

YBN UNIVERSITY, RANCHI

**ELECTROCHEMISTRY**

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**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

$$\Delta G = \Delta G^{\circ} + RT \ln K_c$$

**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  $dS = \frac{dQ}{T}$  [reversible process]  $dS > \frac{dQ}{T}$ , [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<sup>o</sup>):**

"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.

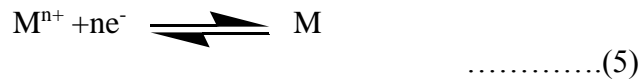
$$\therefore -\Delta G = nFE \dots \dots \dots (3)$$

Under standard condition

$$-\Delta G^{\circ} = nFE^{\circ} \dots \dots \dots (4)$$

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

Consider a reversible electrode reaction



According to Vanthoff's reaction isotherm

$$\Delta G = \Delta G^{\circ} + RT \cdot \ln K_c \quad \dots\dots\dots(6)$$

Where,  $K_c$ =Equilibrium constant

Substitute the value of  $K_c$ , we have

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

Divide the equation (6) by  $-nF$

From equation (3) and (4)

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

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

Then, we have

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

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

$$E = E_0 + \frac{2.303}{n} \frac{RT}{F} \cdot \log [M^{n+}] \quad \dots\dots\dots(11)$$

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

$$E = E_0 + 0.0591 \cdot \log [M^{n+}] \quad \dots\dots\dots(12)$$

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

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

$$E_{cell} = E_{ocell} + 0.0591 \cdot n \cdot \log \left[ \frac{\text{Species at Cathode}}{\text{Species at Anode}} \right]$$

□

**Problems**

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

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

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

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

$$E_{cell} = 1.27 V$$

2. An electrochemical cell consists of iron electrode dipped in 0.1M  $FeSO_4$  and silver electrode in 0.05M  $AgNO_3$ . Write the cell representation cell reaction and calculate the emf of the cell at 298K. (The standard reduction potentials of iron and silver are  $-0.44V$  and  $0.8V$  respectively).

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

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

$[Ag^+] = 0.05M$

cell representation:  $Fe_{(s)} \parallel FeSO_4(0.1M) \parallel AgNO_3(0.05M) \parallel Ag_{(s)}$

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

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

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

$$n \text{ [Fe}^{2+}\text{]}$$

$$\frac{0.0591}{2}$$

$$\frac{[0.05]^2}{[0.1]}$$

$$E_{cell} = 0.8 - (-0.44) + \log$$

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

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

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

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

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

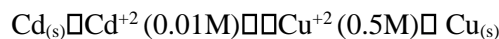
Ans: 
$$E_{cell} = E_{cell}^0 + \frac{0.0591}{n} \log \frac{[\text{Cd}^{+2}]}{[\text{Mg}^{+2}]}$$

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

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

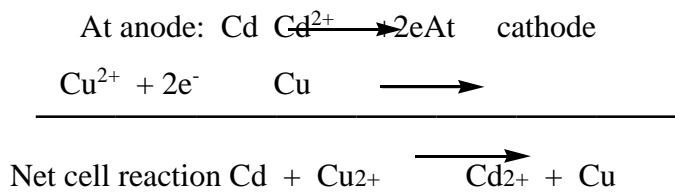
$$E_{cell} = 1.6699 \text{ V.}$$

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:  $E^{\circ}_{\text{Cd}} = -0.4\text{V}$ ;  $E^{\circ}_{\text{Cu}} = 0.34\text{V}$ ;  $[\text{Cd}^{2+}] = 0.01\text{M}$ ;  $[\text{Cu}^{2+}] = 0.5\text{M}$  Ans:



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

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

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

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

5. Calculate the emf of Copper concentration cell at  $25^{\circ}\text{C}$ , where the copper ions ratio in the cell is 10.

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

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

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

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

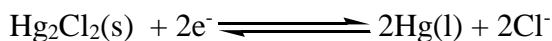
**Reference electrodes:** “Reference electrodes are the electrode with reference to those, the electrode potential of any electrode can be measured”. The Primary reference electrode used for cell potential measurement is the SHE, whose potential is Zero. The secondary reference electrodes are Calomel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

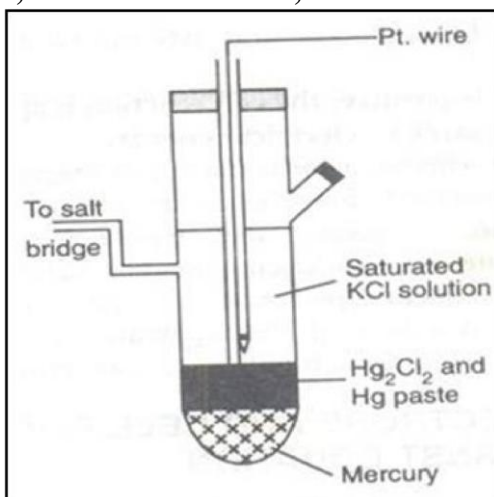
$$E = E^0 - \frac{2.303 RT}{2 F} \log[\text{Cl}^-]$$

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

F

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

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”.

