Engineering Chemistry

Sub. Code : 15CHE12 I.A.Marks:25
Hours/ week : 04 Exam.Hours:03
Total Hours : 50 Exam. Marks : 100

Module-1

Electrochemistry and Battery Technology

Electrochemistry: Introduction, Derivation of Nernst equation for electrode potential.. Referenceelectrodes: Introduction; construction, working and applications of calomel and Ag/AgClelectrodes. Measurement of standard electrode potential using calomel electrode. Constructionand working of glass electrode, determination of pH using glass electrode. Concentration cells:Electrode & Electrolyte, numerical problems on electrolyte concentration cells.

Battery Technology: Introduction, classification - primary, secondary and reservebatteries.Characteristics - cell potential, current, capacity, electricity storage density, energyefficiency,cycle life and shelf life. Construction, working and applications of Zinc-Air, Nickel- metalhydride batteries. Lithium batteries: Introduction, Li-MnO2 and Li-ion batteries.

Fuel Cells: Introduction, difference between conventional cell and fuel cell, limitations &advantages. construction &working of methanol-oxygen fuel cell with H2SO4 electrolyte.

10 hours

Module-2

Corrosion and Metal Finishing:

Corrosion: Introduction, electrochemical theory of corrosion, galvanic series. Factorsaffectingthe rate of corrosion: ratio of anodic to cathodic areas, nature of metal, nature of corrosion product, nature of medium – pH, conductivity, andtemperature. Types of corrosion-Differential metal , differential aeration(Pitting and waterline) and stress (caustic embrittlement in boilers).Corrosion control:, inorganic coatings-Anodizing of Al and phosphating, metal coatings-Galvanizationand Tinning. Cathodic protection (sacrificial anodic and impressed current methods).

Metal Finishing: Introduction, Technological importance. Electroplating: Introduction,principles governing-Polarization, decomposition potential and overvoltage. Factors influencingthe nature of electro deposit-current density, concentration of metal ion & electrolyte;pH, temperature & throwing power of plating bath, additives-complexing agents, brighteners,levellers, structure modifiers & wetting agents. Electroplating of chromium and Ni(Watt's bath). Electro less plating: Introduction, distinction between electroplating and electroless plating, electro less plating of copper & manufacture of double sided Printed Circuit Boardwith copper. **10 hours**

Module-3

Fuels and Solar Energy:

Fuels: Introduction, classification, calorific value- gross and net calorific values, determinationof calorific value of fuel using bomb calorimeter, numerical problems Cracking: Introduction,fluidized catalytic cracking, synthesis of petrol by Fishcher-Tropsch process, reformation ofpetrol, octane and cetane numbers. Gasoline and diesel knocking and their mechanism, antiknocking agents, , power alcohol, biodiesel.

Solar Energy: Introduction, utilization and conversion, photovoltaic cells-importance, construction and working. Design: modules, panels & arrays. Advantages & disadvantages of PV cells. production of solar grade silicon(union carbide process), doping of silicon-diffusion technique (n&p types) andpurification of silicon(zone refining). **10 hours**

Module-4

Polymers:

Introduction, types of polymerization: addition and condensation, mechanism of polymerizationfreeradical mechanism taking vinyl chloride as an example. Molecular weight of polymers:number average and weight average, numerical problems. Glass transition temperature (Tg):Factors influencing Tg-Flexibility, inter molecular forces, molecular mass, branching & crosslinking, and stereo regularity. Significance of Tg. Structure property relationship: crystallinity,tensile strength, elasticity, plastic deformation & chemical resistivity. Synthesis, properties andapplications of PMMA (plexi glass), , Polyurethane and polycarbonate. Elastomers:Introduction, synthesis, properties and applications of Silicone rubber. Adhesives: Introduction,synthesis, properties and applications of epoxy resin. Polymer Composites: Introduction,synthesis, properties and applications of kevlar. Conducting polymers:Introduction, mechanism of conduction in Polyaniline and applications of conductingpolyaniline. **10 hours**

Module-5

Water Technology and Nanomaterials:

Water Technology: Introduction**,** sources and impurities of water; boiler feed water, boiler troubles with disadvantages -scale and sludge formation, priming and foaming, boiler corrosion(due to dissolved O2, CO2 and MgCl2). Determination of DO, BOD and COD, numerical problems. Sewage treatment: Primary, secondary (activated sludge method) and tertiary methods. Softening of water by ion exchange process. Desalination of sea water by reverse osmosis & electrodialysis (ion selective)..

Nano Materials: Introduction, properties (size dependent). Synthesis-bottom up approach (solgel,precipitation, gas condensation, chemical vapour condensation. Nano scale materials-fullerenes, carbonnano tubes, nano wires . **10 hours**

Index Sheet

MODULE-1

ELECTROCHEMISTRY AND BATTERY TECHNOLOGY

Electrochemistry: Introduction, Derivation of Nernst equation for electrode potential. Reference electrodes: Introduction; construction, working and applications of calomel and Ag/AgClelectrodes. Measurement of standard electrode potential using calomel electrode. Constructionand working of glass electrode, determination of pH using glass electrode. Concentration cells:Electrode & Electrolyte, numerical problems on electrolyte concentration cells.

Contents

- **Electrochemistry:Introduction,Derivation of Nernst equation for electrode potential.**
- **Referenceelectrodes: Introduction, construction, working and applications of calomelelectrodeandAg–AgClelectrode**
- **Measurement of standard electrode potential using calomel electrode.**
- **DeterminationofpH of a solution using glasselectrode, concentrationcells, Electrode and electrolyte**
- **Numerical problems on electrolyte concentration cells.**

ELECTROCHEMISTRY:

INTRODUCTION:

GALVANICCELL

Itisadevice,whichconvertschemicalenergyintoelectricalenergywithredoxreactionattherespectiveelectrodes.

ELECTROLYTICCELL: Thedevice,whichconvertselectricalenergytochemicalenergy,iscalledelectrolyticcell.

ELECTROLYTICCELL	GALVANICCELL
1.Itrequiresexternalelectricsource	1.Itdoesnotrequiresexternalelectricsource
2.Redoxreactionarenonspontaneous	2.Redoxreactionarespontaneous
3.Cathodeisnegativeelectrode	3.Cathodeispositiveelectrode
4.Anodeispositiveelectrode	4.Anode is negative electrode
Ex: Electroplating And Electroless Plating	**Ex:** Daniel cell fuel cell

ELECTROCHEMICALCONVENSIONS

1.RepresentationofElectrode:

Itoxidationreactiontakesplaceatanode,thentheelectrodeisrepresentedasM/M^{n+}

ItreductionreactiontakesplaceatthecathodethentheelectrodeisrepresentedasM^{n+}/M

Theverticallinesindicatedthecontactbetweenmetalelectrodesandmetalions.

2.RepresentationofCell:

Thefollowingpointshavetobenotedtorepresentanelectrochemicalcell

a>AnodeisalwayswrittentoLHS.

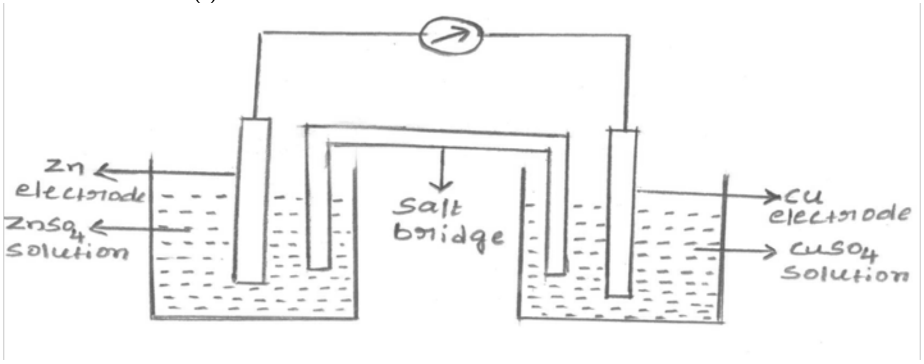
b>CathodeofthecelliswrittentoRHSoftheanode.

c>The2verticallinesdenotesthesaltbridgeandinterfacebetweenthe2electrodes.

Cellnotationisgivenby

$M / M^{n+} // M^{n+}/M$

Ex.$Zn_{(s)} / Zn^{+2}//Cu^{+2}/Cu_{(s)}$



3.Calculationofemfofthecell:

Accordingtoelectrochemicalapplication

$$E_{cell}=E_{cathode}-E_{anode}.$$

IftheEMFvalueis+vethenthereactionisspontaneous&ifitis–vethereactionisnonspontaeous.

SINGLEELECTRODEPOTENTIAL(E)

Singleelectrodepotentialisdefinedasthepotentialdevelopedattheinterfacebetweenthemetalanelectr olyticsolution,whenitiscontactwithsolutionofitsownions.

STANDARDELECTRODEPOTENTIAL(E^0)

Itisthepotentialmeasured,whentheelectrodeisincontactwithsolutionofunitconcentrationat298K. Iftheelectrodeinvolvesgas,thengasisat1atmpressure.

EMFOFTHECELL(E_{cell})

Thepotentialdifferencebetweenthetwoelectrodesofthegalvaniccellwhichcausestheflowofcurrentfromoneelectrode(higherpotential)totheother(lowerpotential)isknowasEMFofthecell.

MEASUREMENTOFELECTRODEPOTENTIAL

ThepotentialofanymetalelectrodeismeasuredusingStandardHydrogenElectrode[SHE]whosepotentialiszeroanditinvolvesthefollowingsteps.

1.CONSTRUCTIONOFTHECELLASSEMBLY

TheelectrodeiscoupledwithSHEthroughsaltbridgeasshowninfigure.Theemfismeasuredusingelectronicvoltmeter.

Forexample:Tomeasuretheelectrodepotentialofzincelectrode,itiscombinedwithSHEandthecellnotationisgivenby

$Zn_{(s)}/Zn^{2+}_{(aq)}//H^+(1M) / H_{2(g)}/Pt$

2.ASSINGINGTHESIGNONTHEELECTRODE

Theanodeandthecathodeofthecellcanbeidentifiedbyconnectingtheelectrodestothe appropriateterminalsofthevoltmeter.TheemfismeasuredonlywhenZnelectrodeisconnected to the –ve terminal andhydrogenelectrodeto+veterminalofthevoltmeter.Thentheemfvalueobservedis0.76V

3CALCULATIONOFELECTRODEPOTENTIAL

$$E^0cell=E_{cathode}-E_{anode}$$
$$0.76v= E_{SHE} – E^0zn^{2+}{}_{/Zn}$$
$$0.76=0V– E^0zn^{2+}{}_{/Zn}$$

Therefore$E^0zn^{2+}{}_{/Zn}$=-0.76V

Similarlytheelectrodepotentialisdeterminedforothermetalelectrodes.

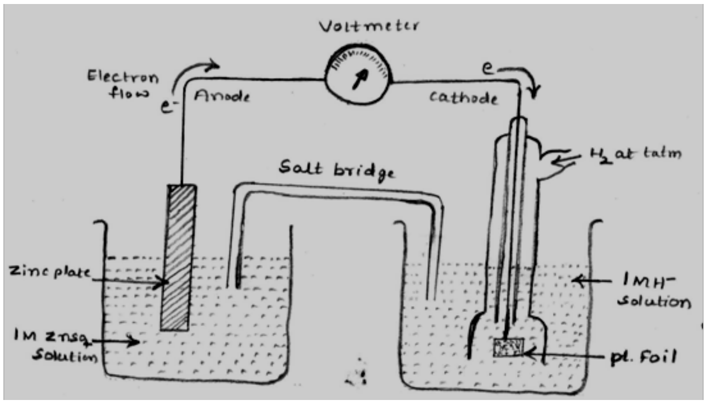


Fig.DeterminationofelectrodepotentialofZincelectrodeusingSHE

NERNSTEQUATION:

Itrelateselectrodepotentialandconcentrationoftheelectrolytespecies

Considerthefollowingreversibleelectrodereaction

$M^{n+} + neM \rightleftharpoons$--------------1

Thedecreaseinfreeenergy($-\Delta G$)representsthemaximumamountofworkthatcanbeobtainedi.e.-

ΔG=Wmax-----------------2

Themax. workdoneisgivenby

Wmax.=No. ofCoulombsxEnergyavailable/Coulomb-----3

Wmax=nFxE-----------------------4

Equatingequations2&4

$-\Delta G=nFE$----------------------5

Understandardconditions$-\Delta G^0= nFE^0$----------------------6

Accordingtothermodynamicequation

$-\Delta G=-\Delta G^0-RT\ln Kc$--------------------------7

WhereR-gasconstant,T-temperature,Kc-equilibriumconstant

Kcforforwardreactionofequationno.1is

$Kc=[M]/[M^{n+}]= 1/[M^{n+}]$since$[M]=1$

Substitutethevaluesof$-\Delta G$,$-\Delta G^0$&Kcinequation7

$nFE=nFE^0-RT\ln 1/[M^{n+}]$----------------------------------8

Convertlntolog$_{10}$bymultiplyingwith2.303anddividetheequationthroughoutbynF

$E=E^0-2.303RT/nF\log 1/[M^{n+}]$--------------------------------9

SubstitutethevaluesofR,Fandtemperatureat25^{0}C

$E=E^0 -0.0591/n\log 1/[M^{n+}]$or

$E =E^0+0.0591/n\log[M^{n+}]$--------------------------------------10

NernstequationforEcellforthefollowingreactionat25^{0}Cis

$aA+bB \rightleftharpoons cC+dD$

$Ecell=E^o cell+0.0591/n\log[A]^a][B]^b/[C]^c[D]^d$

.

Reference electrodes:It is the electrode of known potential and are used to measure electrode potential of other electrodes.

Types of reference electrodes

Primary reference electrodes eg;SHE

Secondary reference electrodes eg;Calomel and Silver-silver chloride electrode.

CalomelElectrode:

Itisametal-metalsaltionelectrode.Itconsistsofaglasstubehavingasidetubeoneach side.Mercury(Hg)isplacedatthebottomofthetubeanditiscoveredbyapasteofHg_2Cl_2withHg.AsolutionofKClisintroducedabovethepastethroughsidetube.Aplatinumwiresealedintotheglasstubeisdippedintomercurywhichgivestheexternalelectriccontact.

Elecroderepresentation:$Hg_{(l)}/Hg_2Cl_{2\,(s)}/Cl^-$ (Sat.)

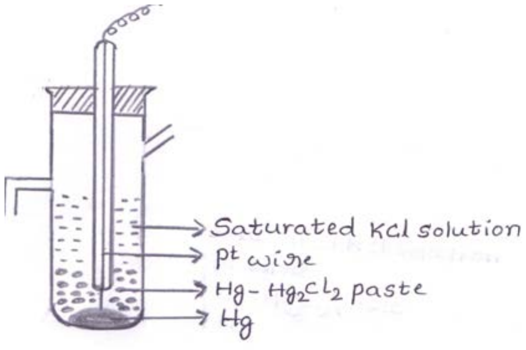


Fig.SaturatedCalomelelectrode.

Working:Itactsasanodeorcathodedependingonnatureoftheotherelectrode.

Whenitactsasanode,theelectroderepresentationis

$$2Hg+2Cl^- \rightarrow Hg_2Cl_2 +2e$$

Whenitactsascathodetheelectrodereactionis

$$Hg_2Cl_2 + 2e \rightarrow 2Hg+2Cl^-$$

Thenetreversibleelectrodereactionis

$$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg+2Cl^-$$

AcordingtoNernstequationelectrodepotentialis

$E=E^0-0.0591\log[Cl^-]$at298K

Theelectrodepotentialisdecidedbytheconcentrationofchlorideions.

Uses:

Itisusedassecondaryreferenceelectrodetomeasureelectrodepotential

Usedasreferenceelectrodeinpotentiometricdetermination

UsedasreferenceelectrodeinpHdetermination

Advantages:Easytoconstruct,electrodepotentialisreproducible,andstableforlongperiod,cellpotentialdoesnotvarywithtemperature.

Silver–Silverchlorideelectrode:ItispreparedbycoatingathinlayerofAgClelectrolyticallyontoasilverwire. Thiswirewhenplacedinasolutionofpotassiumchloridedevelopsadefinitepotentialdependingontheconcentrationoftheelectrolyteused.

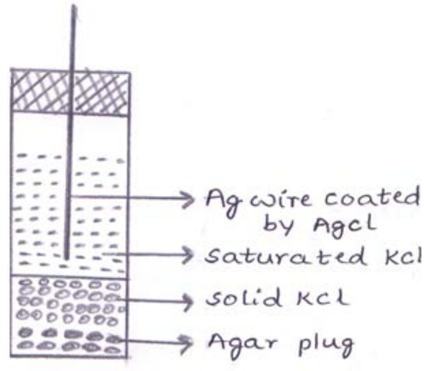


Fig.Silver–Silverchlorideelectrode.

Electroderepresentation:$Ag_{(s)}/AgCl_{(s)}/Cl^-$

Electrodereaction:$AgCl_{(s)}+e \rightarrow Ag_{(s)}+Cl^-$

ElectrodepotentialisgivenbyE=$E^0-0.0591\log[Cl^-]$at298K

TheelectrodepotentialdependsonconcentrationofchlorideionsandforthesaturatedKClthepotentialis 0.199V

Uses:

Usedassecondaryreferenceelectrodetomeasureelectrodepotential

Referenceelectrodeinionselectiveelectrode

Usedtodeterminepotentialdistributionuniformity.

Measurment of standard electrode potential using calomel electrode:

The given electrode is coupled with calomel electrode(Reference electrode)

The emf of the cell is measured using a device.Knowing the potential offered by the reference electrode,the potential of given electrode is calculated.

The potential is measured using a vacuum tube voltmeter,because it draws a minium current for working.

Zinc electrode is coupled with Saturated calomel electrode using salt bridge.

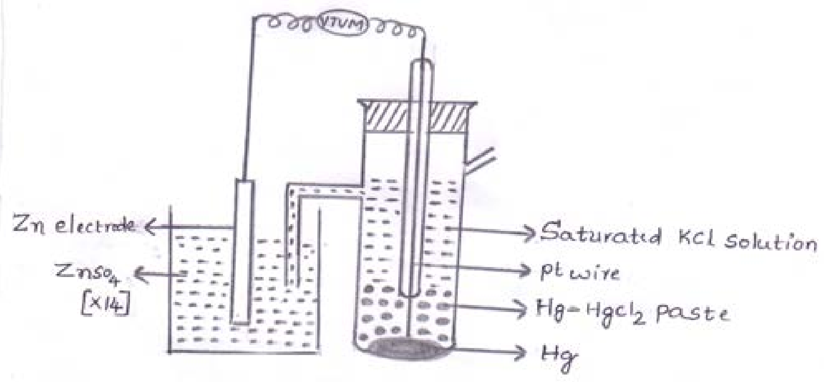
Cell representation:

$Zn/ZnSO_{4(XM)}//$Satured KCl solution$/Hg_2Cl_2/Hg,Pt$

The cell is connected to vacuum tube voltmeter and emf is read out

$E_{Cell} = E_{SCE} - E_{Zn^{2+}/Zn}$

$E_{Zn^{2+}/Zn} = E_{SCE} - E_{Cell}$



Construction and woring of Glasselectrode:

Principle:Thepotentialdevelopedacrossthemembraneisafunctionoftheconcentrationoftheanalyteandreferencesolution.Whentheconcentrationofthereferencesolutioniskeptconstantthepotentialdevelopedatthemembraneisthelinearfunctionofconc.ofanalytesolution.

GlasselectrodeConstruction:Itconsistsofaglassmembranemadeupofspecialtypeofglass(22%Na_2O,6%CaOand72%SiO_2)oflowermeltingpointandhighelectricalconductance.TheglassbulbisfilledwithasolutionofconstantpH(0.1MHCl)andAg-AgClelectrodeisinserted.whichservesasinternalreferenceelectrodeandalsoasexternalelectriccontact.

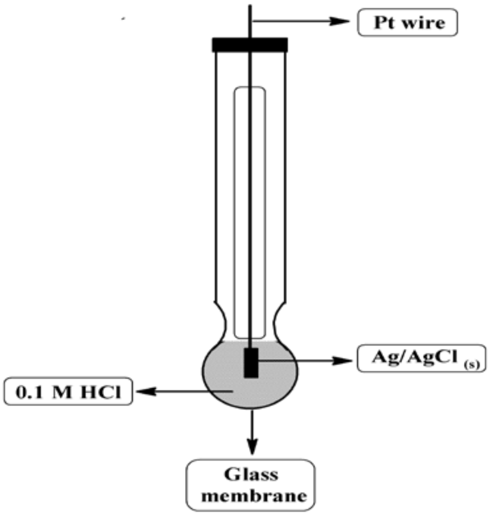


Fig.Glasselectrode

Electroderepresentation:$Ag_{(s)}/AgCl_{(s)}/0.1MHCl$/glassmembrane.
Themembraneundergoesanionexchangereactionasfollows.

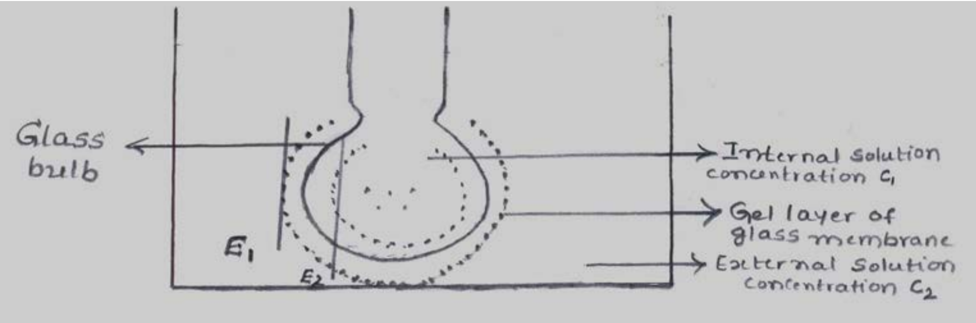
$$H^{+}+Na^{+}Gl^{-}Na^{+}+\rightleftharpoons H^{+}Gl^{-}$$

Advantages:i.Itcanbeusedinoxidizingandreducingenvironments
ii.AccurateresultsareobtainedbetweenpHrange1-9
,iii.Electrodedoesnotpoisoned.

Limitations:
i.Ordinarypotentiometerscannotbeusedii.ItcanbeuseduptopH13butbecomes sensitivetoNa^{+}ionsabovepH9resultingalkalineerror,iii.Itdoesnotfunctionproperlyinpurealcoholandsomeorganicsolvents.

<u>DeterminationofpH</u>:
TodeterminethepHofagivensolutiontheglasselectrodeisdippedinasolutionwhosepHneedtobedetermined.Itiscombinedwithsaturatedcalomelelectrodeasshowninfig.
Thecellassemblyisgivenby
$Hg_{(l)}/ Hg_2Cl_{2(s)}/Cl^{-}$//Unknown pH solution/Glass membrane/0.1M HCl$_{)}$/$AgCl_{(s)}/ Ag_{(s)}$
The EMF of the cell is given by$E_{cell}= E_G-E_{\text{sat.calomelelectrode}}$ -------------1
TheboundarypotentialestablishedduetoexchangeofH^{+}withglassmembraneismainly responsibleforglasselectrodepotential$E_G$andgivenby

$$E_G = E_b + E_{Ag/AgCl}+E_{Asy}\text{----------}2$$



$E_{Ag/AgCl}$is internalreferenceelectrodepotential,E_b –boundarypotentialand$E_{Asy}$is asymmetric potentialobservedwhenConcentration$C_1=C_2$

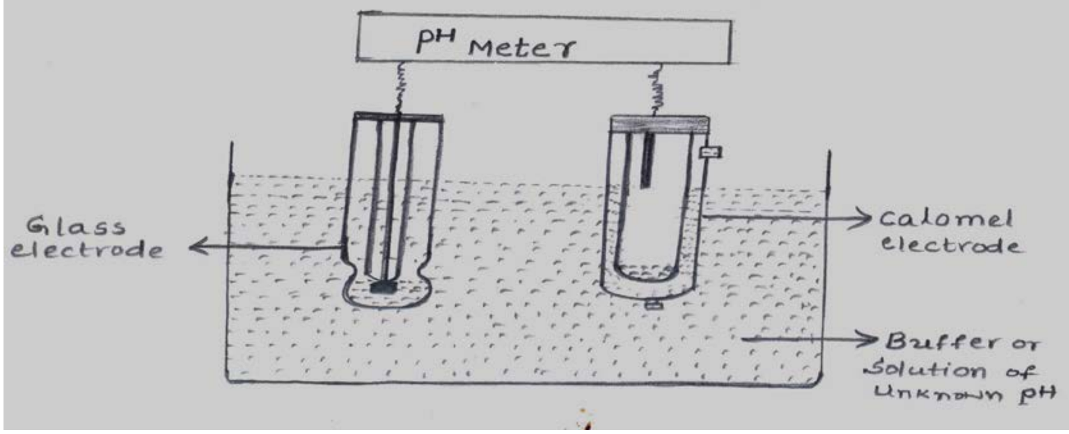


Fig.DeterminationofpH

TheboundarypotentialisgivenbyNernstequationatmembrane$E_b=E_1–E_2$-------3

SinceE_1=Const.+0.0591logC_1

E_2=Const.+0.0591logC_2

Therefore$E_b=0.0591\log C_1-0.0591\log C_2$sincen=1

$E_b=L+0.0591\log C_1$-------------4,whereconstant$L=-0.0591\log C_2$,since $C_2=(H^+)$=const.

$E_b=L+0.0591\log(H^+)$since$C_1=(H^+)$

$E_b=L–0.0591pH$-----------5,where$pH=-\log(H^+)$

Therefore$E_G=L–0.0591pH+E_{Ag/AgCl}+E_{Asy}$-------6

Combineallconstantvaluesintheaboveequation,ie.$L'=L+E_{Ag/AgCl}+E_{Asy}$

$E_G=L'–0.0591pH$-----------7

Thereforeequation1becomes

$$E_{cell}=L'–0.0591pH-E_{sat.calomelelectrode}$$

$$\text{or}\,pH=\frac{L'-E_{sat.calomel\ electrode}-E_{cell}}{0.0591}\text{-----------8}$$

$$\text{or}\,pH=\frac{K-E_{cell}}{0.0591}\text{---------9}$$

where$K=L'-E_{sat.calomelelectrode}$which is constant

ToevaluateKtheelectrodeassemblyisdippedinastandardbuffersolutionandpHmeteriscalibratedtothepHofthebuffersolution.

$$PH(b)=\frac{K-E_{cell(b)}}{0.0591}\text{---------10}$$

NexttheelectrodeassemblyisdippedinasolutionofunknownpHandpH(u)isgivenby

$$PH(u)=\frac{K-E_{cell(u)}}{0.0591}\text{---------11}$$

Subtractequation10from11,$PH(u)=PH(b)-\frac{E_{cell(u)}+E_{cell(b)}}{0.0591}$---------12

ConcentrationCells:

Electrode ConcentrationCells:

In this type of concentration cell the electrode themselves have different concentration, they may be electrode operating at different pressure or amalgams of different concentration.

Electrolytic ConcentrationCells:

Itisanelectrochemicalcellthatgenerateselectricalenergywhentwoelectrodesofsamemetalareincontactwithsolutionofitsownionsofdifferentconcentration.

Considerthefollowingconcentrationcellrepresentedby

$$Cu_{(s)}/Cu^{2+}_{(C1)}//Cu^{2+}_{(C2)}/Cu_{(s)}$$

WhereC_1andC_2aremolarconcentrationsoftheCu^{2+}ionsinthetwohalfcells.

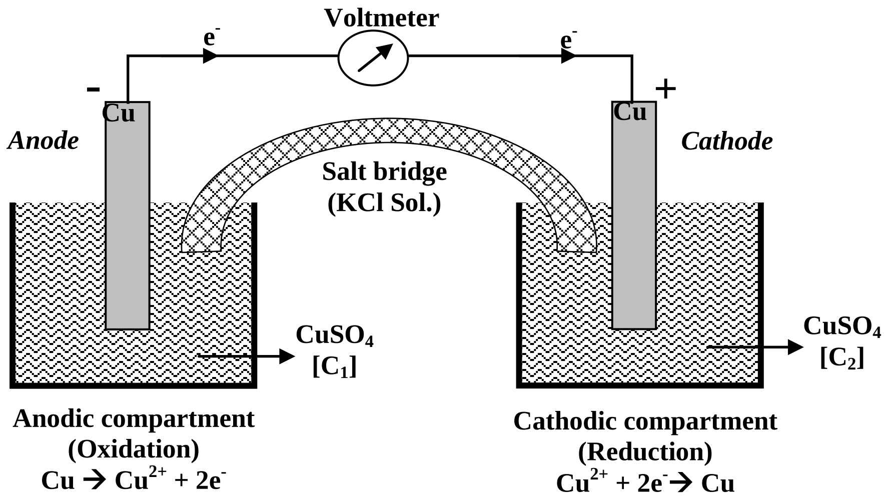


Figure 2: Concentration cell

Byelectrochemicalconventionif$C_1<C_2$,theleftelectrodeisanodeandrightelectrodeis cathode.Thecellreactionsare

Atanode$Cu_{(s)} \longrightarrow Cu^{2+}_{(C1)} + 2e$

Atcathode$Cu^{2+}_{(C2)} + 2e \longrightarrow Cu_{(s)}$

Thenetcellreactionis $Cu^{2+}_{(C2)} \longrightarrow Cu^{2+}_{(C1)}$

Thevoltageofthecellexistsaslongas$C_1<C_2$

TheEMFoftheconcentrationcellisgivenby$E_{cell}=E^0_{Cathode} - E^0_{Anode}$

Therefore$E_{cell} =[E^0_{Cu2+/Cu} + 0.0591/2 \log C_2] – [E^0_{Cu2+/Cu} + 0.0591/2 \log C_1]$

or $E_{cell} = 0.0591/2 \log C_2/C_1$ Where $E^0_{Cu2+/Cu} - E^0_{Cu2+/Cu} = 0$

IngeneraltheEMFoftheconcentrationcellisgivenby

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Fromtheaboveequationfollowingconclusionsmaybedrawn

i.When$C_1=C_2$theconcentrationcelldoesnotgenerateelectricalenergy

ii.When$C_2/C_1>1$,logC_2/C_1ispositiveandE_{cell}ispositive

iii.Higherthe ratioofC_2/C_1higheristhecellpotential.

Battery Technology:

Introduction,classification–primary,secondaryandreservebatteries charecteristics: cell potential, current, capacity, electricity storage density,energy efficiency, cycle life and shelf lifeConstruction,workingandapplicationsof Zn–air, Ni–metalhydride batteries, Lithium batteries,Introduction Li–MnO_2 and Li-ion batteries.
Fuelcells– Introduction, Differencesconventional cellandfuelcell, Limitations and Advantages. Construction andworkingof$CH_3OH–O_2$fuelcells with H_2SO_4 as electrolyte.

