a coal sample from the following data:

Weight of coal sample taken = 8.5×10^{-4} kg

Weight of water taken in the calorimeter = 3.5 kg

Water equivalent of calorimeter = 0.5 kg

Initial temperature of water = 25 °C

Final temperature of water = 27.5 °C

Percentage of hydrogen in the coal sample = 2.5

Latent heat of steam = 2455 kJ/kg

4. When 0.935g of a fuel undergoes complete combustion in excess of oxygen, the increase in temperature of water in a calorimeter containing 1365 g of water was 2.4 °C. Calculate the higher calorific value of the fuel, if the water equivalent of calorimeter is 135g.
5. On burning 0.83×10^{-3} kg of a solid fuel in a bomb calorimeter, the temperature of 3.5 kg of water increased from 26.5 °C to 29.2 °C. The water equivalent of calorimeter and latent heat of steam are 0.385 kg and 4.2×587 kJ / kg respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific values.
6. A coal sample with 93% C, 5% H₂ and 2% ash is subjected to combustion in a bomb calorimeter. Calculate the gross and net calorific value given that mass of coal sample taken is 0.0095kg, mass of water in copper calorimeter is 2 kg, water equivalent of calorimeter is 0.7 kg, rise in temperature of water is 2.8K and latent heat of steam is 2457.182 kJ/kg. Specific heat of water = 4.187 kJ/kg/K
7. Following observations were made in a bomb calorimeter experiment. Wt of fuel 0.835 g, Weight of water taken in the calorimeter 1550g, Water equivalent of

calorimeter 145g, rise in temperature 2.8 °C. Calculate the higher calorific value of the fuel.

8. Calculate the calorific value of a fuel sample from the following data:

Weight of coal sample taken = 0.6g

Water equivalent of calorimeter = 2200g

Rise in temperature of water = 6.52 °C

Specific heat of water = 4.187 kJkg⁻¹

9. On burning 0.96g of a solid fuel in a bomb calorimeter, the temperature of 3500g of water increased by 2.7 °C. The water equivalent of calorimeter and latent heat of steam are 385g and 587 cal/ g respectively. If the fuel contains 5% hydrogen, calculate its gross and net calorific values.

Knocking:

The performance of a vehicle is measured in terms of Km / L of petrol, depends on quality of fuel. More power can be obtained from petrol by increasing the compression ratio of the engine. Compression ratio is the ratio of the initial volume of petrol air mixture which is sucked into the cylinder to the final volume after compression. By increasing the compression ratio, efficiency of the engine can be increased, and fuel can be saved.

The combustion reaction is initiated by a spark in the cylinder due to which flame spreads rapidly & smoothly through the gaseous mixture. When petrol undergoes combustion, under normal conditions, pressure inside the cylinder rises, & rate of flame propagation is 20m/s.

But beyond a particular compression ratio, the petrol-air mixture suddenly bursts into flames & flame propagation increases to 2500m/s. This process is accompanied by a sharp knock in the engine due to explosive combustion, producing a shock wave which dissipates its energy by hitting the cylinder walls & piston. As a result, rattling sound is heard which is called knocking.

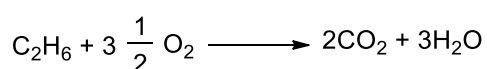
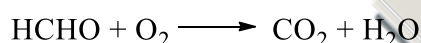
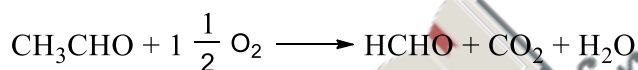
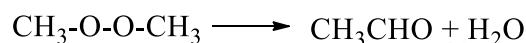
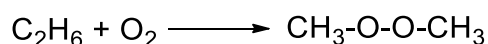
Therefore knocking is the production of a shock wave in an IC engine, as a result of an explosive combustion of fuel-air mixture, resulting in an increase in compression ratio, beyond a certain value, leading to a rattling sound.

Knocking increases the fuel consumption, decreases engine power, damages engine parts by overheating of cylindrical parts.

Mechanism:

Under normal conditions, there is a slow oxidation of the fuel during which oxygen combines with a few hydrocarbon molecules and activates those forming peroxides. The activated molecules combine with the hydrocarbons resulting in a smooth combustion.

Knocking occurs when the chain reactions proceed at a very fast rate. The unstable peroxides formed decompose to give a number of gaseous compounds. This give rise to stock waves which knocks against the engine walls and a rattling sound is heard. The reactions are as follows.

Normal combustion**Explosive combustion****Prevention of knocking:**

Knocking can be prevented by

1. Using anti knocking agents
2. Using high rating gasoline

Antiknocking agents: Antiknocking agent like $\text{Pb}(\text{C}_2\text{H}_5)_4$ (Tetra ethyl lead) is added to fuel, reacts with peroxy compounds & decomposes them preventing knocking. This is called leaded petrol.

Unleaded petrol: The octane number can also be increased by mixing straight chain hydrocarbons with high octane components like isopentane, isooctane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether, etc. hence enhancement of octane number is done without adding lead compounds. This is called unleaded petrol.

Use of leaded petrol is avoided due to ill effects of lead compounds that are discharged through the exhaust. One of the major advantages of using unleaded petrol is that it allows the use of a catalytic converter attached to the exhaust in

automobiles. Catalytic converter contains Platinum & Rhodium catalyst which converts the toxic gases like CO and NO to harmless CO₂ and N₂. It also oxidizes unburnt hydrocarbons into CO₂ and H₂O. However leaded petrol cannot be used with catalytic converters as the lead present poisons the catalyst, destroying the active sites.

Power alcohol:

Power alcohol is a mixture of ethyl alcohol and petrol which is used as a fuel in internal combustion engines. Blends containing up to 25% of alcohol with petrol are used. Industrial alcohol containing 95% alcohol and 5% of water can be mixed with petrol but by using some mixing (blending) agents such as benzene, ether etc. Without the use of blending agents industrial alcohol does not mix with petrol. The main objective of the power alcohol is to provide an alternative renewable energy source.

The advantages of power alcohol:

1. The power out-put is good.
2. Alcohol has an octane number of 90. Addition of power alcohol to petrol (octane number 60-70) increases the octane number. Hence alcohol blended petrol possesses better anti-knock properties.
3. Due to better antiknock property, it can be used in engines with higher compression ratio.
4. The use of ethanol in petrol blends increases the oxygen content of the fuels and promotes more complete combustion of the hydrocarbons and reduces carbon monoxide and volatile organic compound emissions.
5. Petrol – alcohol blend has the same lubrication as the pure petrol has.
6. Ethanol is produced from agricultural products (corn, molasses). It is a sustainable fuel.

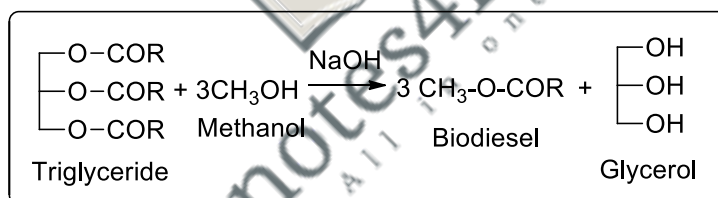
Disadvantages of power alcohol:

1. Alcohol lowers calorific value of petrol.
2. Alcohol is easily oxidized to acids, hence can cause corrosion.
3. Air entering the cylinder has to be regulated as less air is required for combustion.
4. Alcohol absorbs moisture; as a result separation of alcohol & petrol layers occurs at low temperature. Hence blending agents like benzene or toluene are added.

Biodiesel:

Biodiesel is the clean burning fuel obtained from renewable resources such as vegetable oils. Vegetable oils such as soya bean oil, palm oil, peanut oil or sunflower seed oil are triglycerides. These esters have high viscosity, high flash point and low volumetric heating value and hence cannot be used as such in conventional diesel engines. These oils are converted into biodiesel by transesterification reaction, where oils are treated with excess of methanol in the presence of catalysts. The products are a mixture of mono- methyl esters of long chain fatty acids and glycerine. The mixture is allowed to settle and the bottom glycerine layer is drawn off. The upper layer of methyl ester is washed and purified further to remove excess of methanol. The mixture of methyl esters is called the biodiesel. It has the desired characteristics of diesel fuel with cetane numbers 50-62 depending on the vegetable oil used for transesterification.

Synthesis: Vegetable oils or animal fats contain triglycerides (lipids). Biodiesel is synthesised by transesterification of lipids with methanol and NaOH as catalyst at 60-70 °C. Transesterification is a process of exchanging alkoxy (-COR) group of an ester with alcohol.

**Advantages:**

- Used as an alternative fuel for compression ignition engine.
- It is blended with diesel.
- Biodiesel is completely biodegradable, non-toxic and free from sulphur compounds.

Fuel Cells

A fuel cell is defined as a galvanic cell in which the chemical energy is directly converted into electrical energy by electrochemical process in which fuel is oxidised at the cathode.

A fuel cell is represented as;

Fuel / electrode / electrolyte / electrode / Oxidant

At anode: Fuel \longrightarrow Oxidation product + ne^-

At cathode : Oxidant + $ne^- \longrightarrow$ Reduction product

Advantages

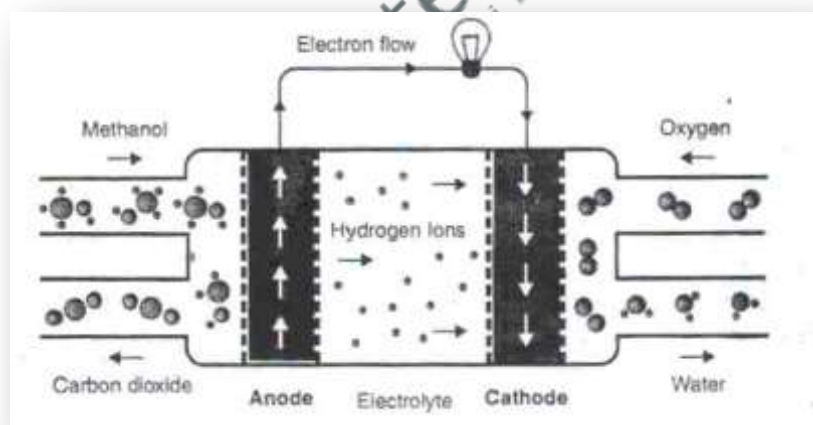
- Highly efficient energy conversion process
- No need of charging
- Absence of harmful waste products
- Silent process

Limitations

- Cost of power is high because of cost of electrodes
- Fuels are stored as gasses under high pressure
- Power output is moderate

Construction, working and applications of Methanol-Oxygen (MeOH-O₂) fuel cell.

In methanol oxygen fuel cell, methanol is used as fuel and oxygen as oxidant. A typical methanol oxygen fuel cell is shown in the figure.



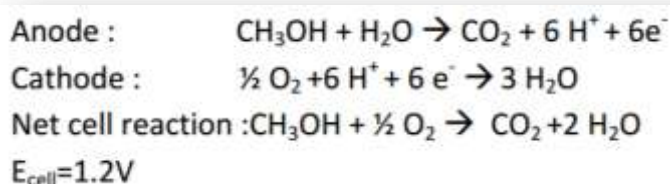
Construction: Has two electrodes, anode and cathode

- Anode – porous nickel electrode impregnated with Pt/Pb catalyst
- Cathode-porous nickel sheet coated with silver catalyst
- Electrolyte-H₂SO₄
- Voltage-1.2V

Working:

- Process begins when methanol molecules enter anode

- A catalyst, which speeds the reactions at the electrodes
- Electrolyte allows protons to move towards cathode, but not electrons
- Instead electrons are directed through an external circuit which creates electrical current
- Oxygen molecules pass through cathode
- Oxygen and protons combine with electrons after they have passed through the external circuit
- Oxygen and protons combine with electrons to produce water and heat
- Overall reaction is split into two partial reactions: oxidation and reduction



Solid Oxide Fuel Cell (SOFC)

A class of fuel cells which use a solid oxide material as the electrolyte

Construction & Working of SOFC:

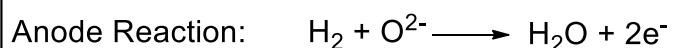
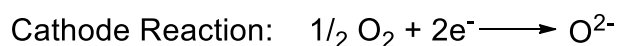
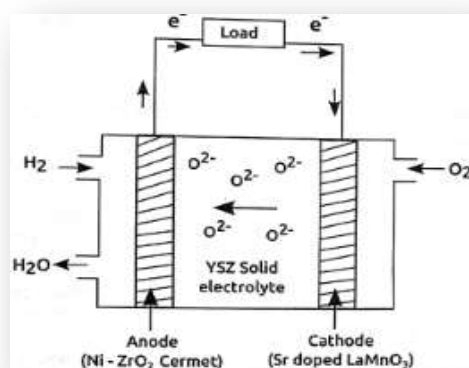
Construction: Electrodes:

- Anode – Ni-ZrO₂ (Porous, Heat resistant ceramic & Sintered material- cermet)
- Cathode – Sr-doped lanthanum manganite (Porous, High electronic conductivity, good oxygen reduction)
- Electrolyte: Ytria stabilized Zirconia (YSZ) (Thin, O²⁻ conductor & electrical insulator)

Working:

As shown in the figure, oxygen atoms are reduced on the porous cathode surface by electrons.