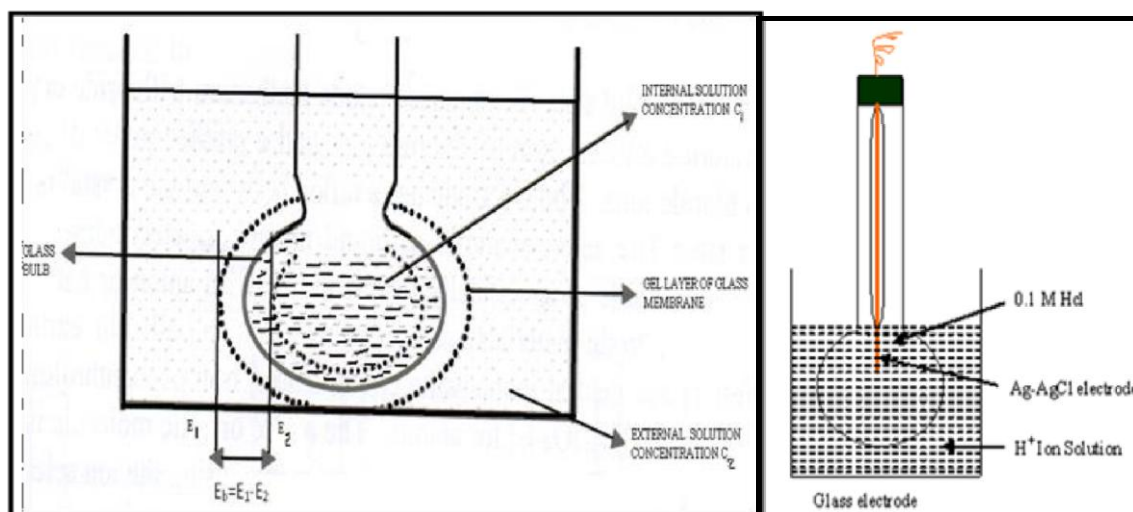
**Uses:-** To determine the concentration of a number of cations and anions such as H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, CN<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup> etc.

There are Four types of membranes, They are

- 1) Glass membranes
- 2) Heterogeneous membranes
- 3) Solid State 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<sub>G</sub> 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<sup>+</sup> concentration inside the glass bulb is a constant. The first term on RHS of the



above equation becomes constant. ....5

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

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

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

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**

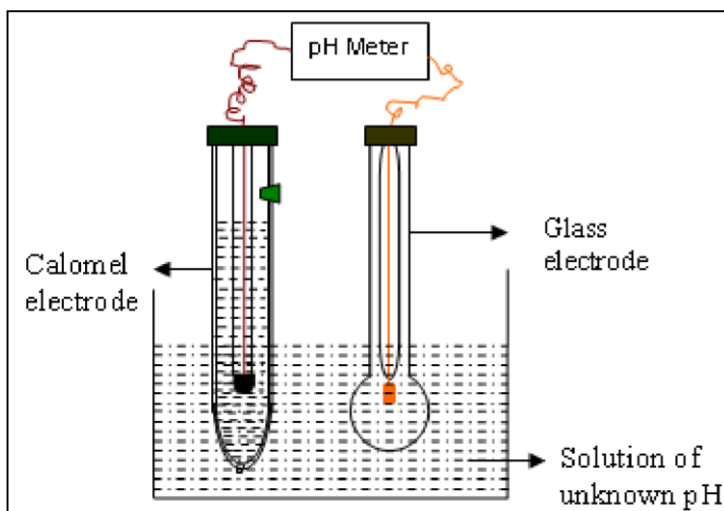
1. This electrode can be used to determine pH in the range 0-9, with a special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