- **Battery Technology: Introduction,classification–primary,secondaryandreservebatteries charecteristics: cell potential, current, capacity, electricity storage density,energy efficiency, cycle life and shelf life**

- **Construction,workingandapplicationsof Zn–air, Ni–metalhydride batteries**

- **Construction,workingandapplicationsofLithium batteries, Li–MnO_2**

- **Construction,workingandapplicationsof Li-ion batteries.Fuelcells– Introduction, Differencesconventional cellandfuelcell, Limitations and Advantages.**

- **Construction andworkingof$CH_3OH–O_2$fuelcells with H_2SO_4 as electrolyte**

BATTERYTECHNOLOGY

INTRODUCTION:

Definition:Abatteryisadevicethatconsistsofoneormorecellsconnectedinseriesorparalleltosupplythenecessarycurrent.

Cell: Itisadevicethatconsistsofonlytwoelectrodesthatgenerateelectricalenergy.

Classification:

1)Primarybatteries: Inthistypeelectricalenergycanbeobtainedattheexpenseofchemicalenergyonlyaslongastheactivematerialsarepresent.Thesebatteriescannotberechargedandreused.

Eg:Zn-MnO_2

2)Secondary batteries::Inthistypeofbatteriesonceusedcanberechargedbypassingcurrentthroughit.Theredoxreactiongetsreversedduringrecharging.

Hereelectricalenergyisstoredintheformofchemicalenergyandutilizedforsupplyingcurrentwheneverneeded.Thereforesecondarybatteriesarealsoknownasstoragebatteries.

Eg.Pb-acid,Ni-Cd

3)Reservebatteries: Thebatterieswhicharestoredinaninactivestateandmadereadyforusewhileactivatingthembeforeuseareknownasreservebatteries.Inthistypeoneofthecomponentisseparatedfromtherestofthebattery.Usuallytheelectrolyteisthecomponentthatisisolated.Theelectrolyteeliminatestheselfdischargeofbatterypriortouse.Theseareusedforlongtermstorage.

Ex.Ag-MnO_2.

BATTERYCHARACTERISTICS

Batteriesaredesignedtoaparticularapplicationbasedontheirperformancecharacteristics.

Cell potential(Voltage):thevoltageavailabledependsonEMFofthecellandEMFinturndependsonfreeenergychange.Considertheequation

$$E_{cell}=E^0_{cell}-2.303\ RT/nF\ \log Q$$

Where$E^0_{cell}=E^0_{cathode}-E^0_{anode}$,Qisthereactionquotientie.[products]/[reactant]

Fromtheaboveequationwecanconcludethat

a)Ifthedifferenceinstd.electrodepotentialismore,EMFofthecellisalsohigher

b)asthetemperatureincreasestheEMFofthecelldecreases.

c)asthevalueofQincreasesie,whencurrentisdrawnfromthecellthecellreactionproceedsandEMFofthecelldecreases.

Toderivemaximumvoltageinadditiontoabovetheelectrodereactionmustbefasttoreducetheoverpotentialsandtheresistanceofthecellmustbelow.

Current: Itisthemeasureoftherateatwhichabatteryisdischarging.Forefficientworkingofthecelltheremustbealargequantityofelectroactivespecieswhichhelpinrapidelectrontransfer.

Capacity:ItisthetotalamountofaelectriccurrentinvolvedintheelectrochemicalreactionandexpressedinatermofcoulombsorAmperehour(Ah).Itdependsonasizeofabatteryandgivenby

C=WnF/MwhereWisthemass&Misthemolarmassofactivematerials

Electricitystoragedensity:Itisthemeasureofchargeperunitweightstoredinthebattery.ie.itisthecapacityperunitweight.

Energyefficiency:itisgivenby

$$\%\text{energyefficiency}=\times100\ \frac{\text{energyreleasedondischarge}}{}$$

energyrequiredforcharging

Itdependsonrateofchargeordischarge,currentefficiencyoftheelectrodeprocessandtheoverpotentialduringchargeanddischargereactionsaswellasthebatteryresistance.

CYCLELIFE:Itisthenumberofchargeordischargeprocessthatarepossiblebeforefailureoccurs.Primarybatteriesaredesignedforsingledischargebutsecondarybatteriesischargeable.
Thecyclelifeofastoragemustbehigh.
Itdependsonchemicalcomposition,morphologicalchangesanddistributionofactivematerialsinthecell

Shelflife:Thedurationofstorageunderspecifiedconditionsattheendofwhichacellorbatterystillretainstheabilitytogiveaspecifiedperformanceiscalledshelflife.Itmustbegoodforstoragecells.Goodshelflifeforbatteriesisexpectedwhenthereisnoselfdischargeorcorrosionofcurrentcollectorscausinglossofperformance

Zinc-AirBattery:

ThisisatypeofmetalairbatterywhichusesoxygendirectlyfromatmospheretoproduceElectrochemical Energy.
Aloosegranulatedpowderofzincismixedwithelectrolyte(30%KOH)actsasanodematerial.Theoutermetalactsascathodeofthebatterywhichisfilledwithsmallamountofcatalystandcarbontooptimizetheevolutionofoxygeninalkalinesolutionandforbetterreduction.Thetwoelectrodesareseparatedbyplasticgasketasinsulator.Astheelectrodeiscompact,highenergydensitiesareobtained.
BatteryNotation:Zn|KOH|air,C

TheCellReactions:

$2Zn+4OH^- \rightarrow 2ZnO+2H_2O+4e^-$ atAnode

$O_2 +2H_2O+4e^- \rightarrow 4OH^-$ atCathode

OverallReaction:

$2Zn+O_2 \rightarrow 2ZnO$

Ithasenergydensityofabout100WhKg^{-1}threetimesthatofLeadacidbatteryortwicethatofNi-CdBattery.

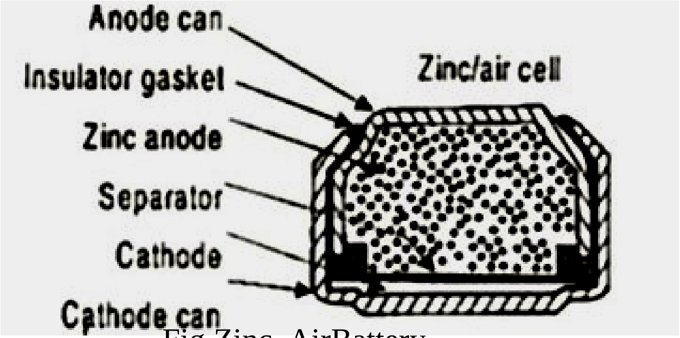


Fig.Zinc–AirBattery

Advantages: Highenergydensity,longshelflife,lowcost,noecologicalproblem.

Uses: Itfindsapplicationsinmilitaryradioreceivers,Powersourceforhearingaids,medicaldevices,remotecommunicationsetc.

Nickel-MetalHydride(Ni-MH)battery:

ItissimilartoNi-Cdcell.InsteadofCadmiummetalhydridebatteryuseshydrogenadsorbedonametalalloyfortheanodeactivematerialAnodeactivematerialssuchasVH_2,ZrH_2andTiH_2areused.Theactivematerialatthecath

odeisNiO(OH).
Themetalalloyiscapableofundergoingareversiblereactionasthebatteryischargedor discharged.ThecathodecellcanisfilledwithNiO(OH)andanodeishighlyporousstructuredwithaNiwiregaugeintowhichhydrogenstoragealloyiscoated.
Thetwoelectrodesareseparatedwithaninsulatormaterialatthetopandtheactivematerialsbyanaqueous solutionofKOHsoakedwithabsorbentmaterialwhichactsaselectrolyte.

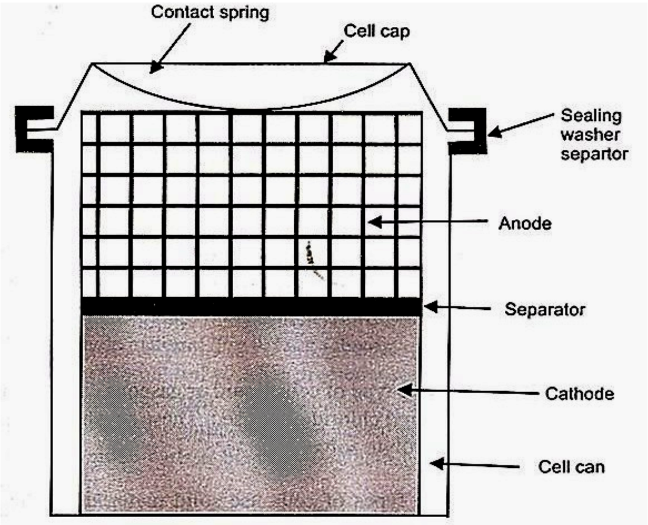


Fig.Nickel–MetalHydridebattery

<u>ThebatteryRepresentation:</u>
$MH|KOH|Ni(OH)_2,NiO(OH)$
<u>TheCellReactions:</u>
$MH+2OH^- \rightarrow H_2O+M+2e^-$ Anode
$2NiO(OH)+2H_2O+2e^- \rightarrow Ni(OH)_2+2OH^-$ Cathode
<u>OverallReaction:</u>
$$MH+2NiO(OH) \rightarrow Ni(OH)_2+M$$
Potentialvaluesvariesfrom1.25Vto1.35V
Uses: ItisusedinComputers,CellularPhones,camcorders,electricvehicles.
Advantages: Highcapacity,longcyclelife,shelflife,lessenvironmentalproblems.

Lithium Batteries are disposable (primary) batteries that have lithium metal or lithium compounds as an anode. They stand apart from other batteries in their high charge density (long life) and high cost per unit. Depending on the design and chemical compounds used, lithium cells can produce voltages from 1.5 V (comparable to a zinc–carbon or alkaline battery) to about 3.7 V.By comparison, lithium-ion batteries are rechargeable batteries in which lithium ions move between the anode and the cathode, using an intercalated lithium compound as the electrode material instead of the metallic lithium used in lithium batteries.Lithium batteries are widely used in products such as portable consumer electronic devices.

<u>Li–MnO_2Batteries:</u>

Li–MnO_2cellisoneofthemostwidelyusedbatteriesItconsistsofLianodeandMnO_2as cathode.Lithiumhalideinorganicsolventsolutionisusedaselectrolyte.TheMnO_2pelletandanodedisc areseparatedbypolypropyleneseparatorpastedwithelectrolyte.Thecellissealedwithcanservingasthe cathodeterminalandcapastheanodeterminal.

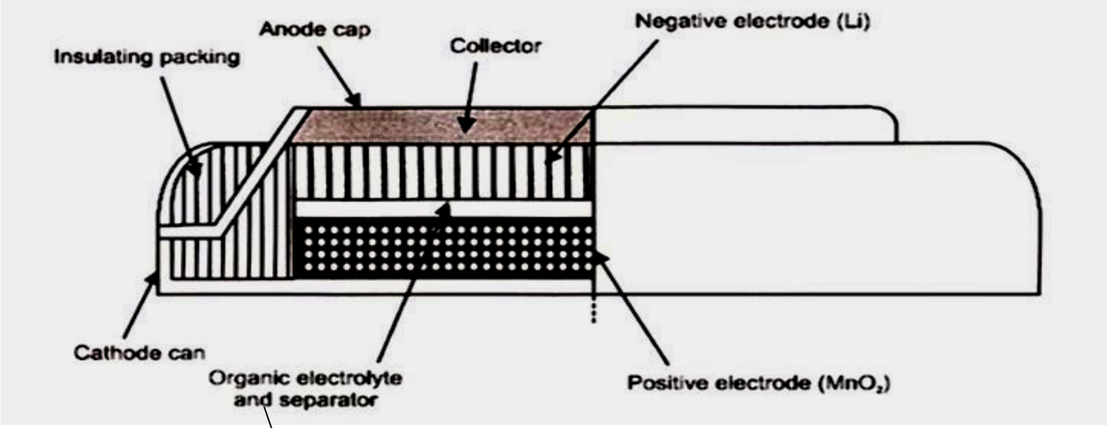


Fig.Li-MnO_2Cell

<u>CellReactions:</u>

$Li \rightarrow Li^+ + e^-$ Anode

$Mn^{IV} + Li^+ + e^- \rightarrow LiMn^{III}O_2$ Cathode

<u>OverallReaction:</u>

$Mn^{IV}O_2 + Li \rightarrow LiMn^{III}O_2$

IntheabovecellreactionMnreducesfrom+4oxidationstateto+3oxidationstate.LithiumionentersintotheMnO_2crystallattice.

Thevoltageofthecellisupto4Vdependingonthecathodeused

Uses:Itismainlyusedinapplicationswatches,calculators,cameras,lightingequipmentsandlongtimememorybackups.

Advantages: Highcurrentdensityduetolowatomicmassoflithium
Operatesbetweenwiderangeoftemperature(-40to70^{0}C)
Lowselfdischargerateandshelflifeishigh.

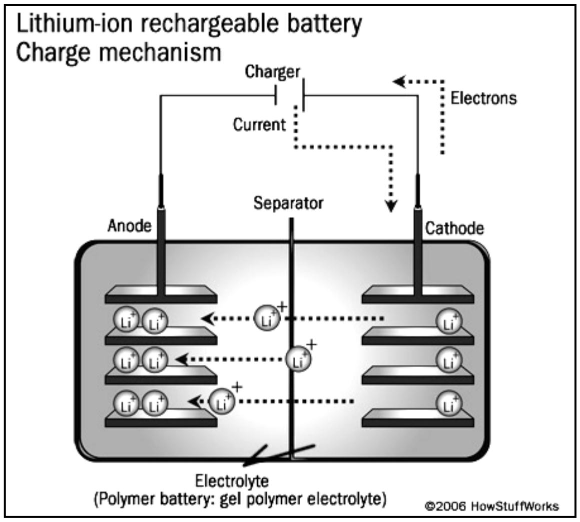
Lithium-ion battery (Li-ion Battery)

1.Li-ion batteries are secondary batteries.
2.The battery consists of a anode of Lithium, dissolved as ions, into a carbon.
3.The cathode material is made up from Lithium liberating compounds, typically the three electro-active oxide materials,
4.Lithium Cobalt-oxide ($LiCoO_2$)
5.Lithium Manganese-oxide ($LiMn_2 O_4$)
6.Lithium Nickel-oxide ($LiNiO_2$)

Principle

1. During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery.
2. Simply, the Li-ion is transfers between anode and cathode through lithium Electrolyte. .Since neither the anode nor the cathode materials essentially change, the operation is safer than

that of a Lithium metal battery.



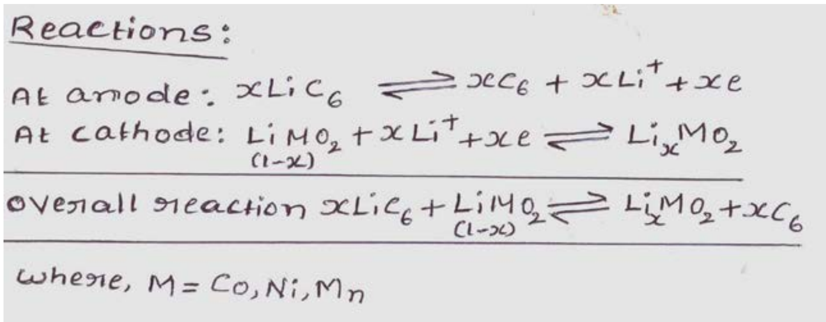
Construction:

1. Li-ion cell has a four-layer structure.
2. A positive electrode made with Lithium Cobalt Oxide has a current collector made of thin aluminum foil – cathode.
3. A negative electrode made with specialty carbon has a current collector of thin copper foil – anode.
4. A separator is a fine porous polymer film.
5. An electrolyte made with lithium salt in an organic solvent.
6. The electrolytes are selected in such a way that there should be an effective transport of Li-ion to the cathode during discharge.
7. The type of conductivity of electrolyte is ionic in nature rather than electronic

Working:

1. The traditional batteries are based on galvanic action but Lithium ion secondary battery depends on an "intercalation" mechanism.
2. This involves the insertion of lithium ions into the crystalline lattice of the host electrode without changing its crystal structure.
3. These electrodes have two key properties. One is the open crystal structure, which allow the insertion or extraction of lithium ions and the second is the ability to accept compensating electrons at the same time. Such electrodes are called intercalation hosts.
4. The chemical reaction that takes place inside the battery is as follows, during charge and discharge operation:
5. The lithium ion is inserted and exerted into the lattice structure of anode and cathode during charging and discharging
6. During discharge current flows through external circuit and light glows
7. During charging, no the electrons flows in the opposite direction.
8. During charging, lithium in positive electrode material is ionized and moves from layer to layer and inserted into the negative electrode.
9. During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode.

10. At the same time the compensating electrons travel in the external circuit and are accepted by the host to balance the reaction.
11. The process is completely reversible. Thus the lithium ions pass back and forth between the electrodes during charging and discharging.
12. A typical Li-ion battery can store 150 watt-hours of electricity in 1 kilogram of battery as compared to lead acid batteries can sore only 25 watt-hours of electricity in one kilogram.
13. All rechargeable batteries suffer from self-discharge when stored or not in use. Normally, there will be a three to five percent of self-discharge in lithium ion batteries for 30 days of storage



Reactions:

At anode: $xLiC_6 \rightleftharpoons xC_6 + xLi^+ + xe$

At cathode: $Li_{(1-x)}MO_2 + xLi^+ + xe \rightleftharpoons Li_xMO_2$

overall reaction $xLiC_6 + Li_{(1-x)}MO_2 \rightleftharpoons Li_xMO_2 + xC_6$

where, M = Co, Ni, Mn

Advantages

1. They have high energy density than other rechargeable batteries
2. They are less weight
3. They produce high voltage out about 4 V as compared with other batteries.
4. They have improved safety, i.e. more resistance to overcharge.
5. No liquid electrolyte means they are immune from leaking.
6. Fast charge and discharge rate

Disadvantage:

1. They are expensive.
2. They are not available in standard cell types.

Applications

1. The Li-ion batteries are used in cameras, calculators.
2. They are used in cardiac pacemakers and other implantable device.
3. They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.
4. They are used to operate laptop computers and mobile phones and aerospace application.

FUELCELLS

Introduction:

Definition:Itisanelectrochemicaldevicethatcontinuouslytransformfreeenergychangeofredoxreactionsofafueltoelectricalenergyattheelectrodes.

AFuelcellisrepresentedasfollows

Fuel/Electrode,Electrolyte,Electrode/Oxidant

AtanodeFuelOxidationproduct+ne

AtCathodeOxidant+neReductionproducts

Advantages:

1.Highefficiencyoftheenergyconversionprocess.
2.Rechargingoffuelcellnotrequired.
3.Absenceofharmfulwasteproducts.
4.Silentoperation.

Difference between conventional cell and fuel cell

Conventional cell	**Fuel cell**
It needs more time for charging	It needs less time for charging
Limited cycle life	Long cycle life
High energy density	Low energy density
Heat produce after long usage	Heat do not produce even after long usage
Ex: Ni-Cd battery.Li-MnO_2 battery	Ex: Methanoloxygenfuelcell

LIMITATIONS:

1.Stroage of fuel and oxidant.
2.electrolytes and electrodes are costly.
3.Gives DC output and should be converted into AC.

ADVANTAGES:

1. High power effianccy appxromateally 75%
2. Eco-friendly
3.Space required for fuel cell is less.
4.Produce DC for a long time.

Construction and working of Methanol-oxygenfuelcell :

Itconsistsoftwoporouscarbonelectrodes.Anodeiscoatedwithplatinumcatalystand cathodewithsilvercatalyst.TheelectrolyteisanaqueoussolutionofH$_2$SO$_4$.TheMethanegasiscontinuouslysuppliedattheanodeandoxygenissuppliedatthecathode.AstheMethanegasdiffusesthroughanodeitisadsorbedontheelectrodesurfaceandreactswithHydroxylionstoformwater. AtthecathodeOxygendiffusingthroughtheelectrodesisadsorbedandreducedandgetreducedtohydroxylions.

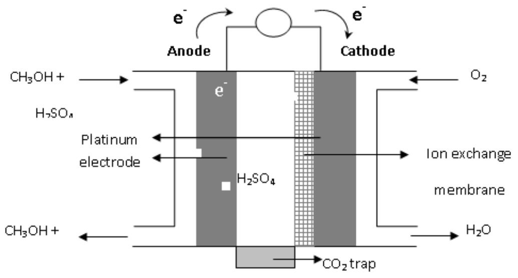


Fig.Methanoloxygenfuelcell

Theelectrodesreactionsare

Atanode,$CH_3OH+6OH^- \longrightarrow CO_2+5H_2O+6e$

Atcathode,$3/2O_2+3H_2O+6e \longrightarrow 6OH^-$

Net cellreaction$CH_3OH + 3/2O_2 \longrightarrow CO_2 +2\ H_2O$

MODULE- 2
CORROSION AND METAL FINISHING

Corrosion : Introduction, electrochemical theory of corrosion, galvanic series. Factors affecting the rate of corrosion: ratio of anodic to cathodic areas, nature of metal, nature of corrosion product, nature of medium – pH, conductivity, and temperature. Types of corrosion- Differential metal , differential aeration(Pitting and waterline) and stress (caustic embrittlement in boilers).Corrosion control: inorganic coatings-Anodizing of Al and phosphating, metal coatings-Galvanization and Tinning. Cathodic protection (sacrificial anodic and impressed current methods). 5 Hours

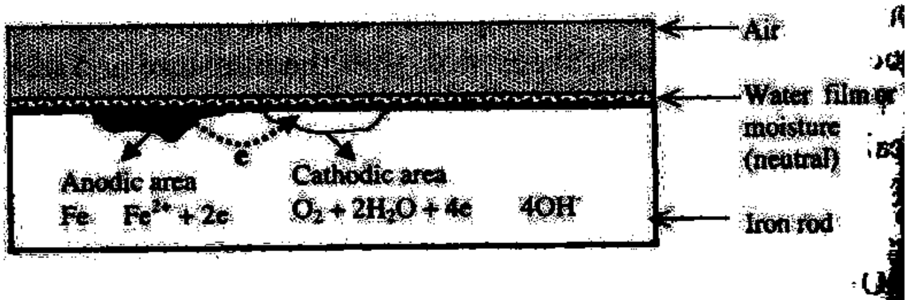
Contents:

- **Introduction, electrochemical theory of corrosion, galvanic series.**
- **Factors affecting the rate of corrosion**
- **ratio of anodic to cathodic areas, nature of metal, nature of corrosion product nature of medium – pH, conductivity, and temperature.**
- **Types of corrosion- Differential metal , differential aeration(Pitting and waterline) and stress (caustic embrittlement in boilers).**
- **Corrosion control: Design and selection of materials**
- **inorganic coatings-Anodizing of Al and phosphating,**
- **metal coatings-Galvanization and Tinning.**
- **Cathodic protection (sacrificial anodic and impressed current methods).**

CORROSIONANDITSCONTROL

DefinitionThedestructionordeteriorationofmetalbysurroundingenvironmentthroughchemicalorelectrochemicalattackisknownascorrosion.
Ex.FormationofreddishbrownscaleonironduetoformationofFe$_2$O$_3$
GreenscaleoncoppervesselduetoCuCO$_3$&Cu(OH)$_2$
Drycorrosionisdirectchemicalattackintheabsenceofmoisturebydrygaseslike SO_2,CO_2,Cl_2,H_2S etc.
Wetcorrosioniscommoninnature&occursbyelectrochemicalattackonthemetalwiththemoistureandoxygenpresentintheatmosphere.

Electrochemicaltheoryofcorrosion.
Whenanironrodisexposedtotheenvironmentthefollowingelectrochemicalchangestakesplace,
i)Formationofanodiccathodicareas,atanodeoxidationtakesplaceproducingelectronsandmetalion(M^{n+}).Atcathodeelectronsaretakenupbyreductionreaction
ii)Corrosiontakesplaceattheanode.
iii)ReductionofwaterandoxygenintheatmospheretoOH$^-$occursatcathodicarea.



Rusting of iron

Considerthemetallikeironexposedtothecorrosiveenvironmentthereactionsthatoccurareasfollows,**Anodicreaction:**Oxidationtakesplaceresultingcorrosionofmetal

$$Fe^{2+}+2e \xrightarrow{} Fe$$

Cathodicreaction: Atcathodereductionreactiontakesplacedependinguponthenatureofelectrolyte.Thedifferentpossiblereductionreactionare
i.IfthesolutionisaeratedandneutraloxygenandwaterarereducedtoOH$^-$ions

$$O_2+2H_2O+4e \xrightarrow{} 4OH^-$$

ii.IfthesolutionisdeaeratedandneutralcathodicreactioninvolvesliberationofH$_2$gasand OH$^-$ions $2H_2O+2e \xrightarrow{} H_2+2OH^-$

iii. IfthesolutionisdeaeratedandacidiccathodicreactioninvolvesliberationofH$_2$gas

$$2H^++2e \xrightarrow{} H_2$$

CorrosionofironprodusesFe^{2+}atanodeandOH$^-$ atcathode.TheseionsdiffusetowardscathodeandformFe(OH)$_2$nearcathode.Inoxidizingenvironmentitisoxidizedtoferricoxideandtheyellowrusthydratedferricoxide.

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

$$4Fe(OH)_2+O_2+2H_2O \xrightarrow{} 2Fe_2O_3.3H_2O$$

Galvanic Series:

In galvanic series the active metals are arranged in the order of their tendency to undergo corrosion in sea water under standard condition.

It is useful as a guide for selecting metals to be joined Alloys are also given position in the galvanic series.

Magnesium tops the list in galvanic series and readily undergo corrosion Pt is at the bottom of the series which is a noble metal.

Factorsinfluencingtherateofcorrosion

Natureofmetal

Themetalswithlowerelectrodepotential(higherupinseries)aremorereactivethanwithmetalofhigherpotential.Themorereactiveme talsaremoresusceptibleforcorrosion. Thusthetendencyofametaltoundergocorrosiondecreaseswithincreaseinelectrode potential. ForexampleK,Na,Mg,Znetc.withlowelectrodepotentialvaluesaremoresusceptibleto corrosion.ThenoblemetalsAg,Au,Ptetc. withhighelectrodepotentialvaluesarelesssusceptibletocorrosion.

Hydrogenovervoltage

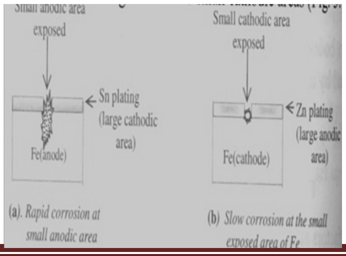
Themetalwithlowhydrogenovervoltageonitssurfaceismoresusceptibleforcorrosionwhencathodicreactionishydrogenevolution.Whenthehydrogenovervoltageislowhydrogengasisliberatedeasilyandthusthecathodicreactionisfaster.Thiswillalsomakestheanodicreactionfasterandhenceintencecorrosiontakesplace.Whenthehydrogenovervoltageishighcathodicreactionisslowerandcorrosionalsobecomesslow.

Natureofcorrosionproduct

Thecorrosionproductisusuallytheoxidelayerformedonmetalsurfacedeterminesthe corrosionrate. Ifthelayerformedisstoichiometric,highlyinsoluble,andnon-porouswithlowelectronicconductivitythenthelayerformedpreventsfurthercorrosion.Thethinlayerformedactsasabarrierbetweenfreshmetalsurfaceandthecorrosionenvironment. Ontheotherhandifthecorrosionproductformedisnon-stoichiometric,soluble,porousandnon-uniformthenthelayerformedcannotcontrolcorrosion. MetalslikeAl,Cr,Tietc.formsthinoxidelayerincorrosiveenvironmentontheirsurfaceandbecomepassivetocorrosion.

Anode and cathode areas

Therateofcorrosiongreatlyinfluencedbytherelativesizesofanodeandcathodicareas.Ifthemetalhassmalleranodicareacomparedtolargecathodicareaintencecorrosintakesplaceatanode. Sincealltheelectronsliberatedatsmallanodeareaarerapidlyconsumedbythelargecathodearea.Ifthecathodeissmallertheconsumptionofelectronswillbeslowerandcorrosionwillbecomeslower. Forexamplewhentiniscoatedonironinsuchawaythatsomepinholesareleftresultsinsmallanodeareaandlargecathodearea.Sincetiniscathodictoironcorrosionoccursatthesmallanodeareaexposed.ontheotherhandwhenzinccoatedonironleavingbehindsmallpinholesresultslargeanodicandsmallcathodicares.Sincezincisanodictoironcorrosionofironwillnotoccur.



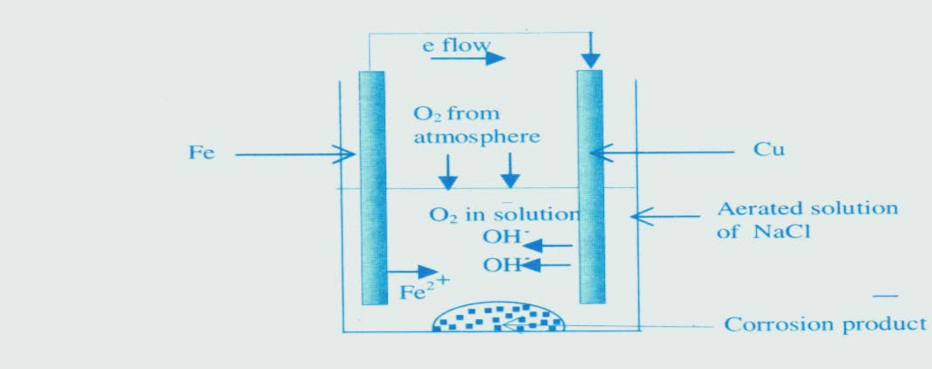
(a). *Rapid corrosion at small anodic area*

(b) *Slow corrosion at the small exposed area of Fe*

Temperature: Withtheincreaseintemperaturethereactionaswellasdiffusionrateincreasestherebycorrosionrateisgenerallyenhanced.Inthecaseofcorrosionresistantpassivemetalstheriseintemperaturereducespassivityandleadstoanincreaseincorrosion.
p^H: Generallyacidicmediaaremorecorrosionthanalkalineandneutralmedia.HoweversomemetalslikeAl,Znetc.undergoesfastcorrosioninhighlyalkalinemedium.

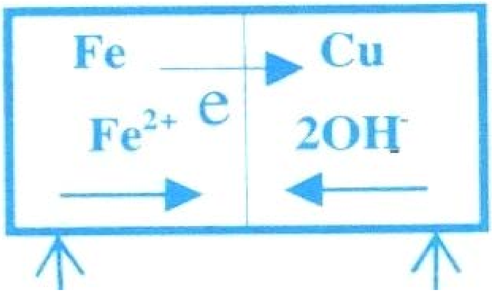
Conductivity :
If the medium to which metal part is exposed is conducting then it induces corrosion. If the conductance of the soil or medium is high the rate of corrosion is severe and fast.
Ex: Metal corrodes high in sea water than in river water.

