

# *Engineering Chemistry Notes*

**For vtu students**

**(Common to all Branches)**

**(Effective from the academic year 2015-16)**

*Subject Code: (15CHE12/22)*



By

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## MODULE-1

### ELECTROCHEMISTRY & ENERGY STORAGE SYSTEMS

**Free energy:** For a reversible cell, the standard free energy (G) of the cell reaction, can be equated to the standard emf  $E^\circ$ , it is defined as the amount of internal energy of a thermodynamic system that is available to perform work.

$$-\Delta G^\circ = nFE^\circ$$

On such occasions using van't Hoff isotherm we can write

$$\Delta G = \Delta G^\circ + RT \cdot \ln K_c$$

**Entropy:** Entropy is the degree of disorder in the movement of molecules making up a thermodynamic system. The higher the disorder, the higher is the system's entropy. For example, the entropy of a gas is higher than the entropy of a crystal at the same temperature and pressure. Entropy is denoted by S (unit: JK<sup>-1</sup>). For its total differential dS we write

$$dS = \frac{dQ}{T} \quad [\text{reversible process}]$$

$$dS > \frac{dQ}{T}, \quad [\text{irreversible process}]$$

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

**Single electrode potential or Cell potential (E):**

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

OR

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

**STANDARD ELECTRODE POTENTIAL (E°):**

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

**EMF OF THE CELL:**

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

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

**Nernst equation for single electrode potential:**

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

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

$$-\Delta G = W \text{ max} \dots \dots \dots (1)$$

$$W \text{ max} = nFE \dots \dots \dots (2)$$

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

$$\therefore -\Delta G = nFE \dots \dots \dots (3)$$

Under standard condition

$$-\Delta G^0 = nFE^0 \dots \dots \dots (4)$$

Where,  $-\Delta G^0$ =Decrease free energy under standard condition,  $E^0$ =Standard electrode potential

Consider a reversible electrode reaction



According to Vanthoff's reaction isotherm

$$\Delta G = \Delta G^0 + RT \cdot \ln K_c \dots \dots \dots (6)$$

Where,  $K_c$ =Equilibrium constant

Substitute the value of  $K_c$ , we have

$$\Delta G = \Delta G^0 + RT \cdot \ln \frac{[M]}{[M^{n+}]} \dots \dots \dots (7)$$

Divide the equation (6) by  $-nF$

From equation (3) and (4)

$$E = E^0 - \frac{RT}{nF} \cdot \ln \frac{[M]}{[M^{n+}]} \dots \dots \dots (8)$$

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

Then, we have

$$E = E^0 - \frac{RT}{nF} \cdot \ln \frac{1}{[M^{n+}]} \dots \dots \dots (9)$$

$$E = E^0 + \frac{RT}{nF} \cdot \ln [M^{n+}] \dots \dots \dots (10)$$

$$E = E^0 + \frac{2.303RT}{nF} \cdot \log [M^{n+}] \dots \dots \dots (11)$$

Substitute the value of  $R=8.314\text{J/K/mol}$ ,  $T=298\text{K}$ ,  $F=96500\text{C/mol}$  to the eq. (11)

$$E = E^0 + \frac{0.0591}{n} \cdot \log [M^{n+}] \dots \dots \dots (12)$$

Eq.n (12) is the Nernst equation for a single electrode.

Then, **Nernst equation for emf of cell** is given by

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

### Problems

1. Calculate the potential of Ag-Zn cell at 298 K, if the concentration of  $\text{Ag}^+$  and  $\text{Zn}^{+2}$  are  $5.2 \times 10^{-6}$  M and  $1.3 \times 10^{-3}$  M respectively.  $E^0$  of the cell at 298K is 1.5V given:  $T=298\text{K}$ ;  $E^0_{\text{cell}} = 1.5\text{V}$ .

$$[\text{Ag}^+] = 5.2 \times 10^{-6} \text{M}$$

$$[\text{Zn}^{+2}] = 1.3 \times 10^{-3} \text{M}$$

$$\text{Ans: } E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{+2}]}$$

$$E_{\text{cell}} = 1.5 + \frac{0.0591}{2} \log \frac{(5.2 \times 10^{-6})^2}{1.3 \times 10^{-3}}$$

$$E_{\text{cell}} = 1.27 \text{ V}$$

2. An electrochemical cell consists of iron electrode dipped in 0.1M  $\text{FeSO}_4$  and silver electrode in 0.05M  $\text{AgNO}_3$ . Write the cell representation cell reaction and calculate the emf of the cell at 298K. (The standard reduction potentials of iron and silver are  $-0.44\text{V}$  and  $0.8\text{V}$  respectively).

$$\text{Given: } T=298\text{K}; E^0_{\text{Fe}} = -0.44\text{V}; E^0_{\text{Ag}} = 0.8\text{V}$$

$$[\text{Fe}^{+2}] = 0.1\text{M}$$

$$[\text{Ag}^+] = 0.05\text{M}$$

cell representation:  $\text{Fe}_{(s)} | \text{FeSO}_4(0.1\text{M}) || \text{AgNO}_3(0.05\text{M}) | \text{Ag}_{(s)}$

$$\text{Ans: } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E^0_{\text{cathode}} + \frac{0.0591}{n} \log [\text{Ag}^+] - E^0_{\text{anode}} - \frac{0.0591}{n} \log [\text{Fe}^{2+}]$$

$$E_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]}{[\text{Fe}^{2+}]}$$

$$E_{\text{cell}} = 0.8 - (-0.44) + \frac{0.0591}{2} \log \frac{[0.05]^2}{[0.1]}$$

$$E_{\text{cell}} = 1.19 \text{ V.}$$

3. Calculate the voltage of the cell  $\text{Mg}_{(s)} | \text{Mg}^{+2} (1\text{M}) || \text{Cd}^{+2} (7 \times 10^{-11}\text{M}) | \text{Cd}_{(s)}$ , where  $E^0_{\text{cell}} = 1.97\text{V}$ .

$$\text{Given: } E^0_{\text{cell}} = 1.97\text{V}$$

$$[\text{Mg}^{+2}] = 1\text{M}$$

$$[\text{Cd}^{+2}] = 7 \times 10^{-11}\text{M}$$

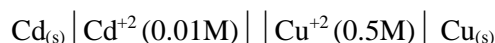
$$\text{Ans: } E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{Cd}^{+2}]}{[\text{Mg}^{+2}]}$$

$$E_{\text{cell}} = 1.97 + \frac{0.0591}{2} \log 7 \times 10^{-11}$$

$$E_{\text{cell}} = 1.97 - 0.3001$$

$$E_{\text{cell}} = 1.6699 \text{ V.}$$

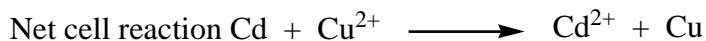
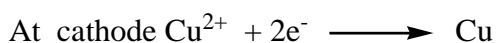
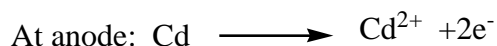
4. Write the half cell and net cell reactions for the cell



The standard reduction potentials of Cd and Cu are  $-0.4\text{V}$  and  $0.34\text{V}$  respectively. Calculate the emf of the cell.

Given:  $E^0_{Cd} = -0.4V$ ;  $E^0_{Cu} = 0.34V$ ;  $[Cd^{2+}] = 0.01M$ ;  $[Cu^{2+}] = 0.5M$

Ans:



$$E_{cell} = E^0_{cathode} - E^0_{anode} + \frac{0.0591}{n} \log \frac{[Cu^{2+}]}{[Cd^{2+}]}$$

$$E_{cell} = 0.34 - (-0.4) + \frac{0.0591}{2} \log \frac{0.5}{0.01}$$

$$E_{cell} = 0.74 + 0.0502$$

$$E_{cell} = 0.7902 \text{ V.}$$

5. Calculate the emf of Copper concentration cell at 25<sup>o</sup> C, where the copper ions ratio in the cell is 10.

Given:  $\frac{[Cu^{+2}]_{cathode}}{[Cu^{+2}]_{anode}} = \frac{C_2}{C_1} = 10$

Ans:  $E_{cell} = \frac{0.0591}{n} \log \left( \frac{C_2}{C_1} \right)$ ; at 298 K

$$E_{cell} = \frac{0.0591}{2} \log(10)$$

$$E_{cell} = 0.0296 \text{ V.}$$

**Reference electrodes:** “Reference electrodes are the electrode with reference to those, the electrode potential of any electrode can be measured”. The Primary reference electrode used for cell potential measurement is the SHE, whose potential is Zero. The secondary reference electrodes are Calomel and Silver-Silver chloride electrode.

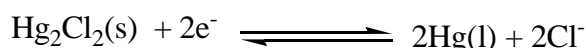
### **Calomel electrode:**

Calomel electrode is a metal-metal salt ion electrode. It consists of mercury, mercurous Chloride and a solution of KCl. Mercury is placed at the bottom of a glass tube.

A paste of mercury and mercurous chloride is placed above the mercury. The space above the paste is filled with a KCl solution of known concentration. A platinum wire is kept immersed into the mercury to obtain an electrical contact. Calomel electrode can be represented as, **Hg|Hg<sub>2</sub>Cl<sub>2</sub>|Cl<sup>-</sup>**.

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

The net cell reversible electrode reaction is,



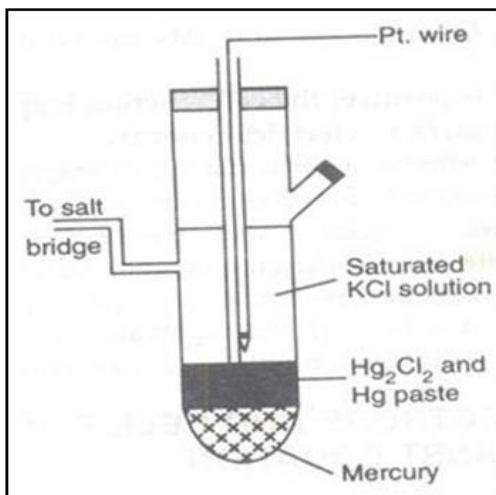
The Nernst equation is given by,

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

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

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

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



**Advantages:-**

1. Simple to Construct.
2. Cell potential does not vary with temperature.
3. The cell potential is reproducible and constant over a long period.

**Applications:**

1. It is used as a secondary reference electrode in the measurement of a single electrode.
2. It is used as a reference electrode in all potentiometer determinations.

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

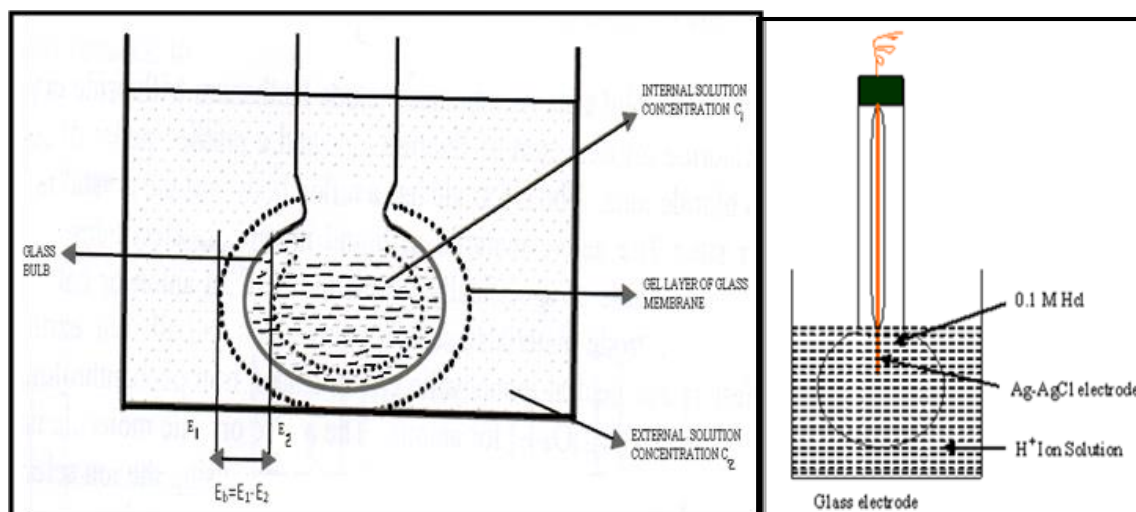
**Uses:-** To determine the concentration of a number of cations and anions such as H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, CN<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> etc.

There are Four types of membranes, They are

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

**Glass electrode:**

**Principle:** - A thin-walled glass bulb containing an acid is immersed in another solution a potential is developed across the glass membrane. The potential difference, E<sub>b</sub> at the interface is referred to as boundary potential is the difference in potential (E<sub>1</sub>-E<sub>2</sub>) developed across the layer of the glass membrane b/w the two liquids.



The potential of glass electrode  $E_G$  is given by

$$E_G = E_1 - E_2 \quad \dots\dots\dots 1 \quad \text{Where, } E_1 \& E_2 \text{ are the electrode potential of outer \& inner membrane}$$

$$E_G = [E^0 + 0.0591 \log [C_2]] - [E^0 + 0.0591 \log [C_1]] \quad \dots\dots\dots 2 \quad \text{Where } C_1 \& C_2 \text{ are the concentration inner \& outer acid solutions.}$$

$$E_G = 0.0591 \cdot \log \frac{[C_2]}{[C_1]} \quad \dots\dots\dots 3 \quad \text{Or} \quad E_G = 0.0591 \cdot \log \frac{[C_2]}{[C_1]}$$

$$E_G = -0.0591 \cdot \log [C_1] + 0.0591 \cdot \log [C_2] \quad \dots\dots\dots 4$$

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

$$E_G = \text{Constant} + 0.0591 \cdot \log [C_2] \quad \dots\dots\dots 5$$

$$E_G = \text{Constant} + 0.0591 \cdot \log [H^+] \quad \dots\dots\dots 6 \quad \text{Since, } C_2 = [H^+]$$

$$E_G = \text{Constant} - 0.0591 \cdot \text{pH} \quad \dots\dots\dots 7 \quad \text{Where } \text{pH} = -\log [H^+]$$

A glass electrode is an ion selective electrode where potential depends on upon the pH of the medium. The glass electrode consists of a glass bulb made up of a special type of glass (22%Na<sub>2</sub>O, 6%CaO, and 72%SiO<sub>2</sub>) which has low melting point and relatively high electrical conductivity. The glass bulb is filled with a solution of constant pH (0.1MHCl) and inserts with an Ag-AgCl electrode, which is the Internal reference electrode and also serves as the external electrical contact. The electrode dipped in a solution containing H<sup>+</sup> ions. The electrode representation is,



**Advantages**

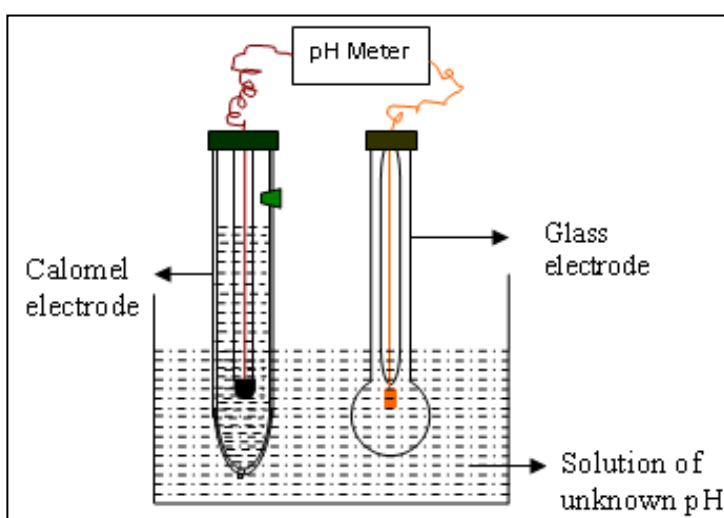
1. This electrode can be used to determine pH in the range 0-9, with a special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

**Limitations**

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.
2. This electrode cannot be used to determine the pH above 12.

**Determination of pH using glass electrode:**

**Principle:** When a thin glass membrane is placed between two solutions of different pH values, a potential difference arises across the membrane. The potential difference varies as the pH of these solutions varies. In practice, pH of one of these solutions is kept constant and therefore the electrode potential depends on pH of the other solution i.e. Experimental solution.



**Procedure:** glass electrode is immersed in the solution; the pH is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge. The cell assembly is represented as,



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

The emf of the cell is given by

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \dots\dots\dots(1)$$

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{SCE}} \dots\dots\dots(2)$$

Since  $E_{\text{SCE}}$  is known EMF of the cell,

Substitute the value of  $E_G$  to equation (2)

$$E_{\text{cell}} = \text{Constant} - 0.0591 \cdot \text{pH} - E_{\text{sce}} \dots\dots\dots(3)$$

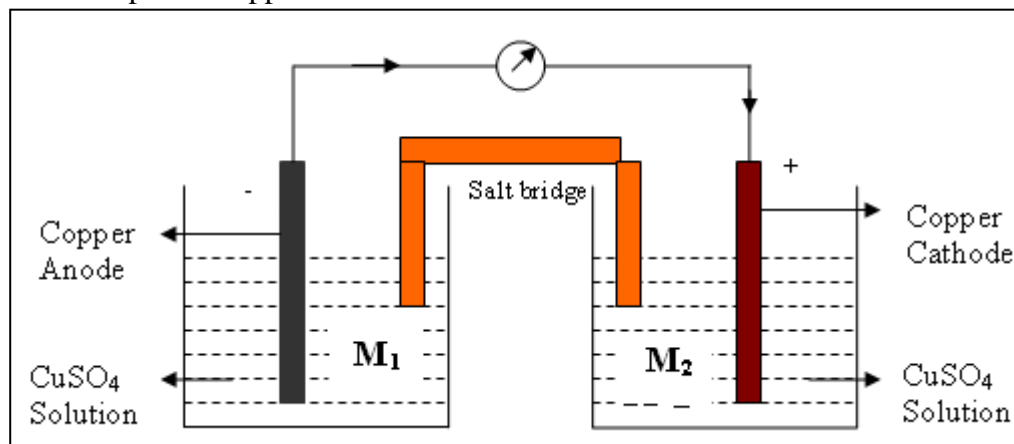
$$\text{pH} = \frac{\text{Constant} - E_{\text{cell}} - E_{\text{sce}}}{0.0591} \dots\dots\dots(4)$$



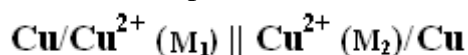
### Electrolyte Concentration cells:

“Electrolyte Concentration cell is an electrochemical cell in which the electrode material and the solution in both the electrodes are composed of the same substances but only the concentrations of the two solutions (electrolyte) are different”.

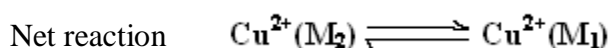
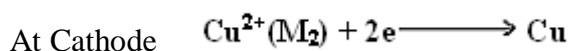
A typical example of Copper concentration cell is shown below.



It consists of two Copper electrodes are immersed in two different concentration of  $\text{CuSO}_4$  solutions. These two electrodes are externally connected by metallic wire and internally by a salt bridge. The cell can be represented as,



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



The net cell reaction is merely the change in concentration as a result of current flow.

#### Emf of concentration cell:

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

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \dots\dots\dots 1$$

$$E_{\text{cell}} = \frac{0.0591}{n} \cdot \log [M_2] - \frac{0.0591}{n} \cdot \log [M_1] \quad \dots\dots\dots 2$$

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

From equation (3) following conclusions may be drawn.

1. When the two solutions are the same concentrations,  $\log \frac{[M_2]}{[M_1]} = 0$  and no electricity flows. Hence,  $E_{\text{cell}} = 0$
2. When  $M_2/M_1 > 1$  i.e.  $M_2 > M_1$ ,  $\log M_2/M_1$  is positive & electrode potential is positive.
3. Higher the ratio of  $M_2/M_1$ , higher is the value of cell potential.

**Problems:**

1. Calculate the potential of Daniel cell at 25<sup>0</sup> C, given the electrode potentials of Cu and Zn are 0.34V and -0.76V respectively.

Given:  $E^0_{Zn} = -0.76V$ ;  $E^0_{Cu} = 0.34V$

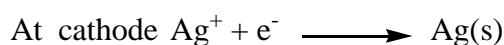
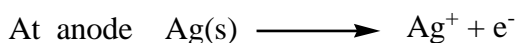
Ans:  $E_{cell} = E_{cathode} - E_{anode}$

$$E_{cell} = 0.34 - (-0.76)$$

$$E_{cell} = 1.1 \text{ V.}$$

2. Write the electrode reactions and Calculate the EMF of the given concentration cell at 298K,  $Ag(s) | AgNO_3(0.018M) || AgNO_3(1.2M) | Ag(s)$ .