**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 ie. Experimental solution.



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



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 knowing EMF of the cell,

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

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

$$\text{Constan } t - E_{\text{cell}} - E_{\text{sce}}$$

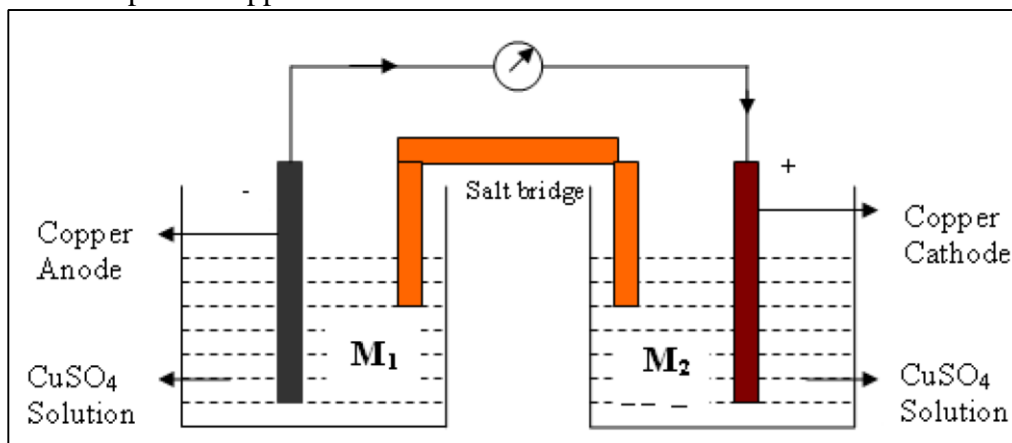
**Electrolyte Concentration cells:**

“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”.

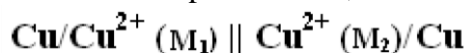
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$$0.0591 \dots\dots\dots(4)$$

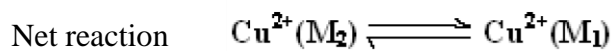
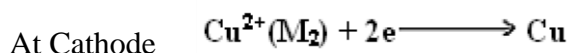
A typical example of Copper concentration cell is shown below.



It consists of two Copper electrodes are immersed in two different concentration of CuSO<sub>4</sub> 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

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

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

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

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.

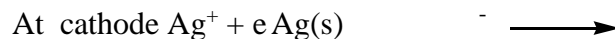
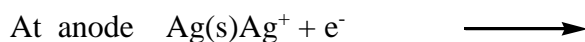
Given:  $E^0_{Zn} = -0.76V$ ;  $E^0_{Cu} = 0.34V$

Ans:  $E_{cell} = E_{cathode} - E_{anode}$   
 $E_{cell} = 0.34 - (-0.76)$   $E_{cell}$   
 $= 1.1 V.$

2. Write the electrode reactions and Calculate the EMF of the given concentration cell at

298K,  $Ag(s) \parallel AgNO_3 (0.018M) \parallel AgNO_3 (1.2M) \parallel Ag(s).$

Ans:



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

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

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

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

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

$$E_{cell} = \frac{0.0591 \cdot 10}{2}$$

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

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  $\text{Cu}^{+2}/\text{Cu}$  is 0.34V at 298K Given:  $T=298\text{K}$ ;  $E^0_{\text{Cu}}= 0.34\text{V}$   
 $[\text{Cu}^{+2}] = 0.1\text{M}$

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

$$\begin{matrix} \text{Cu}^{+2} \\ \text{Cu} \end{matrix} \quad E = 0.34 + \frac{0.0591}{2} \log(0.1)$$

$$E = 0.34 - 0.0296$$

$$E = 0.3104 \text{ V.}$$

**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.

**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.

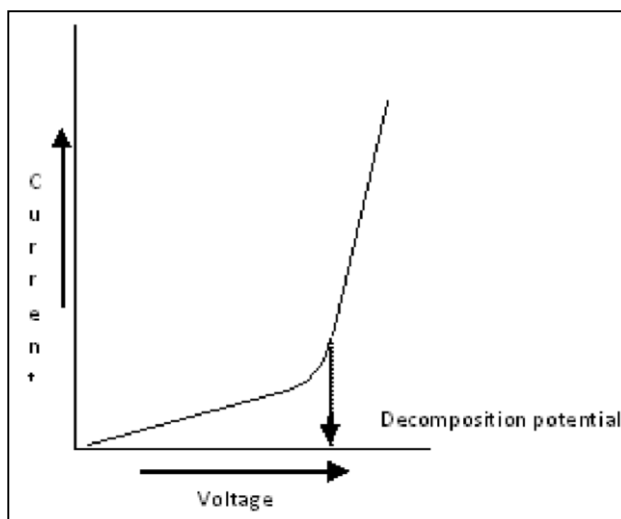
### **b) Decomposition potential:**

“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.