The oxide ions diffuse through the solid electrolyte to the fuel rich and porous anode, where they react with the fuel (H₂) and give off electrons to an external circuit.



Solar energy

Solar energy has the greatest potential to replace fossil fuels as they are fast depleting. A wide range of power technologies exist which makes use of solar energy reaching the earth & convert them into useful forms. Solar energy can be utilized in 2 ways.

1. Direct solar power
2. Indirect solar power

Direct solar power involves only one step transformation. Eg: Sunlight hits a photovoltaic cell, generating electricity.

Indirect solar power involves more than one transformation. Eg: During photosynthesis, solar energy is converted in to chemical energy by plants. These are burnt as fuels to generate electricity.

Advantages of solar energy:

1. Pollution free
2. Local source
3. More economical.

Disadvantages:

1. Practical only in certain areas with favorable climate & latitude.
2. Not available at night.
3. Solar cell technologies produce DC power, which must be converted in to AC power before using.

Photovoltaic cells:

Photovoltaic cells are semiconductor devices that convert sunlight into direct current electricity. As long as light falls on the solar cell it generates electrical power. Solar cells never need recharging.

Construction and Working of a Photovoltaic cell:

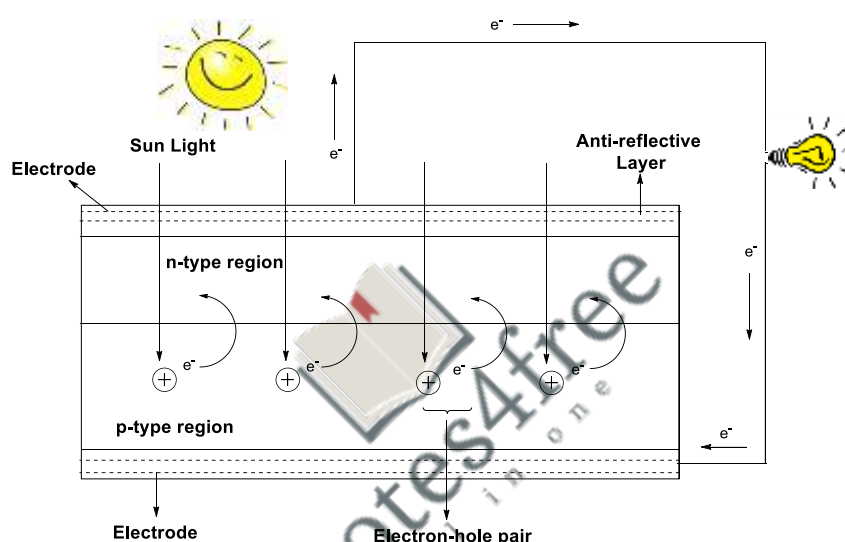
Principle: PV cells rely on photoelectric effect, i.e., the ability of certain elements to emit electrons when electromagnetic radiation of sufficient energy falls on it. The photons possess certain amount of energy as evident from the Plank quantum equation, $E=h\nu$.

Semiconductors have the capacity to absorb light & deliver a portion of energy to carriers of electric current i.e., electrons & holes. A semiconductor diode

separates & collects the current carriers & conducts the generated current in a specific direction.

A typical silicon photovoltaic cell is composed of a thin wafer consisting of an ultra-thin layer of Phosphorous doped silicon (n – type) on top of Boron doped silicon (p- type). Hence a p-n junction is formed between the two.

A metallic grid forms one of the electrical contacts of the diode & allows light to fall on semiconductor between the grids. An antireflective layer (silicon nitride or TiO_2) between the grids increases the amount of light transmitted to the semiconductor. A metallic layer on the back of the solar cell is used as other side electric contact.



When light radiation falls on the p-n junction diode, electron – hole pairs are generated by the absorption of the radiation. The electrons are collected at the n-type and holes are collected at the p-type end. When these two ends are electrically connected through a conductor, there is flow of current through the external circuit. Thus photoelectric current is produced.

Importance of Photovoltaic cells:

- With the conventional energy reserves fast depleting, photovoltaic cells are considered to be future sustainable energy systems. Solar energy being unlimited, inexhaustible, renewable, photovoltaic cells are means to make use of this energy.
- Photovoltaic cells can be used for telecommunication equipment, solar home systems, large scale electricity generation, etc.

- During the production of photovoltaic energy, no harmful emission or transformation of matter occurs, no noise is produced.
- Global warming due to CO₂ can be avoided.
- Photovoltaic cells can be used as roof integrated systems, providing power & also serving as optical shading for the space below & preventing overheating in summer.
- Photovoltaic cells can provide power for spacecraft & satellites.

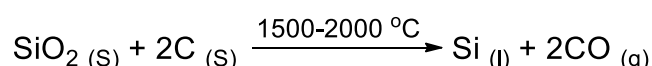
Properties of silicon relevant to photovoltaics:

- Silicon is a semiconductor with a band gap of 1.12eV at 25°C.
- Si is stable in tetravalent state & has a strong affinity for oxygen, forming stable oxides & silicates.
- C is also tetravalent, hence Si & C combine forming strong Si-C covalent bonds. Therefore silicon carbide formed has several applications in solar cells & electronic devices. SiC is an abrasive & can be sliced in to wafers for use as semiconductors.
- Silicon combines with H to form silanes, which are raw materials for the production of amorphous Si & for purification of Si to get semiconductor grade.
- Si also reacts with halogens. Chlorosilanes are highly volatile & can be decomposed to elemental Si at low temperature. Hence they are used in purification of Si.

Production of solar cell grade silicon by Union carbide process:

1. Metallurgical Grade Si (98%):

Step 1: Silica reduced to silicon in electric arc furnace: Quartz and carbon are taken in a crucible. Two carbon electrodes are submerged in the crucible and an electric arc is struck. The mixture gets heated to high temperature and the following reaction takes place.

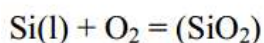
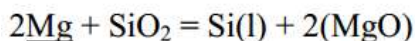
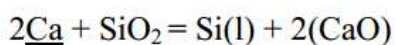
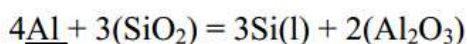


Silicon is obtained in molten state from the bottom of crucible. CO is further oxidized to CO₂ and released into the atmosphere.

Step 2 (Refining): Molten Si treated with fresh silica as flux to remove Al, Mg &

Ca: Molten silicon obtained is treated with oxygen and silica sand. The elements like

Al, Ca and Mg react with silica sand (SiO_2) to form slag and silicon. The slag is removed and molten silicon is poured into moulds when Si solidifies. The silicon obtained is called metallurgical grade silicon.

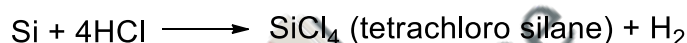
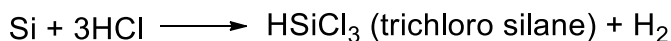


Oxides form slag and separated from Molten Si: $\text{MgO} + \text{SiO}_2 = \text{MgSiO}_3$ (Slag)

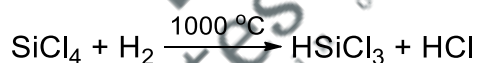
Production of solar grade silicon from metallurgical grade silicon:

Metallurgical grade silicon obtained is further processed in 4 stages to get semiconductor grade silicon or polysilicon.

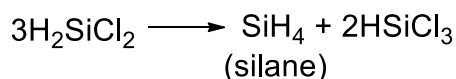
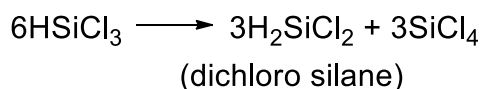
Step 1: Hydrogenation: Metallurgical grade silicon is treated with dry HCl gas at 300°C to form trichlorosilane and a small amount of tetrachlorosilane.



Step 2: Re-Hydrogenation: Tetrachlorosilane is reduced with hydrogen at 1000°C in a reactor, trichlorosilane is obtained.

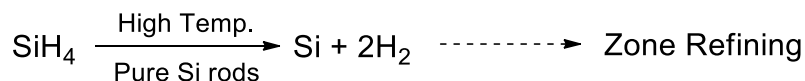


Step 3: Production of Silane (Quaternary ammonium ion exchange resin): The trichlorosilane is then passed through fixed bed columns filled with quaternary ammonium ion exchange resins acting as catalyst. Dichlorosilane and tetrachlorosilane are obtained.

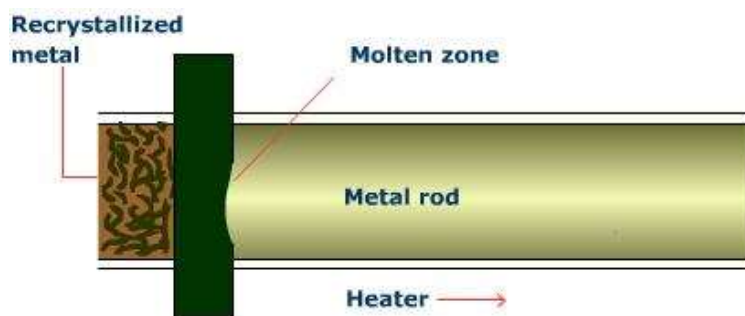


The products are separated by distillation; SiCl_4 & HSiCl_3 are recycled to the hydrogenation reactor & exchange resin respectively.

Step 4: Pyrolysis: Silicon hydride or Silane is further purified by distillation and passed into a reactor containing heated Si rods. Silane gets pyrolyzed to form Silicon.



Purification by Zone Refining:



It is a special method for purification of silicon. It is based on the principle that impurities are more soluble in molten than in the solid material. A zone refiner is used in purification of Si.

A rod of silicon to be purified is clamped to a zone refiner and is heated by RF coil to the melting point of silicon. The heater is moved very slowly from left side to right side. Impurities move towards the molten part of the material as the coil is moved from left to right. Pure silicon solidifies at the left side portion. When the process is complete, right side portion of the rod where impurities are concentrated is removed. This process is repeated to get ultra-pure silicon.

notes4free
All in one

Environmental Pollution

“There is an ecology of the world within our bodies. In this unseen world even minute causes produce mighty effect”.

Today almost every aspect of modern living poses potential health risks. The air we breathe, the water we drink and the places where we live and work may be contaminated with toxic substances or chemical additives. Pollution is the introduction of contaminants into the natural environment that causes adverse change. Environmental Pollution occurs when pollutants contaminate the surroundings; which brings about changes that affect our normal lifestyles adversely. Pollutants are the key elements or components of pollution which are generally waste materials of different forms. Pollution disturbs our ecosystem and the balance in the environment. Environmental Pollution occurs in different forms; air, water, soil, radioactive, noise, heat/ thermal and light.

Types of Pollution

- Air Pollution
- Water Pollution
- Soil pollution
- Noise pollution
- Radioactive pollution
- Light pollution

Air Pollution

The atmosphere (the layer of air that surrounds the earth) is about 150 km thick. However more than half of its total weight concentrated in the troposphere, which is just up to 6.5 km above the earth. The upper portion is called as stratosphere. The air pollution concerned mainly the state of troposphere. The average percentage composition of clean, dry air near sea level is: $N_2 = 78.09$, $O_2 = 20.94$, $Ar = 0.9$, $CO_2 = 0.031$, $Ne = 0.018$, $He+Kr+Xe+H_2+CH_4+ O_3+ CO_x+ NO_x +SO_x = rest$.

Air pollution is most crucial from the public health point of view, because every individual person breathes approximately 22,000 times a day, inhaling about 15-20 kgs of air daily. Air pollution occurs when harmful or excessive quantities of substances including gases, particulates, and biological molecules are introduced into Earth's atmosphere. It may cause diseases, allergies and even death to humans; it may also cause harm to other living organisms such as animals and food crops, and may damage the natural or built environment. Both human activity and natural processes can generate air pollution.

Air Pollutants

An air pollutant is a material in the air that can have adverse effects on humans and the ecosystem. The substance can be solid particles, liquid droplets, or gases. A pollutant can be of natural origin or man-made. Pollutants are classified as primary or secondary.

Primary air pollutants

Primary air pollutants are the pollutants that are directly emitted into the atmosphere through natural or human activities. Examples for Primary air pollutants:

- ❖ Oxides of Sulfur (SO_x)
- ❖ Oxides of Nitrogen (NO_x)
- ❖ Carbon monoxide (CO)
- ❖ Volatile organic compounds (VOC) such as hydrocarbons
- ❖ Particulate matter
- ❖ Toxic metals, such as lead and mercury

Secondary air pollutants

Secondary pollutants are air pollutants that are not directly released into the atmosphere but form when primary pollutants react or interact in the atmosphere. Examples for secondary air pollutant:

- ❖ Ground level Ozone

Oxides of Sulfur (SO_x)

Sulphur dioxide (SO₂) and Sulphur trioxide (SO₃) are referred together as oxides of Sulphur (SO_x).

