

Engineering Chemistry

Fundamentals and Applications

A photograph of laboratory glassware, including a blue rubber bulb with a glass tube, a clear glass beaker containing a red liquid, and several colorful plastic containers (red, green, yellow, pink) in the background.

MOHAMMED OWAIS

ABOUT THE BOOK

First Published OCTOBER, 2023

All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means without the prior permission in writing of the publisher, nor be otherwise circulated in any form of binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

The copy right holder of this book is **MOHAMMED OWAIS**, the student of **MJCET COLLEGE**.

BOOK DEVELOPMENT COMMITTEE

CONTENT BY	: Prof. Amina Sarwar (CHEMISTRY DEPT- CSE - MJCET)
WRITER & EDITOR	: Mohammed Owais (STUDENT OF CSE DEPARTMENT, MJCET)
COVER PAGE DESIGNER	: Mohammed Owais (STUDENT OF CSE DEPARTMENT, MJCET)

FOREWORD

Education is a process of human enlightenment and empowerment. Recognizing the enormous potential of education, all progressive societies have committed themselves to the Universalization of Elementary Education with a strong determination to provide quality education to all. As a part of its continuation, universalization of Secondary Education has gained momentum.

CONTENTS

UNIT 1

1.1 ELECTROCHEMISTRY

1.2 BATTERY CHEMISTRY

UNIT 2

2.1 WATER CHEMISTRY

2.2 CORROSION

2.3 CORROSION CONTROL METHODS

2.4 SURFACE COATING METHODS

UNIT 3

3.1 ENGINEERING MATERIALS

3.2 CONDUCTING POLYMERS

3.3 BIODEGRADABLE POLYMERS

UNIT 4

4.1 CHEMICAL FUELS

4.2 SOLID FUELS

4.3 LIQUID FUELS

4.4 GASEOUS FUELS

4.5 COMBUSTION

UNIT 5

5.1 GREEN CHEMISTRY

5.2 COMPOSITES

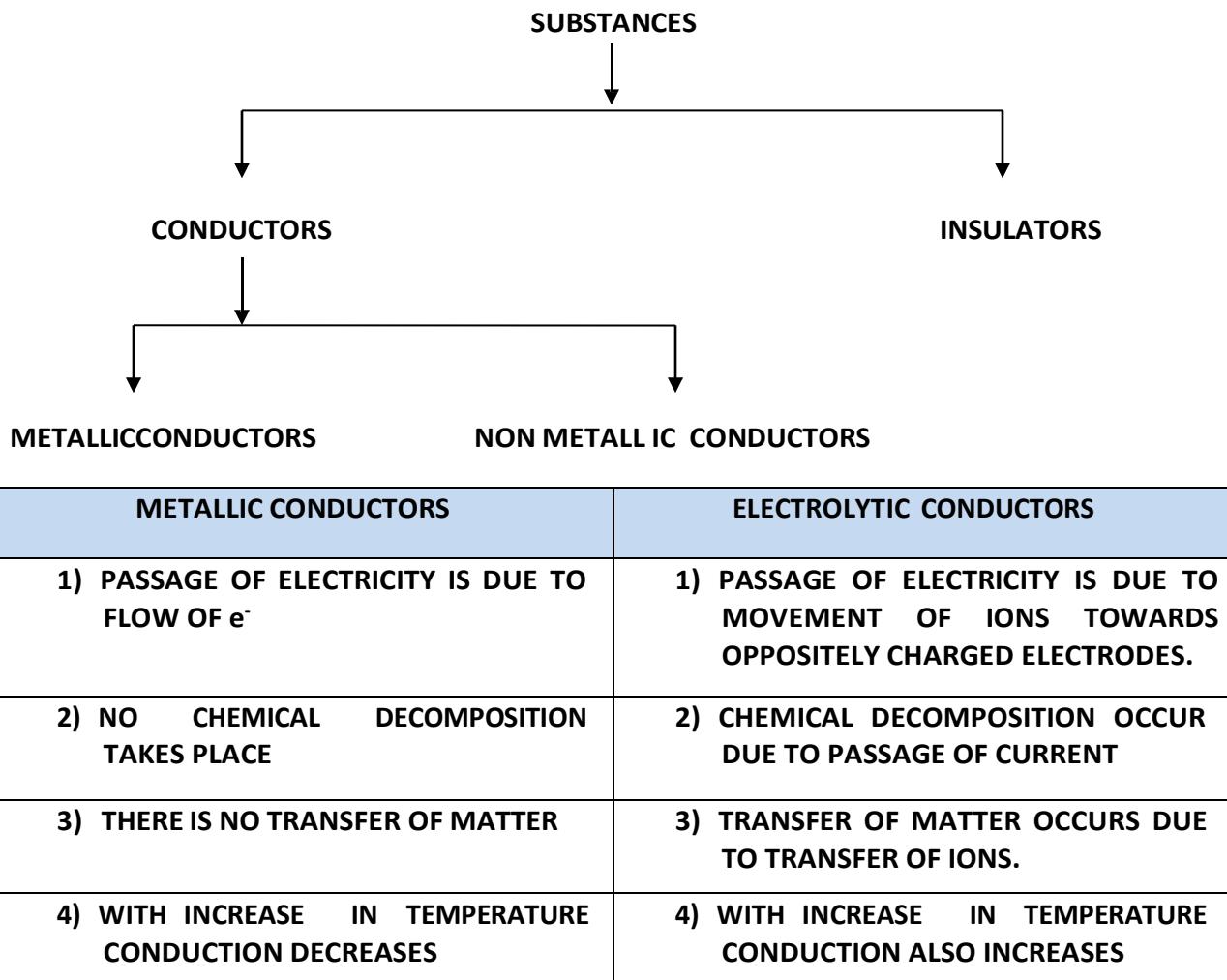
UNIT 1.1

ELECTROCHEMISTRY

It is a branch of chemistry which deals with study of chemical reactions brought about by electrical energy.

It is the study of process involved in the inter-conversion of electrical energy and chemical energy.

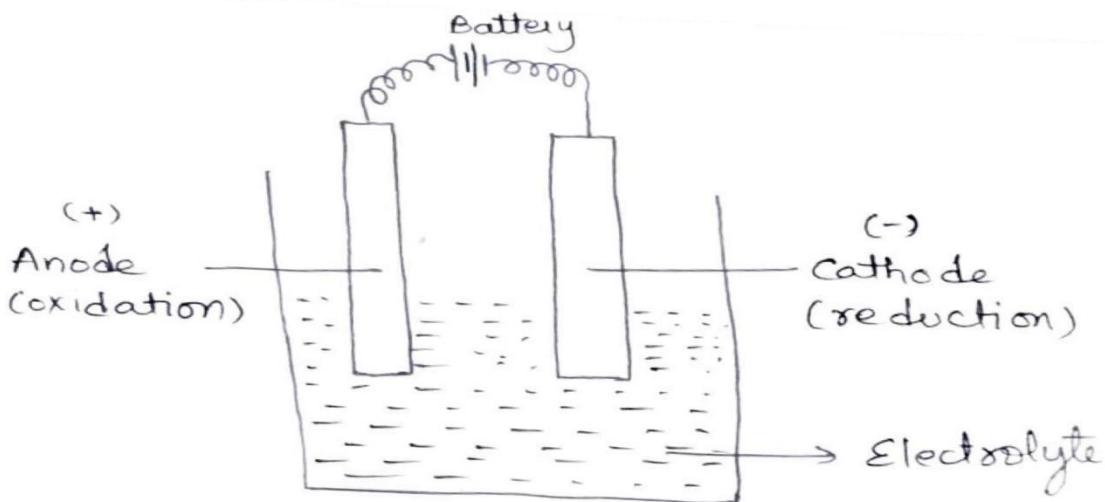
TYPES OF CONDUCTORS :



ELECTROLYtic CELL :

Electrolysis is the process of decomposition of an electrolyte by passage of electric current.

An electrolyte consists of an electrolyte in which two electrodes are immersed, which are connected to the terminals of the battery. The anode is connected to the positive terminal and cathode to the negative terminal. The anions (negatively charged) migrates to the anode and cations (positively charged) migrates to the cathode. Therefore at anode oxidation takes place and at cathode reduction takes place.



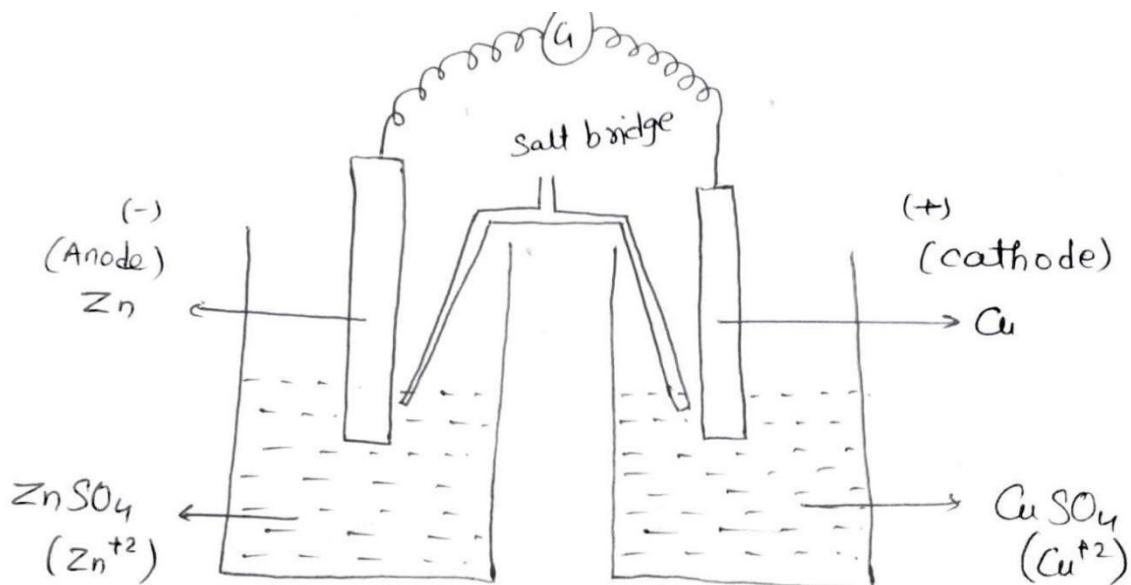
ELECTROCHEMICAL OR GALVANIC CELL:

An electrochemical cell converts chemical energy into electrical energy i.e. electric current is generated by spontaneous redox reactions.

DANIEL CELL:

It is a typical voltaic cell, which consists of Zinc(Zn) rod as anode, placed in $ZnSO_4$ solution, and copper rod as cathode, placed in $CuSO_4$ solution. The two electrodes are joined by a wire and a salt bridge is introduced to connect two solutions. The flow of electrons is from anode to cathode but the flow of current is from cathode to anode.

CELL DIAGRAM:



CELL REACTIONS:



CELL NOTATION :

Cell notation is the symbolic representation of an electrochemical cell. A single vertical line represents phase boundary between the electrode and electrolytic solution. A double vertical line represents the salt bridge. The Anodic Half cell is written on LHS and the cathodic half cell is written on RHS. The value of cell emf is written to the extreme right side



The flow of current through the circuit is determined by the push of e^- by cathode. This driving force that sends the electron to the circuit is called as **CELL POTENTIAL** or **ELECTROMOTIVE FORCE** which is measured as cell voltage in volts.

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

$$= E_{\text{Cu}} - E_{\text{Zn}}$$

$$= +0.34\text{V} - (-0.76\text{V})$$

$$= +1.10\text{ V}$$

SALT BRIDGE :

It is an inverted U shaped tube open at both the ends, containing salts like KCl, NH_4NO_3 in agar-agar gel.

FUNCTIONS OF SALT BRIDGE:

- 1) It connects the 2 solutions in a galvanic cell and prevents intermixing of the 2 solutions.
- 2) It allows the flow of ion from cathodic solution to anodic solution.
- 3) It prevents the accumulation of charges around the electrodes.
- 4) It maintains electro-neutrality of solution and completes the circuit.

Q) Differentiate between electrochemical and electrolytic cells.

ELECTROCHEMICAL CELLS	ELECTROLYTIC CELLS
1) Spontaneous redox reaction takes place.	1) Spontaneous redox reaction does not takes place.
2) Chemical energy is converted to electrical energy	2) Electrical energy is converted into chemical energy
3) Anode is negative electrode cathode is positive electrode	3) Anode is Positive electrode cathode is Negative electrode.
4) The 2 half cells are connected by a salt bridge	4) The electrodes are kept in same electrolytic solution
5) Electrical energy is generated by spontaneous redox reaction	5) Electrical energy brings about the chemical reaction
6) Ex: batteries	6) Ex: electroplating and purification of copper

ELECTRODE POTENTIAL

* The EP is the tendency of an electrode to lose or gain electrons when in contact with its own ions in solution.

* The Elements having tendency to lose e and get oxidized are said to possess oxidation potential and those having tendency to gain e and get reduced are said to possess reduction potential. #Standard Electrode Potential (E°)

It is the potential developed at electrode-electrolyte interface when a metal electrode is in contact with its soluble salt solution as electrolyte having one molar concentration at 25°C or 298K temperature and if gases are involved, then they act at 1 atm.

SINGLE ELECTRODE POTENTIAL(E)

It is the potential developed at electrode-electrolyte interface when a metal electrode is in contact with its soluble-salt solution as electrolyte, having concentration other than one molar, than 1 atm and temperature may or may not be 25°C (or) 298 K.

STANDARD REDUCTION POTENTIAL(SRP)

The potential developed at Electrode - Electrolyte interface when a metal electrode gains e and gets reduced when in contact with its concentration at soluble-salt solution having one molar concentration at 25°C or 298 K temperature and if gases are involved they act at 1 atm pressure.

Electrochemical Series

The series in which the reduction potential of various electrodes have been arranged increasing order downwards with Hydrogen electrode taken as 0 volts is termed as Electrochemical Series.

Applications of Electrochemical Series

*The elements lying above Hydrogen lie up in the series with $-E^\circ$ values are strong reducing agents.

*The elements lie up in the series with lower SRP values act as anode

*Elements above H₂ can easily displace H₂ from acids to release H₂ gas.

*It is used to predict the spontaneity of any redox reaction.

*It helps us to decide anodic or cathodic coating to prevent corrosion.

Elements	E°_{srp} (in volts)
Li	-3.04
K	-2.9
Ca	-2.8
Na	-2.71
Mg	-2.3
Al	-1.66
Zn	-0.76
Fe	-0.44
H ²	0.0
Cu	+0.34
Ag	+0.71
Pt	+1.18
Au	+1.50

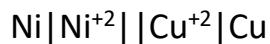
Q) Write the cell notation, cell reaction and cell emf for the following

1) Cu | Ni

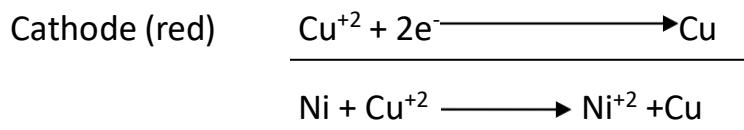
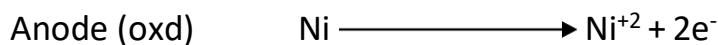
$$E^\circ_{\text{Cu}^{+2}/\text{Cu}} = +0.34\text{V} \text{ (Cathode)}$$

$$E^\circ_{\text{Ni}^{+2}/\text{Ni}} = -0.24\text{V} \text{ (Anode)}$$

Cell notation:



Cell reaction:



$$\text{Emf} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= +0.34 - (-0.24)$$

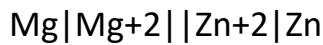
$$= +0.58\text{V}$$

2) Mg | Zn

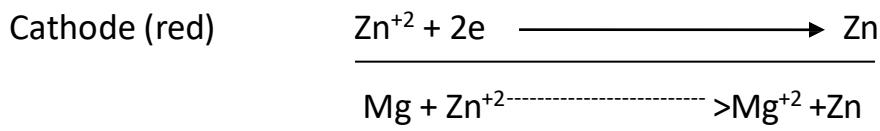
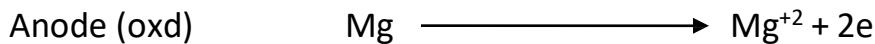
$$E^\circ_{\text{Mg}^{+2}/\text{Mg}} = -2.3\text{V} \text{ (Anode)}$$

$$E^\circ_{\text{Zn}^{+2}/\text{Zn}} = -0.76\text{V} \text{ (Cathode)}$$

Cell notation:



Cell reaction:



$$\text{Emf} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= -0.76\text{V} - (-2.3\text{V})$$

$$= +1.54\text{V}$$

#Nernst equation: (Thermodynamics of emf of cells)

The Nernst equation gives relationship between cell reactions and cell emf. It establishes the relationship between electrode potential and standard electrode potential.

For a general chemical reaction:



Nernst equation is derived from Vant - hoff's isotherm

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{--- (1)}$$

Where

ΔG = change in Gibbs free energy

ΔG° = Change in standard Gibbs free energy

R = Gas Constant (8.314 J/K mol)

T= Temperature in Kelvin

$$Q = \text{equilibrium constant} = \frac{[C][D]}{[A][B]}$$

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

Substitute this in Equation 1

$$-nFE = -nFE^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Divide by $-nF$ on both the sides

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

BASIC NERNST EQUATION

At 298K/25°C Substituting R=8.314, F=96,500 C

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where

E = SINGLE ELECTRODE POTENTIAL

E° = STANDARD ELECTRODE POTENTIAL

F = FARADAY (96,500°C)

n = No. of electron transfer

ANODE



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[M^+]}{[M]}$$

WHERE $[M] = 1$

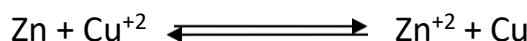
CATHODE



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[M]}{[M^+]}$$

WHERE $[M] = 1$

REDOX REACTION



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]}$$

where $[Zn]$ & $[Cu] = 1$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

Applications of Nernst Equation

- 1) It is used to study the effect of electrolyte concentration on Electrode potential.
- 2) It is used to calculate single electrode potential of a half cell.
- 3) It is used for calculations of cell potential under non standard conditions.
- 4) pH of a solution can be calculated from Nernst Equation using

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - 0.0591 \text{pH}$$

- 5) It is possible to determine the unknown concentration of one of the Species in a cell if E_{cell} and the concentration of the other Species is known.
- 6) It is used to find the valency of an ion (or) the no. of e^- involved in a reaction.
- 7) It gives equations for potentiometric and pH metric experiments.

NOTE

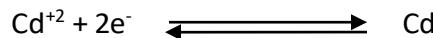
For a spontaneous reaction $\Delta G < 0, E > 0$

For reaction at Equilibrium $\Delta G = 0, E = 0$

For a non-spontaneous reaction $\Delta G > 0, E < 0$

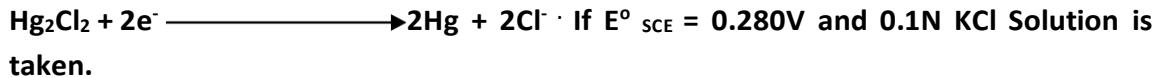
NUMERICAL PROBLEMS

- 1) Calculate the ΔG° value for standard Cd cell at 298K If $E^\circ_{\text{Cd}^{+2}/\text{Cd}} = +1.02\text{V}$



$$\begin{aligned}\Delta G^\circ &= -nFE^\circ \\ &= -2 * 96500 * 1.02\text{V} \\ \Delta G^\circ &= -196800\end{aligned}$$

- 2) Calculate the electrode potential for calomel electrode at 25°C if



$$\begin{aligned}E_{\text{SCE}} &= E^\circ_{\text{SCE}} - \frac{0.0591}{n} \log [\text{Cl}^-]^2 \\ &= 0.280 - \frac{0.0591}{2} \log [0.1]^2 \\ &= 0.280 - \frac{0.0591}{2} 2 \log [0.1] \\ &= 0.3391\text{ V}\end{aligned}$$

- 3) Calculate the single electrode potential of Cu at 25°C, If $E^\circ_{\text{Cu}^{+2}/\text{Cu}} = +0.34\text{V}$ and 0.01M CuSO_4 Solution is taken.

$$\begin{aligned}E_{\text{Cu}^{+2}/\text{Cu}} &= E^\circ_{\text{Cu}^{+2}/\text{Cu}} - \frac{0.0591}{2} \log [1/0.01] \\ &= 0.34 - \frac{0.0591}{2} \log [10]^2 \\ &= 0.34 - \frac{0.0591}{2} 2\end{aligned}$$

$$= 0.2809V$$

- 4) Calculate the cell potential of Daniel cell if ratio of concentration of $Zn^{+2} | Cu^{+2}$ = 0.1 If

$$E^o_{cell} = +1.10V.$$



$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$= 1.10 - \frac{2.303 \times 8.314 \times 303}{2 \times 96500} \log[0.1]$$

$$E_{cell} = 1.130 V$$

- 5) Calculate the Emf of following at $25^\circ C$, such that

$$Fe^{+2} | Fe || H^+ | H_2 \quad E^o_{Fe^{+2}|Fe} = -0.44V \quad E^o_{2H^+|H_2} = 0.00V$$

$$E^o_{cell} = E^o_{2H^+|H_2} - E^o_{Fe^{+2}|Fe} = 0 - (-0.44) = 0.44V$$



$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Fe^{+2}][H_2]}{[H^+]^2}$$

$$E_{cell} = 0.44 - \frac{0.0591}{2} \log \frac{[0.001]}{[1]^2}$$

$$= 0.5286V$$

- 6) Calculate the Emf of following at $25^\circ C$, such that

$$Zn | Zn^{+2} || Cu^{+2} | Cu \quad E^o_{Zn^{+2}|Zn} = -0.76V \quad E^o_{Cu^{+2}|Cu} = +0.34V$$

$0.05M, 0.01M$



$$E^o_{cell} = E_{cathode} - E_{anode}$$

$$= E^o_{Cu^{+2}|Cu} - E^o_{Zn^{+2}|Zn}$$

$$= +0.34V - (-0.76V)$$

$$= 1.10 V$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

$$E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log \frac{[0.05]}{[0.01]}$$

$$= 1.079 \text{ V}$$

REVERSIBLE & IRREVERSIBLE CELLS

A cell is said to be **REVERSIBLE** if it satisfies the 3 conditions, when connected to an external source of emf, acting in the opposite direction. If anyone of the conditions is not satisfied, then it is **IRREVERSIBLE CELL**.

- 1) If $E_{\text{ext}} > E_{\text{cell}}$ then the current flows from the external source and reactions takes place within the cell.
- 2) If $E_{\text{ext}} < E_{\text{cell}}$ then the current flows from the cell and reactions occur In the reverse direction.
- 3) If $E_{\text{ext}} = E_{\text{cell}}$ then no current flows in the circuit and no reactions takes place

TYPES OF REVERSIBLE ELECTRODES

- 1) Metal-Metal ion electrode (Ex: Daniel Electrode)
- 2) Metal-metal insoluble electrode (Ex: Calomel Electrode)
- 3) Gas-ion electrode (Ex: Hydrogen Electrode)
- 4) Redox electrode (Ex: Quinhydrone Electrode)
- 5) Ion-selective electrode(Ex: Glass Electrode)
- 6) Metal-amalgam electrode

REFERENCE ELECTRODE

Reference electrode is an electrode of standard potential, with which we can compare, the potential of other electrodes. It's reactions doesn't change, the emf of the cell.

Reference electrode are broadly classified as primary and secondary electrodes.

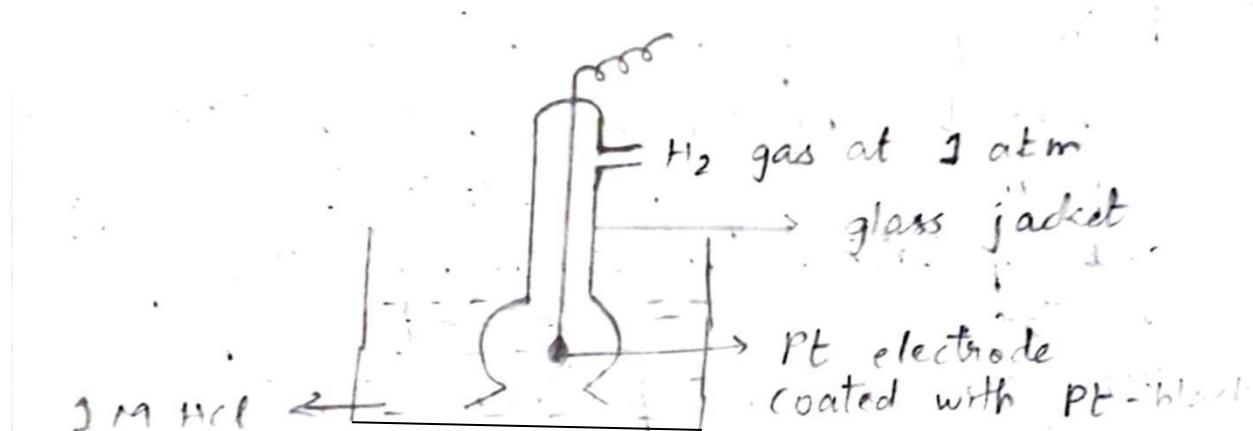
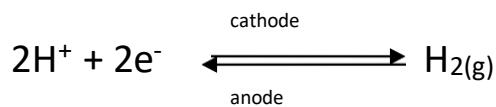
PRIMARY REFERENCE ELECTRODE

Standard Hydrogen electrode (SHE) is a primary reference electrode, used for cell potential measurements, its potential is taken as '0' at all temperatures.

SHE consists of Platinum (Pt) electrode coated with platinum black immersed in 1M HCl solution at 25°C, which is welded in a glass Jacket having side tube.

The H₂ gas is bubbled at 1atm pressure through the glass jacket over the Pt electrode, which causes in the solution.

It is quite difficult to setup hydrogen electrode at 1 atm pressure and with 1M HCl concentration and it cannot be used in solutions containing redox systems. It easily gets poisoned by Hg, As, and oxidizing Agents like MgO_4^- , $Cr_2O_7^{2-}$ and hence it cannot be used in the solutions containing these ions.



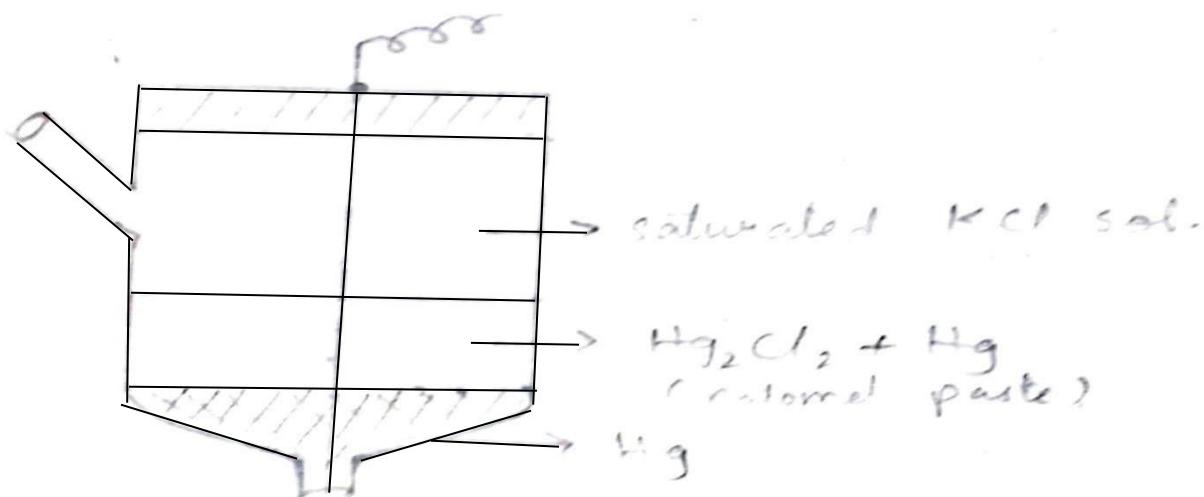
SECONDARY REFERENCE ELECTRODES

To overcome the difficulties encountered by SHE, secondary reference electrodes are used (Ex: Calomel electrode, Quinhydrone Electrode, Glass electrode).

1. SATURATED CALOMEL ELECTRODE(METAL-METAL INSOLUBLE ELECTRODE)

SCE consists of Pt wire dipped into mercury layer placed at the bottom, covered with a paste of $Hg_2Cl_2 + Hg$ (Calomel Paste) which is in contact with sat. KCl solution. The potential of calomel electrode depends on the conc. of KCl solution used.

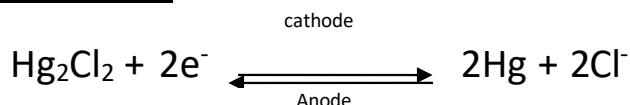
- 1) For SCE, saturated KCl is used and $E^\circ_{SCE} = 0.242$ V.
 - 2) For normal calomel electrode 1N KCl solution is used and $E^\circ_{NCE} = 0.282$ V.
- For Deci-normal Calomel Electrode 0.1N KCl solution is used and $E^\circ_{DNCE} = 0.336$ V.



ELECTRODE REPRESENTATION



ELECTRODE REACTION



ELECTRODE EMF

0.0591

$$E_{\text{SCE}} = E^{\circ}_{\text{SCE}} - \frac{0.0591}{n} \log [\text{Cl}^-]^2$$

0.0591

$$= 0.243 - \frac{0.0591}{2} \log [\text{Cl}^-]$$

$$E_{\text{SCE}} = 0.242 - 0.0591 \log [\text{Cl}^-]$$

The electrode is reversible to Cl^- ion

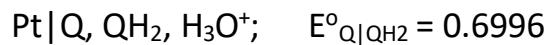
ADVANTAGES OF SCE

- 1) Simple to construct
- 2) Free from surface sensitivity
- 3) Results are stable over a long period of time at various Temperatures.