Ans:



$$E_{cell} = \frac{0.0591}{n} \log\left(\frac{C_2}{C_1}\right) \quad \text{at 298K}$$

$$E_{cell} = 0.0591 \log\left(\frac{1.2}{0.018}\right) \quad (n=1)$$

$$E_{cell} = 0.1078 \text{ V.}$$

3. Calculate the emf of Copper concentration cell at 25<sup>0</sup> C, where the copper ions ratio in the cell is 10.

Given:  $\frac{[Cu^{+2}]_{cathode}}{[Cu^{+2}]_{anode}} = \frac{C_2}{C_1} = 10$

Ans:  $E_{cell} = \frac{0.0591}{n} \log\left(\frac{C_2}{C_1}\right); \quad \text{at 298 K}$

$$E_{cell} = \frac{0.0591}{2} \log(10)$$

$$E_{cell} = 0.0296 \text{ V.}$$

4. Calculate the electrode potential at a copper electrode dipped in a 0.1M solution of Copper sulphate at 298K, assuming copper sulphate to be completely dissociated. The standard electrode potential of  $Cu^{+2}/Cu$  is 0.34V at 298K Given:  $T=298K$ ;  $E^0_{Cu} = 0.34V$

$[Cu^{+2}] = 0.1M$

Ans:  $E_{Cu^{+2}/Cu} = E^0 + \frac{0.0591}{n} \log[Cu] \quad \text{at 298 K}$

$$E_{Cu^{+2}/Cu} = 0.34 + \frac{0.0591}{2} \log(0.1)$$

$$E_{Cu^{+2}/Cu} = 0.34 - 0.0296$$

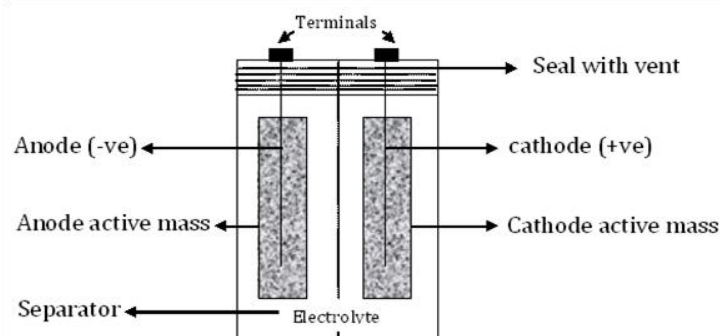
$$E_{Cu^{+2}/Cu} = 0.3105 \text{ V.}$$

## Energy storage systems

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

**Principle components** of a battery are:

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



### Classification of batteries:

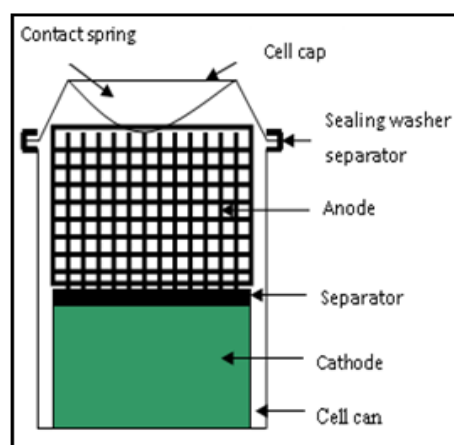
1. Primary batteries: In these batteries the cell reaction is not reversible after discharging cannot be rechargeable. e.g. Zn-MnO<sub>2</sub> dry cell.
2. Secondary batteries: In this battery the cell reaction is completely reversible after discharging can easily rechargeable. e.g. Lead-acid battery, Ni-MH battery.
3. Reserve batteries: In these batteries, one of the active components (e.g. electrolyte) of the battery is separated from the rest of the components. It is assembled just before the use. e.g. Mg-water activated the battery.

### Nickel-metal hydride battery:

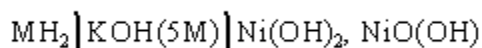
**Construction:** In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed. The active material for the anode is a mixture of a metal hydride (such as TiH<sub>2</sub>, VH<sub>2</sub>, or ZrH<sub>2</sub>) and a hydrogen storage alloy (such as LaNi<sub>5</sub> or TiNi). The active material for the cathode is nickel oxyhydroxide, NiO(OH). An aqueous solution of KOH acts as the electrolyte. Polypropylene is used as the separator.

The anode material has (i) a good hydrogen storage capacity capable of adsorbing and desorbing hydrogen as the battery is discharged and charged.

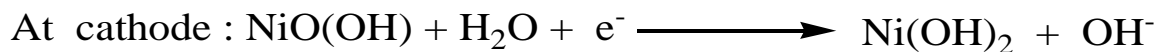
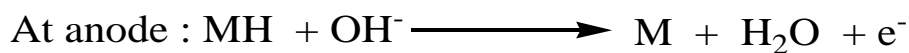
(ii) high resistance to chemical oxidation and corrosion and (iii) high electrochemical reactivity.



**Cell representation:**



**Cell reactions:**



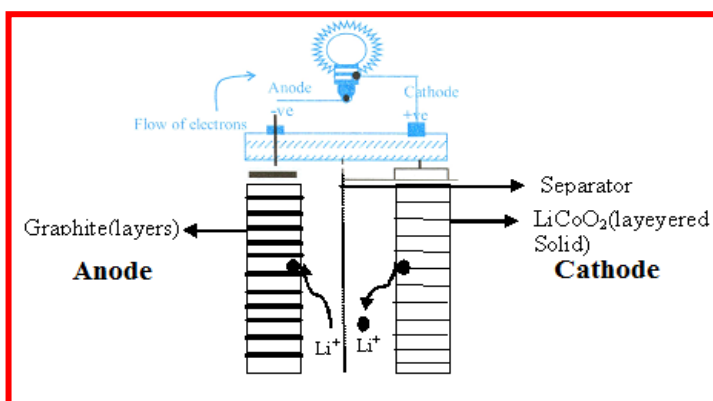
**Uses:** Used in cellular phones, camcorders and laptop computers.

**Lithium batteries:** These batteries with high energy density, high energy efficiency, high voltage and long life cycle. Lithium has the following characteristics.

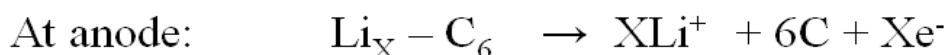
- (i) It is light weight. (ii) It has high electrochemical equivalence ( $3.86 \text{ Ah g}^{-1}$ ). (iii) It has good electrical conductivity. (iv) It has high standard electrode potential ( $-3.05\text{V}$ ).

**Li- ion battery:**

A conventional lithium ion battery consists of and a metal oxide such as carbon (graphite) forms the anode and lithium cobalt oxide ( $\text{LiCoO}_2$ ) as a cathode. The electrolyte consists of a lithium salt in an organic solvent. The salts include lithium hexafluorophosphate  $\text{LiPF}_6$ , lithium tetrafluoroborate  $\text{LiBF}_4$  and lithium perchlorate  $\text{LiClO}_4$ . The solvents used are ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The cell delivers an emf of 4V.



**Cell reaction:**



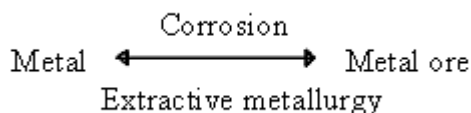
With discharge, the Co is oxidized from  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ . The reverse process (reduction) occurs when the battery is being charged.

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

## MODULE-2

### CORROSION and METAL FINISHING

**Def<sup>n</sup>:** Corrosion is a destruction reaction taking place spontaneously by chemical or electrochemical reaction of the metal by the surrounding environment on the surface of the metal.



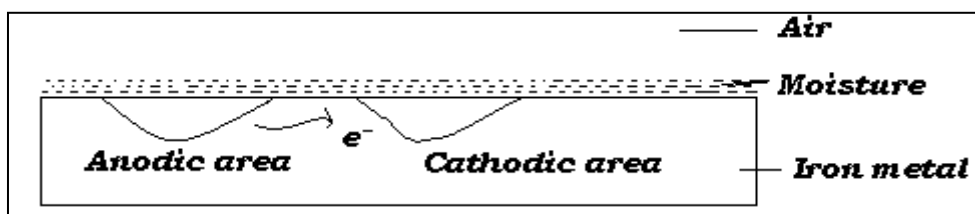
A slow and continuous process of destruction of a metallic substance through spontaneous chemical and electrochemical attack by its environment starting at its surface is called corrosion.

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

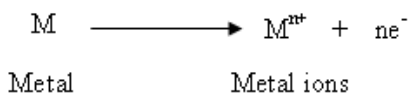
#### Electrochemical theory of corrosion

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

- 1) A large number of minute galvanic cells are formed which acts as anodic and cathodic areas.
- 2) At anode, the metal undergoes oxidation and electrons are liberated which migrates towards cathodic region
- 3) Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxyl ions at the cathode



Anodic reactions: At anode, the metal undergoes oxidation-liberating electrons

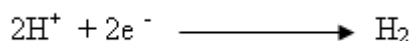


Ex: when iron is exposed to the environment it undergoes oxidation as

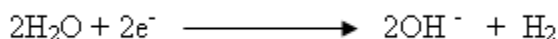


Cathodic reactions: The electrons released at anode migrate to the cathodic area and reduces oxygen to hydroxyl ions. The different cathodic reactions are,

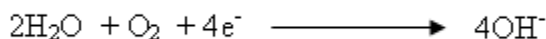
- a). In acidic medium: In acidic medium and in the absence of oxygen, hydrogen ions are reduced to hydrogen gas



b) In alkaline and in the absence of O<sub>2</sub>. If the solution is alkaline and in the absence of oxygen the cathodic reaction is,



c) In neutral and aerated medium: when the solution is neutral and aerated, hydroxyl ions are formed as follows.



d) Formation of corrosion product: The hydroxyl ions migrate towards the anode and react with metal ions (M<sup>n+</sup> ions) and forms corrosion product. In the case of iron OH<sup>-</sup> reacts with Fe<sup>2+</sup> ions and forms an insoluble hydrated ferric oxide known as brown rust.



If  $i_{\text{corr}}$  (corrosion current) is the current flowing,

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

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

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

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

Mn <sup>+</sup> /Mn	E°(V)	Mn <sup>+</sup> /Mn	E°(V)
Li <sup>+</sup> /Li	-0.305	Sn <sup>2+</sup> /Sn	-0.14
K <sup>+</sup> /K	-2.93	Pb <sup>2+</sup> /Pb	-0.126
Ca <sup>+</sup> /Ca	-2.87	H <sup>+</sup> /H <sub>2</sub>	0.000
Na <sup>+</sup> /Na	-2.71	Cu <sup>2+</sup> /Cu	0.34
Zn <sup>2+</sup> /Zn	-0.76	Ag <sup>+</sup> /Ag	0.80
Fe <sup>2+</sup> /Fe	-0.44	Hg <sup>2+</sup> /Hg	0.85
Cd <sup>2+</sup> /Cd	-0.40	Pt <sup>2+</sup> /Pt	1.20
Ni <sup>2+</sup> /Ni	-0.236	Au <sup>3+</sup> /Au	1.38

- 1). A negative value indicates oxidation tendency and a positive value indicates reduction tendency with respect to hydrogen.
- 2).The metal with lower electrode potential is more reactive and as the electrode potential increases, the reactivity decreases and metals with higher electrode potentials are nobler.
- 3).Metals with lower electrode potentials have the tendency to replace metals with higher electrode potential from their solutions, for example, Zn displaces Cu, Cu displaces Ag.
- 4).Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

### **Primary Factors (Related to metal)**

**1. Nature of the metal & its surface state:**

Corrosion is a surface phenomenon smaller the size more will be the area exposed & more will be the corrosion. The rough surface will suffer more corrosion compared to the smooth surface. Impure metal is more corrosive.

**2. Nature of the corrosion product:**

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

### **Secondary factor (Related to Environment)**

**1. pH of the medium:**

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

**2. Temperature:**

The rate of corrosion reaction always increase with temperature, higher temperature increases the rate of diffusion of ions, it also decreases the passivity of certain metals hence more corrosion is seen at elevated temperature.

**3. Relative anodic & cathodic area:**

Larger the cathodic area and smaller the anodic area exposed more will be the corrosion of anodic metal & vice versa.

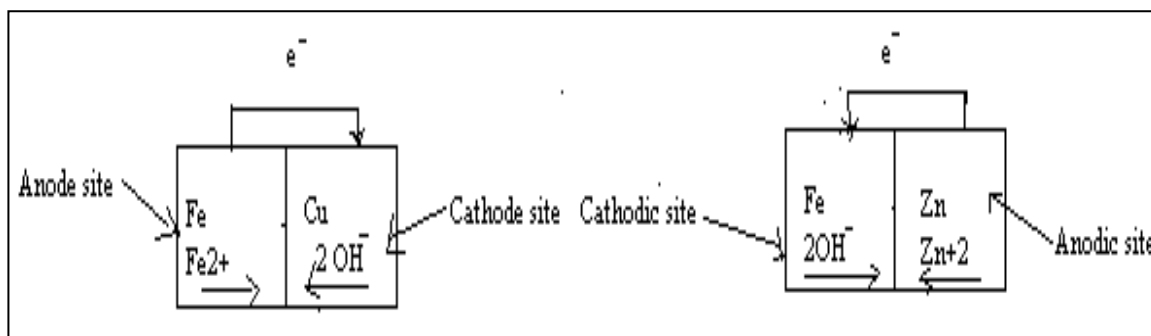
**4. Conductivity of the corroding medium:**

Higher the conductance more will be the flow of corrosion current, hence corrosion of metal buried in clay and mineralized soils will be more than those under dry sandy soils.

## **Types of Corrosion**

### **1). Differential metal corrosion:**

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



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

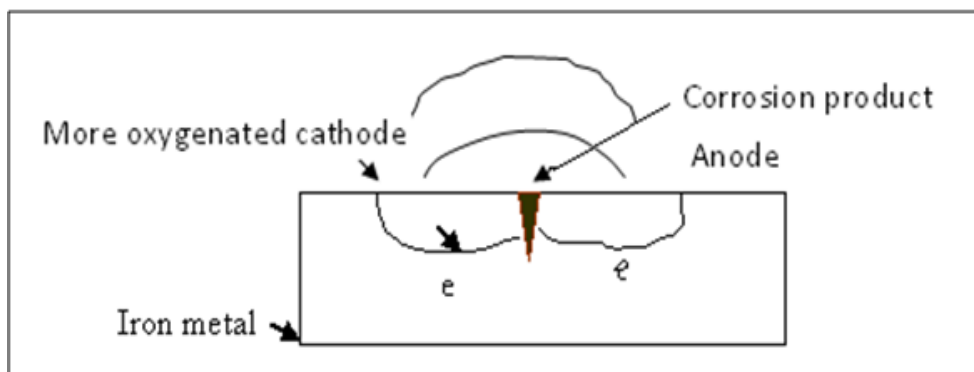
electrochemical series forms cathode hence protected from corrosion. The extent of corrosion depends on the difference in the electrode potential of the two metals and also their relative areas exposed if the potential difference between the electrodes is high, greater the extent of corrosion. **Eg:**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

## 2). Differential Aeration Corrosion:

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

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

### a. Pitting Corrosion:

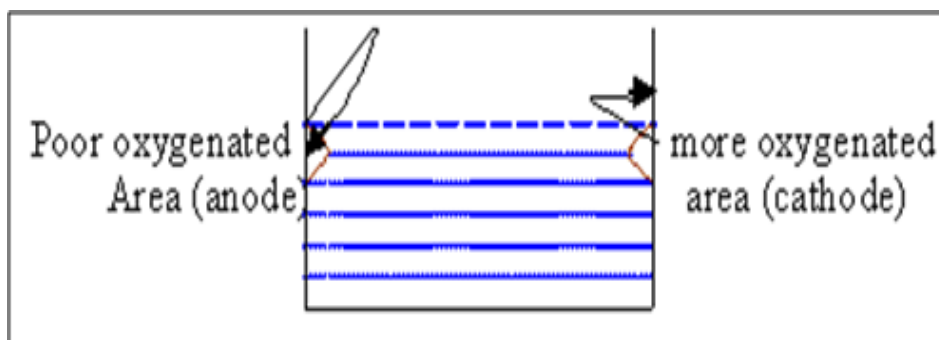


- **Pitting corrosion** is a localised accelerated attack in which only small areas of the metal surface are attacked whilst the remainder is largely unaffected. This localised attack results in pitting. The pits may initiate and propagate to a certain depth resulting in the formation of cavities and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

### b. Water line corrosion:

- Differential aeration accounts for the corrosion of metals partially immersed in a solution, just below the water line. This type of differential aeration corrosion is also known as **water line corrosion**.





- Consider a steel tank containing water. The maximum corrosion takes place along a line just beneath the level of water meniscus. The area above the waterline is highly oxygenated and acts as the cathodic and completely unaffected by corrosion. (Eg. Marine plants attacking themselves on the sides).

### Corrosion control:

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

### Anodizing:

**Def<sup>n</sup>:** - 'A process in which a protective active oxide is formed chemically on metals is called anodization'.

### Anodization of Al

Anodization of Al consists of the following steps.

**Step 1:** - Preparation of Al base metal surface.

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

**Step 2:** - Al base metal is placed in an oxidizing bath like chromic acid or boric acid, H<sub>2</sub>SO<sub>4</sub>

**Step 3:** - The base metal is made anode and connected to a battery while lead is used as cathode. A current of 150mA/Cm<sup>3</sup> at 10-28v at 25-40°C is passed Al<sub>2</sub>O<sub>3</sub> gets deposited. Then it is washed with water.

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



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

### Application:

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

### Cathodic protection:

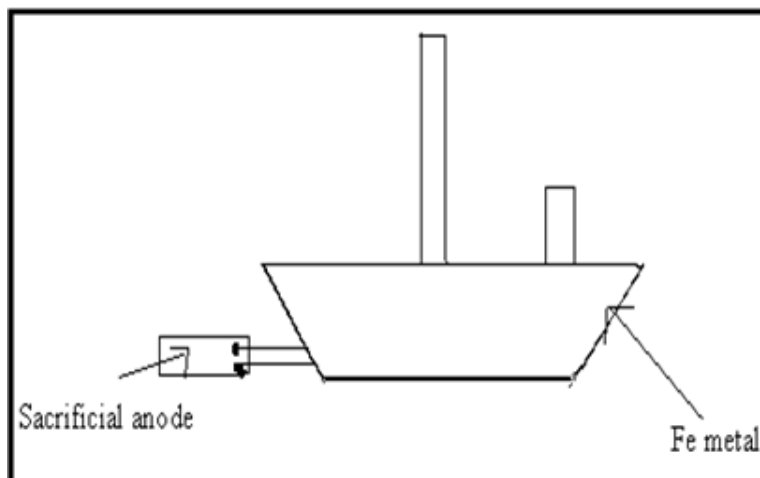
The principle of this method is to convert the corrosive base metal into a cathode. This is done by

1. Sacrificial anodic protection.
2. Impressed current technique.

### 1. Sacrificial anode method:

The metallic structure to be protected is made relatively a cathode by using another anodic metal contact with it. So that the corrosion is now concentrated on more anodic metal

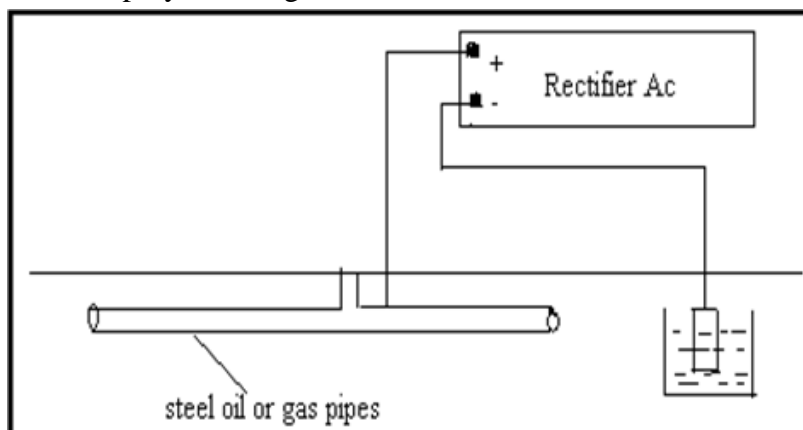
protecting the base metal from corrosion. The sacrificial anodes to be replaced by fresh ones as and when it is required. Commonly used sacrificial anodes are: Mg, Zn, Al etc.



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

## **2. Impressed current technique:**

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



## **Metal coating:**

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

## **Galvanizing:**

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

**Step 1: Preparation of base metal surface.**

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

**Step 2: Hot dipping.**

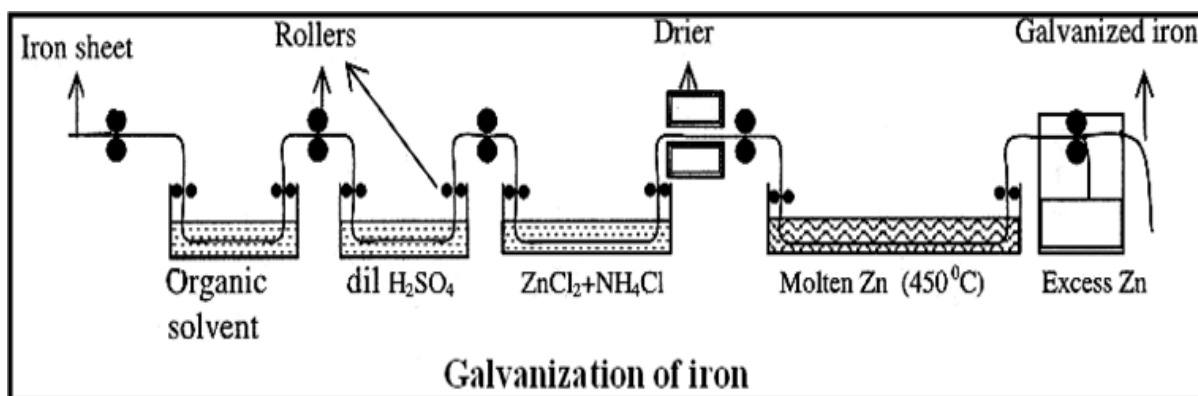
The base metal is dipped in molten Zn at 425-432°C with ammonium chloride or ZnCl<sub>2</sub> as flux.

