Engineering Chemistry Notes
For vtu students

(Common to all Branches)

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unit-1

ELECTROCHEMISTRY

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

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

On such occasions using van‟t Hoff isotherm we can write

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

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^{-1}). For its total differential dS we write

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

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

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

Single electrode potential or Cell potential (E):

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

OR

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

STANDARD ELECTRODE POTENTIAL (E°):

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

EMF OF THE CELL:

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

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

Nernst equation for single electrode potential:

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

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

$$-\Delta G = W\ max \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$W\ max = nFE \ldots\ldots\ldots\ldots\ldots (2)$$

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

$$.'\ .\ -\Delta G= nFE \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Under standard condition

$$-\Delta G^o = nFE^o \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

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

Consider a reversible electrode reaction

$$M^{n+} + ne^- \rightleftharpoons M \quad \ldots\ldots\ldots\ldots(5)$$

According to Vanthoff's reaction isotherm

$$\Delta G = \Delta G^0 + RT.\ln K_c \ldots\ldots\ldots\ldots(6)$$

Where, K_C=Equilibrium constant

Substitute the value of K_C, we have

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

Divide the equation (6) by -nF

From equation (3) and (4)

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

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

Then, we have

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

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

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

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

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

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

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

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

Problems

1. Calculate the potential of Ag-Zn cell at 298 K, if the concentration of Ag^+ and Zn^{+2} are $5.2x10^{-6}$ M and $1.3x10^{-3}$M respectively. E^0 of the cell at 298K is 1.5V given: T=298K; E^0_{cell} = 1.5V.

$[Ag^+] = 5.2x10^{-6}M$

$[Zn^{+2}] = 1.3x10^{-3}M$

Ans:

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

$$E_{cell} = 1.5 + \frac{0.0591}{2}\log\frac{(5.2x10^{-6})^2}{1.3x10^{-3}}$$

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: $Fe_{(s)} | FeSO_4(0.1M) || AgNO_3(0.05M) | Ag_{(s)}$

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

$$E_{cell} = E^0_{cathode} + \frac{0.0591}{n}\log[Ag+] - E^0_{anode} - \frac{0.0591}{n}\log[Fe2+]$$

$$E_{cell} = E^0_{cathode} - E^0_{anode} + \frac{0.0591}{n}\log\frac{[Ag^+]}{[Fe2+]}^2$$

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

E_{cell} = 1.19 V.

3. Calculate the voltage of the cell $Mg_{(s)} | Mg^{+2}$ (1M) || Cd^{+2} ($7x10^{-11}$M) | $Cd_{(s)}$, where E^0_{cell}=1.97V.

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

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

$[Cd^{+2}] = 7x10^{-11}M$

Ans:

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

$$E_{cell} = 1.97 + \frac{0.0591}{2}\log 7X10^{-11}$$

E_{cell} =1.97-0.3001

E_{cell} =1.6699 V.

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

$Cd_{(s)} | Cd^{+2}$ (0.01M) || Cu^{+2} (0.5M) | $Cu_{(s)}$

The standard reduction potentials of Cd and Cu are –0.4V and 0.34V respectively. Calculate the emf of the cell.

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

Ans:

At anode: $Cd \longrightarrow Cd^{2+} + 2e^-$

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

Net cell reaction $Cd + Cu^{2+} \longrightarrow Cd^{2+} + Cu$

$$E_{cell} = E^0_{cathode} - E^0_{anode} + \frac{0.0591}{n}\log\frac{[Cu^{2+}]}{[Cd2+]}$$

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

$E_{cell} = 0.74+0.0502$

$E_{cell} = 0.7902$ V.

5. Calculate the emf of Copper concentration cell at 25^0 C, where the copper ions ratio in the cell is 10.

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

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

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

$E_{cell} = 0.0296$ 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, **$Hg|\ Hg_2Cl_2|Cl^-$.**

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,

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

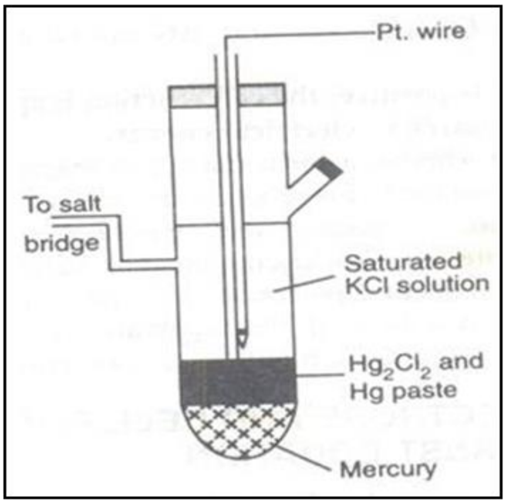
The Nernst equation is given by,

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

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

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

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".

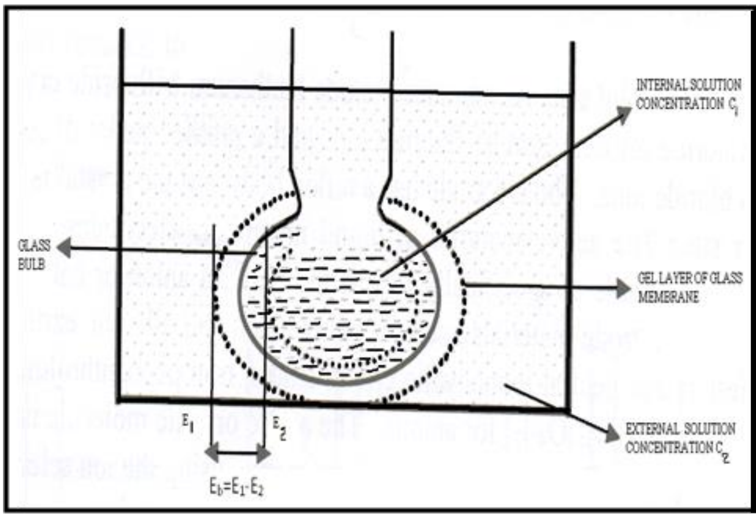
Uses:- To determine the concentration of a number of cations and anions such as H^+, Li^+, Na^+, K^+, Pb^{2+}, Cu^{2+}, Mg^{2+}, CN^-, NO_3^-, F^- etc.

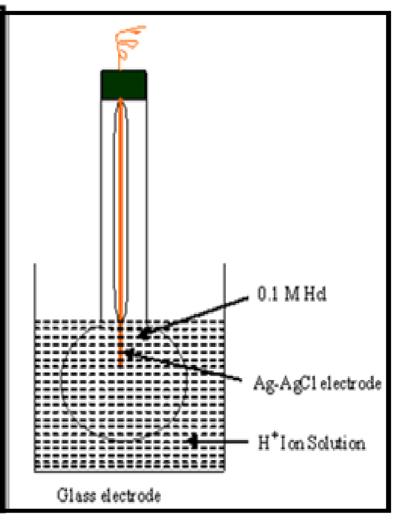
There are Four types of membranes, They are

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

Glass electrode:

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





The potential of glass electrode E_G is given by

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

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

$$E_G = 0.0591.\log \frac{[C_2]}{[C_1]} \text{ ……………3 \textbf{Or} } E_G = 0.0591.\log \frac{[C_2]}{[C_1]}$$

$$E_G = -0.0591.\log[C_1] + 0.0591.\log[C_2] \text{……4}$$

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

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

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

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

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_2O, 6%CaO, and 72%SiO_2) which has low melting point and relatively high electrical conductivity. The glass bulb is filled with a solution of constant pH (0.1MHCl) and 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^+ ions. The electrode representation is,

Glass | 0.1M HCl | Ag-AgCl.

Advantages

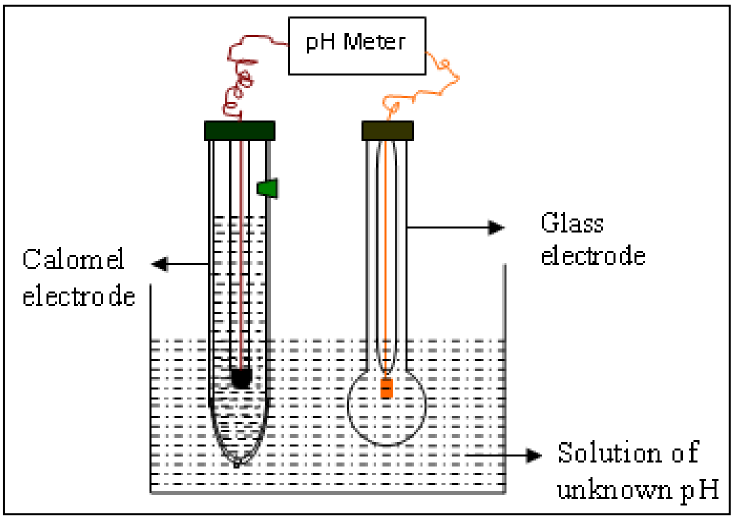
1. This electrode can be used to determine pH in the range 0-9, with a special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

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,

$$\mathbf{Hg|\,Hg_2Cl_2|Cl^-||Solution\ of\ unknown\ pH|glass|0.1M\ HCl|Ag^+|AgCl}$$

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

$\mathbf{E_{cell} = E_{cathode} - E_{anode}}$ ……………..(1)

$\mathbf{E_{cell} = E_{glass} - E_{SCE}}$ ……………..(2)

Since E_{SCE} is knowing EMF of the cell,

Substitute the value of E_G to equation (2)

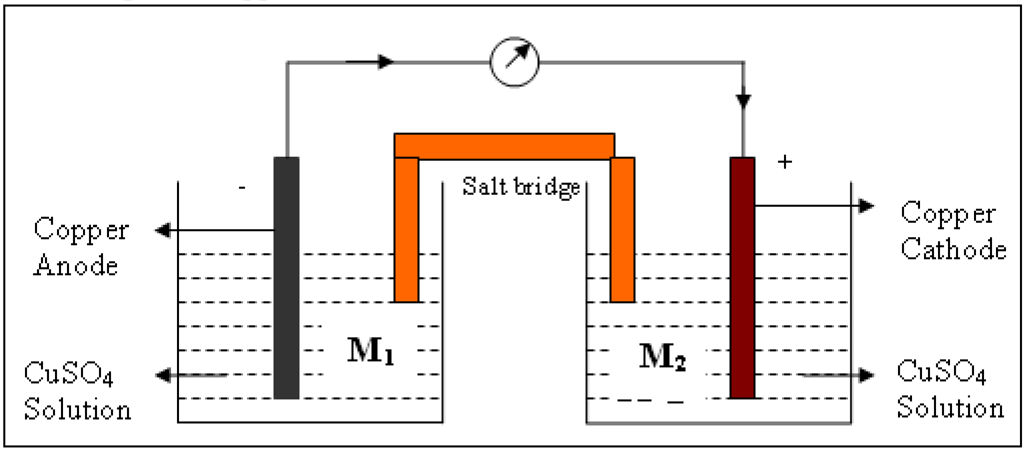
$$E_{cell} = Constant - 0.591.pH - E_{sce} \quad \text{……….(3)}$$

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

Electrolyte Concentration cells:

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

A typical example of Copper concentration cell is shown below.



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

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

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

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

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

Net reaction $Cu^{2+}(M_2) \rightleftharpoons Cu^{2+}(M_1)$

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

Emf of concentration cell:

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

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

$$Ecell = \frac{0.0591}{n}.\log[M_2] - \frac{0.0591}{n}.\log[M_1] \qquad \ldots\ldots\ldots2$$

$$E_{cell} = \frac{0.0591}{n}\log\frac{[M_2]}{[M_1]} \quad \text{at, 298K} \qquad \ldots\ldots\ldots3$$

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, Ecell=0
2. When $M_2/M_1>1$ i.e $M_2>M_1$, log M_2/M_1 is positive & electrode potential is positive.
3. Higher the ratio of M_2/M_1, higher is the value of cell potential.

Problems:

1. Calculate the potential of Daniel cell at 25^0 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, $Ag_{(s)} | AgNO_3\,(0.018M) || AgNO_3\,(1.2M) | Ag_{(s)}$.

Ans:

At anode $Ag(s) \longrightarrow Ag^+ + e^-$

At cathode $Ag^+ + e^- \longrightarrow Ag(s)$

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

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

$E_{cell} = 0.1078$ V.

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

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

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

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

$E_{cell} = 0.0296$ V.

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

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

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

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

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

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

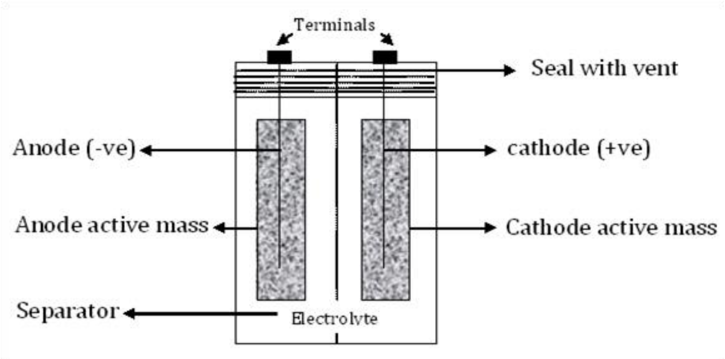
Unit-2

BATTERY TECHNOLOGY

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

Principle components of a battery are:

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



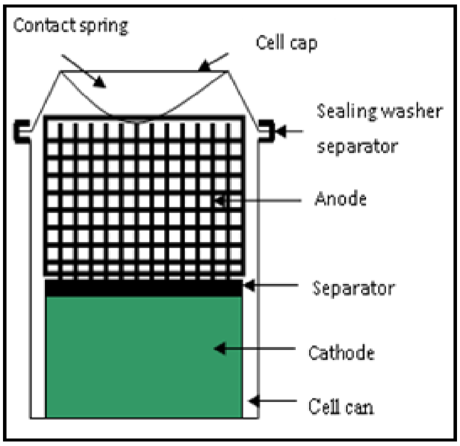
Classification of batteries:

1. Primary batteries: In these batteries the cell reaction is not reversible after discharging cannot be rechargeable. e.g. Zn-MnO_2 dry cell.

2. Secondary batteries: In this battery the cell reaction is completely reversible after discharging can easily rechargeable. e.g. Lead-acid battery, Ni-MH battery.

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

Nickel-metal hydride battery:



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

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

Cell representation:

$$MH_2 \,|\, KOH(5M) \,|\, Ni(OH)_2,\ NiO(OH)$$

Cell reactions:

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

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

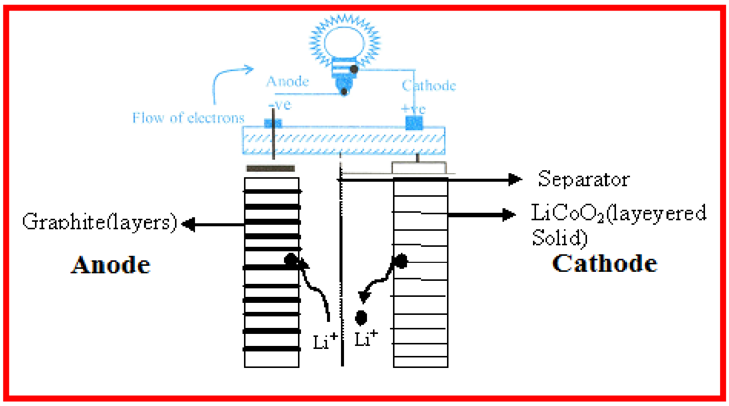
Over all reaction: $MH + NiO(OH) \rightleftharpoons M + Ni(OH)_2$

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

Lithium batteries: These batteries with high energy density, high energy efficiency, high voltage and long life cycle. Lithium has the following characteristics.
(i) It is light weight. (ii) It has high electrochemical equivalence (3.86 Ah g^{-1}). (iii) It has good electrical conductivity. (iv) It has high standard electrode potential (-3.05V).

Li- ion battery:

A conventional lithium ion battery consists of and a metal oxide such as carbon (graphite) forms the anode and lithium cobalt oxide ($LiCoO_2$) as a cathode. The electrolyte consists of a lithium salt in an organic solvent. The salts include lithium hexafluorophosphate $LiPF_6$, lithium tetrafluoroborate $LiBF_4$ and lithium perchlorate $LiClO_4$. The solvents used are ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The cell delivers an emf of 4V.