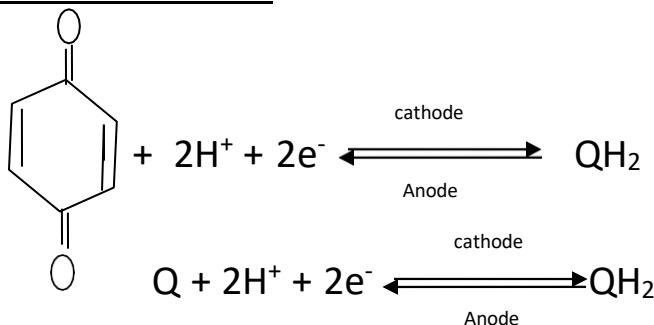
2. QUINHYDRONE (REDOX) ELECTRODE

It is an 1:1 Equimolar mixture of Quinone and hydroquinone, which consists of equilibrium in presence of H^+ ions. The electrode consists of Platinum (Pt) electrode, dipped in He solution, which is saturated in quinhydrone.

ELECTRODE REPRESENTATION:



ELECTRODE REACTIONS:



ELECTRODE EMF:

$$E_{\text{Q/QH}_2} = E^{\circ}_{\text{Q/QH}_2} - \frac{0.0591}{n} \log \frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]}$$

$$E_{Q|QH_2} = 0.6996 - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$E_{Q|QH_2} = 0.6996 - 0.0591 \log \frac{1}{[H^+]}$$

$$E_{Q|QH_2} = 0.6996 - 0.0591 \text{pH}$$

The electrode is reversible to H⁺ ions
Potential depends on pH of a solution.

ADVANTAGES:

- 1) Simple to setup
- 2) Reversibility equilibrium is achieved quickly
- 3) Best for acid-base titration
- 4) Can be used in presence of ions of many metals.

DISADVANTAGES:

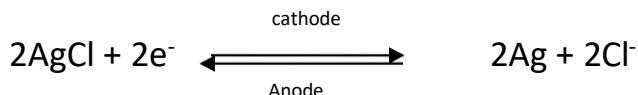
- 1) At high pH, EMF values fluctuate.
- 2) Cannot be used in redox system
- 3) Works well in pH < 8
- 3) **GLASS ELECTRODE (ION- SELECTIVE ELECTRODE)**

The Glass electrode consists of thin wall pH sensitive glass bulb at the lower end containing AgCl, coated Ag electrode or Pt wire, dipped in 0.1M HCl solution. When the electrode is placed in H⁺ test solution, Potential develops across the Glass membrane, due to the pH changes inside and outside the membrane which helps to measure pH of the solution.

CELL REPRESENTATION:



ELECTRODE REACTION:



ELECTRODE EMF:

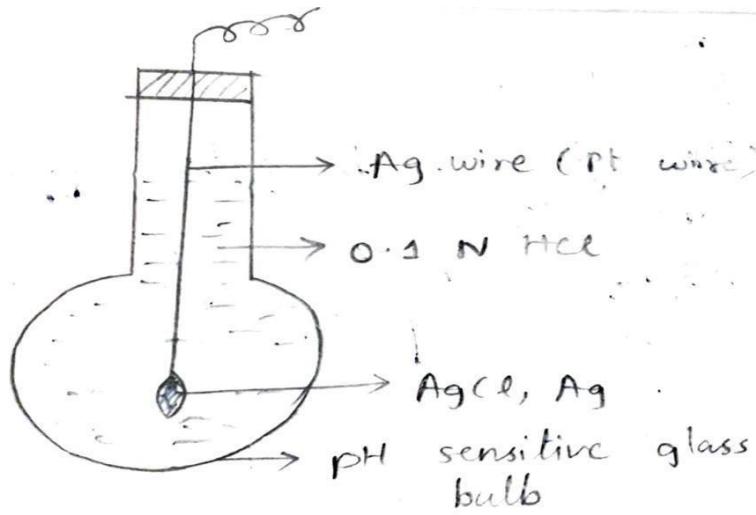
$$E_G = E^{\circ}_G - 0.0591 \text{pH}$$

ADVANTAGES:

- 1) Simple and easy to use.
- 2) Equilibrium is rapidly attained.
- 3) Accurate results.
- 4) Not easily poisoned.
- 5) Cannot be used in turbid, colloidal and colorless solutions.

DISADVANTAGES:

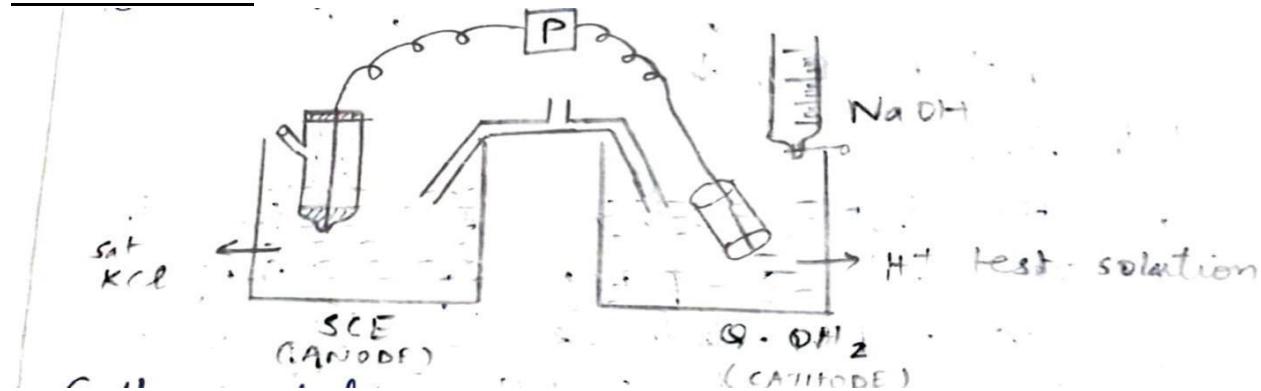
- 1) The glass bulb gets attached in pH above 12
- 2) Highly sensitive glass membrane requires special electronic potentiometer.



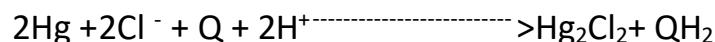
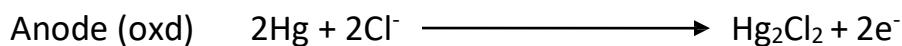
DETERMINATION OF pH OF A SOLUTION USING QUINHYDRONE ELECTRODE POTENTIOMETRIC ACID-BASE TITRATIONS

- 1) Reference electrode(ANODE)-SCE acts as anode. It consists of Hg metal covered with $\text{Hg}_2\text{Cl}_2 + \text{Hg}$ paste in contact with standard KCl solution and a Pt wire for electrical contact. $E^\circ_{\text{SCE}} = 0.242 \text{ V}$.
- 2) Indicator electrode(CATHODE)-QUINHYDRONE is the working electrode. It is 1:1 equimolar mixture of QUININE AND HYDROQUINONE. $E^\circ_{\text{Q|QH}_2} = 0.6996 \text{ V}$.

CELL DIAGRAM:



CELL NOTATION:



EMF:

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

$$E_{\text{cell}} = E_{\text{Q|QH}_2} - E_{\text{SCE}}$$

$$E_{\text{cell}} = (0.6996 - 0.0591\text{pH}) - 0.242$$

$$E_{\text{cell}} = 0.458 - 0.0591\text{pH}$$

$$\text{pH} = \frac{0.458 - E_{\text{cell}}}{0.0591}$$

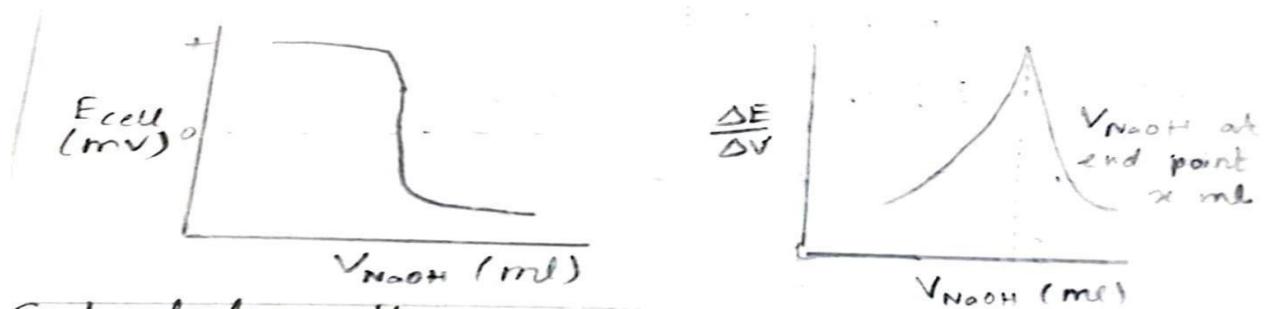
E_{cell} is a function of pH

They both are inversely proportional to each other if value of one of them increases then the value of the other decreases.

TITRATIONS

The H⁺ test solution is taken in a burette and a pinch of Quinhydrone is added. Pt electrode is dipped into the solution and NaOH is taken in the burette. In another beaker SCE is placed in saturated KCl solution. The two boxes are connected by a salt bridge and the electrodes are connected to the terminals of a potentiometer. The initial end is noted before adding NaOH solution. As NaOH is added from the Burette, The emf values gradually decrease and near the end point sudden decrease in emf occurs to the extent that the values change from +ve to -ve. This titration gives approx V_{NaOH} required and to find the exact end point the titration is repeated by adding NaOH in 0.1 ml intervals in the vicinity of the end point.

GRAPH



Q) Calculate the pH of a solution when QH₂ is used along with SCE at 25°C if E_{cell} = 0.2640 V, write the cell notation.

ANS (-)Pt|Hg,Hg₂Cl₂|KCl|H⁺ (test)|Q, QH₂|Pt⁽⁺⁾

$$\text{pH} = \frac{0.458 - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{0.458 - 0.2640}{0.0591}$$

$$= 3.28$$

Q) The potential Ag, AgCl with respect to SCE is -0.22V. Find the value of SRP of Ag, AgCl electrode.

$$\begin{aligned}E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\&= E^{\circ}_{\text{Ag|AgCl}} - E^{\circ}_{\text{SCE}} \\-0.022 \text{ V} &= E^{\circ}_{\text{Ag|AgCl}} - 0.242 \text{ V}\end{aligned}$$

$$E^{\circ}_{\text{Ag|AgCl}} = 0.220 \text{ V}$$

R) The EMF of a cell is 0.3089 V, when SCE & QH₂ are used to construct a cell. Calculate the pH of a test solution. Also calculate the pH if E_{cell} is 0.

Case I

$$E_{\text{cell}} = 0.3089$$

$$\text{pH} = \frac{0.458 - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{0.458 - 0.3089}{0.0591}$$

$$= 2.52 \text{ V}$$

Case II

$$E_{\text{cell}} = 0$$

$$\text{pH} = \frac{0.458 - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{0.458 - 0}{0.0591} = 7.7$$

UNIT 1.2

BATTERY CHEMISTRY

A Battery is a device which transforms chemical energy into electrical energy. Batteries are classified into primary, secondary and flow batteries, depending on their recharging capacities.

1. PRIMARY BATTERIES

These are non - rechargeable cells, which are meant for single use, i.e. they are to be disturbed after use. It works only as a galvanic cell, because the cell reactions are irreversible. The electrical energy is obtained at the expense of chemical reactions, the battery becomes dead, when the reactions get completely converted to products. These cells cannot be recharged.

2. SECONDARY BATTERIES

These are **RECHARGEABLE CELLS**, which are meant for multi-cycle use, it behaves both as electrolytic cell and as galvanic cell. The cell reactions are reversed by external application of current in opposite directions. Secondary batteries can be used to a number of cycles of charging and discharging, till the capacity of battery is discharged, till the capacity of the battery is lost, due to decay, leakage or short-circuit.

Ex: Lead Acid Battery, Lithium ion battery, Nickel Cadmium Battery , etc..

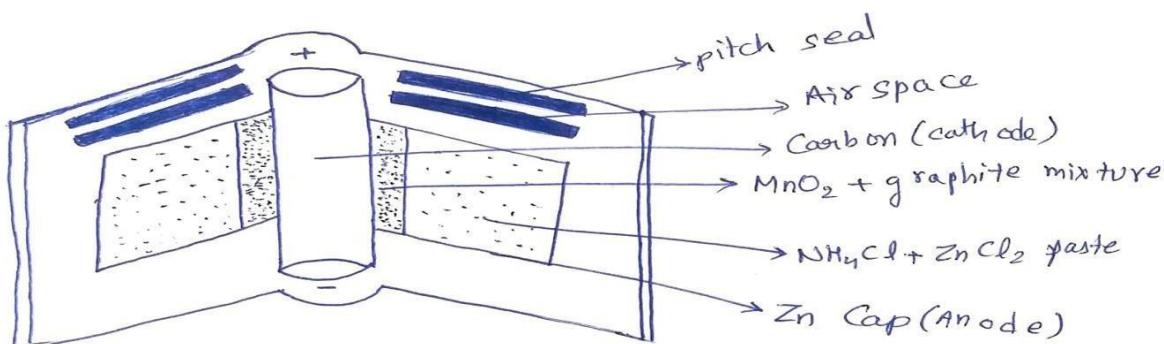
3. FLOW BATTERIES (FUEL CELLS)

It is an electrochemical cell, that converts the chemical energy of fuel and oxidant into electricity.

Ex: H₂-O₂ fuel cell

CH₃OH-O₂ fuel cell

DRY CELL (ZINC-CARBON BATTERY) (LECLANCHE-CELL)



A dry cell is a primary battery which consists of Zn anode and Carbon cathode.

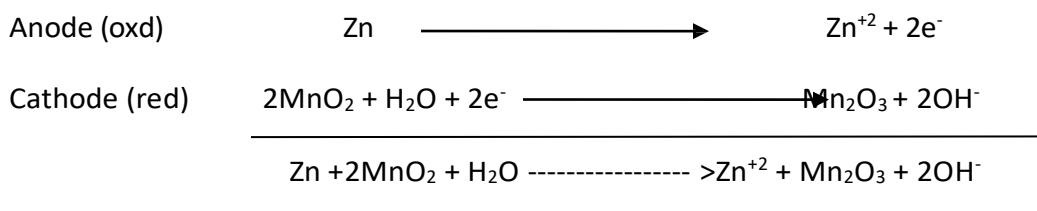
The outer container is made of Zn Sheet which acts as Anode and a graphite rod with a metal cap at the centre acts as cathode.

The Cathode is surrounded by thick moist paste of MnO_2 + Graphite. The outer layer consists of a paste of NH_4Cl + ZnCl_2 as electrolyte. To the electrolyte, starch or methyl cellulose is added so that the battery becomes stable, against discharging. The entire setup is packed-in propylene or cardboard material and a plastic coating is given to prevent any leakage from the battery.

It is called as **DRY CELL** due to the absence of any mobile liquid.

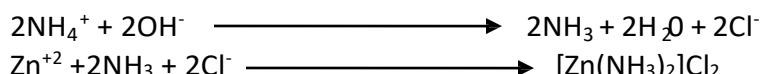
CELL REACTIONS

PRIMARY REACTION



SECONDARY REACTION

The OH^- produced at the electrodes react with NH_4Cl to produce ammonia which disrupts the flow of current. This is prevented by reacting NH_3 with ZnCl_2 to form a complex.



OVERALL REACTION



ADVANTAGES

- 1) Maintains better voltage as current is drawn from it
- 2) Low cost and readily available
- 3) Reasonable power density & reliable performance
- 4) Gives voltage of 1.5 V
- 5) Zn does not readily dissolve in basic medium

DISADVANTAGES

1. Not suitable for high voltage applications
2. Not Rechargeable
3. Optimum Temperature range
4. Self Discharging takes place by evolution of H_2
5. The cell runs down slowly even when not in use.

APPLICATIONS /USES

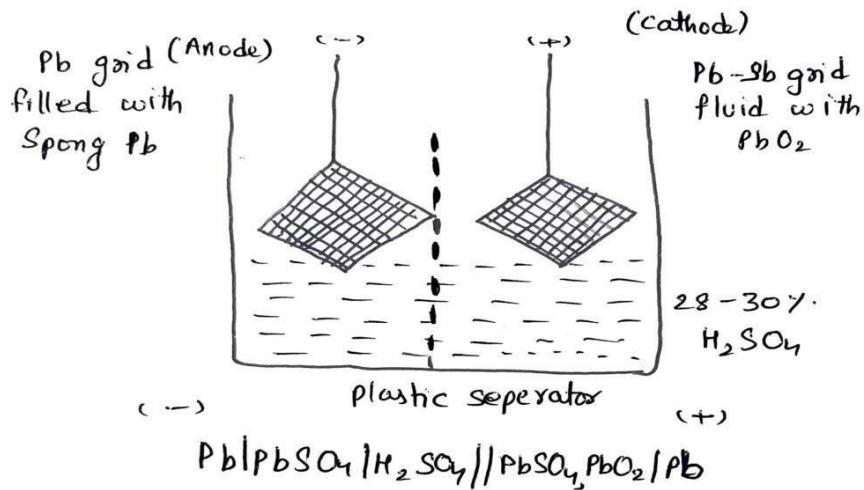
Used in Calculators, portable electric or electronic devices, watches, photographic equipments, Transistors, etc.

LEAD-ACID BATTERY (SECONDARY STORAGE CELL)

The Lead-Acid Battery is so-called because the electrolyte is an acid and the electrodes largely comprises of lead plates. The Anode is lead grid filled with spongy lead while the Lead(Pb)-Antimony(Sb) grid filled with PbO₂ and an inert porous material separates the 2 electrodes. The electrolyte comprises of 23-30% H₂SO₄, specific gravity is 1.2. The Battery consists of 3-6 such cells, joined together in series enclosed in an bonite case.

Each cell gives the voltage of 2 volts and 6 such cells can generate 12 volts.

CELL DIAGRAM

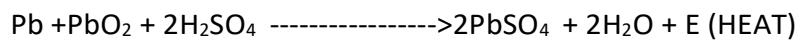
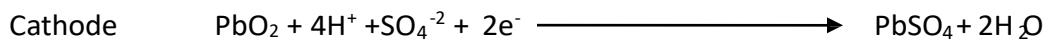
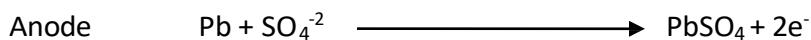


That the EMF of the cell depends on the concentration of H₂SO₄ used during discharging to density of the battery decreases from 1.2g/cc to 1g/cc indicating the weakening of the battery.

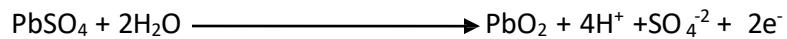
This when the concentration of H₂SO₄ decreases to 5% the battery is charged by connecting it to an external source of EMF.

During discharging the battery acts as a galvanic cell & during charging it acts as a electrolytic cell.

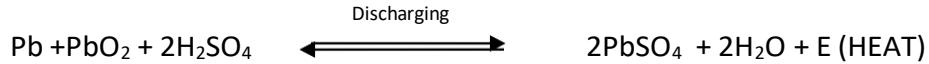
DISCHARGING (GALVANIC CELL)



CHARGING (ELECTROLYTIC CELL)



OVERALL REACTION



Charging

APPLICATIONS/USES

It is used in Automobiles, Electric vehicles, UPS, Submarines, Hospitals, Laboratories, etc..

LITHIUM - ION BATTERY

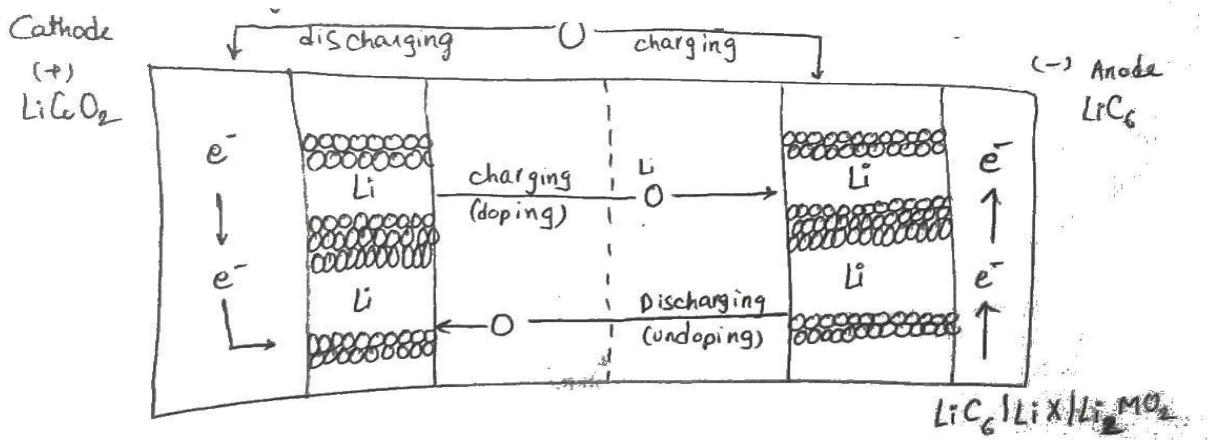
The cell reaction is lithium-ion battery involved the migration of lithium ions between positive & negative electrodes. They are no chemical reactions at the electrodes or in the electrolytic or change in the electrolytic concentration in LIB, the anode is carbon & the graphite in which the lithium is introduced to form lithium graphite intercalated Compounds [LIGIC]. The cathode comprises of lithium metal Oxide complexes. Like to LiCoO_2 , LiMnO_2 .

The electrolyte is complex lithium salts in solvents like LiPF_6 . A Porous membrane acts as a separator b/w the anode and the cathode.

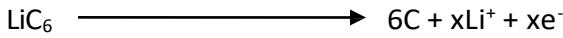
During charging of LIB, the lithium ions are extracted by electrochemical oxidation from the cathode and doped by electrochemical reduction into LIGIC carbon Anode.

During Discharging the lithium ions are extracted from anode by oxidation & inserted into cathode by reduction process.

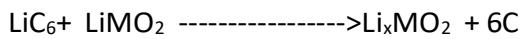
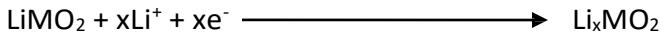
Thus Li doping is charging and undoping is discharging.



Anode



Cathode



APPLICATIONS/USES:

Widely used in mobile phones, laptops, video cameras, electric vehicles, etc..

FUEL CELL

A Fuel cell is a galvanic cell that converts chemical energy of a fuel (H_2 , CH_4 , CH_3OH) and an oxidant(air/ O_2) into electricity.

ADVANTAGES

1. High efficiency of energy conversion.
2. Silent operation therefore no noise pollution.
3. Free from vibration heat transfer & thermal pollution.
4. The waste products are harmless and eco-friendly.
5. Recharging of fuel is not required.
6. Requires less attention and low maintenance cost.
7. Saves fossil fuels.

DISADVANTAGES

1. Initial cost is high
2. Fuel in form of gas & O_2 needs to be stored in tanks under pressure
3. Power output is moderate.
4. For appreciable voltage, a battery of fuel cell must be available.

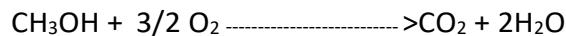
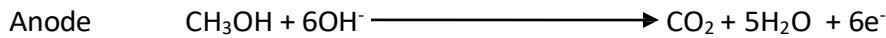
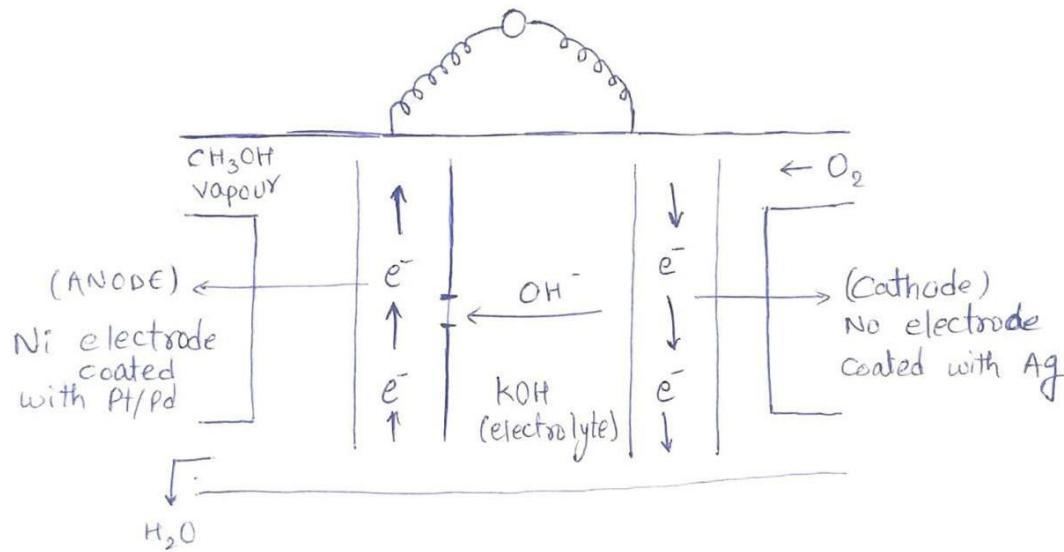
Methanol- Oxygen Fuel Cell ($\text{CH}_3\text{OH} + \text{O}_2$)

In Methanol Oxygen fuel cell CH_3OH vapors are used as fuel at Anode and oxygen as oxidant at cathode. The Anode is porous nickle sheet coated with platinum-palladium catalyst. Cathode is porous nickle sheet coated with silver catalyst.

Alkaline KOH is taken b/w the 2 electrodes as electrolyte. For continuous supply of electricity CH₃OH vapors are passed through Anode and O₂ and oxygen through cathode.

ADVANTAGES & APPLICATIONS

1. Can store high energy content in small space.
2. Produces limited power with high efficiency.
3. Produces no toxic effluence.
4. Used in military equipments as battery charger, also used in space crafts, submarines, etc.



UNIT 2.1

WATER CHEMISTRY

water is the most essential element required by human beings.

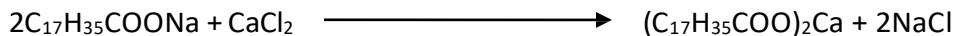
It has wide applications in Engineering as it is used in industries such as paper, textile, laundry, boiler, chemical industries, etc..

SOURCES OF WATER

- 1) Rainwater is the purest form of natural water but gets contaminated due to the pollutants in atmosphere.
- 2) River water dissolves the minerals of soil as it flows.
- 3) Lake water contains constant chemistry composition but high quantity of organic matter
- 4) Sea water is the most impure form of natural water containing high amounts of salts.
- 5) Underground water contains more of dissolved salts but is of high organic purity.

HARDNESS OF WATER

Hardness is caused due to the presence of dissolved salts of Ca & Mg and other heavy metals which prevents lathering of soaps. When hard water is treated with the soap it does not produce lather but instead produces a white scum or ppt due to formation of insoluble salts of Ca & Mg.



TYPES OF HARDNESS

CARBONATE HARDNESS (TEMPORARY)

It is caused due to presence of dissolved carbonates of Ca & Mg and other heavy metals.

It can be destroyed by boiling.



PERMANENT HARDNESS (NON-CARBONATE HARDNESS)

Caused by chlorides & Sulphates of Ca & Mg and other heavy metals. It cannot be removed by boiling. But requires chemical treatment for its removal.

$$\text{TOTAL HARDNESS} = \text{TEMPORARY HARDNESS} + \text{PERMANENT HARDNESS}$$

UNITS OF HARDNESS

PPM (PARTS PER MILLION) – No. of parts of CaCO_3 equivalents hardness present in 1 MILLION (10^6) parts of water.

MILLIGRAMS PER LITRE (mg/l) – No. of Mg CaCO₃ equivalents hardness present in 1 litre of water.

DEGREE CLARKE (°Cl) – No. of parts of CaCO₃ equivalents present in 70k parts of water.

DEGREE FRENCH (°Fr) – No. of parts of CaCO₃ equivalents present in 10⁵ parts of water.

MILLIEQUIVALENTS PER LITRE (mg/l) – No. of milli equivalents of CaCO₃ equivalents hardness present in 1 litre of water

$$1\text{PPM} = 1 \text{ mg/l} = 0.07^\circ\text{Cl} = 0.01^\circ\text{Fr} = 0.02\text{m.eq/l}$$

Q) Why is Hardness always expressed in terms of CaCO₃?

Hardness is always expressed in terms of equivalents of CaCO₃. As the weight of CaCO₃ & equivalent weight is 50. So, expressing hardness in terms of CaCO₃ is easy. Moreover it is the most insoluble salt that can be easily precipitated in water treatment, hence hardness is always expressed in terms of CaCO₃.

Q) Calculate the hardness present in water sample containing 168mg/l MgCO₃ salt.

Ans:

$$\begin{aligned} &\frac{168 \times 100}{\text{M.wt. of MgCO}_3} \rightarrow \text{M.wt. of CaCO}_3 \\ &\text{M.wt. of MgCO}_3 \leftarrow 84 \\ &= 200 \text{ mg/l} \\ &= 200 \text{ ppm} \end{aligned}$$

Q) Calculate hardness caused by 2 g of CaCO₃ present in 500 ml of water.

Ans

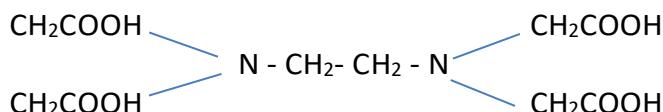
$$\begin{aligned} &\frac{2000 \text{ mg}}{0.5 \text{ l}} \\ &= 4000 \text{ mg/l} \\ &= 4000 \text{ ppm} \end{aligned}$$

Q) Calculate the temporary and permanent hardness in a water sample containing 7.3mg/l Mg(HCO₃)₂, 16.2 Ca(HCO₃)₂, 9.5 mg/l MgCl₂, 13.6 mg/l CaSO₄ and 4mg/l NaCl.

