Question Papers solution

MODULE-1

ELECTROPOTENTIAL&CELLS

Jan 2013

1 a) An electrochemical cell consist of metallic Zn immersed in 0.1M$Zn(NO_3)_2$solution and metallic Cu immersed in 0.2M $CuSO_4$ solution.CalculateEMF of the cell at 25^0C and change in free energy of the cell reaction .E^0 of cell=1.1V (05M)

Ans)) Zn-------Zn2+ + 2e

Cu2+ + 2e-------Cu

Zn + Cu2+------ Zn2+Cu

E_{cell}=E^0+(.0591/2)xlog[Cu2+]/[Zn2+]

=.1.1255V

b) EMF of the cell Ag/$AgNO_3$(C_1)//(C_2=0.2M)$AgNO_3$/Ag is 0.8V. Calculate C_1 of the cell (05M)

Ans) EMF=.0591xlog C2/C1

.08 ==0591xlog 0.2/x

X=0.008 M

c) What are ion selective electrode? Discuss the construction of glass electrode and derive an expression relating glass electrode potential and pH (06M)

Ans) <u>Ion selective electrodes</u>:The electrodes that are able to respond to certain specific ions only their by developing a potential with respect to that ions and ignoring all other ions in a solution are called ion selective electrodes.

Ex. Glass electrode ,Crystalline membrane electrode , Solid state membrane electrode.

Uses:1.Used to determine concentration of cations like H^+,K^+,Na^+,Mn^{2+},Cu^{2+},Mg^{2+} Etc.

2.Anions like F^-,CN^-,and halides.

3.Used to determine the pH of the solution

4.Used to determine concentration of gas using gas sensing electrode.

<u>Glass electrode principle</u>:The potential developed across the membrane is a function of the concentration of the analyte and reference solution.When the concentration of the reference solution is kept constant the potential developed at the membrane is the linear function of conc. of analyte solution.

Glass electrode Construction:It consists of a glass membrane made up of special type of glass (22%Na_2O, 6%CaO and 72%SiO_2)of lower melting point and high electrical conductance.The glass bulb is filled with a solution of constant pH(0.1M HCl)and Ag-AgCl electrode is inserted which serves as internal reference electrode and also as external electric contact.

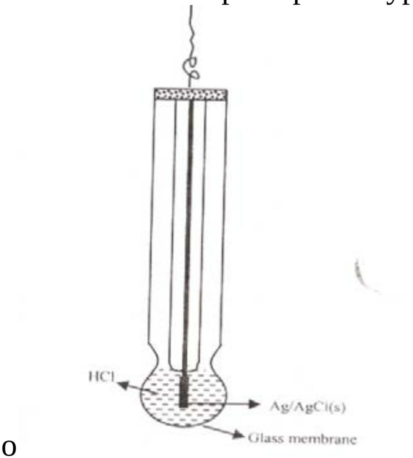


Fig. Glass electrode

Electrode representation: $Ag_{(s)}/AgCl_{(s)}$ /0.1M HCl/glass membrane.

The membrane undergoes an ion exchange reaction as follows.

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

Advantages:i.It can be used in oxidizing and reducing environments ii. Accurate results are obtained between pH range 1-9,iii.Electrode does not poisoned.

Limitations: i. Ordinary potentiometers cannot be used ii.It can be used up to pH 13 but becomes sensitive to Na^+ ions above pH 9 resulting alkaline error, iii.It does not function properly in pure alcohol and some organic solvents.

To determine the pH of a given solution the glass electrode is dipped in a solution whose pH need to be determined. It is combined with saturated calomel electrode as shown in fig.