**Step 3: Removal of the excess coating of Zn.**

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

**Step 4: Annealing**

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



**Advantages:**

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

**Disadvantages:**

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

**Uses:**

To make galvanized articles.

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

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

## **METAL FINISHING:**

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

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

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

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

## **Principles of Metal Finishing:**

### **a) Polarization:**

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

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

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

### **Factors affecting the electrode polarization:**

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

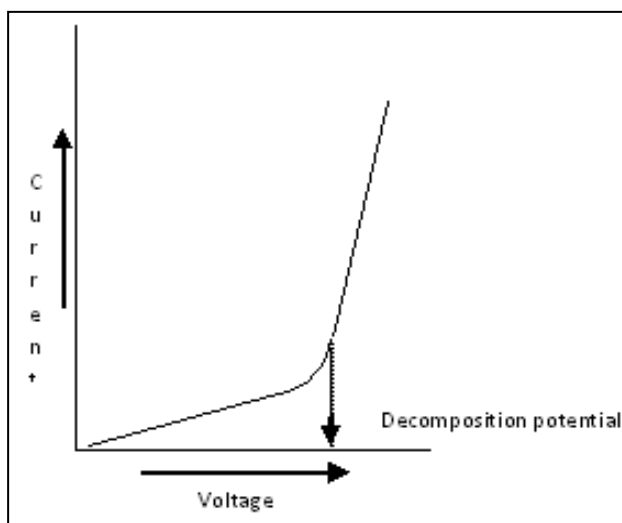
### **b) Decomposition potential:**

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

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

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

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



The magnitude of the back emf is same as the decomposition potential.

### **c) Over voltage (over potential) ( $\eta$ ):**

**Def<sup>n</sup>:**- Over voltage is defined as the excess voltage that has to be applied above the theoretical decomposition potential to start the electrolysis.

$$\eta = \text{Experimental decomposition potential} - \text{Theoretical decomposition potential.}$$

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

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

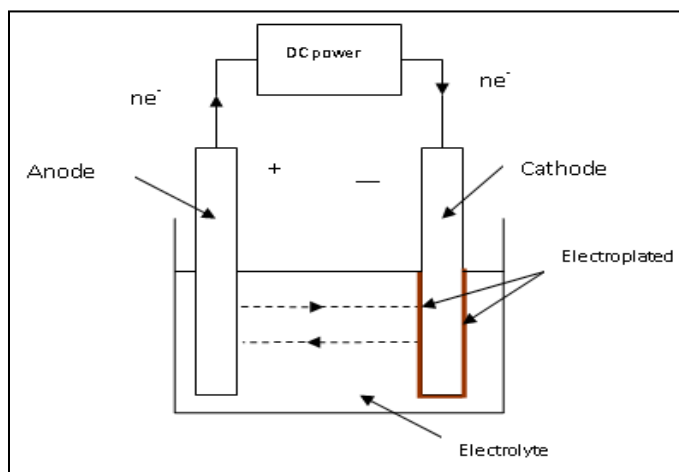
## Electroplating:

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

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

The main components are:

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

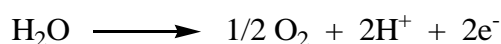


### Reactions at anode and cathode during electroplating:

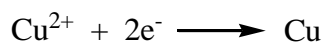
At anode oxidation takes place



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



At the cathode, reduction occurs. The metal gets deposited on the cathode surface. For example:



### Surface preparation (Pretreatment):

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

Surface cleaning involves following steps:

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

**1. Removal of organic substances – degreasing process:**

a) Organic solvent cleaning: It is used to remove oils, greases etc. from the surface. For cleaning, organic solvents such as trichloroethylene ( $\text{CCl}_2 = \text{CHCl}$ ), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), carbon tetrachloride ( $\text{CCl}_4$ ) etc. are used.

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

b) Alkali cleaning: Residual oil and grease from the surface are removed by treatment with alkaline solutions ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  etc.) Alkali cleaning is made more effective by making the metal cathodic in a hot alkali solution. The hydrogen gas liberated at the cathode helps to dislodge the greasy matter.

**2. Removal of inorganic substances – descaling process:**

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

b) Pickling: It is used to remove oxide scales and rust present on the metal surface by dissolution. Pickling involves dipping the object in dilute acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  or a mixture) for a considerable period of time.

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

**Electroplating of chromium:-**

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

1. Plating bath composition	Chromic acid ( $\text{H}_2\text{CrO}_4$ ) + $\text{H}_2\text{SO}_4$ in the weight ratio 100 : 1
2. Operating temperature	45-60 °C
3. Current density	100 – 200 mA cm <sup>-2</sup>
4. Current efficiency	8 – 12 %
5. Anode	Insoluble anode: Pb-Sb or Pb-Sn alloy coated with $\text{PbO}_2$ .
6. Cathode	Object to be plated
7. Anodic reaction	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow 1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
8. Cathodic reaction	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$
9. Applications	1. Used in the decorative coating. 2. Used in corrosion resistant coating.

In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3+ state by a complex anodic reaction in the presence of sulphate ions. The  $\text{Cr}^{3+}$  then gets reduced to Cr on the substrate surface. For a good deposit, the  $\text{Cr}^{3+}$  concentration must be low. The  $\text{PbO}_2$  oxidizes a part of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ , thus reducing the concentration of  $\text{Cr}^{3+}$ .

In chromium plating, we do not use chromium metal as anode due to the following reasons.

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

### **ELECTROLESS PLATING:**

**Def<sup>n</sup>:**- Electroless plating is a method of depositing a metal over a substrate by controlled chemical reduction of metal ions by a suitable reducing agent **without** using electrical energy.

**Metal ions + reducing agent  $\rightarrow$  Metal + oxidized product.**

#### **Advantages of electroless plating:**

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

### **Distinction between electroplating and electroless plating:**

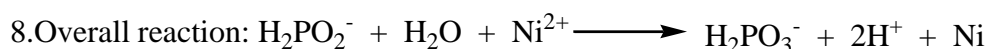
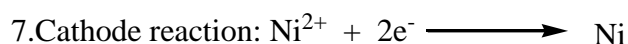
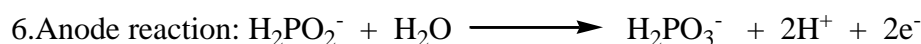
<b>Property</b>	<b>Electroplating</b>	<b>Electroless plating</b>
Source	Electrical energy is obtained from an external source.	No electrical energy is required
The site of anodic reaction.	The anodic reaction takes place at separate anode used in the electrolytic cell.	The site of anode reaction is the article to be plated.
The site of cathodic reaction.	Article to be plated acts as cathode	Catalytic surface on the article to be plated
Anode	Metal	Reducing agent in solution
Type of deposit obtained	Pure	Contaminated
Type of cathode used for plating	Plating is carried out on metals.	Plating may be carried out on insulators (ex: plastics) and semiconductors.
Anode reaction	$\text{M} \longrightarrow \text{M}^{n+} + n\text{e}^- \quad \text{OR}$ $\text{H}_2\text{O} \longrightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	Reducing agent $\rightarrow$ Oxidized product + $n\text{e}^-$
Cathode reaction	$\text{M}^{n+} + n\text{e}^- \longrightarrow \text{M}$	$\text{M}^{n+} + n\text{e}^- \longrightarrow \text{M}$



## Electroless plating of Ni :-

Before electroless plating, the surface is thoroughly cleaned. Then, electroless plating is done under the following conditions:

1. Plating bath solution : NiCl<sub>2</sub>
2. Reducing agent : Sodium hypophosphite.
3. Complexing agent & exaltant : Sodium succinate.
4. Buffer (p<sup>H</sup> = 4.5) : Sodium acetate.
5. Temperature : 93 °C



(Since H<sup>+</sup> ions are produced during the reaction, the p<sup>H</sup> decreases. To maintain the p<sup>H</sup> at 4.5, buffer salt (sodium acetate) is added during the reaction.)

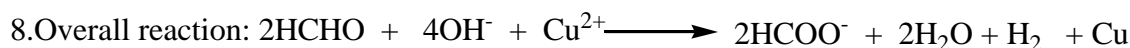
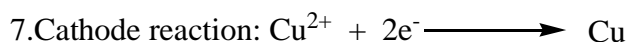
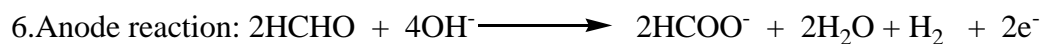
### Applications:

1. Used to obtain a wear resistant surface.
2. Ni coating on aluminum improves the solderability.
3. Ni coating on polymers is used to obtain decorative knobs in hi-fi equipment, tops on bottles etc.

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

Before electroless plating, the surface is cleaned thoroughly. Insulators such as plastics and printed circuit boards are activated by dipping first in stannous chloride (SnCl<sub>2</sub>) and then in palladium chloride (PdCl<sub>2</sub>). Then, the electroless plating is done under the following conditions:

1. Plating bath solution : CuSO<sub>4</sub>
2. Reducing agent : Formaldehyde (HCHO)
3. Complexing agent and exultant : EDTA
4. Buffer (pH = 11) : Sodium hydroxide and Rochelle salt (Na-K-tartrate)
5. Temperature : 25 °C



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

### Applications:

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

## Module – 3

### Energy Systems

#### Chemical Fuels:

**Def<sup>n</sup>:** - Fuel is a carbonaceous combustible substance which on combustion liberates a large amount of energy in the form of heat.

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

Based on occurrence fuels are classified as.

1) *Primary fuels or Natural fuels*

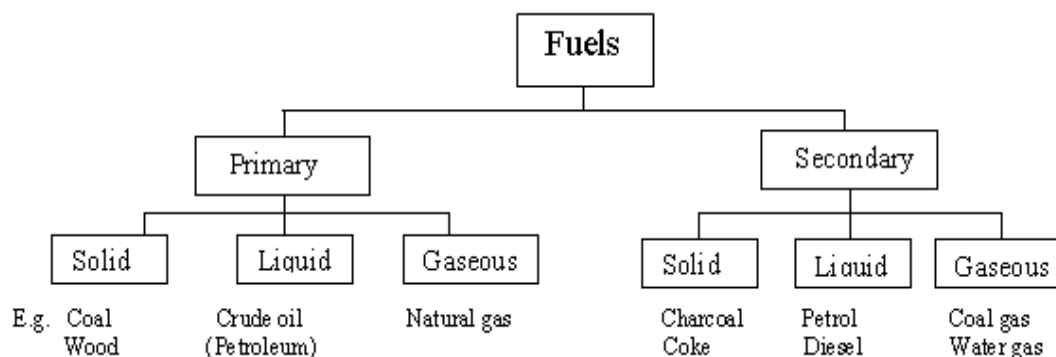
Primary fuels are carbonaceous fuels which are occurring in nature.

Eg. Wood, coal, petroleum, natural gas etc.

2) *Secondary fuels or Artificial fuels.*

Secondary fuels are those which are derived from primary fuels.

Eg. Coke, charcoal, diesel, producer gas etc.

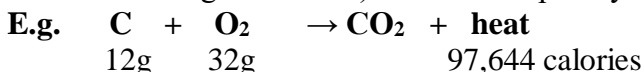


#### Characteristics of a good fuel:

1. High calorific value
2. Moderate ignition temperature
3. Low ash content
4. Low moisture content
5. No harmful combustion products
6. Combustion control
7. Ease of availability
8. Ease of storage and transport

#### Calorific value:

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



i.e 12g of carbon on burning liberates 97,644 calories of heat energy on complete combustion. Therefore 1g of carbon on complete combustion liberates 8137 calories of heat energy.

Calorific value is expressed in 'Kilojoules/Kg' for solids & liquids types of fuels & 'Kilojoules /m<sup>3</sup>' for gaseous fuels. It's also expressed as calorie/gm or Kilocalories / Kg.

#### Types of calorific value:

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

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

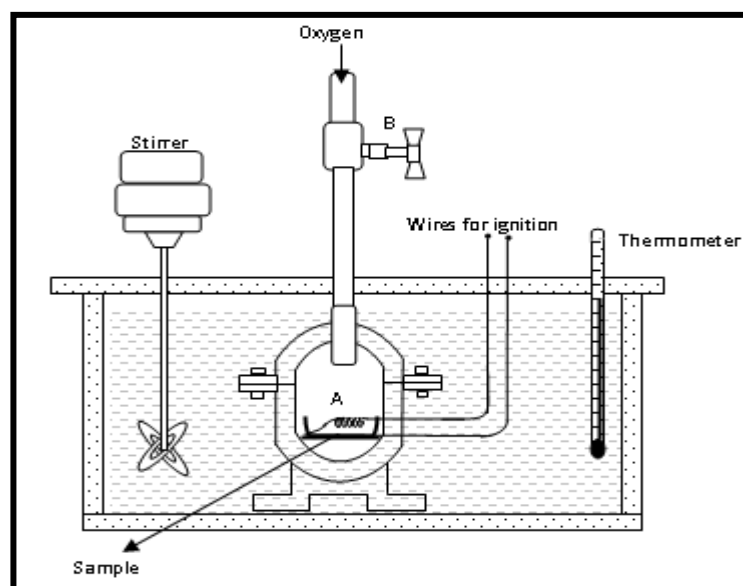
Fuels generally contain some amount of hydrogen during combustion the hydrogen is converted into steam. When the products are cooled to the room temperature the latent heat of condensation of steam gets included in the experimentally measured calorific value, therefore, the experimentally measured calorific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

$$\text{GCV} = \text{NCV} + \text{Latent heat of condensation}$$

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

$$\text{NCV} = \text{GCV} - \text{Latent heat of condensation}$$

### Determination of calorific value of solid & liquid fuel using Bomb Calorimeter:



**Principle:** A known weight of the sample is burnt completely in excess of oxygen. The liberated heat is absorbed by the surrounding water & calorimeter. Thus the heat liberated during the combustion of fuel is equal to the heat absorbed by water and calorimeter.

#### Construction:

- The bomb calorimeter (shown in the fig.) consists of an outer cylindrical steel vessel (bomb) with an airtight screw and an inlet for oxygen.
- The bomb has a platinum crucible with a loop of wire. The ends of the wire project out and can be connected to a source of electric current.
- The bomb is immersed in the rectangular vessel (calorimeter) containing water, which is continuously stirred.
- A Beckmann thermometer is introduced into the calorimeter.

**Working:**

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

**Observation & calculations:**

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

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

Let the fuel contain H percentage of hydrogen



2 atoms of hydrogen produce one molecule of water

2g of hydrogen produce --- 18 g of water

x g of hydrogen produce ---- 9 g of water

$$x \% \text{ hydrogen} \quad \equiv \quad \frac{9 \times x}{100} \text{ g of water} = 0.09 \times x \text{ g of water}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - \text{latent heat of steam formed} \\ &= \text{GCV} - 0.09 \times x \times \text{latent heat of steam} \end{aligned}$$

$$\text{Latent heat of steam} = 2454 \text{ kJ kg}^{-1}$$

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

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 2454$$

1) When 0.84 g of coal was burnt completely in Bomb calorimeter the increase in temperature of 2655 grams of water was 1.85 °C if the water equivalent calorimeter is 156g Calculate GCV.

**Solution:**  $\text{GCV} = \frac{(W+w) \times S \times \Delta t}{M}$

$$= \frac{(2655+156) \times 10^{-3} \times 1.85 \times 4.187}{0.84 \times 10^{-3}}$$

$$= 25921.26 \text{ KJ/Kg}$$

2) Calculate GCV and NCV of a fuel from the following data. Mass of fuel=0.75 g, W=350 g.  $t = 3.02$  °C, Mass of water = 1150, %  $\text{H}_2 = 2.8$ .

**Solution:**  $\text{GCV} = \frac{(W+w) \times \Delta t \times S}{M}$

$$= \frac{(1150+350) \times 10^{-3} \times 3.02 \times 4.184}{0.75 \times 10^{-3}}$$

$$\text{GCV} = 25271.36 \text{ KJ/Kg}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times \text{H} \times 587 \times 4.184 \\ &= 25271.36 - 0.09 \times 2.8 \times 587 \times 4.184 \\ \text{NCV} &= 24652.44 \text{ KJ/Kg} \end{aligned}$$

3) Calculate GCV and NCV of a fuel from the following data.

Mass of fuel = 0.83 g, W = 3500 g, w = 385 g,  $t_2 = 29.2^\circ\text{C}$ ,  $t_1 = 26.5^\circ\text{C}$ , % H<sub>2</sub> = 0.7 and S = 4.2 kJ/kg/°C.

**Solution:** 
$$\text{GCV} = \frac{(W+w) \times \Delta t \times S}{M}$$

$$= \frac{(3.5 + 0.385) \times (29.2 - 26.5) \times 4.2}{0.83 \times 10^{-3}}$$

$$\begin{aligned} \text{GCV} &= 53079.39 \text{ KJ/Kg} \\ \text{NCV} &= \text{GCV} - 0.09 \times \text{H} \times 587 \times 4.184 \\ &= 53079.39 - 0.09 \times 0.7 \times 587 \times 4.2 \\ \text{NCV} &= 52924.07 \text{ KJ/Kg} \end{aligned}$$

4) Calculate the gross calorific value and net calorific value of a sample of coal 0.5g when burnt in a bomb calorimeter, raised the temperature of 1000g of water from 293K to 301.6K. The water equivalent of the calorimeter is 350 g. The specific heat of water is 4.187 kJ kg<sup>-1</sup>K<sup>-1</sup>, latent heat of steam is 2457.2 kJkg<sup>-1</sup>. the coal sample contains 93% carbon, 5% hydrogen and 2% ash.

**Solution:**

m = mass of the fuel	= 0.5 g
W = mass of water taken	= 1000 g
w = water equivalent of calorimeter	= 350 g
t <sub>1</sub> = initial temperature of water	= 293 K
t <sub>2</sub> = final temperature of water	= 296.4 K
s = specific heat of water	= 4.187 kJ kg <sup>-1</sup> K <sup>-1</sup>

$$\begin{aligned} \text{GCV (solid fuel)} &= \frac{(W+w) \times (t_2-t_1) \times s}{m} \\ &= \frac{(1000 + 350) \text{ g} \times (296.4 - 293) \text{ K} \times 4.187 \text{ kJ kg}^{-1} \text{K}^{-1}}{0.5 \text{ g}} \\ &= \frac{1350 \text{ g} \times 3.4 \text{ K} \times 4.187 \text{ kJ kg}^{-1} \text{K}^{-1}}{0.5 \text{ g}} \\ &= 97222.14 \text{ kJ kg}^{-1} \end{aligned}$$

$$\begin{aligned} \text{NCV (solid fuel)} &= \text{GCV} - \text{latent heat} \\ &= \text{G.C.V} - (0.09 \times \% \text{ of H}) \times \text{latent heat} \\ &= 97222.14 \text{ kJ kg}^{-1} - (0.09 \times 5) \times 2457.2 \text{ kJ kg}^{-1} \\ &= 97222.14 \text{ kJ kg}^{-1} - 1106 \text{ kJ kg}^{-1} \\ &= 94764.94 \text{ kJ kg}^{-1} \end{aligned}$$

**Octane Number:**

**Def<sup>n</sup>:** It's the percentage of Isooctane present in a standard mixture of isooctane and n-heptanes which knocks at the same compression as the petrol being tested.

**Cetane number:**

**Def<sup>n</sup>:** It's the percentage by volume of Cetane present in a mixture of cetane or hexadecane and α- Methyl naphthalene which has the same knocking characteristics as the diesel under test.

### **Knocking:**

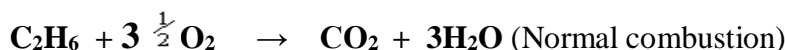
“The production of shock waves in an IC engine as a result of an explosive combustion of fuel-air mixture consequent to an increase in the compression ratio, beyond a certain value leading to a rattling sound”.

$$\text{Compression ratio} = \frac{\text{Volume of cylinder at the end of suction stroke}}{\text{Volume of cylinder at the end of compression stroke}}$$

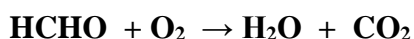
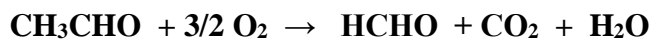
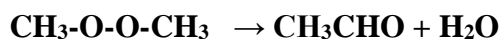
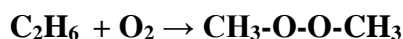
Under ideal conditions, in an IC engine, the petrol-air mixture drawn into the cylinder of the engine undergoes compression and then ignited. The hydrocarbons in the petrol undergo complete combustion and the flame propagates smoothly. But sometimes due to deposits of carbon on the walls of the cylinder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

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

Under ideal conditions:



Under Knocking conditions: (Explosive combustion)



The overall reaction is the same under both the conditions. One molecule of ethane reacts with  $3 \frac{1}{2}$  molecules of oxygen forming carbon dioxide and water with the release of energy. Under ideal condition, the energy is released at a uniform rate but under knocking conditions, the energy is released slowly at first followed by a lag (formation of peroxide) and finally the energy is released at a very fast rate (decomposition of peroxides).