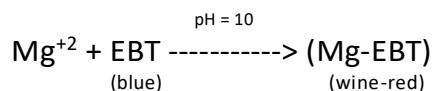
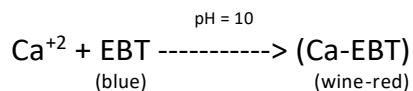
DETERMINATION OF HARDNESS BY EDTA

The hardness of water is usually measured as concentration of Ca²⁺ and Mg²⁺ ions only. Its determination by EDTA involves complexo-metric titrations.

EDTA is **ETHYLENE DI-AMINE TETRA-ACETIC ACID** which is available as its di-sodium salts obtained in high purity state and can be used as standard solution. EDTA solution serves as a valuable titrant because the reagent combines with metal ions in 1:1 ratio.

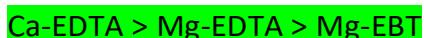


In order to determine the equivalence point EBT(ERIOCHROME BLACK T) indicator is used. The EBT is blue in colour and forms weak unstable wine-red complexes with Ca²⁺ and Mg²⁺ ions. As EBT indicator functions in pH = 10, the hard water to which it is added is buffered using NH₄OH + NH₄Cl.



During the titration against EDTA solution first the free Ca^{+2} and Mg^{+2} ions combine with EDTA to form **stable, colourless (M-EDTA) complexes**. After all the free ions are consumed, the next drop of EDTA displaces EBT from (M-EBT) complexes, thereby releasing free EBT.

Hence at the end point colour changes from **wine red to blue**.



This gives total hardness in water

To estimate the permanent hardness first, temporary hardness is removed by boiling. The solution is filtered to remove the ppt and then titrated with EDTA.

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

Temporary hardness is calculated by subtracting permanent hardness from total hardness.

PREPARATION OF SOLUTIONS

- 1) STD. HARD WATER (1g CaCO_3 dissolved in HCl and made upto 1litre by distilled water.)
- 2) EDTA SOLUTION (4g of EDTA crystals made upto 1 litre)
- 3) EBT INDICATOR (0.5 EBT in 100ml of alcohol)
- 4) BUFFER SOLUTION (67.5g of NH_4Cl + 570 ml of NH_4OH)

PROCEDURE

1) PREPARATION OF STD. HARD WATER

1g of CaCO_3 dissolved in HCl and made upto 1 litre with distilled water.

2) STANDARDIZATION OF EDTA SOLUTION (V_1 ml)

20 ml standard water + 5 drops EBT + buffer

Titrate against EDTA till wine red changes to blue.

3) DETERMINATION OF TOTAL HARDNESS (V_2 ml)

20ml sample water + 5ml EBT + buffer

Titrate against EDTA till wine-red changes to blue.

4) DETERMINATION OF PERMANENT HARDNESS (V_3 ml)

100ml of sample water is boiled to 1/4th of its original volume to remove temporary hardness. It is then filtered to remove the ppt & the filtrate is made up-to the mark of 100ml with distilled water.

20ml boiled water + 5 drops EBT + buffer

Titrate against EDTA till wine-red changes to blue.

CALCULATIONS

1) STANDARDIZATION OF EDTA SOLUTION (V_1 ml)

20 ml standard hard water = V_1 ml EDTA

20ml x 1mg CaCO₃ equivalents = V_1 ml EDTA

1ml EDTA = $20 \times 1 / V_1$ mg CaCO₃

$$1\text{ml EDTA} = \frac{20}{V_1} \text{ mg CaCO}_3 \text{ equivalents}$$

2) DETERMINATION OF TOTAL HARDNESS (V_2 ml)

20 ml sample water = V_2 ml EDTA

$$= V_2 \times \frac{20}{V_1} \text{ mg CaCO}_3 \text{ equivalents}$$

1000 ml or 1litre sample water = $1000 \times v_2 \times 20/v_1 \times 1/20$ mg/l

$$\text{Total hardness} = \frac{v_2}{v_1} \times 1000 \text{ ppm}$$

3) DETERMINATION OF PERMANENT HARDNESS (V_3 ml)

20 ml of boiled water = V_3 ml EDTA

$$= V_3 \times \frac{20}{V_1} \text{ mg CaCO}_3 \text{ equivalents}$$

1000 ml or 1litre sample water = $1000 \times v_3 \times 20/v_1 \times 1/20$ mg/l

$$\text{Permanent hardness} = \frac{v_3}{v_1} \times 1000 \text{ ppm}$$

4) TEMPORARY HARDNESS

$$\begin{aligned}\text{TEMPORARY HARDNESS} &= \text{TOTAL HARDNESS} - \text{PERMANENT HARDNESS} \\ &= 1000(V_2/V_1) - 1000(V_3/V_1)\end{aligned}$$

$$\text{Total hardness} = \frac{1000(v_2-v_3)}{v_1} \text{ ppm}$$

1) Standard Hard water contains 15g of CaCO_3 in 1l of water, 20ml of this solution requires 25ml of EDTA solution during titration, 100 ml of sample water required 18ml of EDTA using EBT indicator, after boiling cooling & filtering the solution requires 12ml of EDTA. estimate the types of hardness present in the water sample.

20 ml std - 25ml EDTA

20 ml x 15 mg CaCO_3 eq - 25 ml EDTA

1ml EDTA = $(20 \times 15)/25$ mg CaCO_3 .

$$1\text{ml EDTA} = 12\text{mg } \text{CaCO}_3 \text{ eq}$$

DETERMINATION OF TOTAL HARDNESS (V2 ml)

$$\begin{aligned}100\text{ml sample} &= 18\text{ml EDTA} \\ &= 18 \times 12 \text{ mg } \text{CaCO}_3 \\ &= 216 \text{ mg } \text{CaCO}_3\end{aligned}$$

For 1000 ml = $(216 \times 1000)/100$

$$\text{TOTAL HARDNESS} = 2160 \text{ ppm}$$

DETERMINATION OF PERMANENT HARDNESS (V3 ml)

$$\begin{aligned}100\text{ml boiled water} &= 12 \text{ ml EDTA} \\ &= 12 \times 12 \text{ mg } \text{CaCO}_3 \text{ eq.} \\ &= 144 \text{ mg } \text{CaCO}_3 \text{ eq.}\end{aligned}$$

For 1000 ml = $(144 \times 1000)/100 = 1440 \text{ ppm}$

$$\text{PERMANENT HARDNESS} = 1440 \text{ ppm}$$

$$\begin{aligned}\text{TEMPORARY HARDNESS} &= 2160 - 1440 \\ &= 720 \text{ ppm}\end{aligned}$$

METHOD II

PREPARATION OF STANDARD HARD WATER

$$N_{SHW} = \frac{\text{Wt}}{\text{Eq wt}} \times \frac{1000}{Vml}$$

$$N_{SHW} = \frac{15}{50} \times \frac{1000}{1000} = 0.3N$$

STANDARDIZATION OF EDTA

$$N_{EDTA} = \frac{N_{SHW} \times V_{SHW}}{V_{EDTA}}$$

$$N_{EDTA} = \frac{0.3 \times 20}{25} = 0.24$$

DETERMINATION OF TOTAL HARDNESS (V₂ ml)

$$N_{sample\ water} = \frac{N_{EDTA} \times V_{EDTA}}{V_{SW}}$$

$$N_{sample\ water} = \frac{0.24 \times 18}{100} = 0.0432$$

Wt.of CaCO₃ eq. = N x eq wt. = 0.0432 x 50 = 2.16 gpl = 2.16 x 1000= 2160 mgL⁻¹ = 2160 ppm²

DETERMINATION OF PERMANENT HARDNESS (V₃ ml)

$$N_{Boiled\ water} = \frac{N_{EDTA} \times V_{EDTA}}{V_{Boiled}}$$

$$N_{Boiled\ water} = \frac{0.24 \times 12}{100} = 0.0288$$

Wt. Of CaCO₃ eq. = N X eq.wt. = 0.0288 x 50 = 1.44gpl

Permanent Hardness = 1.44 x 1000= 1440 ppm

Temporary Hardness = 2160 - 1440 = 720 ppm

2) 250ml of sample hard water required 17ml of 0.025 M EDTA solution. Calculate the total hardness in water sample

DETERMINATION OF TOTAL HARDNESS

$$M_{sample\ water} = \frac{M_{EDTA} \times V_{EDTA}}{V_{water\ sample}}$$

$$M_{\text{sample water}} = \frac{0.025 \times 17}{250} = 0.0017$$

$$\begin{aligned}\text{Wt of CaCO}_3 \text{ eq.} &= M \times \text{mol. Wt.} \\ &= 0.0017 \times 100 \\ &= 0.17 \text{ gpl}\end{aligned}$$

$$\begin{aligned}\text{Total Hardness} &= 0.17 \times 1000 \\ &= 170 \text{ mg/l} \\ &= 170 \text{ ppm}\end{aligned}$$

3) 250ml of sample water was boiled, cooled and filtered and made up-to its original volume with distilled water. It required 3 ml of N/50 EDTA solution. Estimate the type of hardness.

DETERMINATION OF PERMANENT HARDNESS

$$N_{\text{Boiled water}} = \frac{N_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{Boiled water}}}$$

$$N_{\text{Boiled water}} = \frac{0.02 \times 3}{250} = 0.00024$$

$$\text{Wt. Of CaCO}_3 \text{ eq.} = N \times \text{eq.wt.} = 0.0024 \times 50 = 0.012 \text{ gpl}$$

$$\text{PERMANENT HARDNESS} = 0.012 \times 1000 = 12 \text{ mg/l} = 12 \text{ ppm}$$

4) 50ml of standard hard water containing 1mg of CaCO₃ per ml consumes 25ml of EDTA solution. 50ml of sample water consumes 25ml of EDTA solution using EBT indicator. Estimate the type of hardness present.

$$N_{\text{HW}} = \frac{\text{Wt}}{\text{Eq wt}} \times \frac{1000}{V_{\text{ml}}}$$

$$= \frac{0.0019}{50} \times \frac{1000}{1} = 0.02$$

$$N_{\text{EDTA}} = \frac{N_{\text{HW}} \times V_{\text{HW}}}{V_{\text{EDTA}}}$$

$$= \frac{0.02 \times 50}{25} = 0.04$$

$$N_{\text{sample water}} = \frac{N_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample water}}}$$

$$N_{\text{sample water}} = \frac{0.04 \times 25}{50} = 0.02$$

Wt. Of CaCO_3 eq. = $N \times \text{eq.wt.} = 0.02 \times 50 = 1 \text{ gpl}$

TOTAL HARDNESS = $1 \times 1000 = 1000 \text{ mg/l} = 1000 \text{ ppm}$

5) 100ml of sample water consumed 30 ml of 0.01M EDTA solution during the titration using EBT indicator. After, boiling, cooling and filtering, the sample water required 10ml of the same EDTA solution. Calculate the hardness.

$$M_{\text{sample water}} = \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample water}}}$$

$$= \frac{0.01 \times 20}{100} = 0.003$$

Wt. Of CaCO_3 eq. = $M \times \text{mol.wt.} = 0.003 \times 100 = 0.3 \text{ gpl}$

TOTAL HARDNESS = $0.3 \times 1000 = 300 \text{ mg/l} = 300 \text{ ppm}$

$$M_{\text{Boiled water}} = \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{Boiled water}}}$$

$$= \frac{0.01 \times 10}{100} = 0.001$$

Wt. Of CaCO_3 eq. = $M \times \text{mol.wt.} = 0.001 \times 100 = 0.1 \text{ gpl}$

TOTAL HARDNESS = $0.1 \times 1000 = 100 \text{ mg/l} = 100 \text{ ppm}$

TEMPORARY HARDNESS = TOTAL HARDNESS - PERMANENT HARDNESS = $300 - 100 = 200 \text{ ppm}$

6) 50ml of sample water required 10 ml of 0.01M EDTA solution during the titration to estimate the hardness. The sample water was boiled, cooled and filtered, and made upto its original volume with distilled water. It required 4 ml of EDTA solution. Calculate the hardness.

$$M_{\text{sample water}} = \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample water}}} = \frac{0.01 \times 10}{50} = 0.002$$

Wt. Of CaCO_3 eq. = $M \times \text{mol.wt.} = 0.002 \times 100 = 0.2 \text{ gpl}$

TOTAL HARDNESS = $0.2 \times 1000 = 200 \text{ mg/l} = 200 \text{ ppm}$

$$M_{\text{Boiled water}} = \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{Boiled water}}} = \frac{0.01 \times 4}{50} = 0.0008$$

Wt. Of CaCO_3 eq. = $M \times \text{mol.wt.} = 0.0008 \times 1000 = 0.08 \text{ gpl}$

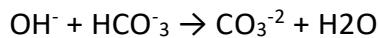
TOTAL HARDNESS = $0.1 \times 1000 = 100 \text{ mg/l} = 100 \text{ ppm}$

PERMANENT HARDNESS = $0.08 \times 1000 = 80 \text{ mg/l} = 80 \text{ ppm}$

TEMPORARY HARDNESS = TOTAL HARDNESS - PERMANENT HARDNESS = $200 - 80 = 120 \text{ ppm}$

ALKALINITY OF WATER

Alkalinity is a measure of ability of water to neutralize the acids. It is defined as the total content of those substances which cause an increase in the hydroxide concentration upon dissociation or due to hydrolysis. The alkalinity of water is caused due to: i) Caustic alkalinity - CO_3^{2-} , OH^- ii) Temporary hardness - HCO_3^- But all the three types of ions cannot exist together because:



Alkalinity in water is estimated by titrating against a standard acid using phenolphthalein and methyl orange as indicators.

- i) $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$
- ii) $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$
- iii) $\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2$

The titration of water sample against Standard acid upto [P] end point marks. the completion of reactions & and & i-e. Complete neutralization of OH^- ions and half of CO_3^{2-} ions. Whereas titration up-to [M] end point corresponds to completion of reactions 1, 2 & 3

PROCEDURE

100 ml of sample water is taken in a conical flask and 2-3 drops of phenolphthalein indicator is added.

It is titrated against 0.02N HCl solution or H₂SO₄ solution till the pink colour disappears [P]. then to the same solution methyl orange indicator is added and the titrations are continued till the solution changes to red colour [M].

CARBONATES : (CO₃⁻²)

$$N_{CO_3^{2-}} = \frac{N_{HCl} \times V_{HCl}}{V_{CO_3^{2-}}}$$

Wt. Of CO₃⁻² = N_{CO₃⁻²} X eq.wt.

Wt. Of CaCO₃ eq. = wt of CO₃⁻² x (50/30) = x gpl x 1000 = _____ ppm

BICARBONATES : (HCO₃⁻)

$$N_{HCO_3^-} = \frac{N_{HCl} \times V_{HCl}}{V_{HCO_3^-}}$$

Wt. Of HCO₃⁻ = N_{HCO₃⁻} X eq.wt.

Wt. Of CaCO₃ eq. = wt of HCO₃⁻ x (50/61) = y gpl x 1000 = _____ ppm

HYDROXIDES : (OH⁻)

$$N_{OH^-} = \frac{N_{HCl} \times V_{HCl}}{V_{OH^-}}$$

Wt. Of OH⁻ = N_{OH^-} X eq.wt.

Wt. Of CaCO₃ eq. = wt of OH⁻ x (50/17) = z gpl x 1000 = _____ ppm

RESULTS OF TITRATIONS:

- i) when p=0, alkalinity is only due to HCO₃⁻ ions.
- ii) when p=m, alkalinity is due to OH⁻ ions.
- iii) when p= 1/2m, then only carbonate (CO₃⁻²) ions are present [As 1/2 of CO₃⁻² neutralisation is with phenolphthalein and complete neutralisation is with methyl orange. Alkalinity due to CO₃⁻² = 2p].
- iv) when p> 1/2M, the ions present are CO₃⁻² and OH⁻ Alkalinity due to CO₃⁻² is equal to 2 (M-P) and OH⁻ = 2P-M.
- iv) when p < 1/2m, both carbonates and bicarbonates are present. Alkalinity due to carbonates = 2p and bicarbonates= m-2p

S.no.	RESULT	OH^-	CO_3^{2-}	HCO_3^-
1	$P=0$			M
2	$P=M$	$P=M$		
3	$P = 1/2 M$		$2P$	
4	$P > 1/2 M$	$2P-M$	$2(M-P)$	
5	$P < 1/2 M$		$2P$	$M-2P$

Q) 50ml of sample water required 5ml of N/50 HCl using methyl orange indicator but did not give any colour with phenolphthalein: Estimate the alkalinity present.

As $P=0$, Alkalinity is due to HCO_3^- ions

$$N_{\text{HCO}_3^-} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{HCO}_3^-}} = \frac{0.02 \times 5}{50} = 0.02$$

$$\text{Wt. Of } \text{HCO}_3^- = N_{\text{HCO}_3^-} \times \text{eq.wt.} = 0.02 \times 61 = 0.122$$

$$\text{Wt. Of CaCO}_3 \text{ eq.} = \text{wt of } \text{HCO}_3^- \times (50/61) = 0.122 \times (50/61) = 0.1 \text{ gpl} = 0.1 \times 1000 = 100 \text{ mg/l} = 100 \text{ ppm}$$

Alkalinity due to HCO_3^- ions = 100 ppm.

Q) 200ml of water sample on titration with 0.02N HCl solution using phenolphthalein Indicator required 10ml of the acid. Another lot of 200ml sample, water also required 10ml of the acid to obtain methyl orange end point. Determine the alkalinity..

As $P= M$, Alkalinity is due to OH^- ions

$$N_{\text{OH}^-} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{OH}^-}} = \frac{0.02 \times 10}{200} = 0.001$$

$$\text{Wt. Of } \text{OH}^- = N_{\text{OH}^-} \times \text{eq.wt.} = 0.001 \times 17 = 0.017$$

$$\text{Wt. Of CaCO}_3 \text{ eq.} = \text{wt of } \text{OH}^- \times (50/17) = 0.017 \times (50/17) = 0.05 \text{ gpl} = 0.05 \times 1000 = 50 \text{ mg/l} = 50 \text{ ppm}$$

Alkalinity due to OH^- ions = 50 ppm

Q) 100ml of water sample required 30ml of N/50 HCl upto P-end point and another 20ml for complete neutralisation upto M-end point. Determine the type of alkalinity present in the water sample.

$$P = 20 \text{ ml}, M = 20+30 = 50 \text{ ml}$$

As $P > 1/2M$, Alkalinity due to $\text{OH}^- = 2P-M$ and $\text{CO}_3^{2-} = 2(M-P)$

$$\text{OH}^- = 2P-M = (2 \times 30) - 50 = 10 \text{ ml}$$

$$\text{CO}_3^{2-} = 2(\text{M}-\text{P}) = 2(50 - 30) = 40 \text{ ml}$$

$$N_{\text{OH}^-} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{OH}^-}} = \frac{0.02 \times 10}{100} = 0.002$$

$$\text{Wt. Of OH}^- = N_{\text{OH}^-} \times \text{eq.wt.} = 0.002 \times 17 = 0.034$$

$$\text{Wt. Of CaCO}_3 \text{ eq.} = \text{wt of OH}^- \times (50/17) = 0.034 \times (50/17) = 0.1 \text{ gpl} = 0.1 \times 1000 = 100 \text{ mg/l} = 100 \text{ ppm}$$

$$N_{\text{CO}_3^{2-}} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{CO}_3^{2-}}} = \frac{0.02 \times 40}{100} = 0.008$$

$$\text{Wt. Of CO}_3^{2-} = N_{\text{CO}_3^{2-}} \times \text{eq.wt.} = 0.008 \times 30 = 0.24$$

$$\text{Wt. Of CaCO}_3 \text{ eq.} = \text{wt of CO}_3^{2-} \times (50/30) = 0.24 \times (50/30) = 0.4 \text{ gpl} = 0.4 \times 1000 = 400 \text{ mg/l} = 400 \text{ ppm}$$

Alkalinity due to OH^- ions = 100 ppm and due to CO_3^{2-} = 400 ppm

$$\text{Total alkalinity} = 100 + 400 = 500 \text{ ppm}$$

Q) 500 ml of water sample on titration with N/50 H₂SO₄ gave a titre value of 29 ml upto P. end point and another 500ml Sample on titration with same and gave a titre value of 58ml upto M-end point. Determine the type of alkalinity.

$$P = 29 \text{ ml}, M = 58 \text{ ml}$$

$$\text{As } P = 1/2M, \text{ Alkalinity is due to CO}_3^{2-} = 2P$$

$$\text{CO}_3^{2-} = 2P = 2 \times 29 = 58 \text{ ml}$$

$$N_{\text{CO}_3^{2-}} = \frac{N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4}}{V_{\text{CO}_3^{2-}}} = \frac{0.02 \times 58}{500} = 0.00232$$

$$\text{Wt. Of CO}_3^{2-} = N_{\text{CO}_3^{2-}} \times \text{eq.wt.} = 0.00232 \times 30 = 0.0696$$

$$\text{Wt. Of CaCO}_3 \text{ eq.} = \text{wt of CO}_3^{2-} \times (50/30) = 0.0696 \times (50/30) = 0.116 \text{ gpl} = 0.116 \times 1000 = 116 \text{ mg/l} = 116 \text{ ppm}$$

Alkalinity due to CO_3^{2-} ions = 116 ppm

Q) 100 ml of sample water required 4 ml of N/50 HCl solution up-to P end point. It requires another 16ml of the same acid for further titration up-to M - endpoint. Determine the type of alkalinity present.

$$P = 4 \text{ ml}, M = 16 + 4 = 20 \text{ ml}$$

$$\text{As } P < 1/2M, \text{ Alkalinity is due to :}$$

$$\text{CO}_3^{2-} = 2P = 2 \times 4 = 8 \text{ ml}$$

$$\text{HCO}_3^- = M - 2P = 20 - 8 = 12 \text{ ml}$$

$$N_{\text{CO}_3^{2-}} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{CO}_3^{2-}}} = \frac{0.02 \times 8}{100} = 0.0016$$

Wt. Of CO_3^{2-} = $N_{\text{CO}_3^{2-}} \times \text{eq.wt.} = 0.0016 \times 30 = 0.048$

Wt. Of CaCO_3 eq. = wt of $\text{CO}_3^{2-} \times (50/30) = 0.048 \times (50/30) = 0.08 \text{ gpl} = 0.08 \times 1000 = 80 \text{ mg/l} = 80 \text{ ppm}$

Alkalinity due to CO_3^{2-} ions = 80 ppm

$$N_{\text{HCO}_3^-} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{HCO}_3^-}} = \frac{0.02 \times 12}{100} = 0.0024$$

Wt. Of HCO_3^- = $N_{\text{HCO}_3^-} \times \text{eq.wt.} = 0.0024 \times 61 = 0.1464$

Wt. Of CaCO_3 eq. = wt of $\text{HCO}_3^- \times (50/61) = 0.1464 \times (50/61) = 0.12 \text{ gpl} = 0.12 \times 1000 = 120 \text{ mg/l} = 120 \text{ ppm}$

Alkalinity due to HCO_3^- ions = 120 ppm.

Total alkalinity = 120 + 80 = 200 ppm

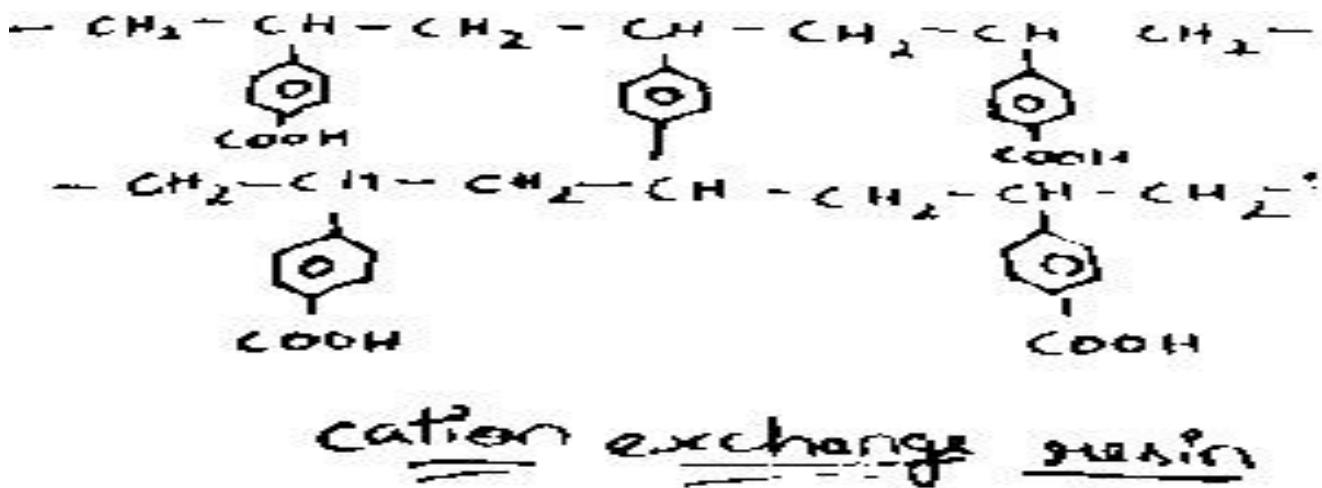
WATER SOFTENING METHOD:

Ion Exchange Process (De-ionization or De-mineralization):

In this process, water is passed through two cylinders containing the cation exchange resin and the anion exchange resin where the H^+ replace the cations. (Mg^{+2} , Ca^{+2}) and OH^- replace the anions (HCO_3^- , Cl^- , SO_4^{2-}) respectively which are responsible for causing hardness in water. The water softened by this method has by 10 ppm hardness and it is as good as distilled water. When the resins get used up, they are said to be exhausted and are regenerated by acid or alkaline treatment.

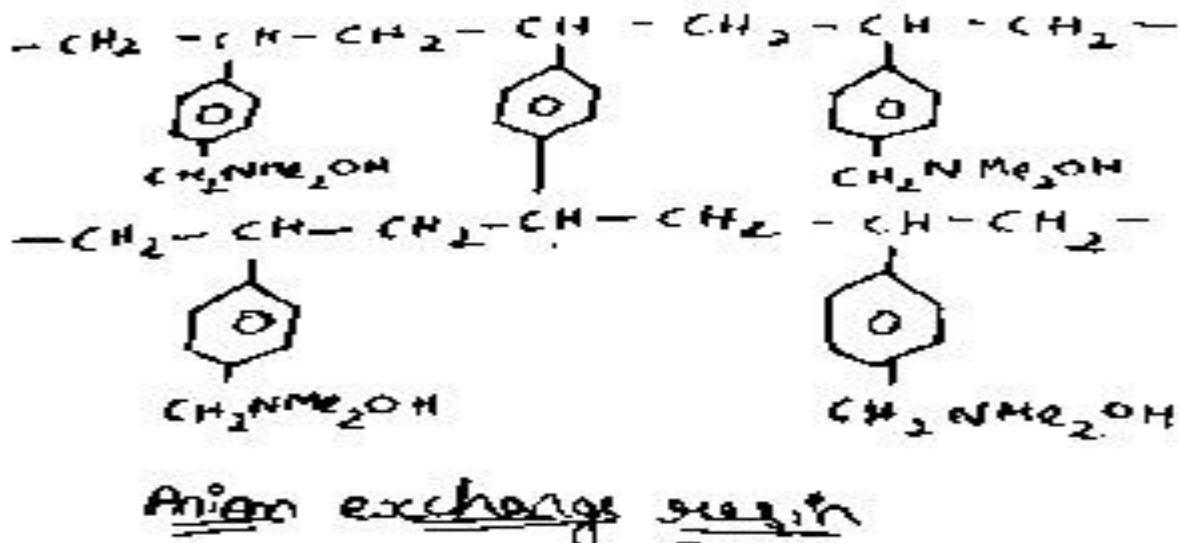
Cation exchange resin (R-H):

These are insoluble, cross-linked porous polymeric materials containing replaceable " H^+ " ions. Ex: Styrene divinyl benzene co-polymer substituted with acidic groups Like -COOH - SO_3H .



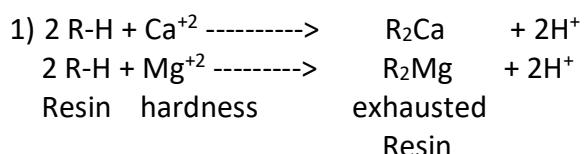
Anion exchange resin (R-OH)

These are insoluble cross-linked porous polymeric materials containing replaceable OH ion). E: Styrene divinyl benzene co-polymer substituted with amino group or quarternary ammonium group

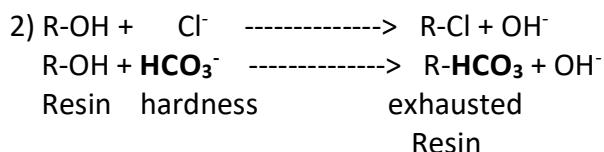


PROCESS:

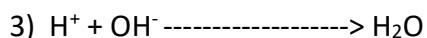
The hard water is passed through cation exchange column where all the Ca^{+2} , Mg^{+2} cations are replaced with H^+ ions from the resin and an equivalent amount of H^+ is released in water



Then the water is passed through anion exchange column where all the anions Cl^- , HCO_3^- , SO_4^{2-} are replaced with an equivalent amount of OH^- ions.

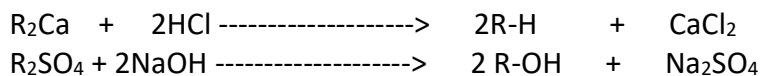


The H^+ and OH^- ions combine to produce water.