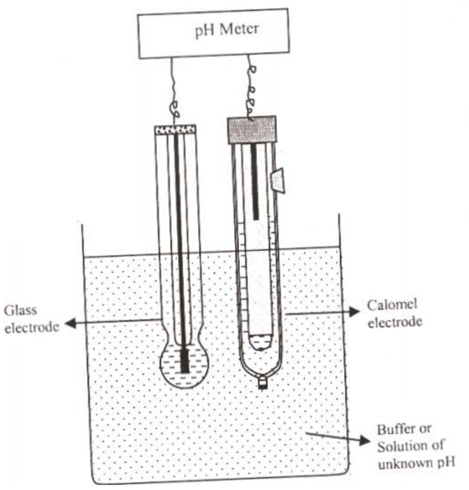
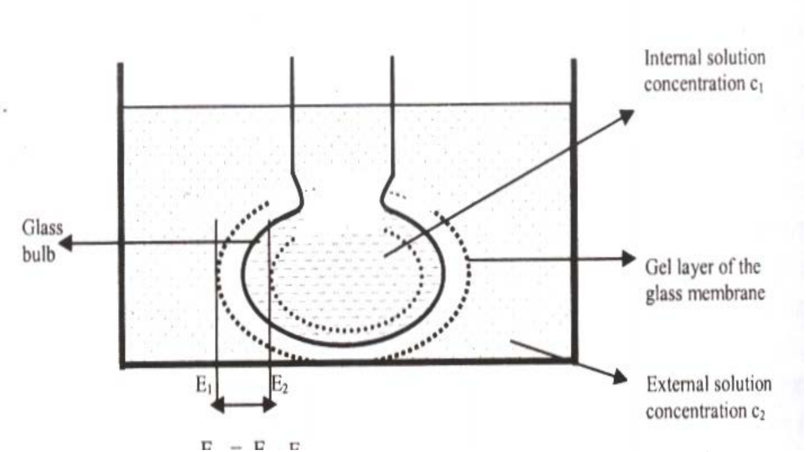


Fig.Determination of pH

The cell assembly is given by

$Hg_{(l)}/ Hg_2Cl_{2\,(s)}/Cl^-$//Unknown pH solution/Glass membrane/0.1M HCl)/$AgCl_{(s)}/ Ag_{(s)}$

The EMF of the cell is given by $E_{cell} = E_G - E_{\text{sat.calomel electrode}}$ -------------1



The boundary potential established due to exchange of H^+ with glass membrane is mainly responsible for glass electrode potential E_G and given by

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

$E_{Ag/AgCl}$ is internal reference electrode potential, E_b –boundary potential and E_{Asy} is asymmetric potential observed when Concentration $C_1 = C_2$

The boundary potential is given by Nernst equation at membrane $E_b = E_1 - E_2$ -------3

Since $E_1 = \text{Const.} + 0.0591 \log C_1$

$E_2 = \text{Const.} + 0.0591 \log C_2$

Therefore $E_b = 0.0591 \log C_1 - 0.0591 \log C_2$ since n=1

$E_b = L + 0.0591 \log C_1$ -------------4, where constant $L = -0.0591 \log C_2$,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

Combine all constant values in the above equation,ie. $L' = L + E_{Ag/AgCl} + E_{Asy}$

$E_G = L' - 0.0591pH$ -----------7

Therefore equation 1 becomes

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

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

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

where $K = L' - E_{\text{sat.calomel electrode}}$ which is constant

To evaluate K the electrode assembly is dipped in a standard buffer solution and pH meter is calibrated to the pH of the buffer solution.

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

Next the electrode assembly is dipped in a solution of unknown pH and pH(u) is given by

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

Subtract equation 10 from 11, $$PH(u) = PH(b) - \frac{E_{cell(u)} + E_{cell(b)}}{0.0591} \text{ ---------12}$$

June/July13

2 a) Derive Nernst equation for the potential of electrode (05M)

Ans) It relates electrode potential and concentration of the electrolyte species

Consider the following reversible electrode reaction

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

The decrease in free energy (- ΔG) represents the maximum amount of work that can be obtained

i.e. $-\Delta G = W_{max}$ ------------------2

The max. work done is given by

Wmax.=No. of Coulombs x Energy available/Coulomb-----3

Wmax = nF xE ----------------------------4

where n-No. of electrons,F-Faraday value ,E-Electrode potential

Equating equations 2&4

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

Under standard conditions $-\Delta G^0 = -nFE^0$ ----------------------6

According to thermodynamic equation

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

Where R-gas constant,T-temperature,Kc-equilibrium constant

Kc for forward reaction of equation no. 1 is

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

Substitute the values of $-\Delta G$, $-\Delta G^0$ & Kc in equation 7

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

Convert ln to $\log_{10}$ by multiplying with 2.303 and divide the equation through out by nF