Cell reaction:

At anode: $Li_X - C_6 \rightarrow XLi^+ + 6C + Xe^-$

At cathode: $XLi^+ + Xe^- + Li_{1-X}CoO_2 \rightarrow LiCoO_2$

Oveall reaction: $Li_X - C_6 + Li_{1-X}CoO_2 \leftrightarrow LiCoO_2 + 6C$

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

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

Unit-3
CORROSION

Def^{n}: Corrosion is a destruction reaction taking place spontaneously by chemical or electrochemical reaction of the metal by the surrounding environment on the surface of the metal.

$$\text{Metal} \underset{\text{Extractive metallurgy}}{\overset{\text{Corrosion}}{\longleftrightarrow}} \text{Metal ore}$$

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

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

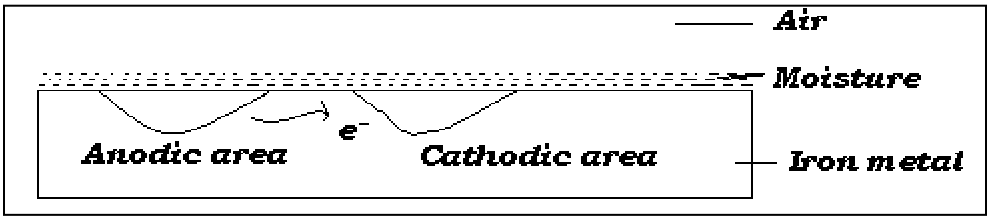
Electrochemical theory of corrosion

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

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

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

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



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

$$\underset{\text{Metal}}{M} \longrightarrow \underset{\text{Metal ions}}{M^{n+}} + ne^{-}$$

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

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

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

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

$$2H^{+} + 2e^{-} \longrightarrow H_2$$

b) In alkaline and in the absence of O_2. If the solution is alkaline and in the absence of oxygen the cathodic reaction is,

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

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

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

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

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

$$2Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2(Fe_2O_3 . 3H_2O) \textbf{ rust}.$$

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

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

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

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

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

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

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

Primary Factors (Related to metal)

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

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

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

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

Secondary factor (Related to Environment)

1. **pH of the medium:**

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

2. **Temperature:**

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

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

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

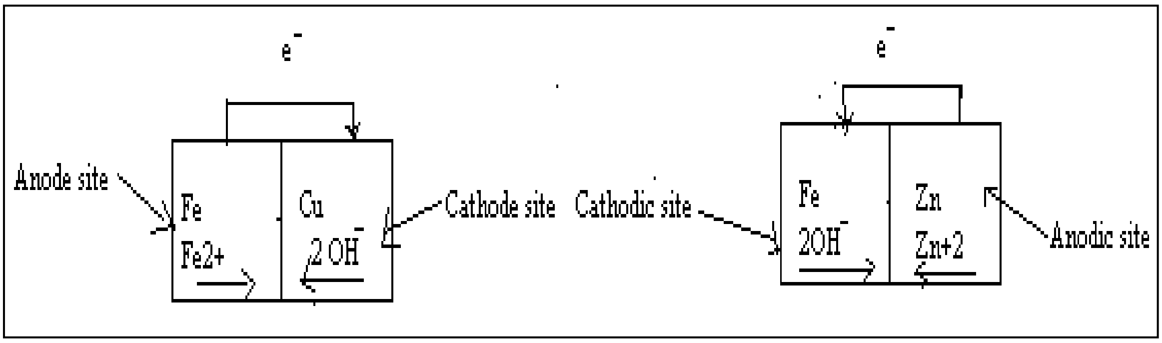
4. **Conductivity of the corroding medium:**

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

Types of Corrosion

1). Differential metal corrosion:

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



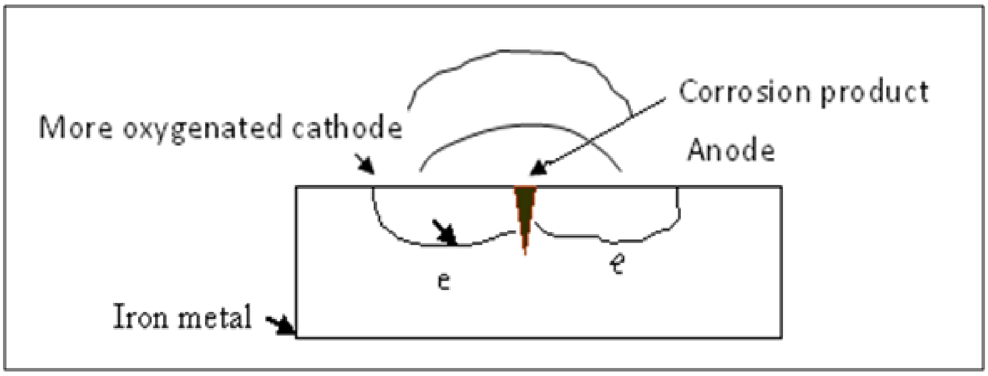
When Zn & Cu metals are electrically connected and exposed to an electrolyte , Zn metal higher in galvanic series forms the anode and suffers from corrosion whereas Cu lower in electrochemical series forms cathode hence protected from corrosion. The extent of corrosion depends on the difference in the electrode potential of the two metals and also their relative areas exposed if the potential difference between the electrodes is high, greater the extent of corrosion. **Eg:** 1). Brass taps fixed to an iron pipe. 2). Steel screws in a brass marine hardware.

2). Differential Aeration Corrosion:

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

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

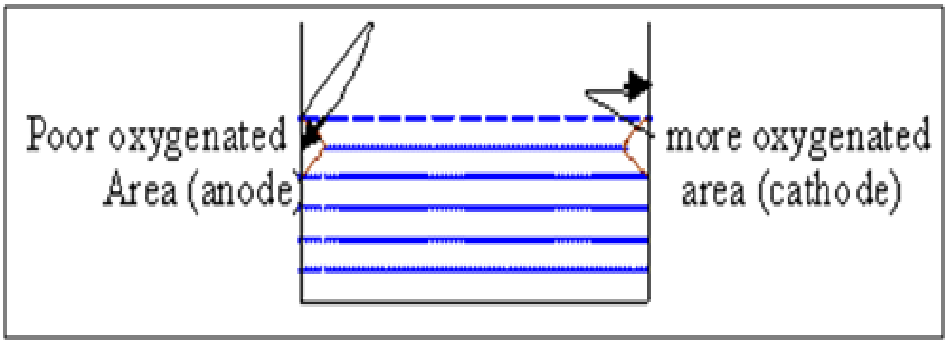
a. Pitting Corrosion:



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

b. *Water line corrosion:*

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



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

Corrosion control:

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

Anodizing:

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

Anodization of Al

Anodization of Al consists of the following steps.

Step 1: - Preparation of Al base metal surface.

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

Step 2: - Al base metal is placed in an oxidizing bath like chromic acid or boric acid, H_2SO_4

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

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

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

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

Application:

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

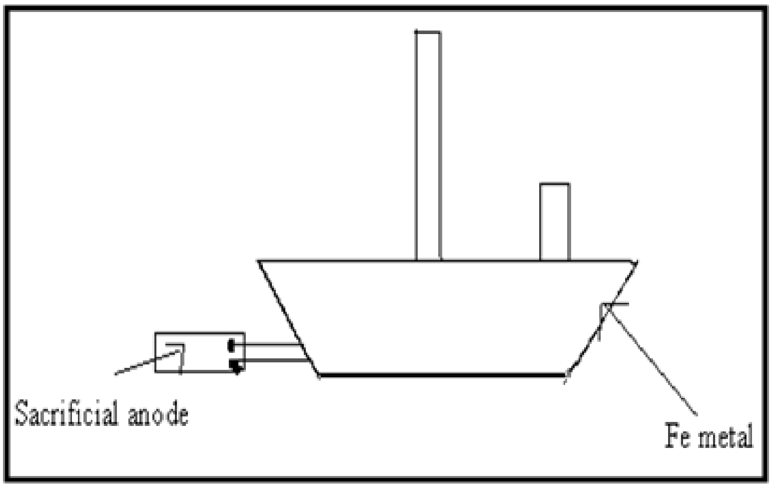
Cathodic protection:

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

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

1. Sacrificial anode method:

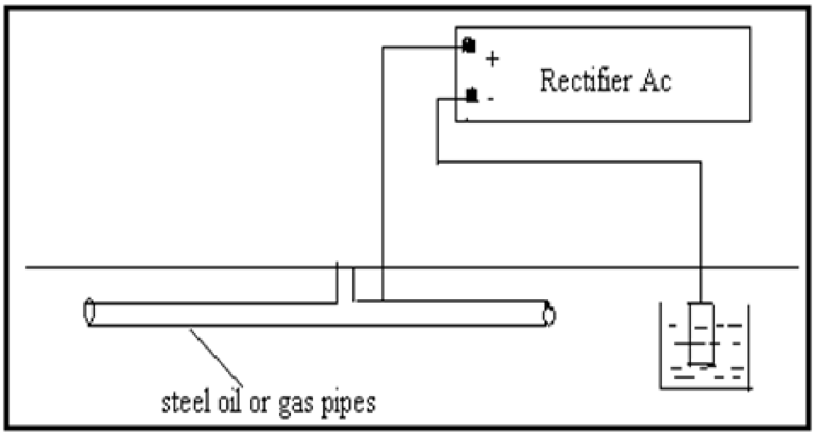
The metallic structure to be protected is made relatively a cathode by using another anodic metal contact with it. So that the corrosion is now concentrated on more anodic metal protecting the base metal from corrosion. The sacrificial anodes to be replaced by fresh ones as and when it is required. Commonly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



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

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

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



Metal coating:

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

Galvanizing:

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

Step 1: Preparation of base metal surface.

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

Step 2: Hot dipping.

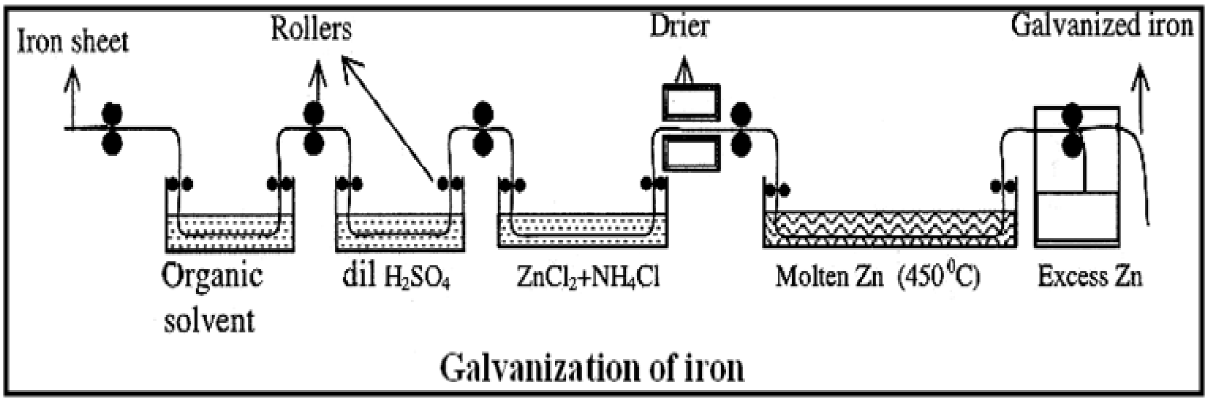
The base metal is dipped in molten Zn at 425-432^oC with ammonium chloride or $ZnCl_2$ as flux.

Step 3: Removal of the excess coating of Zn.

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

Step 4: Annealing

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



<u>Advantages</u>:

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

<u>Disadvantages:</u>

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

<u>Uses</u>:

To make galvanized articles.

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

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

Unit-4

METAL FINISHING:

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

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

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

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

Principles of Metal Finishing:

a) Polarization:

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

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

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

Factors affecting the electrode polarization:

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

5. The rate of stirring of the electrolyte: Stirring helps in minimizing the polarization effects.

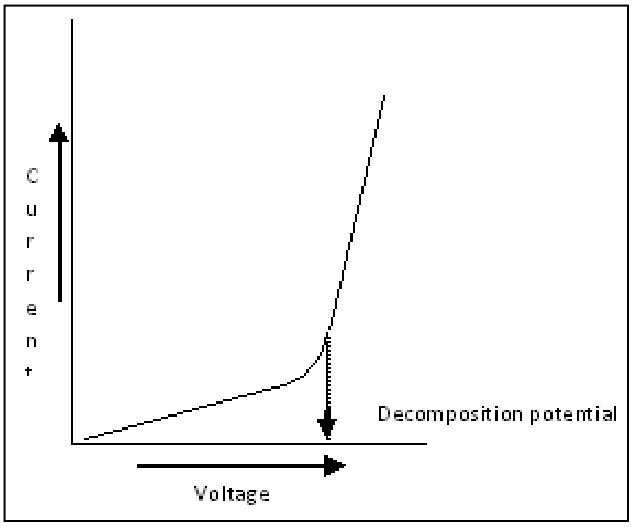
b) Decomposition potential:

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

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

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

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



c) Over voltage (over potential) (η):

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

η = Experimental decomposition potential - Theoretical decomposition potential.

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

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

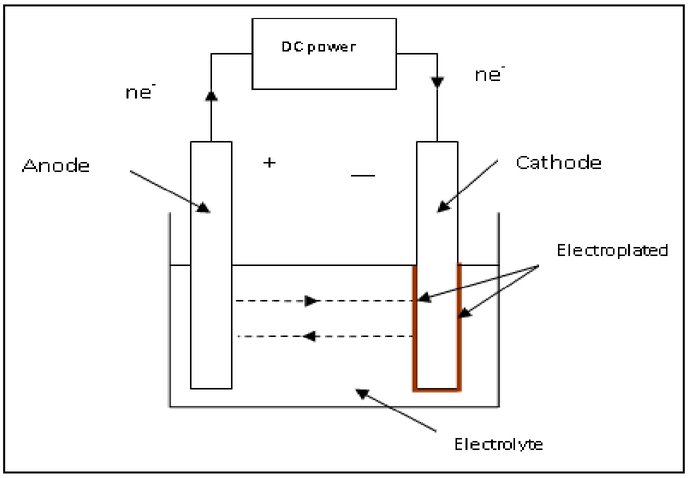
Electroplating:

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

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

The main components are:

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



Reactions at anode and cathode during electroplating:

At anode oxidation takes place

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

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

$$H_2O \longrightarrow 1/2\,O_2 + 2H^+ + 2e^-$$

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

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

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 ($CCl_2 = CHCl$), methylene chloride (CH_2Cl_2), carbon tetrachloride (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 ($NaOH$, Na_2CO_3 etc.) Alkali cleaning is made more effective by making the metal cathodic in a hot alkali solution. The hydrogen gas liberated at the cathode helps to dislodge the greasy matter.

2. Removal of inorganic substances – descaling process:

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

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

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

Electroplating of chromium:-

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

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

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

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

ELECTROLESS PLATING:

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

Metal ions + reducing agent → Metal + oxidized product.

Advantages of electroless plating:

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

Distinction between electroplating and electroless plating:

Property	Electroplating	Electroless plating
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	$M \longrightarrow M^{n+} + ne-$ OR $H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$	Reducing agent → Oxidized product + n e^-

Cathode reaction	M^{n+} + ne- $\longrightarrow$ M	M^{n+} + ne- $\longrightarrow$ 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 : $NiCl_2$
2. Reducing agent : Sodium hypophosphite.
3. Complexing agent & exaltant : Sodium succinate.
4. Buffer (p^H = 4.5) : Sodium acetate.
5. Temperature : 93 °C

6.Anode reaction: $H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^-$

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

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

(Since H^+ ions are produced during the reaction, the p^H decreases. To maintain the p^H 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 ($SnCl_2$) and then in palladium chloride ($PdCl_2$). Then, the electroless plating is done under the following conditions:

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

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

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

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

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

Applications:

1. Widely used for moralizing (PCB's) printed circuit boards.
2. For producing through hole connections.

3. For plating on non-conductors.
4. As an undercoat for electroplating.
5. For decorative plating on plastics.

Unit-5
Energy Systems

Chemical Fuels:

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

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

Based on occurrence fuels are classified as.

1) *Primary fuels or Natural fuels*

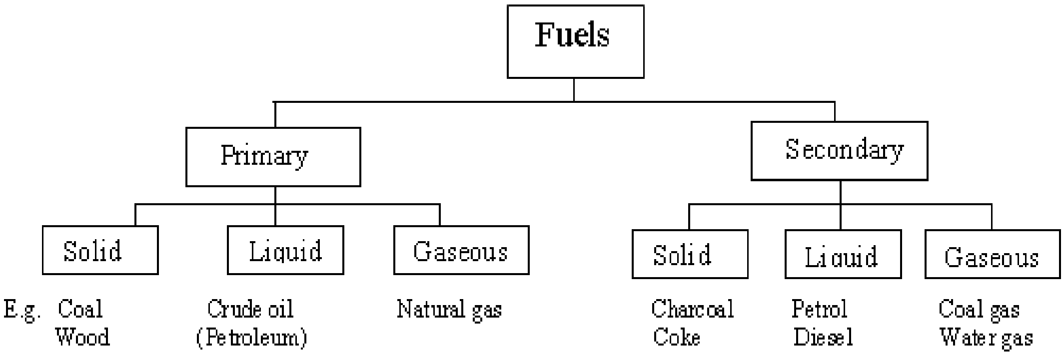
Primary fuels are carbonaceous fuels which are occurring in nature.

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

2) *Secondary fuels or Artificial fuels*.

Secondary fuels are those which are derived from primary fuels.

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



Characteristics of a good fuel:

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

Calorific value:

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

E.g. $\mathbf{C + O_2 \rightarrow CO_2 + heat}$

12g 32g 97,644 calories

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

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

Types of calorific value:

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

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

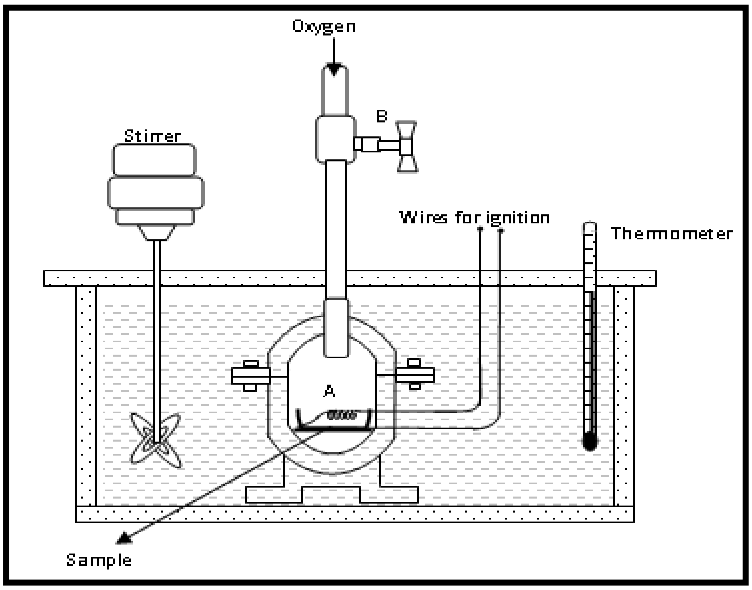
Fuels generally contain some amount of hydrogen during combustion the hydrogen is converted into steam. When the products are cooled to the room temperature the latent heat of condensation of steam gets included in the experimentally measured calorific value, therefore, the experimentally measured calorific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

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

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

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

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



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

Construction:

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

- The bomb has a platinum crucible with a loop of wire. The ends of the wire project out and can be connected to a source of electric current.
- The bomb is immersed in 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 ºC
Final temp. of water = t_2 ºC
Specific heat of water = S KJ/kg/ ºC

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

Let the fuel contain H percentage of hydrogen

$$2H + \frac{1}{2} O_2 \rightarrow H_2O$$

2 atoms of hydrogen produce one molecule of water
2g of hydrogen produce --- 18 g of water
x g of hydrogen produce ---- 9 g of water

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

NCV = GCV - latent heat of steam formed
= GCV - 0.09 × x × latent heat of steam

Latent heat of steam = 2454 kJ kg^{-1}
1 calorie = 4.187 kJ kg^{-1}

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

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 ºC if the water equivalent calorimeter is 156g Calculate GCV.

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

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

= 25921.26 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 ºC, Mass of water = 1150, % H_2=2.8.

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

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

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

$$NCV = GCV - 0.09 \times H \times 587 \times 4.184$$

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

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

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_2 =29.2 ^oC, t_1 = 26.5 ^oC, % H_2 = 0.7 and S = 4.2 kj/kg/ ^oc.