### ***Effects of knocking:***

0. Decreases life of the engine.
1. Causes piston wrap.
2. Consumption of fuel is more.

### ***Prevention of Knocking***

1. The use of a fuel with high octane rating, which increases the combustion temperature of the fuel and reduces the proclivity to detonate
2. Enriching the air–fuel ratio which alters the chemical reactions during combustion, reduces the combustion temperature and increases the margin above detonation
3. Reducing peak cylinder pressure.
4. Decreasing the manifold pressure by reducing the throttle opening or boost pressure.
5. Reducing the load on the engine
6. Retarding (reduce) ignition timing

### Unleaded Petrol(MTBE):

Methyl tertiary butyl ether (MTBE) is added to petrol (unleaded) to boost its octane number. The oxygen of MTBE brings about complete combustion of petrol preventing peroxide formation and hence knocking is prevented.

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

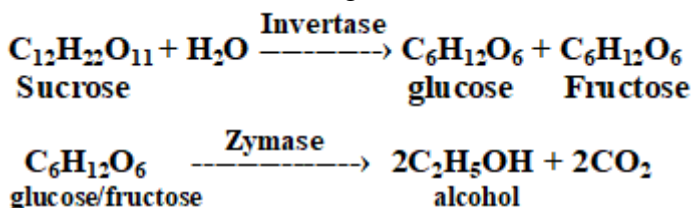
### Power Alcohol:

When ethanol (C<sub>2</sub>H<sub>5</sub>OH) is used as an additive to motor fuels to act as a fuel for IC engines, is called power alcohol. Power alcohol is a gasoline blend containing ethanol.

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

Ethanol is manufactured from saccharine such as molasses – a dark coloured viscous liquid left after the crystallization of cane sugar from cane juice or suger cane.

Molasses - 50-55% total suger of which 35 – 40% is sucrose or cane suger.



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

#### **Advantages**

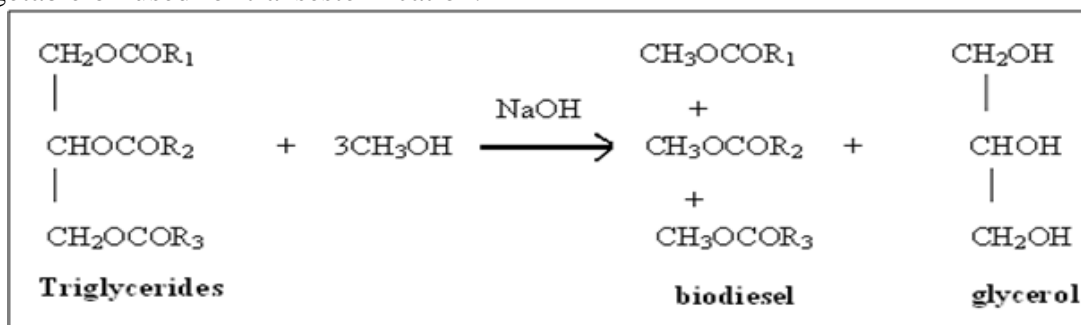
- 1). Power output is high.
- 2). Doesn't release CO, causes less pollution.
- 3). Alcohol is obtained from molasses, an agricultural product and hence renewable.
- 4). Biodegradable.

#### **Disdvantages**

- 1). Alcohol lowers the calorific value of petrol.
- 2). Alcohol is easily oxidized to acids, hence alcohol may cause corrosion.
- 3). Alohol absorbs moisture and as a result separation of alcohol and petrol layers takes place especially at low temperature.

### Biodiesel

It's a clean burning fuel obtained from the renewable resources such as vegetable oils like palm, soya bean, peanut etc. which are all triglycerides. But they cannot be conventionally used in diesel engines because they have high viscosity , high flash point & low volumetric heating value hence they are subjected to trans esterification reaction with excess methanol in presence of catalyst. The product mixture is monomethyl ester of long chain fatty acids & glycerin. The mixture is allowed to settle & the bottom glycerin layer is drawn off. The upper layer of methyl esters is washed & purified further to remove excess amount of methanol. This mixture of methyl esters is called as biodiesel & has the desired characteristics of diesel fuel with cetane no in the range of 50-62 depending on the vegetable oil used for transesterification.



### **Advantages**

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

## **FUEL CELLS:**

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

### **Differences between a Conventional cell (battery) and a fuel cell**

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

### **Limitations of fuel cells:**

1. Fuel cells produce energy only as long as fuels and oxidants are supplied
2. They cannot be recharged because either the raw materials or the products are gases.
- 3.

### **Advantages of fuel cells:**

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

### **Methanol – Oxygen fuel cell:**

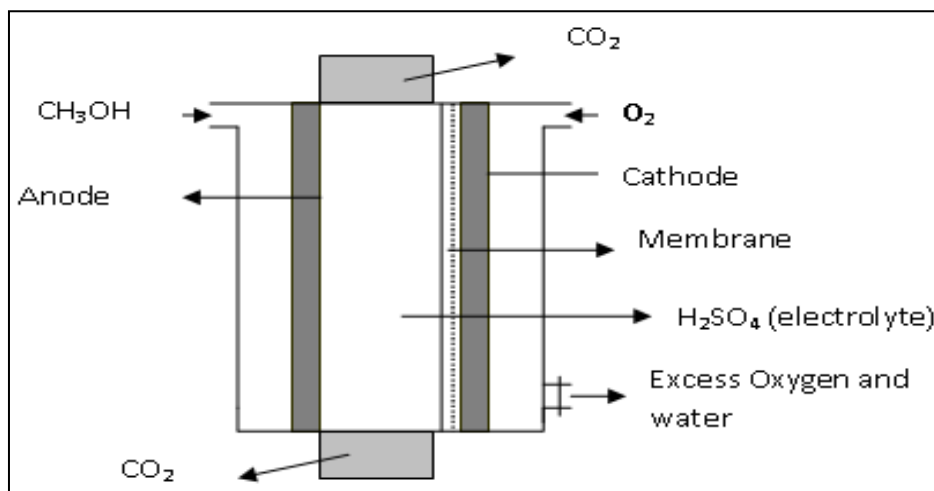
Methanol is an efficient electroactive organic fuel at low temperature. The advantages of methanol are (i) It has low carbon content.

(ii) It has a readily oxidizable OH group.

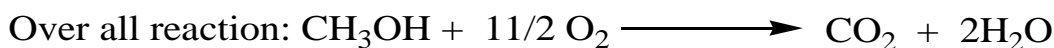
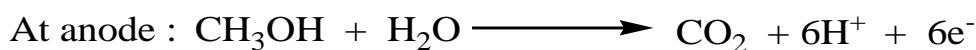
(iii) It has high solubility in aqueous electrolytes.

**Construction:** It consists of anode and cathode made of platinum. Sulphuric acid acts as the electrolyte. A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode. Methanol – H<sub>2</sub>SO<sub>4</sub> mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.





**Cell reactions:**

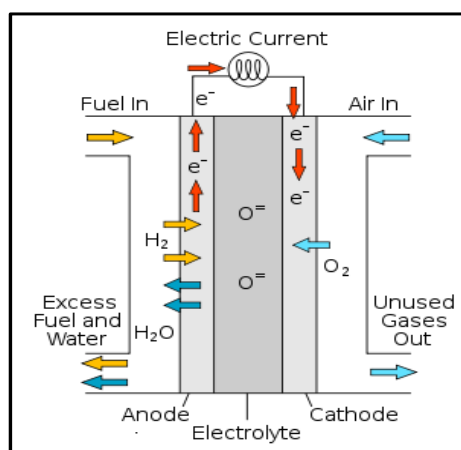


- Uses:** 1) Used in Military applications.  
2) Used for large scale power production stations.

**Solid oxide fuel cells**

A **solid oxide fuel cell** (or **SOFC**) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. Fuel cells are characterized by their electrolyte material; the SOFC has a solid oxide or ceramic electrolyte. Solid oxide fuel cells are a class of fuel cells characterized by the use of a solid oxide material as the electrolyte. SOFCs use a solid oxide electrolyte to conduct negative oxygen ions from the cathode to the anode. The electrochemical oxidation of the oxygen ions with hydrogen or carbon monoxide thus occurs on the anode side.

Solid oxide fuel cells have a wide variety of applications, from use as auxiliary power units in vehicles to stationary power generation with outputs from 100 W to 2 MW.



## SOLAR ENERGY

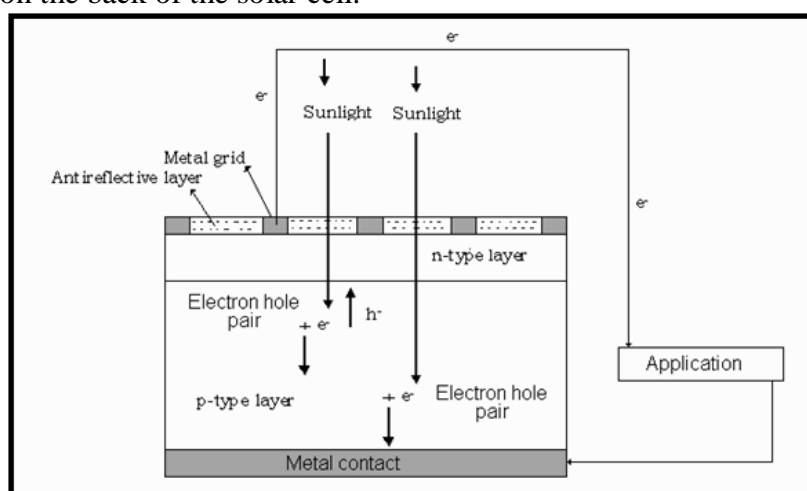
The radiations reaching earth from the sun and converting them into different useful forms of energy is called solar energy. The utilization of solar energy is of two types – Direct solar power and indirect solar power.

### Photovoltaic cells

Photovoltaic cells or solar cells are the devices which generate DC current from semiconductors on illumination.

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

Photovoltaic cell consists of a p-n junction formed from a semiconductor diodes of P-type and n- type brought together to form a metallurgical junction. The diode has two electrical contacts, one of which is in the form of a metallic grid and the other is a layer of nobler metal on the back of the solar cell.



When the light radiation consisting of photon particles incident on the metallic grid of the semiconductor normal to the plane .the photons carry a certain amount of energy given by  $E = hc/\lambda$  Where  $h$  is planck's constant  $c$  is the velocity of light and  $\lambda$  is the wavelength of the radiation . Those photons which posses the energy greater than  $E_g$  are absorbed .The electrons acquire this energy & are removed which leads to the formation of electron hole pair. These electrons are driven out into the external circuit and could be stored and used for various applications such as spinning of fan, working of a motor etc.

### **Advantages:**

1. The Solar power is pollution free.
2. It can operated with little maintenance or intervention after initial setup.
3. The Solar power is becoming more and more economical as costs associated with production decreases, and the technology becomes more effective in energy conversion.
4. The Solar power can be viewed as a local resource because of original climatic variances.

### **Disadvantages:**

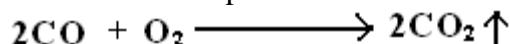
1. The Solar power is only practical in certain areas with a favorable climate and latitude. That is, areas near the tropics and which are relatively cloud free.
2. The Solar power is not available at night.
3. The Solar power decreases during cloudy.
4. The Solar power must be converted into some other form of energy to be stored.
5. Solar cell technologies produce DC power which must be converted to the AC power.

### **Production of solar grade silicon:**

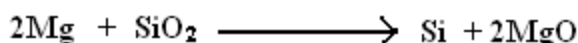
Quartz and carbon are placed in a crucible, two carbon electrodes are submerged in the crucible and an electric arc is struck. The mixture gets heated to a high temperature and the following reaction takes place.



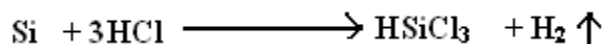
Silicon is obtained in the molten state CO is further oxidized to carbon dioxide & released to atmosphere.



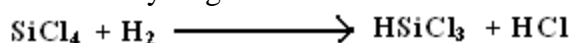
Silicon is further refined by treating with oxygen and slag forming additives such as AL, Ca & Mg. they react with silica to form slag and silicon., the slag is removed and refined melt is poured in moulds where Si solidifies. The silicon obtained is called metallurgical grade silicon.



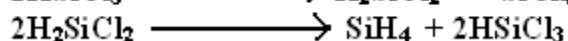
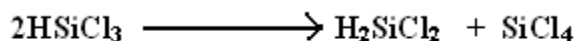
The metallurgical grade silicon is treated with dry HCL gas about 300°C to form trichlorosilane and a small amount of tetrachlorosilane. The mixture is distilled to get pure trichlorosilane.



Silicon tetrachloride is reduced with hydrogen at 1000 °C in a reactor .

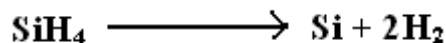


The trichloro silanes is then passed through fixed bed columns filled with quaternary ammonium ion exchange resin acting as catalyst.



The products are distilled & separated tetrachlorosilane & trichlorosilane are recycled to the hydrogenation reactor and the exchange resin respectively.

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



## Module – 4

### Environmental Pollution and Water Chemistry

**AIR POLLUTION:** Air pollution is the undesirable contamination of gas, smoke, dust, mist, odour or chemical particulates of the atmosphere which are dangerous to human beings, plants and animals.

**Composition of atmospheric air:**

Constituents	%
N <sub>2</sub>	78
O <sub>2</sub>	21
Argon (Ar)	< 1
CO <sub>2</sub>	0.037
H <sub>2</sub> O vapour	Remaining
O <sub>3</sub> , H <sub>2</sub> , NH <sub>3</sub>	Trace amount

**Sources of air pollution:** There are two main sources of air pollution.

1. Natural sources
2. Man – made or anthropogenic sources

**Natural Sources:** Natural sources cause large scale air pollution which is beyond the control of man.

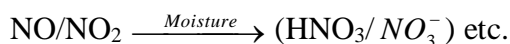
1. Natural contaminants present in the air are pollen, fungal spores, cysts, bacteria and marsh – gas. Methane (CH<sub>4</sub>) or marsh – gas is a hydrocarbon which is formed by decay of vegetable matter in marshy places (i.e. anaerobic decomposition of organic matter).
2. Carbon dioxide from the breakdown of methane
3. Volcanic eruptions release many gases and volcanic ash which cause air pollution.
4. Forest fire releases smoke and harmful trace gases.
5. Electric storms and solar flares pollute the air by the production of the harmful chemicals.
6. Salt spray oceans.
7. Dust storms.

**Man –made or anthropogenic sources:** Industries are the sources of a wide variety of air pollutants like SO<sub>2</sub> gas, NH<sub>3</sub>, NO<sub>2</sub>, HF, HCl and H<sub>2</sub>S gas besides dust, fumes, tar etc. Automobiles too result in emission of hazardous pollutants as by – product of the combustion of fossil fuel. Advanced agricultural techniques like spraying of crops for pest and weed control releases many pollutants like chlorinated hydrocarbon (BHC), organic phosphate, arsenic and lead etc. Nuclear explosions and explosives used in war result in radioactive fallout comprising radioactive pollutants like strontium – 90, cesium – 137, iodine – 131 etc. which have very long range effects.

**Classification of Air pollutants:** According to origin, the pollutants are classified into two types.

**Primary Pollutants:** They are emitted directly from various sources to the atmosphere in a potentially harmful form. Example: CO, ash, smoke, dust, mist, inorganic gases such as SO<sub>2</sub>, H<sub>2</sub>S, Sulphide, nitric acid, ammonia, CO<sub>2</sub>, HF, aromatic hydrocarbons and radioactive substances.

**Secondary Pollutants:** Some of the pollutants may react with one another or with the basic components of air to form new pollutants. They are called as Secondary Pollutants.



H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, smog, formaldehyde, phenoxy - acyl nitrate etc.

**Environmental effect of air pollution:**

**Effect of air pollution on human health:** Air pollutants have many acute as well as chronic effects on human health. These are as follows:

- (i) **Sulphur dioxide (SO<sub>2</sub>):** main contribution of emissions are thermal power plants, in which sulphur-containing coal and diesel are fired. Other sources are petroleum industry, oil refineries, sulphuric acid plants, and sulphide ore-roasting plants. The presence of this gas in the atmosphere cause cardiac (heart), respiratory (pulmonary) diseases to man (Ex: asthma, bronchitis), damage to agriculture, eye-irritation, throat troubles, besides corrosion of metals. Some effects of SO<sub>2</sub> in atmosphere on plants cells are membrane damage, chlorophyll destruction, metabolism inhibition, growth-yield reduction, etc.
- (ii) **Sulphur trioxide (SO<sub>3</sub>)** is formed by the oxidation of sulphur dioxide under the influence of sunlight. Even 1 ppm of SO<sub>3</sub> in air causes breathing discomfort and irritation to the respiratory tract.
- (iii) **Hydrogen sulphide** enter the atmospheric as the pollutants through the decomposition of sewage wastes or organic matter, and from various industries. It is more poisonous than even carbon monoxide and blackens lead paints and causes corrosion of metals.
- (iv) **Oxides of Nitrogen (NO, NO<sub>2</sub>)** 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 vehicles, power plants, industries, etc., the pollution due to nitrogen oxides is increasing day-by-day. In high NO<sub>2</sub> areas, respiratory illness, among children, have been reported. It is unpleasant in odour and leads to irritation of eyes and even lung's congestion. In sunlight, nitrogen oxides and hydrocarbons (from combustion of petroleum products) form smog, which: 1) limits the visibility of roads; 2) causes eye irritation 3) causes difficulty in breathing thereby lung's asthma and bronchitis may result in men living around it.
- (v) **Carbon monoxide (CO)** is released by the partial combustion of fuel in automobiles, industries and oil-refineries. Cigarette and beedi smoke and domestic heat-appliances are the other sources of CO. it is estimated that about 290 million tonnes of CO is discharged into the atmosphere annually. Although it is colourless, odourless, non-corrosive, yet is very toxic in nature. It is headache, visual difficulty, paralysis and even death in the human-beings. Carbon monoxide reacts with the red pigments (haemoglobin) to form carboxy-haemoglobin, thereby impairing the transfer of oxygen to the tissues. In other ward, the presence of CO reduces the oxygen-carrying

capacity of blood. This ultimately causes headache and lassitude, especially by inhaling tobacco smoke. This can lead to such symptoms as laziness, exhaustion of body, headache, decrease in visual perception, and serious effects on the cardiovascular system, thereby causing heart diseases.

- (vi) **Carbon dioxide** is released into the atmosphere in the form of smoke, which is produced by burning of fuels such as coal, wood, petroleum products, and gaseous fuels. The CO<sub>2</sub> is also released into air by the respiration of plants and animals. Increasing population is causing faster increase in concentration of CO<sub>2</sub> in the atmosphere. The concentration of CO<sub>2</sub> is also increased by deforestation. The plants use CO<sub>2</sub> for photosynthesis and release of oxygen. The cutting down of forests makes the environment unhealthy by the decreasing concentration of oxygen. The excess of CO<sub>2</sub> in the atmosphere causes respiratory disorders and suffocation.
- (vii) **Particulates:** (1) **Dust:** main sources of dust are mines and quarries, furnaces, power houses, vehicular traffics, house cleaning dusts, pottery and ceramics factory stacks, agriculture, forest fires, natural winds, combustion operations, material handling and processing, earth movements, engine exhausts, rubber tyre abrasions and a hundred other activities raise dust in the atmosphere.

Effects: on man atmospheric dust causes allergic and respiratory diseases, silicosis, if dust contains silica. Dust also causes corrosion and soiling.

- (2) **smoke** (composed of tiny particles of carbon, ash, oil, etc.) 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 emission are rails, roads, locomotives, domestic wood, coal-grates, industrial power plants, open fires, refuse incinerators, diesel engines, automobile gasoline engines, furnaces, hearths, etc.

Effects: loss of fuel value, through imperfect combustions. Spoiling of clothing, rags and exterior finish of buildings. The incidence of cancer is being increasingly related with smoke.

- (3) **Smog** is a mixture of smoke (from coal combustion) and fog in suspended droplet form.

(4) **Asbestos:** widely used in industry for its mechanical strength and resistance to heat, especially as thermal insulation material in high temperature applications, where the high chemical stability of the silicate structure serves well. However, in recent years it has been established that prolonged exposure to airborne suspensions of asbestos fibre dust can be very dangerous and pose health hazard. Tiny asbestos fibres readily penetrate the lung tissues and the digestive tract, and they remain there over a long period of time. Eventually, lesions, including asbestosis, cancer may result. The symptoms, however, may take years to develop.