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

Substitute the values of R,F and temperature at 25^0 C

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

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

Nernst equation for Ecell for the following reaction at 25^0C is

$aA + bB \rightleftharpoons cC + dD$

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

b)Calculate the voltage of a cell which consist of a rod of iron immersed in 1.0M solution of FeSO4 and a rod of manganese immersed in 0.1M MnSO4 at 25.C .Write the cell reaction .Give EoFe2+/Fe= -0.44V and Eo Mn2+/Mn=1.18V.(05M)

Ans) Fe-------Fe2+ + 2e

Mn2+ + 2e-------Mn

Fe + Mn2+------ Fe2+ +Mn

$E_{cell} = E^0 + (.0591/2) x \log[Ag+]^2/[Cu2+]$

=(-0.44+1.18)+.0591/2xlog[(1)/.1]

=.1.0355V

c) discuss the construction and working of glass electrode to determine pH of a solution. (06M)

Ans)JAN 2013

Dec.2013/Jan.2014

3 a) What are concentration cell? Explain the working of a concentration cell by taking suitable example. (05M)

Ans) **Concentration Cells**: It is an electrochemical cell that generates electrical energy when two electrodes of same metal are in contact with solution of its own ions of different concentration.

Consider the following concentration cell represented by

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

Where C1 and C2 are molar concentrations of the Cu^{2+} ions in the two half cells.

By electrochemical convention if C1<C2, the left electrode is anode and right electrode is cathode.The cell reactions are

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

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

The net cell reaction is $Cu^{2+}_{(C2)} \longrightarrow Cu^{2+}_{(C1)}$

The voltage of the cell exists as long as C1<C2

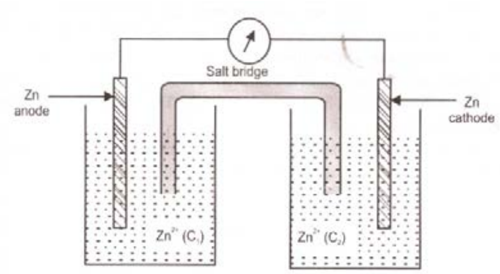


Fig.Concentration cell

The EMF of the concentration cell is given by $E_{cell} = E^0_{Cathode} - E^0_{Anode}$

Therefore $E_{cell} = [E^0_{Cu2+/Cu} + 0.0591/2 \log C2] - [E^0_{Cu2+/Cu} + 0.0591/2 \log C1]$

or $E_{cell} = 0.0591/2 \log C2/C1$ Where $E^0_{Cu2+/Cu} - E^0_{Cu2+/Cu} = 0$

In general the emf of the concentration cell is given by

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

From the above equation following conclusions may be drawn

i.When C1 = C2 the concentration cell does not generate electrical energy

ii.When C2/C1 > 1, log C2/C1 is positive and E_{cell} is positive

iii.Higher the ratio of C2/C1 higher is the cell potential.

b) Explain a method for the determination of single electrode potential. (06M)

Ans: JAN 2013

c) An electrochemical cell consists of magnesium electrode in 0.042m mg(N0$_3$)2 solution and silver electrode in 0.35m AgNO$_3$ Solution. The SEP of Mg and Ag are -2.363V and

+0.80V respectively. Represent the cell. Write the cell reaction and calculate the emf of the cell. (05M)

Ans) Mg-------Mg^{2+} + 2e
Ag^+ + e-------Ag
Mg + 2Ag+------ Mg2+ +2Ag
E_{cell}=E^0+(.0591/2)xlog[Ag+]^2/[Mg2+]

=3.163+.0591/2xlog[(.35)^2/.042]
=3.1908V

June- July .14

4 a) What are secondary reference electrode.Explain Construction & working of calomel electrode (06M)
Ans) jan 2013
b) Explain determination of pH of glass electrode (06M)
Ans)JAN 2013

c) What are reference electrode ? Explain the construction & working of Ag-AgCl electrode (05M)
Ans) reference electrode- Reference electrode are the electrode with reference to those the electrode potential of other electrode can be calculated
Silver –Silver chloride electrode: It is prepared by coating a thin layer of AgCl electrolytically on to a silver wire.This wire when placed in a solution of potassium chloride develops a definite potential depending on the concentration of the electrolyte used.