Sources

Main contributors of emissions are

- Petroleum industries, oil refineries, sulphuric acid plants and sulphides ore-roasting plants.
- Thermal power plants in which Sulphur containing coal and fuels are fired.
$$S + O_2 \longrightarrow SO_2$$
- It is formed by the oxidation of Sulphur dioxide under the influence of sunlight.
$$2SO_2 + O_2 \longrightarrow 2SO_3$$

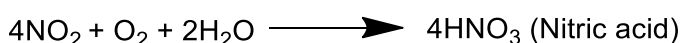
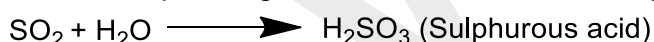
Effects

The presence of this gas in the atmosphere causes

- ❖ Cardiac, respiratory and pulmonary disease
- ❖ Eye irritation, throat troubles
- ❖ Corrosion of metals
- ❖ Damages plants cells such as membrane damage, chlorophyll destruction, growth yield reduction, etc.,
- ❖ Even 1 ppm of SO₃ in air causes breathing discomfort and irritation to the respiratory tract.

Acid rain

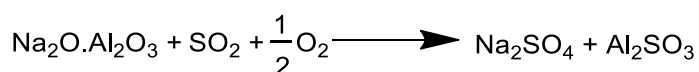
Various industries and automobiles release acidic oxides such as SO₂, SO₃, NO₂, HCl_(g), etc., into the atmosphere. These oxides dissolve in moisture present in atmosphere to form corresponding acids which then fall slowly on the earth as acid rain.



Control

1. Removal of SO₃ from flue gas

Adsorb SO₂ on a suitable adsorbent (sodium aluminate) to form stable sulphates in fluidized bed at 315°C, with subsequent regeneration.



Adsorb SO₂ from flue gases on activated carbon followed by regeneration and conversion to sulphuric acid or elemental Sulphur.

2. Natural dispersion

Natural dispersion of SO_x at high elevation, so that ground level concentrations are acceptable.

3. **Switch to natural gas**, from the conventional high Sulphur fuels like coal and petroleum, reduces SO_x emissions.
4. Use clean Sulphur free nuclear power to generate electricity.

Oxides of Nitrogen (NO_x)

Nitric oxide (NO) and nitrogen dioxide are referred together as oxides of nitrogen.

Sources

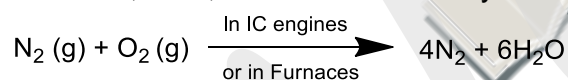
Oxides of Nitrogen are produced from the combustion of fuels (coal, diesel, petrol, etc.). Other sources are acid manufacture, explosive industry and acid pickling plants. Because of continuous increase in the number of vehicle, power plants, industries etc.,

Effects

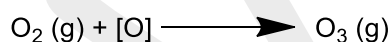
- ❖ In high NO₂ area respiratory illness among children have been reported
- ❖ It is unpleasant in odour and leads to irritation of eyes and even lungs congestion
- ❖ In sunlight, nitrogen oxides and hydrocarbons form 'smog'.

Photochemical Smog: Smog is a mixture of smoke (from coal combustion) and fog in a suspended droplet form. There are two types of smog

(a) Los-Angeles Smog: It is combination of both smoke and fog. It is worst in sunshine with peaks in the afternoon. The oxides of nitrogen (NO and NO₂) along with CO₂, H₂O, CO and unburnt hydrocarbon particles causes Los-Angeles smog.



OR



Hydrocarbons + O₃, O₂, NO_x → Peroxide, ozone, aldehydes, formaldehydes, peroxyacetyl nitrate (PAN) acroline (oxidized hydrocarbon).

These oxidized hydrocarbons and ozone in the presence of humidity cause photochemical smog which dissipates at night.

Photochemical smog causes

- ❖ Irritation to eyes, lungs, nose and throat
- ❖ May damage plants
- ❖ It renders poor atmospheric visibility
- ❖ Cause difficulty in breathing, there by lung's congestion, asthma and bronchitis may results in men living around it.

(b) London Smog: London Smog is a coal smoke and fog. The fog part is mainly SO₂ and SO₃ mixture and humidity. Due to sunlight induced oxidation of SO₂ to SO₃, followed by reaction with humidity, thereby yielding this sulphuric acid aerosol. It is generally bad in the early morning houses becomes worse after sunshine.

Control

There are several methods available to reduce oxides of nitrogen.

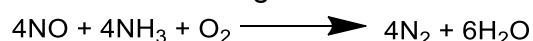
Removal of oxides of nitrogen during combustion

Low NO_x burners ensure that initial fuel combustion occurs within fuel rich conditions that are with low oxygen concentration, such that any gaseous nitrogen produced is reduced to N₂ without oxygen. Advance low NO_x burners can reduce NO_x concentration by up to 30%.

Removal of oxides of nitrogen after combustion

Emission of NO_x generated during the combustion process can be reduced by treating the flue gas. There are number of systems available

- ❖ **Selective catalytic reduction:** In this process ammonia is injected into the flue gas. The nitrogen oxide present in the flue gases react with the ammonia and are converted to nitrogen and water.



- ❖ **Sorption:** Treatment of flue gas by injecting of sorbent (such as carbon, powdered limestone, aluminium oxide) can remove NO_x.

Hydrocarbons

Organic compounds containing only carbon and hydrogen called as hydrocarbons.

Sources

- ❖ Automobile and industrial exhausts are the major sources of hydrocarbons
- ❖ Methane is a naturally occurring hydrocarbon emitted into the atmosphere in large quantities. It is produced by bacteria through anaerobic decomposition of organic matter.



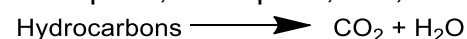
Effects

- ❖ Hydrocarbons at high concentration (>500 ppm) have carcinogenic effects on lungs
- ❖ Inhalation of vapour of benzene, toluene, etc., causes much irritation to the mucous membrane
- ❖ Cyclic hydrocarbons affect nervous system and cause loss of coordination.
- ❖ Methane and benzopyrene creates narcotic effects in human beings

Control

Hydrocarbons and oxides of nitrogen are the major culprits of air pollution. They react to produce peroxy acyl nitrate, O₃, etc., which are chronic secondary pollutants.

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



Particulate Matters

Air born, tiny solid particles and liquid droplets are commonly known as "Particulates". These are also called as "Aerosols". About 2000 million tons of particulate matters per year were released from natural agencies like wind, dust storms, volcanos and salt sprays. About 450 million tons particulates are released by man-made activities like burning of

Environmental Pollution

coal-wood, natural gas etc., and by industrial processes like smelting, mining, fly ash emission from power plants, agricultural burning, forest fires etc.,

The diameter of particulates ranges from 0.0002 μm to 500 μm . Their life varies from a few seconds to several months depending upon the size, density and turbulence of air.

Particulates have the capacity of scattering light and reducing the visibility.

- a. **Dust:** Main sources of dust are mines and quarries, furnaces, power houses, vehicular traffics, house cleaning dusts, poultry, agriculture, forest fire, natural winds, combustion operations, engine exhaust, earth movement, materials handling and processing and a hundred other activities raise dust in the atmosphere.
- b. **Smoke:** Smoke is a composition of tiny particles of carbon, ash, oil, etc., it is invariably formed by incomplete combustion of fuel (due to insufficient supply of air or faulty method of fuel burning). The major sources of smoke emissions are industries, rails, roads, locomotives, woods, coal, open fires, furnaces, diesel engines, power plants, etc.,
- c. **Fly ash:** Fly ash is the fine ash from the penalized fuel (coal) burned in power stations.
- d. **Smog:** Smog is a mixture of smoke and fog in suspended droplet form.
- e. **Fumes:** Fumes are produced by the various chemical reactions like smelting, roasting, calcination, fractionation and distillation.
- f. **Sprays:** Air born tiny droplets or particles emerged from a parent atom by the way of disintegration. **Example:** spraying insecticides, pesticides.

Effects

- ❖ On man, atmospheric dust causes an allergic and respiratory diseases, silicosis (if dust contains silica) and asbestosis (if dust contains asbestos). Dust also causes corrosion and soiling.
- ❖ Loss of fuel values through imperfect combustion. Spoiling of clothing, rags, exteriors finish of buildings. The incidence of cancer is being increasing related with smoke.

Control

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

- a. **Centrifugal cyclones:** Cyclones are low cost, low maintenance centrifugal collectors that are typically used to remove particulates in the size range of 10-100 microns. But the fine dust-removal efficiency of cyclones is typically below 70%, whereas electrostatic precipitators (ESPs) and filter baghouse provide removal efficiency of 99.9% or more.
- b. **Electrostatic precipitator:** Electrostatic precipitator removes particles by using an Electrostatic field to attract the particles onto the electrodes. Collection efficiency for well-designed, well-operated and well-maintained system are typically in the order of 99.9% or more of the inlet dust loading.
- c. **Filter and dust collector (bag-houses):** Filter and dust collector collect dust by passing flue gases through a fabric that acts as a filter. The most commonly used is the bag-filter or bag-house. Accumulated particles are removed by mechanical shaking, reversal of gas flow or a stream of high-pressure air.
- d. **Wet scrubber:** Wet scrubbers rely on a liquid spray to remove dust particles from a gas stream.

Carbon Monoxide (CO)

Sources

CO is released by the partial combustion of fuels in automobiles, industries and oil refineries. Cigarette, beedi smoke and domestic heat appliances are the other sources of CO. It is estimated that about 290 million tons of CO is released into the atmosphere annually. Although it is colourless, odorless, non-corrosive, yet is very toxic in nature.

Effects

- ❖ It causes headache, visual difficulties
- ❖ Paralysis and even leads to death in the human beings
- ❖ CO reacts with red pigment (haemoglobin) to form “carboxyhaemoglobin” thereby impairs the transfer of oxygen to the tissues. In other words the presence of CO reduces the oxygen-carrying capacity of blood. This ultimately causes headache and lassitude, especially by inhaling tobacco smoke.
- ❖ Prolonged exposures can even lead to death.
- ❖ CO also affects the cardio-vascular system, thereby causing heart diseases.

Control

- ❖ Modification of internal combustion engines
- ❖ Development of exhaust system reactor which will complete the combustion process and change the potential pollutant into more acceptable material
- ❖ Development of substitute fuel for gasoline which will yield low concentration of pollutants upon combustion
- ❖ Development of pollution free power sources such as fuel cells to replace the internal combustion engines

Toxic metals, such as Mercury and Lead

Mercury

Sources

- ❖ Natural sources of mercury include volcanoes, natural mercury deposits and release from the oceans.
- ❖ Man-made sources include coal combustion, waste incineration, metal processing industries.
- ❖ Other sources include mercury containing products, for example,
 - Batteries
 - Thermometers and barometers
 - Electric switches and relays in equipment
 - Lamps
 - Dental amalgam
 - Skin lightening products and other cosmetics
 - Pharmaceuticals

Effects

Mercury exists in various forms:

- Elemental (or metallic).
- Inorganic (to which people may be exposed through their occupation).
- Organic (Example: Methylmercury, to which people may be exposed through their diet).

Environmental Pollution

These forms of mercury differ in their degree of toxicity and in their effects on the nervous, digestive and immune systems and on lungs and kidneys.

- Elemental and methylmercury are toxic to the central and peripheral nervous system
- The inhalation of mercury vapour can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys.
- The inorganic salts of mercury are corrosive to the skin, eyes and gastrointestinal tract.
- Symptoms of exposure to different mercury compounds include tremors, insomnia, memory loss, neuromuscular effects, headaches and cognitive and motor dysfunction.

Control

- ❖ Promote the use of clean energy sources that do not burn coal.
- ❖ Eliminate mercury mining and use of mercury in gold extraction
- ❖ Discontinue the usage of non-essential mercury containing products.

Lead

Sources

- ❖ Lead can be found in many products and locations. The most common source of lead poisoning is dust and chips from old paints.
- ❖ 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

Lead is known to be toxic to human metabolism. It enters the body either as inorganic lead (Pb^{2+}) or as TEL.



It is known that lead ions inhibits atleast 2 enzymes that catalyse the reaction for biosynthesis of haemoglobin. Consequently the main symptom is "anaemia".

TEL: (Antiknocking agent used for improving the performance of gasoline in automobiles) is evenmore poisonous than Pb^{2+} . In liver, TEL converted to $(\text{C}_2\text{H}_5)_3\text{Pb}^{2+}$ ions and therefore attack on enzymes in various location such as brain. Consequently brain damages due to acute lead-poisoning. It also affects the CNS and impairs kidney functions.

Lead poisoning is usually treating withchelating substances which can form stable complex ions with Pb^{2+} . Most common effective compounds for removing Pb ions from blood and tissues is EDTA.