- (viii) **Mercury:**

The toxicity of mercury depends very much on its state. Pure mercury is not particularly poisonous; in fact, ingestion of very small amount of mercury (ex; from the dental amalgam) produces no noticeable ill effects, since the metal apparently passes through the body without undergoing chemical change. On the other hand, mercury vapour is very dangerous, because it causes irritation and destruction of lung tissues. Because mercury is so widely used in household (thermometers, etc.) and laboratories, spillage occurs frequently. Simple calculations show that only 3 mL of mercury can saturate a

large room (poor ventilated) with its vapour within a week, thereby making it unsafe to live/work in. spilled mercury is almost impossible to recover completely, because the liquid enters the cracks crevices in the floor. Mercury in vapour form adversely effect the neurological behavior of humans. The toxicity of inorganic mercury compounds dependson their solubilities. For example, the insoluble  $\text{Hg}_2\text{Cl}_2$  is not considered very toxic, and in fact, has been used in medicine as purgative and a drug to kill interstitial worms. Since mercuric salts are generally more soluble they are considerably more toxic. The  $\text{Hg}^{2+}$  ions concentrates chiefly in the liver and kidneys. The harmful effects are usually slow to develop. Symptoms are sore gums and loose teeth. Mercury-poisoning can cause brain damage to unborn infants and can lead to a condition called erethism(charecterizedby jerking, irritability, mental and emotional disturbances). mercury – poisoning is a serious occupational hazard for workers in industries producing mercury, mercury compounds and their solutions. The  $\text{Hg}^{2+}$  ions react with the sulphhyryl groups  $-\text{SH}$  of the proteins and therefore inhabit enzymatic activities. The most toxic of all the mercury compounds are dimethyl mercury and the dimethyl mercury ions. Due to the presence of nonpolar methyl groups these compounds are more soluble in the membrane, separating the blood-stream from the brain. It was once believed that washing of elemental mercury would stay at the bottom of lake or river and be slowly converted into rather harmless  $\text{HgS}$ . However, this is not the case. Certain bacteria and microorganisms metabolizes mercury first to  $\text{Hg}^{2+}$  ions and eventually to  $\text{CH}_3\text{Hg}^{2+}$  and  $(\text{CH}_3)_2\text{Hg}$ . Fish take in bacteria and methyl mercury compound, slowly concentrate in the fatty tissues of their bodies. Small fish are eaten by large fish until, finally, at the end of this food-chain, humans eat these fishes. Because of the cumulative effect, by the time we eat fishes from a mercury contaminated lake the amount of mercury ions in its body may be 50,000 times greater than the mercury concentration in the lake water. The buildup of any poison along a food-chain, is called bio magnification. The best treatment, for mercury-poisoning is a dosage of chelating agents such of EDTA. The impact of mercury pollution has been so strong that many mercury-containing compounds have been banned in industry and agriculture.

Mercury is contained in many products, including:

- batteries
- measuring devices, such as thermometers and barometers
- electric switches and relays in equipment
- lamps (including some types of light bulbs)
- dental amalgam (for dental fillings)
- skin-lightening products and other cosmetics Pharmaceuticals.

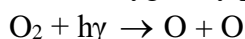
**Effect of air pollution on plants:** Spraying of pesticides and other agricultural practices has exposed the plants to a large number of air pollutants affecting their growth and metabolism by destroying chlorophyll and disrupting photosynthesis.

1.  $\text{SO}_2$  bleaches the leaf surface and cause chlorosis (i.e. loss of chlorophyll and yellowing of the leaf) especially in leaf vegetables.

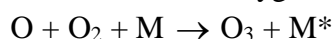
2. NO<sub>2</sub> causes premature leaf fall (abscission) and suppressed growth of plants resulting in reduced yields of crop plants.
3. Ozone causes necrosis (dead areas on a leaf structure) and damages leaves.
4. PAN (peroxyacyl nitrate) damages leafy vegetables causing premature fall, decolouration and curling of sepals.

### Ozone layer depletion:

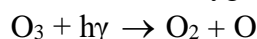
Ozone layer filters out harmful ultraviolet radiations from the sunlight and thus protects various life forms on the earth. Ozone is a form of oxygen. The molecule of oxygen contains two atoms where as ozone contains three oxygen atoms. In the stratosphere ozone is continuously created by the absorption of short wave length ultraviolet radiations. It decomposes molecular oxygen into atomic oxygen by photolytic decomposition.



The atomic oxygen rapidly reacts with molecular oxygen to form ozone.



M is a third body necessary to carry away the energy released in the reaction. Ozone formed is distributed itself in the stratosphere and absorbs harmful ultraviolet radiations and is continuously converted back to molecular oxygen.



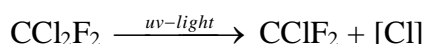
The net result of the above reactions is an equilibrium concentration of ozone. This equilibrium is disturbed by reactive atoms of chlorine, bromine etc., which destroy ozone molecules and results in thinning of ozone layer called ozone hole. Three major activities could destroy the ozone layer.

- i. The use of spray cans and refrigerants that contain Freon gas.
- ii. High flying supersonic jets.
- iii. The detonation of nuclear weapon.

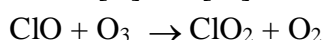
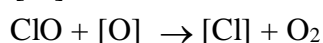
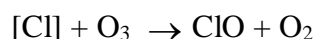
In many developing and developed countries, two Freon are used.

- i. Freon – 11 (trichloromono fluoromethane) is banned by many countries
- ii. Freon – 12 (dichloro difluoromethane) is still used in refrigerators. Air conditioners and freezers. The effects of freons on Ozone layer was occurred through two steps ie., photo dissociation and reduction of ozone as follows

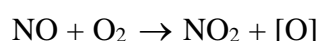
Step I - Photo dissociation of Freon 12



Step II - Ozone depletion or hole formation



Aircrafts and jet engines also produces NO in the stratosphere which also reduce the ozone is as follows.



Due to this effect, leads to the formation of permanent depletion in ozone layer.

### Effects of ozone layer depletion

The effects of ozone layer depletion are penetration of more amount of uv-light which produces skin burns and skin cancer, kills lower fauna and flora. It affects photosynthesis



process, cause mutations and may stop growth. However it also affects the climate change due to the elimination of stratospheric ozone. Yield of vital crops like corn, rice, soybean, bean, cotton, and wheat will decrease. Degradation of paints, plastics and other polymer material will result in economic loss due to effects of UV radiation resulting from ozone depletion.

### **Control of air pollution**

1. Smoke can be reduced during the combustion of fuel. Correct method of burning, allowing required amount of air and using high temperature will considerably reduce the amount of smoke. Uniform quantity of air and fuel supply will reduce the smoke considerably.
2. Smoke from automobile emissions can be considerably reduced by fixing catalytic converters in the exhaust pipes.
3. The installation of tall stacks or chimneys in industrial gas outlets prevents the accumulation of smoke in the ground level.
4. Cottrell electrostatic precipitator is a device used in industrial gas outlets which makes the smoke to settle as carbon particles.
5. By using extraction ventilation method in industries which remove the dust. There are other methods of dust removal which make use of devices such as bag filter, cyclone dust separators, centrifugal separators etc.,
6. Sulphur dioxide gas pollution can be reduced by removing sulphur before combustion or removal of SO<sub>2</sub> gas by passing through various absorbents like alkalized alumina, activated carbon, limestone powder, liquid ammonia, lime water etc.,  
$$2\text{NH}_4\text{OH} + \text{SO}_2 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$$
$$\text{Ca}(\text{OH})_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$$
7. Acid and chemical fumes can be absorbed through a tower filled with coke powder and current water is applied at the top.
8. Proper planning in industrial areas is a must for avoiding pollution. The residential quarters should be built leaving comfortable gap between industrial area and residential area. This kind of planning is known as industrial zoning.
9. Air Pollution can be considerably reduced by avoiding fossil fuels like coal or petroleum. Products and making much use of hydroelectricity, nuclear power, solar energy etc.
10. Growing more vegetation and protecting the existing forests will considerably clean the environment. Plants use carbon dioxide for photosynthesis and evolve oxygen. Hence the help to reduce the carbon dioxide level in the atmosphere. Many plants also absorb notable amount of other gases like H<sub>2</sub>S, NO, N<sub>2</sub>O, NO<sub>2</sub>, etc. The vegetation and forest act like a sieve in settling dust particles which pass through them.

### **Waste Management**

‘Wastes’ are materials which are discarded after use at the end of their intended life-span. Waste management is a collective activity involving segregation, collection, transportation, re-processing, recycling and disposal of various types of wastes. Waste

management differs for different types of wastes and for wastes in different geographical locations such as urban, rural and hilly areas.

**SOLID WASTE:** Rapid industrialization and population explosion in India has led to the migration of people from villages to cities, which generate thousands of tons of MSW daily. The MSW amount is expected to increase significantly in the near future as the country strives to attain an industrialized nation status by the year 2020.

The quantity of waste generated in Indian cities reported to be in the range of 0.2-0.6 kg/capita /day as per the “Manual on Solid Waste Management” prepared by Central Public Health & Environment Engineering Organisation (CPHEEO), Ministry of Urban Development, and Government of India.

The Waste Generation pattern is very much dependant on the living style of the population. As the major share of the population is labour force in Dibrang, the waste generation factor of 0.3 kg/capita/day has been taken into consideration.

**Solid waste management consists:**

**Municipal waste:** Municipal Solid Waste (MSW) or Urban Solid Waste is a waste that includes predominantly household waste (domestic waste) with sometimes the addition of commercial wastes, construction and demolition debris, sanitation residue, and waste from streets , institutes such as hospitals, collected by a municipality within a given area. They are in either solid or semisolid form and generally exclude industrial hazardous wastes.

**Electronic waste (e-waste):** Electronic metal waste, printed circuits boards, e-equipments, machinery, IC, Sockets connections etc.

**Biomedical waste:** Hospitals generate various kinds of wastes from wards, operation theatres and outpatient areas. These wastes include bandages, cotton, soiled linen, body parts, sharps (needle, syringes etc), medicines (discarded or expired), laboratory wastes etc which carry infection and should be properly collected, segregated, stored, transported, treated and disposed to prevent contamination and infection.

India generates a huge quantity of Bio Medical Waste (BMW) every year. Almost 28% of the wastes is left untreated and not disposed finding its way in dumps or water bodies and re-enters our system.

**Following are the major sources of generation of waste at urban level:**

- Solid waste from Residential areas, Institutional/ Community areas
- Solid waste from vegetables markets (retail and wholesale)
- Solid waste from Hotels, and restaurants
- Solid waste from commercial areas
- Biomedical waste from hospitals and dispensaries
- Waste from domestic / stray animals /dairies
- Solid waste from Industries
- Waste from street cleansing

**Methods of solid waste disposal and management:**

- Open burning.
- Dumping into the sea.
- Sanitary Landfills.
- Incineration.
- Composting.
- Ploughing in fields.
- Hog feeding.
- Grinding and discharging into sewers.

**Water Chemistry**

**Introduction:**

1. Water is the most basic and fundamental component of life.
2. It is the most wonderful substance gifted by nature to all the living beings on the earth.
3. 72% of the earth's surface is covered by water. It is distributed as follows :

Oceans	-	97.23%
Ice	-	2.14%
Fresh Water	-	0.03%
Other	-	0.01%
4. Among the three essentials of life i.e., air, water and food, water occupies the second position.
5. Health and wealth of a nation largely depend on the availability and utilization of quality of water.

**Sources of water:** Rainwater, river water, lake water, sea water and well water.

**Impurities in water:**

1) Dissolved impurities:

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

Ex: - When water is in contact with soil (or rock), limestone present in rock combines with water along with CO<sub>2</sub> of water to give Ca(HCO<sub>3</sub>)<sub>2</sub>. This impurity dissolves in water. Hence it acts as a dissolved impurity.



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

2) Suspended impurities:

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

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

3). Dissolved gases:

The water contains mainly CO<sub>2</sub>, O<sub>2</sub> as dissolved gases. Some water may contain ammonia and sulphur compounds such as hydrogen sulphide (H<sub>2</sub>S) as dissolved gas. The presence of these gases imparts a foul smell to the water.

4). Organic matter (microscopic matter):

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

**Boiler feed water:**

Water is mainly used in the boiler for the generation of steam for industries and powerhouses. For such water, all the impurities are not necessarily eliminated and only those impurities which trouble for the operation of boilers are kept within tolerable limits.

A boiler feed water should correspond with the following composition

1. Its hardness should be 0.2 ppm
2. Its caustic alkalinity should lie in between 0.15-0.45 ppm
3. Its soda alkalinity should lie in between 0.45-1ppm

**Boiler troubles**

If exceeds of impurities present in boiler feed water, they lead to the formation of scales, sludge, priming, foaming and caustic embrittlement.

**Sludge and scale formation in boiler:** In boilers, water is evaporated to get steam. This increases the concentration of dissolved salts. Finally, a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed within the boiler are soft, loose and slimy are called **sludge**.

If the precipitates formed within the boiler are hard and strongly adhered to the inner walls of the boiler are called **scales**.

**Disadvantages of scales and sludge**

1. Wastage of fuel: scales have a poor conductor of heat, so the rate of heat transfer from the boiler to water is greatly reduced, hence causes to increase the fuel consumption.
2. Lowering of boiler safety: Due to scale formation, overheating of boiler required for study supply of steam. The overheating boiler tube makes the boiler material softer and weaker.
3. Decrease in efficiency: Deposition of scales in the valves and condensers of the boiler, this results in a decrease in efficiency.
4. The danger of explosion: The scales formation also leads to the expansion of boiler material. Due to uneven expansion, thick scale cracks, water comes suddenly in contact with overheated iron plates which may lead to the explosion of boilers.

**Priming**

The process of passage of water particles along with steam is called priming.

Priming caused by

1. The presence of dissolved impurities particularly the suspended particles
2. The high steam velocities
3. Sudden boiling
4. Improper design of boilers

### Foaming

The process of production of continuous foam or bubbles in boilers is called foaming.

Foaming is caused by the presence of oil and alkalis in boiler feed water.

Foaming can be avoided by the addition of antifoaming agents like sodium aluminates and aluminum sulphate which spreads on the surface of the water and therefore which neutralizes the reduction in surface tension.

### Disadvantages of priming and foaming

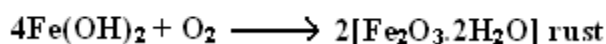
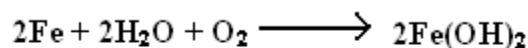
1. It decreases the efficiency of the boiler because the dissolved salts get deposited on turbine blades and superheater by evaporation.
2. The maintenance of the boiler pressure becomes difficult due to the improper judgment of actual height of water column.

### Boiler corrosion

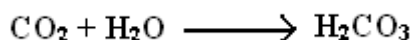
It is decay or disintegration of boiler material either material through chemical or electrochemical reaction with its environment.

Corrosion in boiler is due to the following reasons

1. The presence of dissolved oxygen: this is the most usual corrosion causing factor. When water containing dissolved oxygen is heated in the boiler, the free gas is evolved under the high pressure of the boiler and attacks the boiler materials and forms the rust.

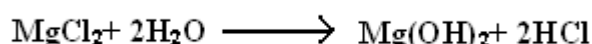


2. The presence of carbon dioxide: carbon dioxide forms carbonic acid in the presence of water which has a slow effect on boiler materials.



3. Presence of Dissolved salts ( $\text{MgCl}_2$ )

Magnesium chloride forms hydrochloric acid in the presence of water which has a slow effect on boiler materials.



### Disadvantages of boiler corrosion

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

### Source of water pollution

#### SEWAGE:

Sewage is the liquid waste, which includes household waste water, industrial wastes, ground wastes etc. Sewage contains both organic and inorganic substances in dissolved, suspended and colloidal form. Sewage is classified into two types namely domestic sewage and industrial sewage.

Domestic sewage: It is the liquid waste comes from residences, institutions. It mainly consists of organic substances which are rich in microorganisms.

Industrial sewage: It is the liquid waste comes from industries. It contains substances like acids, oil, toxic chemicals, metals, animal and plant matters, non-biodegradable compounds etc.

Sewage contains living organisms such as bacteria, algae, fungi and protozoa.

1. Aerobic bacteria:- Which live on free oxygen or on oxygen dissolved in water.
2. Anaerobic bacteria:- Which live and develop in the absence of free oxygen.

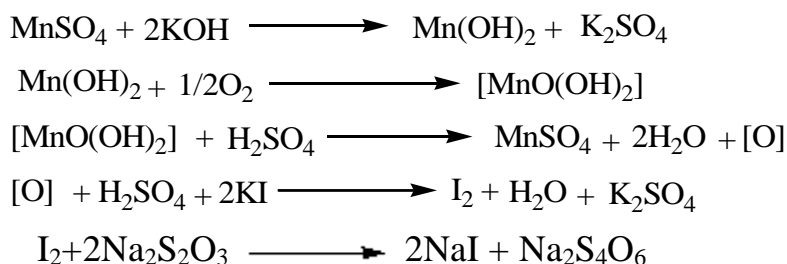
1. Aerobic oxidation: Organic compounds are oxidized by aerobic bacteria's which do not produce any offensive smell. This kind of oxidation is known as aerobic oxidation.
2. Anaerobic oxidation: Organic compounds are oxidized by anaerobic bacteria's which produce an offensive smell. This kind of oxidation is known as anaerobic oxidation.

### **Biological Oxygen Demand**

Def<sup>n</sup>:-The amount of oxygen required for the biological oxidation of the organic matter under an aerobic condition at 20°C and for a period of 5 days.

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

**Principle:-** This method is based on the indirect iodometric titration. Manganese sulphate reacts with an alkaline solution to give manganese hydroxide. Manganese hydroxide reacts with DO to give basic manganese hydroxide and precipitated. Precipitation is dissolved by addition of con. H<sub>2</sub>SO<sub>4</sub> and nascent oxygen are liberated. Nascent oxygen oxidises potassium iodide to iodine. The liberated iodine is titrated against standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.



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

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

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

**Observation and calculation**

D<sub>1</sub> is the DO of the sample in mg/ml at the start of the experiment

D<sub>2</sub> is the DO of the sample in mg/ml after 5 days.

A is ml of the sample before dilution

B is ml of the sample after dilution

$$\text{BOD} = \frac{D_1 - D_2}{A} \times B \text{ mgdm}^{-3}$$

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

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

### Chemical oxygen demand

It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds present in one  $\text{dm}^3$  of waste water using strong oxidizing agent  $\text{K}_2\text{Cr}_2\text{O}_7$  under acidic medium.

**Principle:** A Known amount of water is refluxed with a known excess acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  and a small amount of  $\text{Ag}_2\text{SO}_4$  and  $\text{HgSO}_4$  are added.  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidizes all oxidizable impurities.

The amount of unconsumed  $\text{K}_2\text{Cr}_2\text{O}_7$  is determined by titration with std. FAS (ferrous ammonium sulphate) solution using ferroin indicator. The amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution consumed corresponds to the COD of the sewage sample.

#### Procedure:-

##### Sample or Back titration:-

Pipette 25 ml of waste water into a clean conical flask add 2 test tube of 2N  $\text{H}_2\text{SO}_4$  solution and pipette out 10 ml of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution to the same conical flask. Add 1g of  $\text{HgSO}_4$  followed by 1g  $\text{Ag}_2\text{SO}_4$ . Attach a reflux condenser and reflux contents for 2 hours. Cool and titrate the unconsumed  $\text{K}_2\text{Cr}_2\text{O}_7$  against FAS using ferroin indicator till the color of the solution changes from bluish green color to reddish brown.

Blank titration:- The above procedure is repeated by taking only 10 ml of  $\text{K}_2\text{Cr}_2\text{O}_7$

#### **Observation and calculation:-**

Volume of water sample taken=  $V_1 \text{ cm}^3$

Volume of standard FAS used in sample titration=  $A \text{ cm}^3$

Volume of standard FAS in the blank titration=  $B \text{ cm}^3$

Normality of FAS solution=  $N$

Amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  consumed in satisfying the COD in terms of FAS solution= $(B-A)\text{cm}^3$

$$N_1 \times V = N \times (B - A)$$

$$\text{Normality of COD of the sample } N_1 = \frac{N \times (B - A)}{V}$$

$$\text{COD of the sample} = \frac{N \times (B - A)}{V} \times 8 \text{ g.dm}^{-3}$$

$$\text{COD of the sample} = \frac{N \times (B - A)}{V} \times 8 \times 1000 \text{ mg.dm}^{-3}$$

#### **Importance:**

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

**Problems:-** (1) 20ml of sewage sample for COD is reacted with 25 ml of  $K_2Cr_2O_7$  solution and the unreacted  $K_2Cr_2O_7$  requires 9.0ml of N/4 FAS solution. Under similar conditions, in blank titration 15.0 ml of FAS is used up; calculate the COD of the sample.

Volume of sample taken= 20 ml

Volume of N/4 FAS required to react with unconsumed  $K_2Cr_2O_7$ =9.0ml

Volume of FAS consumed in blank=15.0ml

Amount of  $K_2Cr_2O_7$  consumed to satisfy COD

in terms of FAS solution=15.0-9.0=6 ml

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 20 = 0.25 \times 6.0$$

Therefore, normality of COD Sample  $N_1 = \frac{0.25 \times 6}{20}$

$$\text{COD of the sample} = \frac{0.25 \times 6}{20} \times 8 = 0.6 \text{ g / dm}^3 = 600 \text{ mg / dm}^3$$

(2) 25 cm<sup>3</sup> of sewage water was reacted with 10 cm<sup>3</sup> of 0.25N  $K_2Cr_2O_7$  in Conc.  $H_2SO_4$  medium. The unreacted  $K_2Cr_2O_7$  needed 6.1 cm<sup>3</sup> of 0.1N FAS. 10 cm<sup>3</sup> of 0.25 cm<sup>3</sup> N  $K_2Cr_2O_7$  when titrated under the same condition required 28.2 cm<sup>3</sup> of 0.1N FAS. Calculate the COD.