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

Electrode reaction: $AgCl_{(s)} + e \longrightarrow Ag_{(s)} + Cl^-$
Electrode potential is given by $E = E^0 - 0.0591 \log [Cl^-]$ at 298K
The electrode potential depends on concentration of chloride ions and for the saturated KCl the potential is 0.199 V

Dec.2014/Jan.2015

5 a) Derive Nernst's equation for single electrode potention. (05M)
Ans)JAN 2013
b)Describe the construction and working of calomel electrode. (05M)
Ans) Calomel Electrode:
It is a metal-metal salt ion electrode.It consists of a glass tube having a side tube on each side.Mercury(Hg) is placed at the bottom of the tube and it is covered by a paste of Hg_2Cl_2 with Hg.A solution of KCl is introduced above the paste through side tube. A platinum wire sealed in to the glass tube is dipped in to mercury which gives the external electric contact.

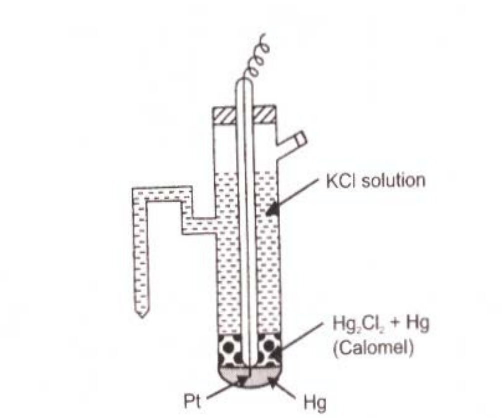


Fig.Saturated Calomel electrode

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

Working: It acts as anode or cathode depending on nature of the other electrode.

When it acts as anode,the electrode representation is

$$2Hg + 2\,Cl^- \longrightarrow Hg_2Cl_2 + 2e$$

When it acts as cathode the electrode reaction is

$$Hg_2Cl_2 + 2e \longrightarrow 2Hg + 2\,Cl^-$$

The net reversible electrode reaction is

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

Acording to Nernst equation electrode potential is

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

The electrode potential is decided by the concentration of chloride ions.

Uses:It is used as secondary reference electrode to measure electrode potential

Used as reference electrode in potentiometric determination

Used as reference electrode in pH determination

Advantages: Easy to construct,electrode potential is reproducible, and stable for long period,cell potential does not vary with temperature.

c) What are reference electrodes? Explain the determination of electrode potential of an unknown electrode using calomel electrode. (05M)

Ans) Reference electrode are the electrode with reference to those the electrode potential of other electrode can be calculated.

d) What are concentration cells? the emf cell of the Ag|$AgNO_3$(0.0083M0)||$AgNO_3$(xm)|Ag was found tobe 0.074V at 298K. calculate the value of and write cell reaction. (05M)

Ans)) EMF=.0591xlog C2/C1

.086 ==0591xlog x/.0083

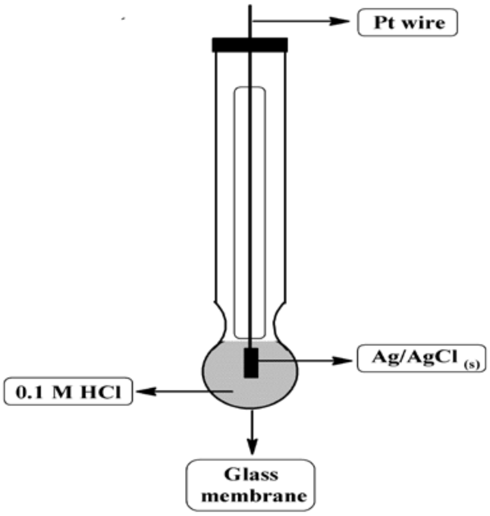
X=7.55M

June/July2015

6a) Explain the construction and working of glass electrode. (05M)

Ans) **Construction and woring of Glasselectrode:**

Principle:Thepotentialdevelopedacrossthemembraneisafunctionoftheconcentrationoftheanalytea