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.



### **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.

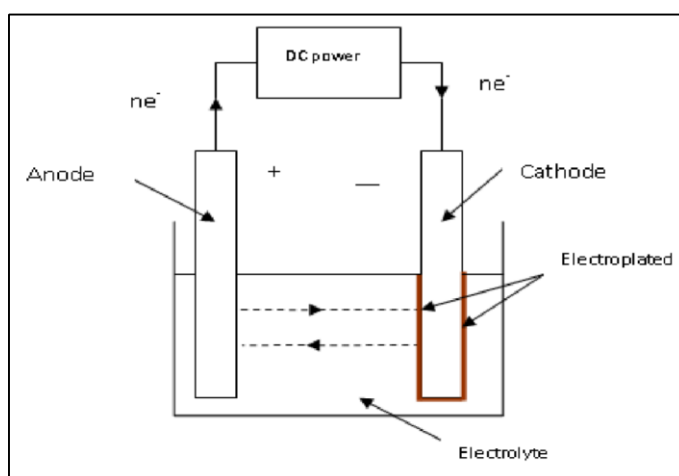
### Electroplating:

**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.



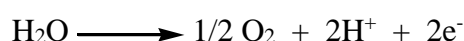
during

### Reactions at anode and cathode electroplating:

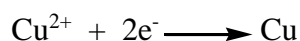
At anode oxidation takes place



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.

### **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

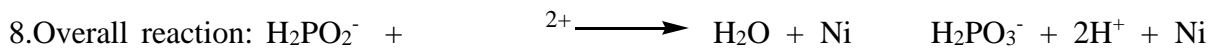
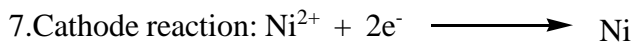
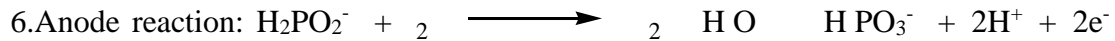


Type of cathode used for plating	Plating is carried out on metals.	Plating may be carried out on insulators (ex: plastics) and semiconductors.
Anode reaction	$\begin{aligned} &\longrightarrow M \quad M^{n+} + \\ &\longrightarrow ne- \quad \text{OR} \\ &H_2O \quad 1/2O_2 + 2H^+ + 2e^- \end{aligned}$	Reducing agent $\rightarrow$ Oxidized product + $ne^-$
Cathode reaction	$M^{n+} + ne^- \rightarrow M$	$M^{n+} + ne^- \rightarrow M$

**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



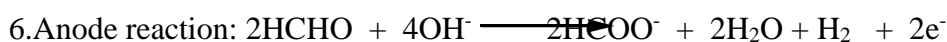
(Since H<sup>+</sup> ions are produced during the reaction, the p<sup>H</sup> decreases. To maintain the p<sup>H</sup> at 4.5, buffer salt (sodium acetate) is added during the reaction.) **Applications:**

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



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

8. Overall reaction:  $2\text{HCHO} + 4\text{OH}^- + \text{Cu} \rightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + \text{Cu}$

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

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

## 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.

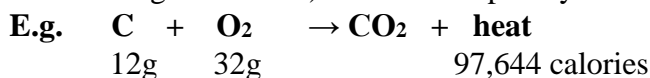
Coke, charcoal, diesel, producer gas etc.

### 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

9. 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).

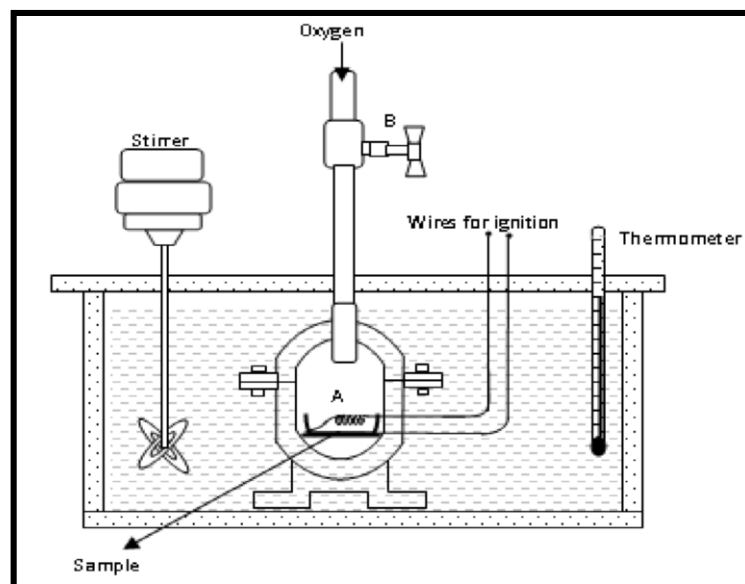
Fuels generally contain some amount of hydrogen during combustion the hydrogen is converted into steam. When the products are cooled to the room temperature the latent heat of condensation of steam gets included in the experimentally measured calorific value, therefore, the experimentally measured calorific 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 % hydrogen      □       $\frac{9 \square x}{100}$  g of water = 0.09 □ x g of water