Volume of 0.1N FAS required to react with unconsumed  $K_2Cr_2O_7$ =6.1 ml

Volume of FAS consumed in blank=28.2ml

Amount of  $K_2Cr_2O_7$  consumed to satisfy COD

in terms of FAS solution=28.2-6.1=22.1 ml

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 25 = 0.1 \times 22.1$$

Therefore, normality of COD Sample  $N_1 = \frac{0.1 \times 22.1}{25}$

$$\text{COD of the sample} = \frac{0.1 \times 22.1}{25} \times 8 = 0.7072 \text{ g / dm}^3 = 707.2 \text{ mg / dm}^3$$

(3) In a COD test, 28.1 and 14.0 cm<sup>3</sup> of 0.05 N FAS solution were required for blank and sample titration respectively. The volume of a test sample used is 25 cm<sup>3</sup>. Calculate the COD of the sample solution.

Volume of 0.1N FAS required to react with unconsumed  $K_2Cr_2O_7$ =14.0 ml

Volume of FAS consumed in blank=28.1ml

Amount of  $K_2Cr_2O_7$  consumed to satisfy COD

in terms of FAS solution=28.1-14.0=14.1 ml

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 25 = 0.5 \times 14.1$$

Therefore, normality of COD Sample  $N_1 = \frac{0.5 \times 14.1}{25}$

$$\text{COD of the sample} = \frac{0.5 \times 14.1}{25} \times 8 = 0.225.6 \text{ g / dm}^3 = 225.6 \text{ mg / dm}^3$$



Chemical analysis of waterDetermination of sulphate by Gravimetric method:

Sulphate ion is one of the major anions present in natural water. It is present in water in the form of  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$  and causes permanent hardness in water and boiler scale. Water containing 250 mg/l sulphate ion is objectionable and is not suitable for drinking as well as for industries.

Gravimetric method gives most accurate results and it is the recommended procedure for determination of sulphate above 10 mg/l.

Principle: Sulphate ion is precipitated as barium sulphate by adding barium chloride to water sample acidified with hydrochloric acid



The  $\text{BaSO}_4$  ppt is filtered through Gooch Crucible and weighed.

To precipitate sulphate ions as completely as possible, excess barium chloride is added. The  $\text{BaSO}_4$  ppt formed is in colloidal condition. Hence this ppt cannot be removed by ordinary filtration procedures.

Procedure: Transfer 200 ml of water sample (if turbid, filter) to a beaker and add concentrated HCl drop wise until it is just acidic, and add 3 drops excess. Boil the sample to reduce the volume to 50 ml. Add hot Barium chloride (10%) solutions slowly with constant stirring until all the sulphate ions are precipitated (Avoid adding excess  $\text{BaCl}_2$ ). Digest the sample at temperature near the boiling point for a few hours, filter through a Gooch crucible and wash the precipitate with hot distilled water until the washings are free from chlorides. Dry the ppt and weigh.

Calculation:-

233.3 g of  $\text{BaSO}_4$  contains 96.0 g of  $\text{SO}_4^{2-}$

$$\text{W gm of BaSO}_4 \text{ Contains} = \frac{96.0 \times W}{233.3}$$

$$\text{Percentage of SO}_4^{2-} = \frac{96.0 \times W \times 100}{233.3} \text{ g / dm}^3$$

$$= \frac{96.0 \times W \times 100}{233.3} \times 1000 \text{ mg / dm}^3$$

Determination of Fluoride by Colorimetric method

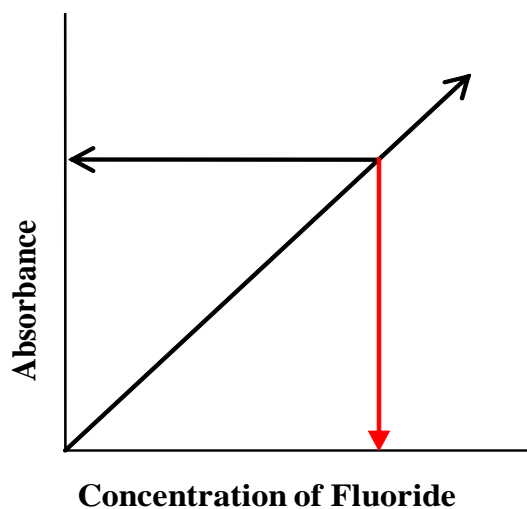
Fluoride ions are present in water as  $\text{NaF}$ ,  $\text{CaF}_2$  etc.

Principle:- Under acidic conditions, fluoride ions react with zirconium SPADNS solution to form complex (Zr-SPADNS). And the colour of Zr-SPADNS gets bleached by the fluoride ions. As the concentration fluoride ion increases, bleaching of Zr-SPADNS

solution is also more. Thus bleaching action of Zr-SPADNS solution indicates the amount of fluoride ions present in water. This complex absorbance is maximum at 570 nm, hence find the absorbance of all the bleached solutions at 570 nm.

**Procedure:-**

1. Preparation of Zirconyl-SPADNS solution: prepare zirconyl chloride solution and SPADNS solution separately. Then mix the two solutions equally.
2. Prepare a reference solution by adding 10 ml SPADNS solution to 100 ml distilled water to which add a solution of HCl(7ml conc.HCl diluted to 10ml). Use this solution to set zero in the colorimeter at 570 nm (Blank)
3. Prepare a std.solution of NaF and pipette out 1, 2, 3ml etc of this solution into different 50 ml volumetric flask.
4. Add 1 drop of NaHSO<sub>3</sub> solution (0.5%) to remove any residual chlorine to each solution.
5. To all the solutions add 10 ml of Zirconyl –SPADNS solution, mix well and find the absorbance at 570 nm.
6. Draw a calibration curve by plotting concentration vs absorbance.
7. Take suitable quantity of water add 10 ml Zirconyl-SPADNS solution and find the absorbance at 570 nm.
8. Using the calibration curve, calculate the concentration of fluoride ions in the given water sample.



**Sewage treatment:**

Sewage water is a waste from the kitchen, laundries, bathroom, laboratories and industries. The domestic sewage contains a heavy load of BOD, pathogens bacteria, colour, odour and bad smell etc. Sewage water is discharged into water bodies, leads to a deficiency of dissolved oxygen and leads to the death of the oxygen. Pathogen bacteria are causing water borne diseases.

**(a) Mechanical or Primary treatments**

Removing of suspended solids is called **primary treatment**. It involves the removing of suspended solids like woods, plastic through screening, filtering and sedimentation.

**Screening:** It is a physical process which removes larger suspended or floating matter in the sewage. Which retain the floating and suspended coarse particles

**Filtration:** The water is passed through conventional sand filter beds to remove the last trace of suspended matter.

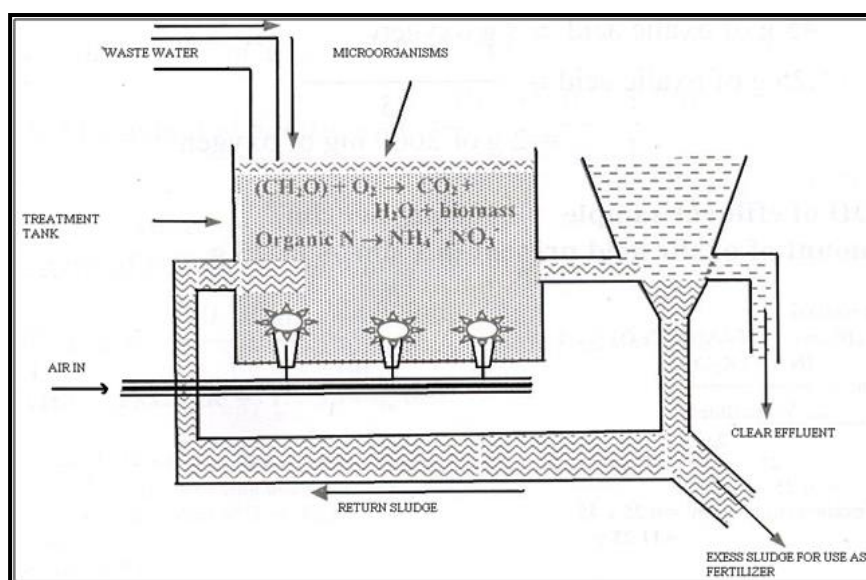
**Sedimentation** is a process of removing suspended impurities present in water by the process of settling.

**Coagulation;** is a process of removing colloidal particles from water by the addition of certain chemicals known as coagulation. Coagulation is carried out for the quick settling of colloidal particles. Alum  $[K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O]$  and ferrous sulphate  $(FeSO_4 \cdot 7H_2O)$  are commonly used coagulants.

**(b) Secondary treatment:** Secondary process involves aerobic oxidation of organic matter.

**Sludge:** The matter which settles down at the bottom after the treatment is called sludge and the liquid is called effluent.

**Activated sludge process:** Activated sludge contains aerobic microorganisms is sprayed over the water is from primary treatment is allowed to flow into large tanks. The microorganisms present in the sludge form a thin layer on the organic wastes in the sewage. Air is passed vigorously from the centre of the tank in order to bring good contact b/w the organic wastes and bacteria in the presence of air and sunlight under these conditions, aerobic oxidation of organic matter occurs. The sludge formed is removed by filtration.



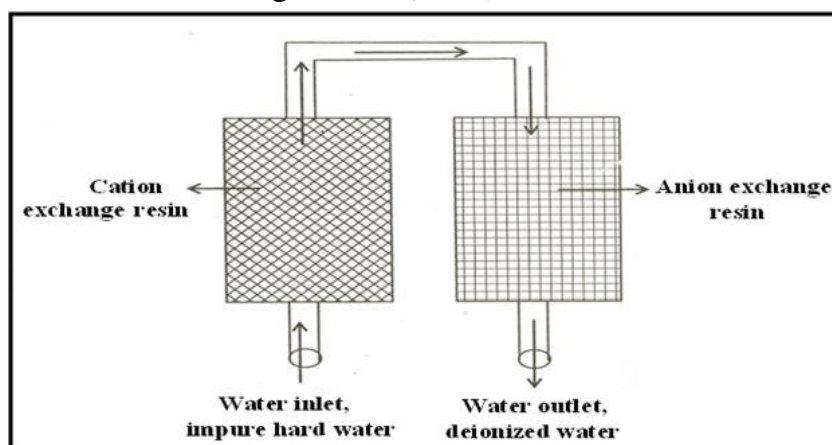
A part of the sludge is reduced and the rest is used as fertilizer. The residual water is chlorinated to remove bacteria and finally discharged into running water. The sludge process operates at 90-95 % efficiency of BOD treatment. If the treated water contains a high concentration of phosphates, heavy metal ions, colloidal impurities and non-degradable compounds then it needs tertiary treatment.

### c) Tertiary treatment:

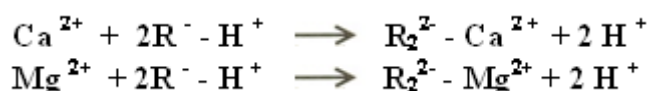
1. Treatment with lime for the removal of phosphates as insoluble calcium phosphates.
2. Treatment with  $S^{2-}$  ions for the removal of metal ions as insoluble sulphides.
3. Treatment with activated charcoal to adsorb remaining organic compounds.
4. Treatment with alum to remove the colloidal impurities not removed in the previous treatments.

### Softening of water by ion exchange process:

Water softening is the removal of calcium, magnesium and certain other metal cations in hard water. In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin. Ion exchange resins are high molecular weight, cross-linked polymers with a porous structure. The functional groups which are attached to the chains are responsible for ion exchange properties. The resins containing acidic groups which are capable exchanging  $H^+$  (or  $Na^+$ ) ions for cations ( $Ca^{2+}$  or  $Mg^{2+}$ ) present in water are known as cation exchange resins ( $RH^+$ ). The resins containing basic groups which are capable exchanging  $OH^-$  for anions ( $Cl^-$ ,  $SO_4^{2-}$ ) present in water are known as anion exchange resins ( $ROH^-$ ).



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



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



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

#### **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.

#### **Disadvantages:**

1. Equipment and process are costly.
2. Turbid water needs to be filtered first before softening.

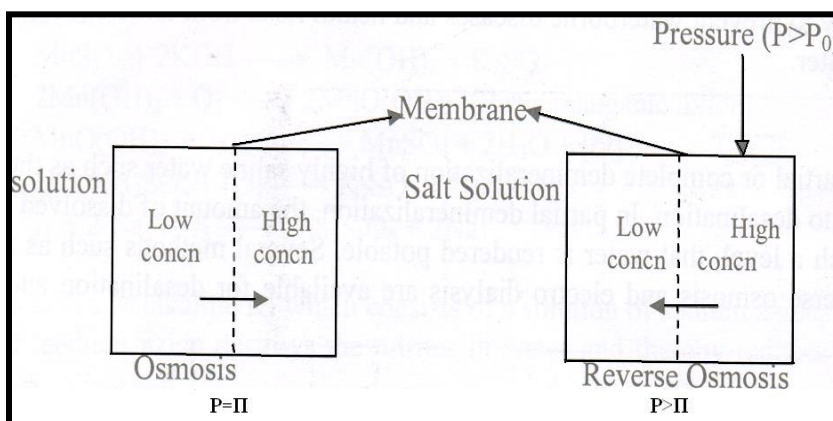
## Desalination or Desalting:

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

### Reverse osmosis

Osmosis is the physical movement of a solvent through a semipermeable membrane. This is based on a difference in chemical potential b/w two solutions (salt solution and water) as the membrane allows only water molecules, not salt. The salt water thus has a greater chemical potential than water on the other side of the membrane. To equalize the difference in chemical potential, water diffuses through the membrane from the water side to the salt water side. This movement is Osmosis, in this case, the pressure is equal to Osmotic pressure ( $\Pi$ ). In Osmosis diffusion from lower concentration to higher concentration.

When pressure is greater than Osmotic pressure ( $P > \Pi$ ) diffusion in opposite direction i.e. from higher concentration to lower concentration. This result water in salt water moves through membrane, not salt. The membrane is generally made up of Cellulose, acetate or Nylon are fabricated in a cylindrical shape.



#### Advantages:

- 1) It is economical, simple, continuous and compact.
- 2) The process needs extremely low energy.
- 3) It has a long life and the membrane is easily replaceable.
- 4) It is possible to connect a number of tubes in parallel, to get more fresh water.
- 5) Ionic, not- ionic, colloidal and high molecular weight organic matters are easily removed.

#### Disadvantages:

- 1) Colloidal silica is not removed by this process.
- 2) The water is usually acidic.
- 3) Some critical contaminants are not removed (volatile organic chemical (VOCs), chlorine and chloramines, pharmaceuticals).

## Module – 5

# Water Technology and Nanomaterials

### **Introduction:**

6. Water is the most basic and fundamental component of life.
7. It is the most wonderful substance gifted by nature to all the living beings on the earth.
8. 72% of the earth's surface is covered by water. It is distributed as follows :
 

Oceans	-	97.23%
Ice	-	2.14%
Fresh Water	-	0.03%
Other	-	0.01%
9. Among the three essentials of life i.e., air, water and food, water occupies the second position.
10. Health and wealth of a nation largely depends on the availability and utilization of quality of water.

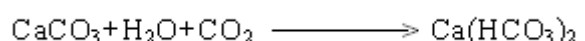
**Sources of water:** Rain water, river water, lake water, sea water and well water.

### Impurities in water:

#### 1) Dissolved impurities:

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

Ex: - When water is in contact with soil (or rock), limestone present in rock combines with water along with CO<sub>2</sub> of water to give Ca(HCO<sub>3</sub>)<sub>2</sub>. This impurity dissolves in water. Hence it acts as a dissolved impurity. .



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

#### 2) Suspended impurities:

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

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

#### 3) Dissolved gases:

The water contains mainly CO<sub>2</sub>, O<sub>2</sub> as dissolved gases. Some water may contain ammonia and sulphur compounds such as hydrogen sulphide (H<sub>2</sub>S) as dissolved gas. Presence of these gases imparts foul smell to water.

#### 4) Organic matter (microscopic matter):

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

### **Boiler feed water:**

Water is mainly used in boiler for the generation of steam for industries and power houses. For such water all the impurities are not necessarily eliminated and only those impurities which troubles for the operation of boilers are kept in tolerable limits.

A boiler feed water should correspond with the following composition

4. Its hardness should be 0.2 ppm
5. Its caustic alkalinity should lie in between 0.15-0.45 ppm
6. Its soda alkalinity should lie in between 0.45-1ppm

### **Boiler troubles**

If exceeds of impurities present in boiler feed water, they lead to the formation of scales, sludge, priming, foaming and caustic embrittlement.

**Sludge and scale formation in boiler:** In boilers water is evaporated to get steam. This increases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed within the boiler are soft, loose and slimy are called **sludge**.

If the precipitates formed within the boiler are hard and strongly adhered on the inner walls of the boiler are called **scales**.

### **Disadvantages of scales and sludge**

5. Wastage of fuel: scales have a poor conductor of heat, so the rate of heat transfer from boiler to water is greatly reduced, hence causes to increase the fuel consumption.
6. Lowering of boiler safety: Due to scale formation, over heating of boiler required for steady supply of steam. The overheating boiler tube makes the boiler material softer and weaker.
7. Decrease in efficiency: Deposition of scales in the valves and condensers of the boiler, this results decrease in efficiency.
8. Danger of explosion: The scales formation also leads to the expansion of boiler material. Due to uneven expansion, thick scale cracks, water comes suddenly in contact with overheated iron plates which may lead to the explosion of boilers.

### **Priming**

The process of passage of water particles along with steam is called priming.

Priming caused by

5. The presence of dissolved impurities particularly the suspended particles
6. The high steam velocities
7. Sudden boiling
8. Improper design of boilers

### **Foaming**

The process of production of continuous foam or bubbles in boilers is called foaming.

Foaming is caused by the presence of oil and alkalis in boiler feed water.

Foaming can be avoided by the addition of antifoaming agents like sodium aluminates and aluminum sulphate which spreads on the surface of water and therefore which neutralizes the reduction in surface tension.

### **Disadvantages of priming and foaming**

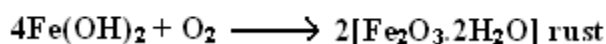
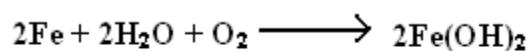
3. It decreases the efficiency of boiler because the dissolved salts get deposited on turbine blades and super heater by evaporation.
4. The maintenance of the boiler pressure becomes difficult due to the improper judgment of actual height of water column.

### **Boiler corrosion**

It is decay or disintegration of boiler material either material through chemical or electrochemical reaction with its environment.

Corrosion in boiler is due to the following reasons

4. Presence of dissolved oxygen: this is the most usual corrosion causing factor. When water containing dissolved oxygen is heated in the boiler, the free gas is evolved under high pressure of the boiler and attacks the boiler materials and forms the rust.



5. Presence of carbon dioxide: carbon dioxide forms carbonic acid in presence of water which has slow effect on boiler materials.



6. Presence of Dissolved salts ( $\text{MgCl}_2$ )  
Magnesium chloride forms hydrochloric acid in presence of water which has slow effect on boiler materials.



### **Disadvantages of boiler corrosion**

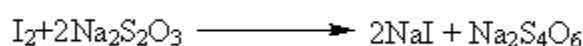
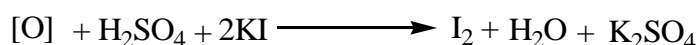
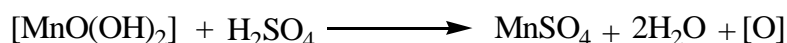
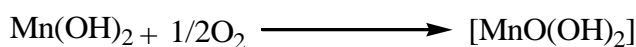
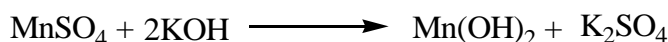
4. Shortening of boiler life.
5. Leakages of joints and riverts.
6. Increased cost of repairs and maintenance.

### **Determination of dissolved oxygen (DO):-**

Oxygen is poorly soluble in water. The solubility of water depends on the concentration of the salts and temperature. Dissolved oxygen is consumed by aquatic animals for their respiration. Aerobic bacteria consume the DO for the oxidation of biodegradable matter. Organic matter present in the water is oxidized by strong oxidizing agent ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) using DO.

DO in water is determined by winklers method.

**Principle:-** This method is based on the indirect iodometric titration. Manganese sulphate reacts with alkaline solution to give manganese hydroxide. Manganese hydroxide reacts with DO to give basic manganese hydroxide and precipitated. Precipitation is dissolved by addition of con.  $\text{H}_2\text{SO}_4$  and nascent oxygen is liberated. Nascent oxygen oxides potassium iodide to iodine. The liberated iodine is titrated against standard  $\text{Na}_2\text{S}_2\text{O}_3$ .





**Procedure:** 150 cm<sup>3</sup> of waste water is taken in a BOD bottle; add 2ml of MnSO<sub>4</sub> and 3 ml of alkaline KI to the reagent bottle containing a known volume of water. Obtained Basic manganese hydroxide Precipitation is dissolved using con H<sub>2</sub>SO<sub>4</sub>. Take a 50 cm<sup>3</sup> of the above reaction mixture into 250 cm<sup>3</sup> conical flask. Add 4-5 drop of starch indicator and titrate the liberated iodine against standard sodium thiosulphate, till the colour changes from blue to colour less.