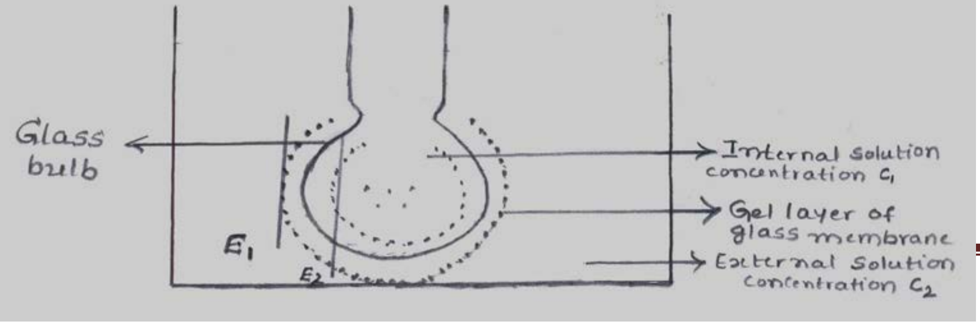
ndreferencesolution.Whentheconcentrationofthereferencesolutioniskeptconstantthepotentialdevelopedatthemembraneisthelinearfunctionofconc.ofanalytesolution.

GlasselectrodeConstruction:Itconsistsofaglassmembranemadeupofspecialtypeofglass(22%Na_2O,6%CaOand72%SiO_2)oflowermeltingpointandhighelectricalconductance.Theglassbulbisfilledwithasolutionofconstantph(0.1MHCl)andAg-AgClelectrodeisinserted.whichservesasinternalreferenceelectrodeandalsoasexternalelectriccontact.Electroderepresentation:$Ag_{(s)}$/$AgCl_{(s)}$/0.1MHCl/glassmembrane.
Themembraneundergoesanionexchangereactionasfollows.
Advantages:i.Itcanbeusedinoxidizingandreducingenvironments
ii.AccurateresultsareobtainedbetweenpHrange1-9
,iii.Electrodedoesnotpoisoned.

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

DeterminationofpH:
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$C_1=C_2$

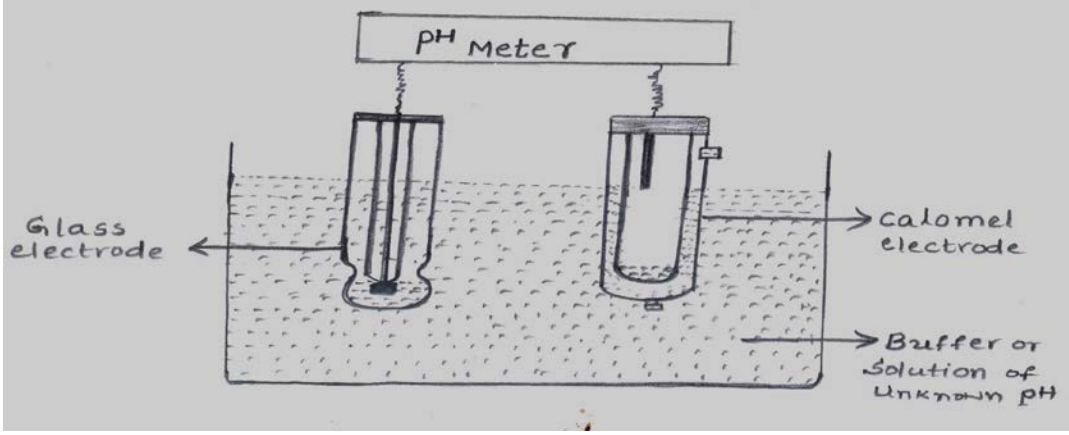


Fig.DeterminationofpH

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

b. Give the construction of calomel electrode. Justify that it is a reversible electrode.

(05M)

Ans) Dec.2014/Jan.2015

c) Define reference electrode. Explain the measurement of standard electrode potential using calomel electrode. (05M)

Ans) 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

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.