REGENERATION OF EXHAUSTED RESIN:

The exhausted cation exchange column is regenerated by passing dilute HCl or dilute H_2SO_4 whereas the exhausted anion exchange column is regenerated using dilute NaOH solution. The columns are then washed and the washings are passed to sink or drain.



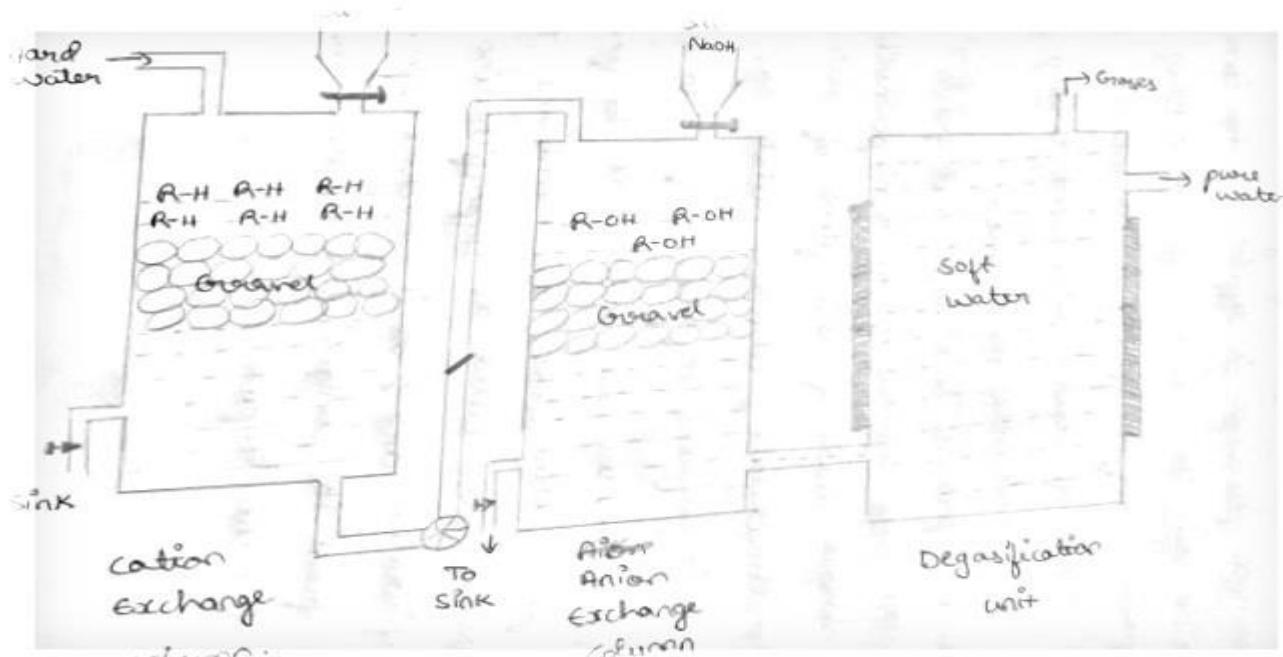
Exhausted Resin regenerated resin washings (sink/drain)

ADVANTAGES:

1. Highly acidic or alkaline water can be Softened by this method.
2. The process is good for treating water very high pressure boilers.
3. Mixed-bed ionizers with only one cylinder are also available.

DISADVANTAGES:

1. Costly equipment and expensive chemicals required.
2. low turbidity water must be used.
3. Temporary hardness must be removed before treating water by this method.



WATER SOFTENING METHOD:

Reverse Osmosis (Desalination): When external pressure greater than the osmotic pressure is applied on the concentrated side, then the solvent is forced to move from region of higher concentration to region of lower concentration through a semi-permeable membrane

Process: In the RO process, salt water and fresh water are separated by a Semi-permeable membrane made of a thin film of cellulose acetate, poly-methacrylate and polyamide polymers. A pressure of 15-40 kg/cm² is applied on the sea water side to force the pure water across the membrane.

This process is also called as hyper-filtration or super-filtration as it involves separating water from its

contaminants rather than removing the impurities.

ADVANTAGES:

1. Simple and reliable.
2. Low capital cost and operating cost.
3. The lifetime of membrane is quite high.
4. Removes ionic, non-ionic, colloidal, high molecular weight organic matter.
5. Extremely low energy consumption
6. Membrane can be easily replaced within a short duration.

DISADVANTAGES:

1. Efficiency of RO plant depends on the maintenance of membrane.
2. pH of water should be around 4.



SPECIFICATIONS OF POTABLE WATER: (DRINKING OR MUNICIPAL WATER)

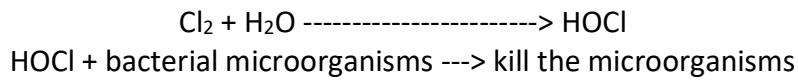
- 1) colourless, odourless and pleasant to taste
- 2) should be free from suspended particles and dissolved impurities.
- 3) should be non-corrosive in nature.
- 4) should be free from disease producing microorganisms and pathogens and objectionable dissolved gases like H_2S .
- 5) pH should be in the range of 6.5 to 8.5.

- 6) Alkalinity should not be more than 200 ppm.
- 7) should not be turbid.
- 8) Total dissolved solids (TDS) should be less than 500 ppm.
- 9) Toxic minerals such as - lead(Pb), Arsenic(As), Chromium(Cr) should not be present.
- 10) should be free from health hazards and sanitary defects.

DISINFECTION: The process of destroying or Killing pathogens (Disease producing micro-organism) and making the water safe for use is called as disinfection or sterilization.

Ex: chlorination ozonisation, U.V Radiation

DISINFECTION BY CHLORINE: Chlorine is the most common disinfectant used in the form of gas/solution (or) bleaching powder. chlorine when added to water forms. hypochlorous acid which is a powerful disinfectant and germicide.



HOCl reacts with the bacterial enzymes and inactivates them which are very much essential for this growth and metabolic processes thus leading to the death of micro-organisms. Chlorine is a most powerful disinfectant at lower pH of 5 to 6.5

FACTORS AFFECTING EFFICIENCY OF CHLORINATION:

1. Time of contact

The death rate of micro-organisms is maximum to start with and it goes on decreasing with time

2. Temperature of water.

With increase in temperature the number of pathogens decreases.

3) pH of water

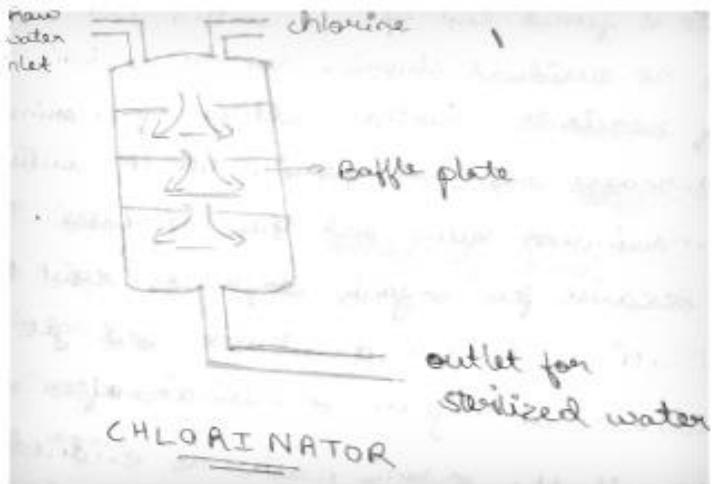
At lower pH of 5 to 6.5 less contact time is required for disinfection

ADVANTAGES OF CHLORINATION:

1. Affective and economical
2. Required less place for storage
3. Stable and does not deteriorate on standing.
4. Most ideal disinfectant.
5. Leaves no salt impurities.
6. No sludge is formed.

DISADVANTAGES:

- 1) Excess chlorine produces unpleasant taste and odour.
- 2) Causes irritation on mucous membrane.
- 3) free chlorine in treated water should not exceed 0.1-0.2 ppm.
- 4) Requires effective dechlorination.



BREAK POINT CHLORINATION:

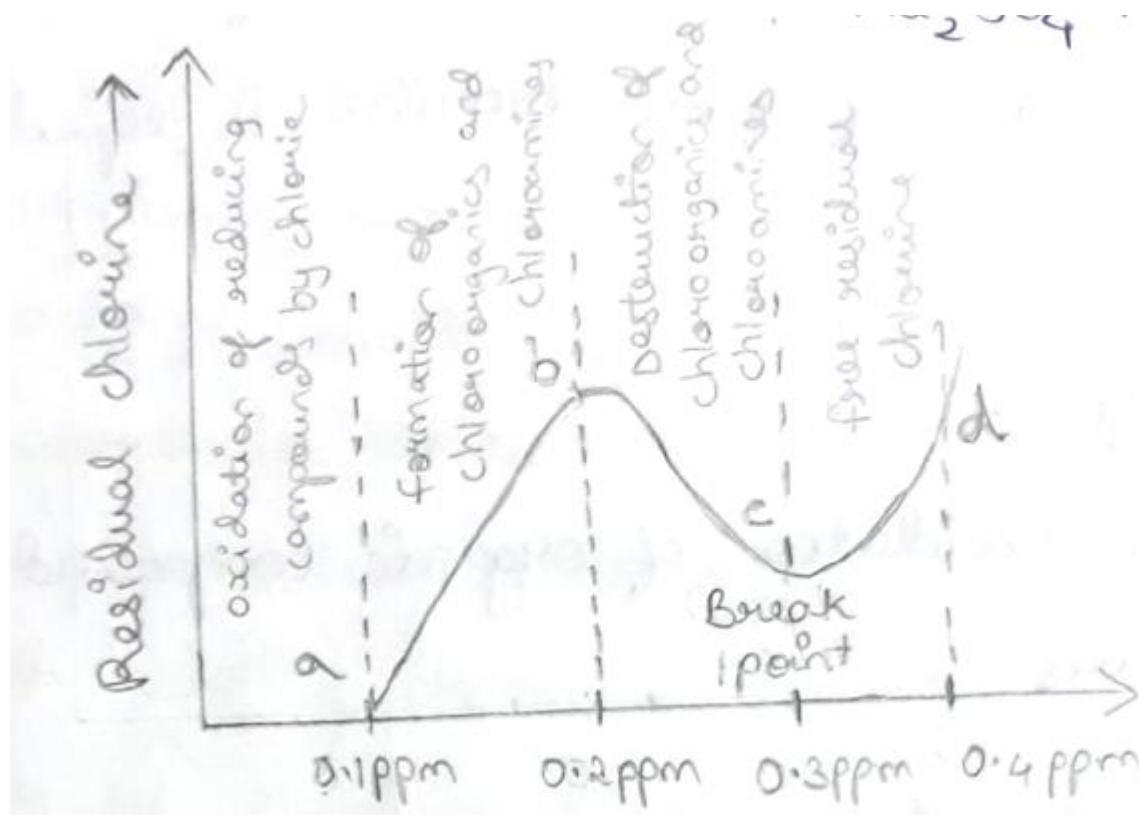
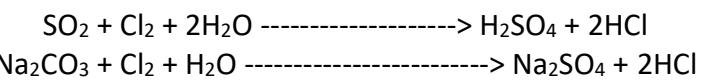
The chlorination of water to such an extent which not only destroys the living organisms but also other impurities like organic matter, reducing substances, free ammonia etc. is called as break point chlorination.

After adding chlorine to water the quantity of residual chlorine is estimated. It is found that up-to a certain level there is no residual chlorine due to oxidation of reactants. Further addition of chlorine increases residual chlorine till it reaches a maximum value and then decreases. This is because few organic compounds resist the oxidation at low concentration and get higher concentration after sometime. When all the organic matter is oxidized, then there is an increase in the level of residual chlorine. This point is called as break point. After this point free residual chlorine increases in water and produces germicidal effects which makes the chlorine an effective disinfectant. Thus after break point quantity of free chlorine is equal to added chlorine.

ADVANTAGES:

- 1) complete oxidation of organic compounds and NH_3 occurs.
- 2) Removes colour.
- 3) Destroys all the pathogens.
- 4) prevents growth of any weeds in water
- 5) Removes odour and taste from water

DE-CHLORINATION: The excess of chlorine in water produces unpleasant taste and odour. Thus the de-chlorination is required to remove the excess chlorine, bad odour and decomposed products. De-chlorination is carried out by passing water through Molecular carbon bed (or) by adding activated carbon (or) by passing SO_2 gas (or) Sodium thiosulphate.



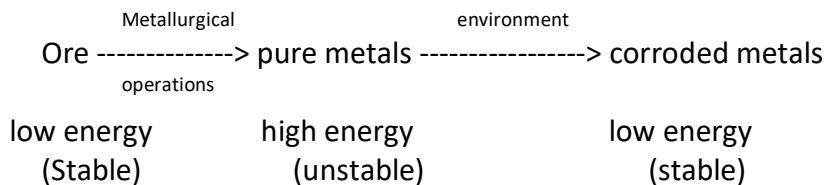
UNIT 2.2

CORROSION

CORROSION: The process of destruction of metallic Surface due to chemical or electrochemical attack by the humid atmosphere on polluted environment is called as corrosion. corrosion is an acidation process starting at the surface of the metals which decreases the strength of metals.

CAUSES OF CORROSION

- 1) During oxidation of metals free energy of the System decreases i.e $\Delta G = -ve$ therefore metal is more stable in combined stage than in free state.
 - 2) Metals exists as there combined state as ores in nature which is thermo-dynamically stable with low energy.
 - 3) To extract pure metals from ore, more energy is required. After metallurgical operations pure metals are obtained but due to their high energy they are thermo-dynamically unstable and professed to reward back to combine state by interacting with the environment which leads to corrosion



EFFECTS OF CORROSION:

- 1) Loss of useful properties of metals and thus case of efficiency.
 - 2) Because in rate of production as replacing corroded equipments is time consuming.
 - 3) Increase in maintenance and production
 - 4) contamination of products.

Ex:

1. Rusting of iron in moist air makes the metal useless.
 2. In sea water rusting of ships is major problem.
 3. Corrosion of the metallic structure decreases the ductile nature resulting in cracks.

TYPES OF CORROSION

There are 2 types of corrosion 1) DRY OR CHEMICAL CORROSION
2) WET OR ELECTROCHEMICAL CORROSION

DRY OR CHEMICAL CORROSION

In this type of corrosion a metal directly comes in contact with the environment gases like H₂SO₂, D₂SO₂, SO₃ etc.. or anhydrous inorganic liquids, acids or bases vapours resulting in chemical reaction between the two

- There are 3 types of corrosion
1. Oxidation corrosion
 2. Corrosion by other gases.
 3. Liquid metal corrosion

OXIDATION CORROSION:

It takes place by direct action of oxygen on metal surface at lower temperature or higher temperature in the absence of moisture to give metal oxide. The extent of corrosion depends upon the nature of oxide layer formed on the metal surface.

A) **STABLE OXIDE LAYER:** It is continuous adherent and covers the entire surface of metal. Hence it is very protective in nature and does not allow further attack of corrosion.

Ex: Aluminium, Lead, chromium etc..

B) **UNSTABLE OXIDE LAYER:** It is formed in case of metals like platinum, silver, gold etc... where the oxide layer reverts back to give the metal and oxygen and hence such metals undergo corrosion.

C) **VOLATILE OXIDE LAYER:** The oxide layer formed does not stay on the metallic surface as it is volatile. The metal is subjected to further attack of corrosion.

D) **POROUS OR NON-PROTECTIVE LAYER:** In case of metals like Fe, alkali and alkaline earth oxide layer is non-continuous, non-adherent, porous and does not cover the entire surface of metals. Hence the metal is exposed to further attack of corrosion leading to severe corrosion.

The PBR (piling bed worth ratio) decides the protective nature of oxide layer, If PBR ≥ 1 , then the oxide layer is protective and If PBR ≤ 1 then it is non-protective

$$PBR = \frac{\text{vol of corrosion product}}{\text{Vol of metal consumed}}$$

CORROSION BY OTHER GASES: It takes place by direct action of gases like Cl₂, SO₂, SO₃, etc.... on the metal. The degree of attack depends on the formation of protective (or) non-protective film formed on the surface of metal.

If protective or non porous film is formed then the extent of corrosion decreases

Eg: AgCl film on Ag

If porous or non-protective film is formed then the degree of attack increases.

Eg. SnCl₄ layer on Sn

LIQUID METAL CORROSION: In this type of corrosion. A liquid metal flowing at a very high temperature attacks on the solid metal due to which it gets dissolved. Also liquid metal can penetrate into solid metal thereby leading to corrosion of the solid metal.

Eg. Nuclear plants.

WET OR ELECTRO CHEMICAL CORROSIONS

This type of corrosion takes place when a conducting liquid is in contact with metal surface (or) when there is heterogeneity on the metallic surface.

When two dissimilar metals are in contact with an electrolyte they form anodic and cathodic areas and electrolyte and current flows through the conducting medium to form a galvanic cell. At anodic areas oxidation occurs and due to the loss of electrons the metal undergoes corrosion. whereas as the cathodic area is uncorroded.

MECHANISM OF WEB CORROSION:

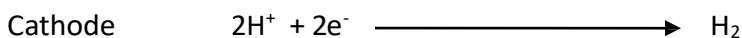
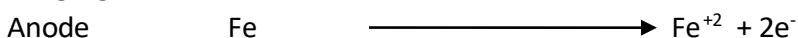
In wet corrosion the current flows from anode to cathode at anode oxidation takes place liberating e^- whereas at cathode the e^- are consumed either by evolution of hydrogen or by absorption of O_2 depending on the nature of corrosive environment.

i) **CORROSION IN ACIDIC MEDIUM (Evolution of H₂):**

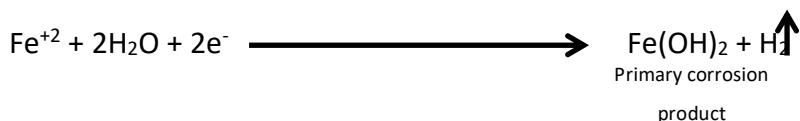
In industrial areas polluting gases like SO_2 , SO_3 , CO_2 , oxides of Nitrogen etc are present which dissolve moisture to form acidic solution.

When such a solution comes in contact with a sheet of iron it forms acidic medium around the metal when the oxide layer form on the surface of metal develops cracks or pores it leads to formation of anodic and cathodic areas resulting in the following reactions.

PRIMARY REACTION



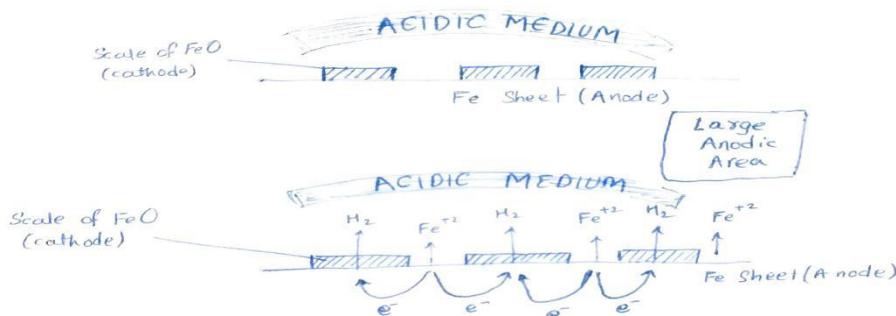
SECONDARY REACTION:



If enough oxygen is present



If oxygen is limited, black crust Fe_3O_4 is formed.

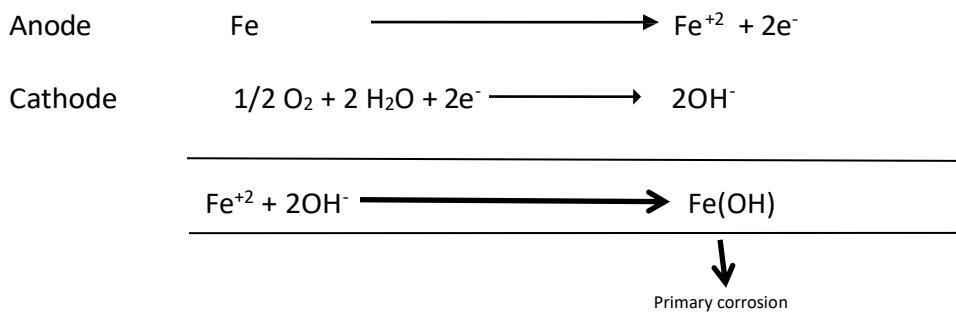


Corrosion in acidic medium is not very severe, but it is generalized. It is so because the anodic areas are very large compared to cathodic area. The evolution of H₂ at the cathode sets up polarization phenomenon and as the solubility of Fe⁺² exceeds its saturation limit the formation of Fe⁺² decreases thus due to these two factors after some time the corrosion of the metal stops.

ii) CORROSION IN BASIC (OR) NEUTRAL MEDIUM: (ABSORPTION OF OXYGEN.)

When salts like NaCl dissolves in moisture it gives neutral solution, whereas salts like Na₂CO₃, NaHCO₃, etc.... give rise to basic or Alkaline medium. When a sheet of iron (or) steel comes in contact with basic (or) neutral medium. An oxide layer is formed on the metal surface. If the oxide layer develops cracks then the electro-chemical cell is formed with small anodic and large cathodic areas.

PRIMARY REACTION



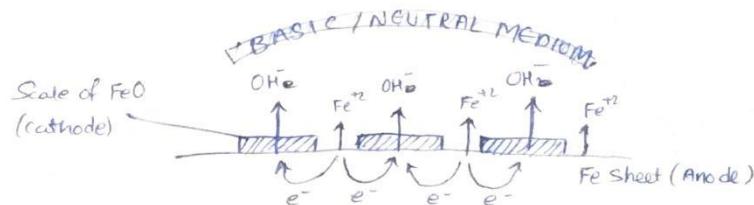
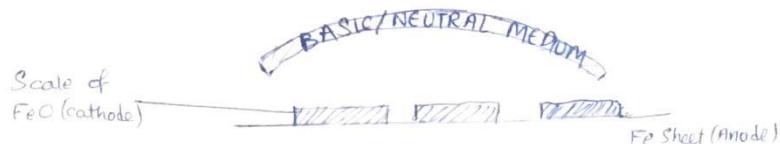
product

SECONDARY REACTION:

If enough oxygen is present



If oxygen is limited, black crust Fe₃O₄ is formed.



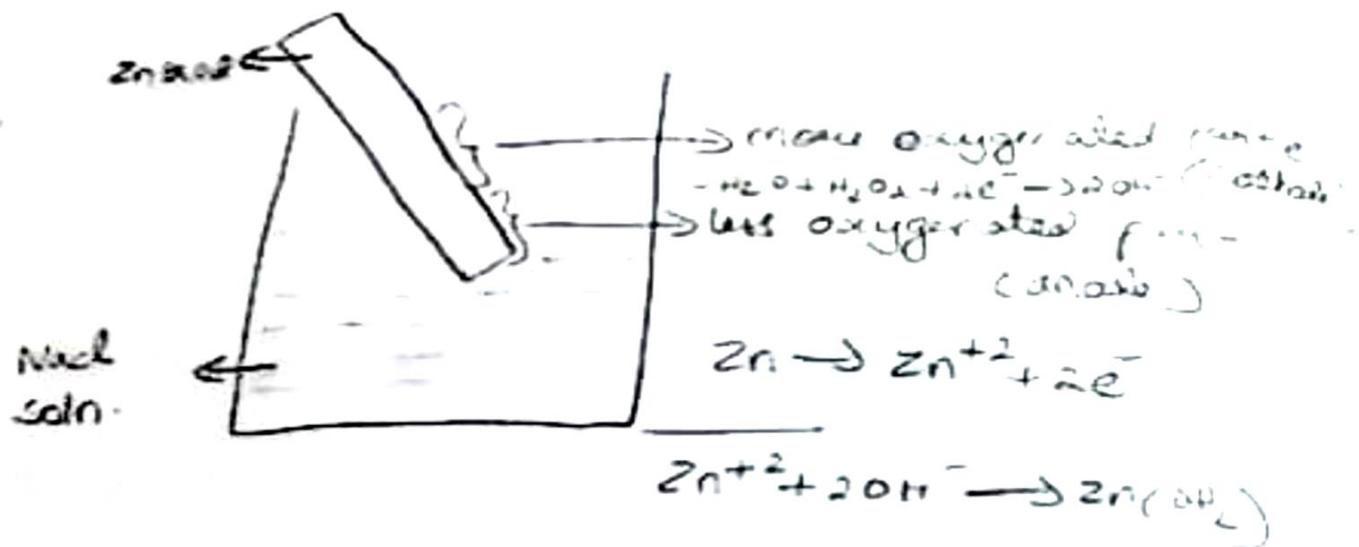
The Fe⁺² formed at anode and OH⁻ formed at cathode combine near the cathode because smaller Fe⁺² ions can diffuse more rapidly, thus the corrosion occurs at anode whereas the rust gets deposited at cathode.

The corrosion in basic medium is more severe and localized leading to pitting corrosion.

DIFFERENTIAL AERATION CORROSION

This is the most common type of concentration cell corrosion in which one part of the metal is exposed to different air concentration from the other part resulting in difference of potential between differently aerated areas. The more oxygenated part (highly aerated area) becomes cathode while the less oxygenated part (poorly aerated area) acts as anode. The corrosion occurs at anode which is poorly aerated.

Ex: zinc metal partially dipped in NaCl solution undergoes corrosion just below the water line which is less oxygenated due to which Zn gets dissolved at the anodic areas

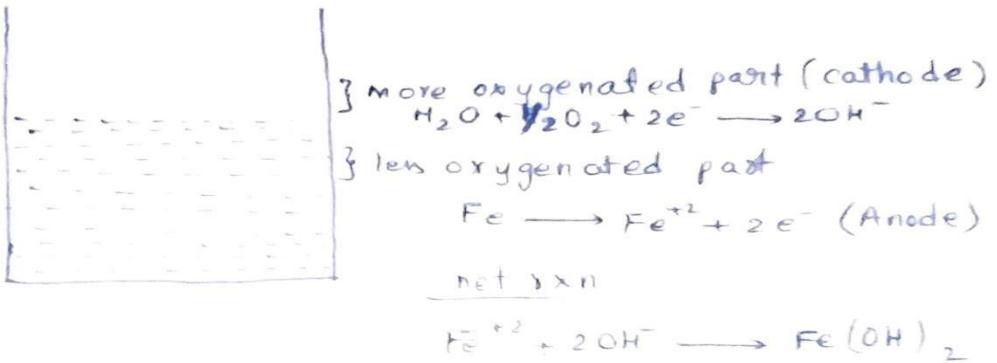


Ex:

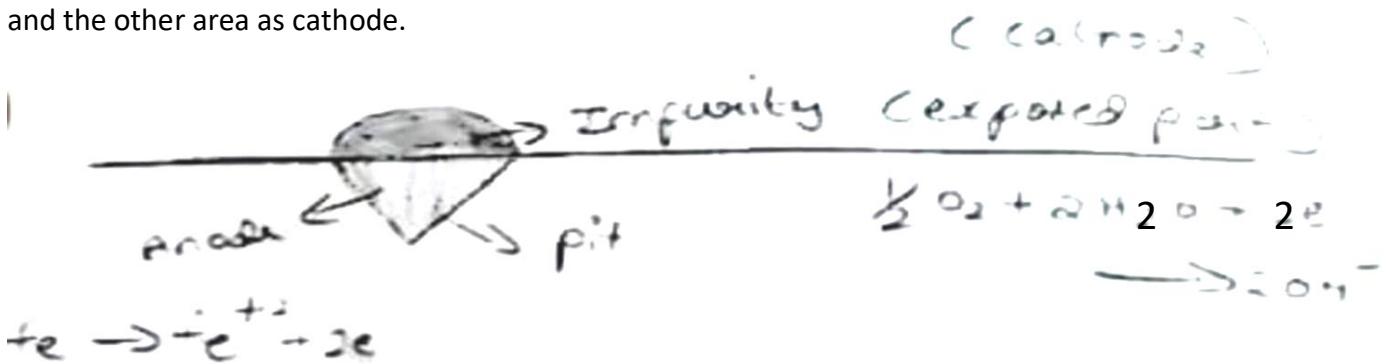
- 1) Metal rod dipped in a solution
- 2) Ship sailing in water
- 3) A nail hammered in a wooden block where head acts as cathode & Stem (Tail) acts as anode.

WATER LINE CORROSION: The water stored in steel tanks or water tankers have maximum amount of corrosion just below the water line. The area of tank above the water level is more aerated area and acts as cathode which is unaffected by corrosion. The area below the water level is poorly aerated and acts as anode which undergoes corrosion.

Ex: Waterline corrosion is commonly found in marine engineering. It is accelerated when aquatic plants stick to the sides of ships also the drinking water stored in iron tanks will have water line corrosion.



PITTING CORROSION: It is a localized corrosion which forms pits or cavities in corrosion. It is caused due to breaking or cracking of protective film on the metal surface. The break down can be due to roughness, scratches, non uniform stress, or chemical action. The pits or cavities formed, small anodic areas and the other exposed part forms large cathodic area. This leads to severe corrosion. The presence of impurities like sand, dust, Scales, also leads to pitting corrosion. The parts of metal below the impurity acts as anode and the other area as cathode.



DIFFERENCES BETWEEN DRY AND WET CORROSION

DRY / CHEMICAL CORROSION	WET / ELECTROCHEMICAL CORROSION
1) Corrosion occurs in the absence of moisture	1) Requires moisture for corrosion (electrolyte as conducting medium)
2) It involves direct chemical attack on the metal surface.	2) It involves formation of electrochemical or Galvanic cell
3) It's a slow process	3) It's a rapid process
4) Corrosion products are formed at the site of corrosion	4) Corrosion occurs at anode but corrosion products are formed at cathode.
5) Uniform corrosion	5) Non-Uniform corrosion
6) Occurs on homogeneous or heterogeneous surfaces.	6) Occurs only on heterogeneous metal surfaces.