Control

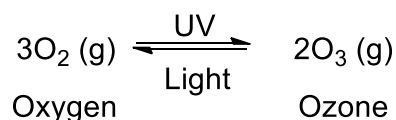
- ❖ Lead smelting plants should design their storage piles in such a way that the movement of lead materials are minimized to lessen exposure to wind and air.
- ❖ Eliminate lead contamination in drinking water by processes such as reverse osmosis, distillation and filtration using carbon filter specifically manufactured for lead removal.

Environmental Pollution

- ❖ To minimize plant absorption of lead content in agricultural soil, it is advised to maintain the soil pH level at 6.3. Another method to minimize plant absorption is by adding organic matter, like composted leaves and manure, because lead contents has the tendency to bind with organic matter.

Ozone

It is an allotrope of oxygen, is produced in the upper layer about 20 km above earth's surface in the atmosphere from oxygen gas by the absorption of ultraviolet light.



Thus air in the upper layer is quite rich in ozone. Ozone checks the entry of UV light from sunlight otherwise sunlight would destroy many of the organic materials necessary for life. Life would not have evolved or existed in the present form, if the UV light were not checked from reaching the surface of the earth. Thus ozone layer formation has helped in the existence of human-life in the present form.

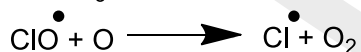
Cause of Ozone depletion

Chlorofluorocarbons (CFCs) are the exhausts of supersonic aircrafts and jumbo jets flying in the upper atmosphere. These got accumulated at high altitudes and undergo decomposition under the influence of UV radiation. One of the main decomposition product is chlorine. Each atom of chlorine so released reacts with more than 10^5 molecules of ozone converting the ozone into oxygen. Consequently gradual depletion of ozone layer takes place and the effective capacity of ozone layer to stop UV radiation entering the environment diminishes.

The typical reaction causing depletion of ozone layer by CFCs are given as



The Cl atoms catalyze the dissociation of ozone



the overall reaction is, $\text{O}_3 + \text{O} \longrightarrow 2\text{O}_2$

The regenerated Cl atom causes further dissociation of ozone. The ozone depletion is produced in stratosphere.

Effects

They cause skin cancer, swelling of skin, sun burn, skin aging, leukemia, cataract of eyes, lung cancer, DNA breakage, alteration and inhibition of DNA's replication, formation of DNA adducts and may even lead to death.

Control

They have started replacing hydro chlorofluorocarbon (HCFC) and hydrofluoro alkanes (HFA) with CFC' but these substances are greenhouse gases. Hence scientists are returning to Hydrocarbon gases like propane, butane, etc., as refrigerators.

Boiler Feed Water

Water is used in many industries directly as well as indirectly. One of the most important applications of water is in industrial boiler. It is known that water can absorb large quantities of heat then it evaporates to form steam at atmospheric pressure and thus formed, carries huge amount of heat with it. Due to these wonderful properties Water becomes an ideal raw material for heating and power generating processes. **“A boiler is a closed vessel which operates under different pressure. 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 boiler is being used for various purposes like power generation, space heating, process heating, drying, etc. it is known that, Natural water contains different kinds of dissolved and suspended matter and dissolved gases as impurities. These impurities create variety of Boiler problem.

Boiler Troubles

Water can cause following important problems in boiler:

1. Scale and Sludge Formation
2. Boiler Corrosion

1. Scale and Sludge Formation

Water is heated under High pressure to High temperature inside the boiler which makes the water to get evaporated in the form of steam. As Boiling Point of Water is much lesser than that of many impurities, the impurities in water get progressively concentrated inside the boiler. On reaching a saturation point, impurities get precipitated out. The resultant precipitate is called as scale if it is in the form of Thick adherent deposit. The precipitate is called as sludge if it is in the form of loose silky precipitate.

Scales

“The hard deposit adhered to the inner surface of boiler which are difficult to remove are called as scales”.

The scales are formed by the impurities in water such as $MgCl_2$, $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, $CaSO_4$ and silica.



Salt of magnesium form scale due to the formation of $Mg(OH)_2$ which has low solubility. Calcium bicarbonate decomposed on heating produces calcium carbonate which has low solubility in water and hence forms scales.



Solubility of the calcium sulphate decreases along with increase in boiler temperature. Thus it also gets precipitated out in the form of scale.

Silica reacts with calcium and magnesium ion present in Water to form silicates of calcium and magnesium. These silicates form hard and glassy scales on the inner surface of boiler.

Problems caused by scale formation

- Loss of Fuel
- Reduction in boiler efficiency
- Boiler explosion
- Loss of strength of boiler
- Expenses of cleaning

Methods to remove scale

- Loose scale can be removed by using wooden scrapers or wire brushes.
- Blow down operation for loose scale; this operation involves removal of very hard water from a tap at the bottom of the boiler.

- By Thermal shocks, which involve alternate heating and cooling, that makes the scale brittle.
- Chemical treatment with 5 – 10% HCl for carbonates and EDTA for Ca/Mg salts.

Sludge

“The loose collection of suspended solids in the cooler, less turbulent part of the boiler and in the distribution pipes is called as sludge”.

The impurities which have more solubility in hot water than in cold water form sludge. Some salts like CaCl_2 , MgCl_2 , MgSO_4 , MgCO_3 soluble in hot water but get precipitated in cooler parts of boiler. Sludge can be removed by blow-down operation.

Problems caused by sludge formation

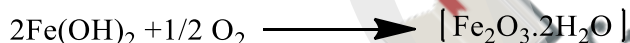
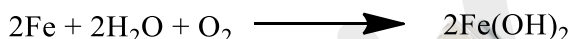
- Loss of Fuel and Reduction in boiler efficiency
- Sludge leads to the clogging of cooler parts of boiler and distribution pipes.
- Expenses of cleaning

2. Boiler Corrosion

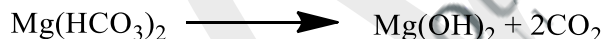
The process of degradation of the boiler surface by the attack of boiler feed water is called as Boiler Corrosion. The dissolved gases like oxygen and carbon dioxide present in the boiler feed water cause boiler corrosion.

Reaction causing boiler corrosion

Natural water usually contains 8 – 9 ppm dissolved oxygen. Generally oxygen level of more than 7ppm present in boiler feed water cause boiler corrosion. The dissolved oxygen present in boiler feed water can attack boiler surface and produce rust as follows:



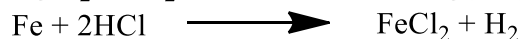
Carbon dioxide is present in the boiler water either from air or due to the presence of residual temporary hardness.



The carbon dioxide dissolves in water to produce carbonic acid, which is slightly acidic in nature and hence cause corrosion.



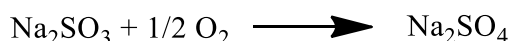
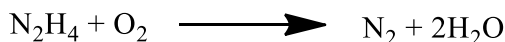
Corrosion also occurs when the pH drops below 8.5 due to acidic nature of feed water. Under this condition, acid may be formed due to the presence of magnesium compounds in feed water.



Controlling of Boiler corrosion

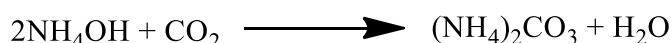
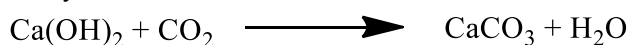
Boiler corrosion can be controlled by reducing the quantity of oxygen, carbon dioxide and any acid from the feed water. This can be achieved by the following ways;

- **By Removing Oxygen:** Dissolved oxygen is first removed by vacuum degasifiers. The remaining traces of oxygen are chemically removed by using oxygen scavengers like hydrazine and sodium sulphite.



Water Chemistry - 2018 Scheme

➤ **By Removing Carbon Dioxide:** Mechanical removal of carbon dioxide can be done by deaeration. Chemical removal of carbon dioxide can be done by treating with lime or ammonium hydroxide.



➤ Finally Acid Impurities if there any, can be removed by treating with alkaline agents like ammonium hydroxide.

Biological Oxygen Demand (BOD)

It is the measure of dissolved oxygen required to oxidize biologically oxidizable impurities. These are the impurities which are oxidized by the microorganisms present in polluted water by utilizing dissolved oxygen present in water.

BOD is defined as **“the amount of dissolved oxygen consumed by microorganisms to oxidize the biologically oxidizable impurities present in 1 litre of water over the period of 5 days at 20°C”**.

BOD is determined by measuring DO of water in the beginning [DO₁] and after the period of 5 days [DO₂].

$$\text{BOD} = [\text{DO}_1 - \text{DO}_2] \text{ mg of O}_2/\text{dm}^3$$

Amount of Dissolved Oxygen (DO) in water can be determination by Winkler's method.

Chemical Oxygen Demand (COD)

COD is defined as **“the amount oxygen required to oxidize all oxidizable impurities present in 1 litre of waste water using a strong oxidizing agent such as acidified K₂Cr₂O₇”**.

Principle

A known volume of the waste water sample is refluxed with K₂Cr₂O₇ solution in sulphuric acid medium. K₂Cr₂O₇ oxidizes oxidizable impurities. The amount of unreacted K₂Cr₂O₇ is determined by titration with standard solution of ferrous ammonium sulphate. The amount of K₂Cr₂O₇ consumed corresponds to the COD of the waste water sample. To find out this, a blank titration without waste water sample is carried out.

Procedure

Back titration: Pipette out 25 cm³ of the waste water sample and 25 cm³ of K₂Cr₂O₇ into a clean conical flask. Add one test tube full of 1:1 sulphuric acid containing silver sulphate and mercury sulphate. Reflux the mixture for half an hour and cool. Add 2-3 drops of ferroin indicator and titrate against the standard ferrous ammonium sulphate solution until the colour changes from bluish green to reddish brown.

Let the normality of the FAS solution be 'Z' N

Let the volume of the FAS solution consumed in titration be 'Y' cm³

Blank titration: Pipette out 25 cm³ of K₂Cr₂O₇ solution. Add one test tube full of 1 : 1 sulphuric acid followed by 2-3 drops of ferroin indicator and titrate against the standard ferrous ammonium sulphate solution until the colour changes from bluish green to reddish brown.

Let the volume of the FAS solution consumed in titration be 'X' cm³

Calculation

$$1000 \text{ cm}^3 \text{ of } 1\text{N FAS solution} = 8 \text{ g of O}_2$$

$$(X-Y) \text{ cm}^3 \text{ of } Z \text{ N FAS solution} = \frac{8 \times (X-Y) \times Z}{1000}$$

$$= \dots\dots\dots \text{g of O}_2 / 25 \text{ cm}^3 \text{ (a)}$$

Water Chemistry - 2018 Scheme

25 cm³ of water sample contains 'a' g of O₂, then 1000 cm³ of water contains

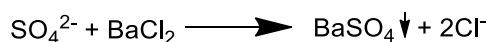
$$\text{COD of water sample} = \frac{a \times 10^6}{25} \quad \text{mg of O}_2 / \text{dm}^3$$

Gravimetric estimation of Sulphate

This method is used if water contains more than 10 ppm of sulphate.

Principle

Gravimetry is a technique in which the amount of analyte in a sample solution is determined by converting (or precipitating) the analyte to some product. In this case sulphate ions in the water sample are quantitatively precipitated as BaSO₄ by treating with BaCl₂ solution containing HCl. Precipitated BaSO₄ is separated by filtration, dried and weighed.



Procedure

Take 200 ml of water sample in a beaker, heat it to boiling and add one test of HCl and heat the solution to near boiling. To the hot solution add one test tube of BaCl₂ solution slowly with constant stirring. Digest the solution on water bath for about 30 min and then allow it to stand for 1 hr. then filter the precipitate through Whatman filter paper and note down the weight of BaSO₄ precipitated (W). Calculate the amount of sulphate using the following formula

233.33 g of BaSO₄ contains 96 g of sulphate

$$\begin{aligned} \text{'W' g of BaSO}_4 \text{ contains} &= \frac{W \times 96}{233.33} \quad \text{g of sulphate/200 ml} \\ &= \frac{W \times 96 \times 1000}{233.33 \times 200} \quad \text{g of sulphate/1000 ml} \end{aligned}$$

Colorimetric estimation of Fluoride by SPADNS method

Principle

Under acidic condition fluorides reacts with zirconium dye (red) such as Zr-SPADNS (sodium 2-sulphophenylazo 1,8-dihydroxy-3,6-naphthalein disulphonate) to form a colourless complex [ZrF₆]²⁻. The red dye becomes progressively lighter as fluoride concentration increases.