**Observation and calculation**

Normality of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solution= N<sub>1</sub>

Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution =V<sub>1</sub> cm<sup>3</sup>

Volume of water take for titration=V<sub>2</sub> cm<sup>3</sup>

Normality of the dissolved N<sub>2</sub>=  $\frac{N_1 \times V_1}{V_2}$

Water of dissolved oxygen per liter of water =  $\frac{V_1 \times N_1 \times 8}{V_2}$  g

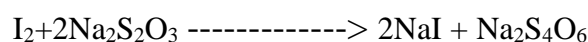
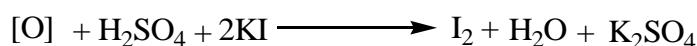
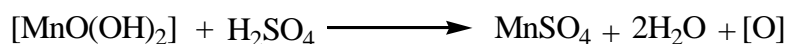
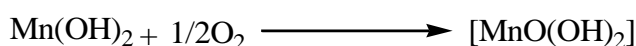
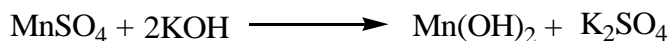
$$= \frac{V_1 \times N_1 \times 8}{V_2} \times 1000mg$$

**Biological Oxygen Demand**

Def<sup>n</sup>:-The amount of oxygen required for the biological oxidation of the organic matter under aerobic condition at 20°C and for a period of 5 days.

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

**Principle:-** This method is based on the indirect iodometric titration. Manganese sulphate reacts with alkaline solution to give manganese hydroxide. Manganese hydroxide reacts with DO to give basic manganese hydroxide and precipitated. Precipitation is dissolved by addition of con. H<sub>2</sub>SO<sub>4</sub> and nascent oxygen is liberated. Nascent oxygen oxides potassium iodide to iodine. The liberated iodine is titrated against standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.



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

**Blank titration:** DO content of the one bottle determined immediately add 2ml of MnSO<sub>4</sub> and 3 ml of alkaline KI to the reagent bottle containing a known volume of water. Obtained Basic manganese hydroxide Precipitation is dissolved using con H<sub>2</sub>SO<sub>4</sub>. Take a 50 cm<sup>3</sup> of the above reaction mixture into 250 cm<sup>3</sup> conical flask. Add 4-5 drop of starch

indicator and titrate the liberated iodine against standard sodium thiosulphate, till the colour changes from blue to colour less.

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

**Observation and calculation**

D<sub>1</sub> is the DO of the sample in mg/ml at the start of the experiment

D<sub>2</sub> is the DO of the sample in mg/ml after 5 days.

A is ml of the sample before dilution

B is ml of the sample after dilution

$$\text{BOD} = \frac{D_1 - D_2}{A} \times B \text{ mgdm}^{-3}$$

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

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

## Chemical oxygen demand

It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds present in one dm<sup>3</sup> of waste water using strong oxidizing agent K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> under acidic medium.

**Principle:** A Known amount of water is refluxed with a known excess acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and a small amount of Ag<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub> are added. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidizes all oxidisable impurities.

The amount of unconsumed K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is determined by titration with std. FAS (ferrous ammonium sulphate) solution using ferroin indicator. The amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution consumed corresponds to the COD of the sewage sample.

**Procedure:-**

Sample or Back titration:-

Pipette 25 ml of waste water into a clean conical flask add 2 test tube of 2N H<sub>2</sub>SO<sub>4</sub> solution and pipette out 10 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to the same conical flask. Add 1g of HgSO<sub>4</sub> followed by 1g Ag<sub>2</sub>SO<sub>4</sub>. Attach a reflux condenser and reflux contents for 2 hours. Cool and titrate the unconsumed K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> against FAS using ferroin indicator till the color of the solution changes from bluish green color to reddish brown.

Blank titration:- The above procedure is repeated by taking only 10 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

**Observation and calculation:-**

Volume of water sample taken= V<sub>1</sub> cm<sup>3</sup>

Volume of standard FAS used in sample titration= A cm<sup>3</sup>

Volume of standard FAS in the blank titration= B cm<sup>3</sup>

Normality of FAS solution= N

Amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> consumed in satisfying the COD in terms of FAS solution=(B-A)cm<sup>3</sup>

$$N_1 \times V = N \times (B - A)$$

$$\text{Normality of COD of the sample } N_1 = \frac{N \times (B - A)}{V}$$

$$\begin{aligned} \text{COD of the sample} &= \frac{N \times (B - A)}{V} \times 8 \text{ g.dm}^{-3} \\ &= \frac{N \times (B - A)}{V} \times 8 \times 1000 \text{ mg.dm}^{-3} \end{aligned}$$

**Importance:**

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

**Problems:- (1) 20ml of sewage sample for COD is reacted with 25 ml of  $K_2Cr_2O_7$  solution and the un reacted  $K_2Cr_2O_7$  requires 9.0ml of N/4 FAS solution. Under similar conditions, in blank titration 15.0 ml of FAS is used up. Calculated the COD of the sample.**

Volume of sample taken= 20 ml

Volume of N/4 FAS required to react with unconsumed  $K_2Cr_2O_7$ =9.0ml

Volume of FAS consumed in blank=15.0ml

Amount of  $K_2Cr_2O_7$  consumed to satisfy COD

in terms of FAS solution=15.0-9.0=6 ml

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 20 = 0.25 \times 6.0$$

$$\text{Therefore, normality of COD Sample } N_1 = \frac{0.25 \times 6}{20}$$

$$\text{COD of the sample} = \frac{0.25 \times 6}{20} \times 8 = 0.6 \text{ g / dm}^3 = 600 \text{ mg / dm}^3$$

**(2) 25 cm<sup>3</sup> of sewage water was reacted with 10 cm<sup>3</sup> of 0.25N  $K_2Cr_2O_7$  in Conc.  $H_2SO_4$  medium. The unreacted  $K_2Cr_2O_7$  needed 6.1 cm<sup>3</sup> of 0.1N FAS. 10 cm<sup>3</sup> of 0.25 cm<sup>3</sup> N  $K_2Cr_2O_7$  when titrated under same condition required 28.2 cm<sup>3</sup> of 0.1N FAS. Calculate the COD.**

Volume of 0.1N FAS required to react with unconsumed  $K_2Cr_2O_7$ =6.1 ml

Volume of FAS consumed in blank=28.2ml

Amount of  $K_2Cr_2O_7$  consumed to satisfy COD

in terms of FAS solution=28.2-6.1=22.1 ml

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 25 = 0.1 \times 22.1$$

$$\text{Therefore, normality of COD Sample } N_1 = \frac{0.1 \times 22.1}{25}$$

$$\text{COD of the sample} = \frac{0.1 \times 22.1}{25} \times 8 = 0.7072 \text{ g / dm}^3 = 707.2 \text{ mg / dm}^3$$

(3) In a COD test, 28.1 and 14.0 cm<sup>3</sup> of 0.05 N FAS solution were required for blank and sample titration respectively. The volume of test sample used is 25 cm<sup>3</sup>. Calculate the COD of the sample solution.

Volume of 0.1N FAS required to react with unconsumed K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>=14.0 ml

Volume of FAS consumed in blank=28.1 ml

Amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> consumed to satisfy COD

in terms of FAS solution=28.1-14.0=14.1 ml

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 25 = 0.5 \times 14.1$$

$$\text{Therefore, normality of COD Sample } N_1 = \frac{0.5 \times 14.1}{25}$$

$$\text{COD of the sample} = \frac{0.5 \times 14.1}{25} \times 8 = 0.225.6 \text{ g / dm}^3 = 225.6 \text{ mg / dm}^3$$

### SEWAGE:

Sewage is the liquid waste, which includes house hold waste water, industrial wastes, ground wastes etc. Sewage contains both organic and inorganic substances in dissolved, suspended and colloidal form. Sewage is classified into two type's namely domestic sewage and industrial sewage.

Domestic sewage: It is the liquid waste comes from residences, institutions. It mainly consists of organic substances which are rich in microorganisms.

Industrial sewage: It is the liquid waste comes from industries. It contains substances like acids, oil, toxic chemicals, metals, animal and plant matters, non-biodegradable compounds etc.

Sewage contains living organisms such as bacteria, algae, fungi and protozoa.

1. Aerobic bacteria:- Which live on free oxygen or on oxygen dissolved in water.
2. Anaerobic bacteria:- Which live and develop in the absence of free oxygen.

1. Aerobic oxidation: Organic compounds are oxidized by aerobic bacteria's which do not produce any offensive smell. This kind of oxidation is known as aerobic oxidation.

2. Anaerobic oxidation: Organic compounds are oxidized by anaerobic bacteria's which produce offensive smell. This kind of oxidation is known as anaerobic oxidation.

**Sewage treatment:-** Sewage water is a waste from kitchen, laundries, bathroom, laboratories and industries. The domestic sewage contains heavy load of BOD, pathogens bacteria, colour, odour and bad smell etc. Sewage water is discharged into water bodies, leads to deficiency of dissolved oxygen and leads to the death of the oxygen. Pathogen bacteria are causing water borne diseases.

#### **(a). Mechanical or Primary treatments**

Removing of suspended solids is called **primary treatment**. It involves the removing of suspended solids like woods, plastic through screening, filtering and sedimentation.

**Screening:** It is a physical process which removes larges suspended or floating matter in the sewage. Which retain the floating and suspended coarse particles

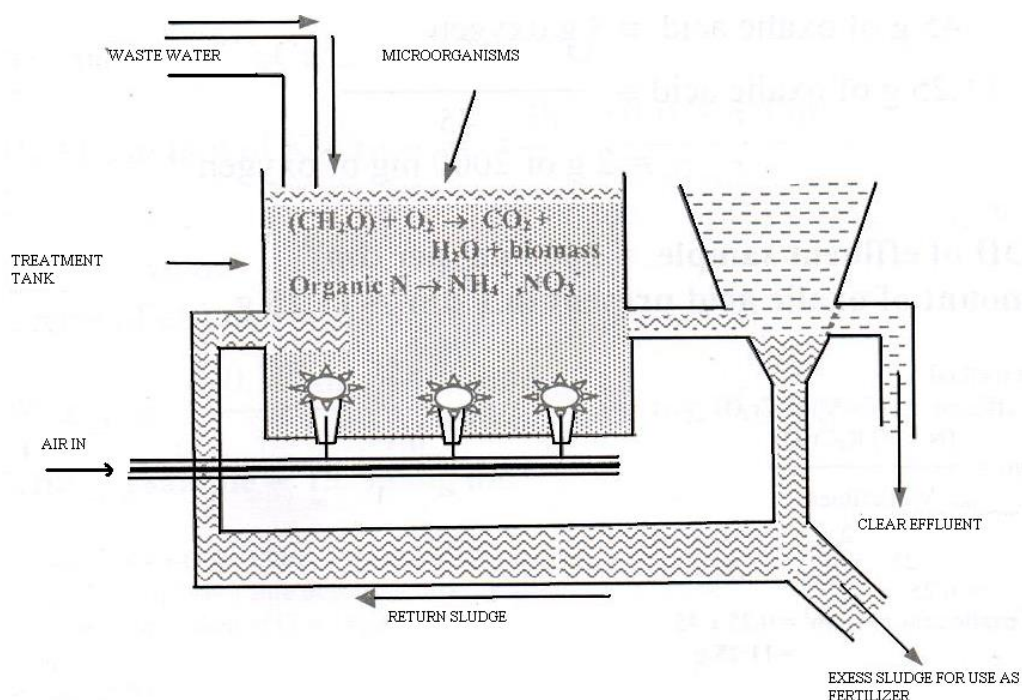
**Filtration:** The water is passed through conventional sand filter beds to remove the last trace of suspended matter.

**Sedimentation:** is a process of removing suspended impurities present in water by the process of settling.

**Coagulation;** is a process of removing colloidal particles from water by the addition of certain chemicals known as coagulation. Coagulation is carried out for quick settling of colloidal particles. Alum [ $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$ ] and ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) are commonly used coagulants.

**(b). Secondary treatment:** Secondary process involves an aerobic oxidation of organic matter.

**Sludge:** The matter which settles down at the bottom after the treatment is called sludge and the liquid is called effluent.



**Activated sludge process:** Activated sludge contains aerobic microorganisms is sprayed over the water is from primary treatment is allowed to flow into large tanks. The microorganisms present in the sludge form a thin layer on the organic wastes in the sewage. Air is passed vigorously from the centre of the tank in order to bring good contact b/w the organic wastes and bacteria in the presence of air and sunlight under these conditions, aerobic oxidation of organic matter occurs. The sludge formed is removed by filtration. A part of the sludge is reduced and the rest is used as fertilizer. The residual water is chlorinated to remove bacteria and finally discharged into running water. The sludge process operates at 90-95 % efficiency of BOD treatment. If the treated water contains a high concentration of phosphates, heavy metal ions, colloidal impurities and non-degradable compounds then it needs tertiary treatment.

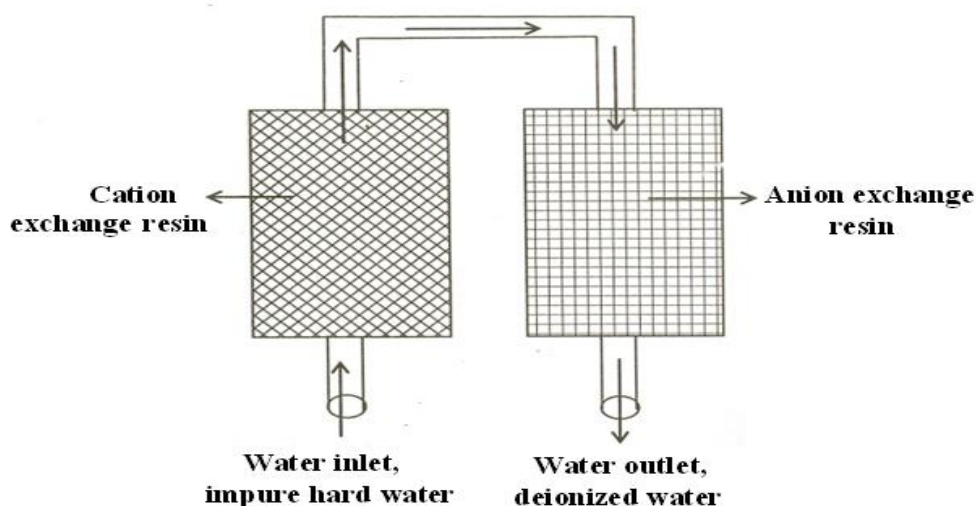
**c). Tertiary treatment:**

- i). Treatment with lime for the removal of phosphates as insoluble calcium phosphates
- ii). Treatment with  $S^{2-}$  ions for the removal of metal ions as insoluble sulphides.

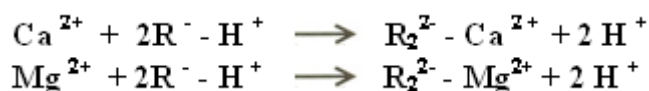
- iii). Treatment with activated charcoal to adsorb remaining organic compounds.
- iv). Treatment with alum to remove the colloidal impurities not removed in the previous treatments.

### Softening of water by ion exchange process:

Water softening is the removal of [calcium](#), [magnesium](#), and certain other metal [cations](#) in [hard water](#). In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin. Ion exchange resins are high molecular weight, cross linked polymers with a porous structure. The functional groups which are attached to the chains are responsible for ion exchange properties. The resins containing acidic groups which are capable exchanging  $H^+$  (or  $Na^+$ ) ions for cations ( $Ca^{2+}$  or  $Mg^{2+}$ ) present in water are known as cation exchange resins ( $RH^+$ ). The resins containing basic groups which are capable exchanging  $OH^-$  for anions ( $Cl^-$ ,  $SO_4^{2-}$ ) present in water are known as anion exchange resins ( $ROH^-$ ).



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



Hard water is then passed through anion exchange resin where ions like  $Cl^-$ ,  $SO_4^{2-}$  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 demineralize water.

#### **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.

4. Residual hardness is very low and thus water is suitable for high pressure boilers also.

**Disadvantages:**

1. Equipment and process is costly.
2. Turbid water needs to be filtered first before softening.

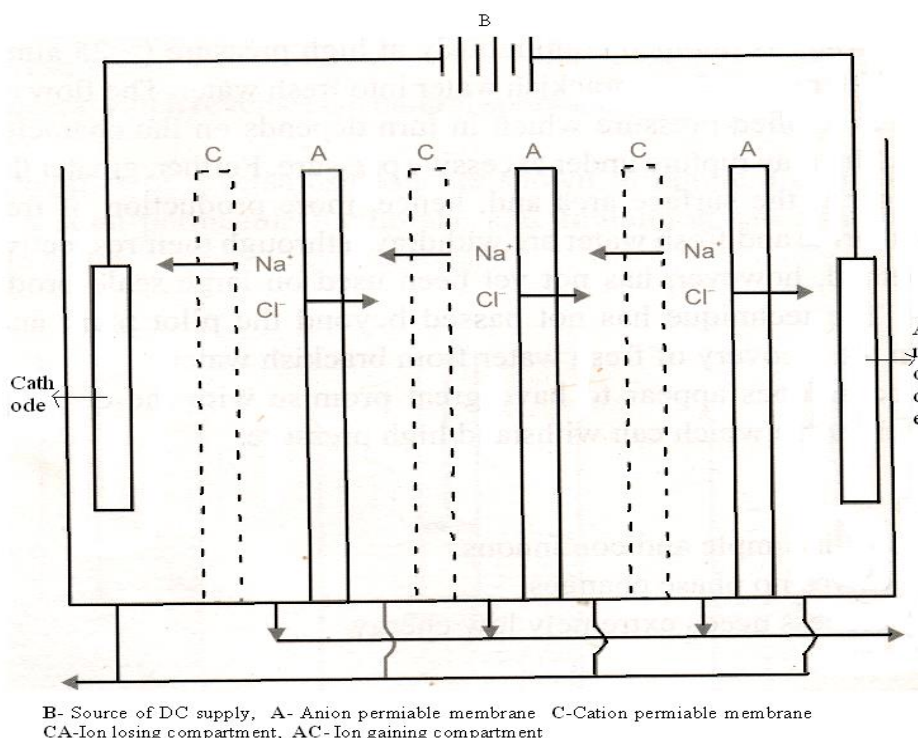
**Desalination or Desalting:**

Desalination is a process of partial or complete demineralization of highly saline water (sea water). The important methods of desalination are 1) Electro dialysis and 2) Reverse osmosis

**Electro dialysis:**

Principle: When electricity is passed through a solution, ions migrate towards the oppositely charged electrodes. The direction of ion's movement can be made specific by using ion selective permeable membranes. The cation membrane is permeable to only cations and anion membrane is permeable to only anions. This is the principle of this process. "The process of decreasing the concentrations of salts in saline water using selective membranes under the influence of an applied emf is called as Electro dialysis".

Procedure: The arrangement of an electro dialysis unit is as shown in figure.



An electro dialysis cell consists sea water in which a series of alternative cation and anion permeable membranes(C & A)are placed . The anode is placed near the anion permeable membrane while cathode is placed near the cation semipermeable membrane. A suitable emf is applied across the two electrodes immersed in the brine. Under the influence of the applied emf, sodium ions move through the cation permeable membrane(C) while anions (Cl<sup>-</sup>) move through the anion permeable membrane(A) from each compartment of CA. The net result is the depletion of salt content in the 'CA' compartments and increase in salt concentration in 'AC' compartments. Thus the fresh

water produced in CA compartments is collected and pumped off. The concentrated brine is discharged through the outlet.

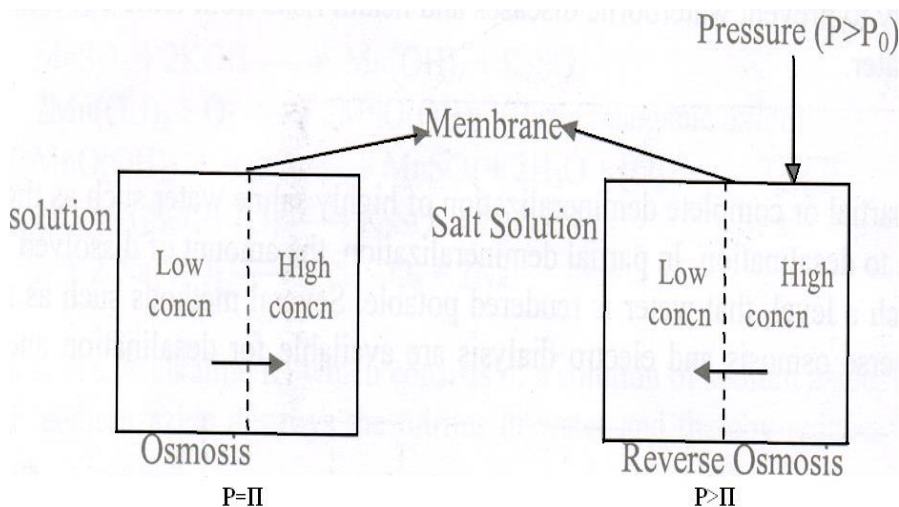
**Advantages:**

- 1). It is economical.
- 2). It is convenient and may applicable at room temperature.
- 3). It is more compact in size and requires only electricity for operation.