FACTORS INFLUENCING RATE OF CORROSION

I) **NATURE OF METALS:**

Position of Metal / Alloy in the galvanic series :

When two metals or alloys are in electrical contact in presence of electrolyte then the more active metal present higher up in series will act as anode & undergoes corrosion. Thus greater the difference b/w the metals faster is the rate of corrosion.

Relative areas of anode & cathode :

When 2 dissimilar metals are in contact then the corrosion of the anodic part is directly proportional to the ratio of areas of cathodic part and anodic part. In case of small anodic areas corrosion is more severe, rapid or localized because the great demand for electron by the large cathodic area can be fulfilled by smaller anode by undergoing continuous rapid corrosion.

Purity of metals:

The impurity in a metal Leads to heterogeneity forming small electrochemical cells at the exposed part of metal which causes anodic areas undergo corrosion. Pure metals are less corroded than impure metal.

Nature of surface oxide film

If the corrosion product is soluble or volatile, then corrosion proceeds at faster rate until all the metal is consumed. If corrosion product is insoluble, continuous and coherent then it covers the metal surface & acts as a physical barrier thereby decreasing further rate of corrosion. If corrosion product is discontinuous or porous then, corrosion will be severe.

II) **NATURE OF ENVIRONMENT:**

Temperature

With increase in temperature of environment the rate of corrosion also increases.

Humidity

The corrosion of metal is rapid in humid atmosphere because atmospheric gases dissolves in moisture to produce an electrolyte which sets up an electrochemical cell. Also sometimes the oxide layer absorbs moisture which leads to electrochemical corrosion.

Effect of pH

The acidic medium is more corrosive than basic/neutral medium i.e. lower the pH greater the rate of corrosion. The corrosion of metals attacked by lower pH can be reduced by increasing the pH of attacking Environment.

WILL BE CONTINUED.....

UNIT 2.3

CORROSION CONTROL METHODS

CATHODIC PROTECTION:

The principle involved in the cathodic protection method is to force the metal to be protected to behave as cathode as a result of which corrosion does not take place. Such type of corrosion control can be achieved by connecting the base metal to external source of energy which may be a metal, rectifier or a generator.

Cathodic protection is of two types:

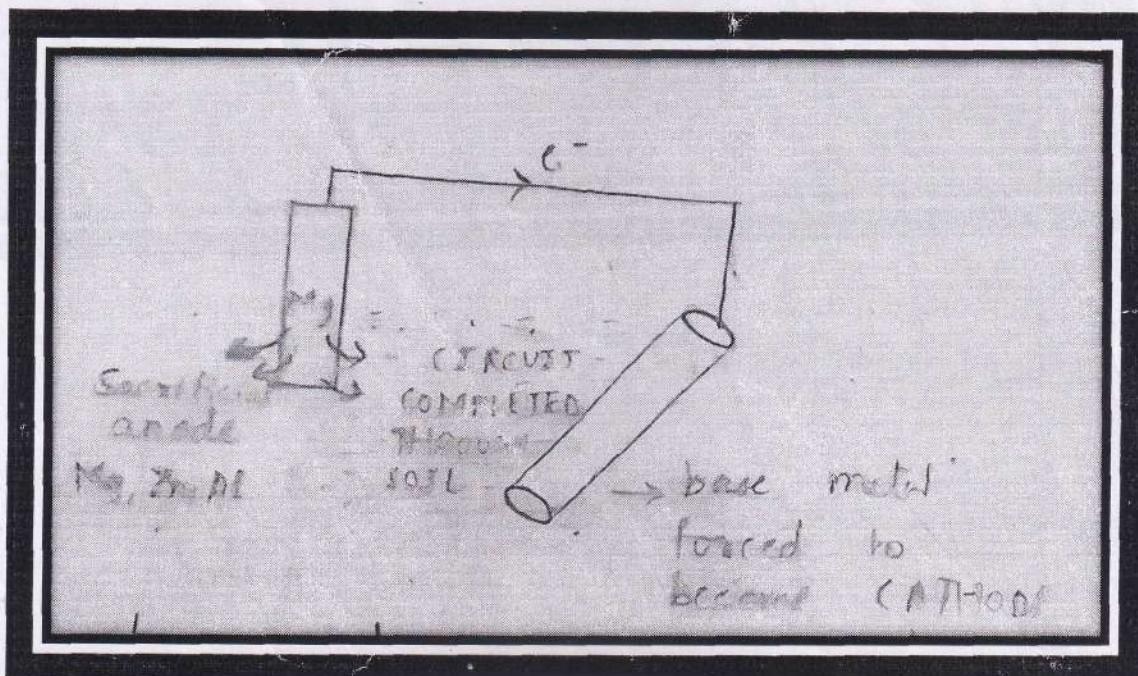
1. Sacrificial anodic protection
2. Impressed current cathodic protection

1. SACRIFICIAL ANODIC PROTECTION

In this method, the metallic structure to be protected is connected by a wire to a more anodic metal so that all the corrosion takes place at the anode. The parent structure thus becomes cathodic and is protected whereas the more active metal gets corroded. As the anode sacrifices itself to protect the base metal, it is termed as Sacrificial anode which is replaced after it gets consumed. The usually used metals for sacrificial anode are Mg, Zn, Al and their alloys.

APPLICATIONS :

Used for protection of buried pipe line underground cables, marine structures, ship hulls, water tanks.

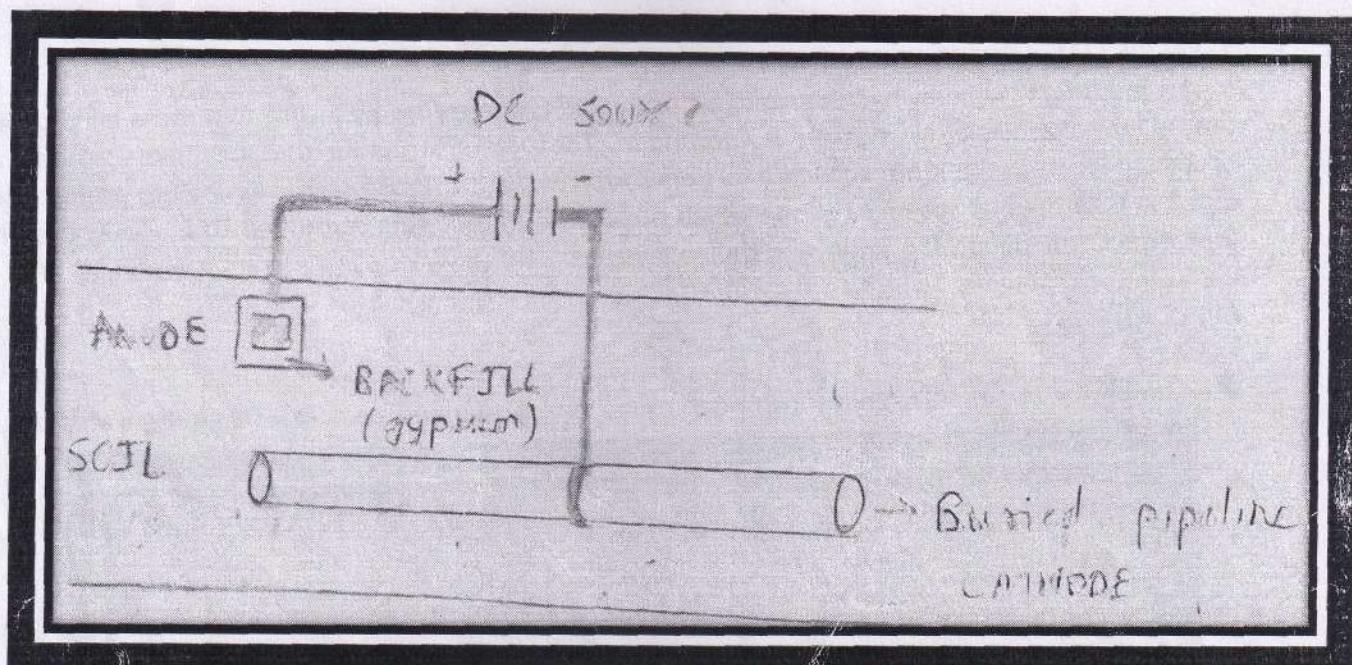


2. IMPRESSED CURRENT CATHODIC PROTECTION:

In this method, an impressed current is applied in the opposite direction to nullify the corrosion current and convert the metal undergoing corrosion from anode to cathode. The impressed current is derived from a DC source connected to an insoluble anode (graphite or Pt) The anode is usually placed in a backfill (gypsum) so as to increase the electrical contact with the surrounding soil. The external source produces current in the direction reversed to corrosion current such that the parent structure forced to behave as cathode and is protected. This kind of protection is useful for large structures for long term operations.

APPLICATIONS :

Used to protect water tanks, buried oil pipelines, condensers, transmission lines, towers, laid-up ships, etc...



UNIT 2.4

SURFACE COATING METHODS

SURFACE COATING – METALLIC COATING

Coating provide physical barrier between the base metal and its environment and protects the metal from corrosion. When the base metal is coated with another metal, it is called as metallic coating.

Metallic coating is of 2 types

- 1) ANODIC COATING
- 2) CATHODIC COATING

1. ANODIC COATING

The coating metal has lower SRP than the base metal due to which it itself gets corroded and protects the base metal.

Ex: Galvanisation of the steel

2. CATHODIC COATING

The coating metal has highest corrosion resistance due to its noble character as it is less reactive.

Ex: Tinning/coating of tin.

HOT DIPPING BY GALVANIZATION

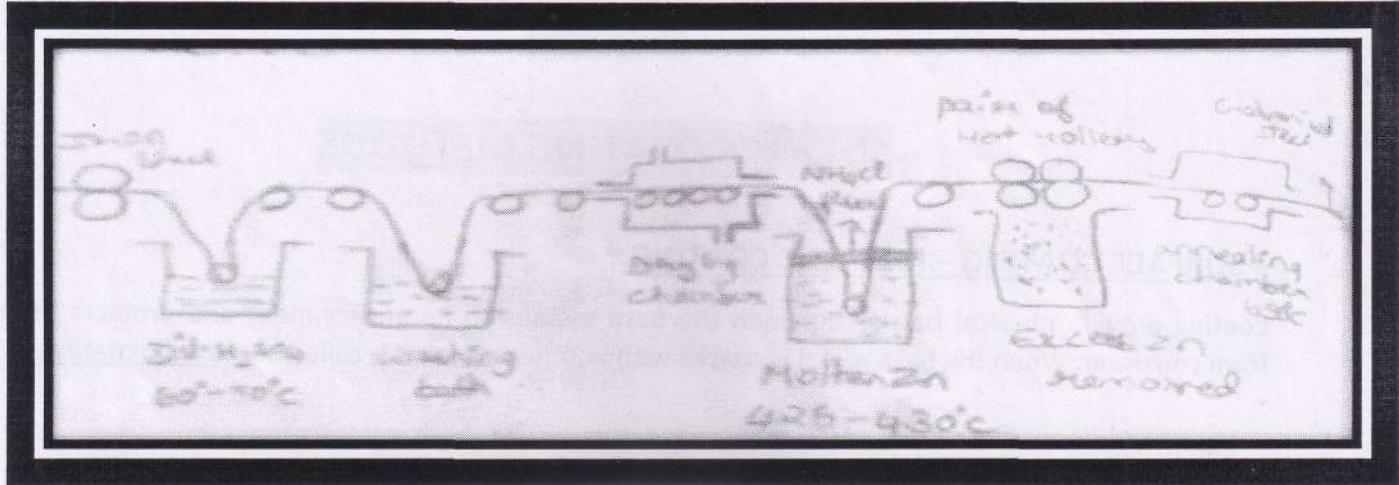
Hot dipping is a common method of coating in which the metals with low melting point such as Pb, Zn, Al are coated on metals with high melting point such as iron, steel and copper. The process consists of dipping the base metal in a bath containing molten coating metal with a layer of flux. The most widely used hot dipping method is galvanization.

Galvanisation is a process of coating iron with zinc to prevent it from rusting. The steps involved are:

1. **Acid pickling:** The base metal is cleaned with water and organic solvents to remove the oil, grease and other impurities. It is then treated with dilute H_2SO_4 for 15-20 minutes at 60-90°C to remove scales of oxides, rust or impurities.
2. **Washing and coating:** The base metal or the article is then washed with water and dried. It is dipped in a hot bath of molten zinc at 425-430°C covered with a layer of NH_4Cl flux. The flux prevents the oxidation of molten zinc and acts like a binder for proper adhesion of zinc on the surface.
3. **Rolling:** The coated article is passes through a pair of hot rollers to remove the excess zinc so that the thin film of uniform thickness is achieved.
4. Annealing: The zinc coated article is then passed through the annealing chamber at 650°C and finally cooled down.

USES:

Used in coating of wires, pipes, nuts, bolts, screws, nails, tubes, roofing sheets, etc..



Q) Can Galvanised utensils be used for preparing or storing food ?

No, because Zn dissolves in dilute acids to form highly toxic or poisonous compounds.

Q) Why Aluminium does not undergo corrosion ?

Metals like Al, Cr, Mg, Ni are passive and exhibit higher corrosion resistance due to the thin protective oxide film formed on the surface which also has self-healing capacity when broken or exposed to environment.

UNIT 5.1

GREEN CHEMISTRY

Green chemistry is the use of chemistry for pollution prevention by environmentally conscious design of chemical products and processes that reduced or eliminate the use or generation of hazardous substances.

Green chemistry is the design of chemical products and processes that are more eco. eco-friendly and reduce the negative impact on human health and the environment.

PRINCIPLES OF GREEN CHEMISTRY

There are 12 twelve principles of green chemistry developed by Paul Anastas and John Warner.

1. Prevention

It is better to prevent waste than to treat or clean-up waste after it has been created.

2. Atom economy

Synthetic methods should be designed to maximise the incorporation of all the materials used in the process into the final product.

3. Less hazardous chemical synthesis -

Wherever practicable, synthetic methods should be designed to use and generate, substances that possess little or no toxicity to human health and environment.

4. Designing safer chemicals

Chemical products should be designed to affect their desired function while minimising their toxicity.

5. Safer solvents and auxiliaries

The use of auxiliary substances should be made unnecessary wherever possible and innocuous when use.

6. Designed for energy efficiency

Energy requirements of chemical processes should be recognised for their environmental and economical impacts and should be' minimised. If possible, If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of renewable feedstock

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce derivates

Unnecessary derivatisation should be minimised or avoided if possible, because such steps require additional reagents and can generate waste

9. Catalysis

Catalytic reagents are superior to stoichiometric reagents

10. Design for degradation

The chemical products should be designed, so that at the end of their function they breakdown into innocuous degradation products and do not persist in the environment.

11. Real time analysis for pollution prevention

Analytical methodologies need to be further developed to allow for real time, in process monitoring and control prior to the formation of hazardous substances

12. Inherently safer chemistry for accident prevention

Substances and the form of a substance used in chemical process should be chosen to minimise the potential for chemical accidents including releases, explosions and fires.

ATOM ECONOMY

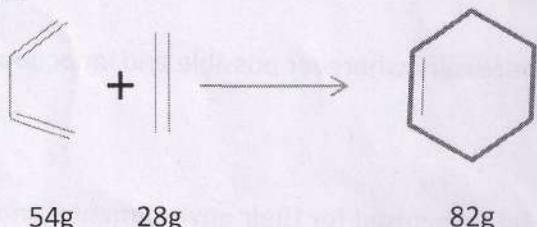
It is a method of determining efficiency with which raw materials i.e. reactants or feedstock are used regardless of the percentage yield obtained in the reaction. The atoms that are not directly involved in the formation of the product are the wasted atoms. The measure of atom economy suggest to find a way of making the same product with lesser wastage of reactant items.

Atom economy is the mass percentage of the reactant atoms used in the final product divided by the total mass of the reactant

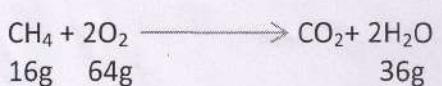
$$\% \text{ atom economy} = \frac{\text{formula weight of atoms utilized}}{\text{formula weight of all reactants}} \times 100$$

The atom economy is a useful tool available for design of reactants with minimum wastage. The term "atom efficiency" signifies that as many as reacting atoms possible should end up in the useful product

Ex.1.



$$\text{Atom economy} = \frac{82}{(54+28)} \times 100 = 100\%$$



$$\text{Atom economy} = \frac{36}{(16+64)} \times 100 = 45\%$$

CATALYSIS

A catalyst is defined as a substance that changes the velocity of the reaction without itself being changed in the process. It lowers the activation energy of the reaction and does not get consumed in the process. Thus, it can be used in small amounts and can be recycled in definitely.

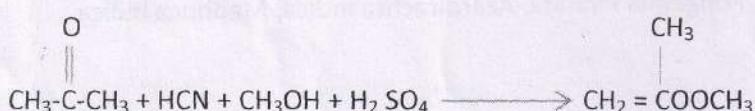
With emergence of green chemistry, Catalysis has been widely applied in pharmaceutical and chemical industry with the main aim of minimising the enormous amount of waste generated by the use of stoichiometric inorganic reagents.

Catalysts are specific in their actions with and are effective at catalysing highly selective processes with complex substrates. Catalysts can be enzymatic in their actions. Enzymes are the most efficient and common catalyst found in nature.

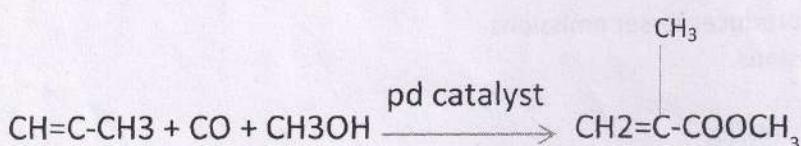
A good catalyst exhibits the following properties:

1. It plays a vital role in environmental synthesis of new and existing chemicals
2. It produces less by-products, co-products and other waste product addressing the benefits of atom economy.
3. It is environmentally safe and minimises the hazards.
4. It reduces the number of steps and time required in a reaction.

Ex.1.

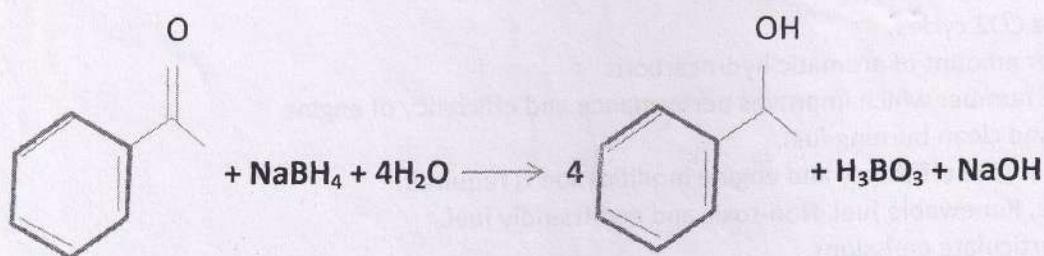


$$\text{Atom economy} = \frac{100}{215} \times 100 = 46.5\%$$

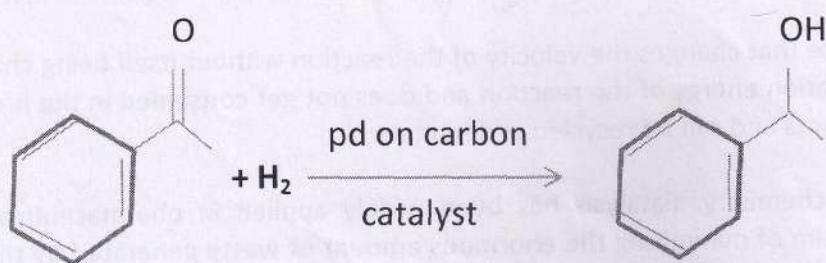


$$\text{Atom economy} = \frac{100}{100} \times 100 = 100\%$$

Ex.2.



81% Atom Efficiency



100% Atom Efficiency

BIODIESEL

Bio diesel is monoalkyl ester of long chain fatty acid which is made from trans-esterification of vegetable oils and animal fats .

Sources of bio-diesel

1. A variety of oils, both edible and non edible are used for production of bio-diesel
Ex Sunflower oil, palm oil, soyabean oil etc
2. The animal fat used for production of bio diesel include chicken fat, fish oil omega-3 fatty acid etc.
3. Plant species include Jatropha curcas, Pongamia Pinnata, Azadirachta indica, Madhuca indica

Properties of bio-diesel-

1. Bio-diesel is light yellow to dark yellow colour liquid
2. It is non-miscible (immiscible) with water
3. High boiling point and low vapour pressure.
4. Low density of 0.88 g/cc
5. Higher flash point than petro diesel.
- 6 Viscosity is similar to petrodiesel
7. It is biodegradable, non-toxic and produces lesser emissions
8. Eco-friendly and sulphur free emissions.
9. Higher cetane rating.
10. Its calorific value is 37.27 MJ/L or MJ/kg
11. It can be blended with diesel easily.

Advantages of bio-diesel (significance / Importance)

- 1) Can be blended with petro diesel and used in diesel engines.
- 2) In India 20% blend is used.
- 3) Reduces CO and CO₂ emissions.
- 4) Completes the CO₂ cycles.
- 5) Contains lesser amount of aromatic hydrocarbons
- 6) Higher cetane number which improves performance and efficiency of engine.
- 7) Sulphur free and clean burning fuel.
- 8) Increases the engine efficiency and engine modification is required.
- 9) Biodegradable, Renewable fuel, Non-toxic and eco-friendly fuel.
- 10) It reduces particulate emissions.
- 11) It works as a lubricant for diesel itself which increases the life of engine.

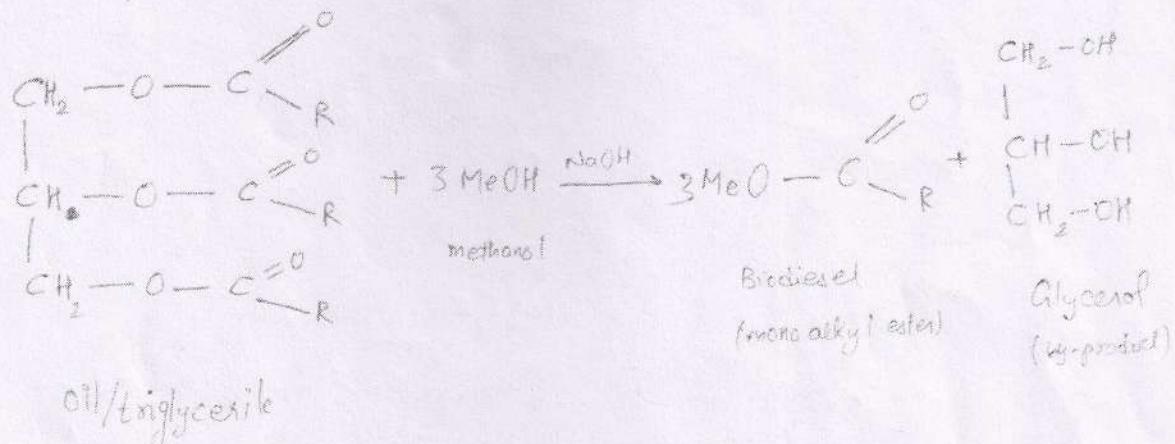
- 12) It possess flashpoint greater than 150°C .
 13) The process of extraction is simple as it involves only 2 steps, i.e, extraction of oil from source and esterification of oil.

TRANSESTERIFICATION

Biodiesel is prepared by trans-esterification reaction of oil or triglyceride with an alcohol.

In trans-esterification reaction methanol reacts with triglycerides in 3:1 ratio in presence of a basic catalyst which gives mono-alkyl ester biodiesel and the by-product glycerol

Glycerol has a wide application in pharmaceutical industry.



Carbon neutrality:

carbon neutral or having net zero carbon foot print, refers to achieving zero carbon emissions by balancing the CO₂ released with renewable sources of energy. Carbon offsetting is done by paying others to remove CO₂ by planting trees or by funding projects or by purchasing carbon credits.

Biodiesel is carbon neutral fuel because the amount of carbon released into the atmosphere upon its combustion is same as the carbon taken from the atmosphere by the plants. As biodiesel releases the same amount of CO₂ that the plants absorb, there is no negative impact on the carbon cycle.

ADVANTAGES OF BIODIESEL OVER PETRO-DIESEL

- 1) The properties of biodiesel are similar to that of diesel fuel.
- 2) Cetane number and lubricating effect of biodiesel is significantly higher than diesel.
- 3) The toxicity of bio-diesel is lower than petro-diesel.
- 4) Bio-diesel can be blended with petro-diesel in any ratio.

UNIT 5.2

COMPOSITES

- # Two or more chemical distinct material which when combined have improved properties over the individual materials are called as Composite.
- # Composites can be natural or synthetic.

PROPERTIES OF COMPOSITES (ADVANTAGES)

- 1) They have high specific strength
- 2) They do not lose their strength even at elevated temperatures
- 3) They are hard and tough.
- 4) They possess good impact resistance & thermal shock resistance.
- 5) They have low specific gravity & low cost
- 6) They have better, creep and fatigue
- 7) They possess high corrosion and oxidation resistance compare to metal.
- 8) They have desirable co-efficient of thermal expansion.
- 9) Conductivity & Electrical conductivity are low & can be controlled
- 10) They have ability to withstand extreme temperature conditions.

EXAMPLES OF COMPOSITES:

1. Wood - (Cellulose fibres & lignen)
2. Bone - (Collagen and Apatite)
3. Raincoat
4. Insulating tape
5. Composite bricks
6. Reinforced concrete

CONSTITUENTS OF COMPOSITES:

Composites generally consists of 2 phases

- 1) matrix
- 2) dispersed phase

1) Matrix

It is the main constituent of composite. It is the continuous body which encloses the composite and gives it the bulk form. It is the bonding material which adheres to the reinforcing material depending on the type of matrix composites are classified as PMC, MMC, CMC.

Functions of a matrix

1. Holds the fibers together
2. Protects the fibers from environment
3. Distributes the loads evenly between fibers so that all fibers are subjected to the same amount of strain
4. Enhances transverse properties Laminate.
5. Improves impact and fracture resistance of a component.
6. Carry inter laminan shear.

Desired properties of a matrix :

1. Reduced moisture absorption
2. Low Shrinkage
3. low coefficient of thermal expansion.
4. Strength at elevated temperature (depending on application)
5. Low temperature capability (depending on application).
6. Excellent chemical resistance (depending on application).

2) Dispersed phase:

It is the structural constituent that determines the internal structure of the composite. It may be fiber, particle, whisker or flakes.

a. FIBRES: fibres are long and thin filament of any polymer, metal or ceramic having high length to diameter ratio, high tensile strength and high stiffness

Eg: Glass fibres, carbon fibres, Boron fibres, aramid fibres, ceramic fibres etc..

b. PARTICLES/PARTICULATES: These are small pieces of hard solid materials which can be metallic (or) non-metallic. They are randomly distributed in the matrix. They increase the Surface hardness, strength and performance. at elevated temperatures reduced shrinkage and friction and modify thermal and electrical Conductivity

eg: concrete, cermit etc...

c. FLAKES: These are thin solids having two dimensional geometry and can be packed more efficiently than fibers and spherical particulates they impart equal strength in a plane compared to fibres (reinforces unidirectionally).

eg: mica flakes - used in electrical and thermal insulating appliances.

d. whiskers: There are thin, strong filaments on fibres of several millimeters in length and several micron in thickness. They have high degree of crystallinity, high elastic modules and higher strength. But their use in composites is limited due to their high cost and difficulty in use.

eg: Graphite silicon, carbide, sapphire Aluminium oxide etc.