NCV = GCV - latent heat of steam formed =

GCV - 0.09 □ x □ latent heat of steam

Latent heat of steam = 2454 kJ kg<sup>-1</sup>

1 calorie = 4.187 kJ kg<sup>-1</sup>

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

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, % H<sub>2</sub>=2.8.

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

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

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

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 587 \times 4.184$$

$$= 25271.36 - 0.09 \times 2.8 \times 587 \times 4.184$$

$$\text{NCV} = 24652.44 \text{ KJ/Kg}$$

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<sub>2</sub> =29.2 °C, t<sub>1</sub> = 26.5 °C, % H<sub>2</sub> = 0.7 and S = 4.2 kJ/kg/ °c.

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

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

$$\text{GCV} = 53079.39 \text{ KJ/Kg}$$

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 587 \times 4.184$$

$$= 53079.39 - 0.09 \times 0.7 \times 587 \times 4.2$$

$$\text{NCV} = 52924.07 \text{ KJ/Kg}$$

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>

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

$$\text{NCV (solid fuel)} = \text{GCV} - \text{latent heat}$$

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

**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  $\alpha$ - Methyl naphthalene which has the same knocking characteristics as the diesel under test.

**Knocking:**

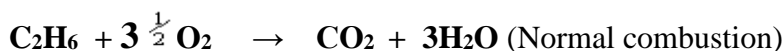
“The production of shock waves in an IC engine as a result of an explosive combustion of fuel-air mixture consequent to an increase in the compression ratio, beyond a certain value leading to a rattling sound”.

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

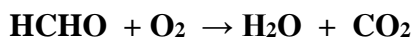
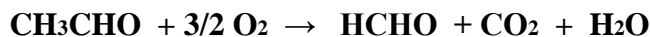
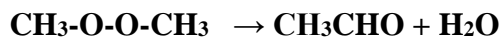
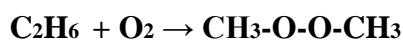
Under ideal conditions, in an IC engine, the petrol-air mixture drawn into the cylinder of the engine undergoes compression and then ignited. The hydrocarbons in the petrol undergo complete combustion and the flame propagates smoothly. But sometimes due to deposits of carbon on the walls of the cylinder 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.

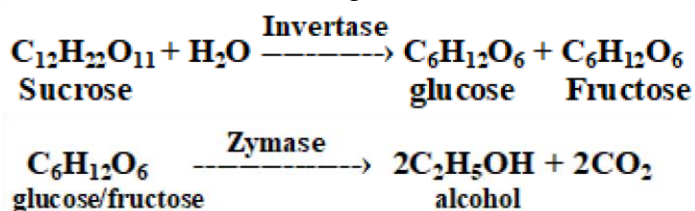
### **Power Alcohol:**

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**

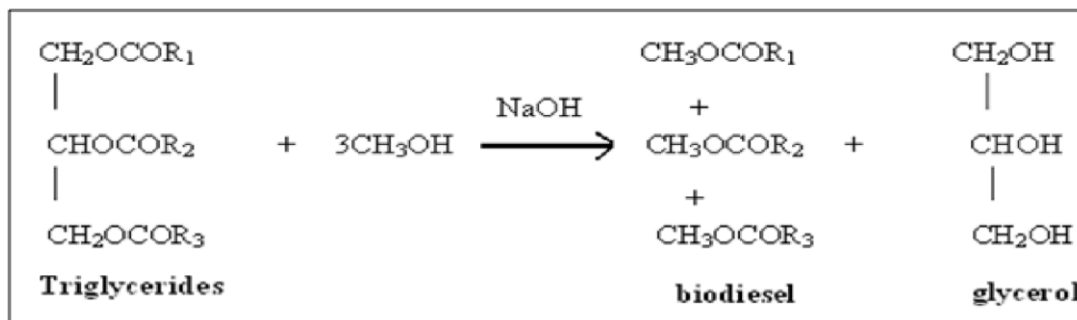
- 1). Power output is high.
- 2). Doesn't release CO, causes less pollution.
- 3). Alcohol is obtained from molasses, an agricultural product and hence renewable.
- 4). Biodegradable.