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

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

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

$$NCV = GCV - 0.09 \times H \times 587 \times 4.184$$

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

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

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 $kg^{-1}K^{-1}$, latent heat of steam is 2457.2 $kJkg^{-1}$. 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_1 = initial temperature of water = 293 K
t_2 = final temperature of water = 296.4 K
s = specific heat of water = 4.187 kJ $kg^{-1}K^{-1}$

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

$$= \frac{(1000 + 350)\text{ g} \times (296.4 - 293)\text{K} \times 4.187 \text{ kJ kg}^{-1}\text{K}^{-1}}{0.5\text{g}}$$

$$= \frac{1350 \text{ g} \times 3.4 \text{ K} \times 4.187 \text{ kJ kg}^{-1}\text{K}^{-1}}{0.5\text{g}}$$

$$= 97222.14 \text{ kJ kg}^{-1}$$

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

$$= \text{G.C.V} - (0.09 \times \text{\% of H}) \times \text{latent heat}$$

$$= 97222.14 \text{ kJ kg}^{-1} - (0.09 \times 5) \times 2457.2 \text{ kJ kg}^{-1}$$

$$= 97222.14 \text{ kJ kg}^{-1} - 1106 \text{ kJ kg}^{-1}$$

$$= 94764.94 \text{ kJ kg}^{-1}$$

Octane Number:

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

Knocking:

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

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

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

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

Under ideal conditions:

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

Under Knocking conditions: (Explosive combustion)

$C_2H_6 + O_2 \rightarrow CH_3\text{-}O\text{-}O\text{-}CH_3$

$CH_3\text{-}O\text{-}O\text{-}CH_3 \rightarrow CH_3CHO + H_2O$

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

$HCHO + O_2 \rightarrow H_2O + CO_2$

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_2H_5OH) 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.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose/fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{alcohol}}{2C_2H_5OH} + 2CO_2$$

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

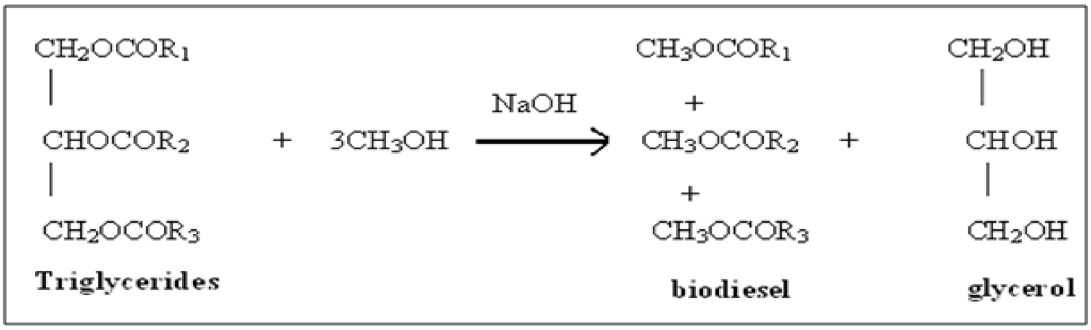
1). Power output is high. 2). Doesn't release CO, causes less pollution. 3). Alcohol is obtained from molasses, an agricultural product and hence renewable. 4). Biodegradable.

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	5. Efficiency is more
Ex: Lead-acid battery, Ni-MH battery.	Ex: H_2-O_2, Methanol-Oxygen Fuel cell.

Limitations of fuel cells:

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

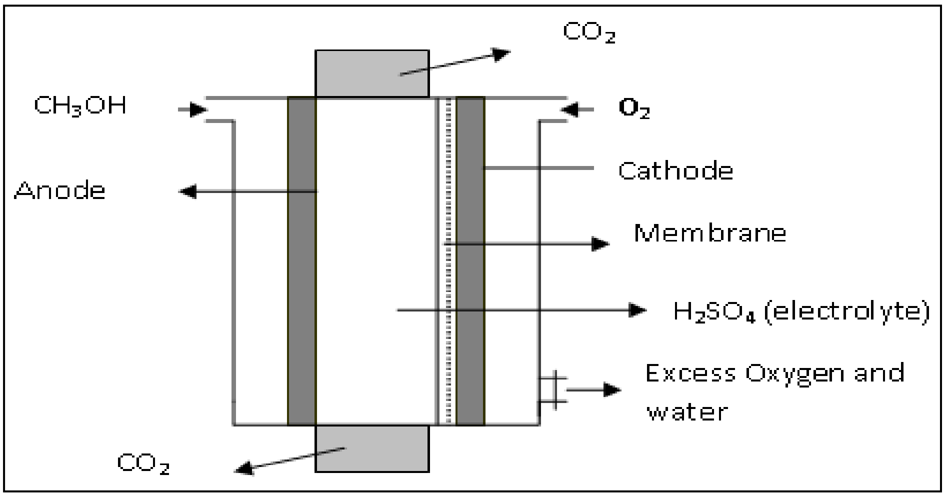
Methanol – Oxygen fuel cell:

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_2SO_4 mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.



Cell reactions:

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

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

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

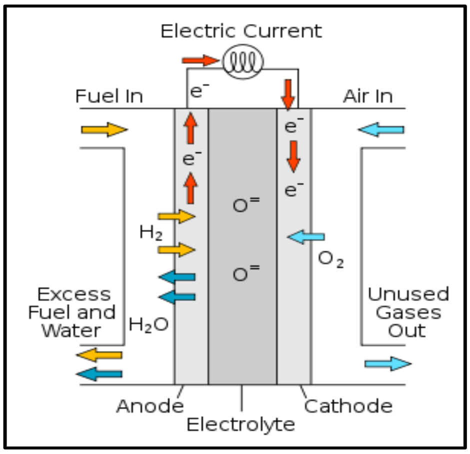
Uses: 1) Used in Military applications.

2) Used for large scale power production stations.

Solid oxide fuel 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

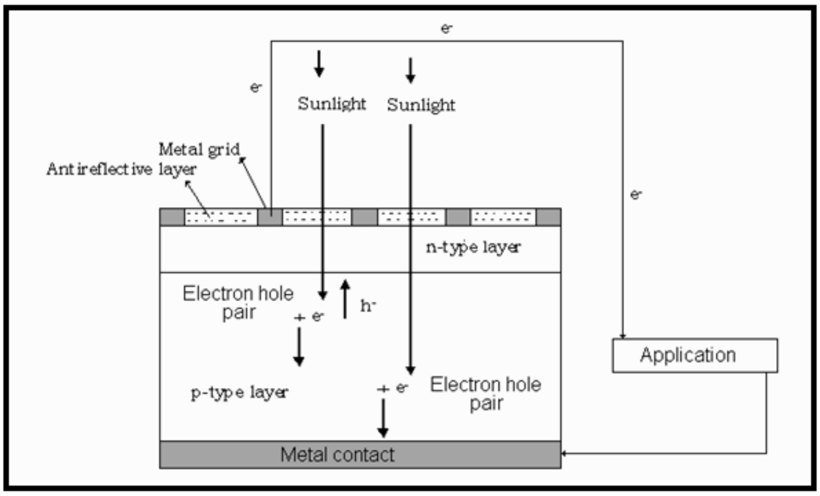
The radiations reaching earth from the sun and converting them into different useful forms of energy is called solar energy. The utilization of solar energy is of two types – Direct solar power and indirect solar power.

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 λ is the wavelength of the radiation . Those photons which posses the energy greater than Eg are absorbed .The electrons acquire this energy & are removed which leads to the formation of electron hole pair. These electrons are driven out into the external circuit and could be stored and used for various applications such as spinning of fan, working of a motor etc.

Advantages:

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

Disadvantages:

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

Production of solar grade silicon:

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.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

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

$$2CO + O_2 \longrightarrow 2CO_2 \uparrow$$

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.

$$4Al + 3SiO_2 \longrightarrow 3Si + 2Al_2O_3$$

$$2Ca + SiO_2 \longrightarrow Si + 2CaO$$

$$2Mg + SiO_2 \longrightarrow Si + 2MgO$$

$$Si + O_2 \longrightarrow SiO_2$$

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

$$Si + 3HCl \longrightarrow HSiCl_3 + H_2 \uparrow$$

$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2 \uparrow$$

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

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

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

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$

$$2H_2SiCl_2 \longrightarrow SiH_4 + 2HSiCl_3$$

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

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).

$$SiH_4 \longrightarrow Si + 2H_2$$

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_2	78
O_2	21
Argon (Ar)	< 1
CO_2	0.037
H_2O vapour	Remaining
O_3, H_2, NH_3	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_4) 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_2 gas, NH_3, NO_2, HF, HCl and H_2S 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_2, H_2S, Sulphide, nitric acid, ammonia, CO_2, 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.

$$NO/NO_2 \xrightarrow{Moisture} (HNO_3/\ NO_3^-)\ \text{etc.}$$

H_2CO_3, H_2SO_4, 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_2):** main contributionof 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: asthama, bronchitis), damage to agriculture, eye-irritation, throat troubles, besides corrosion of metals. Some effects of SO_2in atmosphere on plants cells are membrane damage, chlorophyll destruction, metabolism inhibition, growth-yield reduction, etc.

(ii) **Sulphur trioxide (SO_3)** is formed by the oxidation of sulphur dioxide under the influence of sunlight. Even 1 ppm of SO_3 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_2)** 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_2 areas, respiratory illness, among children, have been reported. It is unpleasant in odour and leads to irritation of eyes and even lung's congestion. In sunlight, nitrogen oxides and hydrocarbons (from combustion of petroleum products) form smog, which: 1) limits the visibility of roads; 2) causes eye irritation 3) causes difficulty in breathing thereby lung's asthma and bronchitis may result in men living around it.

(v) **Carbon monoxide (CO)** is released by the partial combustion of fuel in automobiles, industries and oil-refineries. Cigarette and beedi smoke and domestic heat-appliances are the other sources of CO. it is estimated that about 290 million tonnes of CO is discharged into the atmosphere annually. Although it is colourless, odourless, non-corrosive, yet is very toxic in nature. It is headache, visual difficulty, paralysis and even death in the human-beings. Carbon monoxide reacts with the red pigments (haemoglobin) to form carboxy-haemoglobin, thereby impairing the transfer of oxygen to the tissues. In other ward, thepresence of CO reduces the oxygen-carrying capacity of blood. This ultimately causes headache and lastitude, especially by inhaling tobacco smoke. This can lead to such symptoms as laziness, xhaustion of body, headache, decrease in visual perception, and serious effects on the cardio-vascular 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_2 is also released into air by the respiration of plants and animals. Increasing population in causing faster increase in concentration of CO_2 in the atmosphere. The concentration of CO_2 is also increased by deforestation. The plants use CO_2 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_2 in the atmosphere cause 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, forests fires, natural winds, combustion operations, material handling and processing, earth movements, engine exhausts, rubber tyre abrasions and a hundread 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, refuge incinerators, diesel engines, automobile gasoline engines, furnaces, hearths, etc.

Effects: loads 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 fogin 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 symptons,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, spilage occurs frequently. Simple calculations show that only 3 mL of mercury can saturate a large room (poor ventilated) with its vapour within a week, thereby making it unsafe to live/work in. spilled mercury is almost impossible to recover completely, because the liquid enters the cracks crevices in the floor. Mercury in vapour form adversely effect the neurological behavior of humans. The toxicity of inorganic mercury compounds dependson their solubilities. For example, the insoluble Hg_2Cl_2 is not considered very toxic, and in fact, has been used in medicine as purgative and a drug to kill interstinal worms. Since mercuric salts are generally more soluble they are considerably more toxic. The Hg^{2+} ions concentrates chiefly in the liver and kidneys. The harmful effects are usually slow to develop. Symptoms are sore gums and loose teeth. Mercury-poisoning can cause brain damage to unborn infants and can lead to a condition called errethism(charecterizedby jerking, irritability, mental and emotional disturbances). mercury – poisoning is a serious occupational hazard for workers in industries producing mercury, mercury compounds and their solutions. The Hg^{2+} ions react with the sulphyryl groups –SH of the proteins and therefore inhabit enzymatic activities. The most toxic of all the mercury compounds are dimethyl mercury and the dimethyl mercury ions. Due to the presence of nonpolar methyl groups these compounds are more soluble in the membrane, separating the blood-stream from the brain. It was once believed that washing of elemental mercury would stay at the bottom of lake or river and be slowly converted into rather harmless HgS. However, this is not the case. Certain bacteria and microorganisms metabolizes mercury first to Hg^{2+} ions and eventually to $CH_3Hg^{2+}$and $(CH_3)_2Hg$. Fish take in bacteria and methyl mercury compound, slowly concentrate in the fatty tissues of their bodies. Small fish are eaten by large fish until, finally, at the end of this food-chain, humans eat these fishes. Because of the cumulative effect, by the time we eat fishes from a mercury contaminated lake the amount of mercury ions in its body may be 50,000 times greater than the mercury concentration in the lake water. The buildup of any poison along a food-chain, is called bio magnification. The best treatment, for mercury-poisoning is a dosage of chelating agents such of EDTA. The impact of mercury pollution has been so strong that many mercury-containing compounds have been banned in industry and agriculture.

Mercury is contained in many products, including:

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

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

1. SO_2 bleaches the leaf surface and cause chlorosis (i.e. loss of chlorophyll and yellowing of the leaf) especially in leaf vegetables.

2. NO_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.

$$O_2 + h\gamma \rightarrow O + O$$

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

$$O + O_2 + M \rightarrow O_3 + M^*$$

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.

$$O_3 + h\gamma \rightarrow O_2 + O$$

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

$$CCl_2F_2 \xrightarrow{uv-light} CClF_2 + [Cl]$$

Step II - Ozone depletion or hole formation

$$[Cl] + O_3 \rightarrow ClO + O_2$$

$$ClO + [O] \rightarrow [Cl] + O_2$$

$$ClO + O_3 \rightarrow ClO_2 + O_2$$

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

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO + O_2 \rightarrow NO_2 + [O]$$

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 results 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 exhausts 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 is 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_2 gas by passing through various absorbents like alkalized alumina, activated carbon, limestone powder, liquid ammonia, lime water etc.,
$$\mathbf{2NH_4OH + SO_2 \rightarrow (NH4)_2SO_4 + H_2}$$
$$\mathbf{Ca(OH)_2 + SO_2 \rightarrow CaSO_4 + H_2O}$$
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_2S, NO, N_2O, NO_2, etc. The vegetation and forest act like a sieve in settling dust particles which passes through them.

Waste Management

'Wastes' are materials which are discarded after use at the end of their intended life-span. Waste management is a collective activity involving segregation, collection, transportation, re-processing, recycling and disposal of various types of wastes. Waste management differs for different types of wastes and for wastes in different geographical locations such as urban, rural and hilly areas.

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

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

The Waste Generation pattern is very much dependant on the living style of the population. As the major share of the population is labour force in Dibang, 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_2 of water to give $Ca(HCO_3)_2$. This impurity dissolves in water. Hence it acts as a dissolved impurity.

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

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

2). _Suspended impurities_:

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

Sand, clay, silica oxides of iron and aluminum etc are 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_2, O_2 as dissolved gases. Some water may contain ammonia and sulphur compounds such as hydrogen sulphide (H_2S) as dissolved gas. The presence of these gases imparts a foul smell to the water.

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

Boiler feed water:

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

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

Boiler troubles

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

Sludge and scale formation in boiler:

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

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

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

Disadvantages of scales and sludge

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

Priming

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

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

Foaming

The process of production of continues 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.

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

$$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3.2H_2O] \text{ rust}$$

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

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

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

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

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 type's namely domestic sewage and industrial sewage.

Domestic sewage: It is the liquid waste comes from residences, institutions. It mainly consists of organic substances which are rich in microorganisms.
Industrial sewage: It is the liquid waste comes from industries. It contains substances like acids. oil, toxic chemicals, metals, animal and plant matters, non-biodegradable compounds etc.

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

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

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

Biological Oxygen Demand

Def ^{n}:-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_2SO_4 and nascent oxygen are liberated. Nascent oxygen oxides potassium iodide to iodine. The liberated iodine is titrated against standard $Na_2S_2O_3$.

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

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

$$[MnO(OH)_2] + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O]$$

$$[O] + H_2SO_4 + 2KI \longrightarrow I_2 + H_2O + K_2SO_4$$

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

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

Blank titration: DO content of the one bottle determined immediately add 2ml of $MnSO_4$ and 3 ml of alkaline KI to the reagent bottle containing a known volume of water. Obtained Basic manganese hydroxide Precipitation is dissolved using con H_2SO_4. Take a 50 cm^3 of the above reaction mixture into 250 cm^3 conical flask. Add 4-5 drop of starch indicator and titrate the liberated iodine against standard sodium thiosulphate, till the colour changes from blue to 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_1 is the DO of the sample in mg/ml at the start of the experiment

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

A is ml of the sample before dilution

B is ml of the sample after dilution

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

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 basics, environments design the treatment.

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

Chemical oxygen demand

It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds present in one dm^3 of waste water using strong oxidizing agent $K_2Cr_2O_7$ under acidic medium.

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

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

Procedure:-

Sample or Back titration:-

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

Blank titration:- The above procedure is repeated by taking only 10 ml of $K_2Cr_2O_7$

Observation and calculation:-

Volume of water sample taken= V_1 cm^3

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

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

Normality of FAS solution= N

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

$$N_1 x V = N \text{ x } (B-A)$$

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

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

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

Importance:

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

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

Volume of sample taken= 20 ml
Volume of N/4 FAS required to react with unconsumed $K_2Cr_2O_7$=9.0ml
Volume of FAS consumed in blank=15.0ml
Amount of $K_2Cr_2O_7$ consumed to satisfy COD
in terms of FAS solution=15.0-9.0=6 ml
$\mathbf{N_1 V_1 = N_2 V_2}$
$N_1X20=0.25X6.0$

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

COD of the sample= $\frac{0.25X6}{20}X8 = 0.6\,g/dm^3 = 600\,mg/dm^3$

(2) 25 cm^3 of sewage water was reacted with 10 cm^3 of 0.25N $K_2Cr_2O_7$ in Conc. H_2SO_4 medium. The unreacted $K_2Cr_2O_7$ needed 6.1 cm^3 of 0.1N FAS. 10 cm^3 of 0.25 cm^3 N $K_2Cr_2O_7$ when titrated under the same condition required 28.2 cm^3 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
$N_1 V_1 = N_2 V_2$
$N_1X25=0.1X22.1$

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

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

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

Volume of 0.1N FAS required to react with unconsumed $K_2Cr_2O_7$=14.0 ml
Volume of FAS consumed in blank=28.1ml
Amount of $K_2Cr_2O_7$ consumed to satisfy COD
in terms of FAS solution=28.1-14.0=14.1 ml
$N_1 V_1 = N_2 V_2$
$N_1X25=0.5X14.1$

Therefore, normality of COD Sample $N_1= \frac{0.5X14.1}{25}$

COD of the sample= $\frac{0.5X14.1}{25}X\ 8 = 0.225.6g/dm^3 = 225.6\,mg/dm^3$

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_2SO_4, $CaSO_4$, $MgSO_4$ and causes permanent hardness in water and boiler scale. Water containing 250 mg/l sulphate ion is objectionable and is not suitable for drinking as well as for industries.