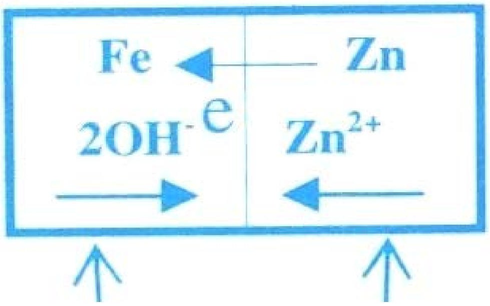
Types of corrosion:
Diffrentialmetal corrosion(Galvaniccorrosion)
Whentwodissimilarmetalsareelectricallyconnectedandexposedtocorrosiveenvironmentthemetalwithlowerelectrodepotential(higherupinelectrochemicalseries)undergoescorrosion.Forexamplewhenzincandcopperareelectricallyconnectedinpresenceofelectrolytethezincmetalwithlowelectrodepotentialactsasanodicarea;getscorrodedasshowninfigure,whereascopperwhichishigherelectrodepotentialbecomecathode.
Therateofthistypeofcorrosiondependsondifferenceinpotential.Higherthedifferenceinpotentialfasteristherateofcorrosion.
Ex.:1)Steelpipeconnectedtocopper



Differential metal corrosion

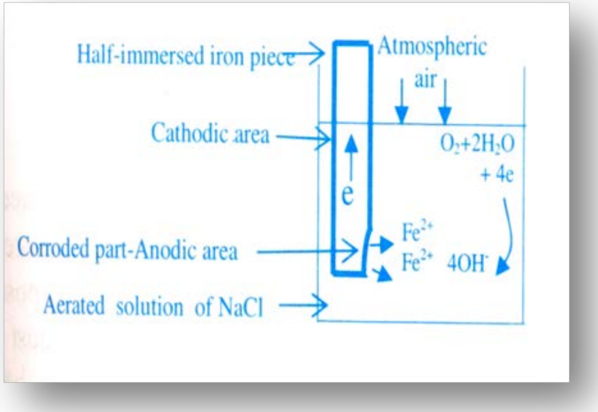
2)Tincoatingoncoppervessel3)Zinccoatingonmildsteel.

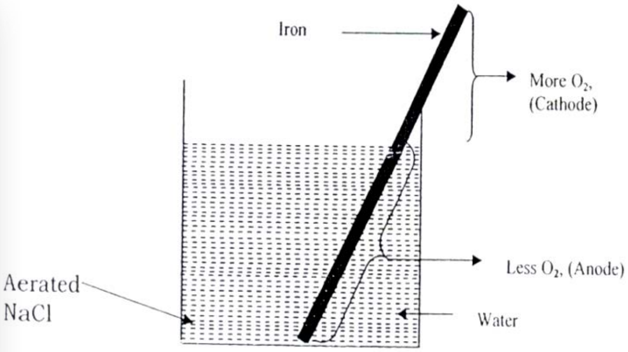




Differential aeration corrosion

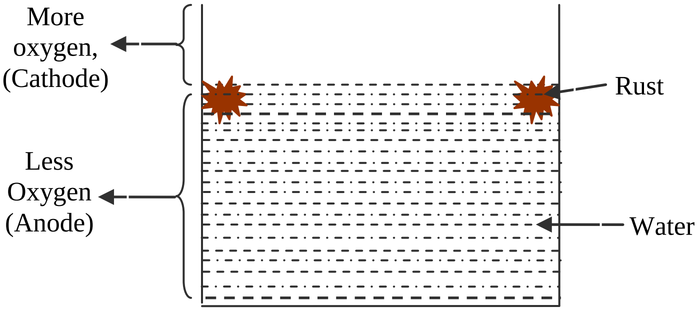
Itoccurswhenametalsurfaceisexposedtodifferentair/oxygenconcentration.Themetalpartexposedtolessoxygenconcentrationactsasanodicareaandcorrodeswhereasthehigheroxygenatedareaisprotectedfromcorrosion(Cathode).Forexamplewhenanironstripispartiallyimmersedinaeratedsolutionofsodiumchlorideasshowninfigure.Themetalpartinsideelectrolytegetcorrodedduetoanodicreactionandthemoreoxygenatedareaofthemetal(cathode)isprotectedEx.:Nailinsidethewallcorrodes,Windowframeinsidewallcorrodes





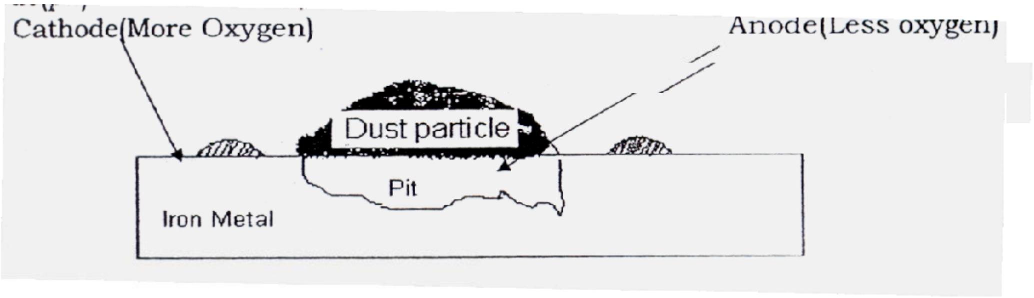
Water-line corrosion

Itisobserved in waterstorage tanks,shipwaterliftingpipesetc.ForexampleinwaterstoragetankthemetalTankpartinsidewaterlevelexposedonlytodissolvedoxygengetorroded(anode)whilethepartabovewaterlineisexposedtohigheroxygenconcentrationisprotected(cathode).



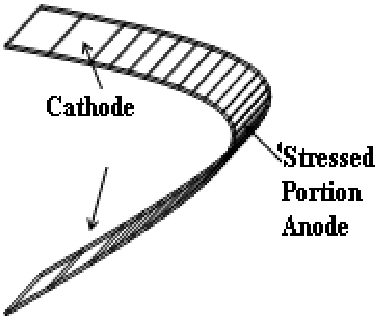
Pittingcorrosion :

Itoccurswhensmallparticlesofdust,waterdroponmetalsurfaceorbreakdownofprotectivefilm. Atypicalpittingcorrosionisillustratedasshowninfigure.Themetalportioncoveredbydustactasanodeduetolessoxygenatedandundergoescorrosionbeneaththedustformingapit.Themetalpartfreefromdustexposedtohigheroxygenconcentrationbecomecathodeandprotectedfromcorrosion.Thecorrosionrat eishigherinthiscaseduetosmallanodeareaandlargecathodearea.Alltheelectronsliberatedatanode(pit)areabsorbedbylargecathodeareaforreductionreaction.



StresscorrosionItisobservedinmetalsunderstressduetothemechanicaloperationssuchaswelding,bending,pressing,rivetingetc.InthiscasecorrosiveagentsarespecificandselectivesuchasKOHorNaOHformildsteel,tracesofammoniaforbrass,solutionofmetalchloridesforstainlesssteel.
Stresscorrosionisexplainedonthebasisofelectrochemicaltheory.Inacorrosiveenvironmentthestressedportionactasanodeundergoescorrosionandstressfreepartbecomecathode.
Themetalwhichisbendedasshowninfigurehasastressatthebentregion.Atthestressedpartthemetalatomsarealwaysathigherenergylevelsascomparetotheonefreefromstress.Thestressedpartofthemetaltherefore becomemore reactiveandundergoescorrosion

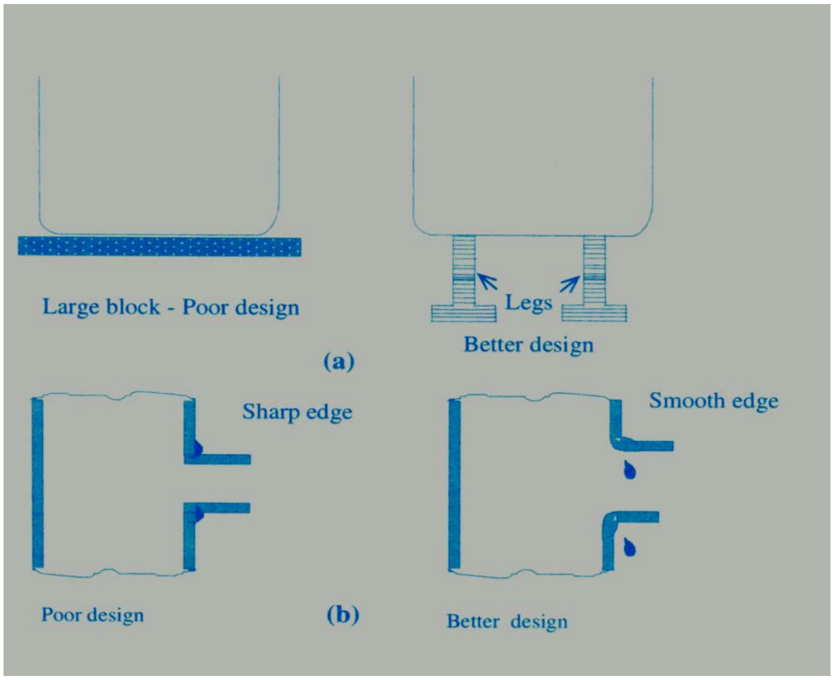
Exampleofstresscorrosion:



Causticembrittlement
Itisobservedinmildsteelboilers.Theboilerwatercontainssmallportionofsodiumcarbonateaddedduringsofteningpurpose.Inboilersthisbreaksuptogivesodiumhydroxideandcarbondioxideandmakeswateralkaline.
$Na_2CO_3+H_2O2NaOH+CO_2 \quad \longrightarrow$
Duetocrackdevelopedatstressedportionthealkalineboilerwaterentersintominutehaircracksbycapillaryaction.Thewater
getevaporatedleavingbehindNaOHatcracks.AstheconcentrationofNaOHincreasesitattacksthemildsteelanddissolvestheironassodiumferratewhichdecomposestomagnetite.
$3Na_2FeO_2+4H_2O \quad 6NaOH+Fe_3O_4+H_2 \longrightarrow$
TheregeneratedNaOHfurtherenhancesthecorrosion.Itispreventedbyaddingsodiumsulphate,tannin,ligninetc.whichblocksthecracksandpreventstheinfiltrationofalkali.

Corrosioncontrol
Design andSelection ofmaterials

- Avoidthecontactofdissimilarmetalsinthepresenceofacorrodingmedia
- Whentwodissimilarmetalsaretobeincontact,theanodicmaterialshouldhaveaslargeareaaspossiblecomparedtocathode.
- Iftwodissimilarmetalsareincontacthavetobeusedtheyshouldbeascloseaspossibletoeachotherinelectrochemicalseries.
- Wheneverthedirectjoiningofdissimilarmetals,isunavoidable,aninsulatingmaterialmaybeplacedbetweenthemtoavoiddirectcontact.
- Sharpcornersandrecessesshouldbeavoided
- Theequipmentshouldbesupportedonlegstoallowfreecirculationofairasshowninfigure



Inorganiccoating

Anodizing of Al:

Theprocessofformationofafilmofmetaloxideonthesurfaceofametalbyelectrochemicaloxidationisknownasanodizing.

Thealuminiumarticletobeanodizedisdegreasedfollowedbyelectropolishingtoremoveimpuritiespresentonthemetalsurface.Itisconnectedtopositiveterminali.e.madeasanodeandsteelorcopperismadeascathode.

Bathcomposition:

Electrolyte: 5-10%Chromicacid/10%H_2SO_4/Oxalicacid

Temperature: 35^0 C

Currentdensity: 10-20mA/cm^2

Electrodereaction:

Anode$2Al_{(s)}+3\,H_2O_{(l)}Al_2O_3+6H^{+}+6e \longrightarrow$ (aq

Cathode$6H^{+}+6e\,3\,H_{2(g)}$ (aq $\longrightarrow$

Finallytheobjectistreatedwithnickelorcobaltacetatefollowedbyboilingwatertreatmenttoimprovecorrosionresistance.

Uses:Usedforsoapboxes,Tiffincarriers,windowframesetc.

Phosphating :

ItisaprocessofconvertingsurfacemetalatomsintotheirPhosphatebychemicalorelectrochemicalprocess. Phosphatingoffersimprovedcorrosionresistanceandalsoimpartsthesurfaceagoodpaintadhesionquantity. Phosphatingbathcontainsfreephosphateions,ametalphosphate(Fe,Mn,Zn)&anaccelerator. ThepHisaboutis1.8to3.2. andtempis35^0C.Thereactioninvolvesthedissolutionofmetalormetalions,metalionsreactingwiththephosphateionstoformametalphosphate&depositionofmetalphosphateonthesurfaceofthemetal.Itisusedinrefrigerators,washingmachinescarbodiestoprovidebetterpaintadhesioninadditiontoimprovecorrosionresistance.

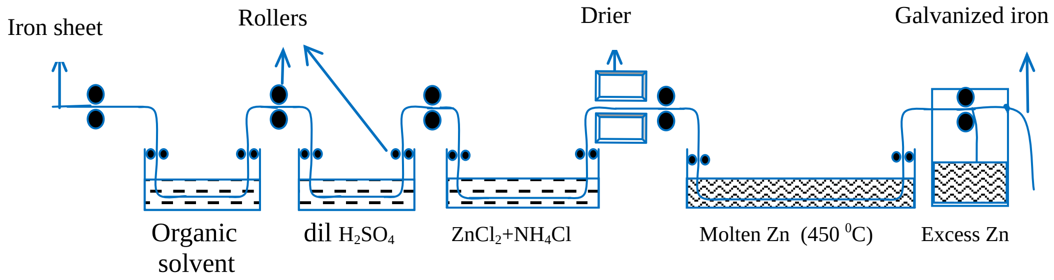
Metalcoating

Depositionofaprotectivemetaloverthesurfaceofabasemetaliscalledmetalcoating.Itisdividedintotwotypes:anodicandcathodiccoating

Anodiccoating(Galvanization)

Galvanizationisaprocessofcoatingabasemetalsurfacewithzincmetalbyhotdippingprocess.Itinvolvesthefollowingsteps:

1. Themetalsurfaceiswashedwithorganicsolventstoremovegreaseandoil.
2. RustandotherdepositsareremovedbywashingwithdiluteH_2SO_4.
3. Finallythearticleiswashedwithwateranddried.
4. Thearticleisthendippedinabathofmoltenzincmaintainedat425-430^0CandcoveredwithNH_4Clfluxtopreventtheoxidationofmoltenzinc.
5. ☐Theexcesszinconsurfaceisremovedbypassingthroughapairofhotrollers,whichwipesoutexcessofzinccoatingandproducesathincoating.

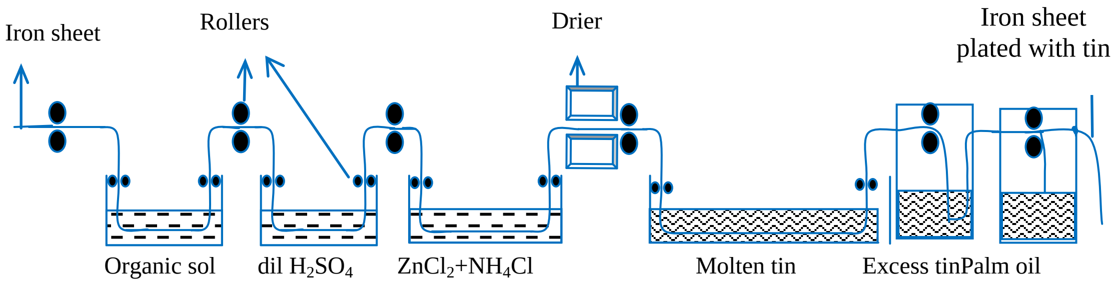


<u>Uses</u>Itisusedtoprotectironfromcorrosionintheformofroofingsheets,fencing wire,buckets,bolts,nuts,nails,screws,pipesetc. Theyarenotusedforpreparingandstoringfoodstuffs,sincezincdissolvesindiluteacidsproducindtoxiczinccompounds.

Tinning :

Itisproducedbycoatingabasemetalwithamorenoblemetalwhichiscathodic.Tinningisthemostcommonlyusedcathodiccoatingonsteelsurfacesbyhotdippingprocessandinvolvesthefollowingsteps

1. Themetalsurfaceiswashedwithorganicsolventstoremovegreaseandoil
2. RustandotherdepositsareremovedbywashingwithdiluteH_2SO_4
3. Finallythearticleiswashedwithwateranddried
4. ☐Thecleananddrysheetispassedthroughmoltenzincchloridefluxwhichhelpsthemoltenmetaltoadhereonthemetalsurface
5. ☐Thenitispassedthroughatankcontainingmoltentin
6. ☐Finallypassedthroughseriesofrollersimmersedinpalmoil.Therollerswipesoutexcessoftindepositsandproducesacontinuous,thincoatingoftin.theoilpreventstheoxidationofthetincoatedsurface .



Itprotectsagainstcorrosiononlyifitcoversthesteelsurfacecompletely.Sincetiniscathodictoironevenifsmallcrackisformedintensecorrosiontakesplaceduetosmallanodeandlargecathodeareas.

Uses: Itisusedforstoringfoodstuffssuchasjam,,instantfood,milkproductsetc.

CATHODICPROTECTION:

Cathodicprotectionisamethodofprotectingametaloralloyfromcorrosionbyconvertingbasemetalcompletelyintocathodicandnopartofitisallowedtoactasanode.

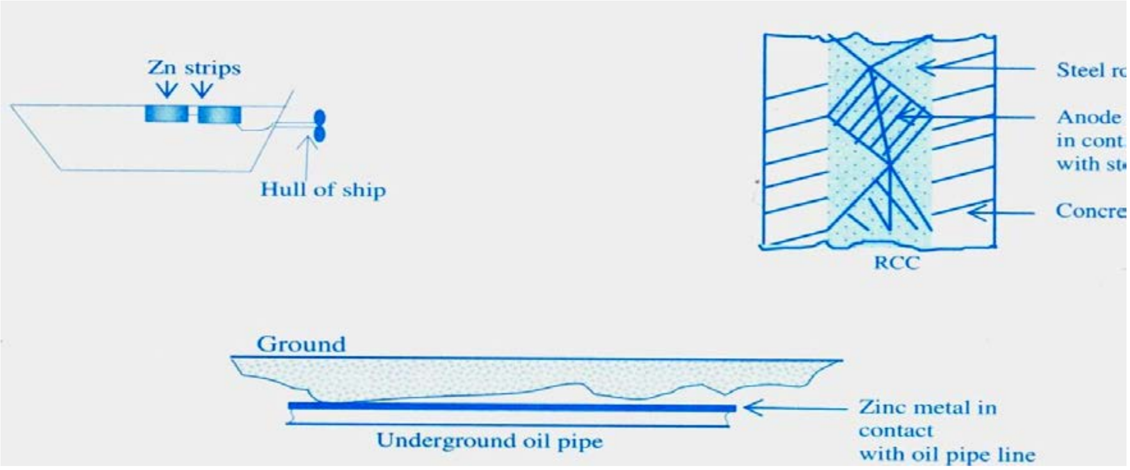
Theprincipleofcathodicprotectionistoreversetheflowofelectronsduringcorrosion.Thiscanbeachievedbyprovidingelectronsfromexternalsourcesthatthespecimenalwaysremainscathodic.Theelectronscanbeprovidedbytwomethods.

Sacrificialanodicmethod:

Inthismethodthemorereactivemetals(sacrificialanodes)likeZn,Mgwhichprovideelectronsconnectedtothemetalstructuretobeprotected.Thebasemetalwillbecomecathodic&morereactivemetalbecomeanode,preferentiallycorrosionoccursatanode.

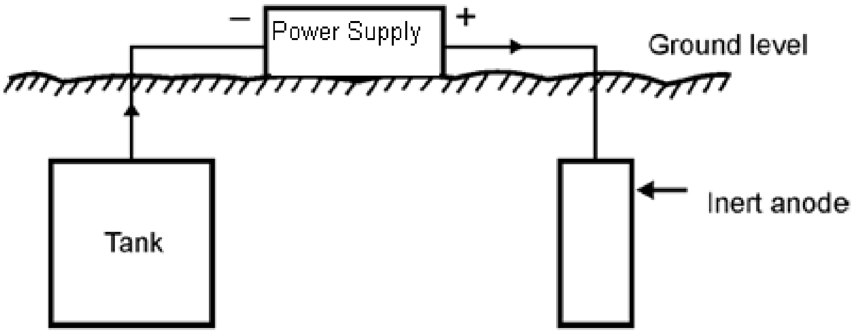
Thesacrificialanodewhichgetscorroded,hastobereplacedtoprotectbasemetalcontinuously.

Example:AMgblockconnectedtoaburiedoilstoragetank.



IMPRESSEDCURRENTMETHOD:

Inthismethodtheelectronsforcathodicprotectionaresuppliedbyasourceofdirectcurrent.Thespecimentobeprotectedshouldbemade–veotherwiseitcorrodes.Thisisusedinburiedoilpipelines,waterstoragetanks.



MetalFinishing

Introduction,Technologicalimportance.Electroplating:introduction,principles governing-Polarization, decomposition potential and overvoltage. Factors influencing the nature of electro deposit-current density, concentration of metal ion & electrolyte;pH, temperature & throwing power of plating bath, additives-complexing agents, brighteners,levellers, structure modifiers & wetting agents. Electroplating of chromium and Nickel (Watt's bath). Electro less plating: Introduction, distinction between electroplating and electroless plating, electro less plating of copper & manufacture of double sided Printed Circuit Boardwith copper. **5 HOURS**

- **Introduction, Technological importance.**
- **Electroplating: Introduction, principles governing**
- **Polarization, decomposition potential and overvoltage.**
- **Factors influencing the nature of electro deposit-current density, concentration of metal ion & electrolyte;**
- **pH, temperature & throwing power of plating bath,**
- **additives-complexing agents, brighteners,levellers, structure modifiers & wetting agents.**
- **Electroplating of chromium and Nickel (Watt's bath).**
- **Electro less plating: Introduction, distinction between electroplating and electro less plating,**
- **electro less plating of copper & manufacture of double sided Printed Circuit Board with copper.**

MetalFinishing:

Definition: Itisdefinedasaprocesscarriedoutinordertomodifythesurfacepropertiesofa metalbydepositionofalayerofanothermetal,polymerorbyformationofoxidelayer.

Technologicalimportanceofmetalfinishing:

Itistheadditionofcertainpropertiestothematerialstoincreasetheutilityofthematerial. Theseinclude

1. toincreasecorrosionresistance
2. toimprovedwearresistance
3. toimpartelectricalandthermalconductingsurface
4. impartingthermalresistance
5. impartinghardness
6. toofferthesurfacethermaloropticalreflectivity
7. manufactureofelectricalandelectroniccomponentssuchasPCBs,capacitors,contacts
8. electroformingprocess
9. electropolishing,electrochemicaletching

Theimportanttechniquesofmetalfinishingareelectroplatingandelectrolessplating .

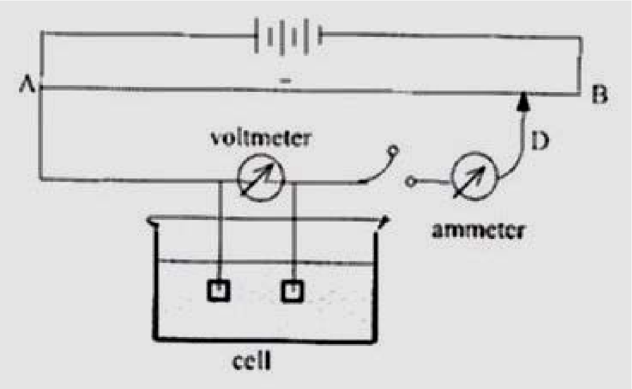
Electroplating:Itisaprocessofelectrolyticdepositionofmetal,alloyorcompositeonthebasemetalby meansofelectrolysis.
Thethreefactorsgoverningtheelectrolysisarepolarisation,decompositionpotentialandovervoltage.

Polarisation:
Itisdefinedasthedepartureoftheelectrodepotential(increaseordecrease)dueto inadequatesupplyofspeciesfromthebulkofsolutiontotheelectrodesurface.
TheelectrodepotentialisgivenbytheNernstequation

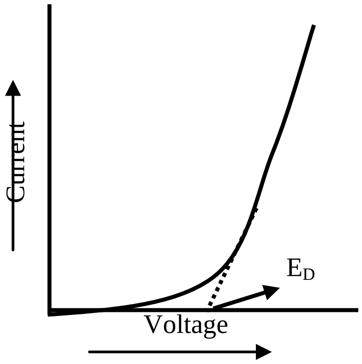
$$E=E^{o}+0.0591/n\log [M^{n+}]$$

WhereE-electrodepotential,E^{o}standardelectrodepotentialand$[M^{n+}]$isthemetalion concentration.Inpresenceofelectriccurrentmetalionconcentrationdecreasesduetodepositionofmetal .Whenthediffusionrateofmetalionisslowthevariationinelectrodepotentialisobserved.Atthatstagetheelectrodeissaidtobepolarized.
Factorsdependingonpolarisationare
i.Natureofelectrode(size&shape)ii.Concentrationofelectrolyteanditsconductanceiii.Temperatureiv.Productsformedatelectrodev.Rateofstirringoftheelectrolyte.Todecreasethepolarisationeffecttheelectrodesurfacemustbelargeandlowconcentrationofelectrolytewithhighconductance.

Decompositionpotential:
Theminimumexternalvoltageappliedinordertocausecontinuouselectrolysisofanelectrolyteiscalled decompositionpotential. Itismeasuredusingan electrolytic cell



Determinationofdecompositionpotential :
Thecellconsistsoftwoplatinumelectrodesimmersedintheelectrolyte.ThevoltageisvariedbymovingthecontactCalongthewireABandthecurrentpassingthroughthecellismeasuredwithammeter.Whendilutesolutionofacidorbaseistakeninthecell,atlowvoltagei.e.Lessthan1.7Vnoreactionisfoundtooccurbecausetheinertplatinumelectrodesareconvertedintoactivehydrogenandoxygengaselectrodes.Thesecondarycellformedproducesbackemfopposingtheappliedemf.Whenthevoltageisincreasedabove1.7VsuddenevolutionofH_2andO_2gastakesplaceattherespectiveelectrodes.Theabruptincreaseincurrentalsoobservedatthispoint.Thedecompositionpotentialiscalculatedbyplottingcurrentversusappliedvoltageasshowninthegraph.



Theintersectionofthesetwostraightlinesgivesthedecompositonpotentialmathematically
$E_{backemf}=E_{cathode}-E_{anode}$
Thedecompositonpotentialvaluesenablesthe
i.Calculationofemfrequiredforcontinuouselectrolysis
ii.usedinseparationofmetalionmixturebyelectrolysis

Overvoltage: TheexcessvoltagethathastobeappliedabovethetheoreticaldecompositionpotentialtostartthecontinuouselectrolysisiscalledOvervoltage.

$E_D= E_{cathode}- E_{anode}+H$,whereH-overvoltage

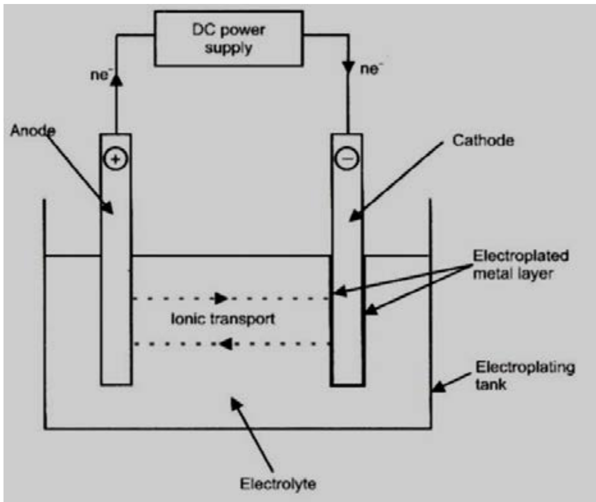
Thefactorsinfluencestheovervoltageare
i.Electrodesurfaceii.Currentdensityiii.
Temperatureiv.Rateofstirringoftheelectrolytev.Natureofsubstancedischarged.
Forexamplethereversibleelectrodepotentialofoxygengaswithsmoothplatinumelectrodesurfaceunderstandardconditionis1.23V.

Butactualgasevolutiontakesplaceatapotentialof1.68V.Thisexcess0.45Vistheovervoltageofoxygen onsmoothplatinumsurface.
Theknowledgeofovervoltageisusedintheelectrolysisfordepositionofmetals.Highertheelectrodepot entialcationswillbeeasilydischargedattheelectrodesurface.

Electroplatingprocess:
Itisaprocessofelectrolyticdepositionofmetal,alloyorcompositeonthebasemetalbymeansof electrolysis. ThedepositsareSinglemetalssuchasSn,Cu,Ni,Cr,Ag,Au,Ptetc.
AlloyslikeCu-Zn,Cu-Sn,Sn-Ni,Ni-Co,Ni-Cretc.
CompositessuchasmetalscontainingsolidslikeWC,SiC
Theprincipalcomponentsofelectroplatingare
1.Anelectroplatingbathcontainingconductingsalt,metaltobeplatedinsolubleform,complexingagent ,additives,bufferingagent.
2.Cathodei.e.thearticletobeplated
3.Anode:Coatingmetalitselforinertelectrode
4.Aninertcontainertoholdallabovecomponents.
Theobjecttobeplatedismadeascathodeandthepossiblereactionsatcathodeis

$$M^{n+}+neM \longrightarrow$$

Thedissolutionofmetalatanodetakesplace.Iftheinertanodeisusedtheoxygenevolutiontakesplaceand metalionsareaddedintheformofmetalsalt.



$$M \quad M^{n+}+ne \longrightarrow$$

Theelectrolysisconditionsaremaintainedinsuchawaythatcurrentefficienciesofbothreactionsaresam e.Forsuccessfulelectroplatingpretreatmentofobject,carefulselectionofanodwithproperplatingbaths olution,currentdensityandotherelectrolysisconditionsarenecessary.

Factorsinfluencingthenatureofelectrodeposit:
Currentdensity: Itisthecurrentperunitareaoftheelectreodesurface(mA/cm^2)
•Atlowcurrentdensitiessurfacediffusionisfastcomparedtoelectrontransferandadatomsfindmostfav orablepositionresultinginwellformeddeposit.

Asthecurrentdensityincreasedsurfacediffusionissloweddowncomparedtoelectrontransferandadatommaynotreachmostfavorablepositionresultinginlessordereddeposit.

- Atveryhighcurrentdensity(belowlimitingvalue)masstransportpredominatesinsolutionresultinginbaddepositwithroughandpowderytexturewhichispoorlyadherenttosurface.
- Whencurrentdensityisincreasedbeyondlimitingcurrentburntandspongyappearanceofdeposittakesplace.ThisisduetodepletionofH$^+$ionsatthecathodeandformationofmetalhydroxidealsotakesplace.