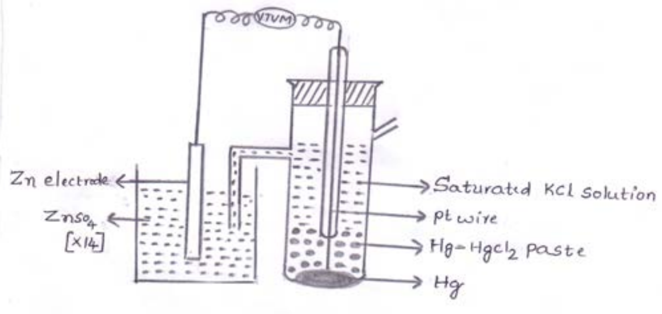
Cell representation:

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

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

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

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



d) A cell is obtained by combining two Cd electrodes immersed in cadmium sulphate solutions of 0.1M and 0.5M at 25^{o}c. Give the cell representation, cell reaction and calculate EMF of the cell. (05M)

Ans) Cd^{2+} + 2e-------Cd

Cd -------Cd^{2+} + 2e

Cd/ Cd^{2+}(.1M) // Cd^{2+}(.5M) / Cd

EMF=.0591/2xlog C2/C1

=.0591/2xlog .5/.1

=.021V

BATTERY TECHNOLOGY & FUEL CELLS

January 2013

1 a)Explain the construction and working of acid storage battery. (07M)

Ans) Pb-acid battery

Construction: It consists of two electrodes of lead grids. The anode grid is filled with spongy lead and cathode grid is filled with PbO_2. Several such electrodes pairs with inert porous partition in between are dipped in 5M sulphuric acid. The battery is enclosed in a plastic container.

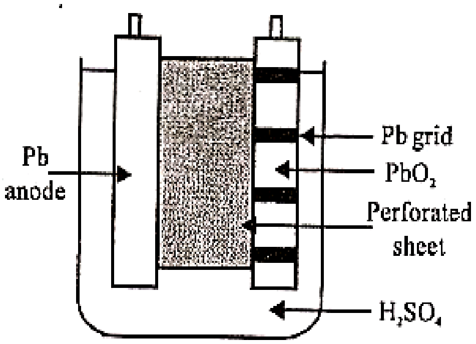


Fig .Lead Acid Battery

At anode: $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e$

Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e \longrightarrow PbSO_4 + 2H_2O$

The over all reaction is given by

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

Cell notation: $Pb/ \ Pb\,SO_4, H_2SO_4, PbSO_4/PbO_2/Pb$

The product $PbSO_4$ formed during discharge get deposited on respective electrode and is available at the sight during charging . The discharge of the battery can be known by finding specific gravity of sulphuric acid.

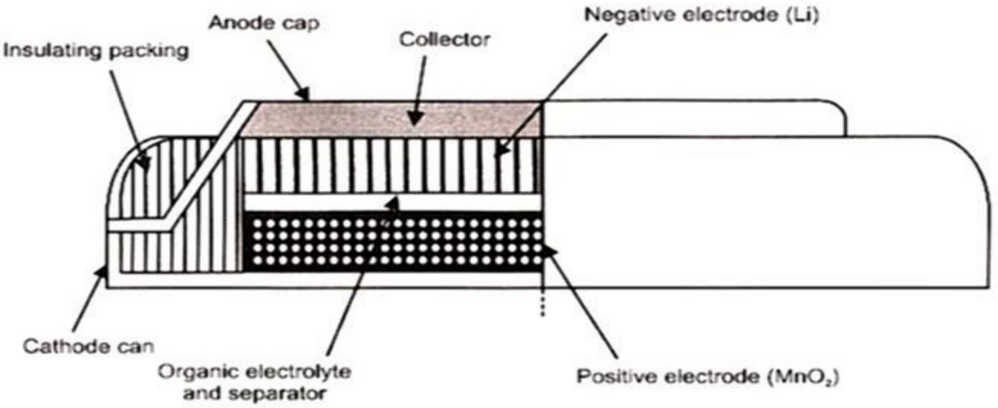
Uses:It is used in lighting , starting and ignition of automobiles such as cars ,trucks, buses etc. ,hospitals,UPS , security alarm system, emergency lighting etc.

The performance required for starting, lighting and ignition of cars are i.capacity 100Ah ii.Ability to provide 25 A for three hours without voltage drop below 10.5V.iii.High cycle life iv.High pulse to permit engine sarting typically 400-450V for 30 seconds without voltage droping 7.2V.

b) Explain the working of lithium ion battery. Write the advantages of Li battery.

Ans) Lithium-ion battery: 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.

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.



(06M)

c)Mention any three advantages of fuel cell. (03M)

Ans) 1. High efficiency of the energy conversion process .
2. Recharging of fuel cell not required .
3. Absence of harmful waste products .
4. Silent operation .