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

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

$$\mathbf{SO_4^{2-} + Ba^{2+} \text{---------------}> BaSO_4 \downarrow}$$

The $BaSO_4$ ppt is filtered through Gooch Crucible and weighed.

To precipitate sulphate ions as completely as possible, excess barium chloride is added. The $BaSO_4$ ppt formed is in colloidal condition. Hence this ppt cannot removed by ordinary filtration procedures.

Procedure: Transfer 200 ml of water sample (if turbid, filter) to a beaker and add concentrated HCl drop wise until it is just acidic, and add 3 drops excess. Boil the sample to reduce the volume to 50 ml. Add hot Barium chloride (10%) solutions slowly with constant stirring until all the sulphate ions are precipitated (Avoid adding excess $BaCl_2$). Digest the sample at temperature near the boiling point for a few hours, filter through a Gooch crucible and wash the precipitate with hot distilled water until the washing are free from chlorides .Dry the ppt and weigh.

Calculation:-

233.3 g of $BaSO_4$ contains 96.0 g of SO_4^{2-}

W gm of $BaSO_4$ Contains $= \frac{96.0\, x\, W}{233.3}$

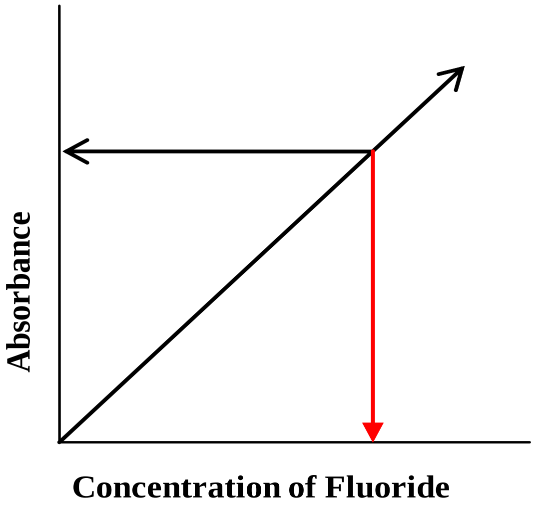
Percentage of $SO_4^{2-} = \frac{96.0\, x\, W\, x 100}{233.3}\, g / dm^3$

$$= \frac{96.0\, x\, W\, x 100}{233.3}\, X\, 1000\, mg / dm^3$$

Determination of Fluoride by Colorimetric method

Fluoride ions are present in water as NaF, CaF_2 etc.

Principle:- Under acidic conditions, fluoride ions react with zirconium SPADNS solution to form complex (Zr-SPADNS). And the colour of Zr-SPADNS gets bleached by the fluoride ions. As the concentration fluoride ion increases, bleaching of Zr-SPADNS solution is also more. Thus bleaching action of Zr-SPADNS solution indicates the amount of fluoride ions present in water. This complex absorbance is maximum at 570 nm, hence find the absorbance of all the bleached solutions at 570 nm.



***Procedure*:-**

1. Preparation of Zirconyl-SPADNS solution: prepare zirconyl chloride solution and SPADNS solution separately. Then mix the two solutions equally.

2. Prepare a reference solution by adding 10 ml SPADNS solution to 100 ml distilled water to which add a solution of HCl(7ml conc.HCl diluted to 10ml). Use this solution to set zero in the colorimeter at 570 nm (Blank)

3. Prepare a std.solution of NaF and pipette out 1, 2, 3ml etc of this solution into different 50 ml volumetric flask.

4. Add 1 drop of $NaHSO_3$ solution (0.5%) to remove any residual chlorine to each solution.

5. To all the solutions add 10 ml of Zirconyl –SPADNS solution, mix well and find the absorbance at 570 nm.

6. Draw a calibration curve by plotting concentration vs absorbance.

7. Take suitable quantity of water add 10 ml Zirconyl-SPADNS solution and find the absorbance at 570 nm.

8. Using the calibration curve, calculate the concentration of fluoride ions in the given water sample.

Sewage treatment:

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

(a) *Mechanical or Primary treatments*

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

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

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

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

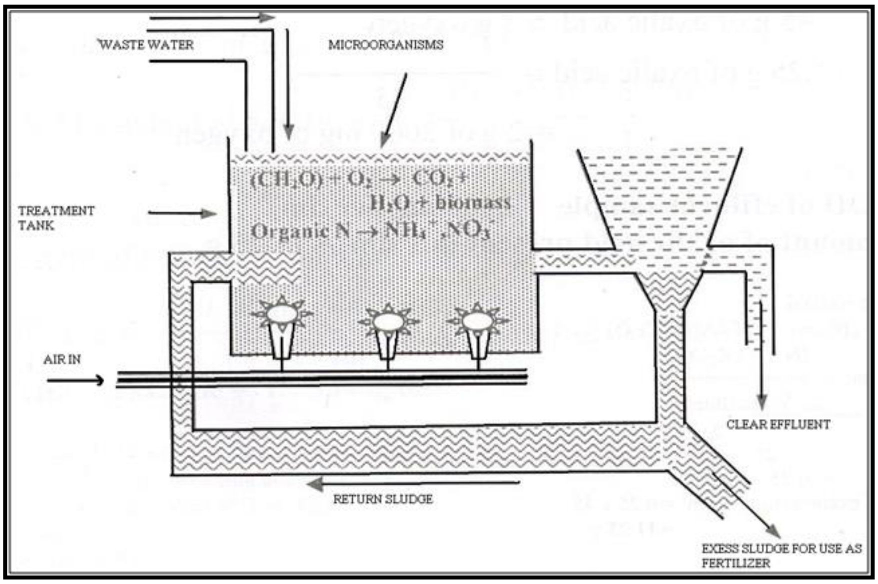
Coagulation; is a process of removing colloidal particles from water by the addition of certain chemicals known as coagulation. Coagulation is carried out for the quick settling of colloidal particles. Alum [$K_2SO_4Al_2\ (SO_4)_3.24H_2O$] and ferrous sulphate ($FeSO_4.7H_2O$) are commonly used coagulants.

(b) Secondary treatment:

Secondary process involves aerobic oxidation of organic matter.

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

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



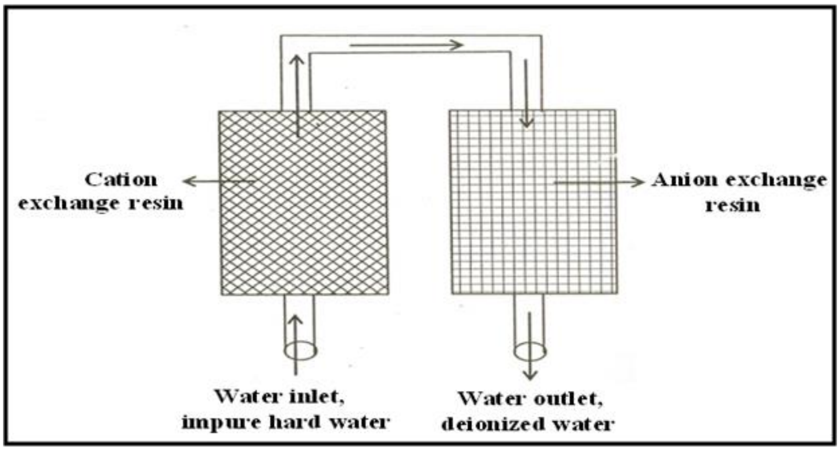
A part of the sludge is reduced and the rest is used as fertilizer. The residual water is chlorinated to remove bacteria and finally discharged into running water. The sludge process operates at 90-95 % efficiency of BOD treatment. If the treated water contains a high concentration of phosphates, heavy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

c) Tertiary treatment:

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

Softening of water by ion exchange process:

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



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

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

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

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

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

Advantages of Ion Exchange process

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

Disadvantages:

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

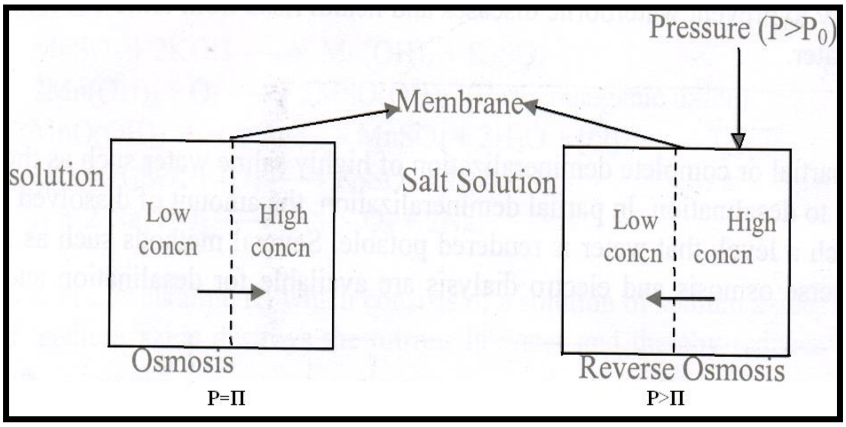
Desalination or Desalting:

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

Reverse osmosis

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

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



Advantages:

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

***Disadvantages*:**

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

Unit-7

Water Technology and Nanomaterials

Introduction:

6. Water is the most basic and fundamental component of life.
7. It is the most wonderful substance gifted by nature to all the living beings on the earth.
8. 72% of the earth's surface is covered by water. It is distributed as follows :
   Oceans - 97.23%
   Ice - 2.14%
   Fresh Water - 0.03%
   Other - 0.01%
9. Among the three essentials of life i.e., air, water and food, water occupies the second position.
10. Health and wealth of a nation largely depends on the availability and utilization of quality of water.

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

Impurities in water:

1) *Dissolved impurities:*

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

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

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

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

2). *Suspended impurities*:

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

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

3). *Dissolved gases:*

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

4). Organic matter (microscopic matter):

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

Boiler feed water:

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

A boiler feed water should correspond with the following composition

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

Boiler troubles

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

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

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

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

Disadvantages of scales and sludge

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

Priming

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

Priming caused by

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

Foaming

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

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

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

Disadvantages of priming and foaming

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

Boiler corrosion

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

Corrosion in boiler is due to the following reasons

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

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

$$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3.2H_2O] \text{ rust}$$

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

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

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

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

Disadvantages of boiler corrosion

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

Determination of dissolved oxygen (DO):-

Oxygen is poorly soluble in water. The solubility of water depends on the concentration of the salts and temperature. Dissolved oxygen is consumed by aquatic animals for their respiration. Aerobic bacteria consume the DO for the oxidation of biodegradable matter. Organic matter present in the water is oxidized by strong oxidizing agent ($K_2Cr_2O_7$) using DO.

DO in water is determined by winklers method.

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

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

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

$$[MnO(OH)_2] + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O]$$

$$[O] + H_2SO_4 + 2KI \longrightarrow I_2 + H_2O + K_2SO_4$$

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

Procedure: 150 cm^3 of waste water is taken in a BOD bottle**;** add 2ml of $MnSO_4$ and 3 ml of alkaline KI to the reagent bottle containing a known volume of water. Obtained Basic manganese hydroxide Precipitation is dissolved using con H_2SO_4. Take a 50 cm^3 of the above reaction mixture into 250 cm^3 conical flask. Add 4-5 drop of starch indicator and titrate the liberated iodine against standard sodium thiosulphate, till the colour changes from blue to colour less.

Observation and calculation

Normality of $Na_2S_2O_4$ solution= N_1

Volume of $Na_2S_2O_3$ solution =V_1 cm^3

Volume of water take for titration=V_2 cm^3

Normality of the dissolved $N_2=\frac{N_1 \, x \, V_1}{V_2}$

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

$$= \frac{V_1 \, x \, N_1 \, x 8}{V_2} X 1000 mg$$

Biological Oxygen Demand

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

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

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$$[O] + H_2SO_4 + 2KI \longrightarrow I_2 + H_2O + K_2SO_4$$

$$I_2 + 2Na_2S_2O_3 \text{------------->} 2NaI + Na_2S_4O_6$$

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

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

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

Observation and calculation

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

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

A is ml of the sample before dilution

B is ml of the sample after dilution

$$\text{BOD} = \frac{D_1 - D_2}{A} xB \quad \text{mgdm}^{-3}$$

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 basics, environments design the treatment.

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

Chemical oxygen demand

It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds present in one dm^3 of waste water using strong oxidizing agent $K_2Cr_2O_7$ under acidic medium.

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

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

Procedure:-

Sample or Back titration:-

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

Blank titration:- The above procedure is repeated by taking only 10 ml of $K_2Cr_2O_7$

Observation and calculation:-

Volume of water sample taken= V_1 cm^3

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

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

Normality of FAS solution= N

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

$$N_1xV=N \text{ x } (B-A)$$

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

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

$$= \frac{N\,x\,(B-A)}{V}\,x\,8\,x\,1000\,mg.dm^{-3}$$

Importance:

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

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

Volume of sample taken= 20 ml

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

Volume of FAS consumed in blank=15.0ml

Amount of $K_2Cr_2O_7$ consumed to satisfy COD
in terms of FAS solution=15.0-9.0=6 ml

$N_1 V_1 = N_2 V_2$

$N_1X20=0.25X6.0$

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

COD of the sample= $\frac{0.25X6}{20}X8 = 0.6\,g/dm^3 = 600\,mg/dm^3$

(2) 25 cm^3 of sewage water was reaccted with 10 cm^3 of 0.25N $K_2Cr_2O_7$ in Conc. H_2SO_4 medium. The unreacted $K_2Cr_2O_7$ needed 6.1 cm^3 of 0.1N FAS. 10 cm^3 of 0.25 cm^3 N $K_2Cr_2O_7$ when titrated under same condition required 28.2 cm^3 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

$N_1 V_1 = N_2 V_2$

$N_1X25=0.1X22.1$

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

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

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

Volume of 0.1N FAS required to react with unconsumed $K_2Cr_2O_7$=14.0 ml
Volume of FAS consumed in blank=28.1ml
Amount of $K_2Cr_2O_7$ consumed to satisfy COD
in terms of FAS solution=28.1-14.0=14.1 ml
$N_1 V_1 = N_2 V_2$
N_1X25=0.5X14.1

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

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

SEWAGE:

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

Domestic sewage: It is the liquid waste comes from residences, institutions. It mainly consists of organic substances which are rich in microorganisms.
Industrial sewage: It is the liquid waste comes from industries. It contains substances like acids. oil, toxic chemicals, metals, animal and plant matters, non-biodegradable compounds etc.

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

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

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

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

(a). Mechanical or Primary treatments

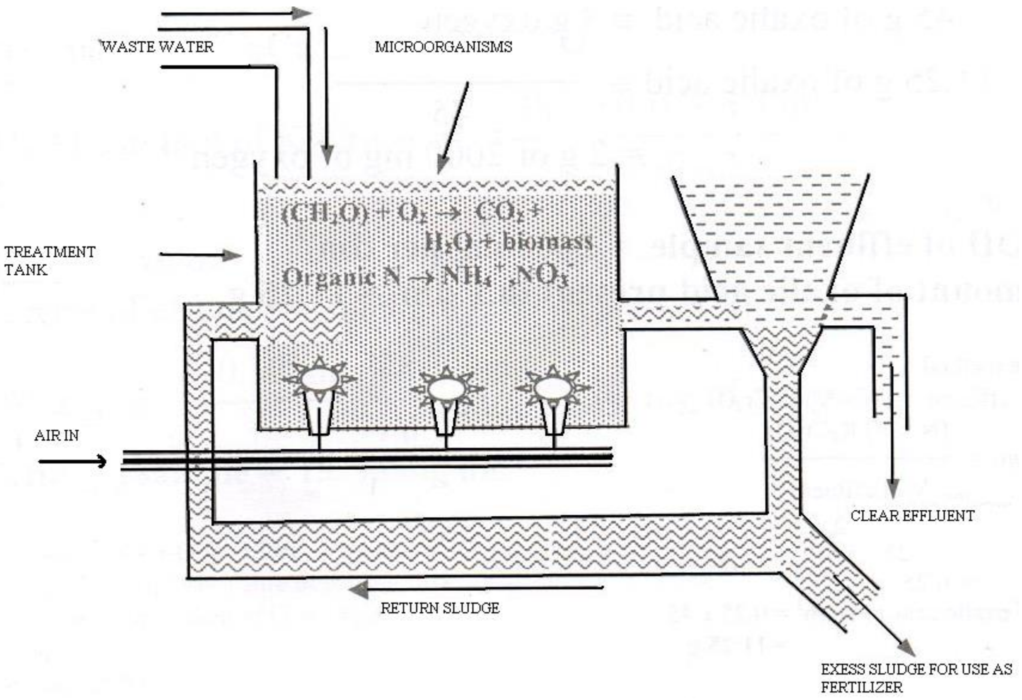
Removing of suspended solids is called **primary treatment**. It involves the removing of suspended solids like woods, plastic through screening, filtering and sedimentation.
Screening: It is a physical process which removes larges suspended or floating matter in the sewage. Which retain the floating and suspended coarse particles
Filtration: The water is passed through conventional sand filter beds to remove the last trace of suspended matter**.**

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

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

(b). <u>Secondary treatment</u>: Secondary process involves an aerobic oxidation of organic matter.