**Reverse osmosis:**

Osmosis is the physical movement of a solvent through a semipermeable membrane. This is based on a difference in chemical potential b/w two solutions (salt solution and water) as the membrane allows only water molecules not salt. The salt water thus has a greater chemical potential than water on the other side of membrane. To equalize the difference in chemical potential, water diffuses through the membrane from the water side to the salt water side. This movement is Osmosis, in this case the pressure is equal to Osmotic pressure ( $\Pi$ ). In Osmosis diffusion from lower concentration to higher concentration.

When pressure is greater than Osmotic pressure ( $P > \Pi$ ) diffusion in opposite direction i.e. from higher concentration to lower concentration. This result water in salt water move through membrane not salt. The membrane is generally made up of Cellulose, acetate or Nylon are fabricated in a cylindrical shape.



**Advantages:**

- 6) It is economical, simple, continuous and compact.
- 7) The process needs extremely low energy.
- 8) It has long life and membrane is easily replaceable.
- 9) It is possible to connect number of tubes in parallel, to get more fresh water.
- 10) Ionic, non- ionic, colloidal and high molecular weight organic matters are easily removed.

**Disadvantages:**

- 4) Colloidal silica is not removed by this process.
- 5) Discharged Brackish is harder than the previous one.



## NANOTECHNOLOGY

**Introduction:** *Nanotechnology* originates from the Greek word meaning “*dwarf*”. A nanometre is one billionth ( $10^{-9}$ ) of a metre, which is tiny, only the length of ten hydrogen atoms, or about one hundred thousandth of the width of a hair! Although scientists have manipulated matter at the nanoscale for centuries, calling it physics or chemistry, it was not until a new generation of microscopes was invented in the nineteen eighties in IBM, Switzerland that the world of atoms and molecules could be visualized and managed.

**Definition:** *Nanotechnology can be defined as the manipulation of atoms and molecules (one billionth) scale (1-100 nm) to produce devices, structures or systems having at least one novel or superior property.*

*Materials having at least one dimension in the nano scale are called **nanomaterials**. Conceptualization of nanotechnology was done by Richard Feynman in 1959.* The impact of nanotechnology is quite significant. When the bulk materials are reduced to nanometer size, the properties exhibited by these nanomaterials are of tremendous use. For example,

1. Opaque materials become transparent (copper),
2. Insoluble substances become soluble (gold),
3. Stable materials become combustible (aluminium).

*In fact, at normal scales, gold is chemically inert but at nanoscales, gold nanoparticles can serve as potent chemical catalysts.* The study of these nanomaterials is known as **nanoscience**.

**Properties of nanomaterials:** *Physical and chemical properties of nanomaterials are significantly different from those of single atoms/molecules and bulk material of the same chemical composition. Difference in properties are related to,*

1. The spatial arrangement of molecules/structure,
2. Electronic structure,
3. Energetic,
4. Chemical reactivity
5. Phase change or catalytic activity.

*Properties remain same at first (size being reduced from macro to micro), and slowly small changes begin to take place as the particle size is reduced further from micro to nanoscale range (generally observed below, 100 nm).*

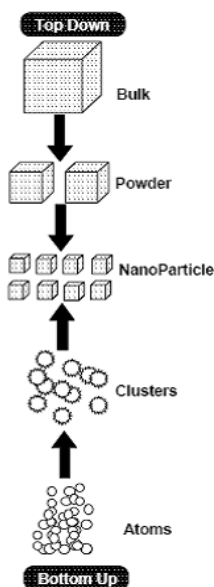
### **Size dependant properties**

1. **Surface area** : If a macroscopic object is divided into smaller parts, the ratio of surface atoms to interior atoms becomes a significant number of total fraction of atoms.

**The inverse relation between the particle size and surface area is responsible for the remarkable changes in the physical properties of nanomaterials.**

Properties like catalytic activity, gas adsorption, chemical reaction depends on surface area.

Ex: Gold is catalytically inactive in bulk but nano gold is highly catalytically active.



2. Electrical properties: Electronic bands in bulk material are continuous due to overlap of billions of atoms, but in nano size material very few molecules are present so electrical band separates. Hence some metals which are good conductors in bulk become semiconductor and insulator at nano level.

3. Optical Properties: Nano materials exhibit different colors from bulk materials. The discrete electronic state of nano material allow absorption and emission of light of specified.

### General methods of Synthesis:

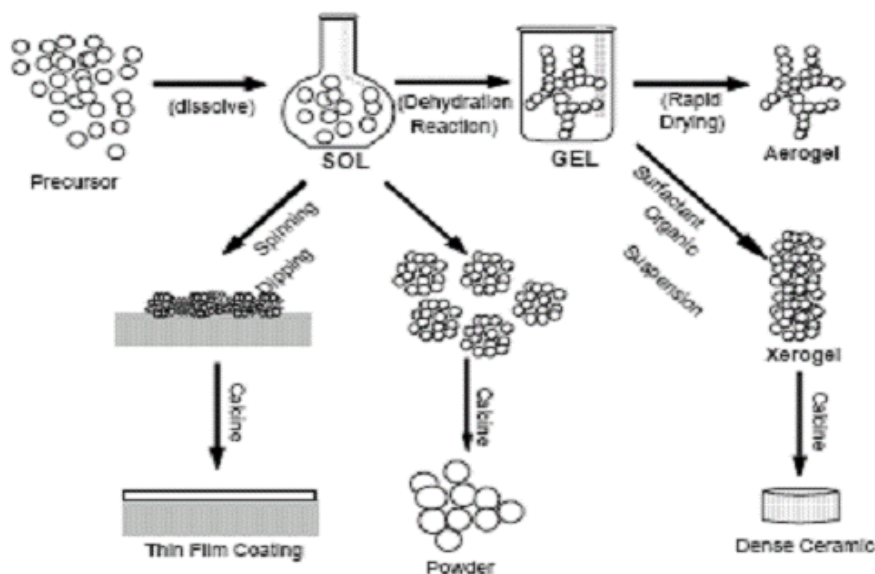
- There are two approaches for synthesis of nano materials and the fabrication of nano structures. Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle. Bottom up approach refers to the build up of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster. Both approaches play very important role in modern industry and most likely in nano technology as well. There are advantages and disadvantages in both approaches.

Figure: Schematic representation of the building up of Nanostructures.

### Bottom-up approach

#### 1.Sol-gel process:

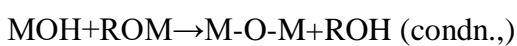
Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials.



The sol-gel process can be characterized by a series of distinct steps.

**Step 1:** Formation of different stable solutions of the alkoxide or solvated metal precursor (**the sol**).

**Step 2: Gelation** resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation or polyesterification reaction that results in a dramatic increase in the viscosity of the solution.



**Step 3: Aging of the gel (Syneresis)**, during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

**Step 4: Drying of the gel**, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period.

If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.

**Step 5:** Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800°C.

**Step 6:** Densification and decomposition of the gels at high temperatures ( $T > 800^\circ\text{C}$ ). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

## II. Precipitation method

Ultrafine particles are produced by precipitation from a solution, the process being dependent on the presence of the desired nuclei.

An inorganic metal salt, such as chloride, nitride and so on, is dissolved in water. Metal cations exist in the form of metal hydrate species, for example,  $\text{Al}(\text{H}_2\text{O})^{3+}$  or  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . These hydrates are added with basic solutions, such as NaOH or  $\text{NH}_4\text{OH}$ .

The hydrolyzed species condense and then washed, filtered, dried and calcined in order to obtain the final product.

e.g., i).  $\text{TiO}_2$  powders have been produced with particle sizes in the range 70-300 nm from titanium tetraisopropoxide.

### III. Gas Condensation Process (GPC)

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys.

A metallic or inorganic material, e.g. a suboxide, is vaporised using thermal evaporation sources such as Joule heated refractory crucibles/electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar of He (or Ar, Ne, Kr).

Cluster form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase. Particle size depends critically on-the residence time of the particles in the growth regime and can be influenced by the gas pressure of He, Ar or Kr, and on the evaporation rate/vapour pressure of the evaporating material. With increasing gas pressure, vapour pressure and mass of the inert gas; the average particle size of the nanoparticles increases.

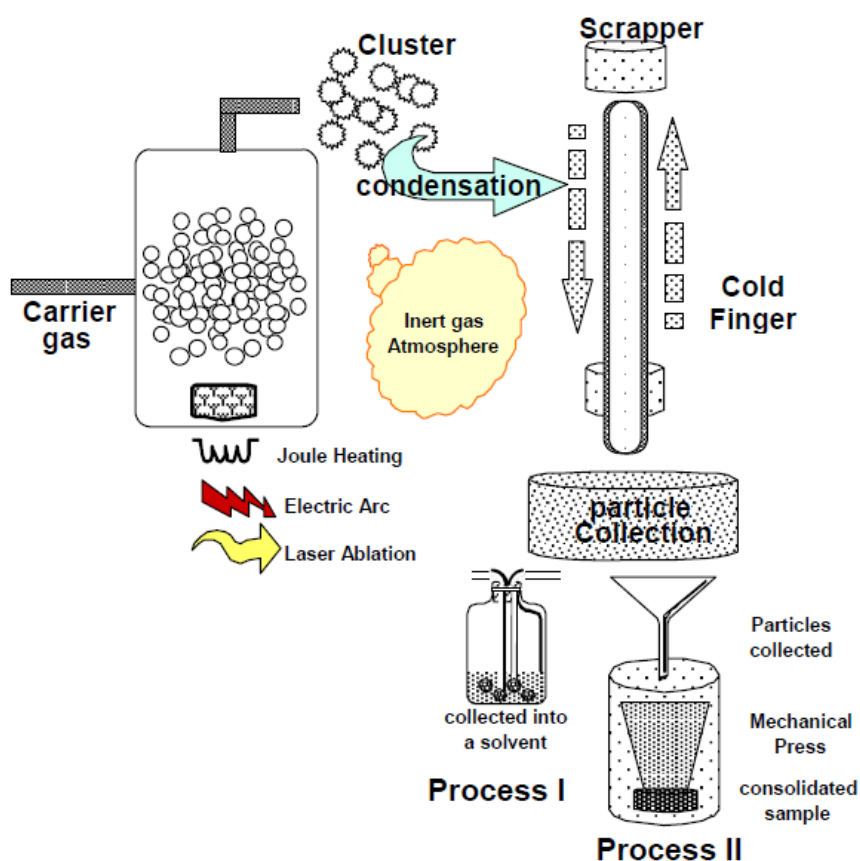


Fig: Schematic representation of typical set-up for gas condensation synthesis.

A rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no agglomeration.

The nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate usually by this cold finger device or corona discharge, or any aerosol science technique.

Methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders.

#### **IV. Chemical Vapour Condensation (CVC) method**

Chemical vapor condensation (CVC) was developed in Germany in 1994. It involves pyrolysis of vapors of metal organic precursors in a reduced pressure atmosphere. Particles of  $ZrO_2$ ,  $Y_2O_3$  and nanowhiskers have been produced by CVC method.

As shown schematically in Figure, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation or the CVC process. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed.

By adjusting the residence time of the precursor molecules either by changing the gas flow rate, the pressure difference (between the precursor delivery system and the main chamber) or the temperature (of the hot wall reactor), one can have prolific production of nanosized particles of metals and ceramics.

#### **Nanowire**

A **nanowire** is a nanostructure, with the diameter of the order of a nanometer ( $10^{-9}$  meters). It can also be defined as the ratio of the length to width being greater than 1000. Alternatively, nanowires can be defined as structures that have a thickness or diameter.

At these scales, quantum mechanical effects are important and this lead to the term "quantum wires".

Many different types of nanowires exist, including metallic (e.g., Ni, Pt, Au), semiconducting (e.g., Si, InP, GaN, etc.), and insulating (e.g.,  $SiO_2$ ,  $TiO_2$ ).

Molecular nanowires are composed of repeating molecular units either organic (e.g. DNA) or inorganic (e.g.  $Mo_6S_9-xI_x$ ).

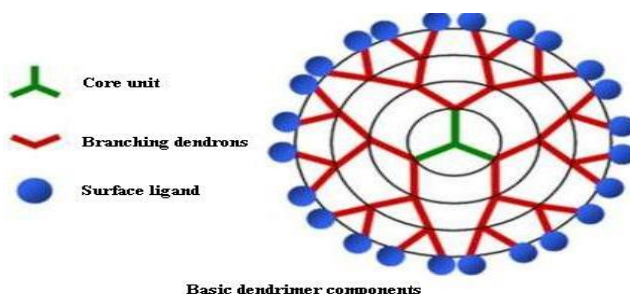
**Electrons** in nanowires are quantum confined laterally and thus occupy energy levels that are different from the traditional continuum of energy levels or bands found in bulk materials and hence manifest themselves in discrete values of the electrical conductance.

1. Nanowires can be synthesised/grown by (i) Solution-phase synthesis, (ii) Non-catalytic growth and (iii) Vapor-Liquid-Solid (VLS) synthesis/growth.
2. Nanowires are being studied for use as photon ballistic waveguides as interconnects in quantum dot/quantum effect well photon logic arrays. Photons travel inside the tube, electrons travel on the outside shell.
3. When two nanowires acting as photon waveguides cross each other the juncture acts as a quantum dot.
4. There are many applications where nanowires may become important in electronic (they may complement or replace carbon nanotubes), opto-electronic and nanoelectromechanical devices, as additives in advanced composites, for metallic interconnects in nanoscale quantum devices, as field-emitters and as leads for biomolecular nanosensors.

## Nanorods

1. Nanorods are solid nanostructures morphologically similar to nanowires but with aspect ratios of approximately 3-to-5.
2. They are formed from a variety of materials including metals, semiconducting oxides, diamonds (aggregated diamond nanorods produced from fullerenes are the hardest material so far discovered), and organic materials.
3. Nanorods are produced by a number of techniques, including: a vapor-liquid-solid approach; mechanical alloying; direct chemical synthesis using ligands for shape control; plasma arc discharge; laser ablation; and catalytic decomposition methods.
4. They are under considerable investigation for applications such as gas sensors; video displays, computer components, nanoelectronic/nano optoelectronic components, MEMS ([microelectromechanical systems](#)) devices and solar energy conversions.
5. Gold nanorods are considered excellent candidates for biological sensing applications because the absorbance band changes with the refractive index of local material.
6. Nanorods with near-infrared absorption peaks can be excited by a laser at the absorbance band wavelength to produce heat, potentially allowing for the selective thermal destruction of cancerous tissues.
7. As sensors for testing humidity.

## Dendrimers



**Dendrimers** are repetitively branched molecules. The name comes from the Greek word (**dendron**), which translates to "tree". Synonymous terms for dendrimer include **arborols** and **cascade molecules**.

1. Dendrimers are highly branched, star-shaped macromolecules with very well defined chemical structures with a regular and highly branched 3-dimensional architecture (in nanometer-scale dimensions with three components: a central core, an interior).
2. The varied combination of these components yields products of different shapes and sizes with shielded interior cores that are ideal candidates for applications in both biological and materials sciences.
3. The attached surface groups affect the solubility and chelation ability, the varied cores impart unique properties to the cavity size, absorption capacity, and capture-release characteristics.

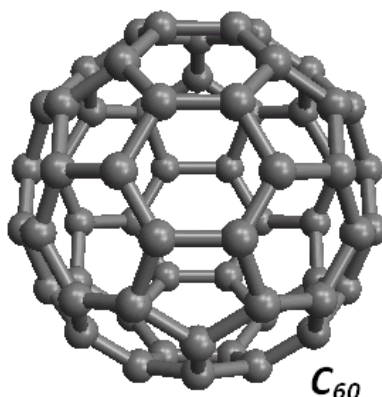
4. Applications includes drug delivery, gene transfection, catalysis, energy harvesting, photo activity, molecular weight and size determination, rheology modification, and nanoscale science and technology.
5. Diameter in the range of 1–100 nm corresponds to molecular mass in the interval  $10^4$ – $10^7$  Da and a number of atoms within  $10^3$ – $10^9$  atoms.
6. The dendrimeric nanostructures possess improved quality of physical, chemical, and biological properties such as solubility, stability, ability to work as delivery systems, and many others. The immense potential of nanotechnology reaches to prevention, detection, diagnosis, and treatment of cancer, viral, and bacterial diseases.
7. Dendrimers are potential nanocarriers of agents because they are highly biocompatible and water soluble. Their solubility is related to the surface functional groups, their generation and even the core synthesis. Consequently, drugs that appear to have poor pharmacokinetic parameters, such as the hydrophobic ones, may be efficiently administered with these nanomolecules. Furthermore dendrimers show low toxicity and organ accumulation.

### **Nanocomposites**

- Nanocomposites are materials that incorporate nanosized particles into a matrix of standard material.
- In nanocomposites, the nanoparticles (clay, metal, carbon nanotubes) act as fillers in a matrix, usually polymer matrix.
- Addition of nanoparticles results in an improvement in properties that can include mechanical strength, toughness, impermeability, optical clarity and electrical or thermal conductivity.
- Two principal factors cause the properties- increased relative surface area (high surface-to-volume ratio), and quantum effects changes/enhance properties such as reactivity, strength and electrical characteristics.
- Properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.
- Inorganic components can be zeolites (having 3D framework), clays, metal oxides, metal phosphates, chalcogenides (having 2D) and even one-dimensional and zero-dimensional materials such as  $(\text{Mo}_3\text{Se}_3)_n$  chains and clusters.
- Organic/inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization in which *in-situ* growth and polymerization of biopolymer and inorganic matrix is occurring.
- Lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized.
- All types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts.
- Nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, gas barriers, oxygen barriers, food storage/packaging (Nanoclay polymer composites are currently tried to keep food for 3 yrs without refrigeration) non-linear optics, fuel tanks, battery cathodes and ionics, nano-wires, sensors and other systems.

### **Fullerenes**

Fullerene a new allotrope of carbon, in which the atoms are arranged in closed shells, having the structure of a truncated icosahedron (a polyhedron). (Nobel Prize, 1996 for Kroto, Curl and Smalley). Named as Buckminsterfullerene (after Buckminster Fuller who designed geodesic domes in the 1960's).



1. First time produced isolable quantities of  $C_{60}$  by causing an arc between two graphite rods to burn in a helium atmosphere (extracting the carbon condensate so formed using an organic solvent).
2. Other carbon clusters such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{84}$  are also studied, with new and unexpected properties, which lead to new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.
3. Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of an icosahedral symmetry closed cage structure, with each carbon atom is bonded to three others and is  $sp^2$  hybridised.
4.  $C_{60}$  molecule has two bond lengths - the 6:6 ring bonds can be considered "double bonds" and are shorter than the 6:5 bonds.  $C_{60}$  is not "superaromatic" as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalisation and hence  $C_{60}$  behaves like an electron deficient alkene, and reacts readily with electron rich species.
5. The most striking property of the  $C_{60}$  molecule is its high symmetry. There are 120 symmetry operations (*most symmetric molecule*), like rotations around an axis or reflections in a plane, which map the molecule onto itself.

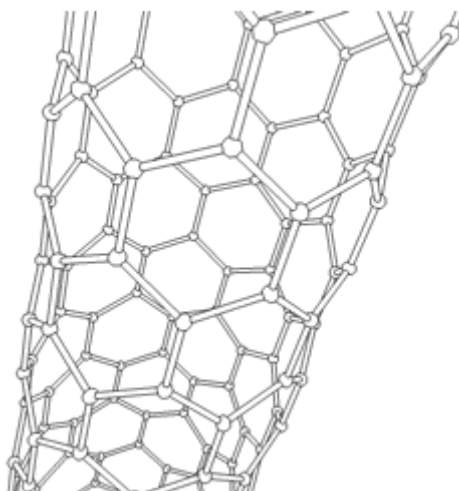
### Carbon Nanotubes

#### **Carbon nanotubes:**

- In 1991, during the optimization of the fullerene-synthesis by arc-discharges, small tubes were found (by Sumio Iijima, characterized by transmission electron microscopy TEM).
- Nanotubes are members of the fullerene structural family (name derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called [graphene](#)).
- These sheets are rolled at specific and discrete ("[chiral](#)") angles, and the combination of the rolling angle and radius decides the nanotube properties.
- Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking.



- Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) and Double-wall Nanotubes (DWNT).



- The chemical bonding of nanotubes is composed entirely of  $sp^2$  bonds, similar to those of graphite. These bonds, which are stronger than the  $sp^3$  bonds found in [alkanes](#) and diamond, provide nanotubes with their unique strength.

**Preparation :**

Nanocyl uses the "Catalytic Carbon Vapor Deposition" method for producing Carbon Nanotube Technologies. This proven industrial process is well known for its reliability and scalability. It involves growing nanotubes on substrates, thus enabling uniform, large-scale production of the highest-quality carbon nanotubes worldwide.

**Properties :**

- Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength (~100 GPa) and elastic modulus respectively (due to covalent  $sp^2$  bonds).
- Standard single-walled carbon nanotubes can withstand a pressure up to 25 GPa without deformation.
- Maximum electrical conductance of a single-walled carbon nanotube is  $2G_0$ ,
- All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction".

**Applications:**

Conductive plastics, Structural composite materials, Flat-panel displays, Gas storage Antifouling paint, Micro- and nano-electronics, Radar-absorbing coating, Technical textiles , Ultra-capacitors, Atomic Force Microscope (AFM) tips, Batteries with improved lifetime, Biosensors for harmful gases, Extra strong fibers.

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