#### **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.	1. It is a galvanic cell in which the electrical energy is directly derived from the combustion of chemical fuels supplied continuously.
2. Store chemical energy.	2. Do not store chemical energy.
3. Reactants are within the cell.	3. Reactants are supplied continuously.
4. Products remain within the cell.	4. Products are continuously removed from the cell.
5. Efficiency is less Ex: Lead-acid battery, Ni-MH battery.	5. Efficiency is more Ex: H <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.

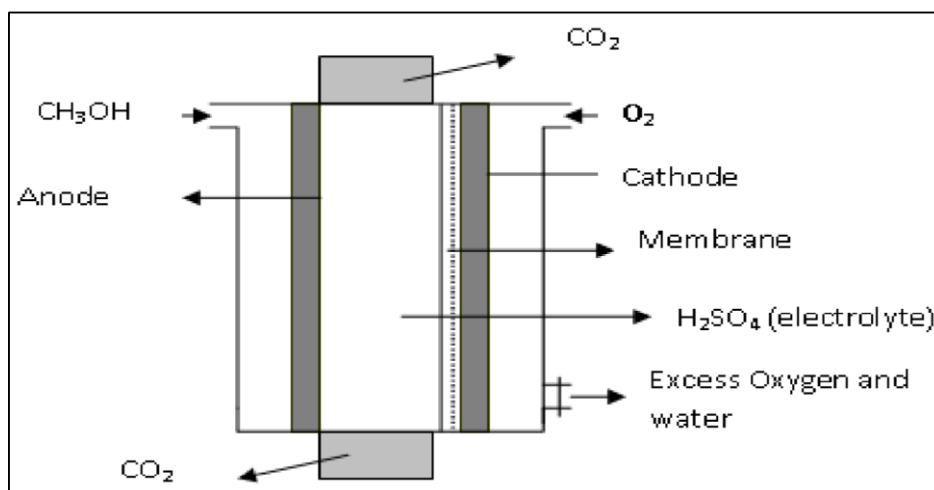


2. Harmful products are absent. Hence fuel cells are environment-friendly.
3. No need for charging.
4. Silent operation.
5. No moving parts. Hence wear and tear are eliminated.

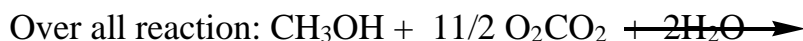
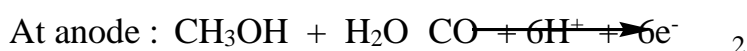
### Methanol – Oxygen fuel cell:

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.

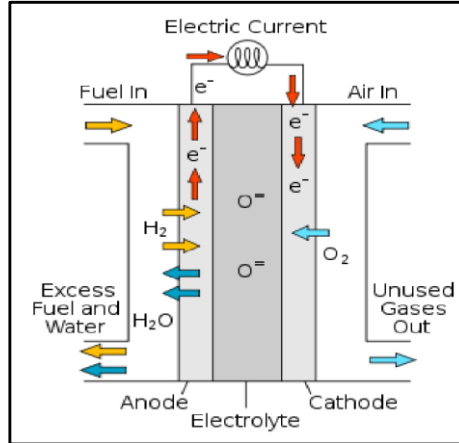
2) Used for large scale power production stations.

#### 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**

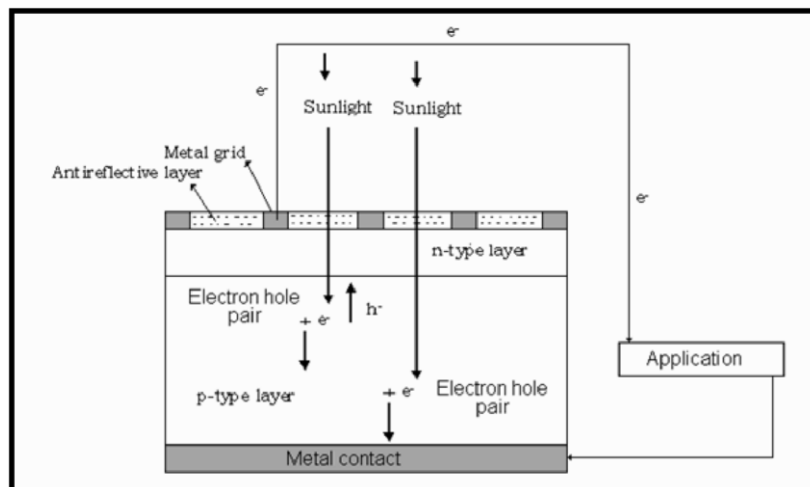
The radiations reaching earth from the sun and converting them into different useful forms of energy is called solar energy. The utilization of solar energy is of two types – Direct solar power and indirect solar power.