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



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

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

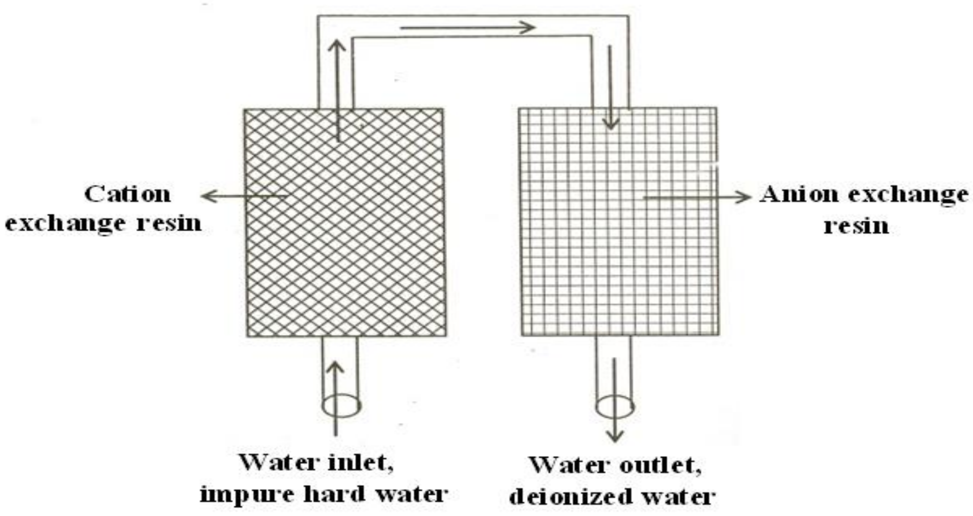
i). Treatment with lime for the removal of phosphates as insoluble calcium phosphates

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

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

Softening of water by ion exchange process:

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



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

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

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

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

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

Advantages of Ion Exchange **Process**

1. The ion exchange apparatus, once set up, is easy to operate and control.
2. Both acidic and alkaline water can be softened.

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

Disadvantages:

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

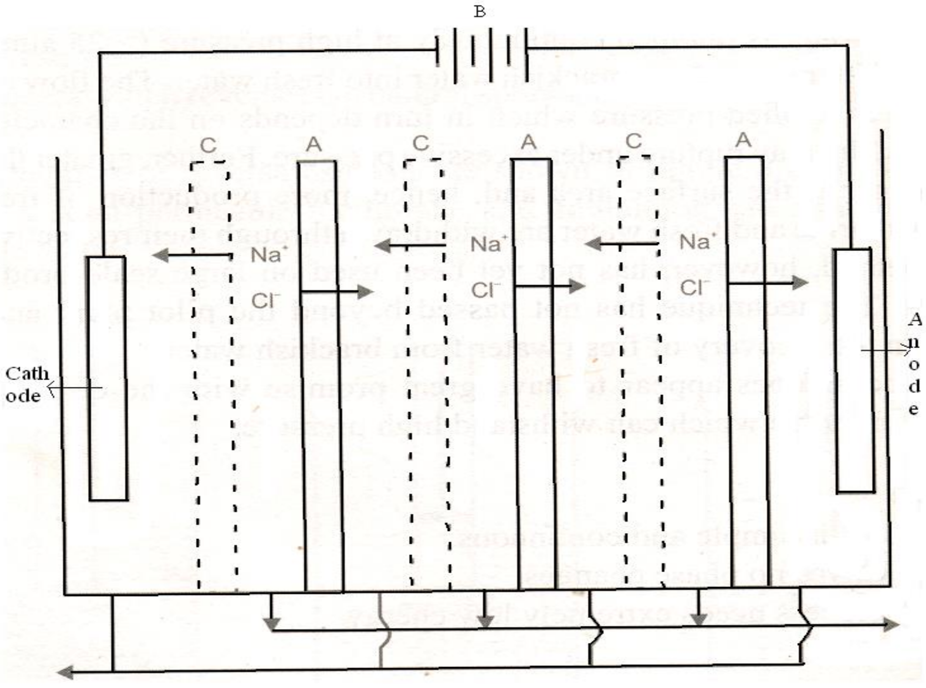
Desalination or Desalting:

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

Electro dialysis:

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

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



B- Source of DC supply, A- Anion permiable membrane C-Cation permiable membrane
CA-Ion losing compartment, AC-Ion gaining compartment

An elecrodialysis cell consists sea water in which a series of alternative cation and anion permeable membranes(C & A)are placed . The anode is placed near the anion permeable membrane while cathode is placed near the cation semipermiable membrane. A suitable emf is applied across the two electrodes immersed in the brine. Under the influence of the applied emf, sodium ions move through the cation permeable membrane(C) while anions (Cl^-) move through the anion permeable membrane(A) from each compartment of CA. The net result is the depletion of salt content in the 'CA' compartments and increase in salt concentration in 'AC' compartments. Thus the fresh water produced in CA compartments is collected and pumped off. The concentrated brine is discharged through the outlet.

Advantages:

1). It is economical.

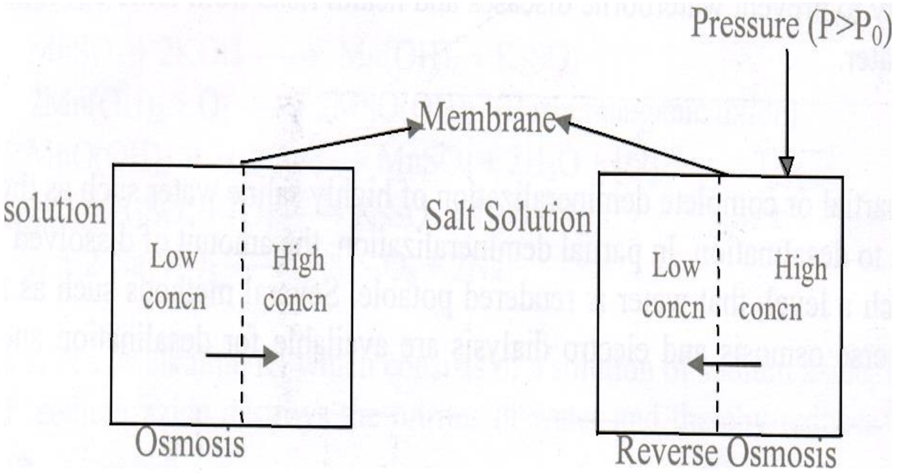
2). It is convenient and may applicable at room temperature.

3). It is more compact in size and requires only electricity for operation.

Reverse osmosis:

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

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



P=Π P>Π

Advantages:

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

Disadvantages:

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

PHASE RULE

Phase rule is an important generalisation dealing with the behaviour of heterogeneous systems in equilibrium.. By the application of phase rule, it is possible to predict the number of phases qualitatively, by means of a diagram, the effect of changes in pressure, temperature and concentration on a heterogeneous equilibrium.

A single graph depicting the overall relationships among the various phases (solid, liquid and vapour phases) of a substance is known as a **phase diagram**. A phase diagram summarises the conditions at which a substance exists as a solid, liquid or gas.

The understanding of phase diagrams for alloy systems is extremely important because there is a strong correlation between microstructure and mechanical properties and the development of microstructure of an alloy is related to the characteristics of its phase diagram. In addition, phase diagrams provide valuable information about melting, casting, crystallization and other phenomena.

Phase diagrams are of considerable commercial and industrial significance, particularly for semiconductors, ceramics, steels, polymers, composites and alloys. They are also the basis of separation procedures in the petroleum industry and cosmetic preparations.

Statement:

The number of degrees of freedom (F) of a heterogeneous system at equilibrium at a definite temperature and pressure is related to the number of components (C) and of phases (P) by the phase rule equation,

$$P + F = C + 2 \qquad \text{or} \qquad F = C - P + 2$$

Where P=No of phases in the system

C= No of Components of the system

F= No of degrees of freedom or variables of the system(T,P and Composition or concentration)

PHASE :

A phase is defined as any homogeneous physically distinct and mechanically separable part of a system which is separated from other parts of the system by definite boundary lines .

E.g.1) A mixture of Ice, liquid water and water vapour is a two-phase system.

2)Every solid in a system constitutes an individual phase, each is separated from the others by a definite bounding surface viz., outside of the crystal.

3)Two miscible liquids -is one phase system. e.g. Ethanol and water is a one phase system.

4) Two immiscible liquids- is two phase system.e.g. Chloroform and water constitutes a two-phase system. Ether and water constitutes a two-phase system.

5)An aqueous solution of a solid substance such as sodium chloride or sugar is a one-phase system.

6) However, a saturated solution of sodium chloride in contact with excess of sodium chloride is a two-phase system.

7)All gases mixture freely to form a homogeneous mixture. Therefore, any mixtures of gases, say oxygen and nitrogen is a one-phase system.

8)Decomposition of calcium carbonate to calcium oxide and CO_2 is a three phase system with two solid phases and one gaseous phase.

$$CaCO_3(s) \Longleftrightarrow CaO(s) + CO_2(g)$$

COMPONENT : (C)

It is the smallest (least) number of independent chemical constituents by means of which the composition of each phase present in the particular system can be expressed, either directly by formula or in the form of a chemical equation.

One component :-

1)Water system has three phases i.e. Ice(s) ↔ Water(l) ↔ Water vapour(g)
The composition of all the three phases is expressed in terms of one chemical constituent, H_2O. Thus water system is a one component system.

2) Sulphur has four phases : i) rhombic ii) monoclinic iii) liquid and iv) sulphur vapour.
The composition of all these phases can be expressed by one chemical individual, S(sulphur). Thus sulphur system has one component only.
3)A mixture of gases Nitrogen Oxygen –is a one phase two component system.
4) Two miscible liquids -is one phase two component system.
5) Two immiscible liquids- is two phase two component system.
6) An aqueous solution of a solid substance such as sodium chloride is a one-phase two component system.
7) A saturated solution of a solid substance such as sodium chloride is a two-phase two component system.

8) Dissociation of ammonium chloride in a closed vessel is a two-phase one component system.

$$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$$

The composition of both NH_3 and HCl can be expressed in terms of NH_4Cl vapour.

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Two component :-

8) Decomposition of calcium carbonate.

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$$

It has three phases; solid $CaCO_3$, solid CaO and gaseous CO_2. The composition of all the phases can be expressed in terms of any two (of three) chemical substances in equilibrium.

CaO and CO_2 as components

Phase ***Components***
$CaCO_3 = CaO + CO_2$
$CaO = CaO + 0CO_2$
$CO_2 = 0CaO + CO_2$

$CaCO_3$ and CaO as components

Phase ***Components***
$CaCO_3 = CaCO_3 + 0CaO$
$CaO = 0CaCO_3 + CaO$
$CO_2 = CaCO_3 - CaO$

$CaCO_3$ and CO_2 as components

Phase ***Components***
$CaCO_3 = CaCO_3 + 0CO_2$
$CaO = CaCO_3 - CO_2$
$CO_2 = 0CaCO_3 + CO_2$

9)Dissociation of copper sulphate is a two component system.

$$CuSO_4.5H_2O(s) \leftrightarrow CuSO_4.3H_2O(s) + 2H_2O(g)$$

Components are $CuSO_4$ and H_2O

10)Dissociation of ammonium chloride in a open vessel is a two-phase two component system.

$NH_4Cl(s) \leftrightarrow x\ NH_3(g) + y\ HCl(g)$

The Components are NH_4Cl and NH_3 in excess or HCl in excess

DEGREES OF FREEDOM OR VARIANCE (F):

The number of degrees of freedom of a system is the minimum number of independently variable factors, such as temperature, pressure and composition which need to be fixed in order that the condition of a system at equilibrium may be completely defined.

Eg. 1) Thus, the state of a pure gas can be specified by two variables, pressure and temperature or pressure and volume. This means that a pure gas has two degrees of freedom.

2) A system consisting of boiling water.

In this system, water (l) and steam (g) are in equilibrium and does not have a composition variable since both water and steam contain molecules of the same fixed formula, H_2O. To define the system, it is necessary to specify only the steam pressure because the temperature of boiling is automatically fixed (or vice versa). Application of the phase rule to the system gives,

$P + F = C + 2$; $F = C - P+2$: $F = 1-2+2 = 1$ i.e. either pressure or temperature but not both.

A system with F = 1 is referred to as univariant or monovariant.

3) Ice(s) $\leftrightarrow$ Water (l) $\leftrightarrow$ Water vapour (g)

In the above system all the three phases are present in equilibrium. All the three phases co-exist only at one particular temperature and pressure. If variables like T or P is altered one of the phase disappears.

A system with F = 0 is known as invariant.

A system with F = 1 is referred to as univariant.

A system with F = 2 is called bivariant.

Calculate the number of components and degrees of freedom in the following equilibria.

i). $Na_2SO_4.10H_2O\ (s) \leftrightarrow Na_2SO_4\ (s) + 10H_2O\ (g)$

$P = 3$; $C = 2$; $F = C-P +2 = 2-3 +2 =1$

ii).$N_2\ (g) + O_2\ (g) \leftrightarrow 2NO\ (g)$

$P = 1$; $C = 2$; $F = C-P +2 = 2-1 +2 =3$

iii) $N_2O_4\ (g) \leftrightarrow 2NO_2\ (g)$

$P = 1$; $C = 1$; $F = C-P +2 = 1-1 +2 =2$

iv) $NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$, when $pNH_3 = pHCl$

$P =2$; $C = 2$; $F = C-P +2 = 1-2 +2 =1$

v) $Fe(s) + H_2O(g) \leftrightarrow FeO_{(s)} + H_2(g)$

$P= 3$; $C=3$; $F= C-P +2 = 3-3+2 = 2$

Derivation of phase rule

Gibbs phase rule is derived from the thermodynamic result

Consider a system with component number C is existing altogether in P number of phases in equilibrium.

Total number of variables may be calculated as,

One variable Temperature– same for all phases.

One variable pressure – same for all phases .

Another variable concentration or composition is independent variable.

For a system of one phase, the independent concentration variable in respect of C components is C−1.

(The concentration variable is left over value).

For a system of P phases it is P (C−1) concentration or composition terms must be specified in order to define the composition completely.

In addition to composition or concentration, the temperature and pressure of the system which are the same in all phases must be known.

Therefore, the total number of independent variables which must be specified is P (C−1)+2.

According to thermodynamics for a system in equilibrium at constant temperature and pressure, the chemical potential (μ) of any given component has the same value in every phase.

In a system of phases at equilibrium, the total quantity of material in any phase does not matter, it is the composition of the phase that is important.(Eg., In a saturated solution of a pure solid, the composition of the solution is independent of the total quantity of solution and undissolved solid).

The chemical potential of any component is the same in all phases at equilibrium according to equations:

$\mu_{1(a)} = \mu_{1(b)} = \text{--------} = \mu_{1(P)}$

$\mu_{2(a)} = \mu_{2(b)} = \text{--------} = \mu_{2(P)}$

$\mu_{C(a)} = \mu_{C(b)} = \text{--------} = \mu_{C(P)}$ for C components in P phases.

For one component this give rise to (P-1) restrictions for the P number of phases.

For C component this give rise to C (P-1) restrictions for the P number of phases.

(Chemical potential μ is a function of temperature, pressure and concentration or composition.)

The number of variables remaining undetermined for the system at equilibrium is given by F=Total number of independent variables specified-The number of variables defined.

$F= [P(C-1) + 2] - [C(P-1)] = C-P + 2$

In order to define the system completely, the number of variables must be arbitrarily fixed and hence it must be equal to F. Therefore, F = C-P + 2.

Application of phase rule to one component system

THE WATER SYSTEM:

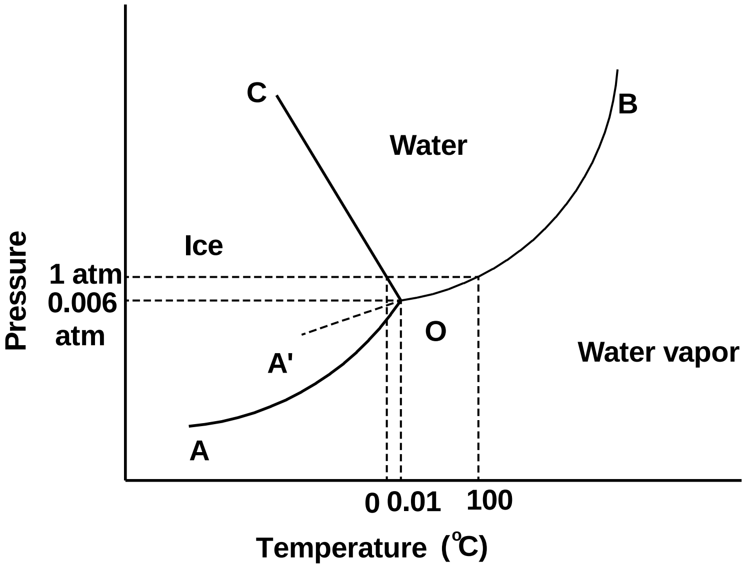
Consider water system Ice (s) ↔ Water (l) ↔ Water vapour(g)

Water can exist in three possible phases, namely, solid ice, liquid water and water vapour. Hence there can be three forms of equilibria,

1. Ice(s) ↔ Liquid water(l)
2. Ice(s) ↔ Water vapour(g)
3. Water(l) ↔ Water vapour(g)

The phase diagram or P-T graph for water system is obtained by plotting the pressure against temperature. It consists of

i) Three areas, namely, COA, COB and AOB.
ii) Three curves, OA, OB and OC.
iii) One triple point,O.



Curves:
In the phase diagram, the curve OA represents the vapour pressure curve of liquid water. Along this curve two phases co-exist.

Water (l) ↔ Water vapour (g)

The point N on the curve OA indicates the B.P. of water is 100 ^{o}C at 1 atms.pressure. Keeping pressure constant at 1 atms. rise in temperature behind 100 ^{o}C brings about a change in the phase from water to water vapour along the line NH. And decrease in temperature below 100 ^{o}C reverse is the phase change. The curve OA terminates at A which is the critical point (Critical pressure = 218 atms.pr. & Critical temperature = 374 ^{o}C). Behind the critical point water phase merge into vapour phase.

The curve OB is known as sublimation curve and it shows the variation of vapour pressure with temperature for the solid ice. The vapour pressure increases with increase in temperature. Along this curve two phases exist in equilibrium.

Ice (s) ↔ Water vapour (g)

The point B is a natural limit at -273 ^{o}C, behind this point vapour phase merge into ice.
The dotted curve $OA^{|}$ which is the continuous extension of OA is obtained for water below 0 ^{o}C. Liquid water may be cooled below its freezing point without solidifying. This is called super cooling. The dotted curve $OA^{|}$ represents the super cooled state of water. This curve represents a meta-stable system.

The curve OC represents the melting curve of ice or freezing curve of water. Along this curve two phases exist in equilibrium.

Ice (s) ↔ Water (l)

The slope of OC towards the pressure axis shows that the melting point of ice is decreases by increase in pressure. It may be seen from the phase diagram that the point M on the curve OC represents the freezing point (0 ^{o}C temperature & 1 atms.pr). Any increase in pressure on ice keeping temperature constant ice melts into water along MK.

Along the curves OA, OB and OC two phases exist in equilibrium and the number of component of the system is one. By applying the phase rule,

F = C - P + 2
F = 1 - 2- + 2
F = 1

It means that only one variable, either pressure or temperature is sufficient to define the system. It implies that pressure is not freely variable, if the temperature is set.