Thereforeoptimumcurrentdensityshouldbeappliedtogetgooddeposit.

Platingbath:

Metalsaltandelectrolyteconcentration:Themetalsaltconcentrationiskepthightodecreasethemasstransferotherwisethequalityofplatingisadverselyaffected.Electrolytesarealsoaddedtoincreasetheconductivityoftheplatingbath.TheyalsohavetheroleofcontrollingthepHofbathsolutionparticularlyiftheevolutionofH_2orO_2atcathodeoranode.H_2SO_4isaddedtopreventhydrolysisofsalt.Boricacidisusedasbufferingagent.

Complexingagents:

Theseareaddedtoconvertfreemetalionsintocomplexingionstogetfinegrainedandmoreadherentdeposit.Theyarealsoaddedforthefollowingreasons

- Topreventthereactionofcathodemetalandplatingions
- Topreventpassivationofanodeandincreaseincurrentefficiency
- Toimprovethrowingpowerofplatingbath
- Toincreasethestabilityofslightlysolublemetalsalts
- TomakepotentialofplatingM^{n+}more-vetocarryoutplatingatlowerpotential.

Themostcommoncomplexingagentsarecyanides,hydroxides,sulphamates,citrates,tartaratesetc.

Organicadditives

:Awiderangeoforganiccompoundsareaddedinlowconcentrationtomodifythestructure,morphologyandpropertiesofthedeposit.Thecommonadditivesare

a)Brightners

:Theseareaddedtogetbrightandlightreflectingdeposit.Thereflectiontakesplaceonlywhengrainsizeofdepositislowerthanthewavelengthoftheincidentlight.Brightnersusedtoproducemicroscopicallyfinedepositparalleltosubstratesurface.Ex.AromaticsuphonesorsulphonatesandcompoundscontainingC=N,N=C=S,or>C=Ogroups.

b)Levellers:Substratesurfacemaycontaindislocationswhereplatingtakesplacefasterresultinguneventhickness.Whenlevelersareusedtheyabsorbatsuchregionswhererapiddepositiontakesplaceandpreventrateofelectrontransfer.ex.Sodiumallylsulphonates.

c)Stressrelieversorstructuralmodifiers: Anelectroplatingprocessinvolvesinternalstress.Ifthestresslevelishighcrackingtakesplace.Stressrelieversreducestheformationofinternalstressbymodifyingthestructureofthedeposit.Ex.Saccharin

d)Wettingagents:Inelectroplatinghydrogengasevolvedatcathodeandthesegasbubblesadheretothecathodesurface.Thegasmaytrytoescapewhentheplatingisoverandmakesthedepositporousandbrittle.Wettingagentsaddeddetachadsorbedhydrogengasonthecathodesurfaceandimprovetheadhesionofthedeposit. Ex.Sodiumlaurylsulphate.

P$^{H:}$AtlowpHvalue,hydrogengasevolutiontakesplacecausingdepositbrittleandburnt.AthigherpHdepositsofinsolublemetalhydroxidestakesplace.HenceoptimumpHismaintainedbyusingsuitablebuffers.

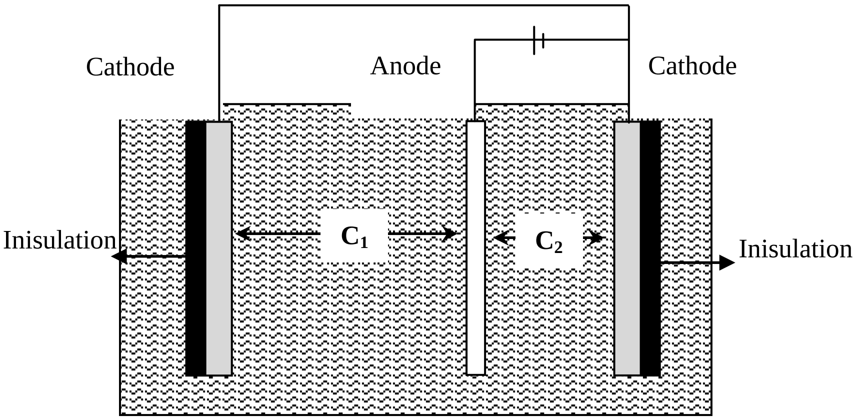
Temperture:Atslightlyhighertemperaturegooddeposittakesplaceduetoincreaseinthesurfacediffusionofions.Butathightemperaturedecompositionoforganicadditives,corrosionofequipmentandhydrogenevolutionmaytakesplace.Hanceoptimumtemperatureisused(30to60^{o}C)

Throwingpower:Theabilityoftheplatingbathtogiveuniformandevendepositontheentiresurfaceofcathodeofirregularshape.
ItisdeterminedbyHaringblumcell.Itconsistsofinsulatingcontainerfilledwithelectrolytewhosethrowingpoweristobedetermined.Anodeisplacedatthecenterandtwocathodes(C_1&C_2)areplacedatdifferentdistancesd_1&d_2(d_1>d_2)asshowninthefig.

Electroplatingiscarriedoutforsufficienttimeandweightsw_1&$w_2$depositedoncathodesC_1&C_2aredetermined.
Theweightofdeposit(w_1)oncathodeC_1islessbecauseofitsloweroverpotential.Itiscalculatedbytheequation

$$\%OfTP=100(x-y)/(x+y-2)$$

wherex= d_1/d_2&$y=w_2/w_1$



Determinationofthrowingpower

Electro-plating of Chromium:

Bath:$Cr_2O_3$250g+2.5gH_2SO_4(100:1)
Temperature:45-55^{O}C
Currentdensity:100-200mA/Cm^2.
Currentefficiency:10-15%
Anode:InsolubleanodePb-SborPb-SncoatedwithPbO_2
Cathode:Objecttobeplated.

Atanode:$CrO_3+H_2OH_2CrO_4 \longrightarrow$
$2\ H_2CrO_4H_2Cr_2O_7 \rightarrow + H_2OCr_2O_7^{-2} + 2H^{+}+H_2O \longrightarrow$
$Cr_2O_7^{-2}+ 14\ H^{+}+ 6e2Cr^{+3}+ 7\ H_2 \rightarrow O$
$Cr^{+3}+3eCr \longrightarrow$
AtCathode:$2H_2OO_2+4H^{+}+ 4e \longrightarrow$

SulphuricacidsactsascatalystinconvertingCr(VI)toCr(III)bycomplexanodicreaction. TomaintaintheconcentrationofCr(III)ionsinsolubleanodeslikePb-Sb,Pb-Sn,alloysareusedcoveredPbO_2whichoxidizeCr(III)toCr(VI)&controlstheconcentrationofCr(III)ions.
1)Crmetalpassivatesstronglyinacidsulphatemedium.
2)ItgivesCr(III)ionsondissolution.InpresencelargeCr^{3}ionsablockCrdepositisobtained.
3)Differenceinefficiencyofanodeandcathode(anode-100%cathode-20%).

Uses: Usedindecorativeandcorrosiveresistantfinish.Decorative&durablefinishlikecycles,automobiles,furniture,householdfittings,surgicalanddentalinstruments,otherslikeopticalinstruments,machinetools,electronicsparts,pistonrings,cylinderlinersofdieselengines&aircraftscylinders.

Electroplatingof Nickel (Watt's bath) :

Watts nickel plating solutions

Nickel electroplating is a process of depositing nickel on a metal part. Parts to be plated must be clean and free of dirt, corrosion, and defects before plating can begin.[2] To clean and protect the part during the plating process a combination of heat treating, cleaning, masking, pickling, and etching may be used.[1] Once the piece has been prepared it is immersed into an electrolyte solution and is used as the cathode. The nickel anode is dissolved into the electrolyte in form of nickel ions. The ions travel through the solution and deposit on the cathode

Watts solution was developed by Oliver P. Watts in 1916. Now it is most popular nickel electroplating solution. Plating operation in Watts solutions is low cost and simple.

Bath composition:

Nickel sulphate, $NiSO_46H_2O$: 32-40 oz/gal (240-300 g/l)
Nickel chloride, $NiCl_26H_2O$: 4-12 oz/gal (30-90 g/l)
Boric acid, H_3BO_3: 4-6 oz/gal (30-45 g/l)

Operating conditions:

Temperature: 105-150°F (40-65°C)
Cathode current density: 20-100 A/ft² (2-10 A/dm²) PH: 3.0-4.5

Mechanical properties:

Tensile strength: 50000-70000 psi (345-485 MPa)
Elongation: 10-30%
Hardness: 130-200 HV
Internal stress: 18000-27000 psi (125-185 MPa)

Brighteners:

- Carrier brighteners (e.g. paratoluene sulfonamide, benzene sulphonic acid) in concentration 0.1-3 oz/gal (0.75-23 g/l). Carrier brighteners contain sulfur providing uniform fine Grain structure of the nickel plating.
- Levelers, second class brighteners (e.g. allyl sulfonic acid, formaldehyde chloral hydrate) in concentration 0.0006-0.02 oz/gal (0.0045-0.15 g/l) produce (in combination with carrier brighteners) brilliant deposit.
- Auxiliary brighteners (e.g. sodium allyl sulfonate, pyridinum propyl sulfonate)in concentration 0.01-0.5 oz/gal (0.075-3.8 g/l).
- Inorganic brighteners (e.g. cobalt, zinc) in concentration 0.01-0.5 oz/gal (0.075-3.8 g/l). Inorganic brighteners impart additional luster to the coating.

.

Electroless plating:
ItisdefinedasdepositionofmetaloralloyfrommetalsaltsolutionontoaelectrilyticallyactivesurfacebycontrolledchemicalreductionofM^{n+}ionsbysuitablereducingagentswithoutusingelectricalenergy.

Advantages:

1)Doesnotrequireelectricalpowersource.
2)Semiconductors&insulatorslikeplasticcanbecoated.
3)Goodthrowingpower,henceuniformcoatingisachievedonarticleofirregularshape.
4)Platingisharderthanelectro-plating.
5)Depositshaveuniquechemical,mechanicalandmagneticproperties.
6)Levelersarenotused.

DistinctionbetweenElectro-platingandelectroless-plating

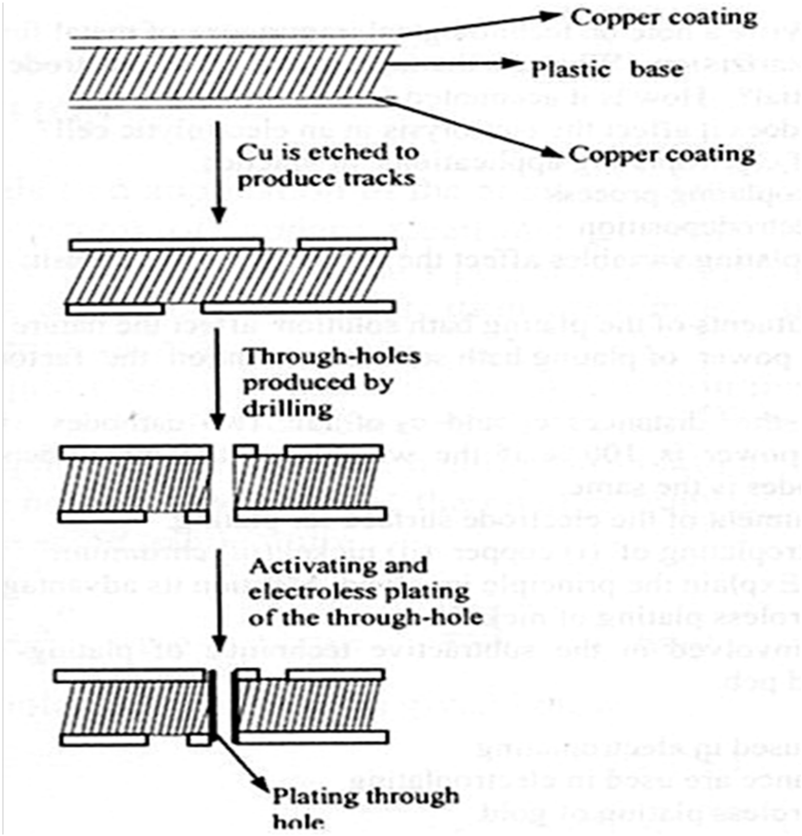
	Electro-plating	**Eelectroless-plating**
Anodereaction	$M \longrightarrow M^{n+} + ne$	R $\longrightarrow$ Oxidizedproduct+ne
Drivingforce	powersupply	auto-catalyticredoxreaction
Siteofanodereaction	separateanode	articletobeplated
Siteofcathodereaction	articletobeplated	articletobeplatedwith Catalyticallyactivesurface
Natureofdeposit	puremetalordefinitealloy	Metalcontaminatedwith O/R species
Throwingpower	Satisfactory	Good
Application	applicableonlytoconductors	applicablebothforconductors andnonConductors

Electrolessplatingofcopper

Pretreatmentandactivationofsurface:Thesurfaceistreatedtoremovegreaseandotherimpurities.Incaseofinsulators,thesurfaceisactivatedbydippinginstannouschlorideandtheninpalladiumchloride.Thesurfaceisdried.

Platingbath:
Bath:Coppersulphate12gperlitre
Reducingagent:Formaldehyde8gperlitre
Buffer:NaOH15g/litre&Rochellesalt14g/litre
Complexingagent:EDTA20g/litre
pH:11
Temperature:25^{0}C

Reactions
Atanode2HCHO+4OH2HCOO+$2H_2O+H_2 \longrightarrow$+2e
AtcathodeCu^{2+}+2eCu $\longrightarrow$



DoublesidedPrintedcircuitboard

Uses: Used in printedcircuitboard,plating on conductors,plating through hole connections

Module-3

Fuels and Solar Energy

Fuels:Introduction, classification, calorific value-gross and net calorific values,determination of calorific value of fuel using bomb calorimeter,numerical problems.Cracking: Introduction,fluidized catalytic cracking,synthesis of petrol by Fishcher-Tropsch process,reformation of petrol ,octane and cetane number.Gasoline and diesel .Knocking and their mechanism,antiknocking agents, power alcohol,biodiesel.

5HOURS

Content :

- **Introduction, classification.**
- **Calorific value-gross and net calorific values,determination of calorific value of fuel using bomb calorimeter,numerical problems.**
- **Cracking: Introduction,fluidized catalytic cracking,synthesis of petrol by Fishcher-Tropsch process,reformation of petrol.**
- **octane and cetane number.**
- **Gasoline and diesel .Knocking and their mechanism,antiknocking agents.**
- **power alcohol,biodiesel.**

Fuels

Introduction: Energy is the fundamental aspect of human life. Energy is defined as the capacity to do work. Everything we do is connected to energy in one form or the other. Chemical fuels are used in transportation, communication and illumination etc,.

Chemical fuels: It isdefined as naturally occurring or artificially manufactured combustible carbonaceous material used mainly as source of light and heat in few cases as a source of raw material.

Classification of fuels: On the basis of origin, fuels are classified as primary and secondary fuels.

Physical state	Primary fuels	Secondary fuels
Solid	Wood,Coal	Charcoal,coke
Liquid	Petroleum	Petrol,diesel
Gas	Natural gas	LPG

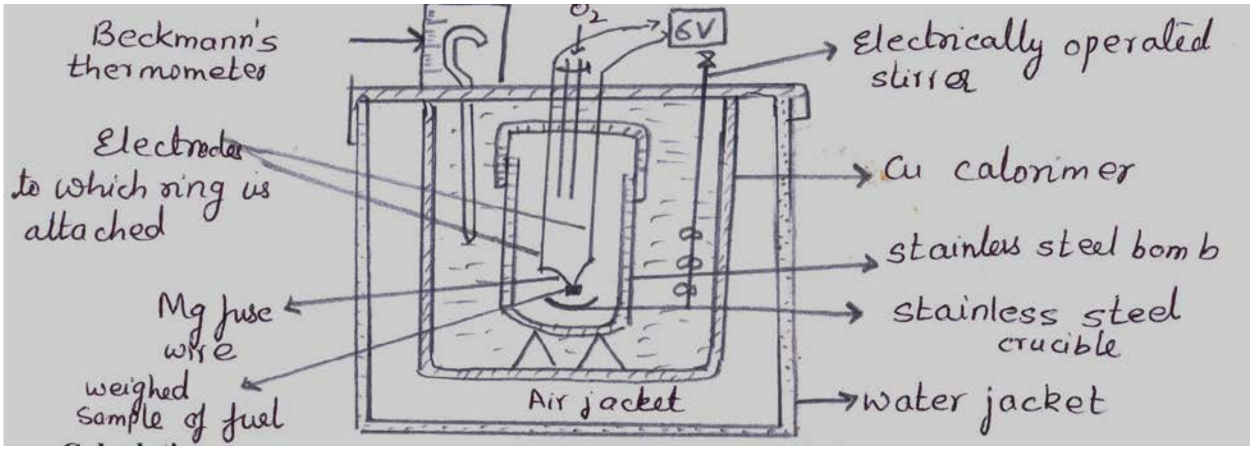
Primary fuels: It is the one which is natural and doesn't require any chemical processing before utilization.
Ex: wood, coal, crude petroleum and natural gas.
Secondary fuels: They are produced from naturally occurring substances by subjecting to treatments, which alter their chemical composition and improve their calorific value.
Ex: Coke, gas-LPG, Diesel, Petrol, Kerosene
Hydrocarbon fuels: Fuels which contain hydrogen and carbon are called hydrocarbon fuels. Ex: Petrol, diesel, kerosene.

Calorific value of a fuel: It is measured in terms of heating efficiency.
It is defined as the amount of heat evolved by the complete combustion of unit quantity (mass or volume) of the fuel in air or oxygen.
It is expressed in J/Kg for solid and liquid fuels and J/m^3 for gaseous fuels.
Calorific values are expressed in two ways:
1. Gross calorific value (GCV) 2. Net Calorific value (NCV)
Gross calorific value: Gross calorific value is defined as the quantity of heat evolved by the complete combustion of unit quantity of the fuel in air or oxygen and the products of combustion are brought down to room temperature.
Most of the fuels contain carbon and hydrogen. On combustion carbon and hydrogen are converted into CO2 and steam respectively.
On cooling, the combustion product steam gets condensed to water and liberates its latent heat. Hence, GCV is made up heat of combustion of fuel plus the latent heat of condensation of steam.
Therefore, GCV is always higher than the net calorific value.
Net Calorific value: It is defined as the quantity of heat evolved by the complete combustion of unit quantity of the fuel and the products of combustion are let off into the atmosphere.
i.e., the combustion products are not cooled to room temperature but they are allowed to escape into the atmosphere. Hence, this calorific value does not include latent heat of steam.Therefore, Net calorific value is always lower than GCV.
NCV = GCV - % of H_2 x 0.09 x latent heat of steam

Determination of calorific value of a solid or liquid fuel using Bomb Calorimeter:
Bomb calorimeter is used to determine the Calorimeter value of solid as liquid fuels
Principle: A Known wt of a liquid as solid fuel is completely burnt and liberated heat is absorbed by a Known weight of water by recording the rise in temperature of water and Knowing specific heat water calorific value is calculated

Construction: It consist of an air tight stainless steel bomb placed inside the copper colorimeter the colorimeter is surrounded by air and water jacket to prevent the heat loss to surrounding because of radiation the calorimeter is also fitted with an electrically operated stirrer to mix water mg fuse wire to start combustion an 0_2 inlet to support combustion and Beckmanns thermometer to read the temperature.

Working : A known wt (x) of the fuel in the form of pellet is taken in a crucible and placed inside the bomb. The bomb is kept inside a copper calorimeter containing a know weight of water Initial temperature (T_1) of water is noted after stirring.Oxygen is pumped into the bomb through O_2 value and the fuel is ignited using mg fuse wire and it is absorbed by water calorimeter .The maximum temperature (T_2) attained by water is noted



Calculation:
Heat Liberated due to combustion of x gm of fuel = XL absorbed by water and apparatus =(w+w) (T_2- T_1) H eat liberated = Heat absorb
W= Mass of water in Calorimeters in g= WxS
W= Water equivalent of the calorimeter in g
W= Wt of apparatus x Specific heat = W^1 S
L= H C V in cal/g
HCV$= \underline{(W+W)x\ S\ (T_2 - T_1)}$ Kj/kg
X
LCV =HCL –Latent heat of water formed
=(HCL -0.091xHxSx587) Cal /gm
Where latent heat of steam =587 Cal/g

Numericals problems on Bomb calorimeter

A) On burning 0.76 x 10^{-3} Kg a solid fuel in a bomb calorimeter, the temperature of 2.5 Kg of water is increased from 25^{0} C to 28^{0}C.The water equivalent of calorimeter and latent heat of steam are 0.486Kg 2457 Kj /Kg respectively. Caculate its GCV and NCV.Given Sp . heat = 4.187 Kj / Kg/ ^{0}C and % of H_2 is 2.5

Ans) Givenm=0.75g=0.76× 10^{-3}kg

w_{1+W2}=(2.5+0.486) kg=2.986kg

$\Delta t = t_2 - t_1 = 28-25 = 3^oC$

s =4.2kJkg^{-1o}C^{-1} = 4.2× 10^3 J kg^{-1o}C^{-1}

L=2457kJkg^{-1}=2457×10^3J kg^{-1}

$$\text{a)GrossC.V.} = \frac{(w_1+w_2)s\Delta t}{m} = \frac{2.986X3X4.2X10^3}{0.756X10^{-3}} J/Kg = 49351.5kJ/Kg$$

NCV=[GCV-Latentheatofsteam]=[49351.5–2.5X0.09X2457]KJ/Kg

=48798.2KJ/Kg

b)0.78g of coal containing 1.9% hydrogen. When burnt in a bomb calorimeter, increased the temperature of 2.7kg water from 27.20c to 29.70C. if the water equivalent of calorimeter is 1.2kg. calculate gross and net calorific value (specific neat of water 4.187kJ/kg/0C, latent of steam 2457kJ/Kg.

Ans) Givenm=0.78g=0.78× 10^{-3}kg

w_{1+W2}=(2.7+1.2) kg=3.986kg

$\Delta t = t_2 - t_1 = 2.5^oC$

s =4.2kJkg^{-1o}C^{-1} = 4.2× 10^3 J kg^{-1o}C^{-1}

L=2457kJkg^{-1}=2457×10^3J kg^{-1}

$$\text{GrossC.V.} = \frac{(w_1+w_2)s\Delta t}{m} = \frac{3.986X2.5X4.2X10^3}{0.78X10^{-3}} J/Kg = 5365.5kJ/Kg$$

NCV=[GCV-Latentheatofsteam]=[5365.5–2.5X0.09X2457]KJ/Kg

=48126.2KJ/Kg

Petroleum: It is found under the rocky strata of the earth crust. It is non renewable energy source as it takes millions of years to form. It is naturally occurring substance made up of several hydrocarbons.

Petroleum is subjected to fractional distillation to get various fractions like petrol, diesel, kerosene.The process of separating various components of petroleum from one another having different boiling points is called fractional distillation. This process is known as refining of petroleum.

Chemical processing of petroleum: Fractional distillation of petroleum physically separates the fractions of crude oil into its constituent fractions. These fractions are further converted into useful products by subjecting to various chemical process. The two important process used to achieve these objectives are i) Cracking ii) Reforming

<u>Cracking</u>: Breaking up of high molecular weight hydrocarbons into more useful low molecular weight hydrocarbons in presence of heat is called cracking. This involves the change in molar mass.

$$C_{10}H_{22} \xrightarrow{\text{Cracking}} C_5H_{12} + C_5H_{10}$$

n-decane n-pentane pentene

bp; 174 ^{o}C bp; 35 ^{o}C bp; 35 ^{o}C

There are two types of cracking process have been recognised

Thermal cracking: In this process petroleum is subjected to high pressure and temperature (700 C) in the absence of air and a catalyst. This method is not used since there is no control over the product of cracking and the efficiency is low.

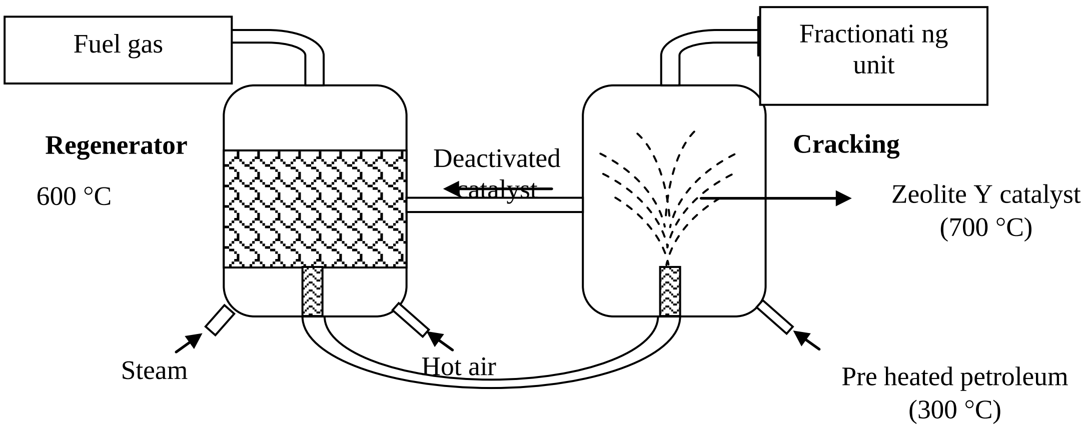
Catalytic cracking: In this process petroleum is subjected to low pressure and temperature in presence of catalyst. This cracking process is control over the end products.

<u>Fluidized catalytic cracking:</u>

Catalyst used: $Al_2O_3 + SiO_2$
Pressure : 1-2 atm
Temperature; 480-600^{O}C
Feed stock: Heavy oil
Yield: 70-80%(octane gasoline 40% , gas 6% and gas oil 37-47%)

Working or method:

In this process, oil is preheated to about 300^{0}C is sprayed from the bottom into a riser column containing the catalyst. Oil mixes with powdered catalyst at 700 ^{0}C. Then it carries the catalyst and the oil mixture in a fluidized state into the reactor, then cracking takes place.Cracked products are taken and transferred into a fractionating column for further separation.Spent catalyst is pumped from the catalyst chamber into a regeneration chamber. Hot air is blown through the chamber to burn the carbon deposit on the catalyst surface. The regenerated catalyst is sent back to the catalyst chamber. Thus the process of cracking is continuous.



Advantages of the method:

1)The yield of petrol is higher
2) The quality of petrol produced is better
3)Cracking process can be controlled

4)Catalyst can be regenerated and used again

5)The product contain a very little amount of undesirable sulphur and posses better anti-knocking properties.

Synthesis of petrol by Fischer-Tropsch process: (Indirect conversion of coal)

This method involves the following steps

a) Production of water gas: Water gas (CO+H2) is obtained by passing steam over white hot coal.

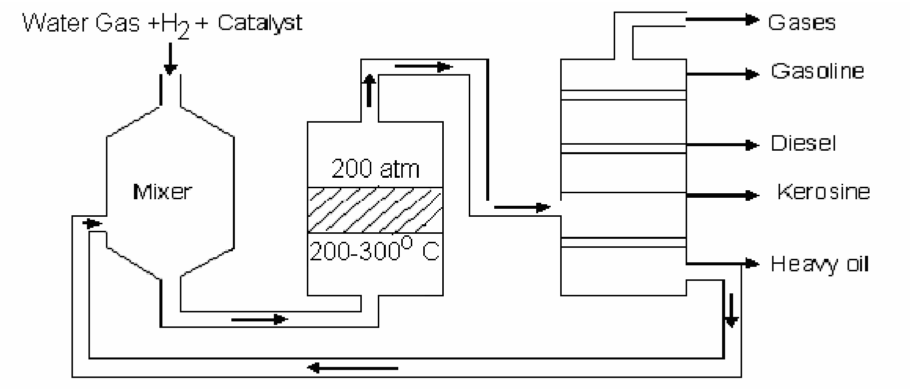
$C + H_2O \longrightarrow CO + H_2$ (water gas)

b) Production of synthesis gas the water gas obtained above is freed from dust, H2S and organic Sulfur compounds and blend water gas with hydrogen to form synthesis gas (CO + 2H2).

c) Hydrogenation of carbon monoxide: the Synthesis gas (CO + 2H2) is compressed to 5-10 atm pressure and admitted into a catalytic reactor containing the catalyst (mixture of cobalt (100 parts), thoria (5 parts) and magnesia (8 parts)). The reactor is heated to about 250^0CHydrogenation, reactions takes place to form saturated and unsaturated. These mixture of saturated and unsaturated hydrocarbons are passed through a fractionating column for separation petroleum fractions.

$$n\,CO + 2n\,H_2 \longrightarrow C_nH_{2n} + n\,H_2O$$

$$n\,CO + (2n + 1)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O$$



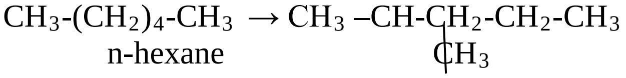
Reforming of petrol:

Reforming is a process which involves molecular rearrangement of hydrocarbons without any change in number of carbon atoms to form new compounds. This process is used to produce highoctane number of petrol.

A few important reforming reactions are

1.Isomerisation 2. Dehydrogenation 3. Cyclization and dehydrogenation 4. Ploymerization

Isomerisation: This process refers to chemical rearrangement of straight chain hydrocarbons into branched chain hydrocarbons.



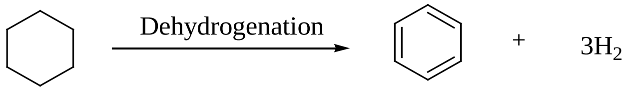
$$CH_3\text{-}(CH_2)_4\text{-}CH_3 \rightarrow CH_3\text{–}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

n-hexane

2-Methyl pentane

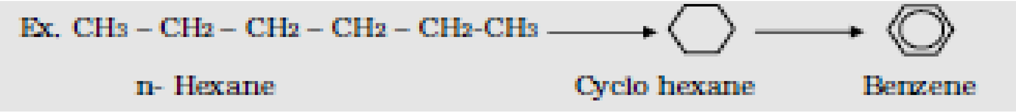
Dehydrogenation: This process involves the conversion of cycloalkanes into aromatic compounds.

$$\underset{\text{Cyclohexane}}{C_6H_{12}} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + 3H_2$$

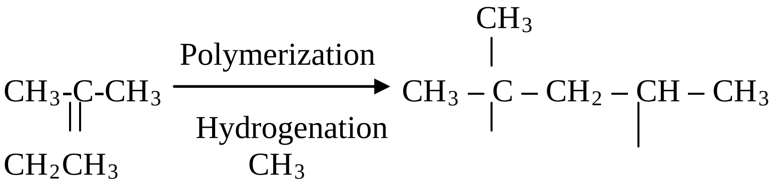


Cyclohexane Benzene

Cyclization and dehydrogenation: This process refers to the conversion of straight chain hydrocarbons into cyclic compounds followed by dehydrogenation.