June/July13

2 a) Explain the construction & working of Zn-air battery (05M)

Ans) Zinc-Air Battery:

This is a type of metal air battery which uses oxygen directly from atmosphere to produce Electrochemical Energy. A loose granulated powder of zinc is mixed with electrolyte(30%KOH) acts as anode material. The outer metal acts as cathode of the battery which is filled with small amount of catalyst and carbon to optimize the evolution of oxygen in alkaline solution and for better reduction. The two electrodes are separated by plastic gasket as insulator. As the electrode is compact, high energy densities are obtained.

Battery Notation:_ Zn | KOH | air ,C

The Cell Reactions:

$2\,Zn + 4\,OH^- \longrightarrow 2ZnO + 2\,H_2O + 4e^-$ at Anode

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

Over all Reaction:

$$2Zn + O_2 \rightleftharpoons 2ZnO$$

It has energy density of about 100W h Kg^{-1} three times that of Lead acid battery or twice that of Ni- Cd Battery.

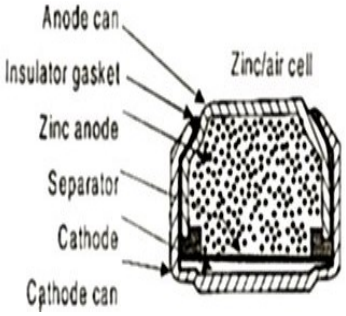


Fig.Zinc –Air Battery

Advantages:High energy density,long shelf life,low cost ,no ecological problem.
Uses: It finds applications in military radio receivers,Power source for hearing aids,medical devices,remote communications etc.

b) Explain the following battery characteristics
i) Voltage ii) Cycle life iii) Energy efficiency (06M)

Ans) Voltage: the voltage available depends on EMF of the cell and EMF in turn depends on free energy change.Consider the equation

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

Where $E^0_{\ cell} = E^0_{\ cathode} - E^0_{anode}$,Q is the reaction quotient ie. [products]/[reactant]
From the above equation we can conclude that

a) If the difference in std.electrode potential is more ,EMF of the cell is also higher
b) as the temperature increases the EMF of the cell decreases
c) c) as the value of Q increases ie, when current is drawn from the cell the cell reaction proceeds and EMF of the cell decreases.
d) To derive maximum voltage in addition to above the electrode reaction must be fast to reduce the overpotentials and the resistance of the cell must be low

CYCLE LIFE: It is the number of charge or discharge process that are possible before failure occurs . Primary batteries are designed for single discharge but secondary batteries is chargeable. The cycle life of a storage must be high.
It depends on chemical composition, morphological changes and distribution of active materials in the cell
Energy efficiency: it is given by

$$\%\text{energy efficiency} = \frac{\text{energy released on discharge}}{\text{energy required for charging}} \times 100$$

It depends on rate of charge or discharge,current efficiency of the electrode process and the overpotential during charge and discharge reactions as well as the battery resistance.

c) Explain the construction & working of H2-O2 fuel cell. (05M)

Ans)) **<u>Hydrogen-oxygen fuel cell :</u>** It consists of two porous carbon electrodes .Anode is coated with platinum catalyst and cathode with silver catalyst .The electrolyte is an aqueous solution of KOH .The hydrogen gas is continuously supplied at the anode and oxygen is supplied at the cathode . As the Hydrogen gas diffuses through anode it is adsorbed on the electrode surface and reacts with Hydroxyl ions to form water . At the cathode Oxygen diffusing through the electrode is adsorbed and reduced and get reduced to hydroxyl ions .