Thus each system is **univariant**.

Areas:

The phase diagram can be divided into three areas, COB, COA and AOB. Each area contains one pure phase only as mentioned here under.

Area	**Phase**
COB	Ice
COA	**Water**
AOB	Water vapour

Application of phase rule gives ($P = 1$; $C = 1$),

$$F = C-P+2;\ F = 1-1+2;\ F = 2$$

Thus each area of phase diagram represents a bivariant system. Both the variables (temperature and pressure) can be varied independently without changing the number of phases.

Thus each system namely ice, water & water vapour is **bivariant** system.

The phase rule predicts that both the variables T & P are necessary to locate any point G in an area.

Triple point:

The three curves OA, OB & OC meet at point O, the point O is called triple point. The triple point shows the conditions under which all the three phases solid, liquid and vapour can exist in equilibrium.

$$\text{Ice(s)} \leftrightarrow \text{Water (l)} \leftrightarrow \text{Water vapour (g)}$$

At the triple point, $P = 3$, $C = 1$ and $F = C-P+2 = 1-3+2 = 0$.

All the variables are fixed for this system at this point. If any of the variables is altered, the equilibrium will be disturbed and one of the phases will disappear. The triple point is fixed for water system. It occurs at 0.01 ^{o}C & 0.006 atms.pressure.

Thus the system is **zero variant** or **invariant**.

Application of phase rule to two component system

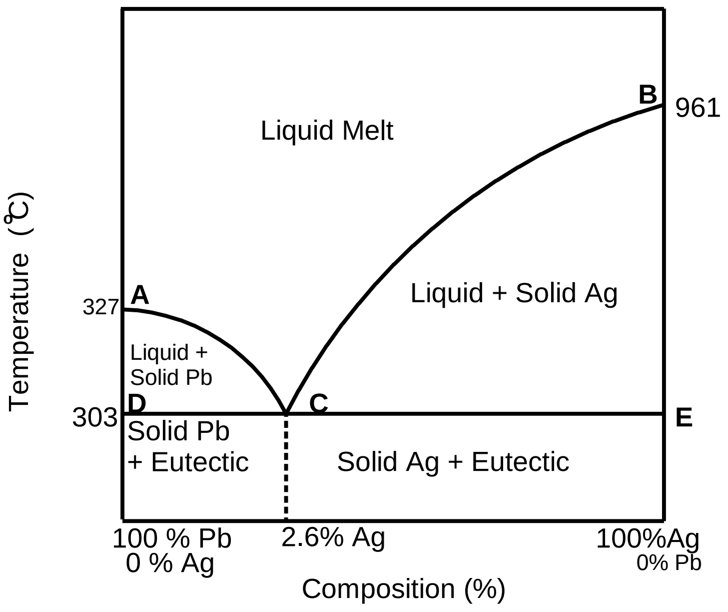
LEAD-SILVER SYSTEM:

Lead-silver system is a two component system. It is a solid / liquid system.

Lead-silver system is a condensed system. A system in which only solid and liquid phases are present with gaseous phase being absent is called a condensed system. The degrees of freedom in such a case is calculated by a reduced phase rule equation,

$$F = C-P+1.$$

The phase diagram for lead-silver system is obtained by plotting temperature on Y-axis and % composition on X-axis.



The various features of the phase diagram or P-T graph are illustrated here under.
The phase diagram consists of curves, areas and eutectic point.

Curves (OA & OB)
Pure lead melts at 327 ^{o}C and the addition of silver lowers its freezing point along AO. This is called freezing point curve for the lead. Along AO the melting point of lead gradually falls on the addition of Ag till lowest point O (303^{o}C) is reached where liquid melt gets saturated with respect to Ag and the melting point of Pb does not fall further. On cooling further whole mass (Eutectic composition) crystallize out. Pure silver melts at 961 ^{o}C and the addition of lead lowers its freezing point along BO and is called freezing point curve of silver. This curve indicates that the melting point of Ag falls gradually on adding Pb, along BO till the lowest point O (303^{o}C) is reached Where liquid melt gets saturated with respect to pb and m.p. of Ag does not fall further .On cooling further whole mass (eutectic composition) crystalize out.
The phase diagram has the following two curves.
Curve OA - Along this curve, solid lead and liquid mixture of Pb + Ag co-exist i.e. P = 2.
Curve OB- Along this curve solid silver and liquid mixture of Ag +Pb co-exist i.e. P = 2.
Applying reduced phase rule,

$$F = C-P+1$$
$$= 2-2+1$$
$$= 1$$

The systems solid Pb / liquid mixture of Pb + Ag and solid Ag / liquid mixture of Ag +Pb are **univariant systems**. For a point on the line change in either T or % composition changes the phase. On the other hand along any of the line one variable T or % C is specified and the other is fixed automatically.

Areas :
There are three areas in the phase diagram, namely, AOB, AOC and BOD. The phases present in each of these are,

AOB - 1 (liquid melt)
AOC - 2 (solid Pb + liquid mixture of Pb + Ag)
BOD - 2 (solid Ag + liquid mixture of Ag +Pb)

Area AOB: By applying phase rule, we have

$$F = C-P+1 = 2-1+1 = 2.$$

It is necessary to specify the temperature as well as the % composition in order to define any point in this area. This system (liquid melt) is a **bivariant system**. Both T & % C are needed to locate any point in this area AOB. Within this area when two variables are altered no change in phase.

Area AOC and BOD: In the areas AOC and BOD, P = 2, C = 2

F = C-P+1 = 2-2+1 = 1.

The composition of each phase is fixed, each being a pure component and so only one variable is the temperature. These systems have one degree of freedom. These are **univariant systems.** To locate any point in these areas either T or %C is needed.

Ex: If an alloy of Ag & Pb of %composition Z is heated to a point U & cooled and no solid separates till it reaches a point V on the line BO. At V pure Ag separates out which will be in equilibrium with the liquid melt of Ag+Pb. If it is cooled further to a point Z more silver separates out along VX. The %composition of the liquid melt at Z will be same as that at point X on the line BO.

If T is known, the %C of the liquid melt in the areas AOC & BOD can be known or vice-versa.

Eutectic point :

At the point O, where the curves AO and BO meet, both the solids Pb and Ag are in equilibrium with the liquid melt and is called the eutectic point. The point ‘O’ is the lowest temperature at which any liquid mixture of silver and lead will freeze and consequently represent the lowest melting point of any mixture of solid lead and solid silver.

At eutectic point,

F = C-P+1 = 2-3+1 = 0

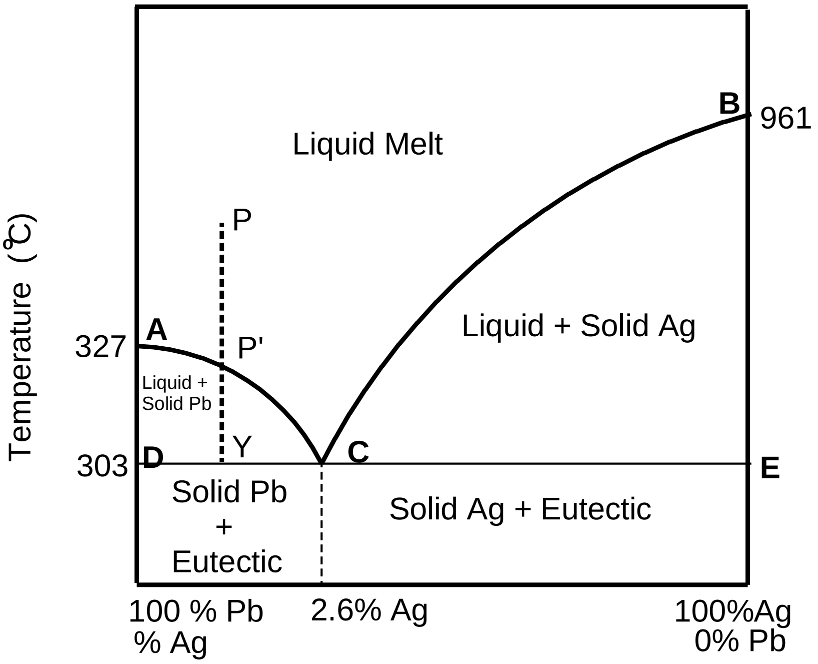
This is a **invariant system or Zero variant system**

The variables, both temperature (303^o C) and composition (97.4% Pb and 2.6% Ag) are fixed.

The eutectic mixture, although has a definite melting point, is not to be regarded as a compound. A mixture containing two components which are not miscible in the solid state is called a eutectic mixture. The eutectic composition is 2.6% Ag & 97.4% Pb. The eutectic temperature is 303^o C.

Desilverisation of lead by Pattinson’s process:

The phase diagram of Pb-Ag has a special significance in the desilverisation of lead. The argentiferrous lead contains a very small percentage of silver (0.1%). The argentiferrous lead is first heated well above the melting point of lead so that the system consists only of a liquid phase which is represented by the point, p in the figure. The liquid melt is allowed to cool. The temperature of the melt falls along pp′. As the temperature corresponding to p′ is reached on the curve AC, lead will begin to solidify and the liquid will contain relatively higher silver.



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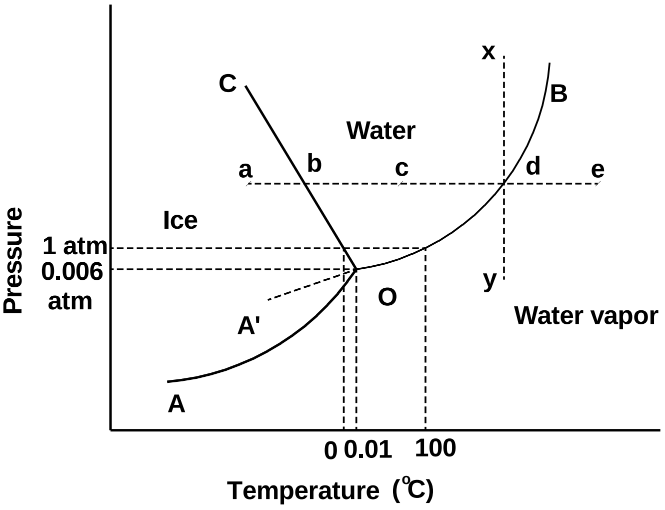
Lead continues to separate out and is removed constantly by means of ladles. The melt continues to be richer and richer in silver until the point Y is reached when the percentage of silver rises to 2.6. Thus the original argentiferrous lead which contains 0.1% silver now contains about 2.6% silver. The process of raising the relative proportion of silver in argentiferrous lead is known as Pattinson's process

Explain the changes that occur when the pressure is decreased from x to y and temperature is increased fro a to e. Calculate the number of degrees of freedom at x, y, a, b, c, d and e.



Unit-8

HIGH POLYMERS

Definition of polymers:

Polymers are the macromolecules of high molecular weight, which are obtained by the repeated union of many simple molecules of low molecular weight. The process of manufacture of a polymer is called the polymerization.

Monomers:

Monomers are nothing but simple molecules of low molecular weight, the repeated union of which gives rise to polymers. Hence monomers are considered as the building blocks of polymers.

Polymerisation:

The process of conversion of low molecular weight monomers in to high molecular weight polymers with or without the elimination of by products under suitable conditions is called Polymerisation.

Types of polymerization:

Based on the type of chemical reaction, which occurs during polymrisation, it is of two types. Namely,

1.Addition polymerization.

2.Condensation polymerization.

1.Addition (chain) polymerization:

It is a type of polymerization reaction in which many number of simple molecules (monomers) unite together to give high molecular weight polymers without the elimination of any by products such as water, ammonia, etc.

It is also known as **Chain polymerization**. Generally monomers containing one or more unsaturated (double) bonds are used. It is usually carried out in the presence of initiators.

Ex: Formation of polythene.

$$\underset{\text{Ethene}}{n\,CH_2{=}\,CH_2} \longrightarrow \underset{\text{Polythene}}{[-\,CH_2 - CH_2\,-]_n}$$

The main features of addition polymerization are:

1. Only olefinic compounds are used as monomers.
2. It does not involve the elimination of any byproducts.
3. Double bond provides required bonding sites(ie Monomer units are linked through Carbon-carbon covalent linkages).
4. Reaction is very fast.
5. It gives rise to linear polymers.
6. It generally proceeds through free radical mechanism.
7. The molecular weight of the polymer is an integral multiple of the monomer.
8. The elemental composition of the polymer is same as that of monomer.
9. Initiator is necessary.

2.Condensation polymerization:

It is a type of polymerization reaction in which many number of poly functional monomers undergo intermolecular condensation with the continuous elimination of by products such as water, ammonia, etc.

It is also known as **Step polymerization**. Generally monomers with bi or poly functional groups are used It is usually carried out in the absence of initiators.

Ex. Formation of Nylon -66

$$\underset{\text{Hexamethylene diamine}}{n\ NH_2\text{-}(CH_2)_6\text{-}NH_2} + \underset{\text{Adipic acid}}{n\ HOOC\text{-}(CH_2)_4\text{-}COOH}$$

$$\downarrow$$

$$\underset{\text{Nylon -66}}{[\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}]_n} + 2n\ H_2O$$

<u>The main features of condensation polymerization are:</u>

1. The monomers having two or more functional groups are used.
2. It involves the elimination of by products.
3. Functional groups of the monomers provide bonding sites (i.e. monomer units are linked through functional atoms.
4. It is a slow process and stepwise.
5. Polymerization proceeds through normal stepwise condensation.
6. It gives rise to either linear or cross-linked polymers
7. It is generally catalysed by acids or alkali.
8. The elemental composition of the polymer is different from that of the monomers.
9. Initiator is not necessary.

<u>Degree of polymerization:</u> The number of monomers used in the process is called degree of polymerization.

<u>Functionality:</u> The total number of functional groups or bonding sites present in a monomer molecule is called the functionality of the monomer.
Examples: ethylene (bifunctional), methylmethacrylate (bifunctional), adipic acid (bifunctional), phenol (trifunctional), glycerol (trifunctional).

<u>Classification of polymers</u>:

Polymers are classified based on many factors. Namely,

I. Based on the source of the polymer.
II. Based on the thermal behaviour of the polymer.
III. Based on the method of polymerization.
IV. Based on the nature of the monomer.
V. Based on the structure and properties.

I. <u>Based on the source of the polymer:</u>

1. <u>Natural polymers</u>: The polymers, which are obtained from natural sources such as Plants and animals are called natural polymers.
Ex: Silk, Wool, Cotton, Proteins, Natural rubber etc.

2. <u>Synthetic polymers:</u> The man made polymers are called Synthetic Polymers. They are generally synthesized from simple organic molecules
Ex: Nylon-66, PVC, Teflon, Plexiglass, Polyethylene etc.

II.<u>Based on the thermal behaviour</u>:

Based on the thermal behaviour, polymers are classified in to two types.

1.<u>Thermoplastics</u>: The polymers, which become soft on heating and get harden on Cooling, are called Thermoplastics. They can be repeatedly moulded again and again without affecting their properties.
Ex: PVC, Polyethylene etc.

2. <u>Thermosetting plastics</u>: The polymers, which undergo permanent chemical change

And develops cross-links upon heating and becomes permanently hard on cooling, are called Thermo setting plastics. They will not soften on reheating instead they degrade.
Ex: Bakelite, Urea-Formaldehyde etc.

III.__**Based on the method of polymerization:**__

Based on the method of polymerization by which they are produced, polymers are classified into

1. __**Addition polymers**__: The polymers, which are obtained by the addition polymerization Of the unsaturated monomers without the elimination of the simple molecules are called Addition polymers.
Ex: PVC, Polyethylene etc.

2. __**Condensation polymers**__: The polymers, which are formed by intermolecular condensation reactions through functional groups of monomers with continuous elimination of by products are called condensation polymers.
Ex: Phenol-formaldehyde, Polyester, Epoxy resin, Nylon66 etc.

IV. __**Based on their properties they are classified into**__

1. Elastomers: The polymers, which undergo elongation under the application of force (stress) and return to their original length on release of force are called elastomers. Elastomers are coiled and long chain polymers. They will have negligible intermolecular forces except weak vander waals forces.
Ex: Natural rubber, Buna-S, Butyl rubber, Silicon rubber etc

2. Fibres: Fibers are long, thin and thread like polymers, whose length is at least 100 times greater its diameter. They will not undergo stretching and deformation likes elastomers. They are linked up to each other by hydrogen bonding.
Ex: Natural fibers like-Jute, Wood, Silk etc and synthetic fibers like-Nylon66 and Terylene.

3. Resins: These are the low molecular weight polymers available either in liquid or solid form. They are generally used as Adhesives.
Ex: Phenol- Formaldehyde, Urea- Formaldehyde, Epoxy resins, etc

4. Plastics: The polymers, which can be moulded into desired shapes by the application of heat and pressure, are called plastics.
Ex: Polyethylene, Plexiglass, PVC, PC, Teflon etc.

__**Free radical mechanism of addition polymerization:**__

The polymerization of ethylene monomer in the presence of initiator such as organic peroxides gives polythene.

$$\underset{\text{Ethene}}{n\,CH_2{=}\,CH_2} \longrightarrow \underset{\text{Polythene}}{[-\,CH_2 - CH_2\,-]_n}$$

__**Mechanism:**__ Addition polymerization is a chain reaction. It proceeds through free radical mechanism. It involves three distinct stages. Namely

1.Chain initiation.
2.Chain propagation.
3.Chain termination.