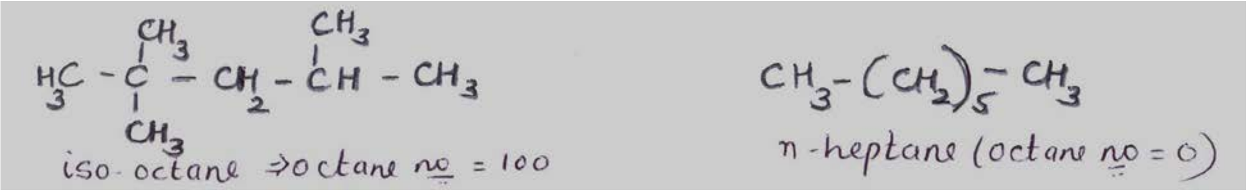


Polymerization: This process involves the formation of high molecular mass followed by hydrogenation.

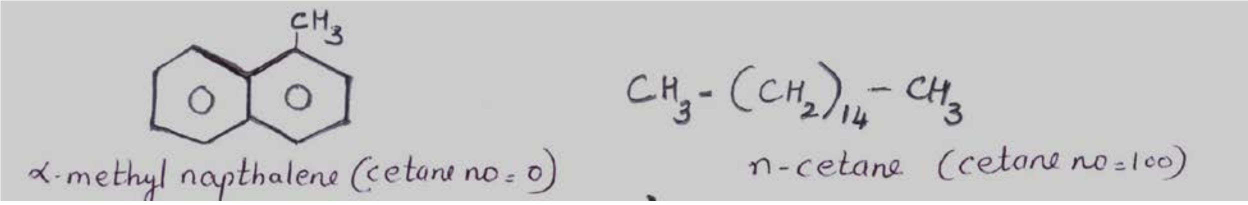


$$CH_3\text{-}\underset{\underset{CH_2CH_3}{\|}}{C}\text{-}CH_3 \xrightarrow[\text{Hydrogenation}]{\text{Polymerization}} CH_3 - \overset{\overset{CH_3}{|}}{\underset{|}{C}} - CH_2 - \underset{|}{CH} - CH_3 \qquad CH_3$$

Octane number: The knocking characteristics of petrol sample are described by the octane number. Higher the octane number lower is the tendency to knock and better is the quality of the petrol.Isooctane (2,2,4-trimethyl-pentane) has least knocking tendency and its octane number is arbitrarily fixed as 100. N-heptane a straight chain hydrocarbon has the highest tendency to knock and its octane number is fixed as 0.Therefore, octane number is defined as the % of isooctane present in a standard mixture of isooctane and n-heptane which knocks at the same compression ratio as the petrol being tested.



Cetane number: Quality of petrol sample is expressed in terms of its octane number. Where as the quality of diesel is expressed by means of cetane number.Cetane or hexadecane ($C_{16}H_{34}$) is an ideal fuel with a cetane number 100. α-methyl naphthalene has a cetane number of zero.“ Cetane number is defined as the % of hexadecane present in a standard mixture of cetane and α-methyl naphthalene which knocks at the same compression ratio as the diesel being tested.



Gasoline knocking : The performance of motor car is measured in terms of Km/l of petrol, which depends on the quality of the fuel.

Important method of obtaining more power from petrol is increasing the compression ratio of the engine.

$$\text{Compression ratio of engine} = \frac{\text{Intial volume of petrol and air mixture sucked into cylinder}}{\text{Final volume of petrol and air mixture after compression}}$$

Increases the compression ratio of the engine increases the efficiency of the engine. In the cylinder, combustion reaction is initiated by a spark as a result flame spreads rapidly and smoothly through gaseous mixture. By this petrol undergoes combustion under thermal conditions and the pressure increases inside the cylinder.However, beyond a particular compression ratio, the mixture of air and petro suddenly bursts into flames. This process is accompanied by a sharp knock in the internal combustion engine due to explosive combustion producing a shock wave which lose its energy by hitting the walls of the cylinder and piston. As a result a rattle sound is heard which is referred as knocking.

“Knocking is defined as the production of shock wave in an IC engine due to explosive combustion of mixture of petrol and air which increases compression ratio beyond a certain value leading to rattle sound.”

Affects of Knocking:

Knocking causes the following effects

1.Produces undesirable rattling sound

2.Decreases efficiency of engine and power out put

3.Increases the fuel consumption

4.Causes the mechanical damage to engine parts

5.The driving becomes rather unpleasant

Mechanism of Knocking:

Under ideal conditions, there is a slow oxidation of fuel, during which oxygen combines with a few hydrocarbon molecules and activates them.The activated molecules combine with hydrocarbon molecules and a chain reaction is set up resulting in a smooth combustion.In case of knocking conditions, all the hydrocarbon molecules activated and they combine at a faster rate to set up a chain reaction. Hence knocking occurs.The knocking is due to the formation of unstable peroxide decomposes rapidly to give a number of gaseous compounds. This give rise to pressure waves which knock against the engine walls.

$C_2H_6 + O_2 \longrightarrow 2CO_2 + 3H_2O$ (Normal combustion)

$$\underset{\text{Fuel}}{C_2H_6 + O_2} \longrightarrow \underset{\text{Ethane peroxide}}{CH_3\text{-}O\text{-}O\text{-}CH_3} \text{ (Under knocking conditions)}$$

$$CH_3\text{-}O\text{-}O\text{-}CH_3 \longrightarrow CH_3CHO$$

$$CH_3CHO + O_2 \longrightarrow HCHO + CO_2 + H_2O$$

$$HCHO + O_2 \longrightarrow CO_2 + H_2O$$

Diesel knocking: The diesel engine work on the principle of compression.air is drawn into the cylinder and compressed and the temperature risrs to 500oC .The fuel is injected at this point as in finely divide spray.hydrocarbons in the fuel absorb heat from the air ,vapouiize and burn on attaining ignition temperature.Knocking in diesel engine occur due to ignition delay which is caused by the chemical nature of hydrocarbons in diesel ie straight chain hydrocarbons have shorter ignition delay than branched and aromatics hydrocarbons. ignition delay is caused because time is required for vapourization of fuel and raising the temperature of the vapour to its ignition temperature ie accumulation of of fuel in the engine which leads to explosive combustion.this is called diesel knocking

Antiknocking agents in gasoline: The substances added to control knocking is called as anti knocking agents. These substances improve the octane number of petrol.example Tetra ethyl lead (TEL) [$Pb(C_2H_5)_4$]:TEL acts as a anti knocking agent it reacts with peroxy compounds and decomposes them there by prevents knocking. TEL is added in the form of ethyl fluid.TEL is a mixture of tetra ethyl lead, dichloroehane and dibromoehtane.It has some disadvantages as follows.

a) After combustion lead is deposited as lead oxide on piston and engine walls it leads to mechanical damage.

b) Lead is a poisonous air pollutant.

c) It spoils the catalyst used in catalytic converter.

Antiknocking agents in diesel:

The substances added to control knocking is called as anti knocking agents. These substances improve the cetane number of diesel.Cetane number can be improved by adding substance called dopents like ethyl nitrate ,acetone ,acetone peroxide which help in starting engine.

Power alcohol:

A mixture of ethyl alcohol and gasoline blend, which can be used as fuel in internal combustion engine, is known as power alcohol or gasohol.

Absolute alcohol is mixed with ether, benzene etc compounds and one volume of this is mixed with four volumes of petrol and is used as a fuel.

“Ethyl alcohol is used as an additive to motor fuels to act as a fuel for IC engines it is called as power alcohol.”

Advantages:

1.The power out put is good.

2.It has better antiknock property.

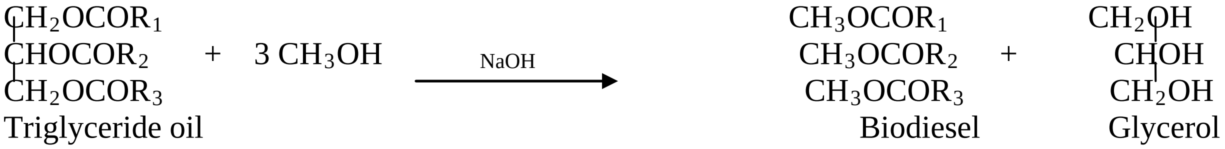
3.Ethanol is biodegradable; hence it is environmental friendly fuel.

4.The use of ethanol in alcohol increases the oxygen content of the fuels and promotes more and complete combustion of hydrocarbons in gasoline.

5.It reduces carbon monoxide emission.

Biodiesel: Biodiesel is a renewable, oxygenated fuel obtained from variety of agricultural resources such as soya beans or rape seeds.Biodiesel is non-toxic, biodegradable, replacement for petroleum diesel. Chemically biodiesel is a fatty acid monoalkyl ester.The oil/fat are triglycerides esters of fatty acids and their use in engines require extensive engine modifications. However, it is possible to convert these triglycerides into substance of diesel quality by transesterification.“Transesterification is alcoholysis of the triglyceride oil in the presence of a base like NaOH to obtain biodiesel. Thus, biodiesel is a mixture of mono alkyl esters of long chain fatty acids.

The transesterification of triglyceride oil with methanol in presence of NaOH is given below:



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + 3\,CH_3OH \xrightarrow{NaOH} \begin{array}{l} CH_3OCOR_1 \\ CH_3OCOR_2 \\ CH_3OCOR_3 \end{array} + \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Triglyceride oil Biodiesel Glycerol

The direct transesterification in presence of alkali results in the formation of soap. This soap forms a semi solid mass at ambient temperature and affects the engine performance. It also affects the separation of glycerol from diesel layer.This soap formation is avoided by first esterifying the free fatty acid in presence of an acid catalyst. This is followed by base catalyzed transesterification to get biodiesel. The transesterification proceeds at RT but the rate can be increased by raising temperature to 60° C.

Advantages of biodiesel:

1.It is made using renewable sources and feed stocks

2.Readily undergoes biodegradation, nontoxic, suitable for sensitive environments.

3.It has higher flash point than the diesel but lower ignition point.

4.It has higher cetane number (48-60) compared to diesel (40-55)

5.Use of biodiesel reduces green house gases.

SolarEnergy : Introduction,utilization and conversion,photovoltaic cells-importance,construction and working.design:modules,panels and arrays.Advantages and disadvantages of PV cells.Production of solar grade silicon (union carbide process),doping of silicon-diffusion technique (n and p types) and purification of Silicon (Zone refining). 5Hours

Content :

- **Introduction,utilization and conversion.**
- **Photovoltaic cells-importance,construction and working.**
- **Design:modules,panels and arrays.Advantages and disadvantages of PV cells.**
- **Production of solar grade silicon (union carbide process).**
- **Doping of silicon-diffusion technique (n and p types),.**
- **Purification of Silicon (Zone refining).**

Solar Energy

Solar Energy:

At presently dominant energy sources are petroleum, natural gas, hydro power and nuclear energy.As the reserves of fossil fuels are very limited and are being depleted very fast, search for alternative sources of energy has gained lot of importance. The world is looking towards the natural resources such as solar energy, wind energy, etc., out of these solar energy is the potential candidate. The energy supplied by this is enormous, continuous and free of cost.

Solar energy provides heat and light. Therefore in last few decades lot of effort has been made towards the use of solar energy. It is also possible to convert heat energy of the sun into electricity.

The solar energy utilization and conversation can be of two types

1) Direct solar power
2) Indirect solar power

Direct solar power: involves one step transformation into a usable form.

Example: a)photovoltaic cell to generate electricity where solar energy is directly converted to electrical energy.

b)Sunlight hits the dark absorber surface of a solar thermal collector and the surface warms.the heat energy may be carried away by a fluid circuit.

c)Sunligt strikes a solar sail on a space craft and is converted directly into a force on the sail which causes motion of the craft.

Indirect solar power: involves more than one transformation to reach usable form.

Ex-a)photosynthesis where solar energy is converted to chemical enegy which can be later used as energy source.

b) photo spliting of water to produce H_2 which can be used as a fuel.

c)Petroleum resources (fossil fuel) is a class of solar energy.

Photo-Voltaic cells: The device which is used to convert heat energy of the sun into electricity is called solar cells or photo voltaic cells. They often referred as semiconductor devices that convert solar energy into electricity.

Advantages:

1. Fuel source is vast and essentially infinite.
2. No emissions, no combustion or radioactive residues for disposal. Does not contribute to global change or pollution.
3. Low operating cost (no fuel).
4. No moving parts and so no wear and tear.
5. High reliability in modules.
6. No recharging
7. They do not corrode.
8. Can be integrated into new or existing building structures

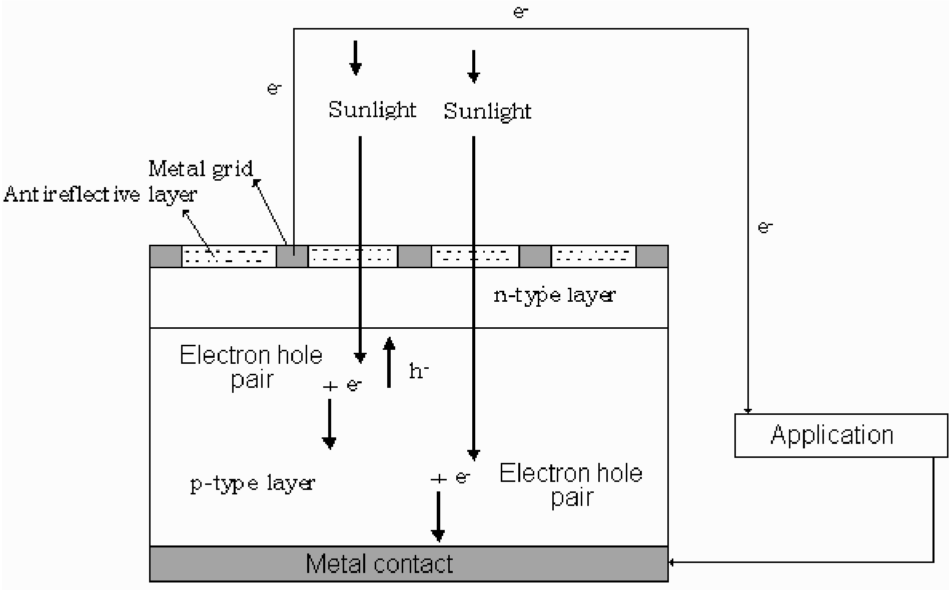
Disadvantages:

1. Sun light is a diffuse, i.c., it is relatively low density energy.
2. High installation cost.
3. Poor reliability of auxiliary elements including storage.
4. Energy can be produced only during the day time.

Construction and Working of Photo-Voltaic cells:

Semiconductors like silicon has the capacity to absorb light and deliver a portion of the energy of the absorbed photons to carry charge carriers (electrons and hole).Thus solar cell is a semiconductor diode that has been designed carefully so that it can absorb the light energy efficiently and convert light energy from the sun into electrical energy.

A conventional solar cell structure is shown in figure:

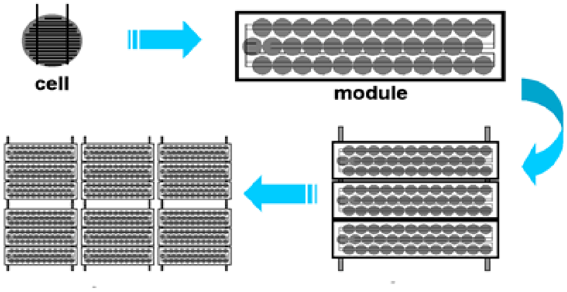


Construction: A typical silicon photo voltaic cell composed of thin layer of phosphorus doped silicon (n-type) on top of boron doped (p-type) silicon. Hence these two layers form p-n junction.A metallic grid is the electrical contact of the diode and allows light to fall on the semiconductor between the grid lines.An antireflective layer between the grid lines increases the amount of light transmitted to semiconductor.

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

Design: modules, panels & arrays:

The current out put of a cell depends on its efficiency and size and is proportional to the intensity of sun light striking the surface of the cell. Therefore, photovoltaic cells are connected electrically in series or parallel circuits to produce higher voltages, currents and power levels. A number of solar cells electrically connected to each other and mounted in a support structure or frame is called a photovoltaic module. Modules are designed to supply electricity at a certain voltage, such as a common 12 volts system. Photovoltaic panels include one or more modules assembled as a pre-wired, field installable unit. A photovoltaic array is the complete power generating unit, consisting of any number of photovoltaic modules and panels.



Advantages:

1. Fuel source is vast and essentially infinite.
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Disadvantages:

1. Sun light is a diffuse, i.c., it is relatively low density energy.
2. High installation cost.
3. Poor reliability of auxiliary elements including storage.
4. Energy can be produced only during the day time.

Production of solar grade silicon by union carbide process :

Silicon is obtained by reducing silicon dioxide (SiO_2) with coke in an electrode arc furnace at about 1300-2000 ° C.

$SiO_2 + C \longrightarrow Si + CO_2$

The obtained liquid silicon collects at the bottom of the furnace. Then it is dried and cooled. The silicon obtained by this process is called metallurgical grade silicon. It is 98 % pure silicon.

This metallurgical grade silicon is not suitable for semiconductor devices. It demands greater purity than the metallurgical grade silicon.

To get high purity silicon, metallurgical grade silicon is refined by treating it with anhydrous HCl at 300 ° C iin a fluidized bed reactor to form trichlorosilanes ($SiHCl_3$).

$Si(s) + 3HCl \longrightarrow SiHCl_3 + H_2$

Trichlorosilanes has low boiling point of 31.8° C, therefore it is purified by fractional distillation to remove halide impurities ($FeCl_3$, $AlCl_3$, BCl_3). In the next step, lighter impurities like Al, B, P, Fe, Cu are eliminated. Finally, pure SiHCl3 is treated with hydrogen at 1100° C for 200-300 hrs to produce a very pure form of silicon. This process is often referred to as Siemens process.

$SiHCl_3 + H_2 \longrightarrow Si + 3HCl$

Doping of Silicon by Diffusion Technique:

Si is Semiconductor and its Conductivity can be increased by doping with minute amount as either trivalent or penta valent atom.Doping is commonly caused out by diffusion technique Typical dopant sources used are BBr_3, $POCL_3$ (liquids) B_2O_3 , P_2O_5 (Solids) PH_5, B_2H_6(gases)

P-doping-In case of p-doping a required quantity of dopant source likeB_2H_6 is subjected to pyrolysis in a reactor containing Si substrate trivalent B atom formed by decomposition diffuse into the lattice of Si.

$B_2H_6 \xrightarrow{950^oC-1250^oC} 2B + 3H_2$

The valency of silicon is 4. When trivalent impurity like boron is doped into silicon it provides three valence electrons. These electrons combine with three valence electrons of silicon atom to form covalent bonds. There is a shortage of electron for the silicon atom to form another covalent bond. This shortage of electron is treated as hole. This makes silicon **p-type** semiconductor. The extent of diffusion is regulate by temperature and concentration of the impurity atom.

N-doping-In case of n-doping a required quantity of dopant source likePH_5 is subjected to pyrolysis in a reactor containing Si substrate. Pentavalent P atom formed by decomposition diffuse into the lattice of Si.

$2PH_5 \xrightarrow{1250^oC} P+ 5H_5$

A n-type silicon can be obtained by heating a silicon walfer below its melting point in an atmosphere of n-type impurity such as Phosphorus. The valency of silicon is 4.

When pentavalent impurity like phosphorus is doped into silicon it provides five valence electrons. Out of 5 valence electrons of phosphorus four will combine with four valence electrons of silicon atom to form bonds. There is an extra electron other than the electrons involved in bonding. This extra electron is treated as negative charge. This makes the silicon **n-type** semiconductor.

Purification of silicon (Zone refining)

The principle of zone refining is that when a solid is melted, the impurities tend to concentrate in the molten zone. A vertical zone refiner is used in the purification of silicon. A rod of silicon to be purified is clamped as shown in fig. and is heated by a RF coil to the melting point of silicon in the presence of argon gas.

1)This methods gives ultra pure silicon.

2) In this method a rod of maternal to be purified is melted and molten zone is moved slowly along the rod from one end to other end during this process impurities show more affinity to words molten zone move along with it leaving behind the puss material.

3) A rod of si is taqen in a furnace Containing high frequency induction coil for heating one end of the rod is heated almost near to its melting point.

4) The coil is now slowly moved to the adjacent along the rod and thereby shifting the molten zone also .

5) During this process impurities show more affinity towards molten zone and more along with it leaving behind pure silicon in this way heating coil is gradually moved to words and of rod .

6) Impurities present throughout the rod also more along with the molten zone and finally get concentrated not other end of the rod.

7) The process is repeated several times and finally the end of rod where impurities have collected in cut off remaining part of the rod containing Si with almost 100% purity .

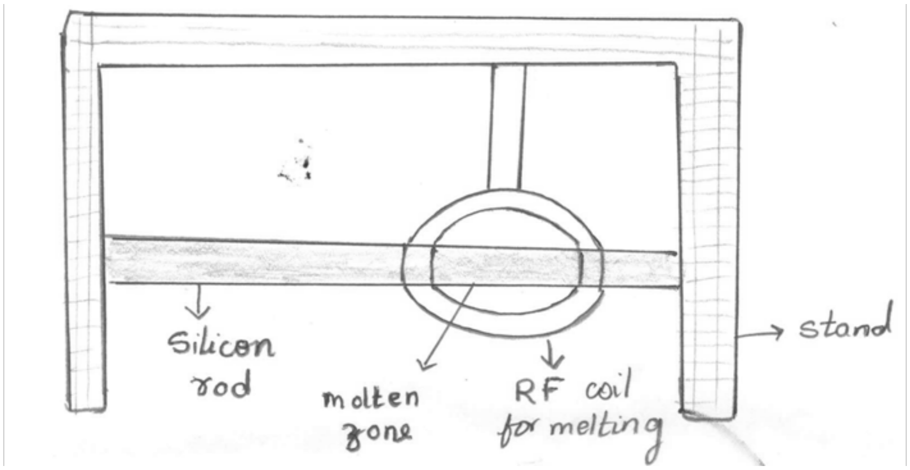


Fig : Zone Refining

MODULE-4

HIGH POLYMERS

Introduction types of polymerization: addition and condensation mechanism of polymerization-free radical mechanism taking vinyl chloride as an example .molecular weight of polymers :number average and weight average ,numerical problems. Glass transition temperature (T_g): Factors influencing T_g-Flexibility, inter molecular forces, molecular mass branching and cross linking. And stereo regularity. Significance of T_g. Structure property relationship: crystallinity. Tensile strength, elasticity , plastic deformation and chemical resistivity ,Synthesis, properties and applications of PMMA (plexi glass), Teflon polyurethane and polyurethane. Elastomers: Introduction, synthesis, properties and applications of silicone rubber. Adhesives: Introduction, synthesis, properties and applications of epoxy resin. Polymer composites Introduction, synthesis properties and applications of Kevlar and carbon fiber. Conducting polymers: Introduction, mechanism of conducting in polyaniline and applications of conducting polyaniline. 10 Hours

Contents:

- **Introduction types of polymerization**
- **Addition Mechanism Of Polymerization-Free Radical Mechanism**
- **Molecular weight of polymers :number average and weight average**
- **Glass transition temperature (T_g)**
- **Molecular Mass Branching And Cross Linking**
- **Synthesis, properties and applications of PMMA**
- **Elastomers: Introduction, synthesis, properties and applications of silicone rubber**
- **Adhesives: Introduction, synthesis, properties and applications of epoxy resin**
- **Polymer composites**
- **Synthesis Properties And Applications Of Kevlar And Carbon Fiber**
- **Conducting polymers: Introduction, mechanism of conducting in polyaniline.**

HIGH POLYMERS

Polymer:

A polymer is a large molecule, made up of small and simple molecules joined together chemically through covalent bond to form one giant macromolecule.

Monomer: A monomer is defined as a simple molecule with two or more bonding sites through which it forms covalent linkage with other monomer molecules to form the macromolecule.

Functionality: The functionality of a monomer is defined as the number of bonding sites present in a molecule of a monomer.

Example:

- All double bonded compounds like $CH_2=CH_2$ are bifunctional, i.e. have a functionality of two
- Similarly glycols ($OH-CH_2-CH_2-OH$), adipic acid ($HOOC-(CH_2)_4-COOH$) bifunctional
- Phenols have their 2,4,6 positions as active sites, hence they are trifunctional.

Degree of Polymerization: The number of times the unit is repeated in a chain is called as Degree of Polymerization. High polymers have a high degree of polymerization and hence large molecular masses.

Molecular weight of a polymer = Molecular weight of repeating unit × Degree of Polymerization

Types Polymerization Process

Addition Polymerization or Chain Polymerization:

The polymerization reaction in which a rapid self-addition of several bifunctional monomers to each other, takes place by chain reaction without the elimination of any by-product is called "Addition or Chain polymerization"

The product has the same elemental composition as the monomer compounds containing reactive double bonds, like alkenes undergo chain polymerization. Addition polymerization is initiated using small amounts of substances called 'initiators'

$$n\,[CH_2 = CH_2] \rightarrow -CH_2 - CH_2-CH_2 -[\,CH_2-CH_2]_n -CH_2 - CH_2-CH_2 -$$

Condensation Polymerization OR Step polymerization:

A polymerization reaction in which a bi- or poly functional monomer undergoes intermolecular condensation with another bi- functional monomer having a suitable functional group resulting in continuous elimination of by-products (of small molecules like H_2O, HCl, NH_3 etc) is called "condensation or step polymerization".

These reactions are normally catalyzed by acids or alkali

Ex: $$n\,HOOC-(CH_2)_4-COOH + n\,{}_2HN-(CH_2)_6-NH_2 \longrightarrow -\!\left[HN-(CH_2)_6-NHOC-(CH_2)_4-CO\right]\!-_n +2n\,H_2O$$

Adipic Acid Hexamethylene diamine Nylon 66

Mechanism of Addition or Chain Polymerization

Compounds containing reactive double bonds undergo a chain polymerization reaction. Chain polymerization consists of 3 major steps, viz. a. Initiation b. Propagation c. Termination. The first step of the process of polymer chain growth can be brought about by either a free radical or an ion (cation or an anion) or a complex formation between the monomer and a catalyst and accordingly follow different mechanisms.

Free Radical mechanism:

The first step in this mechanism involves the production of highly reactive species called free radicals by the hemolytic decomposition of the compounds called `initiators'

Some typical compounds used as initiators are: Azo compounds, Peroxides, Peracids.

Initiation:

The initiators are thermally unstable. In presence of thermal energy it dissociates in to diradical

$$[C_6H_5COO]_2 \longrightarrow 2C_6H_5COO^\bullet \longrightarrow 2C_6H_5^\bullet + CO_2$$

The free radical of the initiator,attacks the double bond in the monomer molecule as

$$C_6H_5^\bullet + CH_2 = CHCl \rightarrow R - CH_2 - C^\bullet HCl$$

Now, the monomer unit linked to the free radical of the initiator through a sigma bond and the free radical site is shifted from the initiator to the monomer unit

Propagation:

In this step, the radical site at the first monomer unit attacks the double bond of a fresh monomer unit results in linking up of second monomer to the first and transfer of the radical site to the second

$$R - CH_2 - C^\bullet HCl + CH_2 = CHCl \rightarrow R - CH_2 - CHCl - CH_2 - C^\bullet HCl$$

The new free radical attacks another molecule of monomer, adds it on and transfers the radical site to it, this proceeds in quick succession leading to a growing chain of polymer

$$R - CH_2 - CHCl - CH_2 - C^\bullet HCl + CH_2 = CHCl \rightarrow R - CH_2 - CHCl - CH_2 - CHCl - CH_2 - C^\bullet HCl$$

$$R - CH_2 - CHCl - CH_2 - CHCl - CH_2 - C^\bullet HCl + CH_2 = CHCl \rightarrow R - [CH_2 - CHCl]_3 - CH_2 - C^\bullet HCl$$

$$R - [CH_2 - HCl]_{n-1} - CH_2 - C^\bullet HCl + CH_2 = CHCl \rightarrow R - [CH_2 - CHCl]_n - CH_2 - C^\bullet HCl$$

Termination:

The propagation lasts till the chain growth is stopped by the free-radical site being killed by a termination step.The process of termination results in deactivated chain of polymer, which is called as “dead polymer chain”. Depending on the conditions, termination may take place in two different ways

(i) Termination by coupling:

Combination of one polymer free radical with another polymer free radical or an initiator free radical to form a dead polymer as

$$R - [CH_2 - CHCl]_m - CH_2 - C^\bullet HCl + R - [CH_2 - CHCl]_n - CH_2 - C^\bullet HCl \rightarrow$$

$$R - [CH_2 - CHCl]_m - CH_2 - CHCl - CH_2 - CHCl - [CH_2 - CHCl]_n - R$$

Dead heavy Polymer

Since this process involves coupling of two lone electrons, it is called `termination by coupling'.

(ii) Termination by Disproportionation:

In this case, one H atom from one growing chain is abstracted by the other (second) growing chain so that two dead polymers, one saturated and one unsaturated are formed

$$R - [CH_2 - CHCl]_m - CH_2 - C^\bullet HCl + R - [CH_2 - CHCl]_n - CH_2 - C^\bullet HCl \rightarrow$$

$$R - [CH_2 - CHCl]_m - CH_2 - CH_2Cl \ + \ R - [CH_2 - CHCl]_n - CH = CHCl$$

This type of termination results in formation of two molecules of shorter chain length.

Glass transition temperature (Tg)

The temperature at which the polymer abruptly transforms from glassy state to rubbery state is known as glass transition temperature. The rotation about the inter unit bonds in the polymer is effectively frozen at Tg and below Tg.

$$\underset{\text{(Hard and brittle)}}{\text{Glassy state}} \xrightarrow[\text{Tg}]{} \underset{\text{(Rubbery)}}{\text{Viscoelastic state}} \xrightarrow[\text{Tm}]{} \underset{\text{(Polymer melt)}}{\text{Viscofluid State}}$$

Factors influencing glass transition temperature.

Chain flexibility: A free rotation about the inter unit bonds in polymer chain imparts flexibility to the polymer. The polymer having simplest chemical structure has lowest Tg like polyethylene. The presence of double bond, aromatic or bulky side group hinder the freedom of rotation and restricts the chain mobility thereby increases Tg value.

Polymeric material	Glass transition temp.(Tg)	Melting temp.(Tm)
Polyethylene(LDPE)	-110^{0}C	110^{0}C
Polyethylene(HDPE)	-90^{0}C	140^{0}C
Polypropylene	-18^{0}C	180^{0}C
PVC	87^{0}C	210^{0}C
Polystyrene	100^{0}C	240^{0}C

Presence of plasticizers*:* Addition of plasticizer to the polymer reduces the Tg, since plasticizer imparts flexibility to the polymer.

Molecular mass*:* Tg decreases as the molecular weight of a polymer decreases. This is because there are more chain ends in low molecular weight polymer. Increase in molecular weight, free rotation of molecules is restricted and Tg increases. It is not significantly affected if the degree of polymerization is above 250.

Branching and cross linking*:* A small amount of branching will lowers the Tg .On the other hand a high density of branching brings the polymer chain closer and reduces the chain mobility resulting an increase in Tg. Cross linked polymers have higher Tg due to presence of strong covalent bond throughout the structure.