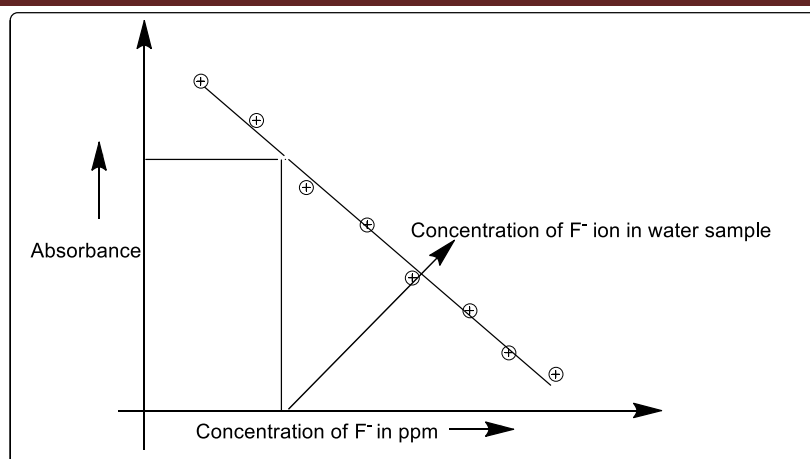
Preparation of reagents

Dissolve 950 mg SPADNS in distilled water and dilute to 500 ml.

Dissolve 133 mg of zirconium chloride octahydrate (ZrCl₂ · 8H₂O) in 25 ml water, add 350 ml of concentrated HCl and dilute to 500 ml with distilled water. Mix equal volume of SPADNS solution and zirconyl acid reagent.

Procedure

1. Prepare a series of standard solutions of sodium fluoride in the concentration range 0 to 2 ppm.
2. Add 10 ml of Zr-SPADNS reagent to each of the solution and dilute to 50 ml and mix well.
3. Measure the absorbance of the solution at 570 nm.
4. Construct calibration graph by plotting absorbance verses concentration.
5. Take suitable aliquot of water sample and repeat step 2 and 3.
6. Using calibration curve calculate the concentration of F⁻ ions in the sample.



Sewage treatment

Water gets contaminated by both industrial as well as domestic waste. Water comes out after industrial use is called as effluent, whereas, water comes out of domestic use is termed as sewage. Domestic sewage mainly consists of organic waste like human waste, food waste, detergents in suspended and dissolved form.

Sewage can treat in different stages to make it to suitable for domestic usage again. Treatment of sewage is carried out in three stages namely,

1. Primary treatments
2. Secondary treatments and
3. Tertiary treatments.

1. **Primary treatments:** In this stage, suspended solids, gases, oil, colour and odour are removed from sewage in different ways. Primary treatment involves,

(a) Screening: Suspended and floating substances are removed in this process. Here, sewage is passed through two metal bar screens or mesh screens. The first one has wide (2-5 cm diameter) and the second one has small openings (0.25 cm diameter). Thus, the first screen retains bigger and the second screen retains smaller floating and suspended matter from the sewage respectively.

(b) Silt and Grit Removal: In this process, water is passed through channels in a grit chamber. Water flows slowly in this chamber (Around 20 meters per minute). As a result of this, silt and grit particles (Heavy pieces like coal particles, pebbles, brick pieces, bone chips and sand) being heavy, settled down at the bottom of chamber.

(c) Oil and grease removal: Oil and grease is removed by passing air under high pressure into sewage water and subsequently, water is passed into low pressure chamber. 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 is removed by skimming.

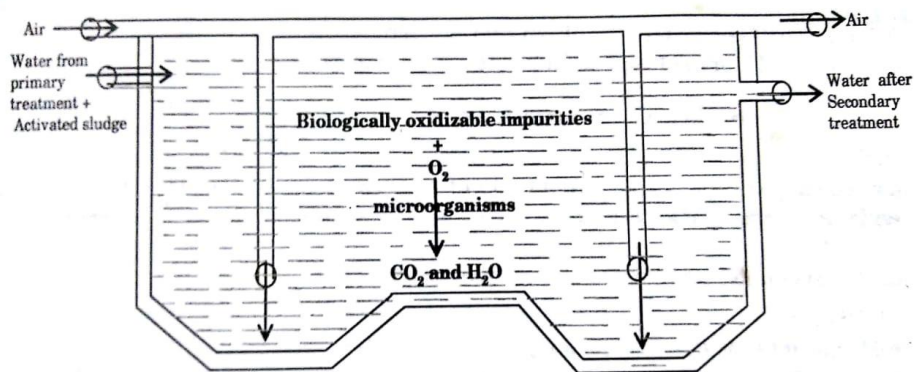
(d) Sedimentation: The finer suspended particles are removed from water in this process. Here, screened water is passed into a sedimentation tank which has a V-shaped bottom provided with an opening. As water enters the tank from the bottom and slowly raising upward, the solid impurities settle down due to gravity. Finally water is taken out of the tank and solid particles in the form of sludge are removed from the bottom.

Finally, dissolved gases are removed by storing the sewage water in large shallow tanks and exposed to the atmosphere, where, gases easily escape from the water surface.

2. **Secondary treatment (Activated sludge process)**

This stage is 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,

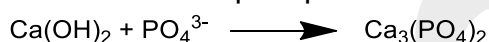
etc.,) taken into large tank. Air is passed into the tank to maintain aerobic conditions. Under aerobic condition, microorganisms oxidize biologically oxidizable impurities into CO_2 and H_2O .



Activated sludge process for secondary (biological) treatment of sewage

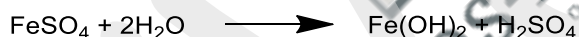
3. Tertiary treatment: In this stage, chemical impurities, bacteria, remaining suspended matter and dissolved gases are removed from waste water.

a) Removal of phosphate: By treating waste water with lime at pH above 11, phosphate is removed as a precipitate of calcium phosphate.



b) Sedimentation with coagulation:

The fine suspended particles are removed by sedimentation in the presence of coagulating agents like alum, FeSO_4 etc. These compounds produce gelatinous precipitate of their metal hydroxides. This gelatinous precipitate adsorbs fine suspended particles on its surface and settles at the bottom of the sedimentation tank.



c) Filtration: The last traces of suspended matter are removed by filtering the water through sand filter beds.

d) Degasification: Dissolved gases like NH_3 , CO_2 , H_2S , etc., are removed from water by passing it through a degasifier. Hot waste water is made to trickle through perforated plates provided on the tower of the Degasifier. High temperature and the exposure to large surface area lead to the stripping out of gases from water.

e) Disinfection: Finally water sample is chlorinated to kill the pathogenic bacteria.



HOCl formed by the above reaction kills all pathogenic bacteria present in water.

Water obtained after tertiary treatment is free from odour, colour, pathogenic bacteria, and has low BOD, hence can be used for domestic purposes.

Softening of Water

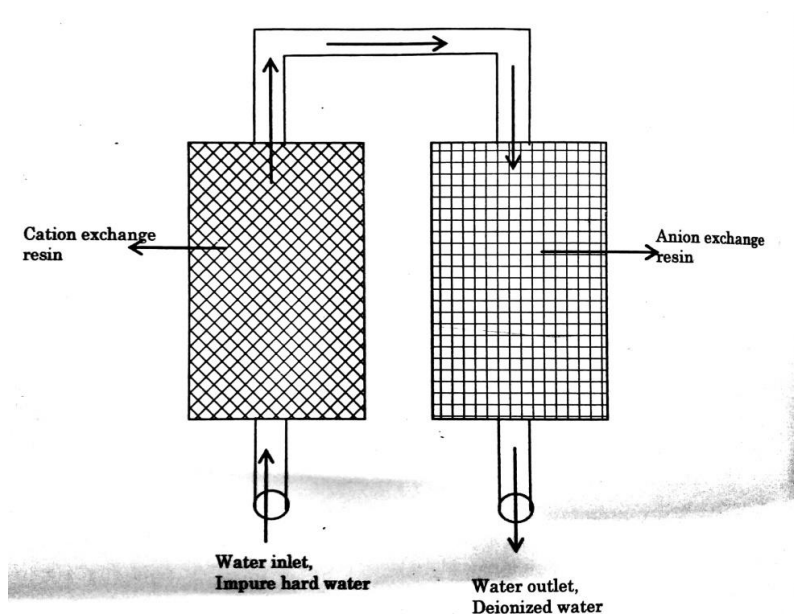
The process of removal of calcium, magnesium, iron salts and other metallic ions (which form insoluble metallic soaps) from water is called softening of water

Softening of water by Ion Exchange Method (Demineralization)

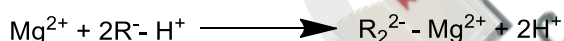
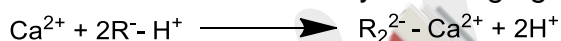
In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin. Ion exchange resins are high molecular weight, cross linked polymers with a porous structure. The functional groups which are attached to the chains are responsible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

Water Chemistry - 2018 Scheme

basic groups which are capable exchanging OH^- for anions (Cl^- , SO_4^{2-}) present in water are known as anion exchange resins (ROH^-).



Process: In this process, cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cations like Ca^{2+} , Mg^{2+} are removed from hard water by exchanging with H^+ ions like as follows:



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

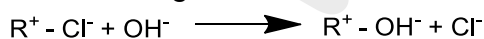


These H^+ and OH^- ions released combine to form water molecule. Thus water coming out of two resins is ions free and called as ion-exchanged or deionized or demineralized water.

Regeneration: When the resins are exhausted and lose their capacity to exchange ions, they are regenerated. The cation exchange resin is regenerated by passing a solution of dilute HCl or H_2SO_4 .



Similarly, anion exchange resin is washed with ammonium or sodium hydroxide solutions.



The columns are finally washed with deionized water and the washings are discarded.

Advantages of Ion Exchange process

1. The ion exchange apparatus, once set up, is easy to operate and control.
2. Both acidic and alkaline water can be softened.
3. Residual hardness is very low and thus water is suitable for high pressure boilers also.

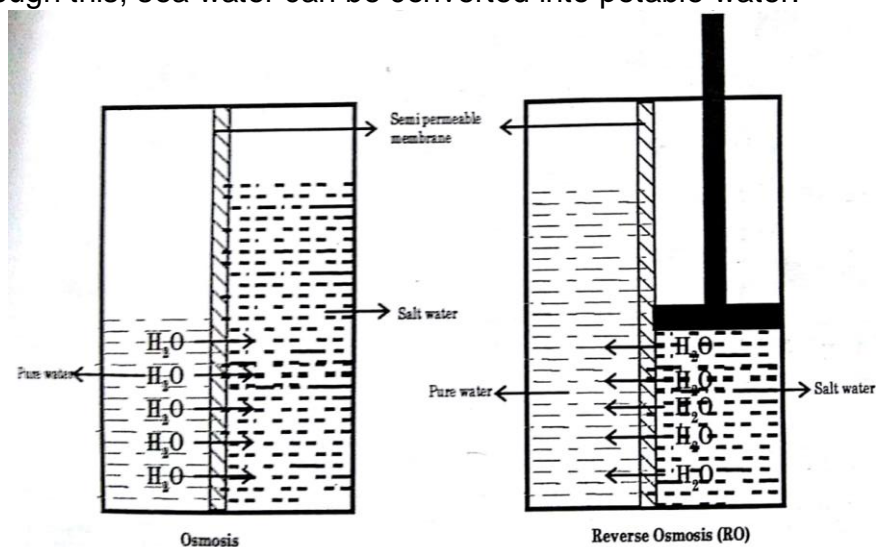
Desalination of water

It is the process of removal of dissolved salts present in water. There are mainly two methods available for desalination.

Reverse Osmosis (RO): If pure water and salt water are separated by a semipermeable membrane, the water molecule flow from pure water (dilute solution) to salt water (concentrated solution). This process of movement of solvent (water) molecule from a dilute

Water Chemistry - 2018 Scheme

solution into concentrated solution through a semi permeable membrane is called as osmosis. Pressure exerted due to osmosis is called as osmotic pressure. Water can be made to flow in reverse direction (from salt water to pure water) by applying pressure on salt water which is greater than the osmotic pressure. This process is called as reverse osmosis. Through this, sea water can be converted into potable water.



A reverse osmosis unit consists of a vessel, a membrane and a high pressure pump. The membranes are generally made of cellulose acetate or nylon. Pressure in the range of 410 – 540 psi is usually applied to bring about reverse osmosis.

Instrumental Methods of Analysis

Analytical chemistry deals with the quantitative and qualitative characterization of materials. The identification of elements/ radicals/ ions/ compounds is called as qualitative analysis. The determination of exact quantity of the constituents present in the substance is called as quantitative analysis. A chemical analysis which involves instruments is called as instrumental analysis.

Advantages

1. It is faster.
2. We get accurate and reproducible result.
3. Low concentration sample solution can be analyzed.
4. Easy to handle large number of samples.
5. Widely applicable in industries.

Disadvantages

1. Instruments are expensive.
2. Calibration is necessary before analysis.
3. Concentration range is limited.
4. Training is needed to handle the instruments.

Potentiometry

Potentiometry is an instrumental analysis in which the amount of a substance in solution is determined by measuring the EMF between two electrodes dipped in the solution.

The potential of an electrode is given by Nernst equation.