__**1.Chain initiation:**__ The addition polymerization is initiated by the initiator free Radical. The initiator free Radical is produced by the thermal decomposition of organic peroxides such as dibenzoyl peroxide. Organic peroxides on heating undergo homolytic cleavage to give a pair of Initiator free radicals. So produced initiator free highly reactive species and contains an odd electron. It adds to vinyl monomer (Ethylene) to produce New free Radical.

$$\underset{\text{Initiator}}{(C_6H_5COO)_2} \xrightarrow{\text{Heat}} 2C_6H_5COO\cdot \xrightarrow{\text{Heat}} \underset{\text{Initiator free Radical }(R\cdot)}{2CO_2 + 2C_6H_5\cdot}$$

$$R\cdot + \underset{\text{Monomer}}{CH_2 = CH_2} \longrightarrow \underset{\text{New free radical}}{R\text{-}CH_2\text{-}CH_2\cdot}$$

<u>2.Chain propagation:</u> In the propagation step, so produced New free radical attacks another monomer to form yet another free radical. This process continues to give long polymer chain until chain termination occurs.

$$R\text{-}CH_2\text{-}CH_2\cdot + CH_2 = CH_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\cdot$$

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\cdot + CH_2 = CH_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\cdot$$

$$\Big\downarrow \, n\ CH_2=CH_2$$

$$\underset{\text{Growing chain of the polymer}}{R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\cdot}$$

<u>3.Chain termination:</u>

This is the last stage of free radical polymerization. At some point, the growing chain of the polymer stops growing and terminates. Termination may take place by

a. Coupling or combination:

The two growing chain may react with each other to give dead polymer.

$$R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\cdot + \cdot CH_2\text{-}CH_2\text{-}(CH_2)_n\text{-}R$$

$$\Big\downarrow$$

$$R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_n\text{-}R$$

b. Coupling of growing chain with initiator free radical:

$$R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\cdot + R\cdot \longrightarrow R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\text{-}R$$

c.Disproportionation: In this kind of termination a hydrogen atom of one growing chain is transferred to another growing chain. This results in the formation of two polymer molecules one saturated and another unsaturated.

$$R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\cdot + R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_2\cdot$$

$$\Big\downarrow$$

$$\underset{\text{Dead polymer}}{R\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_3 + R\text{-}(CH_2)_n\text{-}CH=CH_2}$$

<u>Glass transition temperature (T_g):</u>

The temperature at which the polymer changes abruptly from a hard glassy state to soft rubbery state is called glass transition temperature.It is denoted by **'T_g'.** The hard, brittle state is known as the glassy state and soft flexible state as the rubbery state. In the glassy state, there will be no segmental and molecular motion. On the other hand, in rubbery state, there are only segmental motion but no molecular mobility.

Glassy state	Rubbery state	Polymer melt
	(Viscoelastic state)	(Viscofluid state)
(hard & brittle)	(soft & flexible)	

T_g T_m

<u>Factors affecting T_g:</u>

1. **<u>Flexibility</u> :** Linear polymer chain made of C-C, C-O or C-N single bonds have a higher degree of freedom of rotation on a single bond. Presence of rigid groups such as aromatic or cyclic groups in the chain backbone or bulky groups in the chain backbone carbon atoms hinders the freedom of rotation.
   Ex: Polyethylene (T_g= -110ºC)-linear polymer
   Polyethylene terphthalate (T_g= 69ºC)-aromatic group in chain backbone
   Polystyrene (T_g= 100ºC)-aromatic group attached to one of the carbon atom
2. **<u>Effect of side group</u>**: Poly [α- methyl styrene] has higher T_g (T_g= 170ºC) value while polystyrene has lower T_g (T_g= 100ºC) value, is due to the presence of effective methyl side group which hinders the free rotation about carbon-carbon bond of chain back bone, and restricts the chain mobility, thereby increases T_g value.
3. **<u>Intermolecular forces</u>**: Presence of large number of polar groups in the molecular chain lead to strong intermolecular cohesive forces which restrict the segmental/molecular mobility. This leads to an increase in T_g.
   Ex: polypropylene (T_g= -18ºC) has lower T_g compared to nylon6,6 (T_g= 57ºC).
4. **<u>Branching and crosslinking</u>**: A small amount of branching will reduce the T_g, because with small amount of branching the free volume increases thus decreases the T_g. On the other hand, a high density of branching (crosslinking) brings the polymer chains closer, lowers the free volume thus reduces the chain mobility and hence results in increase of T_g.
   Ex: Low density polyethylene (LDPE)
   Crosslinking low density polyethylene (XLDPE)
5. **<u>Presence of plasticizers:</u>** Addition of plasticizers reduces the T_g value.
   Ex: Diisooctyl phthalate, which is added to PVC to reduce its T_g from 80ºC to below room temperature.
6. **<u>Srereoregularity</u>** of polymers increases T_g. Thus T_g of a isotactic polymer is greater than that of the syndiotactic polymer whose T_g is greater than atactic polymer.
7. **<u>Molecular weight</u>**: The T_g of all polymers, in general, increases with molecular weight up to 20,000 and beyond which the effect is negligible.

Importance(significance) of T_g:

1. T_g value is a measure of flexibility of a polymer and the type of response the polymer would exhibit to mechanical stress.
2. T_g value gives the idea of the thermal expansion, heat capacity, refractive index, electrical and mechanical properties of the polymer.
3. T_g value can decide whether a polymer at the use temperature will behave like rubber or plastic.
4. Knowledge of T_g and T_m is useful in choosing right temperature for fabrication. (fabrication- temperature region in which the polymer material can be converted into finished product through different processing techniques such as injection moulding, compression moulding, calendering, extrusion etc)

Structure-property relationship of polymers:

The structure of polymers have great influence on the fundamental properties, such as crystallinity, tensile strength, elasticity and chemical resistance etc..

Strength: Melt viscosity, impact and tensile strength are a few mechanical properties of a polymer. Tensile strength and impact strength increases with molecular mass up to a certain point and then become constant. The melt viscosity of the polymer initially shows a gradual increase with the molecular mass and steep increase at higher molecular masses. For polymer to be commercially useful it should have low melt viscosity, high tensile and impact strength.

Crystallinity: Polymers are usually consists of crystalline and amorphous part. A requirement for a polymer to crystallize is regularity of molecular structure with greater symmetry such that polymer chains can closely packup with ordered structure.

The degree of crystallinity of the polymers depends on its structure. i.e, linear polymer means highly crystalline, because the atoms along the chain permit closer approach which drops sharply with branching. Which further drops sharply with bulky pendant group in polymer chain.

The polymers chains with polar groups can form hydrogen bonding with their neighbouring chains have high crystallinity.
Ex. Nylon6,6. Polymer with high degree of crystallinity has high tensile strength and impact .

Crystallinity of a polymer also depends on the stereo regular arrangement. Polymers like isotactic and syndiotactic polystyrene etc are highly crystalline. On the other hand atactic polystyrene, will have their substituents in a random arrangement are less crystalline.

Elasticity:

The property by which the polymer undergoes elongation several times by the application of stress and regain their original length on releasing the stress is called elasticity.

Elasticity of a polymer material is mainly because of the uncoiling and recoiling of the molecular chains on the application of force. For a polymer to show elasticity the individual chains should not break on prolonged stretching. Breaking takes place when the chains slip past each other and get separated. In rubber this is avoided by molecular engineering such as

1. Introducing cross- linking at suitable molecular position (Vulcanization)
2. Avoiding bulky side group such as aromatic and cyclic structure in the repeat unit
3. Introducing more non- polar groups in the chains so that the chains do not separate on stretching.
4. The structure should be amorphous, so that the material should have a T_g lower than the temperature at which it is used.

In other words to get a elastomeric material, any factor that introduces crystallinity should be avoided.

Non elastic nature of fibres:

In contrast to elastomers, the high strength and non elastic nature of the fibers is attributed to its crystallizability on pulling. In fibers, the chain mobility is reduced by very close packing of the polymer chain backbone without cross linking. Polar groups and aromatic and cyclic rings in the backbone chain are known to impart a high strength to the polymer fibre.

Ex: Polyamide (nylon6,6), polyethylene terphthalate (tereylene).

Chemical resistivity: The chemical resistance of a polymer depends on the structure of the polymer and also on the nature of attacking reagent. When the chemical attacks on the polymer it first softens, swells and loses the strength then it dissolves. Chemical resistivity of polymers depends on number of factors like presence of polar and non- polar groups, the molar mass, degree of crystallinity, extent of cross linking.

Polymers containing –OH group or –COOH polar group are soluble in polar solvents like water, alcohol etc. Polymers with non– polar groups such as –CH3, –C6H5 are easily swells and dissolves in non–polar solvents like benzene, toluene and carbon tetra chloride etc. Polymer containing ester group (polyester) undergo hydrolysis with strong alkalis at high temperature. Polyamide like nylon containing –NHCO– group, polyurethane contain –NHCOO– group can be attacked by strong acids or alkali.

Higher the molecular mass of the polymer the dissolution decreases. Chemical resistance of a polymer increases with increase in crystallinity. Similarly chemical resistance increases with degree of cross linking.

Types of plastics

Thermoplastic	**Thermosetting plastic**
1. Formed by addition ploymerization	1.Formed by condensation polymerization
2. They are linear ploymers	2.They are cross linked polymers
3. Monomers have bifunctional groups	3. Monomers have higher functional groups have

4. They are low molecular	4.They are high molecular
5. Soft, weak, brittle	5.Hard, strong, brittle.
6. Soluble in organic solvents	6.Insoluble in organic solvents.
7. Softened on heating	7. Do not soften on heating
8. Can be reshaped, recycled	8.Retain their shape and structure.

MOULDING OF PLASTICS INTO ARTICLES

In the moulding process, the compounded polymer in the form of powder, chips or granules is placed in a mould of the required shape and subjected to heat and pressure to get final product.

Important methods of moulding are

(a) Compression moulding
(b) Injection moulding
(c) Extrusion moulding

Compression moulding: This technique is generally employed for producing articles from thermosetting plastic. In this method a plastic material is placed directly into a heated metal mould, then is softened by the heat, and forced to conform to the shape of the mould as the mould closes. The mould is made of two halves, upper and lower halves. The lower half contains a cavity and the upper half has a projection which fits into the cavity when the mould is closed. The gap between the projected upper half and the cavity in the lower half gives the shape of the moulded article.

Process: The process starts with an allotted amount of polymer in the form of powder or pellet inserted into a mould. The material is heated to a molten state in and by the mould. Then the hydraulic press compresses molten polymer against the mould, resulting in a perfectly moulded piece retaining the shape of the inside surface of the mould. The excess material flows out of the mould as a thin film known as flash. Under the influence of heat, the compacted mass gets cured and hardened to shape. The mould can be opened while it is hot to release the moulded product.

Fig

Applications: In the manufacture of electrical parts, dinner wares, gears, buttons, buckles, knobs, handles, radio cases and large containers.

Injection moulding: This process is mainly applicable to thermoplastics. In this method, granular plastic is fed by gravity from a hopper into a heated barrel. As the granules are slowly moved forward by a screw-type plunger, the plastic is forced into a heated chamber, where it is melted. As the plunger advances, the melted plastic is forced through a nozzle that rests against the mould, allowing it to enter the mould cavity. The mould remains cold so the plastic solidifies almost as soon as the mould is filled. When the material has been cured sufficiently, half of the mould is opened to allow the ejection of the finished article.

Fig

Applications: In the manufacture of telephone handsets, television cabinets, electrical switches, DVDs, automotive bumpers, automotive dash boards, battery casings, syringes, disposable razors, craters, recycling boxes, bottle lids etc.

Advantages

- High production rates
- Wide range of materials can be used
- Low labor costs
- Minimal scrap losses
- Little need to finish parts after moulding

Disadvantages

- Equipments are expensive
- Running cost is high
- Parts must be designed with moulding consideration

Extrusion moulding: It is a manufacture process. During this method, the plastic material in the form of powder or granules is fed through the hopper into the feed zone of the cylinder. A motor runs a screw which feeds granules of plastic through a heater. The granules melt into a liquid which is forced through a die, forming a long tube like shape. The shape of the die determines the shape of the tube. The extrusion is then cooled and forms a solid shape.

Applications: In the manufacture of pipes, hoses, drinking straws, curtain tracks, rods and fibres, all in continuous lengths.

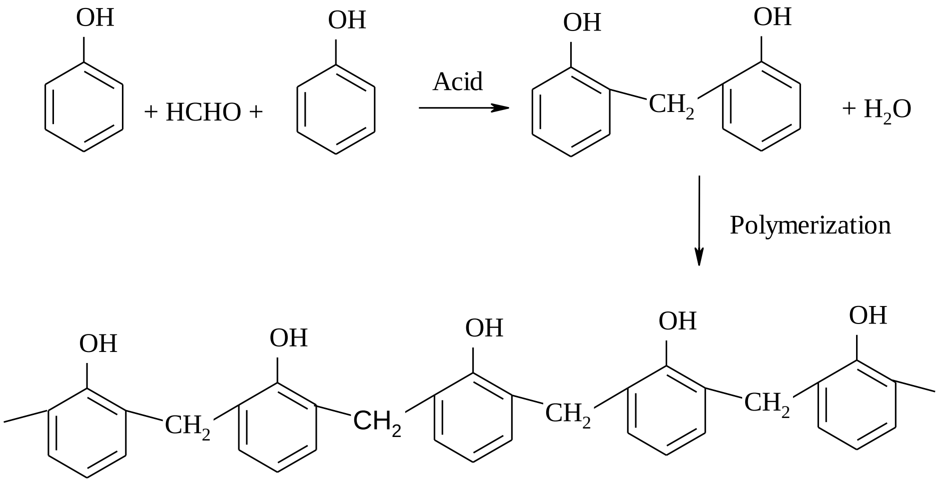
Advantages: It is the most efficient and rapid method for the production of long continuous products such as tooth paste tubes, rods and filaments.

Phenol-formaldehyde resin (Bakelite):

It is also known as Phenoplasts.It is prepared by the condensation reaction between phenol and formaldehyde using acid or base as catalysts.

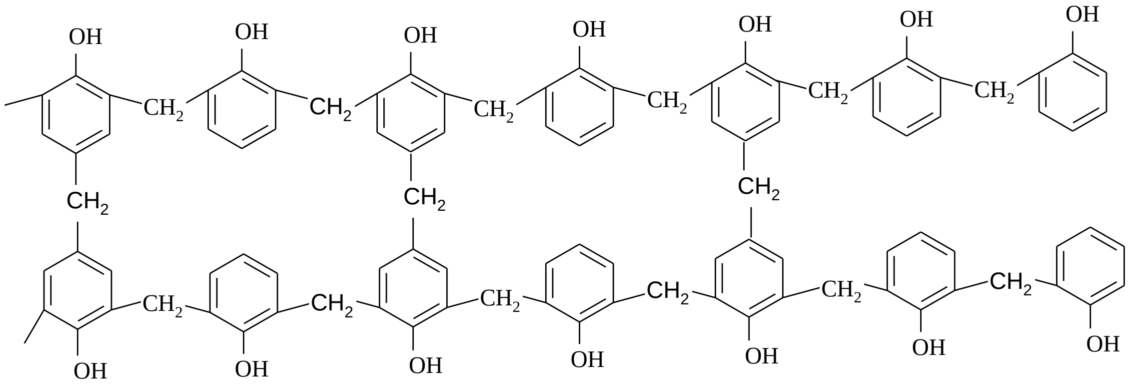
The nature of the product depends on the relative concentrations of phenol and formaldehyde and on whether the acid or base is used as as catalyst.

A large excess of phenol on heating with an aqueous solution of formaldehyde in the presence of acid catalyst gives a polymer called Novalac Resin. It is a linear polymer of low molecular weight.



Novalac Resin

On the other hand, a large excess of an aqueous solution of formaldehyde on heating with of phenol in the presence of base as catalyst gives a polymer called Resol. It is a crossed linked polymer of high molecular weight.



Resol

Further heating of Novolac and Resol in the presence of fillers, thinners, dyes and other additives during moulding process causes excessive cross linking in the formation of a hard rigid, insoluble polymer called **Bakelite.**

Uses:

1. They are used for making electrical parts like switches, plugs, switch holes; heaters etc.
2. They are also used for making moulded articles like telephone, cabins of Radio & TV washing machine agitators etc.
3. Resol is used in the manufacture of laminated plastics.

Teflon (PTFE):

Teflon is the trade name for Poly tetra fluro ethylene(PTFE). The monomer used in the production of Teflon is Tetrafluro ethylene(C_2F_4). It is obtained by treating chloroform with HF and dechlorinating the product.

$$\underset{\text{Chloroform}}{CHCl_3} + 2HF \longrightarrow \underset{\text{Chlorodifluoro methane}}{CHClF_2} + 2HCl$$

$$2CHClF_2 \longrightarrow \underset{\text{TFE}}{CF_2 = CF_2} + 2HCl$$

Teflon is usually manufactured by emulsion polymerization of TFE using peroxide or ammonium persulphate as initiators.

$$n\ CF_2=CF_2 \xrightarrow{\text{peroxide}} \underset{\text{Teflon}}{(-CF_2 - CF_2 -)_n}$$

Uses:

1. It is used for insulation of motors, generator, transformers, coils, capacitors, wires and cables.
2. Teflon is used as lining for food processing equipments such as as bakery trays, frying pans as this is not wetted by oil or water.
3. It is also used in Gaskets, industrial filters, belts which are subjected to wear at elevated

Temperatures.

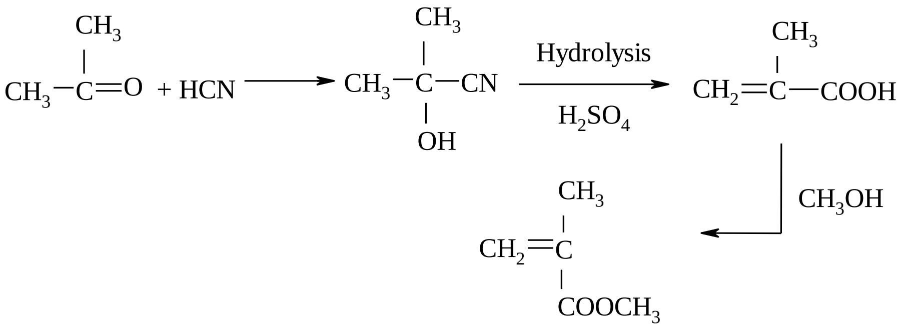
4. It is also used for coating army weapons as an anticorrosive coat.

5.It is used as an ideal lubricant for non- lubricated bearings and as a dry lubricant as it remains slippery over a wide range of temperature..

Poly methyl methacrylate or plexi glass (PMMA):

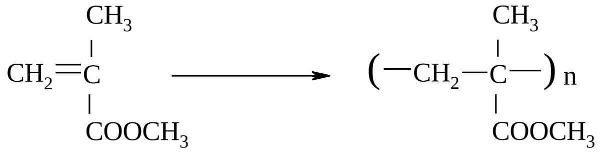
It is also known as Plexi glass. The monomer used in the production of PMMA is Methyl metheacrylate. Methyl metheacrylate is obtained by the following method.

Acetone with hydrogen cyanide gives acetone cyanohydrin. The hydrolysis of acetone cyanohydrin with sulphuric acid, yields methylacrylic acid, which on esterification with methyl alcohol gives methyl methacrylate



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=O + HCN \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CN \xrightarrow[H_2SO_4]{Hydrolysis} CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COOH \xrightarrow{CH_3OH} CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}$$

It is manufactured by the Bulk or suspension polymerization technique of methyl methacrylate using hydrogen peroxide as initiator.



$$CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} \longrightarrow \left(-CH_2-\underset{\displaystyle COOCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\right)_n$$

methyl methacryalate PMMA

Uses:

1.It is used for making lenses, attractive sign boards.