Intermolecular forces*:* Due to presence of large number of polar groups in the polymer chain leads to strong intermolecular forces of attraction which restrict the chain mobility. This leads to increase in Tg. For example polypropylene is -18^{0}C and nylon 66 is 57^{0}C. In nylon 66 the hydrogen bonding takes place between individual polymer chains at –NH and –CO groups of the polymer chain.

Stereoregularity of the polymer*:* In Syndiotactic polymers, the substituent group present alternatively one above and another below the plane have higher Tg than atactic which in turn has higher Tg than its isotactic. Isotactic polymers have all substituent groups on one side where as atactic polymers have random arrangement of substituent groups.

Crystallinity*:* Higher the crystallinity larger is the Tg value of polymer.In crystalline polymer the chains are lined up parallel to each other and are held by strong cohesive forces. This leads to higher Tg.

Significance of Tg:

- It is used to evaluate the flexibility of a polymer and predict its response to mechanical stress.
- It is useful in choosing proper temperature range during processing operations.
- Coefficient of thermal expansion, heat capacity, refractive index, electrical properties etc. at Tg determine the usefulness of a polymer over a temperature range.

Structure – Property Relationship

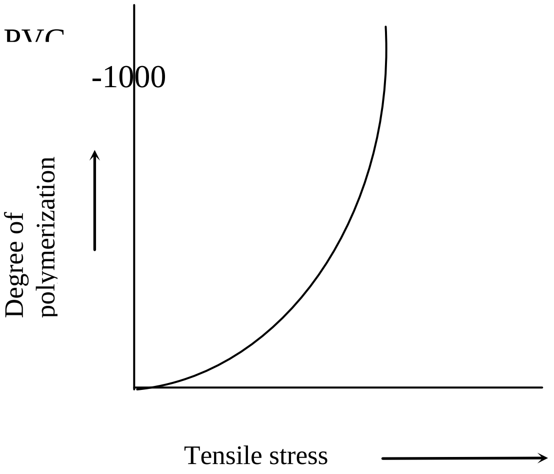
The propertiesof a polymer such as strength, elasticity, chemical resistivity etc dependgreatly on the structure aspects of polymers such as, molecular weight, crystallinity, nature of polymer chains, stereo regularity of the molecule, presence of polar groups etc.

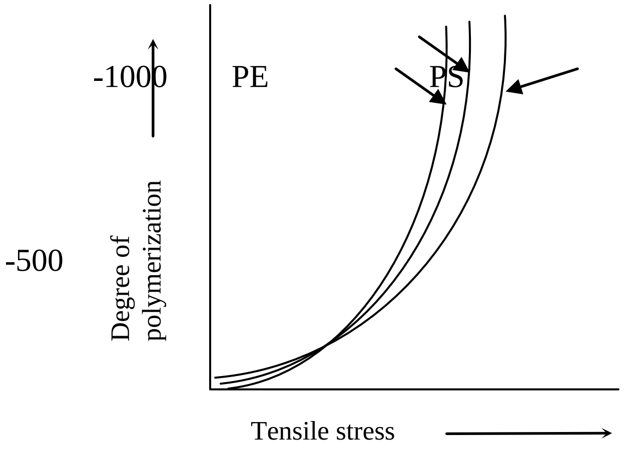
Strength: It is measured by magnitude and distribution of the attraction forces between the molecules, viz., I) primary or chemical bond forces ii) secondary or intermolecular forces.

In straight chain and branched chain polymers the individual chains are held together by weak intermolecular forces of attraction, the strength of which increases with the chain length or molecular weight as shown in fig by plotting DP against Tensile strength. High molecular weight polymers accounts for high softening point and tensile strength. Therefore high molecular weight polymers are tougher and more heat resistant. The intermolecular forces increased by the presence of polar groups like carboxyl, hydroxyl, chlorine, fluorine etc.

Strength of straight chain polymers also depends on the slipping power of one molecule over the other. Shape of the polymer molecules greatly affects the resistance to slip. For example in polyethylene limited restriction to movement of one molecule over other whereas in PVC, movement is much more restricted between molecules due to the presence of large lumps of Cl atoms. Therefore PVC is stronger and tough compare to polyethylene.

In cross linked polymers all structural units are linked by strong covalent force. Therefore they are more strong and tough since the movement of intermolecular chains is restricted.





Crystallinity: The arrangement of the polymer with respect to each other results in crystalline and amorphous state. In amorphous state molecules are arranged in random position and in crystalline state chains can be aligned in orderly arrangement.

Crystallization imparts a denser packing of molecules, thereby increasing the intermolecular forces of attraction. This accounts for higher and sharper softening point, greater rigidity and strength, and greater density as compared to that of amorphous polymer.

The degree of crystallinity determines several factors such as stiffness, yield point, modulus, hardness, permeability, optical property and heat capacity.

Crystalline regions occur when linear polymer chains without branching and no bulky side groups are orderly arranged parallel and close to each other. High degree of crystallinity makes the polymer to exhibit high tensile strength and high impact strength.
Linear polyethylene is highly crystalline because the atoms will become closer approach and it decreases with branching. On the other hand a polymer with bulky side groups prevents closer approach. Crystallinity decreases by copolymerization because it lowers the structural symmetry.

Elasticity: This is a property similar to spring – the polymer elongates on applying force and regains its shape on release of force. It is characterized by recoverance of original shape after a deforming stress is released. For a polymer to show elasticity the individual chains should not break on prolonged stretching. The elasticity increases by

- Introducing cross linking at suitable molecular positions. Cross – links provided at constant interval will hold the molecules and not allow them to slip past each other on stretching.
- Avoiding bulky side groups such as aromatic and cyclic structures on the repeat units
- Inter chain cohesive forces should be low. This is achieved by avoiding polar groups in repeat units.
- Introducing more nonpolar groups on the chain so that the chain don't separate on stretching
- To get an elastic material any factor that introduces crystallinity should be avoided.

Chemical Resistance: The chemical nature of monomeric units and their molecular arrangement determines the chemical resistance of polymers.

- Usually chemical attack causes softening, swelling and loss of strength of material.
- A polymer is generally more soluble in a structurally similar solvent.

For e.g polymers containing polar groups like –OH or –COOH are usually attacked by polar solvents like water, alcohols and ketones but are nearly resistant to non polar solvents like benzene, toluene, CCl_4 etc.
But polymers having non-polar groups such as methyl ($-CH_3$) and phenyl ($-C_6H_5$) are swollen or even dissolved in non –polar solvents but resistant to polar solvents like water, ethyl alcohol etc.
Polymers which are more aliphatic character are more soluble in aliphatic solvents where as those of aromatic character are more soluble in aromatic solvents.

- For a given polymer, swelling character decreases with increase in molecular weight.
- Chemical resistance increases with increase in the degree of crystallinity, due to denser packing of chain molecules which makes penetration of solvent more difficult.
- Polymers containing unsaturation such as poly isoprene (rubber) and poly butadiene are easily attacked by oxygen or ozone and undergo oxidative degradation.
- Polymers such as poly alkenes, PVC ,poly fluorocarbon have high degree of chemical resistance.

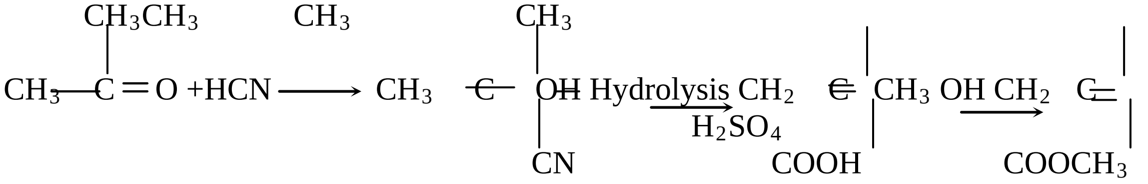
Plastic deformation: It is found in thermoplastics, whose structure is deformed to plastic stage on application of heat or pressure or both. The linear polymers without cross linking or branched structure show the greatest degree of plastic deformation. Under pressure polymers deform at high temperature because at high temperature the Van der Waals forces acting between different molecules become more and more weak.

On cooling they become rigid in the moulded shape, because plasticity of the material decreases with fall of temperature. So plasticity is reversible in linear polymers.
In cross linked polymers deformation does not occur on heating, because only primary covalent bonds are present throughout the structure and no slip between the molecules can occur. Therefore in thermosetting polymers plasticity does not increase with increase in temperature.

Elastic deformation: The elastic deformation arises from the fact that polymers consists of very long chain molecules, having free rotating groups. Since polymers contain both crystalline and amorphous regions the elongation increases proportionately to the load and reacts instantaneously on withdrawal of the load.

The deformation depends upon the degree of crystallinity, degree of cross linking and glass transition temperature.

Polymethyl methacrylate(PMMA): (Plexiglass)

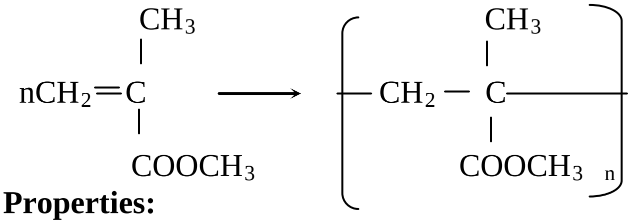


$$CH_3-\underset{}{\overset{CH_3}{C}}=O + HCN \longrightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}-OH \xrightarrow[H_2SO_4]{\text{Hydrolysis}} CH_2=\underset{COOH}{\overset{CH_3}{C}} \xrightarrow{CH_3OH} CH_2=\underset{COOCH_3}{\overset{CH_3}{C}}$$

Acetone Acetone cayanohydrin Methyl Acrylic Acid Methyl methacrylate

Monomer : Methyl methacrylate
Temperature:100^0 C
Initiator :Acetyl peroxide or Hydrogen peroxide

Polymerization process:



$$nCH_2=\underset{COOCH_3}{\overset{CH_3}{C}} \longrightarrow \left[-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-\right]_n$$

Properties:
Amorphous, High resistance to sunlight, High optical transparency
Softening point 130 to 140 ^{0} C
Above 65 ^{0} C it becomes like a rubber structure
Good mechanical properties and resistance to many chemicals but soluble in organic solvents like esters
Low scratch resistance compare to glass

Uses: Lenses, artificial eye, dentures bone (artificial teeth), paints, TV screens, attractive sign boards, used in buildings for decorative purposes.

Polyurethane polymers: Polyurethanes are characterized by the presence of urethane linkage, [-NHCOO-] in their repeat units. They resemble polyamides in their structure, with the presence of one more 'O' making the chain more flexible. They are linear polymers with the structure represented by:

$$[- C – N – (R) – N – C – O – (R') – O -]_n$$

‖|| ‖

O H H O

Polyurethanes are prepared by the addition polymerization reaction between alkyl di-isocyanate with diol. During addition the H atom of the OH group gets attached to N-atom to form NH– CO group as follows:

n O = C = N – (R) – N = C = O + n HO – (R$^{'}$) – OH tert. Amine $\longrightarrow$

Alkyl di –isocyanate diol

HO - R - O - [- C – N – (R) – N – C – O – (R’) – O -]$_n$ -H

‖|| ‖

O H H O

Poly urethane

Ex.Perlon urethane

n HO ─[CH$_2$)$_4$ OH + n O = C = N – [CH$_2$)$_6$ – N = C = O $\longrightarrow$ - O - [- C – N – – [CH$_2$)$_6$ – N – C – O – [CH$_2$)$_4$ – O -]$_n$ - H

‖|| ‖

O H H O

Properties:

Polyurethanes are spongy, transparent linear thermoplastics

They have low melting point and high degree of flexibility

They are resistant to water, oil, and corrosive chemicals.

Applications:

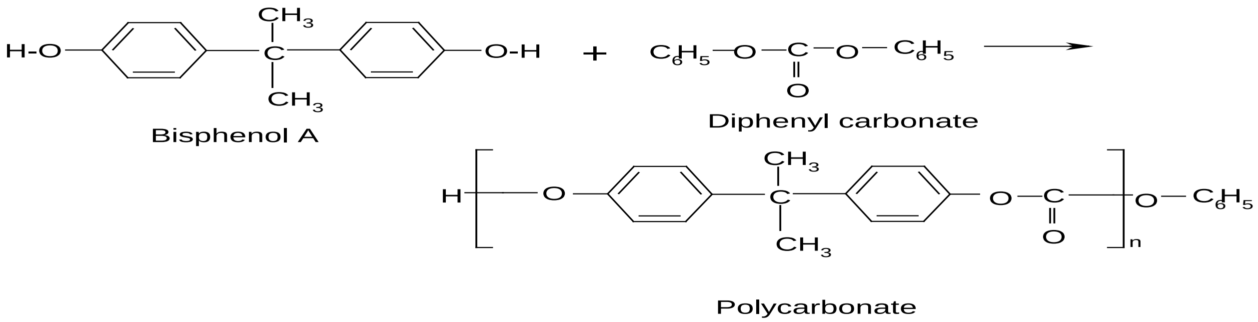
- Due to their resistance to oil , grease and corrosive chemicals, polyurethanes are used in tire treading and industrial wheels.
- Polyurethane fibers are used in light -weight water repellant garment like swim suits.
- Polyurethanes are abrasion resistant and hence they are used as floor coating of gymnasium, dance floors, etc
- Polyurethane foams (U foams) are used in cushions for furniture and car upholsteries.
- The abrasion resistance and superior adhesion properties of polyurethane adhesives have enabled the advancement of recording densities in the form of magnetic binders for various forms of recording media from audio/video tapes, computer disc, and even prepaid cards and transportation tickets.
- Due to polyurethane’s electrical insulation characteristics, they are also used extensively in wire coatings and optical fiber cable.

Polycarbonates:

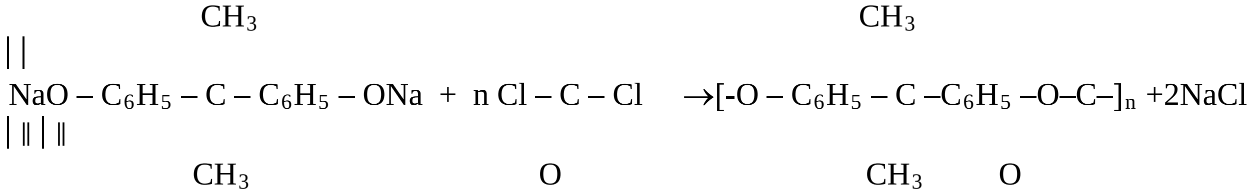
Polycarbonates are condensation polymers - polyesters of phenols and carbonic acid, HO – CO – OH. They contain [- O – CO – O -] linkage.

Preparation:

They are prepared by condensing Bisphenol A with diphenyl carbonate involving elimination of phenol in presence of tert.amine catalyst



They are also prepared by condensation reaction of phosgene and sodium salt of Bisphenol A.



$$\mathrm{NaO-C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5-ONa\ +\ n\,Cl-\underset{O}{C}-Cl\ \rightarrow [-O-C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5-O-\underset{O}{C}-]_n\ +2NaCl}$$

Sodium salt of Bisphenol A Phosgene Polycarbonate

Properties:

- Polycarbonate is a transparent thermoplastic.
- Polycarbonate has a high melting point, around 265^0C
- It has a high tensile strength and impact resistance
- It is resistant to water and many organic compounds but alkalis slowly hydrolyze it.

Applications:

The great commercial success of polycarbonate is due to its unique combination of properties extreme toughness, outstanding transparency, excellent compatibility with several polymers, and high heat distortion resistance.

It finds application in making many useful articles such as safety goggles, safety shields, Telephone parts and automobile light lenses etc

Polycarbonates are clear thermoplastic polymers which are mainly used as molding compounds. CD-ROMs and baby bottles are well known examples of their use.

Used as insulator in electronic and electrical industries

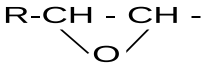
Adhesives:

It is defined as the non metallic polymeric binding materials, which firmly hold two similar or different materials such as metals glasses etc. by surface attraction.

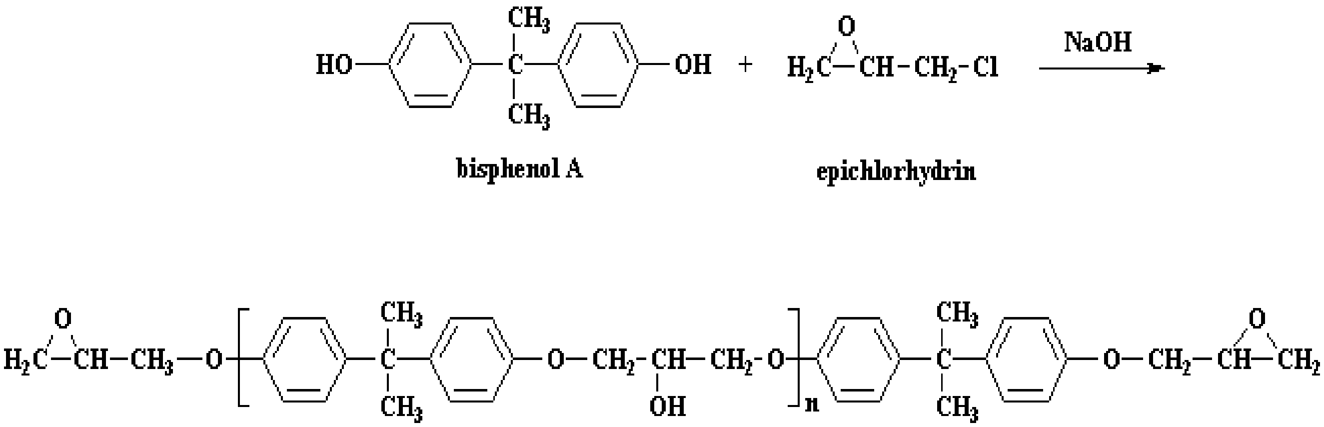
- Some natural adhesives are gum and glue while synthetic adhesives are phenol formaldehyde resin, urea formaldehyde resin, epoxies etc
- Synthetic adhesives are far superior to natural adhesives in their adhesive capacity.
- Each type of adhesive is useful for bonding only a select group of materials, eg. Epoxy resins are good adhesives for metals, wood, glass, concrete, ceramics and leather while phenol-formaldehyde is used for rubber.

Epoxy Resins [Araldite]

Epoxy resins are basically poly ethers and containing epoxy group:



Epoxy resins are combination 2, 2-bis (4-hydroxyphenyl) propane (I) (Bisphenol) and epichlorohydrin in presence of alkaline catalyst at 60^o C. It is made by condensation polymerization.



The reactive epoxide and hydroxyl groups give a three dimensional cross linked structure. Melting point between 145-155^{o}C.

Properties:

- Due to presence of stable ether linkage they are highly resistant to water, various solvents, alkalis, acids.
- They are further cured with polyamines, polyamides etc. there by increasing toughness and heat resistance.
- Epoxy resins are **thermosetting** materials as opposed to **thermoplastic** materials.
- The epoxy resins have excellent adhesion quality for various surfaces
- They have very good electrical insulating property.
- They are flexible due to the presence of reactive groups(OH and Epoxide) which are widely spaced

Applications:

Epoxy resins find a large number of uses due to their remarkable chemical resistance and good adhesion.

- Epoxy resins are excellent structural adhesives for many surfaces like glass, metals, wood etc
- They are used as surface coatings for skid-resistant surfaces for highways
- Mould made from epoxy resins are employed for production of components of aircrafts and automobiles
- Epoxy resins are applied over cotton, rayon and bleached fabrics to impart crease-resistance and shrinkage control
- They are one of the principal constituents of fiber -reinforced plastics
- They are used as laminating materials for electrical equipments.

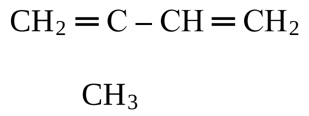
Elastomers:

They are high polymers which undergo very large elongation (500 to 1000%) under stress and regain original size on release of stress.

Natural Rubber (NR)

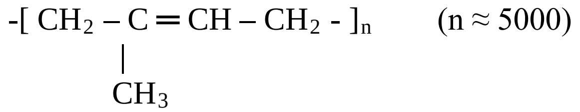
- Natural rubber is obtained in the form of latex from rubber trees.
- Natural rubber is a highly soft and elastic material. It is a poly isoprene, obtained from the

Monomer, isoprene (2 -methyl 1, 3 butadiene),



$CH_2 = \underset{\underset{CH_3}{|}}{C} - CH = CH_2$

and its structure is

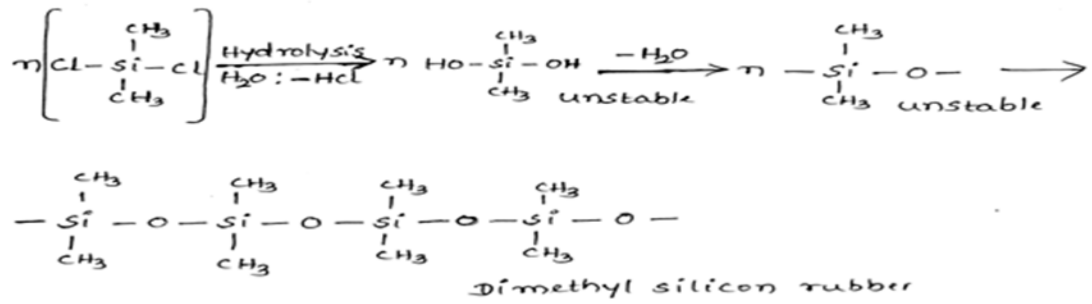


$-[\ CH_2 - \underset{\underset{CH_3}{|}}{C} = CH - CH_2\ -\ ]_n \qquad (n \approx 5000)$

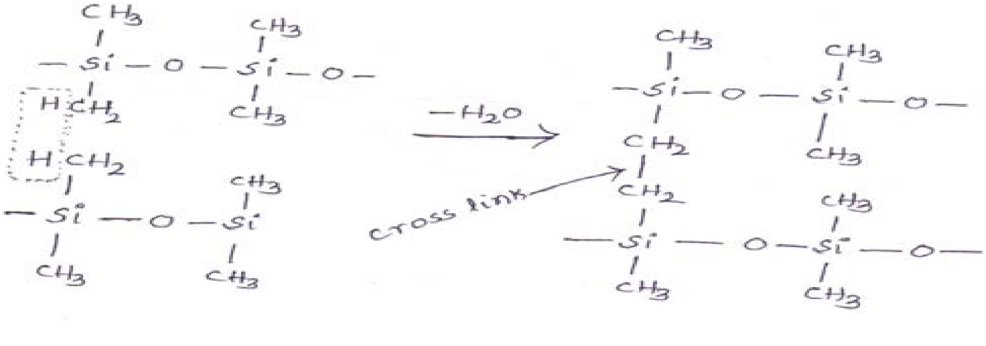
Silicone rubber:

They contain Silicon-Oxygen structure, which has organic radicals attached to silicon atom. Silicon on reaction with alkyl halide in presence of Grignard reagent produces mono methyl and dimethyl silicon chlorides. Further they form very long chain polymers as below

$$\underset{\text{Methyl Chloride}}{CH_3Cl} + \underset{\text{Silicon}}{Si} \longrightarrow CH_3SiCl_3 \text{ and } (CH_3)_2SiCl_2$$



Cross linked silicone rubbers are obtained by mixing linear dimethyl silicone polymers with fillers and curing agents like peroxides. Peroxide causes the formation of cross link through methyl groups of adjacent chains. Bi and tri functional silicon halides also results in the formation highly cross linked silicones.



Properties: Resistance to sunlight, dilute acids and alkalis. Flexible in the temperature range of 90-250^{0}C. Cross linked silicones are thermosetting, good electrical insulating properties and heat resistance.

Uses: Used as sealing material in aircraft engines, manufacture of tires for fighter aircrafts. Used in making lubricants, paints, protective coatings for fabric finishing and water proofing. Used as insulators.

Number average molecular weight ($\overline{Mn}$)

It is measured by colligative properties- Relative lowering of vapor pressure, Elevation of boiling point, Depression of freezing point and Osmotic pressure.

It is defined as the ratio of total mass of all molecules in a polymer sample to the total number of polymer molecules in the mixture.

$\overline{Mn} = w/\Sigma n$ Where w= nM n-number of molecules, M-molecular mass of repeating unit

$$\overline{Mn} = \frac{n_1M_1+n_2M_2+n_3M_3+\ldots\ldots\ldots\ldots n_iM_i}{n_1+n_2+n_3+\ldots\ldots\ldots\ldots n_i} = \frac{\Sigma\, n_iM_i}{\Sigma\, n_i}$$

Weight average molecular weight ($\overline{M}$w)

It is obtained by light scattering and ultracentrifugation techniques. It is also expressed in the similar form. In a mixture, if w is mass and M is the molecular mass of each species then $\overline{M}$w is given by

$$\overline{Mw} = \frac{w_1M_1+w_2M_2+w_3M_3+\ldots\ldots\ldots\ldots w_iM_i}{w_1+w_2+w_3+\ldots\ldots\ldots\ldots w_i} = \frac{\Sigma\, w_iM_i}{\Sigma w_i} \qquad \text{since } n=w/M \text{ or } w=nM$$

$$\overline{Mn} = \frac{n_1M^2{}_1+n_2M^2{}_2+n_3M^2{}_3+\ldots\ldots\ldots\ldots n_iM^2{}_i}{n_1M_1+n_2M_2+n_3M_3+\ldots\ldots\ldots\ldots n_iM_i} = \frac{\Sigma\, n_iM^2{}_i}{\Sigma\, n_i\, M_i}$$

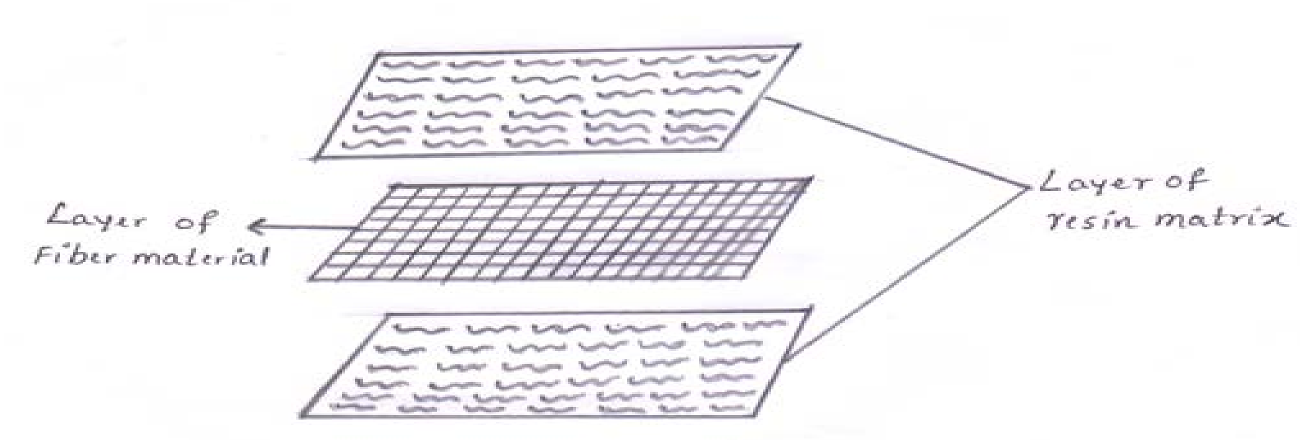
$\overline{Mw}$ of a polymer is either equal or greater than its $\overline{Mn}$, hence $\overline{Mw}/\overline{Mn} \geq 1$ This ratio is called distribution ratio, which is a measure of polydispersity of polymers.

POLYMER COMPOSITES:

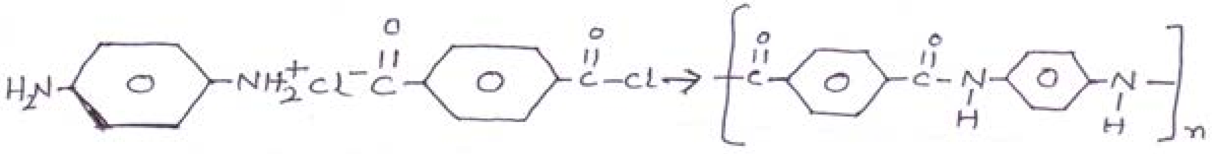
Combination of two or more structurally different components combine to form a new class of material suitable for structural applications is referred as composite material. When one of the component is a polymer, the resulting composite is called a polymer composite.

Fiber reinforced composites are strong and light weight. They are stronger than steel with less weight and hence they can be used in automobiles to achieve fuel efficiency and less pollution. They finds higher strength per unit weight, low cost of fabrication and resistant to corrosion.

Polymeric composites are produced by suitably bonding a fiber material with polymer resin matrix and curing the same under pressure and heat. Alternate layers of resin and fiber are laid in a similar sequence to get the desired thickness. The polymer matrixes generally used are epoxy resin, Phenolic resins, silicone resins, melanine resins etc. The fibers used are glass fiber, carbon fiber and Kevlar.

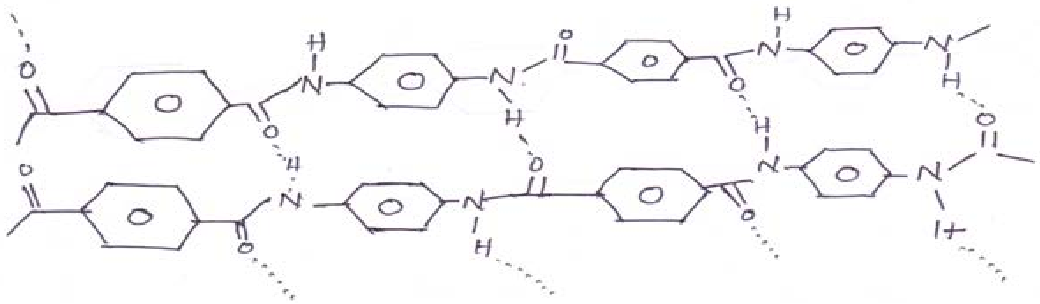


Kevlar(Aramid): It is synthesized from the monomers 1,4-phenylene diamine(para phenylene diamine) and terephthaloyl chloride through a condensation reaction with the liberation of HCl as byproduct.



1,4-phenylene diamine terephthaloyl chloride Kevlar or Poly(para-phenylene terephthalamide)

It is high strength due to presence of inter chain hydrogen bonds formed between carbonyl group and NH group. Additional strength is achieved from aromatic staking interactions between adjacent strands. Kevlar is a synthetic fiber stronger than steel.



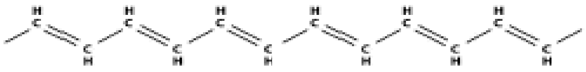
Molecular structure of Kevlar, dashed line indicates hydrogen bonding

Properties: High tensile strength, high chemical inertness, very low coefficient of thermal expansion, flame resistance, high impact resistance, low weight.