**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:**

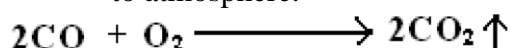
1. The Solar power is only practical in certain areas with a favorable climate and latitude. That is, areas near the tropics and which are relatively cloud free.
2. The Solar power is not available at night.
3. The Solar power decreases during cloudy.
4. The Solar power must be converted into some other 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:**

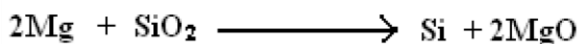
Quartz and carbon are placed in a crucible, two carbon electrodes are submerged in the crucible and an electric arc is struck. The mixture gets heated to a high temperature and the following reaction takes place.



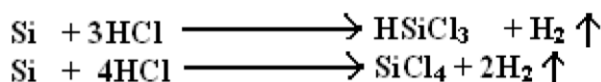
Silicon is obtained in the molten state CO is further oxidized to carbon dioxide & released to atmosphere.



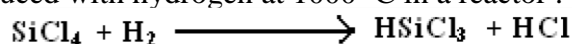
Silicon is further refined by treating with oxygen and slag forming additives such as AL, Ca & Mg. they react with silica to form slag and silicon., the slag is removed and refined melt is poured in moulds where Si solidifies. The silicon obtained is called metallurgical grade silicon.



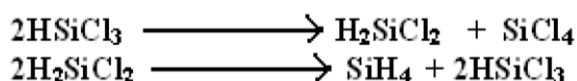
The metallurgical grade silicon is treated with dry HCL gas about 300°C to form trichlorosilane and a small amount of tetrachlorosilane. The mixture is distilled to get pure trichlorosilane.



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).



## Unit-6

### 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.

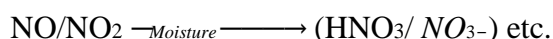
1. Natural contaminants present in the air are pollen, fungal spores, cysts, bacteria and marsh – gas. Methane (CH<sub>4</sub>) or marsh – gas is a hydrocarbon which is formed by decay of vegetable matter in marshy places (i.e. anaerobic decomposition of organic matter).
2. Carbon dioxide from the breakdown 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, noncorrosive, yet is very toxic in nature. It causes 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 words, 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 affects the neurological behavior of humans. The toxicity of inorganic mercury compounds depends on 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 a purgative and a drug to kill intestinal worms. Since mercuric salts are generally more soluble they are considerably more toxic. The  $\text{Hg}^{2+}$  ions concentrate 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 (characterized by 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 sulphhydryl groups  $-\text{SH}$  of the proteins and therefore inhibit 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 metabolize 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 as 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.

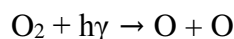
1.  $\text{SO}_2$  bleaches the leaf surface and causes chlorosis (i.e. loss of chlorophyll and yellowing of the leaf) especially in leafy vegetables.
2.  $\text{NO}_2$  causes premature leaf fall (abscission) and suppressed growth of plants resulting in reduced yields of crop plants.



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:

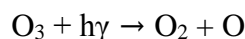
Ozone layer filters out harmful ultraviolet radiations from the sunlight and thus protects various life forms on the earth. Ozone is a form of oxygen. The molecule of oxygen contains two atoms where as ozone contains three oxygen atoms. In the stratosphere ozone is continuously created by the absorption 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.



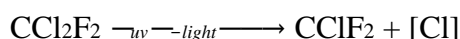
The net result of the above reactions is an equilibrium concentration of ozone. This equilibrium is disturbed by reactive atoms of chlorine, bromine etc., which destroy ozone molecules and results in thinning of ozone layer called ozone hole. Three major activities could destroy the ozone layer.

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

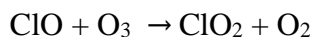
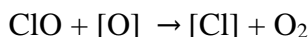
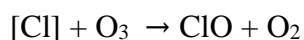
In many developing and developed countries, two Freon are used.