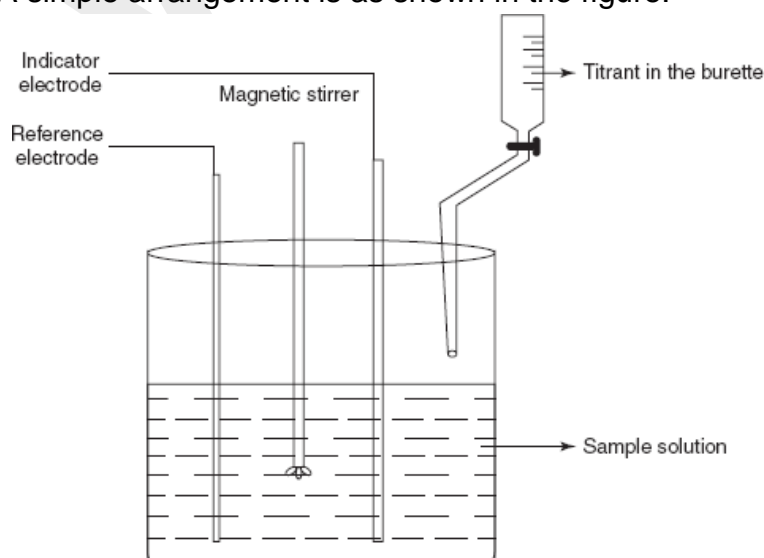
$$E = E^0 + (0.0591/n) \log [M^{n+}]$$

Thus, the potential of an electrode depends upon the concentration of the ion.

Electrode potential is measured by combining the electrode with reference electrode. During titration, concentration of ions changes. Hence potential of the electrode changes. The electrode, whose potential depends on the concentration of the ions to be determined, is called as indicator electrode.

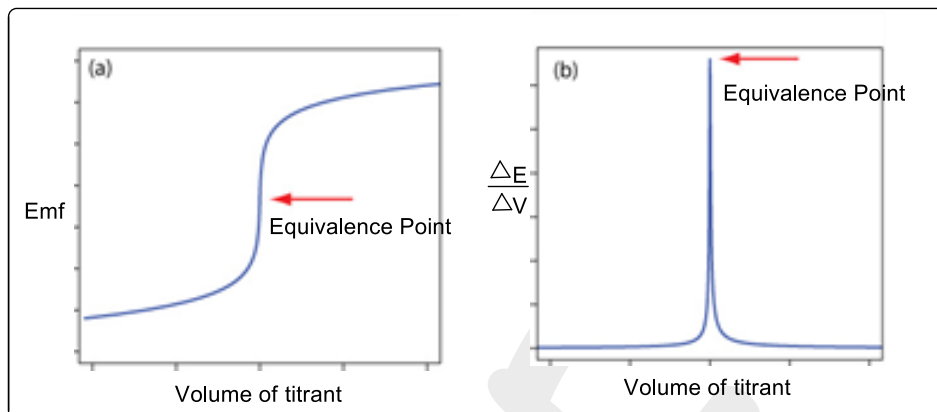
Instrumentation

The potentiometer consists of a reference electrode, an indicator electrode and a potential measuring device. A simple arrangement is as shown in the figure.



Instrumental Methods of Analysis

A known volume of analyte is taken in a beaker and its potential is determined. The titrant is added in increments of 0.5 cm³ and emf is measured for each addition. At the approach of the equivalence point the emf tends to increase rapidly. A few readings are taken beyond the end point. Thus the change in potential at different volumes of titrant are recorded. To locate the end point of the titration emf values are plotted against the volume of titrant or $\Delta E/\Delta V$ values are plotted against the volume of titrant.



Applications

1. To locate end point of the titration.
2. To determine the concentration of the solution by finding emf.
3. To determine pH of the solution using glass electrode.

Potentiometric titration is applicable in oxidation-reduction titration to estimate the concentration of analyte.

In redox titration the indicator electrode is an inert metal such as platinum and the reference electrode is generally a saturated calomel electrode.

The potential of the electrode depends on the concentration of the substance being oxidized or reduced.

$$E = E^{\circ} + (0.0591/n) \log \{[\text{oxidized}] / [\text{reduced}]\}$$

$$E = E^{\circ} + (0.0591/n) \log \{[\text{Fe}^{3+}] / [\text{Fe}^{2+}]\}$$

Immerse a platinum electrode and a reference electrode (calomel electrode) into the given FAS solution in the beaker and connect it to the potentiometer. Add one test tube of dilute H₂SO₄ solution. Measure the emf of the solution. Add standard solution of K₂CrO₇ from the burette in increments of 0.5 cm³. After each addition stir the solution and note the emf. Continue the titration till a sharp increase in emf is obtained and 5 to 6 readings thereafter. Plot $\Delta E/\Delta V$ against volume of K₂Cr₂O₇ and note down the equivalence point.

Colorimetry

Colorimetry is an instrumental analysis in which the amount of a substance in solution which are themselves coloured or which gives colour with a suitable reagent is determined. Colorimetric method of analysis is based on Beer's and Lambert's Law.

Beer's law - states that the intensity of the transmitted light decreases exponentially as the concentration of the media increases arithmetically.

Lambert's law - states that the intensity of the transmitted light decreases exponentially as the path length of the media increases arithmetically.

Instrumental Methods of Analysis

Beer's Lambert's law states that when a monochromatic light is passed through a solution, part of light is absorbed by the solution. The extent of absorption depends on the concentration of the solution and the path length of the light through the solution.

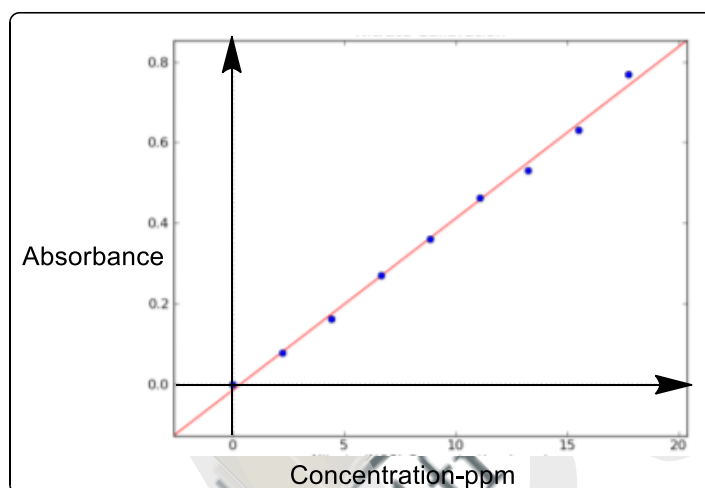
$$A = \epsilon cl$$

A = absorbance c = concentration of the solution, l = path length ϵ = molar absorption coefficient.

If the path length l of the cell is kept constant, absorbance A is proportional to the concentration C.

$$A \propto C$$

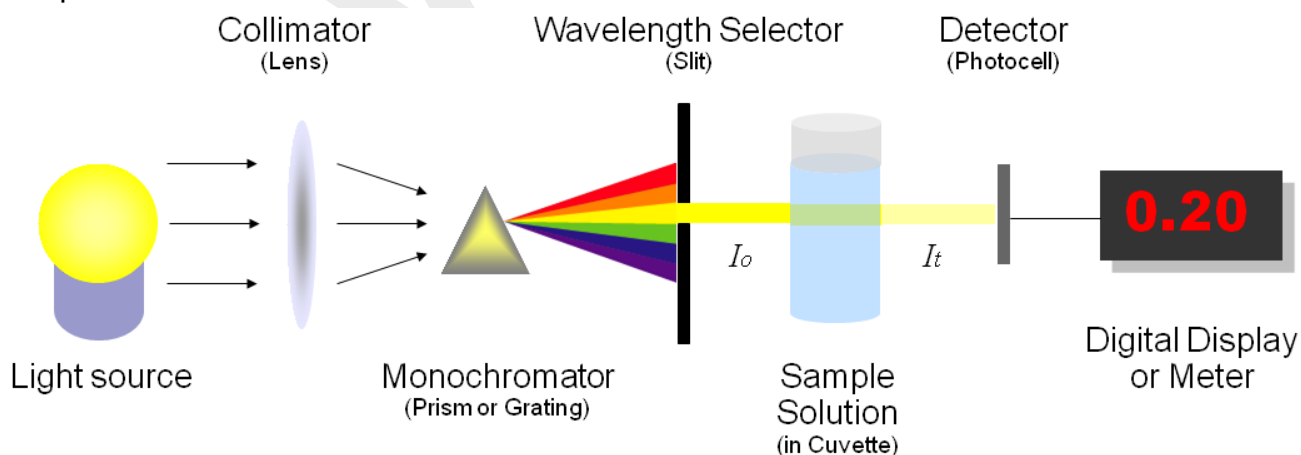
Therefore if absorbance of a series of solution are plotted versus their concentration, a straight line graph result, which is called Beer's-Lambert's curve or calibration curve.



Instrumentation

The instrument used to measure the absorbance of a solution is called photoelectric colorimeter. It consists of,

1. Tungsten lamp as light source
2. A filter which provides the desired wavelength range, where in the solution gives the maximum absorbance.
3. A sample cell
4. A photocell detector



Blank solution is taken in the sample cell and placed in the path of the light beam. Its absorbance is adjusted to zero on the meter. Light from tungsten lamp is allowed to fall on the solution after passing through the filter. The quantity of light absorbed is measured. A plot

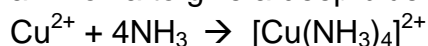
Instrumental Methods of Analysis

of absorbance versus concentration of analyte is used to find the unknown concentration of analyte in the sample.

Applications

1. Used in chemical lab for the analysis of glucose, urea creatinine etc
2. Used in soil testing lab
3. Used in water and food testing lab

Example: Colorimetry is used in the estimation of copper in a solution. Cupric ions react with ammonia to give a deep blue colour due to the formation of cuprammonium complex ion.



Procedure

Prepare 100ml of 0.1M solution of CuSO_4 . Transfer 5, 10, 15, 20, 25 ml of prepared CuSO_4 solution into different 50 ml volumetric flasks using burette. Add 5 ml of ammonia solution to all the flasks and make up to the mark using distilled water. Stopper the flask and shake well.

Prepare a blank solution by taking 5 ml of NH_3 solution in 50 ml of volumetric flask, make up to the mark by using distilled water and shake well. Measure absorbance of all the solutions against blank at 620 nm using a photoelectric colorimeter.

To the given unknown solution add 5 ml of NH_3 and make up to the mark with distilled water. Then a calibration curve is obtained by plotting absorbance against concentration. From the graph the concentration of copper ions is determined.

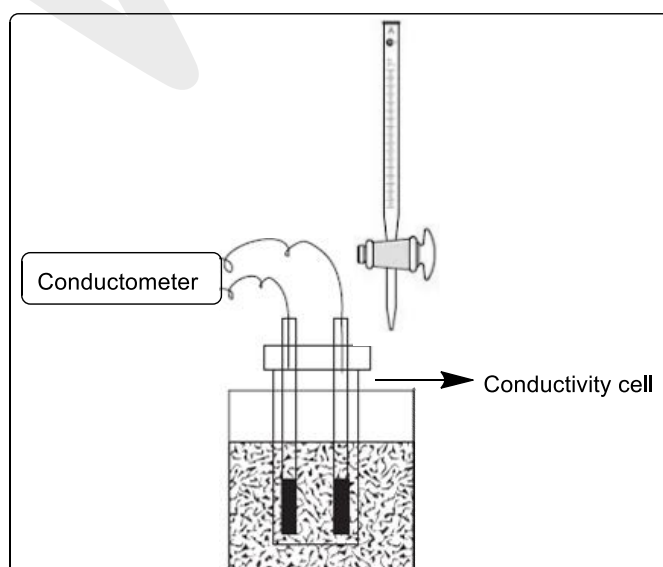
Conductometry

Conductometry is an instrumental analysis in which the amount of a substance in solution can be determined by measuring conductance of the solution.

Theory: Conductivity of the electrolyte solution obeys Ohm's law and at constant temperature it depends on charge, mobility, concentration and size of the ions. Ohm's law states that the current I flowing through a conductor is directly proportional to the applied potential E and inversely proportional to the resistance R of the conductor.

$$E = IR$$

Instrumentation

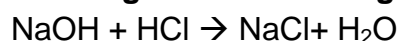


Instrumental Methods of Analysis

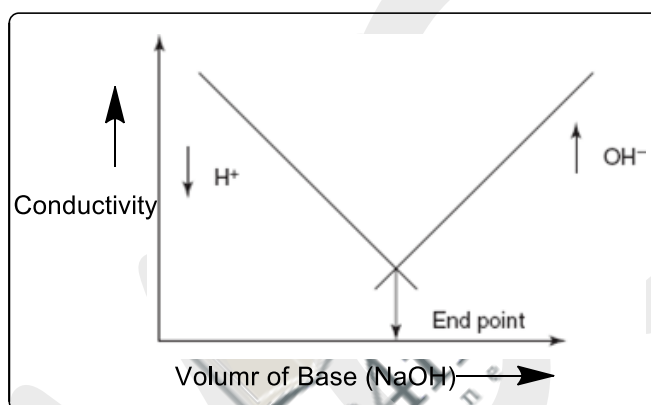
It consists of two platinum electrodes each of unit area of cross section placed unit distance apart. The electrodes are dipped in the electrolyte solution taken in a beaker. Two electrodes are connected to a conductometer and the conductance of the solution is recorded. The titrant is added from the burette in an increment of 0.5 ml. The conductance is measured after each addition. Then a graph of conductance against the volume of titrant is plotted. The point of intersection of the curve gives the end point.