CLASSIFICATION OF COMPOSITES:

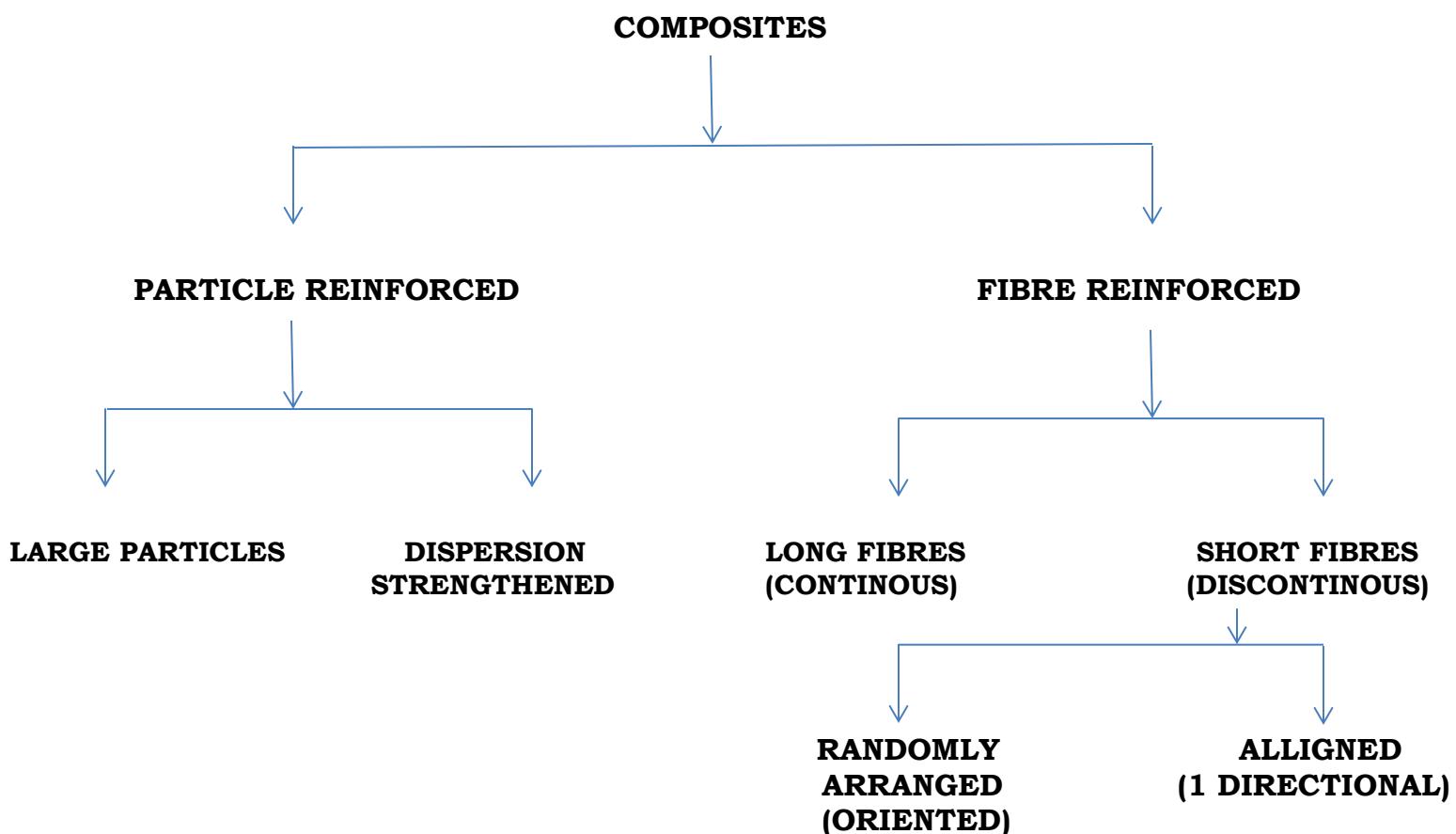
1) On the basis of types of matrix, composites are classified as

Polymer Matrix Composites - PMC

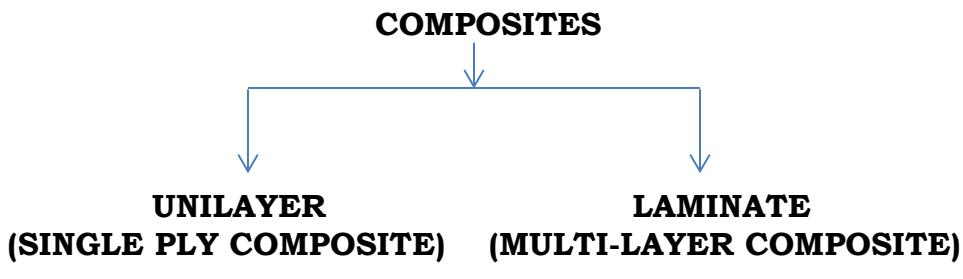
Metal Matrix Composites - MMC

Ceramic Matrix Composite - CMC

2) On the basis of type of reinforcement, composites are classified as



3) On the basis of PLY/LAMINA/LAYERS, composites are classified as



MATRIX BASED COMPOSITES

1. POLYMER MATRIX COMPOSITE (PMC)

Low cost, Light Weight, Tough and Corrosion, resistance but have low strength, stiffness and thermal stability.

Ex: Glass or carbon fibres in thermoset polymer matrix

2. METAL MATRIX COMPOSITE - (MMC)

Ductile, thermal shock resistant, easy to process, high operating temperature, creep resistance but costly.

Ex: Aluminium, Titanium, Copper, steel, molybdenum and their alloys.

3. CERAMIC MATRIX COMPOSITE - (CMC)

Thermally stable, high stiffness, load bearing, high melting point, good resistance to oxidation but low tensile strength, brittle and low shock resistance

Ex: Zirconium particles in Al_2O_3 matrix.

REINFORCED COMPOSITES:

Particle Reinforced Composites:

When reinforcing material is in form of large or Small particles suspended in a matrix then it is called as particulate composites.

i) Large Particle Composites:

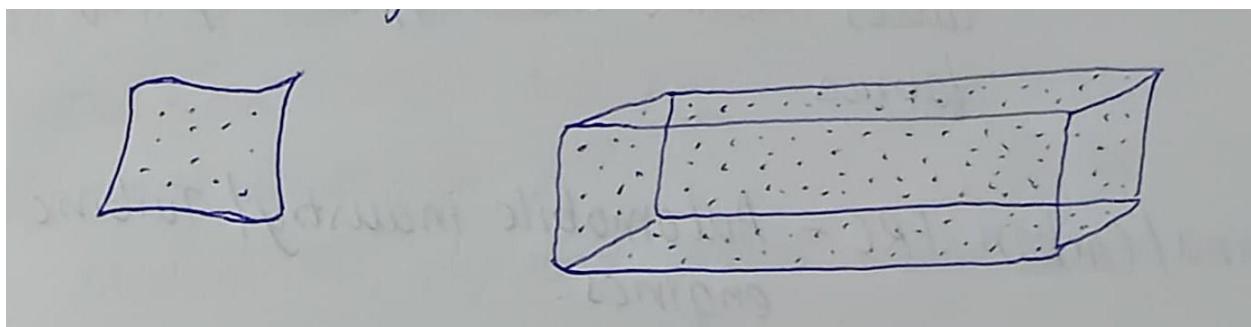
- The particles should be small and should be evenly distributed throughout the matrix.
- The shape must be square, triangular, or round but the dimensions of all sides are usually equal
- The particular phase is harder and stiffer than matrix

Ex: Automobile, tyres, cement, concrete, etc

ii) Dispersion strengthened Composite:

- Very small particles in the range of 10-100nm are Strengthening materials
- Dispersed phase can be metallic or non-metallic
- Such composites retain strength even at elevated temperature for longer periods
- The matrix bears major part of the applied load.

Ex: High temperature strength of nickel alloy is enhanced by adding thoria (ThO_3) particles.



Fibres Reinforced Composite - (FRC)

- These composites involve 3 components - a filament or fibre polymer matrix, bonding agent.
- FRC possess high specific strength, high specific modulus, stiffness, low overall density, high yield Strength, fracture strength and good mechanical properties
- The characteristics of FRC depend upon the nature and properties of matrix and fibre, orientation and distribution of fibres and the bonding between matrix and fibres.
- The fibre and matrix should be chemically compatible with no undesirable reaction between them.
- The fibres should be stable at the room temperature and retain their strength at high temperatures.

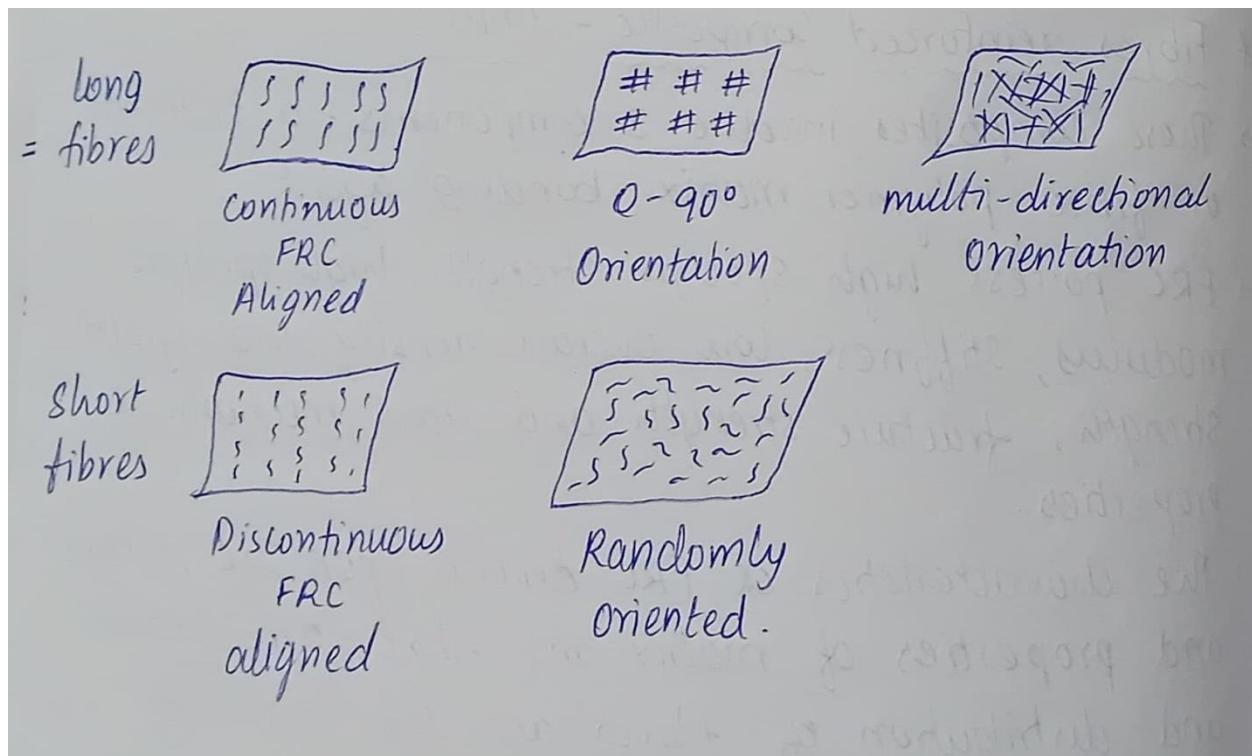
Ex:

Glass FRC - automobile parts, storage tanks, plastic pipes, floorings, underground petrol storage tanks.

Carbon FRC - Aircrafts wings, body, fishing rods, turbine blades, Sports material.

Aramid FRC - Automobile brakes, dutches, ropes, cables, marine industry, bullet proof fabrics.

Aluminal/Carbon FRC - Automobile industry/ Turbine engines.



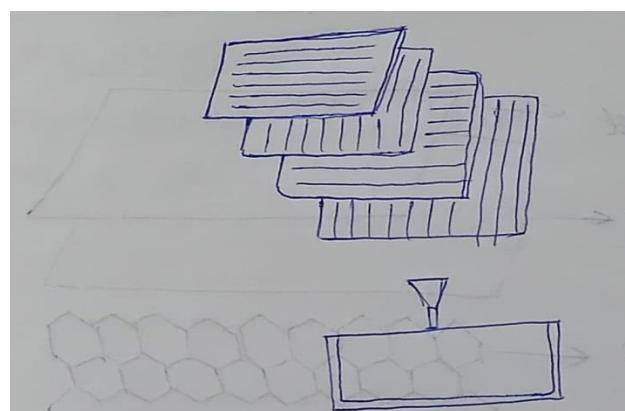
STRUCTURAL COMPOSITE (LAYERED COMPOSITES)

These composites consist of both homogeneous material and composite material bounded together in layers. The layered composites have high strength but possess low shear strength

1. Laminar Composites (unilayer or Single ply)

In laminar composites, two dimensional layers of two different materials are stacked and glued together such that the orientation of high strength direction varies with each successive layer. The individual unidirectional lamina piles are oriented in such a way that the resultant structural component has desired mechanical and physical properties in different directions.

Ex: Modern Ski, plywood, plastic based laminates, etc.

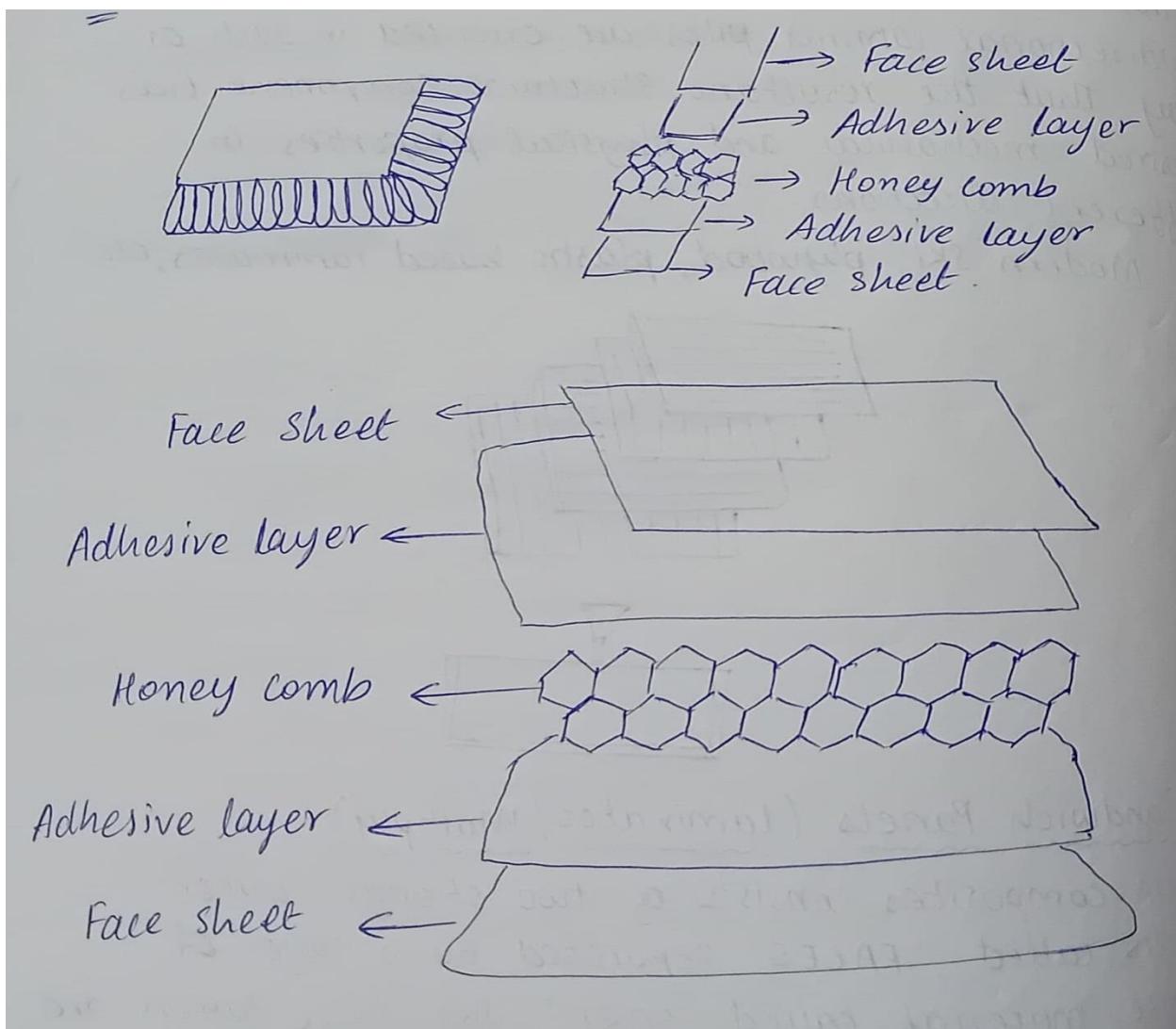


2. Sandwich Panels (laminates / Multiply)

These composites consists of two stronger outer sheets called 'FACES' separated by a layer of dense material called 'CORE'. The three layers are joined together by an adhesive. The core material is of honeycomb structure with low strength and stiffness which resist deformation at right angles to provide rigidity. As thickness of CORE increases, Stiffness also increases. Core material used are synthetic rubber, foamed polymers

The FACE materials bears most of the load and strength.

Ex: FRC, plywood, titanium, steel, Al alloys.



Sandwich panels can be used in variety of applications which include roofs, floors, walls of building and in aircraft for wings, fuse lage and tailplane skins, safety glass, ships and boat hulls.

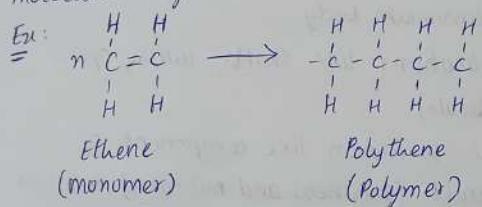
APPLICATION OF COMPOSITES

1. In automobile or transportation industry.
Ex: steel, aluminium body.
2. Marine applications like shafts, hulls, spars (for racing boat)
3. Aeronautical application like components of rockets, aircrafts (business and military), missiles, etc.
4. Communication antenna, electronic circuit boards.
Ex PCB, breadboard.
5. Safety equipment like ballistic protection and airbags of cars.

01/12/2023 UNIT-3: Engineering Materials

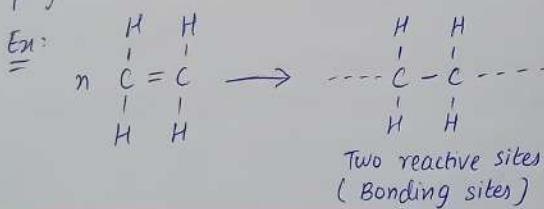
Polymers or macromolecules are giant molecules of high molecular weight which are built together by linking large number of small molecules known as monomers.

A monomer is the single repeating unit in a polymeric chain. These are small molecules of low molecular weight.



* Functionality: The number of bonding sites in a monomer is referred to as its functionality. For a substance to behave as a monomer, it must at least have two reactive sites or bonding sites. i.e. bifunctional.

If a monomer is bifunctional, it produces linear or straight chain polymers whereas if the monomer is trifunctional, it forms cross-linked 3-D Network polymer.



* Degree of Polymerisation: The number of repeating units in a polymeric chain is known as degree of polymerisation.

Polymers with low degree of polymerisation are known as oligo-polymers or oligomers with the molecular weight ranging from 500 - 5000 units. The polymers with high degree of polymerisation are known as high polymers, with molecular weight ranging from 10,000 - 200,000 units.

Q. What is the basic requirement for a substance to behave as a monomer?

A: For a Substance to behave as a monomer,
i. It must have double or triple bond (presence
of unsaturation).
ii. Presence of polar groups (functional groups).

* Classification of Polymers:

Polymers are classified:

1. Based on origin of source,
 - i. Natural
 - ii. Synthetic
 - iii. Semi-synthetic
 2. Based on polymerisation,
 - i. Addition
 - ii. Condensation
 - iii. Co-polymerisation.

3. Based on Structure,
 - i. Linear
 - ii. Branched chain polymers.
 - iii. Cross-linked (3D Network)
4. Based on Main chain,
 - i. Homochain
 - ii. Heterochain
5. Based on Monomers,
 - i. Homopolymers
 - ii. Heteropolymers
6. Based on molecular forces,
 - i. Elastomers
 - ii. Fibres
 - iii. Plastics
 - Thermoplastics
 - Thermosetting plastics

6/12/2023

- I. Based on Source:
 1. Natural polymers: polymers found in nature or isolated from natural materials. Ex: starch, protein, cellulose, etc.
 2. Synthetic polymers: These are man-made polymers or synthesised from low molecular weight compounds. Ex: Nylon, teflon, etc.
 3. semi-Synthetic polymers: It is the blend or mixture of natural or synthetic polymers.

- Ex: Rayon, cellulose derivatives, etc.
- II. Based on Monomers:
 1. Homopolymer: consists of identical monomers.
Ex: polyethene, polystyrene, etc.
 2. Heteropolymer: consists of more than one type of monomer or monomers of different structures.
Ex: Nylon, Terylene, etc.
 - III. Based on Structure:
 1. linear polymers: These are straight chain polymers.
Ex: polyethene, nylon, etc
 2. Branched polymers: The polymeric chain has several branches. Ex: Glycogen.
 3. Cross-linked polymers: The several cross-linkings between the polymeric chain give rise to 3D network. Ex: Bakelite, urea, formaldehyde resin
 - IV. Based on Main chain:
 1. Homochain polymers: The main chain is made of same species of atom.
Ex: polyethylene
 2. Heterochain polymers: The main chain is made up of different species
Ex: Terylene, nylon, etc.

I Based on Application:

1. Fibres: These are natural long chain polymers with high tensile strength, rigidity, stiffness, and are characterised by high melting point.

Ex: Nylon, Kevlon, Terylene, etc.

2. Elastomer (Rubber): These are high polymers with characteristic elasticity as the molecules are arranged in the form of spring-shaped chain of zig-zag pattern.

Ex: Natural rubber, Buna-S, Butyl rubber, Silicon rubber.

3. Plastics: High polymeric materials which can be moulded into various shapes and possess the property of plasticity. They are further classified into two types:

i. Thermoplastics and ii. Thermosetting plastics

Example: Polyethene, PVC, Bakelite, Polystyrene, etc.

i. Thermoplastics: Thermoplastic resins are formed by addition polymerisation. They possess long chain linear structure and can be softened on heating and hardened on cooling. The repeated heating or cooling process does not alter the chemical nature as the change is only physical.

ii. Thermosetting plastics: Thermosetting resins are formed by condensation polymerisation. They possess 3D structure. Once these resins solidify, they cannot be softened again on heating. Thus, these are permanent setting resins.

Differences between Thermoplastic & Thermosetting

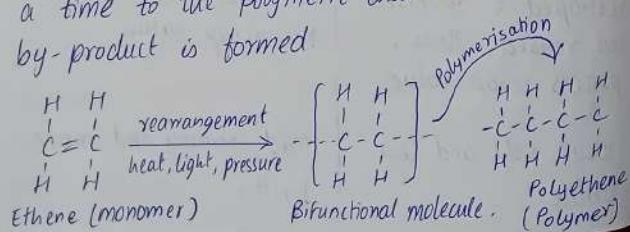
Thermoplastics	Thermosetting
1. Formed by addition or chain polymerisation.	Formed by condensation or step polymerisation
2. Generally long chain linear polymers.	They have 3D network structure.
3. They soften on heating readily.	They do not soften on heating due to strong covalent bonds.
4. They melt on heating	They get charred on prolonged heating
5. They can be softened, reshaped & reversed and reused. Thus, possess scrap value.	They cannot be reused or reshaped. Hence, no scrap value.
6. Weak, soft and less brittle.	Hard, strong and more brittle.

Thermoplastics	Thermosetting
7. Cannot withstand high temperature	Can withstand high temperatures
8. Plasticity is directly proportional to the temperature.	Plasticity is unaffected by change in the temperature.
9. Soluble in some of organic solvents. Ex: Polyethene, PVC, Polystyrene, etc.	Soluble in all types of solvents. Ex: Bakelite, polyester, urea, formaldehyde resin, etc.

Types of Polymerisation:

1. Addition or Chain Polymerisation:

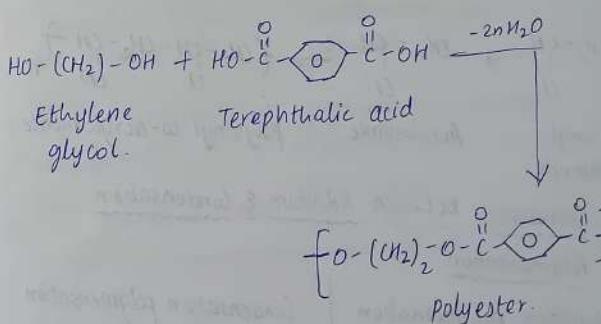
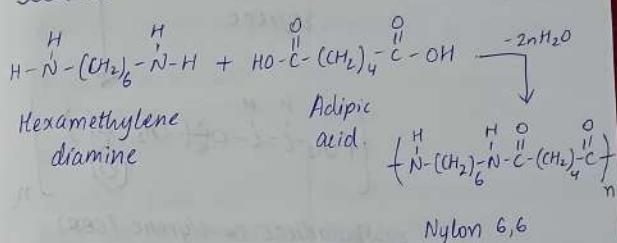
In addition polymerisation, the product formed is an exact multiple of the original monomeric unit. The monomer contains double or triple bond which by intermolecular re-arrangement makes the molecule bifunctional forming a homo chain polymer. The monomer adds one at a time to the polymeric chain and no other by-product is formed



2. Condensation or Step Polymerisation:

It is the polymerisation reaction obtained between monomers containing polar groups with elimination of small molecules like H_2O , HCl , etc. along with the product. The polymerisation proceeds by step-wise mechanism and the rate of reaction is slow.

Examples:

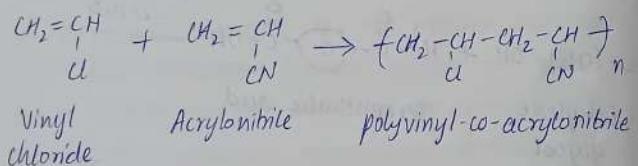
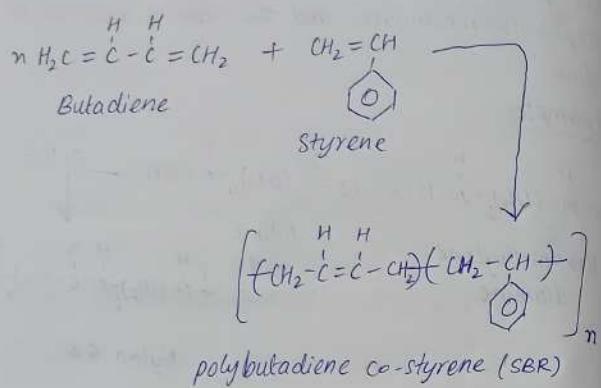


3. Co-polymerisation:

It is a joint polymerisation of two or more

different monomeric species to give high molecular weight compounds known as the co-polymers.

Examples



Differences between Addition & Condensation

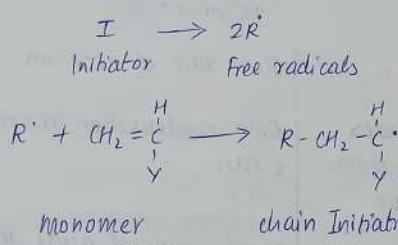
Polymerisation

<u>Addition polymerisation</u>	<u>Condensation polymerisation</u>
1. Only one unit is repeated at a time.	Any two molecular species can react.

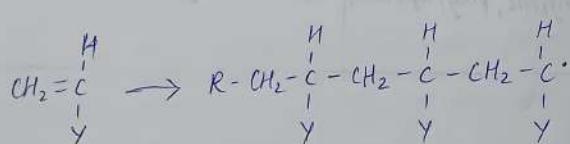
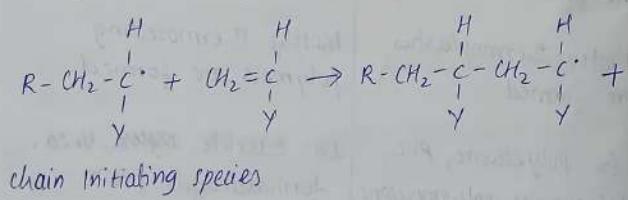
7/12/23

Free Radical Mechanism of addition polymerisation

1. Initiation Step: In this step, free radicals are formed by homolytic fission of an initiator which reacts with the monomeric molecule to form chain initiating species.

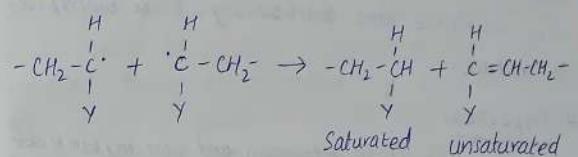


2. Propagation Step: The chain initiating species continues to grow by successive additions of large number of monomer molecules.

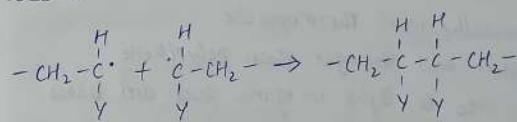


3. Termination Step: The propagation step gets terminated at some point either by disproportionation or by coupling. Once the propagation stops, the polymer is called as dead polymer.

Disproportionation



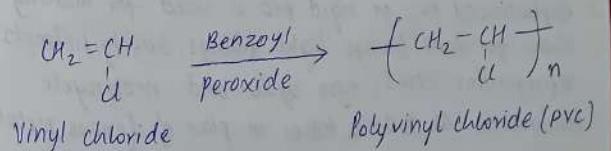
Coupling:



Plastics:

1. PVC (Polyvinyl chloride) :

* Preparation: PVC is prepared by heating a water emulsion of vinyl chloride in presence of Benzoyl peroxide as a catalyst in an autoclave.



Plasticised PVC is prepared by adding the plasticizers such as dibutyl phthalate or tricresyl phosphate or dioctyl phthalate to rigid PVC. It is a good insulator. As compared to leather, it has greater abrasion resistance, flex resistance and washability. It is waterproof in nature.

* Properties:

1. PVC is colourless, odourless and non-inflammable.
2. Its softening point is 148°C .
3. Chemically inert thermoplastic.
4. Tougher and stronger than polyethylene.
5. Resistance to light inorganic acids and bases.
6. Stiff and hard polymer.
7. Excellent oil resistance & resistant to weathering.
8. Superior chemical resistance but soluble in ethyl chloride and THF (Tetra Hydro Furan).

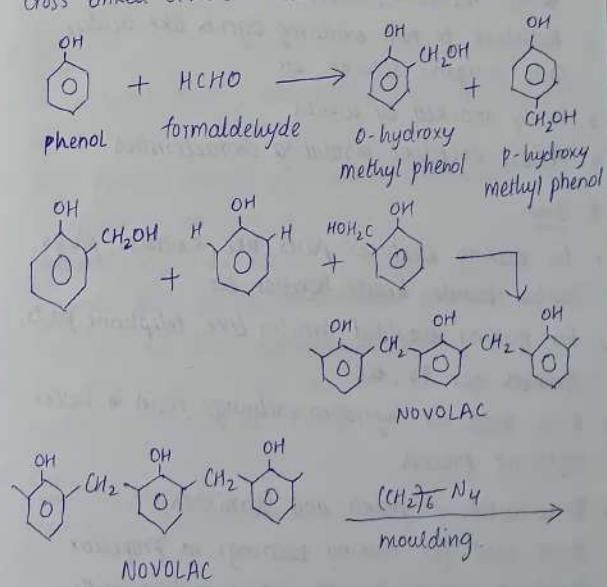
* Uses:

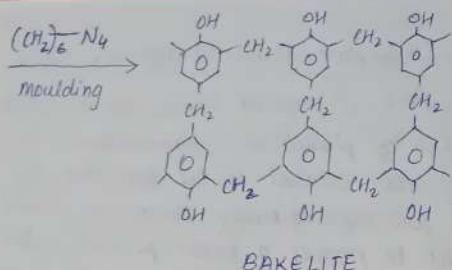
1. Plasticized PVC is used by making dining table mats, raincoats, garden hose, table cloth, curtains, tool handles, toys and gadgets, chemical containers, conveyor belts.
2. Unplasticized PVC or rigid PVC is used for making sheets for tank linings, light fittings, safety helmets, refrigerator items, tyre cable and motorcycle mudguards, as rods & tubes in place of ferrous metals.