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

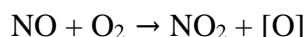
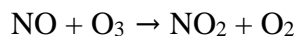
Step I - Photo dissociation of Freon 12



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 0.20.6 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 Dibrugarh, 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.

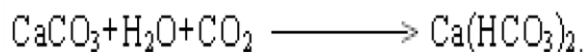
**Sources of water:** Rainwater, river water, lake water, sea water and well water.

### 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 steady 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

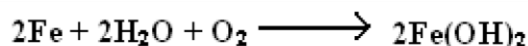
1. It decreases the efficiency of the boiler because the dissolved salts get deposited on turbine blades and superheater by evaporation.
2. The maintenance of the boiler pressure becomes difficult due to the improper judgment of actual height of water column.

### 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.

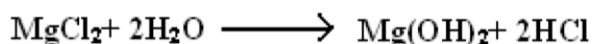


2. The presence of carbon dioxide: carbon dioxide forms carbonic acid in the presence of water which has a slow effect on boiler materials.



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.

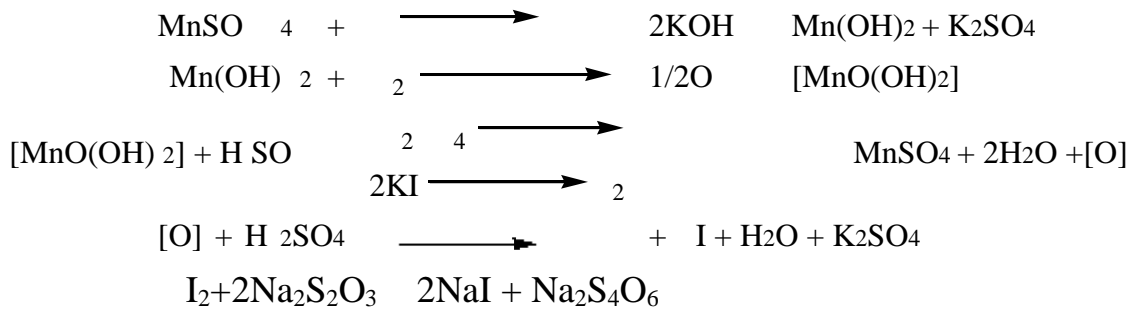
Anaerobic oxidation: Organic compounds are oxidized by anaerobic bacteria's which produce an offensive smell. This kind of oxidation is known as anaerobic oxidation.

### **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 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 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

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

**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 oxidizable 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=(BA)cm<sup>3</sup>

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

$$N \times (B - A)$$

$$\text{Normality of COD of the sample } N_1 = \frac{\quad}{V}$$

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

$$V$$

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



V

**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

$$N_1 V_1 = N_2 V_2$$

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

$$\frac{25 \times 6.0}{20}$$

Therefore, normality of COD Sample  $N_1 =$

$$\frac{25 \times 6.0}{20} \quad 3 \quad 600mg / dm^3$$

$$COD \text{ of the sample} = X_8 = 0.6g / dm =$$

**(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

$$N_1 V_1 = N_2 V_2$$

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

$$\frac{1 \times 22.1 \cdot 10}{25}$$

Therefore, normality of COD Sample  $N_1 =$

$$\frac{1 \times 22.1 \cdot 10}{25} \quad 3 \quad 707.2mg / dm^3$$

$$COD \text{ of the sample} = X_8 = 0.7072g / dm =$$



(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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>=14.0 ml

Volume of FAS consumed in blank=28.1ml

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<sub>1</sub> V<sub>1</sub> = N<sub>2</sub> V<sub>2</sub>

N<sub>1</sub>X25=0.5X14.1

$$\frac{5 \times 14.1 \times 10^3}{25}$$

Therefore, normality of COD Sample N<sub>1</sub>=

$$\frac{5 \times 14.1 \times 10^3}{25} = 225.6 \text{ mg / dm}^3$$

COD of the sample= X 8 = 0.225.6g /dm =

### Chemical analysis of water

#### Determination 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 Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub> 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 BaSO<sub>4</sub> ppt is filtered through Gooch Crucible and weighed.

To precipitate sulphate ions as completely as possible, excess barium chloride is added. The BaSO<sub>4</sub> ppt formed is in colloidal condition. Hence this ppt cannot be removed by ordinary filtration procedures.

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 BaCl<sub>2</sub>). 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 BaSO<sub>4</sub> contains 96.0 g of SO<sub>4</sub><sup>2-</sup>

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

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

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