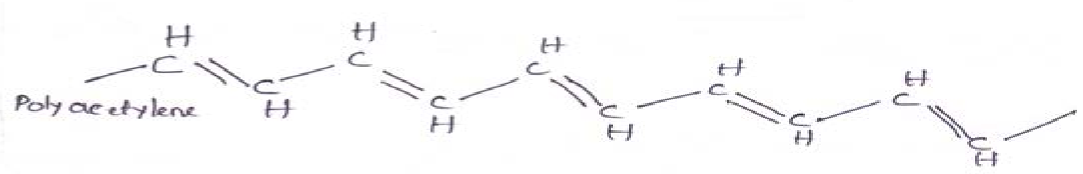
Uses: used as inner lining for tires to prevent punctures, used in table tennis, tennis, badminton and squash racquets, cricket bats, hockey sticks, used in personal armor such as helmets, ballistic face masks, bullet proof vests etc. It is often used in the field of cryogenics for its low thermal conductivity and high strength. Used in boat hulls, helicopter blades etc.

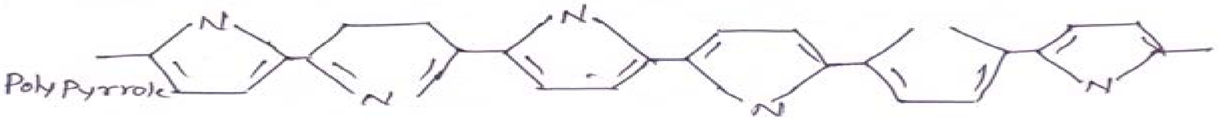
Conducting polymers: An organic polymer with delocalised Π-electron system, having electrical conductance of the same order of a conductor is called conducting polymer.

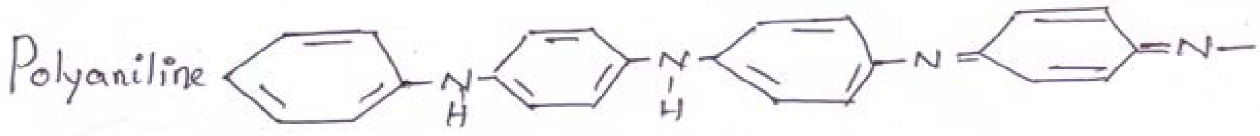
- This is one of the simplest chain polymers it possesses conjugated double bond.



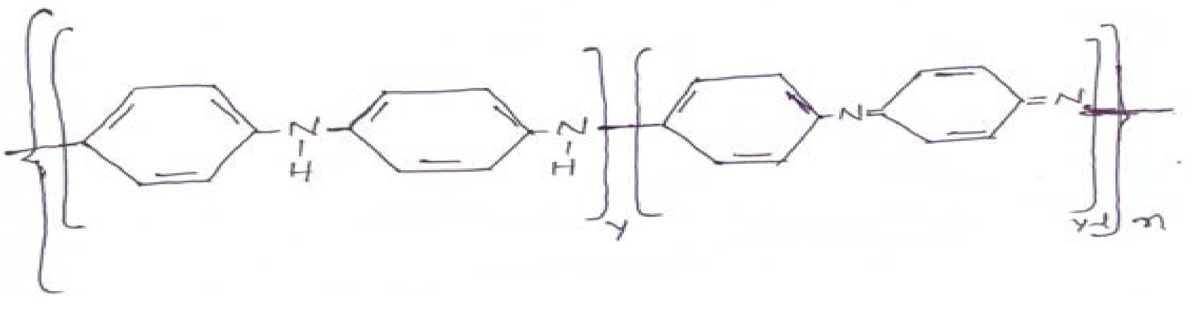
- Conducting polymers are obtained generally by doping (Doping is either the addition of electrons (reduction reaction) or the removal of electrons (oxidation reaction) from an organic polymer with conjugated backbone (consisting of alternating double and single carbon-carbon bonds
- In a conjugated system, as the electrons are only loosely bound, electron flow may be possible. However as the polymers are covalently bonded the electrons are localized and do not take part in conductivity. Hence the material needs to be doped for electron flow to occur. Once doping has occurred, the electrons in the pi-bonds are able to "jump" around the polymer chain. As the electrons are moving along the molecule, electric current occurs.





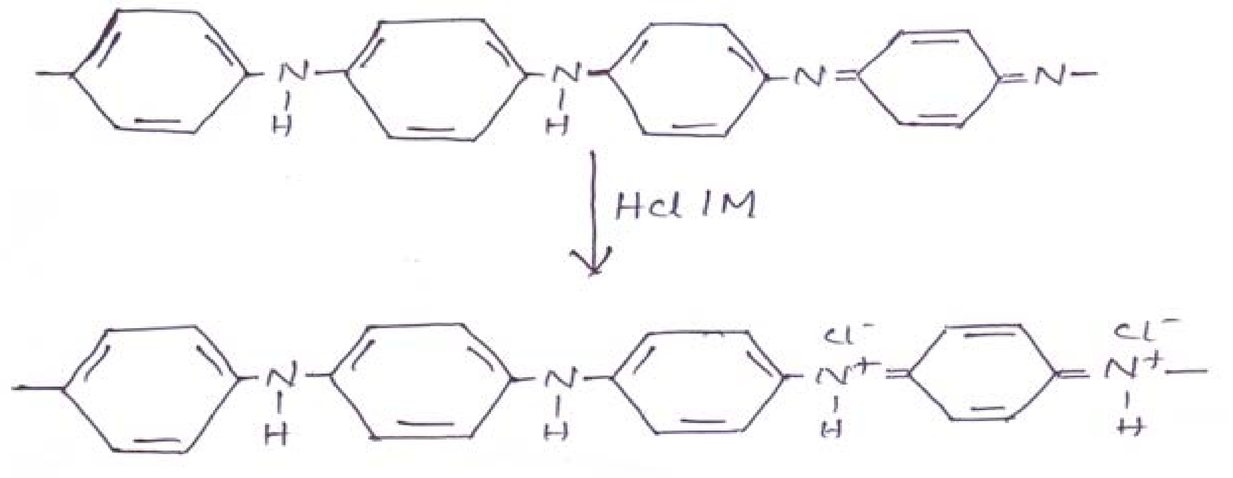


Polyaniline: Distilled 0.2M aniline dissolved in pre cooled 1M HCl solution and maintained at 5^0C. Calculated amount of 0.5M$(NH_4)_2S_2O_8$(oxidizing dopant) dissolved in 1M HCl is added slowly to above prepared solution. Since the polymerization reaction is exothermic, to maintain temperature of 0 to 5^0C the reaction vessel is placed in ice bath. After the complete addition of $(NH_4)_2S_2O_8$ the mixture is stirred for about two hours. Polyaniline finally precipitates in the green form. The dark green precipitate was washed with 1M HCl until the green color disappears. Polyaniline in undoped state is a semiconductor with conductivity 10^{-8}S/cm.
Different oxidation states of polyaniline are.



y=1 Leuco emeraldine
y=0.5 Emaraldine base
y=0 Pernigraniline

Emaraldine base consisting of equal proportions of amine(-NH-) and imine(=N-) sites. On protonic acid doping, imine sites are protonated by acids to form bipolaron bands.



Applications: Used as electrode material for commercial rechargeable batteries, used as conductive tracks on printed circuit boards, used in light emitting diodes, in fuel cells as the electro catalytic materials, used as sensors and biosensors in glucose sensing for medical applications and amine sensing for environmental and food safety applications.

MODULE-5

WATER TECHNOLOGY

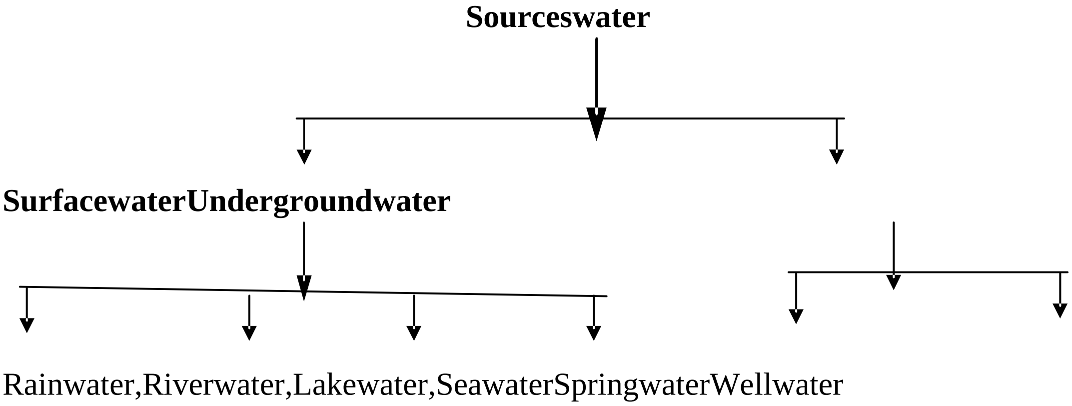
Water Technology: Introduction, sources and impurities of water; boiler feed water, boiler troubles with disadvantages -scale and sludge formation, priming and foaming, boiler corrosion(due to dissolved O_2, CO_2 and $MgCl_2$).Determination of DO, BOD and COD, numerical problems. Sewage treatment: Primary, secondary (activated sludge method) and tertiary methods.Softening of water by ion exchange process.Desalination of sea water by reverse osmosis & electrodialysis (ion selective).5 Hours

Contents:

- **Introduction:Sourcesofwater&impuritiesinwater.**
- **Boiler feed water, boiler troubles with disadvantages -scale and sludge formation.**
- **Priming and foaming, boiler corrosion(due to dissolved O_2, CO_2 and $MgCl_2$).**
- **Determination of DO, BOD and COD, numerical problems.**
- **Sewage treatment: Primary, secondary (activated sludge method) and tertiary methods.**
- **Softening of water by ion exchange process.**
- **Desalination of sea water by reverse osmosis & electrodialysis (ion selective).**

WATER TECHNOLOGY

SourcesofWater: Thesourcesofwaterclassifiedasfollows



1)**Rainwater**:Purestformofwatercontainsmanydissolvedgasesandsuspendedsolidparticles.
2)**Riverwater:**Containsdissolvedmineralsofsoilsuchaschlorides,sulphates,bicarbonatesofsodium, calcium,Mg,Feetc. Itisalsocontainstheorganicmatter,smallparticlesofsoilandsandinsuspension.
3)**Lakewater**:Itcontainslessdissolvedmineralsbuthighqualityoforganicmatters.
4)**Seawater**:Itisthemostimpureformofnaturalwater.
ItcontainsdissolvedsaltssuchasNaCl,sulphatesofsodium,bicarbonatesofK,Mg&Ca,andbromidesof K&Mg.

Undergroundwater:clearinappearancebutcontainsmanydissolvedsaltsandorganicmatter.

Impuritiesinwater: Thewaterfoundinnatureisneverpurewhichcontainslargenumberofimpuritiesin varying amount.Theseimpuritiesmainlydependuponitssourceandareclassifiedintofourdifferenttypes.
1)Dissolvedgases;theseincludesdissolvedoxygen,CO_2,SO_2,NH_3,(NO)x,allofwhichderivedfromatmosphere**.**
2)Dissolvedsolids;theseincludessaltslikebicarbonates,ChloridesandSulphatesofCa,Mg,&Na inadditiontothatsmallamountofnitrates,nitrites,silicates,ammoniaandferroussaltetc.
3)Suspendedimpurities:Suspendedimpuritiesarethedispersedsolidswhichcanberemovedbyfiltrationorsettling
Suspendedimpuritiesareoftwotypes.
i)InorganicImpurities:clay,silica,oxidesofFe&Mgetc.
ii)OrganicImpurities:wood,pieces,deadanimalmatter,leaf,fish,bacteria,algae,protozoaetc.
4)OrganicMatter:organiccompoundsderivedformthedecayofvegetableandanimalmatterincludingb

acteriamaybepresentinwater.Wateralsogetscontaminatedwithsewageandexcretalmatter. Consequentlythepathogenicbacteriaandmicroorganismarethemaincausesforwaterborndiseases.
ChemicalAnalysisofWater:determinationofvariousconstituentpresentinwaterinordertoascertainthequalityofwaterasperWHOslanderedandtherebyutilityofwaterisincreasedisknownaswateranalysis.

Thedifferentconstituentsgenerallydeterminedarehardnessofwater,alkalinity,chlorides,nitrates, sulphates,fluorides,dissolvedoxygenetc.

Boiler feed water:

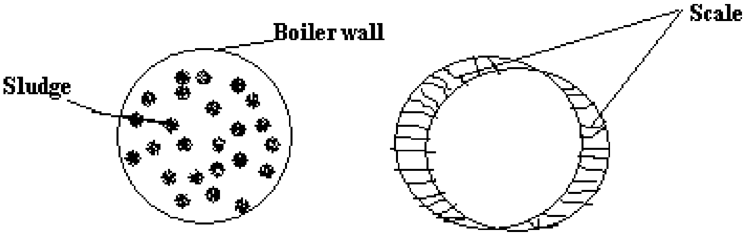
Water is mainly used in boilers for the generation of steam for industries and power house.

Boiler feed water should correspond with the following composition.

1) Its hardness should be below 0.2ppm
2) Its caustic alkalinity (due to $^{-}$OH) should lie in between 0.15 and 0.45 ppm
3) Its soda alkanity (due to Na_2CO_3) should be 0.456 to 1ppm.

If excess of impurities present they lead to the formation of scales, sludges, foaming , Corrosion and caustic embattlement.

Boiler troubles:



Sludge and scale formation in Boilers:

In boilers, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Exceed their solubility product and precipitates thrown out.

Sludge formation in boilers;

The resultant precipitate is called as scale.If it is in the form of thick adherent deposit. The precipitate is known as sludge and it is in the form of loose milky precipitate.

Sludges are formed by substances which have greater solubility in hot water than in cold water.

Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

They are collected at place, Where the flow rate is slow, they can be easily removed with a wire brush.

Disadvantages of Sludge:

Sludge has greater solubility in hot water than in cold water. They are poor conductors of heat and they tend to waste a portion of heat generated and hence decreases the efficiency of boiler. Excessive sludge formation disturbs the working of the boiler. it settles in the region of poor water circulation such as pipe connection plug opening etc.

Causes of scale formation in boilers

If the precipitate is hard and strongly adhering on the inner walls of the boilers is known as scale.Which is difficult remove even with the help of hammer.

Scaler are formed due to

1) Decomposition of Calcium bicarbonate.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$CaCO_3$ is soft and it is the main cause of scale formation in low pressure boilers.
In high pressure boilers $CaCO_3$ is soluble due to formation of $Ca(OH)_2$.

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2$$

2) In high pressure boilers, $CaSO_4$, $CaSiO_3$ and $MgSiO_3$ are sparingly soluble in cold water. They are nearly insoluble in high temperature.
3) Hydrolysis of magnesium salts.

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

4)Presence of Silica: If small quantity of Silica is present it will deposit as calcium silicate or $MgSiO_3$.

Disadvantages of Scale formation
1) It is due to wastage of fuel.
2) It is due to lowering of boiler safety.
3) Due to Decrease in efficiency.
4) Due to danger of explosion.

Priming:
When steam is produced rapidly in the boilers, some droplets of the liquid water carried along with steam. The process of passage of water particle along with steam from boilers is known as priming.
Priming is caused by the,
1) Presence of dissolved impurities and suspended impurities.
2) High steam velocities.
3) Sudden boiling.
4) Improper design of boilers.
Priming can be avoided by rapid change in steaming velocity, blowing off sludge or scaler, Low water levels in boilers and supplying soft water.

Foaming: The process of production of continuous foam or bubbles in boiler is known as foaming.
Foaming is caused by the presence of oil and alkalis in boiler feed water.
Foaming can be avoided by addition of anti foaming agents like castor oil, removal of foaming agent form boiler water by adding Chemicals like Sodium aluminate and Aluminium Sulphate.

Boiler Corrosion: Corrosive compounds, especially O_2 and CO_2 must be removed, usually by use of a deaerator. Residual amounts can be removed chemically, by use of oxygen scavengers. Additionally, feed water is typically alkalized to a pH of 9.0 or higher, to reduce oxidation and to support the formation of a stable layer of magnetite on the water-side surface of the boiler, protecting the material underneath from further corrosion. This is usually done by dosing alkaline agents into the feed water, such as sodium hydroxide (caustic soda) or ammonia. Corrosion in boilers is due to the presence of dissolved oxygen, dissolve carbon dioxide,dissolved salts.

Boiler corrosion: It is decay or disintegration of boiler materal either due to chemical or electrochemal reaction with its environment.

Disadvantages of boiler corrosion

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

Corrosion in boiler due to,

1 Presence of dissolved oxygen: In boilers oxygen is introduced through the raw water supply.water usually contains 8ppm of DO at room temperature. as water is heated the D O is set free and boiler starts corroding. DO reacts with iron the presence of water under high temperature to form ferric hydroxide.

$$4Fe+2H_2O+O_2 \longrightarrow 4Fe(OH)_2$$

$$4Fe(OH)_2+O_2+2H_2O\ 2[Fe_2O_3.2H_2O \rightarrow]$$

Removal of D O is by adding hydrazine or sodium sulphide.

$N_2H_4+O_2N_2+2H_2O \longrightarrow$

$2Na_2SO_3+O_2 \quad 2N_2SO4 \longrightarrow$

$Na_2S+2O_2 \quad Na_2SO_4 \longrightarrow$

A low concentration of 5-10ppm of Na_2SO_3 is maintained because under high pressure it decomposes to give SO_2 which enters steampipe are appears as corrosive because of sulphurous acid(H_2SO_3).

2. Presence Of Dissolved Carbondioxide

There are 2 sources of CO_2 in boiler water

1.Dissolved CO_2 in raw water.

CO_2 formed by decomposition of biocarbonates in water.

$$Mg(HCO_{3)2} \longrightarrow MgCO_3+H_2O+CO_2$$

CO_2 in presence of water forms carbonic acid which has a corrosive effect on boiler materials like any other acid

$$H_2O+CO_2 \longrightarrow H_2CO_3$$

CO2 can be removed by lime stone

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

It also removed by adding ammonium hydroxide

$$NH_4OH+CO_2 \longrightarrow (NH_4)_2CO_3+H_2O$$

2 Magnesium chloride: If it is present in boiler feed water can undergo hydrolysis producing Hcl

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

The liberated acid react with iron material of the boiler to from ferrous hydroxide which is converted to rust in the following way.

$$Fe+2HCl \longrightarrow FeCl_2+H2$$

$$FeCl_2+2H_2O \longrightarrow Fe(OH)_2+2HCl$$

$$2Fe(OH)_2+O_2 \longrightarrow Fe_2O_3.3H_2O$$

As the boiler water is generally alkaline hence acid is neutralised. In case the amount of acid is more calculated quantity of alkali is added outside to prevent the corrosion.

DETERMINATIONOFDISSOLVEDOXYGENPRESENTINA GIVENSAMPLEOFWATERBYWINKLER’SORIODOMETRICMETHOD

Theory:

Theprincipleinvolvedinthedeterminationofdissolvedoxygenisthatthedivalentmanganesesolutionalongwithastrongalkaliareaddedtowatersample.TheDOpresentinwatersampleoxidisesdivalentmanganesetotetravalentmanganese.Thebasicmanganicoxideformedactsasoxygencarriertoenablethedissolvedoxygeninmolecularformtotakepartinthereaction.Uponacidification,tetravalentmanganeserevertstodivalentstatewiththeliberationofnascentoxygen,whichoxidisesKItoI$_2$.Theliberatediodineistitratedagainststandardsodiumthiosulphatesolutionusingstarchasindicator.

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

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2 \text{(Basicmanganicoxide)}$$

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

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

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

Procedure: Pipetteout300cm^{3}ofwatersampleintoacleanglassstopperedbottle.Add3cm^{3}of manganoussulphatesolutionfollowedby3cm^{3}ofalkalinepotassiumiodidesolution.Stopperthebottleandshakewellandallowtheprecipitatetosettledown.Nowadd1cm^{3}ofconcentratedsulphuricacidslowlyandmixwelluntiltheprecipitatedissolvescompletely.
Pipetteout50cm^{3}ofthissolutionintoacleanconicalflaskandslowlytitrateagainst0.02Nsodiumthiosulphatesolutionusing2cm^{3}starchindicatorneartheendpoint.Repeatthetitrationtogetconcordantreadings.

OBSERVATIONANDCALCULATION

PartB:Determinationofdissolvedoxygen*:*

Burette:Na$_2$S$_2$O$_3$solution
Conicalflask:50 cm^{3}oxygensolution
Indicator:Starchsolutionneartheendpoint
Endpoint:Disappearanceofbluecolour

Burette Reading	Trail 1	Trail 2	Trail 3
Final Reading			
Initial Reading			
Volume of Na$_2$S$_2$O$_3$ run down in cm3			

NormalityxVolumeofoxygensolution=NormalityxVolumeofNa$_2$S$_2$O$_3$

$$\text{Normalityofoxygensolution} = \frac{\text{NormalityxVolumeofNa}_2\text{S}_2\text{O}_3}{}$$

Volumeofoxygensolution

$\frac{NxV}{50}$ -----------------a

= 50

Weightofdissolvedoxygen/dm^3=NormalityxEquivalentweightofoxygen

=ax8.0=g -------------------b

=bx1000mg

= mg

RESULT: Theweightofdissolvedoxygeninthegivenwatersample= mg.

WATERPOLLUTION

Dischargeofcertainforeignsubstanceintowaterthataffectsthephysical,biologicalandchemicalpropertiesofwaterwhichinturndecreasestheutilityofwaterisknownaswaterpollution.

Thematterwhichisresponsiblefortheseunhealthychangesinwaterisknownaswaterpollutants.

Eg.Pd,Hg,CN,As,Cu,acidsalkalispesticides,insecticides,fungicides,animalmatter,humanexcreta,radioactivewastesetc.

Thecontaminatedinwateriscalledsewagewateroreffluent.

DependsonthesourcesofwaterPollutant,sewagewaterisclassifiedintotwotype

1.DomesticSewage

2.Industrialsewage

Domesticsewage: Itiswastedischargeawayfromresidence,Institutes,Hospitalsetc.Theseincludecertainorganicwastes,pathogenicbacteria,plantmaterialsPesticides,detergentsandothermaterials.

Domesticsewagecauseswaterborndiseaseslikedysentery,choleratyphoid,andhookworminfection.

Industrialsewage: ThewaterreleasedbyindustriescontainsPd,Hg,CN,As,Cu,acids,alkalis,pesticides,detergents,insecticides,fungicides,soap,phenoletc.

Theindustrialsewagealsocausesseveralenvironmentalproblems.

Thesewagecanberenderharmlessbysuitabletreatments.Theorganicwastepresentinwaterundergoesdegradationandbreakdownintosimplemoleculesbybacteria.Thebacterialdegradationisoftwo types;

1.Aerobicdegradationoroxidation:Broughtaboutbybacteriainpresenceofairanddissolveoxygenofwater.AerobicoxidationproducessimplercompoundslikewaterandCO$_2$.

2.Anaerobicdegradationoroxidation:BroughtaboutbybacteriainabsenceofairandproducesharmfulproductsuchasNH$_3$,H$_2$S,H$_2$S,CH$_4$etc.

BiologicalOxygendemand(BOD):“BODisdefinedastheamountoxygenrequiredbymicroorganismtooxidizeallorganicmatterpresentinonelitreofwastewaterat20^{o}Coveraperiodof5days”.

Determination: TodetermineBODaknownvolumeofsamplesewageisdilutedwithequalvolumeoffreshwatercontainsnutrientforbacterialgrowth,whosedissolveoxygencanbedetermined.

Thesolutioniskeptinaclosedbottleat20^{o}Coveraperiodof5days.After5daystheunusedoxygencontentsinwaterisdetermined.Thedifferencebetweenoxygencontentsinfreshwaterandunusedoxygencontentsinwaterisdetermined.

ThedifferencebetweenoxygencontentsinfreshwaterandunusedoxygeninsolutiongivestheBODvalue.

ChemicalOxygenDemand(COD): Itisdefinedastheamountofoxygenconsumedinthechemicaloxidationoforganicandinorganicimpuritiespresentinonelitreofwastewaterbyusingacidified$K_2Cr_2O_7$solutioninpresenceofsilversulphateandmercuricsulphateascatalyst.

$$3CH_2O+16H^{+}+2Cr_2O_7^{2-}\rightarrow 4Cr^{3+}+3CO_2+11H_2O$$

Determination:

Principal: Themethodconsistsofinaddingexcessstandardsolutionofacidified$K_2Cr_2O_7$toknownvolumeofeffluentsampleandbacktitratingtheexcessof$K_2Cr_2O_7$againstastandardsolutionofFAS.

Procedure: Pipetteout25mlofwastewatersampleintoacleanconicalflaskand10mlof0.25N $K_2Cr_2O_7$, 30mlof6NH_2SO_4, 1g Ag_2SO_4and1gof$HgSO_4$refluxthemixturefortwohours,coolandtitrateagainstFASusingferroinindicatortilltogetreddishbrowncolour. Letthetitervaluebea cm^3.Performablanktitrationinsimilarwayexceptusingwastewatersample.Lettheblanktitervaluebeb cm^3.

CALCULATION

Volumeof$K_2Cr_2O_7$consumedforthesample=(b-a) cm^3

1000cm^3of1NFASsolution=1equivalentofoxygen=8gofoxygen(or8x10^3mgofO_2)

$$(b\text{-}a)cm^3 \text{of......NFASsolution} = \frac{8\times10^3\times(b-a)\times N \text{ of FAS}}{1000\times125cm^3 \text{ of wastewater}} = ...X.\text{mg of oxygen}/$$

25cm^3ofwatersampleconsumedXmgofO_2

$$1000cm^3 \text{ of wastewater sample contains} = \frac{.X\times1000}{25} \text{mg of oxygen}/dm^3$$

CODofwastewatersample=.......................................mgofO_2perdm^3

Problems on COD

1)Calculate the COD of the effluent sample sample when 25cm^3 of the effluent sample requires 8. 5cm^3 of 0.001 N $K_2Cr_2O_7$ Solution for complete oxidation.

Ans) $COD=N\times V_{ofK2Cr2O7}\times48000/V_{ofeffluent}$

$COD=.001\times8.5\times8000/25$

COD**=2.72/dm^3**

2)25cm^{3}of asampleofCODanalysiswasreacted with15cm^{3}of 0.2N$K_2Cr_2O_7$&the unreacted$K_2Cr_2O_7$requires8.2cm^{3}0f 0.2NFAS.25cm^{3}of same$K_2Cr_2O_7$&25cm^{3}of distilledwaterunderthesameconditionrequires16.4cm^{3}0f 0.1NFAS.

Ans) COD=Nx (V_2-V_1) $_{\text{ofK2Cr2O7}}$x8000/V$_{\text{ofeffluent}}$
COD =0.2x6.8x8000/25
COD **=435.2/dm^3**

3) 20ml of sample of COD analysis was reacted with 10ml of 0.25 N $K_2Cr_2O_7$ and the unreacted dichromate required 6.5ml of 0.10N FAS .10ml of the same $K_2Cr_2O_7$and 20ml of distilled water under the same conditions as the sample required 26ml of 0.10 N FAS.What is the COD of the sample.

Ans) Volume of 0.1N FAS required to react with unconsumed $K_2Cr_2O_7$=6.5ml
Volume of FAS consumed in blank=26ml
Amount of $K_2Cr_2O_7$ consumed to satisfy COD
in terms of FAS solution=26-6.5ml
COD of the sample= (26-6.5) xNx8000/V $_{\text{ofeffluent}}$
= (26-6.5) x0.10x8000/20
COD =**780mg/l**

4)CalculatetheCODoftheeffleuentsampleWhen25cm^{3}of effluentsamplerequires8.9cm^{3}of.001M$K_2Cr_2O_7$forcompleteoxidation.

Ans)COD=NxV$_{\text{ofK2Cr2O7}}$x48000/V$_{\text{ofeffluent}}$
=.001x8.9x48000/25
=17.00g/dm^3

5) 25cm3 of a sample of COD analysis was reacted with 15cm^3 of .2N $K_2Cr_2O_7$& the unreacted $K_2Cr_2O_7$ requires 8.2cm^3 0f 0.2N FAS.25cm^3 of same $K_2Cr_2O_7$& 25cm^3 of distilled water under the same condition requires 16.4cm^3 0f 0.1N FAS.What is COD of water.

Ans) COD=Nx(b-a)x8000/25
COD=0.2x(16.4-8.2)x8000/25
COD =**524.8g/dm^3**

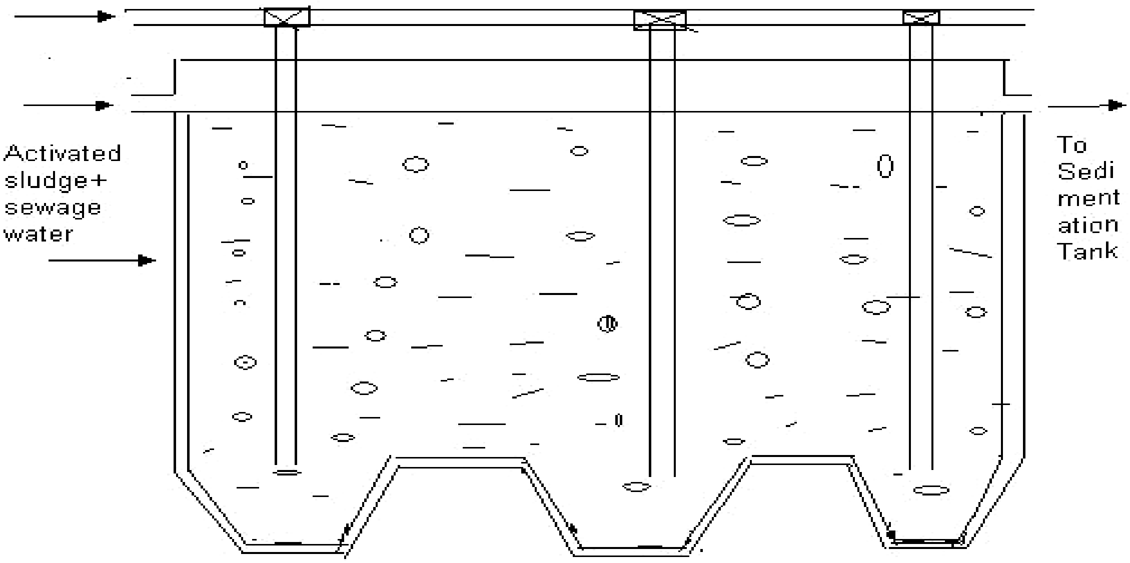
Watertreatmentorsewagetreatment

Removalofharmfulcontaminationfromwastewatercompletelyorpartiallyisknownaswatertreatment orsewagetreatment.
Thetreatmentofsewagewateriscarriedoutbythreedifferentstages.