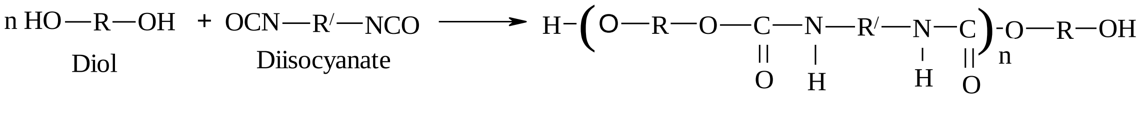
2.It is used for making artificial teeth and eyes.

3. It also finds uses as paints and adhesives.

4.It is also used in moulding process to get transparent moulds and tubes.

Polyurethanes:

Polyurethanes are the polymeric materials in which the monomer units are linked through –NHCOO- group .They are prepared by the poly addition reaction between diisocyanate and diols.



$$\underset{Diol}{n\,HO-R-OH} + \underset{Diisocyanate}{OCN-R'-NCO} \longrightarrow H-\left(O-R-O-\underset{\displaystyle O}{\underset{||}{C}}-\underset{\displaystyle H}{\underset{|}{N}}-R'-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle O}{\underset{||}{C}}\right)_n-O-R-OH$$

POLYURETHANES

Uses:

1. It is used for floor coating for gymnasium and dance floors where high abrasion resistance is required.
2. Used as surface coatings, films, foams and adhesives.
3. They are used for cushions because of improved strength, lower density and easier fabrication.
4. It is used in lightweight garments and swim suits because of its stretching property

Elastomers: Rubbers are high polymers which undergo elastic changes when subjected to an external force but readily regain their original position when external force is removed. Rubbers are therefore referred to as elastomers. A rubber band can be stretched to 4 to 10 times to its original length. Elastomers can be obtained from two processes, which may be natural or synthetic.

Natural rubber: Occurs in the inner bark of tropical plants like heavea brasiliensis, gauyule guttaparcha etc. I n the form of milky suspension called latex. Latex is a dispersion of isoprene.In the treatment of latex, these isoprene molecule polymerized to form long coil chain of polyisoprene.

Natural rubber is a linear high polymer of isoprene hence it may also called as poly isoprene.

Drawbacks (deficiencies)of natural rubber :

1. Plastic in nature
2. It is very weak its tensile strength is low 200 kg/cm^2
3. It becomes hard and brittle at low temperature and soft and sticky at high temperature.
4. It is non resistant to organic solvent, non-polar solvent, water, oxidation by oxygen and other oxidizing agents.
5. It has poor abrasion resistance.

To improve all these drawbacks it is subjected for compounding and vulcanisation.

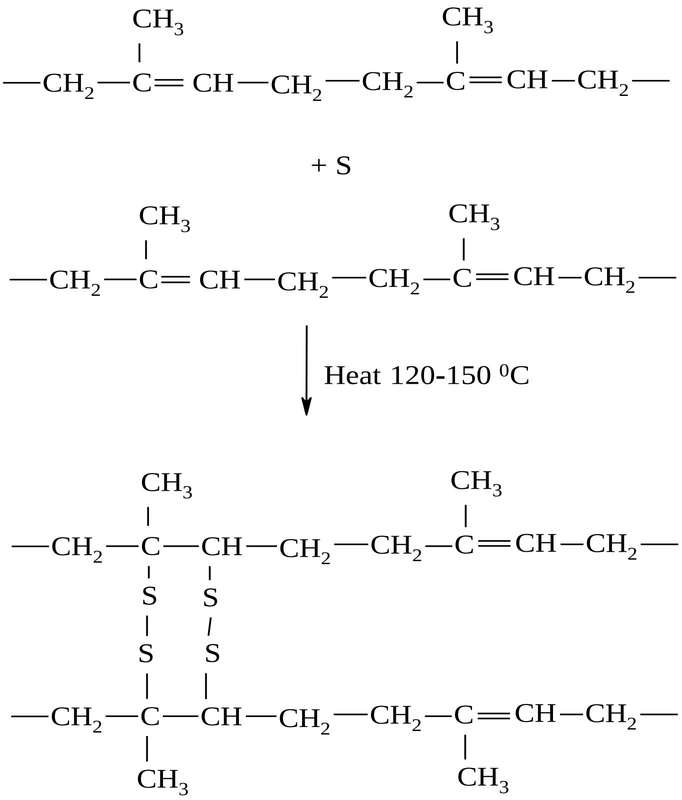
Differences between natural rubber and synthetic rubber(Advantages of synthetic rubber over natural rubber):

Natural rubber	Synthetic rubber
1. It is attacked by sunlight and air sunlight	1.It is not attacked by air and sunlight
2. It is less resistance to heat and cold.	2.It is more resistance to heat and cold
3. Holds less air and water at high pressure.	3. Hold more air and water even at high pressure.
4. It has low tensile strength	4. It has high tensile strength.
5. Rubber property is lost at high temperature.	5. Rubber property is retained over a wide range of temperature.
6. It swells and dissolves in organic solvents.	6. Generally, they donot swells and dissolves in organic solvents
7. It ages quickly and loses lustrous nature in service.	7.Donot ages quickly
8 It has low resistance to the action of chemicals.	8. It has high resistance to the action of chemicals.

Vulcanization of rubber

The treatment that decreases the flow of an elastomer, increases its tensile strength and modules but preserves its extensibility.

Vulcanization was introduced by Goodyear in 1839. It consists of heating raw rubber to 150 ^{0}C with 1-3 % sulfur with small amounts of accelerators, activators and antioxidants. Sulfur attacks the rubber molecules at the position of double bonds forming bridges between the adjoining molecules.



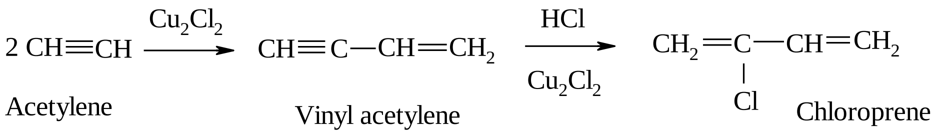
Vulcanized rubber

The degree of vulcanization introduced in vulcanized rubber depends on the amount of sulfur used. Tyre density uses 3-5 % sulfur. If the amount of sulfur is increased to 30%, a hard and rigid rubber called ebonite is produced.

Neoprene rubber

Neoprene is an addition polymer of chloroprene (2-chloro-1,3-butadiene)

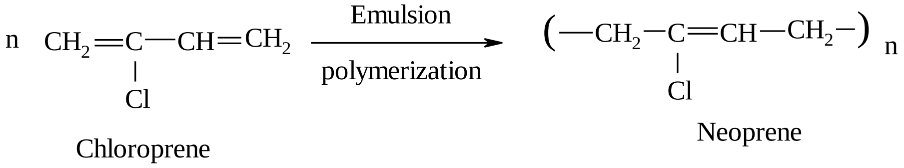
Preparation of chloroprene: Acetylene in the presence of catalyst cupric chloride gives vinyl acetylene. Addition of hydrogen chloride to vinyl acetylene in the presence of cupric chloride gives chloroprene.



$$2\,CH\equiv CH \xrightarrow{Cu_2Cl_2} CH\equiv C-CH=CH_2 \xrightarrow[Cu_2Cl_2]{HCl} CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2$$

Polymerization

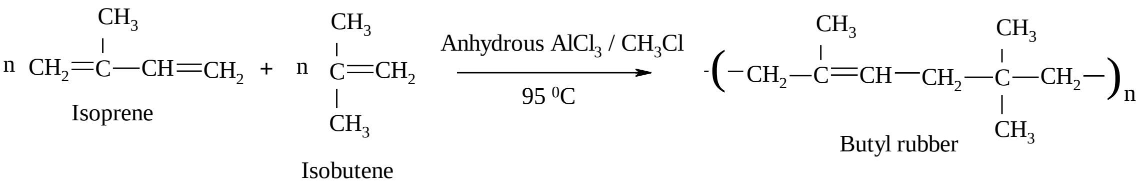
Chloroprene undergoes emulsion polymerization by free radical mechanism to give neoprene rubber.



$$n\ CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \xrightarrow[\text{polymerization}]{\text{Emulsion}} \left(-CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2{-}\right)_n$$

Butyl rubber:

It is a colpoymer.It is manufactured by mixing isobutene with 1.5 to 4.5% of isoprene. The monomers are polymerized in CH_3Cl and anhydrous $AlCl_3$ as catalyst at -95^0c.



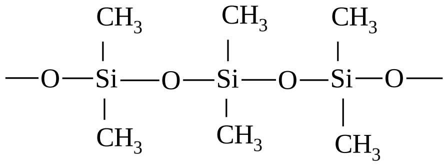
$$n\ CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + n\ \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{=}CH_2 \xrightarrow[95\ ^0C]{\text{Anhydrous } AlCl_3\ /\ CH_3Cl} \left(-CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_2{-}\right)_n$$

Uses:

1. It is used for making inner tubes for tyres, conveyor belts.
2. It is also used for insulating high voltage wires and cables.

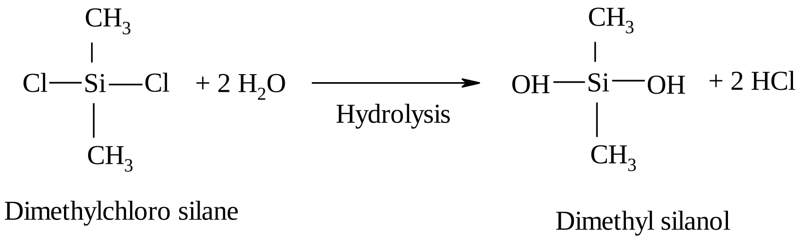
Silicone rubber

Silicone rubber (polymethyl siloxane) is an example for inorganic polymer. It is a chain of alternating silicon and oxygen atoms and each silicon atom carries two methyl groups.

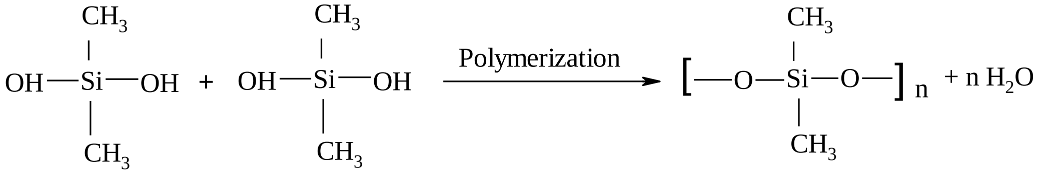


$$-O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-O-$$

Preparation: Silicone rubber is obtained by the condensation polymerization of dimethyl silanol, which is produced by dimethylchloro silane.



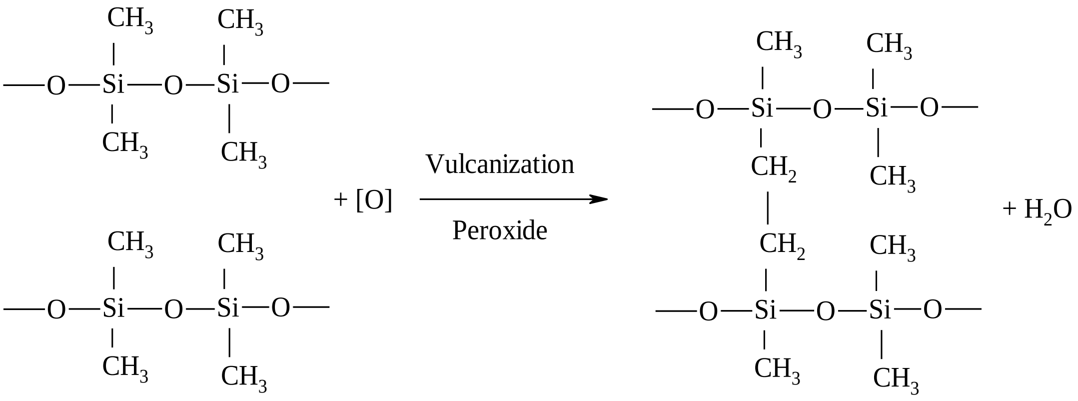
$$Cl-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-Cl + 2\ H_2O \xrightarrow[\text{Hydrolysis}]{} OH-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-OH + 2\ HCl$$



$$OH-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-OH + OH-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-OH \xrightarrow{\text{Polymerization}} \left[-O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{Si}}}}-O-\right]_n + n\ H_2O$$

Vulcanization of silicone rubber

Due to the absence of unsaturation in silicones, vulcanization with sulfur is not possible. It is therefore, vulcanized by using peroxides such as H_2O_2 or benzoyl peroxide. Silicon chains are cross linked through methylene bridges.



Properties

- Silicone rubber possesses high thermal stability (up to 250 ^{0}C)
- Resistance to weathering and lubricating properties
- Not affected by common acids and alkalis
- Water repellent

Applications

- Used in industrial and domestic gaskets
- High temperature cable insulation and safety glass inter layers
- Water proof surfaces and clothing
- Tyres of fighter air-crafts
- Artificial heart valves
- Transfusion tubings
- Padding material in plastic surgery

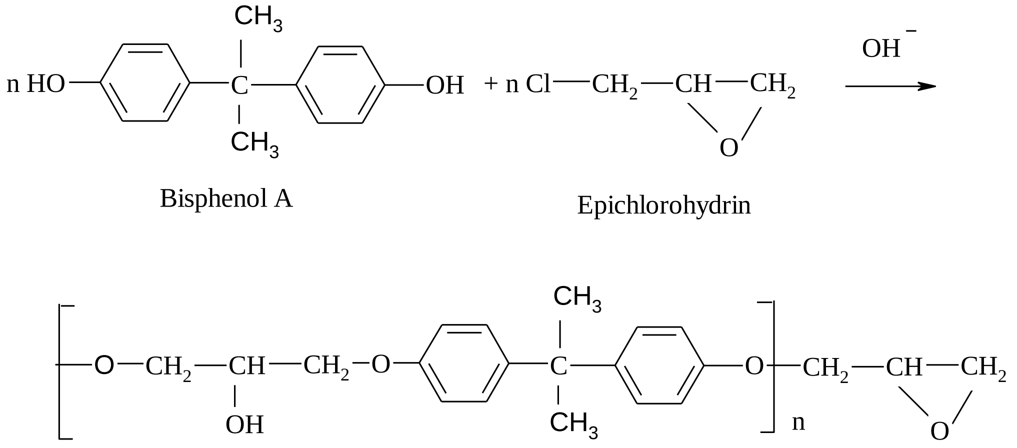
Adhesives

Adhesives are mainly used to join two surfaces together. Adhesive is defined as a non-metallic compound which can hold firmly two materials together by surface attachment. Adhesives develop cohesive strength necessary to hold two surfaces together. They can transfer load from one substance to another.

Adhesion offers many advantages over soldering, riveting, welding, screwing, etc.

Epoxy resin (Araldite):

Epoxy resins are synthetic adhesives and can be obtained by the condensation of excess Epichlorohydrin with Bisphenol A, catalyzed by alkali.



Properties

These are linear, low molecular weight and soluble liquids. These are cross linked at room temperature on mixing with diamines, dicarboxylic acids or acid anhydrides.Epoxy resins are highly resistant to water, solvents, acids and alkalis.

Applications

- Widely used as structural adhesives due to their excellent chemical resistance and good adhesion
- Used for laminating materials
- Used to impart crease and shrinkage resistance to fabrics.

Polymer composites:

Two or more distinct components, which combine to form a new class of material suitable for structural applications are referred to as composite materials. A composite containing polymer matrix is known as polymer composite.

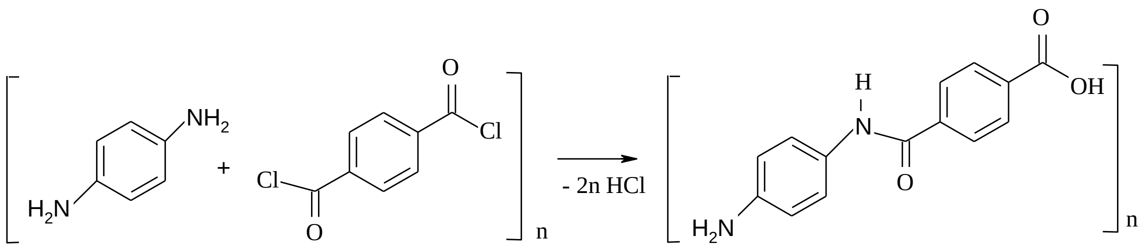
The properties of the composite system are not attainable by the individual components acting alone.

Properties of polymer composites:

1. They are light in weight.
2. They have high strength to weight ratio.
3. They are much stronger and durable than conventional metals like steel and aluminium.
4. They have high fatigue strength.
5. They have good corrosion resistance.
6. They are most suitable for aerospace applications due to their lightweight.

Kevlar: Kevlar belongs to a family of aramids. It is a aromatic polyamide with the name poly [para-phenylene terephthamide]

The linkage through para position s of the phenyl rings gives Kevlar a strong ability to stretch and hence its extra strength.



It has higher tensile strength and modulus than fiberglass. Kevlar fibers are used for structures requiring good stiffness, high abrasion resistance and lightweight.
Used in lightweight boat hulls, aircraft fuselage panels, pressure vessels, high performance racecars, bulletproof vests and puncture resistant bicycle tyres.

Carbon fibre: Carbon fiber is a polymer, which is a form of graphite with carbon ring structure.

Preparation of carbon fiber:
It is made by heating polyacrylonitrile. The polymer cyclises through the cyanogroups to form a polycyclic chain. The resulting solid is heated gradually. Then it is slowly roasted at 400-600^{o}c when the adjacent chains join together losing more hydrogen gas. Then the temperature is gradually raised to 2000^{o}c to get wider ribbon like mass.
Carbon fiber reinforced composites are very strong and are often stronger than steel but lighter. They are used for making parts of aero planes and the space shuttle, tennis rackets and golf clubs, weaving machines, missiles, agricultural etc.

Applications of polymer composites:

1. In aerospace: wings, fuselage, antennae, helicopter blades, landing gears, seats, floors rocket motor cases.
2. In automobiles: body panels, bumpers, shafts, gears, bearings, automobile brakes, clutches.
3. In boats: hulls, decks, masts, engine shrouds.
4. Interior and exterior panels, chairs, tables etc.
5. Protective helmets, archery bows, surfboards, fishing rods, diving boards.
6. Pipes, tanks, pressure vessels, hoppers, valves, pumps etc.