Application

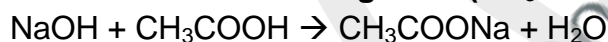
1. Strong acid with strong base (HCl v/s NaOH)



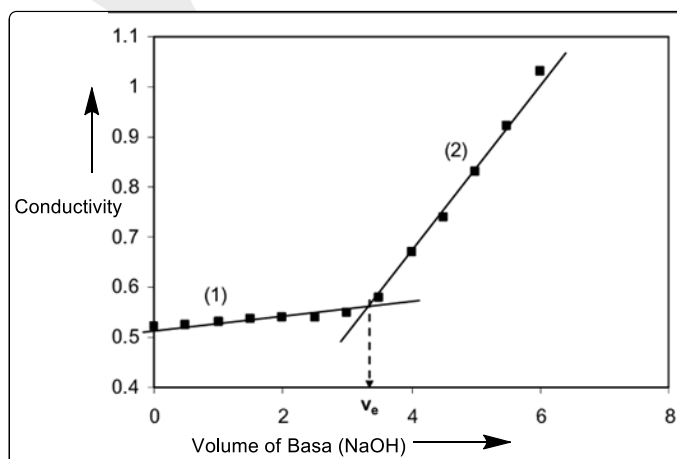
A graph of conductance against the volume of NaOH is as shown in the figure. On addition of NaOH, the conductance decreases because the small and highly mobile H^+ ions in the acid is replaced by heavier and less mobile Na^+ ions. Addition of base beyond the neutralization point leads to increase in the more mobile OH^- ions and conductance increases.



2. Weak acid and strong base (CH_3COOH v/s NaOH)

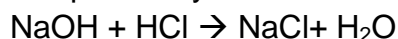


A graph of conductance against the volume of NaOH is as shown in the figure. On addition of NaOH, the conductance increases because the partially dissociated weakly conducting weak acid is converted into fully dissociated conducting salt (sodium acetate). Addition of base beyond the neutralization point leads to increase in the more mobile OH^- ions and conductance increases.

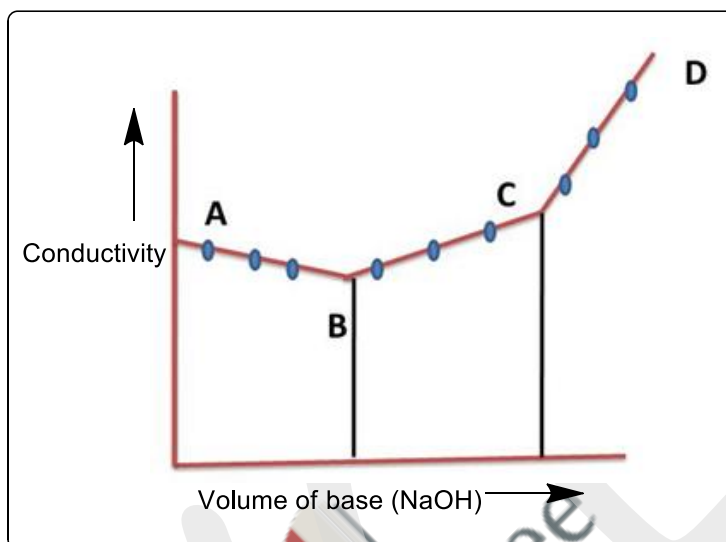


3. Acid mixture with strong base (HCl and CH₃COOH v/s NaOH)

A graph of conductance against the volume of NaOH is as shown in the figure. On addition of NaOH, the conductance decreases because the small and highly mobile H⁺ ions in the acid is replaced by heavier and less mobile Na⁺ ions.



addition of base beyond the first neutralization point leads to moderate increase in conductance because the partially dissociated poorly conducting weak acid is converted into fully dissociated conducting salt (sodium acetate) until the second neutralization point.



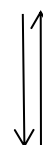
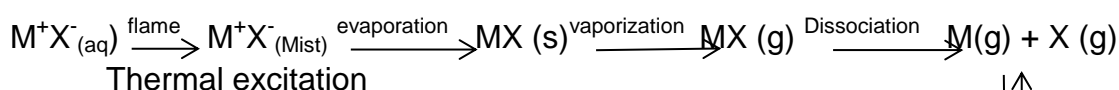
Further addition of base increases the number of more mobile OH⁻ ions and hence conductance increases.

Flame Photometry (Flame Emission Spectroscopy)

Flame Photometry is an instrumental analysis in which alkali and alkaline earth metals such as Na, K, Li, Ca, Ba...are detected and determined. These elements emit characteristic colour to Bunsen flame and the brightness of the flame is directly proportional to the concentration of the element.

Following changes take place when a solution containing a compound of the metal to be investigated is aspirated into a flame.

1. Solvent evaporates leaving behind a solid residue in the form of mist.
2. Vaporization of the solid followed by its dissociation into constituent atoms which are initially in the ground state.
3. Some gaseous atoms get excited by thermal energy of the flame from the ground state to higher energy level (excited state).
4. Excited atoms are unstable and quickly emit photons and return to lower energy state.
5. The intensity of the emitted light is measured using flame photometer.

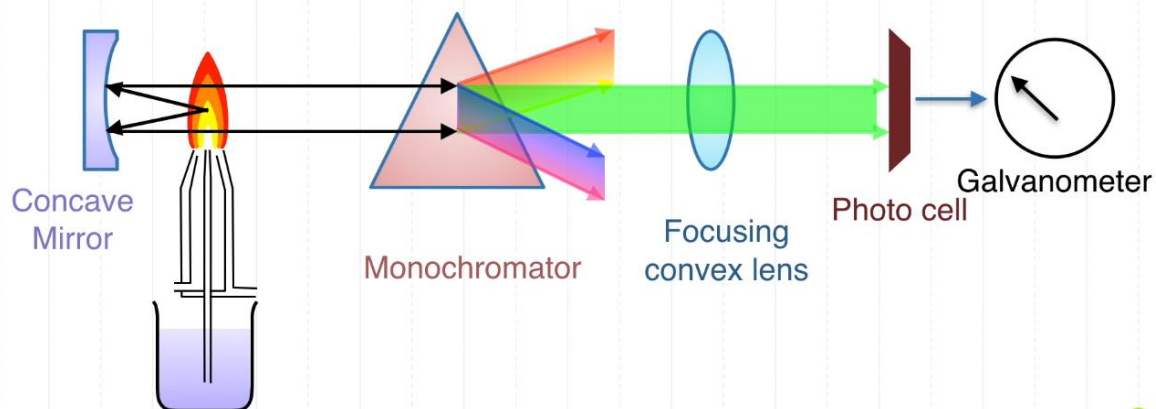


M* (g) excited atom

Instrumental Methods of Analysis

The characteristic wavelength of some metal are Na-589 nm, Ca-623 nm, Li-670 nm, K-766 nm, Ba-554 nm.

Instrumentation



A simple flame photometer consists of the following basic components:

1. Source of flame
2. Nebulizer
3. Optical system
4. Simple colour filters
5. Photo-detector

Applications

- Flame photometer can be applied both for quantitative and qualitative analysis of elements. The radiations emitted by the flame photometer are characteristic to particular metal. Hence with the help of Flame photometer we can detect the presence of any specific element in the given sample.
- The presence of some group II elements is critical for soil health. We can determine the presence of various alkali and alkaline earth metals in soil sample by conducting flame test and then the soil can be supplied with specific fertiliser.
- The concentrations of Na^+ and K^+ ions are very important in the human body for conducting various metabolic functions. Their concentrations can be determined by diluting and aspirating blood serum sample into the flame.
- Soft drinks, fruit juices and alcoholic beverages can also be analysed by using flame photometry to determine the concentrations of various metals and elements.

Example: Determination of Sodium

Prepare 1 ppm of NaCl solution. Transfer 2, 4, 6, 8 and 10ml of standard NaCl solution into 25ml of volumetric flask and dilute up to the mark with distilled water. Measure the emission intensity of each solution and test solution using flame photometry.

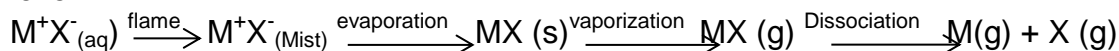
Draw a calibration curve by plotting emission intensity against the concentration of NaCl solution. From the calibration curve, the concentration of sodium in test solution can be obtained.

Atomic Absorption Spectroscopy (AAS)

When a solution containing the sample element is aspirated into the flame, solvent gets evaporated leaving behind the salt in the flame. The salt gets evaporated into vapour of the salt, which further undergo dissociation into the constituent atoms. These metal atoms electrons are excited by the flame energy, but do not have the necessary energy to jump to

Instrumental Methods of Analysis

next quantum energy level. If a light of appropriate energy (wave length) is passed through the flame, the excited electrons absorbs this wavelength photons and jumps to next energy level.



Absorption of radiation

$M^*(g)$ excited atom

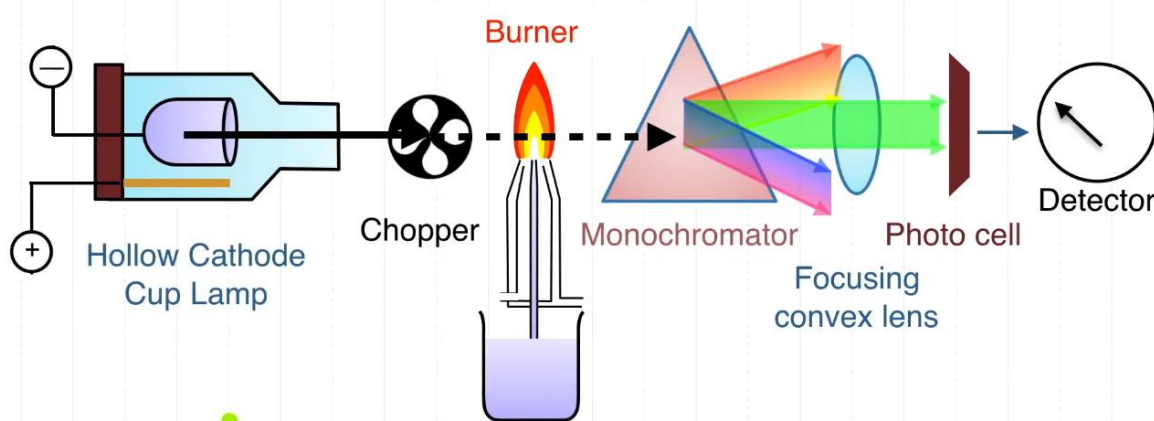
The greater the concentration of metal atoms in solution then more photons are absorbed in the flame. This follows Beer's –Lambert's law.

$$A = \epsilon cl$$

A = absorbance c = concentration of the solution l = path length ϵ = molar absorption coefficient.

The signal strength after the flame, decreases with increase in concentration. So by measuring the absorbance by a suitable detector, the concentration can be determined.

Instrumentation



Atomic absorption spectrometer consists of

1. Hollow cathode lamp: is a source of light in which cathode is coated with a metal to be analysed.
2. Nebulizer: It produces fine spray of the sample and introduce it into the flame.
3. Burner: here the sample is burned with the flame produced by the fuel and oxidant. The sample after evaporation and vapourization leaves a residue of neutral atom.
4. Fuel and oxidant: proper combination of fuel and oxidant are used to produce required temperature commonly used fuel are propane, hydrogen and acetylene and oxidants are air or oxygen.
5. Monochromator and detector: the radiation from the hallow cathode lamp is passed through a monochromator to separate the element specific radiation from other radiation emitted by the radiation source and finally measured by a detector.

Applications

1. Used in the quantitative analysis of metal element in soil sample, body fluids, environmental sample like ground water.
2. Used in food industries.
3. Estimate lead in petroleum product.

Nano Materials (2018- Scheme)

The materials having at least one dimension in the nano scale are called nanomaterials. The study of these nanomaterials is known as nanoscience.

Size dependent properties of nanomaterials

Materials in the nano scale exhibit physical properties different from the bulk. Properties of any bulk material are independent of its size (e.g., melting point of gold remains same whether the size of gold is 1gram or 1Kg. A piece of gold is golden however big or small it is). But in nanoscale range, a material with same structure and composition will show different properties when the size of material is slightly varied. Material in the nano size range exhibits these size dependent properties, because a transition from atom or molecules to bulk form takes place in this size range. Some of the size dependent properties of nanomaterials are,

1. Surface area

If a bulk material is subdivided into individual nanomaterials, surface area is enormously increased. Properties like catalytic activity, gas adsorption and chemical reactivity depend on the surface area. Therefore nanomaterials can show specific surface related properties that are not observed in bulk material.