1.Primarytreatment
2.Secondarytreatment
3.Tertiarytreatment

Primarytreatment: Theremovalofcoarsesolidinthesewagewaterisaffectedbymeansofnarrowrocks,screens,gritchambers,andskimmedtanketc.Thewateristhenpassedintosedimentationtankwhereitisallowedtosettle.Thenonsettledimpuritiesareremovedbyaddingcoagulantsuchaspotashalum

Secondarytreatmentoractivatedsludgemethod: Thewastewaterafterprimarytreatmentisallowedtoflowintoalargetankwherebiologicaltreatmentiscarriedout.Herethewaterissprayedwithactivatedsludge,themicroorganismpresentinsludgeformathinlayeronwaterandbreakdownallorganicimpuritiesintosimplercompounds.
Theairispassedfromthecentreoftankvigorouslyinorderbringeffectiveaerobicoxidation.Theresidualwaterischlorinatedtokillbacteriaandthentreatedwithpotashalumtosettletheimpurities.Thewateristhenfilteranddischargeintodrainage.



Tertiarytreatment: Thewaterevenaftersecondarytreatmentcontainsphosphate,heavymetalions,colloidalimpurities,coloringmatteretc.Hencethewaterissubjectedtotertiarytreatment.
ThetertiarytreatmentincludesthetreatmentwithlimetoremovephosphatestreatmentwithS^{2-}toremoveheavymetalionsasinsolublesulphides,treatmentwithactivatedcharcoaltoabsorbcoloringmatterandthenpotashalumtoremovecolloidalimpuritiesandthendischargetodrainage.

Softening of water by ion exchange process:

Softening of water is the process, where by we remove or reduce hardness of water irrespective of whether it is temporary or permanent is known as softening of water. Ion exchange process is an external treatment of softening of water. Which is done before its entry in the boilers.

It is a process by which ions held on a porous, essential insoluble solid are exchange for ions in solution that is brought in contact.

Ion Exchange softening process:

The Hard water is first passed through cation exchange (styrene divinyl benzene on sulphonation or carboxylation –capable to exchange their hydrogen ions with the cations in the water) column . when all the cations like Ca^{2+}, Mg^{2+} etc. are removed from resin & it equivalent to H^+ ions are released from this column to water.

$$\underset{\text{Solid}}{RSO_3^-H^+} + \underset{\text{solution}}{M^+} \longleftrightarrow \underset{\text{solid}}{(RSO_3)M^+} + \underset{\text{solution}}{XH^+}$$

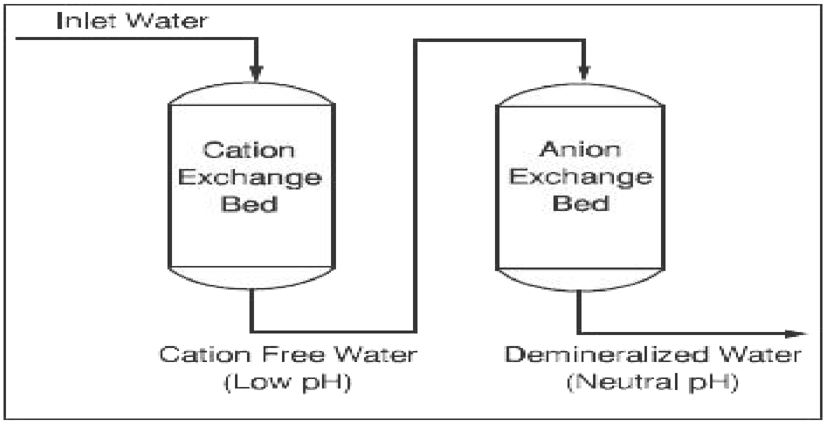
After passing through cation exchange column, the hard water is passed through anion exchange column (Styrene Divinyl Benzene –copolymer) Which contains basic functional group such as amino or quaternary ammonium (N^+R_3) or tertiary sulphonium group as integral part of resin.

When all the anions like $SO^2{}_4$. Cl^- etc. present in the water are removed (taken up by resin) and equivalent amount of ^-OH ions are released from this column to water.

$$X[RN^+(CH_3)_3]^-OH + A^{x-} \longleftrightarrow [RN+(CH_3)_3]_X A^{X-} + X^-OH$$

H+ = -OH ions get combined to produce water. $H^+ + ^-OH \longrightarrow H_2O$

Thus the Water coming out from the exchanger is free from cations as well as anions. Ion free water is known as deionized or demineralized water and it is also free from acidity or alkality and it as pure distilled water.



Finally the dimineralised water is passed through a degasifier. A tower whose rider are heated and which is connected to vaccum pump. High temperature and low pressure reduce the amount of dissolved gases like CO_2 and O_2 in water.

The exhausted cation exchange column and anion exchange column is regenerated by treating with Hcl and NaoH respectively which are then used again.

Advantages:

1) It is used to soften highly acidic or alkaline water.
2) It produce water of very low hardness (O- 2ppm)
3) It is used in industries and domestic purposes.
4) Use of chemical is minimized and can be used any number of times.

Disadvantages:

1) If water contains turbidity then efficiency of process is reduced.
2) The cost is high or It is not economical.

Portablewater: Waterthatisfitforhumanconsumptionandmeetsthemicrobiologicalandchemicalsta ndardsofqualitytopreventwaterborndiseasesandhealthriskfromtoxicchemicalsisknownasportable water.

Desalinationofwater: Theprocessofpartialorcompleteremovalof$NaCl$saltfromhighlysalinewatersuchasseawaterisknownasdesalination.

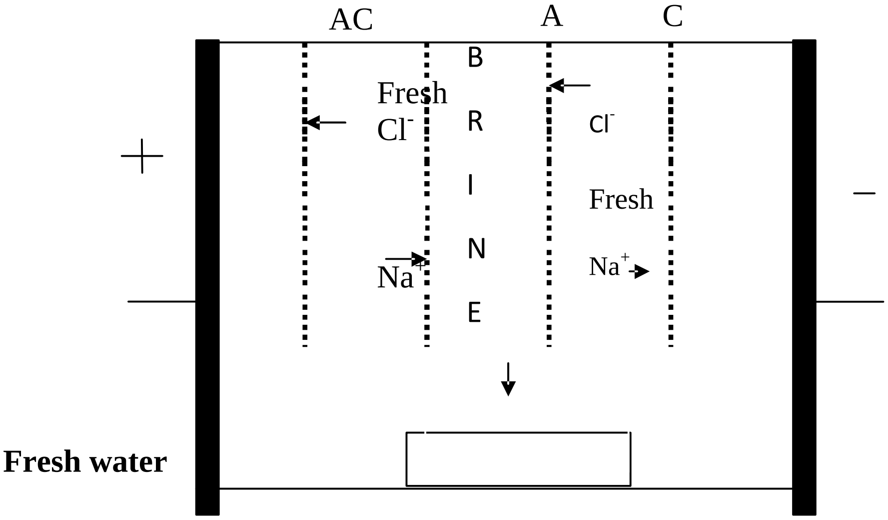
Desalinationcanbecarriedoutbydifferenttechniqueswhichare,

1.Flashevaporation
2.Electrodialysis
3.Reverseosmosis

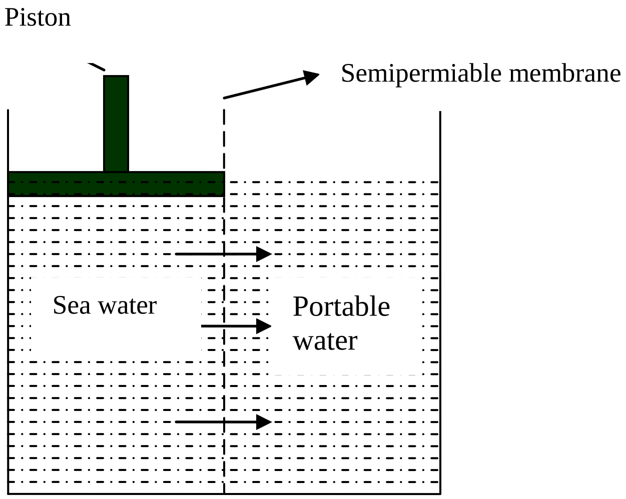
Electrodialysis: Anelectrodialysisunitconsistsofaseriesofalternativecationandanionpermeablemembranewhichpermitsonlyrespectiveions.Thesuitableemfisappliedacrosstheelectrodesthatdependonthelevelofsaltinsalinewater.

UndertheinfluenceofemfNa^+ionsmovetowardsthecathodethroughcationpermeablemembranewhereasCl^-movetowardsanodethroughanionpermeablemembrane.

ThenetresultisthedepletionofsaltinACcompartmentandincreaseofsaltconcentrationinCAcompartment.ThefreshwaterobtainedfromACcompartment. Theanodeis placednearanodepermeablemembranewhilecathodeisplacednearcationpermeablemembraneasshowninfig.



ReverseOsmosis:Osmosisistheprocesswherethesolventmoleculesnaturallydiffusefromlowerconcentrationregiontohigherconcentrationregionthroughsemipermeablemembraneduetoosmoticpressure(Po).Thisnaturalprocessmaybereservedbyapplyingpressureonbrinesidehigherthanthatofsomatic pressure,whenfreshwatertendstoflowfrombrinetofreshwaterregionasshowninfig


Piston
Semipermiable membrane
Sea water
Portable water

NANOMATERIALS

- **Nano Materials: Introduction, properties (size dependent). Synthesis-bottom up approach (solgel, precipitation, gas condensation,chemical vapour condensation processes). Nano scale materials- fullerenes, carbon nano tubes, nano wires, Nano rods,nano composites and dendrimers**

5 Hours

Contents :

- **Introduction, Properties (Size Dependent).**
- **Synthesis-Bottom Up Approach By Solgel,Precipitation,Gas Condensation**
- **Chemical Vapour Condensation**
- **Nano scale materials- Fullerenes, Carbon Nano Tubes, Nano Wires,Nano rods,nano composites and dendrimers**

NANOMATERIALS

1. Introduction:

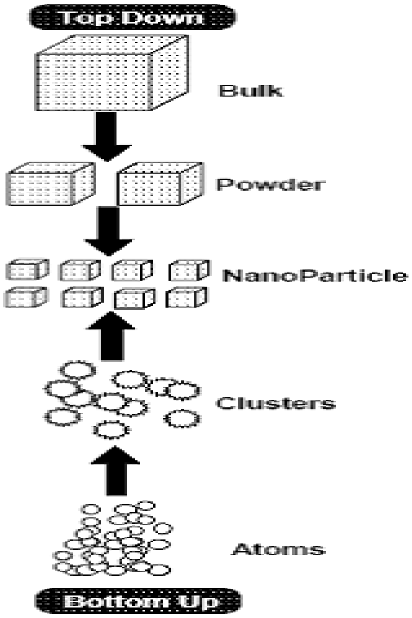
Nanomaterials are corner stones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.



Nanomaterial – synthesis

Nanomaterial can be synthesized by two approaches

1. Top down process
2. Bottom up process

Thetop downprocess:where the material is prepared by the structuraldecompositionofcoarser-grainedstructuresas theresultof severeplastic deformation.

Ex: Milling and mechanical grinding

Thebottomupprocess:where materialscontainingthedesiredprecursors aremixedinacontrolledfashionto forma colloidal solution.

Ex: Sol-gel, Precipitation, Gas condensation, Chemical vapour condensation, Hydro thermal & Thermolysis processes.

Nanomaterials can be defined as an aggregate of atoms between 1nm to 100nm with dimensions less that the characteristic length of some physical phenomenon.Nanomaterials exhibit several size dependent properties few of them are given below.

a)Surface area: Nanomaterials have a significant proportion of atoms existing at the surface. Properties like catalytic activity, gas adsorption and chemical reactivity depend on the surface area. Therefore nanomaterials can show specific related properties that are not observed in bulk materials.

b)Electrical properties: The electronic bands in bulk materials are continuous due to overlapping of orbits of billions of atoms. But in the nanomaterials, very few atoms or molecules are present so the electric band becomes separate and the separation between different electric states varies with the size of the nanomaterials. Hence, some metals which are good conductors in bulk become semiconductors and insulator as their size is decreased to nano level.

c)Optical properties: Nanomaterials in general can have particular optical properties as a result of the way light intersects with their fine nanostructures. The discrete electronic states of nanomaterials allow absorption and emission of light at specific wavelength. Hence, nanomaterials exhibit unique colours different from bulk materials.

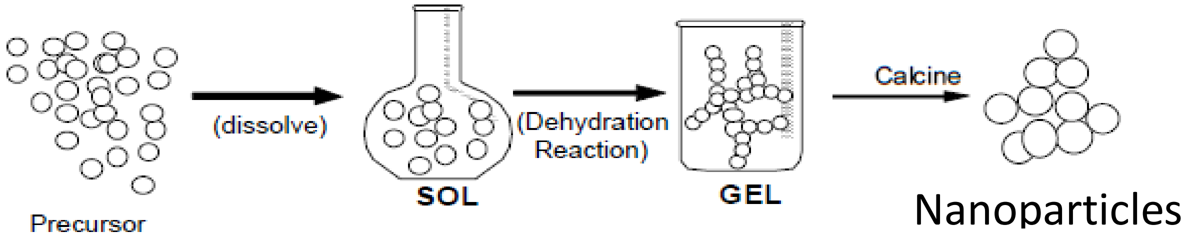
d)Magnetic properties: Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to differing magnetic properties. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles. Gold nanoparticles become ferromagnetic when they are capped with appropriate molecules such as thiol.

e)Mechanical properties: Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of the bulk materials. For example, the bending of bulk copper(wire, ribbon,etc.) occurs readily with the movement of copper atoms/clusters at about 50nm scale. Copper nanoparticles smaller than 50nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper.

Nanoparticles are particles between 1 and 100 nanometers in size. In nanotechonology a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties. Particle are further classified according to diameter. Ultrafine particles are the same as nanoparticles and between 1 and 100 nanometers in size. Coarse particles cover a range between 2,500 and 10,000 nanometer. Fine particles are sized between 100 and 2,500 nanometers.Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields.

Sol-Gel-Method.

The sol-gel process has been mainly used in the synthesis of monodispersed nanoparticles of metal oxide and temp sensitive organic- inorganic hybrid material.The following steps are involved in the synthesis of nanomaterials by sol-gel process.



Examples: Zinc oxide nanoparticles, TiO_2 nanoparticles can be synthesized by this method.

a) preparation of sol: In this method, metal alkoxide is used a precursor to synthesis nanoparticles of a metal oxide. Metal alkoxide is dissolved in alcohol and then water is added under acidic, neutral or basic conditions. Addition of water leads to hydrolysis in which alkoxide ligand is replaced with a hydroxyl ligand.

$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

b) Conversion of sol to gel : The polycondensation reaction between MOH and MOR results in the formation of an oxide – or alcohol – bridged network(gel).

$$MOH + ROM \rightarrow M\text{-}O\text{-}M + R\text{-}OH \text{ (Polycondensation)}$$

c) Aging of the gel: The reaction mixture is allowed to continue polycondensation reactions until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.

d) Removal of a solvent: The water and other volatile liquids are removal from the gel network. If isolated by thermal evaporation, the resulting product is termed a xerogel. If the solvent is extracted under supercritical conditions, resulting product is termed an aerogel.

e) Heat treatment: The sample obtained is calcined at high temperature (800^0C) to obtain nanoparticles.Nanoparticles formed by sol-gel process commonly have a size ranging from 1 to 100 nm.

Advantages

1. Nanomaterials of high purity with good homogeneity can be obtained.
2. Samples can be prepared at lower temperature.
3. Easy to control synthesis parameters to control physical characteristics like shape and size of resulting materials.
4. Simple and inexpensive equipment.

Precipitation Method.

In this method solid nanoparticles are obtained by careful precipitation from their solution. Precipitation method can be used to prepare nanoparticles of metal oxides, metal sulphides and metals.

a) In this method, an inorganic metal salt (such as nitrate, chloride or acetate of metal) is dissolved in water (precursor solution).

b) Metal cations exist in the form of metal hydrate species, for example, $(Al(H_2O)_6)^{3+}$ or $(Fe(H_2O)_6)^{3+}$.

c) These metal hydrates are added to precipitating agent like NaoH or NH4OH, it changes the P^H& causes condensation of precursor.

d) Thus concentration of solution increases and reaches a critical level called super saturation. At this concentration nucleus formation is initiated. The nucleus further grows into particles, which gets precipitate.

e) The precipitate obtained is filtrated, washed with water, air dried and finally calcined at high temperature.

Advantages

1.The process is relatively economical.

2. Wide range of single and multicomponent of oxide nanopowders can be synthesized.

Inert Gas Condensation Method.

The inert gas condensation is one of the simplest techniques for the production of metal nanoparticles.

a) In this method, Metal is vaporized by heating at high temperature inside a chamber.
b) Chamber is previously evacuated and filled with inert gas to a low pressure.
c) Metal atoms present in the vapours collide with the inert gas molecules and condenses into nanoparticles.
d) The particle size is usually in the range 1-100 nm and can be controlled by varying the inert gas pressure.

Advantages:

1. A major advantages is the improved control over the particle size.
2. It is better suited for larger scale synthesis of nanoparticles.

Chemical Vapour Condensation Method.

In this method a mixture of gas reactants are delivered into a reaction chamber. Inside the chamber, the chemical reactions among the gas molecules are induced by an input of energy such as resistant heating, laser and plasma. The product formed in the vapour state on condensation, deposits nanoparticles. The by-products of the reactions are exhausted.

Advantages

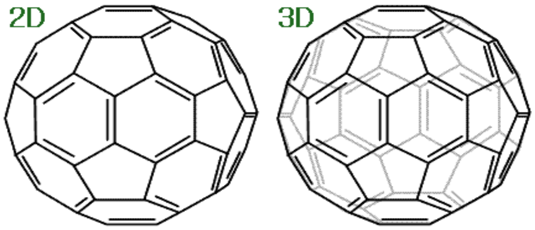
1. Very flexible, can produce wide range of materials.
2. Precursors can be solid, liquid or gas under ambient conditions, but delivered to reactor as vapour.
3. Allows formation of doped or multi- component nanoparticles by use of multiple precursors.

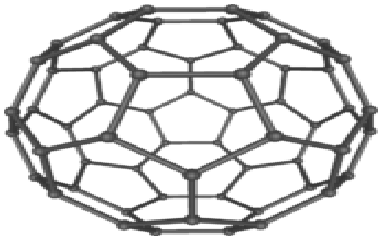
Nano scale materials:

Fullerenes:

Fullerenes are class of molecules made only carbon atoms having closed cage like structure. Fullerenes can be of a different type $C_{60,}$ C_{70}, C_{76}, C_{78}, C_{80} etc.depending on the number of carbon atoms. the most important fullerene is C60 containing 60carbon atoms which is commonly known as Buckminster fullerene. the name of Buckminster fullerene comes from the name of an architect Richard Buckminster fuller who had built the geodesic dome with spherical shape.

A **fullerene** is a molecule ofcarbon in the form of a hollow sphere, ellipsoed, tube, and many other shapes. Spherical fullerenes are also called **buckyballs**, and they resemble the balls used in football (soccer). Cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite,which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.





Molecule with 60 carbon atoms, C_{60}, and with an icosahedral symmetry, Larger molecular weight C_{70}, C_{76}, C_{78}, C_{80}, and higher mass fullerenes, which possess different geometric structure, e.g. C_{70} has a rugby ball-shaped symmetry.

The 60 carbon atoms in C_{60} are located at the vertices of a regular truncated icosahedron and every carbon site on C_{60} is equivalent to every other site.

The average nearest neighbor C-C distant in C_{60} 1.44A is almost identical to that in graphite (1.42 A). Each carbon atom in C_{60} is trigonally bonded to other carbon atoms, as in graphite

Most of the faces on the regular truncated icosahedron are hexagons. There are 20 hexagonal faces and 12 additional pentagonal faces in each C_{60}.which has a molecule diameter of 7.10A.

Fullerenes can be made by vaporizing carbon within a gas medium. (they could form spontaneously in a condensing carbon vapor)Cross-sectional drawing of the supersonic laser-vaporization nozzle used in the discovery of fullerenes.

Properties of fullerenes

1)Fullerenes are heat-resistant and unique, dissolve in common solvent at room temperature.

2)In fullerenes, 12 pentagonal rings are necessary and sufficient to affect the cage closure.

30Fullerenes contain carbon atoms arranged as a combination of 12 pentagonal rings and n hexagonal rings. The chemical formula is C20+2n.

4)Fullerene cages are about 7-15 Å in diameter, and are one carbon atom thick.

Quite stable from chemical and physical points of view (breaking the balls requires temperatures of about 1000 °C).

5)Highest tensile strength of any known 2D structure or element.

6)Highest packing density of all known structures.

7)Impenetrable to all elements under normal circumstances, even to a helium atom with energy of 5 eV.

Applications

1. Fullerenes are extremely flexible and strong nature, therefore are being considered for use in combat armor.
2. Researchers have found that water-soluble derivates of fullerenes inhibit the HIV-1 protease (enzyme responsible for the development of the virus) and are therefore useful in fighting the HIV virus that leads to AIDS.
3. Elements can be bonded with C_{60} or other fullerenes to create more diverse materials, including superconductors and insulators.
4. Fullerenes and their derivatives are also applied to coat materials on some chemical sensors, such as quartz crystal microbalance (QCM) and surface acoustic wave sensors (SAW)

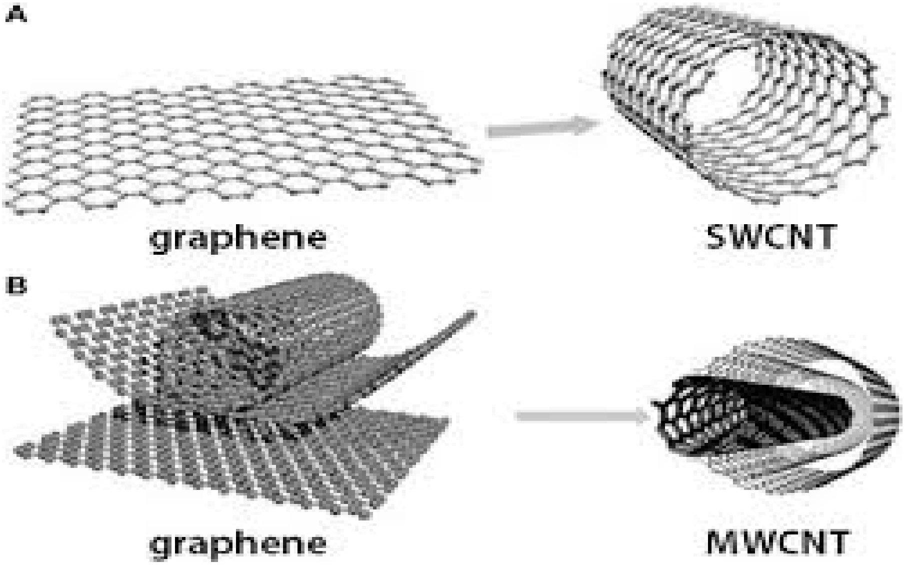
Carbon Nanotubes (CNTs): Carbon Nanotubes are cylindrical tubes with a central hollow core formed by rolling up of graphine sheets. Its ends are capped by hemisphere of fullerene sheets.The diameter of CNT is in the range of 1-50nm and the length can go up to few micrometers. The CNT is a one dimensional material like nanowire, but with the length to width ratio greater than 1000.

Current use and application of nanotubes has mostly been limited to the use of bulk nanotubes, which is a mass of rather unorganized fragments of nanotubes. Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes, but such composites may, nevertheless, yield strengths sufficient for many applications. Bulk carbon nanotubes have already been used as composite fibers in polymer to improve the mechanical, thermal and electrical properties of the bulk product.

Nanotubes are categorized as Single-Walled CNT(SWCNTS)andmulti-walled nanotubes (MWCNTs).

1 Single-Walled CNT(SWCNTs):They are formed by rolling up of single graphine layer.The diameter of SWCNT is 1-4nm and length can go up to few micrometers.

2 Multi-Walled CNT(MWCNTs):They consist of two or more concentric graphine cylindres with vander wall's forces between adjacent tubes.The diameter of MWCNTs is in the range of 30-50nm and length can go up to few micrometers.



Properties and applications:

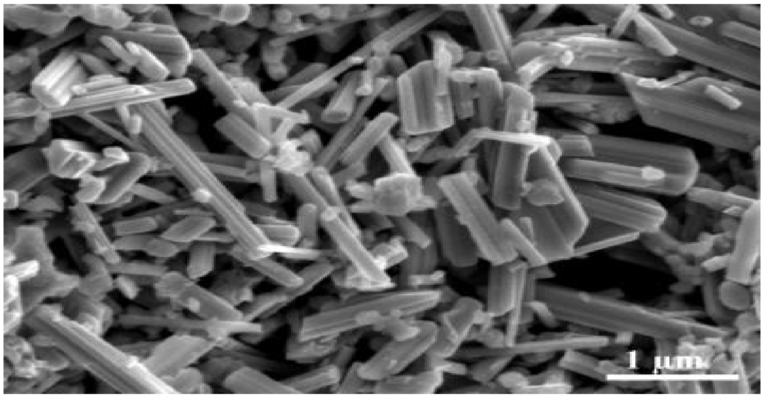
1. CNTs exhibit highnelectrical and thermal conductivty. They have low density and very high mechanical strength.due to these properties they are used as electrode material for lithium ion rechargeable batteries.
2. CNTs can emit electrons when subjected to high electrical field.due to this property they are used in the field emission X-ray tubes.
3. The CNTs are about 20 times stronger than steel and hence find apllications in making automabiles and aircraft body parts.
4. SWCNTs absorb radation in the near IR range(700-1100nm) and convert it to heat.this property is used in caner thermotherapy to selectivty kill caner cells without affecting nearby healthy tissues.

Nano wires: A nano wires is a nanostructure with the diameter of the order of nanometer with the ratio of the length to width being greater than 1000.They are also refered to as quantum wires.nanowires can be metallic(Ni,Pt,Au etcs,)semiconducting(Si,GaN etcs) or insulating(Sio2,Tio2 etcs). They belong to one dimensional(1-D) nanomaterials. Nanowires are prepared by using a number of techniques, including suspension,electrochemical deposition,vapour deposition etc. But the most commonly used technique is vapor-liquid-solid(VLS)synthesisthe nanowires of a given material exhibit thermal,electrical,mechanical and optical properties different from the bulk material.for example the conductivity of a nanowire will be much less than that of the corrsponding bulk material.

Uses:

1. Date storage/transfer-transfer data up to 1000 times faster and store date for as long as 1000000 years without degradation
2. Batteries/generators-tiny,efficient solar panels,turning light into energy, able to hold 10 times the charge of existing batteries.
3. It is also used in transistors,LED’s, Optoelectronic devices,biochemical sensors and thermoelectric devices.

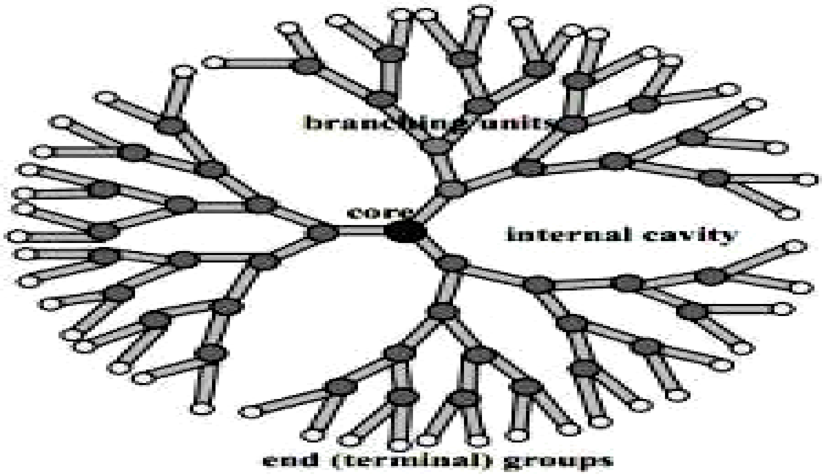
Nanorods : Nanorods are solid nanostructures morphologically similar to nanowires but with aspect ratios(length divided by width)of approximately 3-5.They are formed from a variety of materials including metals,semiconducting oxides,diamonds and organic materials.Nanorods are produced by a number of techniques including a vapor-liquid-solid approach,mechanical alloying,Direct chemical synthesis,plasma arc discharge,laser ablation and catalytic decomposition.direct chemical synthesis method is one of the simple and most commonly used method for the synthesis of nanorods,with a combination of ligands acting as shape control agents.the ligands bond to different facts of the nanorods with a combination of ligands acting as shape control agents.



Uses:

1. In display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field.
2. In microelectromechanical systems(MEMS)
3. Nanorods along with other noble metal nanoparticles, also function as the ragnostic agents.
4. Nanorods absorb radiation in the near IR and convert it to heat.this property is used in cancer thermotherapy to selectively kill cancer cells without affecting nearby healthy tissues.
5. Nanorods based on semiconducting materials as energy harvesting and light emitting davices.

Dendrimers: Dendrimers are large and complex molecules with very well defined chemical structures.the dendrimers are tree like repectitively branched polymer molecules.(In Greek Dendros Means Tree And Meros Means Part) they have a central core of multifunctional molecule to which branched molecules are added repeatedly step by step. Branched multiple in each step in all the directions much in the way as the tree limbs divide to form smaller branches.centre of a dendrimer is less dense ans as the branches grow in multiple fashions, It becomes progressively denser towards the exterior.Each step of addition of branches to a dendrimer is called as a generation.A dendrimer can be grown up to 10-15 generations.low generation dendrimers have a disc-like structure, while higher generations have a globular or spherical shape.



Uses:

1. It is used in medicinal diagnosis, gene therapy, chemical sensors etcs.
2. It is used in adhesives and coatings.
3. It is used in light harvesting material.
4. It is used in catalyst and electronic apllications.
5. It is also used in separating agents.

Nano composities: Nanocomposities are a class of materials in which one or more phases with nanoscale dimensions (0-D, 1-Dand 2-D)are embedded in a metal,ceramic or ploymer matrix.According to their matrix materials.

Nanocomposites can be classified into three types,
1 Ceramic Matrix Nanocomcomposites (CMNCs)
2 Metal Matrix Nanocomcomposites (MMNCs) and
3 Polymer Matrix Nanocomcomposites (PMNCs)

The reinforcing material can be made up of nanoparticles, nanosheets or nanofibres.The mechanical, electrical, thermal, optical, electrochemical,catalytic properties of the nanocomposites differ markedly from that of the component materials.for example adding carbon nanotubes improves the electrical and thermal conductivity of the composite.other kinds of nanoparticulates may result in enhanced optical properties,dielectric properties,heat resistance or mechanical properties such as stiffness,strength and resistance to wear and damage.

Uses:

1. In producing batteries with greater power output.
2. In speeding up the healing process for broken bones.
3. In producing structural components with a high strength to weight ratio.
4. In making lightweight sensors with nanocomposities.
5. As light weight materials in vehicles for fuel economy.
6. It is economically beneficial for artificial joints.