8/12/2023

2 Bakelite : (Phenoplast / Phenol-formaldehyde-resin)

* Preparation: It is prepared by the condensation polymerisation of phenol with formaldehyde in presence of acidic catalyst. In the first step, the ortho and para hydroxy methyl phenol are formed which react to produce a linear polymer, called NOVOLAC. During the moulding step, hexa-methylene tetra amine is added to convert the soluble and fusible NOVOLAC into hard, infusible solid of cross-linked structure called as BAKELITE.





* Properties:

1. It is rigid, hard, scratch resistant, infusible, water resistant, insoluble solid.
2. Resistant to non-oxidising agents like acids, salts, inorganic solvents, etc.
3. Easily attacked by alkalis.
4. Possess excellent insulating characteristics.

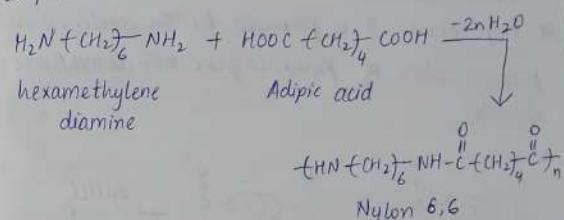
* Uses:

1. For making electrical parts like, switches, plugs, switch boards, heater handles, etc.
2. For making moulded articles like telephone parts, cabinets for TV, etc.
3. It is used as hydrogen exchange resin in water softening process.
4. It is used in paints and varnishes.
5. It is used for making bearings in Propeller shafts for paper industry and rolling mills.

Fibres:

1. Nylon 6,6 (Polyamide):

* Preparation: It is prepared by the condensation reaction between hexamethylene diamine and adipic acid.



* Properties:

1. It is light, thorny and possess high melting point of 265°C.
2. High tensile strength and abrasion resistant.
3. Insoluble in all type of solvents.
4. Thermoplastic in nature.
5. Absorbs little moisture, therefore drip dry in nature.
6. Very flexible and crystalline in nature.
7. On mixing with wool, the strength and abrasion resistance increases.

* Uses:

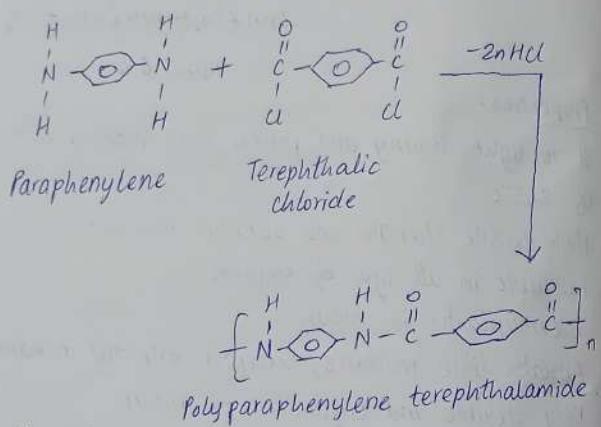
1. Used as a fibre in making socks, carpets, garments, etc.
2. Used in making filaments for ropes, bristles of

toothbrush, tyre cords, etc.

3. Used in oil filters.
4. Used in transmission belts, ribbons for typewriters, insect screens, etc

2. Kevlar (aramid):

* Preparation: It is prepared by the condensation polymerisation of paraphenylen with terephthalic chloride.



* Properties:

1. Light weight, high tensile strength and high modulus.
2. Low thermal expansion. Therefore, it is thermally stable.
3. Abrasion and impact resistant.

* Uses:

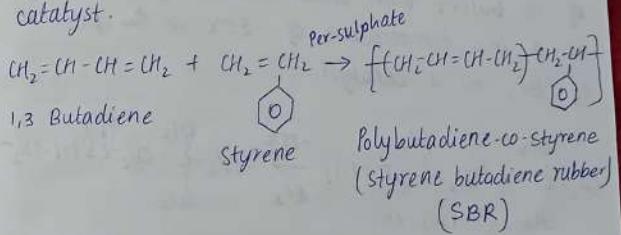
1. Used in light weight boat hulls, race cars, bullet-proof jackets, puncture resistant tyres, aircraft parts, cables and conveyor belts.
2. Used as protective layer on graphite laminate.

13/12/2023

Elastomers:

1. Buna - S:

* Preparation: It is prepared by co-polymerisation of 75% by weight 1,3 Butadiene and 25% by weight styrene in presence of per-sulphate catalyst.



* Properties:

1. Resembles natural rubber in processing characteristics.
2. Possess high abrasion resistance and high load bearing capacity.
3. Low oxidation resistance as it gets oxidized in presence of small amount of ozone.
4. Can be vulcanized to similar to natural rubber.

using Sulphur.

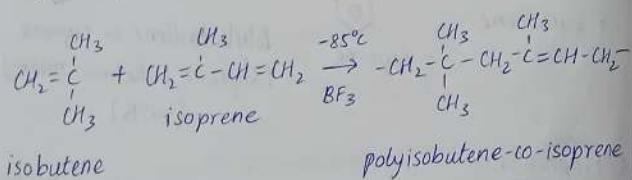
5. It swells in oils ~~and solvents~~. and solvents.

* Uses

1. Mainly used in manufacture of motor tyres.
 2. Also used for wires and cable insulation, foot wear components, floor tiles, shoe soles, water proof fabrics, carpet waterproof fabrics, carpet backings, gaskets, tank linings and other house moulded articles

2. Butyl Rubber

* Preparation: It is prepared by co-polymerisation of iso-butene with small amounts of isoprene at a low temperature of -85°C in the presence of BF_3 as a catalyst.



* Properties.

1. It is cheaper than other synthetic rubbers
 2. It is impermeable to air and ~~water~~ other gases
 3. Excellent resistance to heat, abrasion, chemicals

like HCl , H_2SO_4 , HNO_3 and polar solvents like alcohol and ketones.

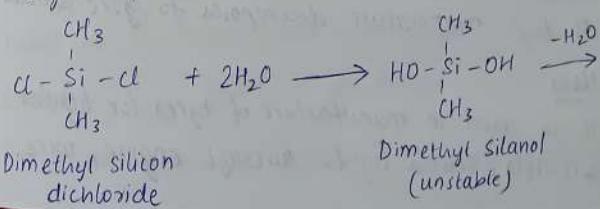
4. High resistance to ozone.
 5. Put electrical insulation properties.
 6. Soluble in hydrocarbon solvents like benzene.
 7. Can be vulcanized but cannot be hardened much.
 8. Becomes soft on oxidative degradation.

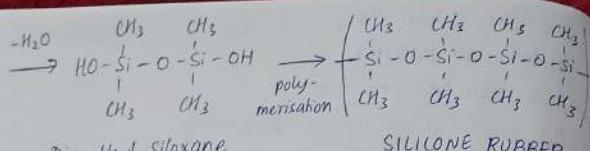
* Uses:

1. For making cycle and automobile tubes, hoses, automobile parts, conveyor belts, tank lining for storing acids, insulation for high voltage wires and cables.

3. Silicone Rubber:

* Preparation: Dimethyl silicon dichloride undergoes hydrolysis to form dimethyl silanol which is unstable and undergoes condensation to produce dimethyl siloxane. The polymerisation of dimethyl siloxane produces Silicone rubber which can be vulcanized in presence of the organic peroxides.

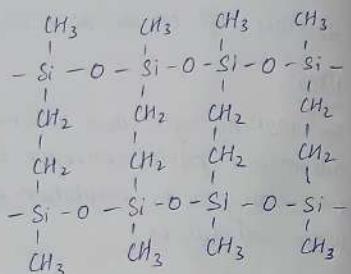




Dimethyl siloxane

SILICONE RUBBER

↓ peroxides



Vulcanised Silicon Rubber.

* Properties:

1. Stable and remains flexible in temperature range of 90-250°C.
2. Resistant to Sunlight, weathering, boiling water, dilute acids and bases.
3. Unaffected by ozone and oxygen.
4. At high temperature, decomposes to give silica.

* Uses:

1. It is used in manufacture of tyres for fighter aircrafts, search lights, aircraft engine, wire

and cable insulation, in preparing lubricants, paints and coatings, used as adhesive, for making artificial heart valves, transfusion tubes, and in plastic surgery, packaging materials, tubes and gaskets.

14/12/2023

CONDUCTING POLYMER

A polymer that conduct electricity is called as conducting polymers. These polymers exhibit the property of conduction due to the presence of extensive configuration in the backbone i.e. presence of alternate π -bonds. The p-orbitals of adjacent carbon atom overlap to form π -bonding molecular orbitals (BMO) and π^* antibonding molecular orbitals (ABMO).

These molecular orbitals spread over the entire length of polymer chain. The BMO are similar to valence band in metals and ABMO similar to the conduction band. When the potential is applied, electrons get excited from valence band to conduction band and as they become mobile, they conduct electricity.

There are different types of conducting polymers.

* Types of Conducting Polymers : (classification)

Conducting polymers are broadly classified into two types:

- Intrinsic conducting polymers,
- Extrinsic conducting polymers.

* Intrinsic conducting polymers:

These polymers have extensive conjugation in the backbone. They are further divided into two types:

1. Undoped Conducting Polymers:

These polymers contain conjugated πe^- which increases their conductivity. The overlapping of conjugated πe^- over the entire backbone results in formation of valence band as well as conduction band which extend over the entire polymer molecule. The bands are separated by a significant band gap. In the presence of an electric field, electrons get excited and become mobile in the conduction band.

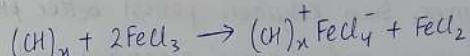
Example: Polyacetylene, Poly pyrrole, Poly aniline, etc.

2. Doped Conducting polymer:

These polymers have πe^- in their backbone & their conductivities are increased by doping. Doping means creating a positive or negative charge on the polymer backbone either by oxidation or reduction. Oxidation gives rise to p-doping and reduction gives rise to n-doping. Doping increases the surface conduction of polymer. Doping is carried out by exposing a polymer to a doping agent in either gaseous or solution phase.

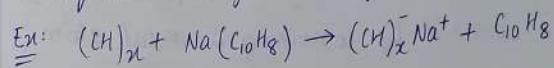
⇒ p-doping:

It is generally done with Lewis acids which extract an electron from the polymer due to which it gets oxidized and acquires a positive charge.



⇒ n-doping:

The polymer is treated with Lewis bases which reduces the polymer as a result of which it acquires a negative charge.



* Extrinsically Conducting Polymers:

In these polymers, conduction is due to the presence of externally added substances. They are of two types:

1. Conductive element filled polymer:

The polymer does not conduct electricity itself. Fillers like carbon black, metallic fibres and metallic oxides are added to the polymers after which they conduct electricity.

Ex: Carbon black filled polypropylene

2. Blended Conducting Polymer:

They are obtained by adding or blending a conventional polymer with a conductive polymer. Such polymers possess better physical, mechanical and chemical properties and can be easily processed.

Ex: Polyanniline + polystyrene, Polyanniline + Polyethene oxide

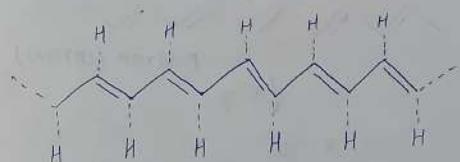
3. Co-ordination Conducting Polymers: (Inorganic polymers)

It is a charge transfer polymer complex containing Polymer obtained by combining a metal atom

with a polydentate ligand. Although the degree of polymerisation is small, yet they exhibit corrosion characteristics.

Polyacetylene:

It is the simplest, organic, intrinsic conducting polymer with the repeating unit $(C_2H_2)_n$. It exists as a flat molecule with a bond angle of 120° . It contains long chain of carbon atoms with alternate single and double bonds. It exists in cis and trans forms where trans-polyacetylene is thermodynamically more stable than the cis form.

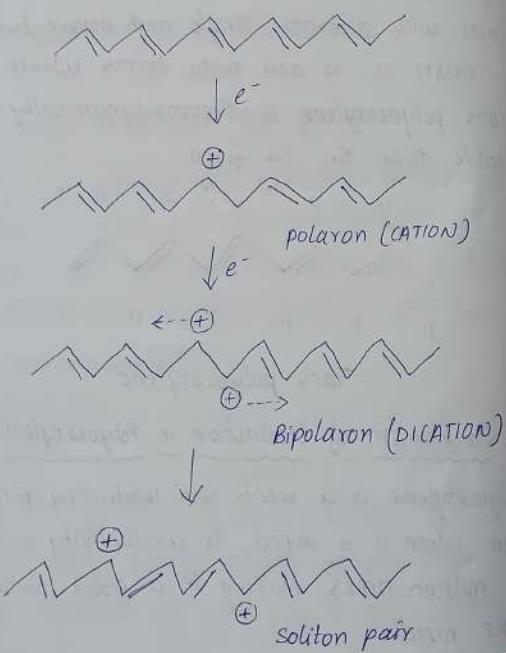


Trans-polyacetylene

* Mechanism of Conduction in Polyacetylene:

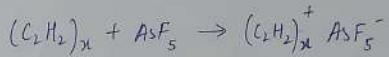
Polyacetylene is a weak semi-conducting polymer but when it is doped, its conductivity increases a million times, making it a good conductor like metals.

1. P-doping: When polyacetylene is subjected to p-dopants like halogens and Lewis acids, they extract an electron from the polymer chain which makes the chain cation and the acceptor as anion. P-doped polyacetylene retains its conductivity even after exposure to air for several days.

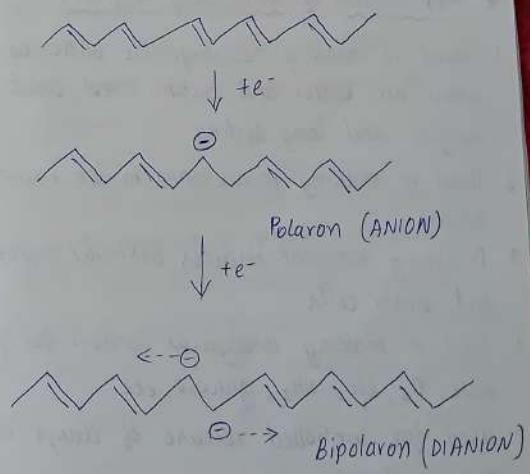


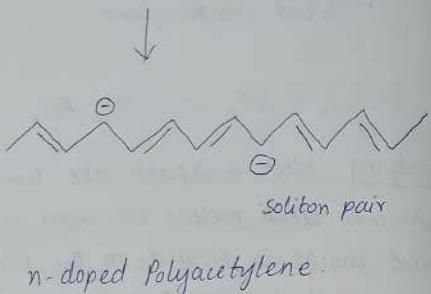
P-doped polyacetylene

OR

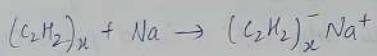


2. n-doping: When n-dopants like Lewis bases and alkali metals are used, a (-ve) negative charge is created on the polymer backbone as it becomes anionic and the donor becomes cation. The doping increases the conductivity but n-doped polyacetylene are highly sensitive to air and moisture.





OR



15/12/23

* Application of Conducting Polymers:

1. Used in making rechargeable batteries, which are better and button sized, light in weight and long lasting.
2. Used in making membranes in ion-exchange resins.
3. Designing artificial muscles, artificial nerves, and brain cells.
4. Used in making analytical sensors for pH, heat, O₂, etc, NH₃, glucose, etc.
5. Used for controlled release of drugs in cancer treatment.

6. Photo conducting polymers are used in the graphic displays, phone displays, etc.
7. Used as ink for printing circuits.
8. Used in battery, fuel and cell technology.
9. Used in solar cells, diodes and transistors.
10. Used in electromagnetic screening materials
11. Used in wiring in aircraft and aerospace components.

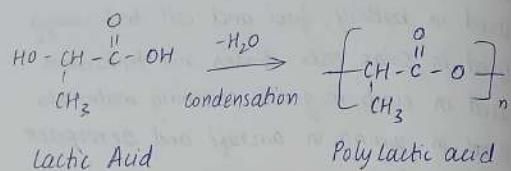
Biodegradable Polymers:

Biodegradation means the enzymatically promoted breakdown of a polymer caused by the micro-organisms such as bacteria, fungi, algae, etc. The extent to which a polymer degrades into smaller fragments is called as degree of biodegradation.

* Polylactic Acid (PLA):

PLA is a thermoplastic polyester made from lactic acid which is a natural molecule widely used in food preservatives and flavouring agents. Lactic acid can be synthesized from microbial fermentation of sugars from potato, starch, corn sugar and other dairy products.

This lactic acid then undergoes fermentation and condensation to form polylactic acid.



* Properties.

1. PLA can be processed into fibres & films like other thermoplastics
 2. It is brittle in nature
 3. Water sensitive and degrades slowly by hydrolysis.
 4. Its melting temperature can be increased from 40-50°C and heat deflection temperature can be increased from 60°C to 190°C by blending it with poly-D-lactide (pDLA)
 5. It is biodegradable, non-toxic, and also eco-friendly.

* Advantages

1. Lactic acid is the raw material for the production of biodegradable lactide polymers.
 2. Possesses advantage over other polymers due to its strength, thermoplastic nature, biocompatibility and availability from renewable sources.
 3. Biodegradable blenders are prepared from PLA mixed with other polymers which improves the biodegradability.

* Degradation of PLA:

PLA degrades quickly to CO_2 and H_2O or CH_4 and H_2O under high temperature and high humidity by undergoing hydrolysis followed by bacterial attack on the fragmented residue. The high molecular weight polymer is then hydrolysed to low molecular weight oligomers.

* Applications of PLA :

1. Used in packaging materials, paper coating and disposable articles
 2. Used in biomedical application like stents, dialysis and drug delivery devices

- 3. Used as medical implants in form of anchors, screws, plates, pins, rods, mesh (as it breaks inside the body in 6 months to 2 years).
- 4. Can be manufactured in the form of fibres, disposable garments and diapers, upholstery and other hygiene products.

20/12/2023

UNIT - 4 : CHEMICAL FUELS

The term fuel includes all the combustible substances that combine with oxygen from atmosphere and undergoes combustion producing a large amount of heat which can be used for domestic and industrial purposes economically.

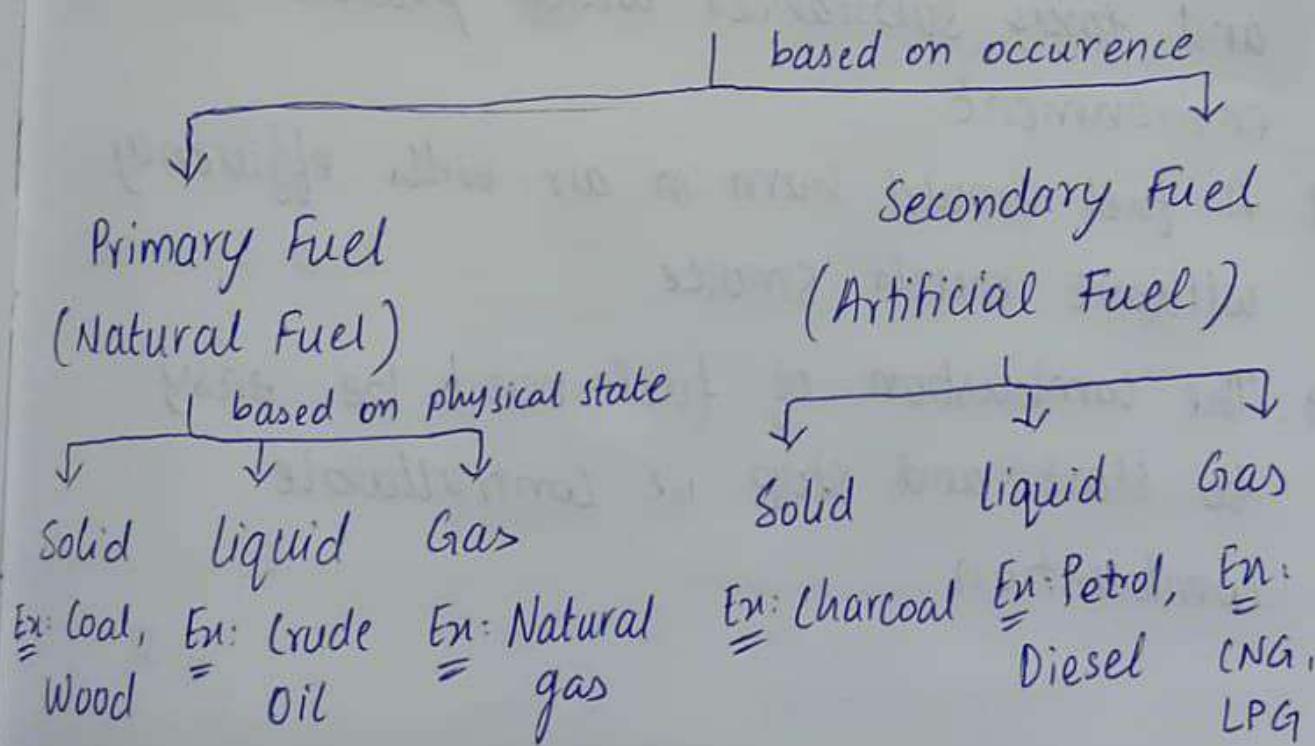


chemical fuels are substances which on exothermic reaction with oxygen during the combustion liberate heat and end products.

* Classification of Fuels:

The chemical fuels may be solid, liquid or gas which are naturally found or artificially prepared.

Chemical Fuels



* Requirements of a Good Fuel:

1. A good fuel should have high calorific value.
2. Fuel must possess low moisture content.
3. An ideal fuel must have moderate ignition temperature.
4. A good fuel should possess low non-combustible matter.
5. fuel should have moderate rate of combustion for continuous supply of heat.
6. A good fuel should be readily available, easy to transport and store and should be of low cost.
7. Fuel should not produce harmful gases and toxic substances which pollute the environment.
8. A fuel should burn in air with efficiency without much smoke.
9. The combustion of fuel must be easy to start and stop. i.e. Controllable Combustion.

Comparison between Solid, liquid, & Gaseous Fuels:

Fuel characteristics	Solid	Liquid	Gaseous
Cost	cheap	costly	costly
Storage	Easy	Require closed containers.	must be stored in leak-proof voluminous storage tanks
Risk of Fire Hazards	least	High	very high as they are highly inflammable
Combustion rate	Slow	Quick	very rapid & effluent
Combustion control	Not easy	can be stopped when needed	possible by controlling air supply
Handling cost	High (requires labour for storage & transport)	Low (can be transported through pipes)	Low
Ash	Disposal of ash is a problem	No ash problem	

Fuel characteristics	Solid	Liquid	Gaseous
Smoke	Invariably produced	Clean burning	No smoke
Calorific value	Least	Higher	Highest
Thermal efficiency	Least	Higher	Highest
Use in the IC Engine	Not possible	Possible	Possible

* Calorific Value:

It is the amount of heat liberated from complete combustion of unit mass or unit volume of fuel in air or oxygen.

Units: Kcal / Kg or Kcal / m³ or Cal / g

* Higher or Gross Calorific Value (HCV/GCV)

The total amount of heat liberated when a unit mass or unit volume of fuel has been completely burnt out and the products of combustion are cooled to room temperature.

* lower or Net Calorific Value (LCV / NCV):

The net heat produced when a unit mass or unit volume of fuel is burned completely and the products of combustion are not cooled to room temperature but are allowed to escape into the atmosphere.

$$LCV = HCV - 0.09H \times 587 \text{ cal/g}.$$

21/12/2023

CHEMISTRY# Theoretical calculation of Calorific Value By
Dulong's formula:

The calorific value of the fuel can be estimated from Dulong's formula when the HCV of carbon,

$C = 8080$, Hydrogen $H = 34500$, Sulphur

$S = 2240 \text{ cal/g}$

$$\text{HCV} = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S \right]$$

$$\text{HCV} = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S \right]$$

$$\text{LCV} = \text{HCV} - 0.09H \times 587 \text{ cal/g.}$$

- Q. Calculate the HCV and LCV for a coal sample having $C = 82\%$, $H = 3.1\%$, $S = 1.1\%$, $N = 0.8\%$, $O = 3.9\%$, ash = 9.1%

$$\text{Sol: } \text{HCV} = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S \right]$$

$$= \frac{1}{100} \left[8080 \times 82 + 34500 \times \left(3.1 - \frac{3.9}{8} \right) + 2240 \times 1.1 \right]$$

$$HCV = 7551.55 \text{ cal/g}$$

$$\begin{aligned}LCV &= HCV - 0.09H \times 587 \text{ cal/g} \\&= 7551.55 - 0.09(31) \times 587 \\&= 7387.77 \text{ cal/g}\end{aligned}$$

- Q. calculate the HCV and LCV of a fuel having C = 80%, H = 7%, S = 3.5%, N = 2.1% O = 3% ash = 4.4%

$$\text{sol. } HCV = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S \right]$$

$$\begin{aligned}&= \frac{1}{100} \left[8080 \times 80 + 34500 \times \left(7 - \frac{3}{8} \right) + 2240 \times 3.5 \right] \\&= 8828.02 \text{ Kcal/Kg}\end{aligned}$$

$$\begin{aligned}LCV &= HCV - 0.09H \times 587 \text{ cal/g} \\&= 8828.02 - 0.09(7) \times 587 \\&= 8458.21 \text{ Kcal/Kg}\end{aligned}$$

- Q. calculate the NCV of a fuel if it contains 6.5% H₂ and the GCV of fuel is 3500 cal/g.

$$\begin{aligned}
 \text{Sols} \quad NCV &= GCV - 0.09H \times 587 \text{ cal/g} \\
 &= 3500 - 0.09(6.5) \times 587 \\
 &= 3500 - 0.09(6.5) \times 587 \\
 &= 3156.6 \text{ cal/g}
 \end{aligned}$$

21

Combustion:

It is an exothermic reaction accompanied by development of heat and light which increases the temperature considerably.

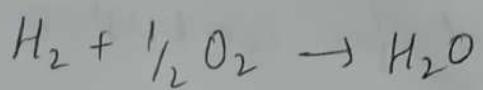
* Ignition Temperature of Fuel:

It is the minimum temperature at which a substance ignites and burns without the further addition of heat externally. The fuel must be preheated to its ignition temperature for proper combustion of fuel.

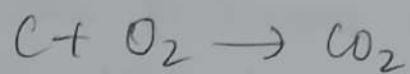
Ex: Coal is preheated by adding kerosene, Petrol, paper, twigs, etc.

* Combustion Calculations:

1. Substances combine in definite proportions which are determined by their molecular mass.



2 : 16 : 18



12 : 32 : 44



32 : 32 : 64

2. Composition of air:

a) By volume: $\frac{100}{21}$ or 4.76 volume of air

provides 1 volume of O_2 for combustion.

b) By weight: $\frac{100}{23}$ or 4.35 weight of air

provides 1 weight of O_2 for combustion.

3. At STP, 1 gram mole of any gas occupies

22.4 litres.

Example: 32 grams of O_2 occupies 22.4 L at STP.