Example: Bulk gold is catalytically inactive. But gold nanoparticles are catalytically very active for some redox reaction.

2. Electrical properties

The electronic bands in bulk material are continuous due to overlapping of orbitals of billions of atoms. But in nano size materials, very few atoms or molecules are present. So the electronic bands become separate and the separation between different electronic states varies with the size of nano materials. Hence some metals which are good conductor in bulk become semiconductors and insulators as their size is decreased to nano level.

3. Optical properties

The discrete electronic states of nanomaterials allow absorption and emission of light of specific wavelength. Hence, nanomaterials exhibit unique colour different from bulk material.

When light hits the surface of metal particles, electrons present on the surface starts oscillating back and forth in a synchronized way in a small space and the effect is called as surface Plasmon resonance (SPR). Resonating electrons have cross sectional area very much higher than the nanoparticle. Depending on the frequency of oscillation, resonating electrons can capture radiation of different wavelength. Therefore nanoparticles of different size can scatter radiation of different wavelength. Hence some nanomaterials exhibit unique colour different from bulk material.

4. Catalytic Property

The catalytic property of material depends on particle size. If the size of the particle reduces from bulk to nano scale surface to volume increases drastically, that leads to very high catalytic activity of the same material.

Example: Catalytic property of gold nanoparticles. Although bulk gold samples are practically inert, nanometer-sized gold particles have been proven to be highly active for several reactions, including

- Low temperature oxidation of CO
- Partial oxidation of hydrocarbons
- Water gas shift reaction
- Reduction of nitrogen oxides when dispersed over certain oxides and carbides

5. Thermal property

Melting point is defined as the temperature at which the atoms, ions or molecules in a substance have enough energy to overcome the inter-molecular force that hold them in a fixed position in a solid.

As the size of the material decreases to nanoscale their melting point decreases. Because the surface atoms are in contact with only fewer atoms in nanomaterial and require lesser energy to overcome inter-molecular force.

Example: 3 nm CdSc nanocrystal melts at 700K compared to bulk CdSc at 1678K.

Synthesis of nano material

There are two approaches for the synthesis of nanomaterials. They are

1. Top down approach
 2. Bottom up approach
1. Top down approach refers to successive cutting of a bulk material to get nanoparticles.
 2. Bottom up approach is the building up of a material from the bottom, that is atom by atom, molecule by molecule or cluster by cluster.

In bottom up approach desired nanomaterials is built from bottom, by orderly assembling the growth species like atoms or ions or molecules. There are many advantages of bottom-up approaches. They are

1. The methods are simple, versatile and economical.
2. These methods provide better control over chemical composition, size, microstructure and aspect ratio.
3. Nanostructures with less defects are high purity can be synthesized.

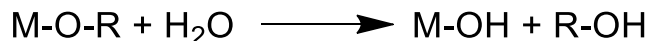
Some of the bottom up approaches are,

1. Sol-gel process

Sol gel process is used to produce nanostructure of metal oxide material. Sol gel process involves following step,

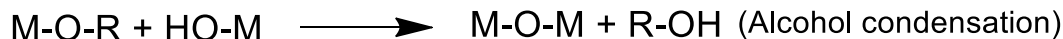
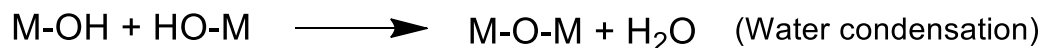
Step-1: Hydrolysis

A sol is prepared by dispersing metal salts or metal alkoxide used as precursors (starting materials) in a solvent and then subjected to hydrolysis as follows.



Step -2: Poly-condensation (aging)

Hydrolyzed species undergo poly-condensation with each other or with unhydrolyzed species.



The metals (M) are Si, Ti, Al, Zr etc.,

Aging process may exceed seven days.

Step 3: Drying

The sample obtained is heat treated to obtain nanoparticles.

Example: TiO₂ nanorods are prepared by sol-gel method using anodic aluminium oxide (AAO). A solution is obtained by dissolving titanium isopropoxide in ethanol. Acetyl acetone dissolved in a mixture of ethanol and water is added to titanium isopropoxide solution to obtain a sol. AAO membrane is dipped in this sol. A required volume of HCl is added to control hydrolysis and condensation reaction resulting in gel. The sample is dried and washed with NaOH to remove AAO. Nanorods of TiO₂ obtained by calcining the sample at 400°C for 24h.

Advantages

- Monosized nano particle can be synthesized by this method,
- Materials like glasses, glass ceramics can be prepared at low temperature.

2. Precipitation method

Precipitation method involves following process.

1. An inorganic metal salts (such as chloride, nitrates, acetate or oxychloride) is dissolved in water.
2. Metal cation in water exists in the form of metal hydrate species such as $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$.
3. The species are hydrolyzed by adding a base solution, such as NaOH or NH₄OH.
4. On increasing the concentration of OH⁻ ions, the hydrolyzed species condense with each other to form either metal hydroxide or hydrous metal oxide precipitate.
5. The precipitate is then washed, filtered and dried to get nanoparticles.

Example: Ruby coloured aqueous solution of gold nanoparticle is obtained by reducing an aqueous gold salt with phosphorus in a mixed solvent (carbon di sulphides/water).

Advantages:

- The process is economical.
- Wide range of single and multi-components of oxide nano powder can be synthesized.

3. Chemical vapour condensation (CVD)

In CVD process, nanoparticles are synthesized from the gaseous phase by a chemical reaction or decomposition of precursors at high temperature. In this method precursors

is vapourized and mixed with an inert carrier gas like N_2 and the mixture is fed into the reactor. Reactor is maintained at a temperature required for the reaction. Precursors undergo reactions producing a product which is deposited over the substrate. The by-products and left over from the reactions are passed on to the gas phase, which are easily removed from reaction chamber. Reaction is often catalyzed by the catalyst present on the substance.

In CVD, proper choice of precursor is very important. Precursor used should be highly pure and stable at room temperature with sufficient volatility.

Example: GaAs semiconductor nanoparticles can be synthesized by CVD from organometallic precursor. Trimethyl gallium and AsH_3 are used as precursors and hydrogen is used as carrier gas as well as reducing agent.

Advantages:

- Nanomaterial can be synthesized in large scale
- CVD does not require ultrahigh vacuum.

Nano scale materials

1. Fullerenes

A fullerene is a class of molecules made of carbon atoms having closed cage like structure. Many number of fullerene molecule with different carbon atoms like C_{60} , C_{70} , C_{74} , C_{76} , C_{78} etc., have been prepared and investigated. The smallest stable and also most abundant fullerene is C_{60} molecule commonly called as Buckminster fullerene.

Structure

Fullerene have closed cage like structure built up of fused pentagons and hexagons. The pentagons provide curvature required to form closed structure. All fullerenes contain 12 pentagons and different number of hexagons. Each fullerene has $2(10+M)$ number of carbon atoms corresponding to 12 pentagons and M number of hexagons. All carbons atoms in C_{60} are sp^2 hybridized and trigonally bonded, similar to graphite.



Synthesis

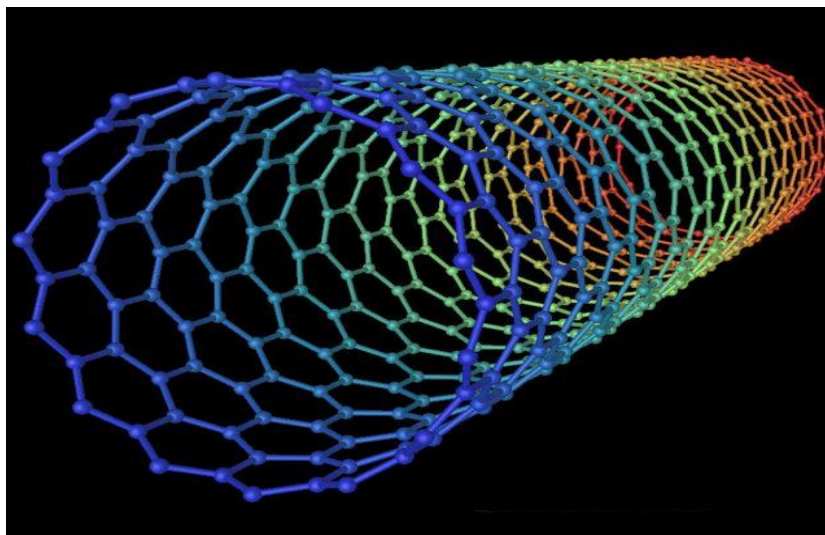
Fullerenes are prepared by vaporization of graphite at very high temperature and condensing the vapour in inert atmosphere. Graphite is vapourized by setting up an electric arc between two graphite electrode in a controlled atmosphere of helium gas. The temperature at the tip of electrode is more than 4000°C and pressure of He gas is 150-200 torr. A mixture of various fullerenes is obtained by condensing the evaporated carbon. The main product is the fullerene C_{60} . It is extracted and crystallized using benzene as solvent.

Properties and application

1. Potassium is intercalated in the crystal structure of C_{60} to get a compound with the composition of K_3C_{60} . This compound has metallic properties and becomes superconducting when cooled.
2. C_{60} molecule is used to protect materials from damage by intense incident light radiation.
3. Polymer composite of C_{60} molecule are used in making organic photovoltaic cells, used as catalyst and some polymer composite of C_{60} molecule are used in photocopying applications.
4. C_{60} molecule is used as hydrogen storage material for fuel cells

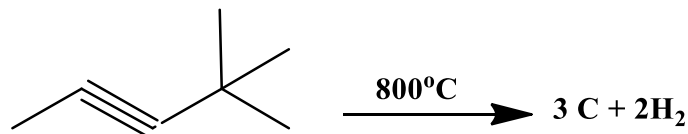
2. Carbon Nano Tubes(CNTs)

A carbon nano tubes is tubular structure made of carbon atoms, having diameter of nano meter but length in micrometers. CNT are regarded as allotrope of carbon. Carbon nano tube is considered as folding of a single layer of graphite sheet. If a single graphite sheets we get single wall carbon nano tube whereas more than two sheets we get multi wall carbon nano tube. Nano tubes have sp^2 hybridized C atoms with a C-C bond. They behave as semiconductors. Doping changes their resistivity characteristics.



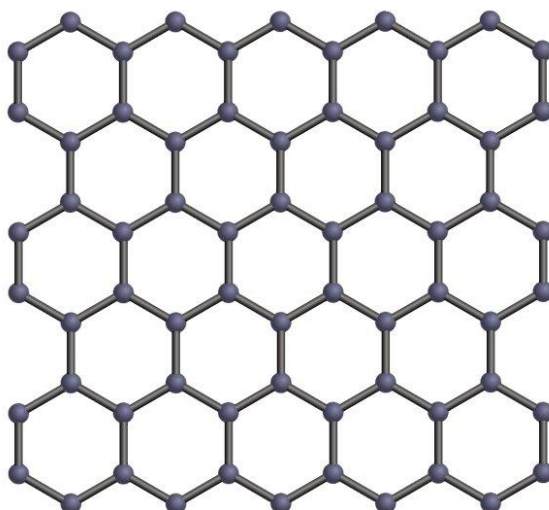
Synthesis of CNTs

Carbon nano tubes Found naturally in the combustion product of graphitic electrode and are also readily synthesized by Chemical Vapour Deposition (CVD) from hydrocarbons, using iron or cobalt catalyst. Carbon nano tube is synthesized by pyrolytic decomposition of propylene at 800°C, using an anodic aluminium oxide (AAO) film as a structure directing template.



3. Graphene

Graphene is a two dimensional crystalline allotrope of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It has high electrical conductivity and act like a semi-metal with a small overlap between the valence and the conduction band.



Its carbon atoms are densely packed in a regular hexagonal pattern. The atoms are about 1.42 Å apart. Each carbon atom is bonded to three other carbon atoms and is sp² hybridized.

Properties

- ❖ Graphene has excellent electronic conductivity, because its conduction and valence bands meet at the Dirac point (zero-gap semiconductor).
- ❖ Graphene has unique optical properties, produces an unexpectedly high opacity for an atomic monolayer in vacuum.
- ❖ Thermal transport in graphene is an active area of research which has attracted attention because of the potential for thermal management applications.
- ❖ Graphene melts at nearly 4125 K, graphene melts into an agglomeration of loosely coupled double bonded chains, before becoming a gas.

Nano Materials (2018- Scheme)

- ❖ Graphene is the strongest material ever tested, with an intrinsic tensile strength of 130.5 GPa.

Applications

- ❖ Graphene is flexible conductor that holds promise for various device applications, including solar cells, light-emitting diodes (LED), touch panels and smart windows or phones.
- ❖ Graphene has also been used in other fundamental electronic devices, such as capacitor and Field Effect Transistors (FETs), in which it can act as an atomically thin channel.
- ❖ Graphene supercapacitor serves as energy storage alternative to traditional batteries. Among advantages are fast charging, long life span and environmentally friendly production.
- ❖ Functionalized graphene holds exceptional promise for biological and chemical sensors.