4. The molecular mass of air is 28.94 g/mole.

5. Theoretical amount of O_2 required for complete combustion of 1 kg of fuel ~~is~~ is

$$\text{Amt. of } O_2 = \frac{32}{12} C + 8 \left[H - \frac{O}{8} \right] + S$$

6. The amount of air required for combustion of 1kg of fuel.

$$\text{wt. of air} = \frac{100}{23} \times \text{wt. of O}_2$$

$$= \frac{100}{23} \left[\frac{\frac{32}{12} C + 8 \left[H - \frac{O}{8} \right] + S}{100} \right]$$

Questions:

1. Calculate the wt. and volume of air required for complete combustion of 1kg of carbon.

$$\text{Sol: wt. of air} = \frac{100}{23} \times \text{wt. of O}_2$$

$$= \frac{100}{23} \times \left(\frac{32}{12} C \right)$$

$$= \frac{100}{23} \times \frac{32}{12} \times 1$$

$$= \frac{100}{23} \times 2.66 \text{ kg O}_2 = 11.59 \text{ kg air}$$

$$\text{Vol. of air} = \frac{100}{21} \times \text{Vol. of O}_2$$

$$= \frac{100}{21} \times 1862 \text{ lit O}_2 = 8866.6 \text{ lit air}$$

Rough work: Volume of O₂

$$\begin{array}{rcl} 32 \text{ g} & - & 22.4 \text{ L} \\ 2.66 \text{ Kg} & - & 1862 \text{ L} \\ \times 1000 \text{ g} & & \end{array}$$

2. Calculate the wt. and volume of air required for complete combustion of 3kg of carbon and calculate the volume in m³.

Sol: wt. of air = $\frac{100}{23} \times$ wt. of O₂

$$= \frac{100}{23} \times \frac{32}{12} \times 3$$

$$= \frac{100}{23} \times 8 \text{ Kg O}_2$$

$$= \frac{100}{23} \times 8 \text{ Kg O}_2 = 34.78 \text{ Kg air}$$

$$\text{vol. of air} = \frac{100}{21} \times \text{vol. of O}_2$$

$$= \frac{100}{21} \times 5600 \text{ lit O}_2$$

$$= 26,666.66 \text{ lit air}$$

$$= 26.6 \text{ m}^3$$

Rough: Volume of O_2 .

$$32 \text{ g} \longrightarrow 22.4 \text{ L}$$

$$8 \text{ kg} \longrightarrow 5600 \text{ L}$$

$$\times 1000 \text{ g}$$

3. Calculate the wt. of air required for the combustion of a sample fuel having:

$$C = 80\%, O = 3\%, H = 4\%, N = 3\%, S = 2\%,$$

$$\text{ash} = 5\%, \text{moisture} = 3\%.$$

Calculate if 60% excess air is supplied.

$$\underline{\underline{\text{Sol:}}} \quad \text{wt. of air} = \frac{100}{23} \times \text{wt. of } O_2$$

$$= \frac{100}{23} \times \frac{32}{12} C + 8 \left[H - \frac{O}{8} \right] + S$$

$$= \frac{100}{23} \times \left[\frac{32}{12} \times 80 + 8 \left(4 - \frac{3}{8} \right) + 2 \right]$$

$$\frac{100}{23}$$

$$= \frac{100}{23} \times 2.44 \text{ kg } O_2$$

$$= 10.62 \text{ kg air}$$

$$\text{For } 60\% \text{ excess air} = 10.62 \times \frac{160}{100} = 16.99 \text{ kg air.}$$

Q) calculate the qty. of air required for a sample fuel having C=72%, H=5%, O=4%, N=2%, S=3%, ash=8% moisture = 6%. Also calculate the air required for 5kg of the fuel.

$$\text{wt. of air} = \frac{100}{23} \times \text{wt. of O}_2$$

$$= \frac{100}{23} \times \frac{32}{12} C + 8\left(H - \frac{O}{8}\right) + S$$

$$= \frac{100}{23} \times \underbrace{\left[\frac{32}{12} \times 72 + 8\left(5 - \frac{4}{8}\right) + 3 \right]}_{100}$$

$$= \frac{100}{23} \times 2.31 \text{ kg O}_2 = 10.04 \text{ kg air}$$

$$\text{for 5kg of fuel} = 10.04 \times 5 = 50.2 \text{ kg air.}$$

Q. Cal the GCV & NCV of air wt. by 1 Kg of
Coal burning C=75%, H=5.2% O₂=12.1% ash=4%

Also calculate if 40% air is supplied

$$\text{A) } \text{GCV} = \frac{1}{100} \left[8080 \times 75 + 34500 \left(5.2 - \frac{12.1}{8} \right) \right]$$

~~at 20°C~~

$$= 73321.8 \text{ kJ}$$

$$\text{NCV} = 73321.8 \times 75 - 0.09 \times 5.2 \times 587$$

$$= 732964.003 \text{ kJ}$$

$$\text{wt. of O}_2 = \frac{1}{100} \left[\frac{32}{12} \times 75 + 8 \left(5.2 - \frac{12.1}{8} \right) \right] \times \frac{100}{23}$$

$$= 2.20295 \times \frac{100}{23} = 9.97 \text{ kg}$$

$$\text{for 40\%} \quad \frac{40}{100} \times 9.97 = 3.99 \text{ kg}$$

27/12/2023

CHEMISTRY

Solid Fuels - COAL

Coal is the solid primary fuel formed by decay and decomposition of plants & animals over the years deep under the earth's crust by the action of heat and pressure.

* Ranking in Coal:

Rank is a qualitative measure of carbon content present in coal. It is defined as the degree or extent of maturation. The soft coals have low percentage of carbon and are termed as low ranked coals whereas the hard coals have high percentage of carbon and are called as high ranked coals.

Wood → Peat → Lignite → Bituminous → Anthracite
coal

% C :	50%	57%	67%	83%	93%
Rank :	low rank	low rank	low rank	High rank	High rank
CV :	4,000 to	4,125 to	6,500 to	8,000 to	8,650 to
(cal/g)	4,500	5,400	7,100	8,500	8,700

* Proximate Analysis of Coal:

In order to assess the quality of coal, it is subjected to proximate analysis which includes determination of moisture, volatile matter, ash, and fixed carbon content. Proximate analysis gives information about practical utility of coal.

1. Moisture: A known weight of finely powdered coal is taken in a silica crucible, and heated in electric hot air oven at 105 - 110°C for 1 hour. The crucible is then removed and cooled in an air dessicator and its weight is noted. The loss in weight is reported as percentage of moisture.

$$\% \text{ moisture} = \frac{\text{loss in weight}}{\text{wt. of coal sample}} \times 100$$

Significance: The presence of high moisture content increases the cost and transportation charges. It lowers the calorific value and quenches the fire in the furnace. High rank coal contains 5-10% moisture.

2. Volatile Matter: The coal sample left in the crucible is covered with a lid and placed in

electric muffle furnace at $925 \pm 20^{\circ}\text{C}$ for 7 minutes. The crucible is then removed and cooled in a dessicator and its weight is noted. The loss in weight is reported as the percentage of volatile matter.

$$\% \text{ volatile matter} = \frac{\text{loss in weight}}{\text{wt. of coal sample}} \times 100$$

Significance: The non-combustible matter present in the fuel does not contribute to the calorific value. Hence, it is undesirable. Coal having high volatile matter burns with long flame, high smoke and possess low calorific value. Also, the volume of furnace required is large.

3. Ash: The sample left in crucible is heated without the lid in presence of air & oxygen at $700 - 750^{\circ}\text{C}$ for $\frac{1}{2}$ hour in electric muffle furnace. The weight of the residue obtained after burning the coal is noted. The heating, cooling and weighing process is repeated till constant weight is obtained.

$$\% \text{ ash} = \frac{\text{wt. of ash formed}}{\text{wt. of coal sample}} \times 100$$

Significance: Ash is the non-combustible, useless matter left behind after burning of coal. It reduces the calorific value and decreases the efficiency of coal. It increases the transporting, handling and storing cost and an additional cost is required for ash disposal. The presence of ash destroys the furnace walls, obstructs the supply of air, leads to pollution and metallurgical problems.

4. Fixed carbon: It is obtained by deducting the sum total of moisture, volatile matter, ash from 100.

$$\% \text{ Fixed C} = 100 - \% (M + VM + A)$$

Significance: High carbon content means high calorific value indicating better quality of coal. It helps in designing the furnace and shape of fire cocks.

* Ultimate Analysis of Coal:

The ultimate analysis helps to assess the quality of coal. It includes determination of Carbon, Hydrogen, Nitrogen, Sulphur, present in coal. This data is useful for industrial purpose.

1. Carbon and Hydrogen: A known quantity of coal is burnt in a current of dry oxygen where carbon and hydrogen get oxidized to CO_2 and H_2O . These gases are passed over two bulbs. In one bulb, anhydrous CaCl_2 is taken which absorbs H_2O and in another bulb, KOH is taken which absorbs CO_2 . The increase in weight of CaCl_2 bulb represents the weight of water formed while the increase in weight of KOH bulb represents the weight of CO_2 formed.

$$\% \text{ C} = \frac{\text{increase in wt. of KOH}}{\text{wt. of coal sample}} \times \frac{12}{44} \times 100$$

$$\% \text{ H} = \frac{\text{increase in wt. of } \text{CaCl}_2}{\text{wt. of coal sample}} \times \frac{2}{18} \times 100$$

Significance: The major combustible constituent of coal are Carbon and Hydrogen. Available hydrogen contributes towards calorific value. Thus, greater the percentage of carbon and hydrogen, better is the quality of coal and higher is its calorific value. High percentage of carbon reduces the size of combustion chamber required.

2. Nitrogen: 1 gram of powdered coal is heated with concentrated H_2SO_4 in Kjeldahl's flask. It is then titrated with NaOH to liberate ammonia which is distilled over and absorbed in a known volume of 0.1 N H_2SO_4 solution (V_1). The un-used acid is determined by back titration with 0.1 N NaOH solution (V_2).

$$\% N = \frac{0.1 (V_1 - V_2) \times 1.4}{\text{wt. of coal sample}}$$

Significance: Nitrogen is an inert, incombustible matter, the presence of which is undesirable. A good quality coal should have very little

Nitrogen content. The nitrogen in fuels gets converted to oxides of nitrogen which reacts with ozone and results in depletion of the ozone layer. It also contributes to acid rains.

3. Sulphur: A known weight of coal is completely burned in bomb calorimeter where sulphur is oxidised to sulphates. The ash from the bomb calorimeter is extracted with dilute HCl and treated with BaCl₂ to precipitate Sulphate as BaSO₄.

$$\% S = \frac{\text{wt. of } BaSO_4 \text{ obtained}}{\text{wt. of coal sample}} \times \frac{32}{233} \times 100$$

Significance: Sulphur is the undesirable content in coal. Though it increases the calorific value, the SO₂ and SO₃ gases produced pollute the environment and contribute to acid rains. Coals having 65-70% sulphur are unsuitable for use in metallurgy and in iron industry.

4. Oxygen: The percentage of Oxygen is directly obtained by deducting the sum total of Carbon, Hydrogen, Nitrogen, Sulphur from 100.

$$\% \text{ O} = 100 - \% (\text{C} + \text{H} + \text{N} + \text{S})$$

Significance: Oxygen is usually present in combined form with hydrogen. High oxygen content coals have high moisture content, low calorific value and low coking power. The good quality coal should have low oxygen content.

Numericals:

1. 2.5 grams of powdered coal sample was taken in a silica crucible and heated for 1 hour at 105°C after which a residue of 2.425 grams was obtained. The crucible was then covered with a lid and heated for 7 minutes at 960°C in a furnace which gave a residue of 1.520 grams. The crucible was then heated without the lid until constant weight of 0.232 grams was obtained. Calculate the percentage results.

Sol: It is Proximate Analysis.

$$\% \text{ Moisture} = \frac{\text{loss in weight}}{\text{wt. of coal sample}} \times 100$$

$$= \frac{2.5 - 2.425}{2.5} \times 100 = 3\%$$

$$\% \text{ Volatile matter} = \frac{\text{loss in weight}}{\text{wt. of coal sample}} \times 100$$

$$= \frac{0.1 (50 - 12.5) \times 1.4}{3.12}$$

$$= 1.68 \%$$

3. 0.1 grams of coal sample was heated in bomb calorimeter and the ash formed was heated with BaCl_2 , which gave a precipitate of 0.01 gram BaSO_4 . Calculate the percentage results.

Sol: % S = $\frac{\text{wt. of } \text{BaSO}_4 \text{ formed}}{\text{wt. of coal sample}} \times \frac{32}{233} \times 100$

$$= \frac{0.01}{0.1} \times \frac{32}{233} \times 100 = 1.37 \%$$

Liquid Fuels

1. Petroleum or Crude Oil:

The crude oil or petroleum is the major source of liquid fuels. Petroleum is usually found way below the earth's crust, floating upon a layer of brine and has a layer of natural gas on top of it.

The petroleum is drilled from the earth's crust and sent to refineries.

* Refining of Crude Oil:

The crude oil is separated into various fractions by fractional distillation. This process is called as refining of crude oil.

- i. Cottrell's Process: The water from the crude oil is separated by cottrell's process. Here, the crude oil is allowed to flow between two highly charged electrodes so that the water droplets combine and

Separate out as water.

ii. Removal of Sulphur: The crude oil is treated with copper oxide to remove the harmful sulphur compounds as copper sulphates.

*** Fractional Distillation: The crude oil is heated in an iron retort to about 400°C where all the volatile constituents are evaporated. The hot vapours are then passed through a tall cylindrical tower known as fractionating column. The column consists of a number of horizontal stainless steel ~~roasted~~ trays at short distances provided with individual chimney which are covered with loose caps. As the vapour moves up, fractional condensation takes place at different heights of the column. The higher boiling fractions condense first while the lower boiling fractions condense later.

Gases (Below 30°C)

Stainless steel trays.

chimney

loose cap

Petroleum ether (30°-70°C)

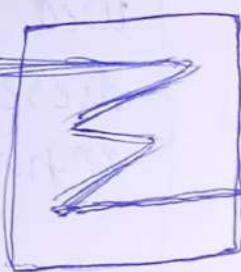
Gasoline (40°-120°C)

Naphtha (120°-180°C)

Kerosene (180°-250°C)

Diesel oil (250°-320°C)

Lubricating oil



IRON RETORT

(400°C)

fractionating column

Heavy oil

(320°-400°C)

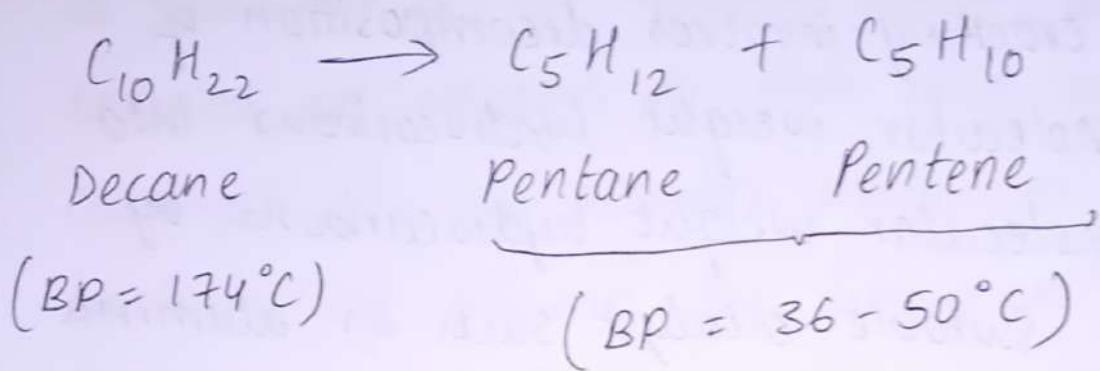
* Major Fractions obtained From Fractional
Distillation:

characteristics	Gasoline/ Petrol.	Kerosene	Diesel
1. Composition	Mixture of hydrocarbons such as C_5H_{12} to C_8H_{18}	Mixture of hydrocarbons such as $C_{10}H_{22}$ to $C_{16}H_{34}$	Mixture of hydrocarbons such as $C_{15}H_{32}$ to $C_{18}H_{38}$

Characteristics	Gasoline / Petrol	Kerosene	Diesel
2. Temperature	obtained b/w 40 - 120 °C	obtained b/w 180 - 250 °C	obtained b/w 250 - 320 °C
3. Calorific value (kcal/kg)	11,250 kcal/g	11,100 kcal/g	11,000 kcal/g
4. Uses	used as a fuel for IC engines in aeroplanes & automobiles. As solvent in dry cleaning.	Used as fuel in stoves, water heater jet engine fuel, for making oil gas & lab gas, used as an illuminant.	used in diesel engine.

* Cracking: It is defined as decomposition of high molecular weight hydrocarbons of high boiling point into simpler low molecular weight hydrocarbons of low boiling point.

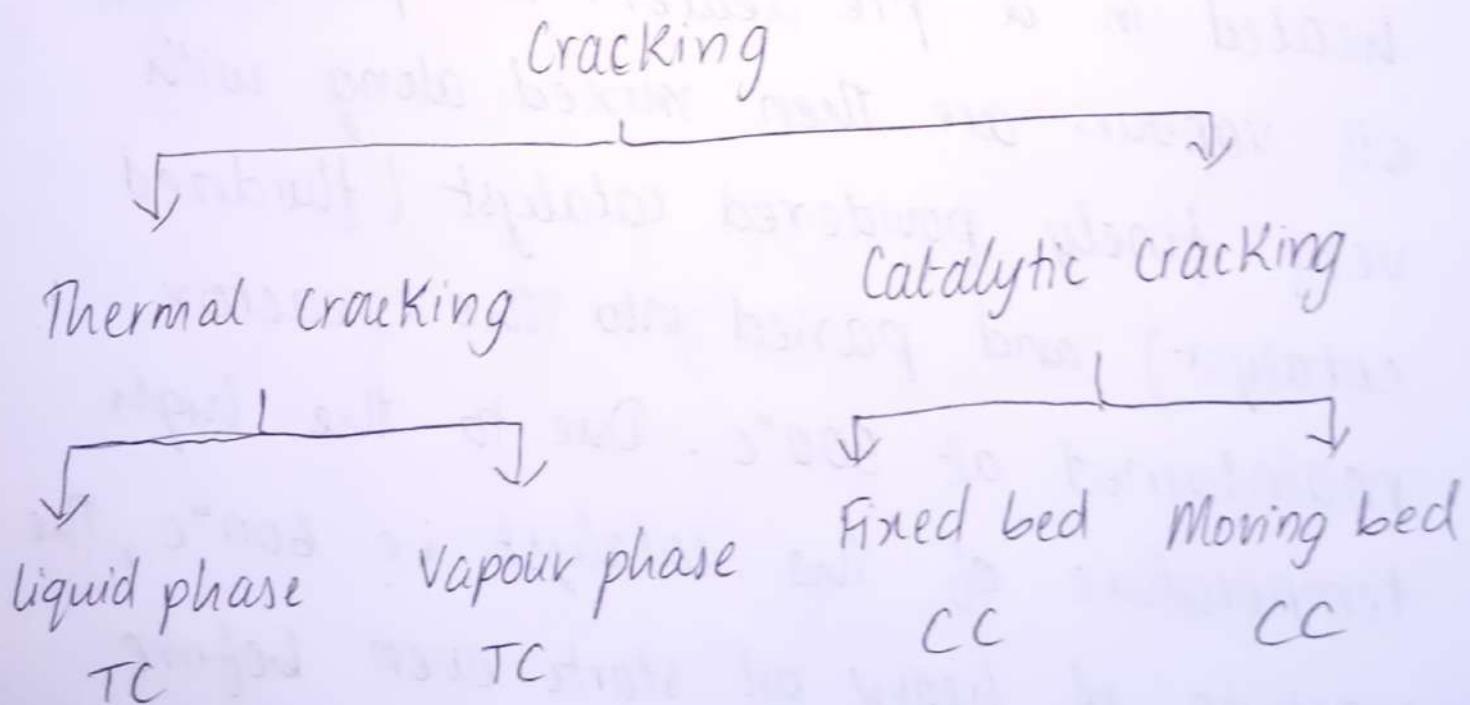
Example:



* Significance:

Cracking helps to overcome the shortage of petrol or gasoline. Also, the petrol obtained through cracking has much better characteristics than straight run petrol.

* Types of Cracking:



Moving Bed Catalytic Cracking:

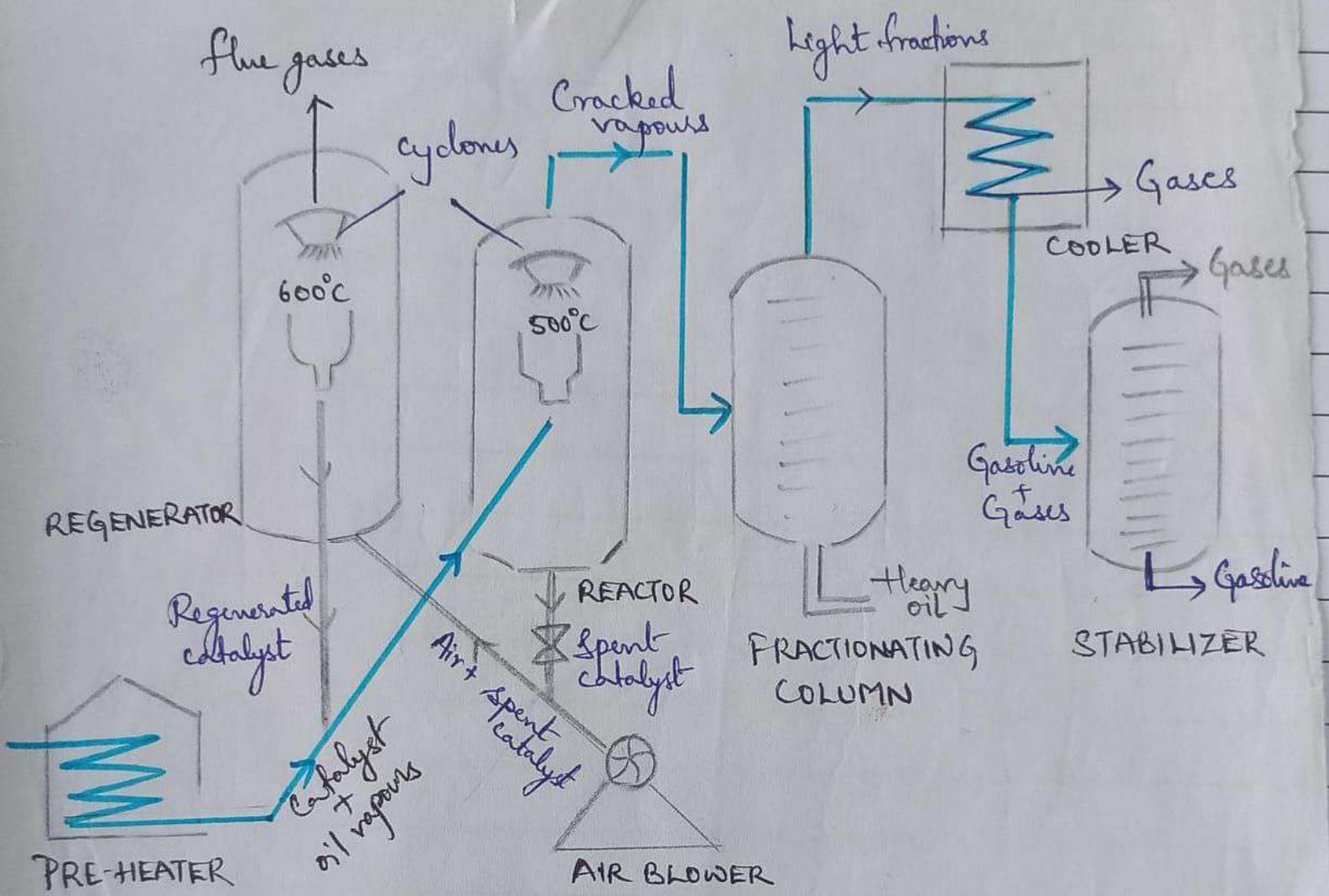
Catalytic cracking involves decomposition of higher molecular weight hydrocarbons into lower molecular weight hydrocarbons by using a suitable catalyst such as alumina or aluminium silicate or zirconium catalyst.

Catalytic cracking requires much lower temperature and pressure when compared to thermal cracking.

The solid catalyst is very finely powdered such that it almost behaves like a fluid (fluidized cracking). In moving bed catalytic cracking, the feed oil is first heated in a pre-heater. The pre-heated oil vapours are then mixed along with very finely powdered catalyst (fluidized catalyst) and passed into the reactor maintained at 500°C . Due to the high temperature of the catalyst i.e. 600°C , the cracking of heavy oil starts even before entering into the reactor. The cracked oil

Vapours are then passed into fractionating column through the internal cyclone fixed at the top of the reactor which allows only cracked oil vapours to pass and retains the catalyst in the reactor itself. In the fractionating column, the heavy oil is separated and the vapours are passed through the cooler where gasoline condenses with other gases. This is then sent to the stabilizer where the dissolved gases are removed and pure gasoline is obtained. In the re-generator, the carbon is burnt and the re-generated catalyst is mixed with fresh incoming oil vapours. The cyclone in the regenerator releases the flue gases.

P. T. O.



* Advantages of Catalytic Cracking :-

- 1) The yield of Petrol obtained is high because the catalyst are selective in their action.
- 2) Better quality of Petrol is obtained because the products contain less amount of sulphur & high amount of aromatic Hydrocarbons.
- 3) No external fuel is required for cracking.
- 4) A much lower temp & pressure are sufficient for catalytic cracking.
- 5) The percentage of gum & gum forming compounds is very less.
- 6) The cost of production is low.
- 7) The products contain less of gas, coke & more of liquid products.

* Knocking In Petrol Engine :-

- It is defined as tutting sound produced while accelerating the engine.
- In an IC engine a mixture of gasoline vapour & air is used as fuel.
- After initiation of combustion reaction by the electric spark in the cylinder. The flame should spread smoothly through the gaseous mixture, thereby the expanding gas drives the piston down.
- Sometimes due to the compression of air + fuel mixture it gets heated to a temperature greater than the ignition temperature which leads to auto ignition even before sparking.
- This produces Knocking. It can also cause multiple flame fronts within the cylinder instead of single flame.
- These flames collide with explosive force producing a sharp metallic ringing noise that is Knocking.
- The pre-ignition of fuel + air mixture also leads to Knocking.

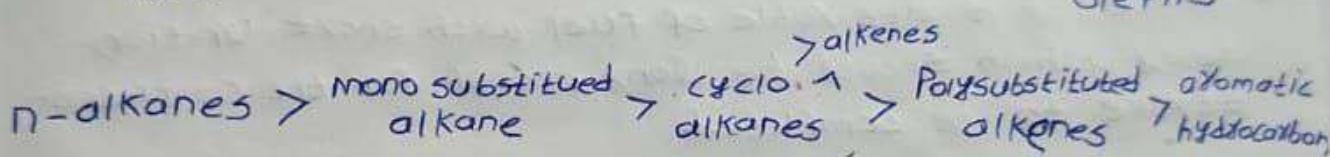
→ In some cases, the state of oxidation becomes so great that the last portion of fuel & air mixture gets ignited instantaneously producing explosive violence known as Knocking, which results in loss of efficiency.

* Disadvantages of Knocking :-

- 1) Knocking results in decreased power output & mechanical damage due to over heating of IC Engine.
- 2) Prolonged Knocking leads to loss in efficiency.

* Factors effecting Knocking :-

- 1) Design of Engine
- 2) Running condition
- 3) chemical structure of fuel where aromatic hydrocarbons have anti-knocking characteristics than paraffins & higher olefins



* Octane Number :-

The Percentage of iso-octane in the mixture of iso-octane + n-heptane which have the same Knocking characteristics as the gasoline sample under the same set of conditions is known as Octane Number.

Ex:- Gasoline sample with ON = 90 has same Knocking characteristics as a mixture of 90% iso-octane + 10% n-heptane

* Anti-Knock Agents

Anti-knock Agents like (TEL) Tetra Ethyl lead, Benzene, di-ethyl telluride etc are added to enhance the octane Number.

* Unleaded Petrol :-

A Petrol whose Octane Number is increased without adding lead compound is called Unleaded Petrol.

→ Octane boosters like MTBE (Methyl tertiary butyl ether)
ETBE (ethyl)
Ethanol, etc are added.

Knocking in diesel engine

The combustion of fuel in diesel engine is not instantaneous. The interval between the start of fuel injection and its ignition is called as ignition delay. The ignition delay is due to the time taken for vapourisation of individual droplets and raising of vapour to its ignition temperature. When ignition delay is long, it leads to fuel accumulation in the engine even before ignition. In such a case, when ignited, an explosion occurs due to the increased temperature and pressure which results in diesel knock. Hence, it is desirable to have fuels with short ignition delay which should be long enough for the compression stroke to be completed.

Cetane number

The percentage of n-hexa decane in a mixture of n-hexa decane + 2-methyl naphthalene which has the same ignition characteristics (knocking) as the diesel sample under the same set of conditions is known as cetane number

Ex- A diesel sample with CN=40 performs with the same efficiency as a mixture of 40% n-hexa decane + 60% 2-methyl naphthalene

Octane number	Cetane number
① It is the percentage of iso-octane in the mixture of iso-octane + n-heptane.	① It is the percentage of n-hexa decane in the mixture of n-hexa decane + 2-methyl naphthalene.
② ON is used to find the suitability of gasoline or IC engine fuels.	② CN is used to find the suitability of diesel fuel
③ ON can be enhanced by adding TEL, Benzene, ETBE, MTBE etc.	③ CN can be increased by adding alkyl nitrates
④ Straight-chain hydrocarbons have low octane number.	④ Straight-chain hydrocarbons have high cetane number.

Gaseous fuels:-

LPG (Liquified Petroleum Gas) :-

or
Bottled Gas or Refinery Gas

LPG is obtained as a by-product during the cracking of heavy oil or from natural gas. LPG is dehydrated, desulphurised and traces of mercaptans (organic sulphides) are added to give the warning of gas leakage. The calorific value of LPG is 27800 kcal/ m^3

Composition:-

LPG mainly consists of hydrocarbons that can exist as gas under atmospheric pressure and can be readily liquified under high pressure. It mainly includes n-butane, iso-butane and butylene along with propane.

Advantages:-

1. High efficiency and ^{high} heating rate.
2. Requires very little care for maintenance.
3. Clean to use, handle and store.
4. Well-designed burners ensure complete combustion.
5. Burns with no smoke. Therefore, eco-friendly.
6. Portable in cylinders even to remote places.
7. Possess less health hazard.
8. Compared to gasoline, LPG easily mixes with air, is cheaper and knock resistant.

Uses:-

1. Widely used as domestic and industrial fuel.
2. Used as a source of petrochemical.
3. Can be used as direct motor fuels.
4. Used in IC engines.

CNG (Compressed Natural Gas) :-

CNG is the natural gas compressed to a high pressure of 1000 atmospheres. Its calorific value ranges between 12000 - 14000 kCal/m³.

Composition

CNG mainly consist of methane. Its simple one carbon molecular structure makes possible complete combustion and ensures clean burning.

CH₄ 80-90%.

Ethane 4-5%.

Propane 1.7-2%.

Oxygen 0.5-0.6%.

C₄ and higher 0.7-0.8%.

C₆ and higher 0.2-0.3%.

CO₂ + N₂ 3-9%.

Hydrocarbon 0.1-0.2%. no need to learn all these except CH₄ (methane)

Advantages

1. Low fuel cost and low maintenance cost.
2. High octane number and high efficiency.
3. Complete and homogenous combustion.
4. Clean burning. Therefore eco-friendly.
5. Produces very low particulate emissions

and unburnt hydrocarbons

- 6. When released in atmosphere, mixes harmlessly with air
- 7. CNG fuel tanks are safer and stronger.
- *8. Compared to LPG, the CNG is much safer fuel as it ignites at a higher temperature, has low operating cost and the conversion of gasoline automobiles to CNG vehicles is easy

Uses:-

Used as a domestic fuel for heating and cooking and also used as fuel in automobiles