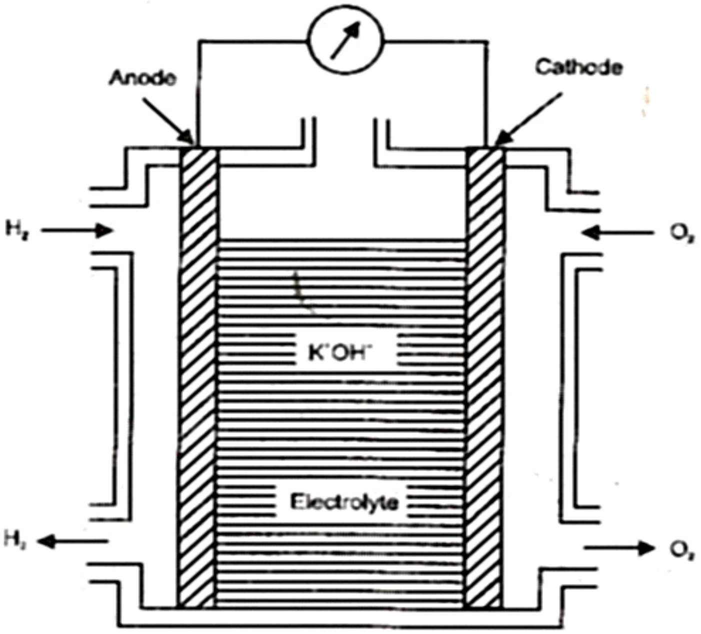


Fig. Hydrogen-oxygen fuel cell

The electrodes reactions are,

$$\text{At anode, } 2H_2 + 4OH^- \longrightarrow 4H_2O + 4e$$
$$\text{At cathode, } O_2 + 2\,H_2O + 4e \longrightarrow 4OH^-$$
$$\text{Net cell reaction } 2H_2 + O_2 \longrightarrow 2\,H_2O$$

water formed in the above cell removed continously because it will dilute the electrolyte and the function of battery stops

Dec.2013/Jan.2014

3 a) What are fuel cells? How it differ from battery? Explain the construction and working of CH3OH-O2 fuel cell. (06M)

Ans) Methanol oxygen fuel cell :

It consists of two porous carbon electrodes .Anode is coated with platinum catalyst and cathode with silver catalyst .The electrolyte is an aqueous solution of KOH .The Methane gas is continuously supplied at the anode and oxygen is supplied at the cathode . As the Methane gas diffuses through anode it is adsorbed on the electrode surface and reacts with Hydroxyl ions to form water . At the cathode Oxygen diffusing through the electrodes is adsorbed and reduced and get reduced to hydroxyl ions .

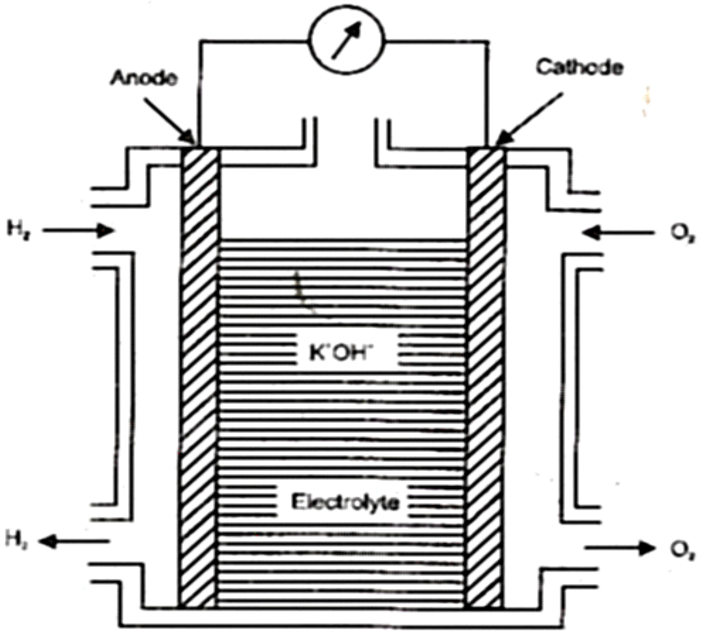


Fig. Methanol oxygen fuel cell

The electrodes reactions are

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

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

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

b)Write the discharing and charing reactions in the following batteries:

i)Ni-Cd battery: ii) Ni-MH battery (05M)

Ans) i)Ni-Cd battery: Cd + 2 Ni(OH)3 ---------- 2Ni(OH)2 + $Cd(OH)_2$

Ni-MH battery **:** <u>The Cell Reactions:</u>

$MH + 2OH^- \longrightarrow H_2O + M + 2e^-$ Anode

$2NiO(OH) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$ Cathode

<u>Over all Reaction:</u>

$$MH + 2NiO(OH) \rightleftharpoons Ni(OH)_2 + M$$

<u>June/July 2014</u>

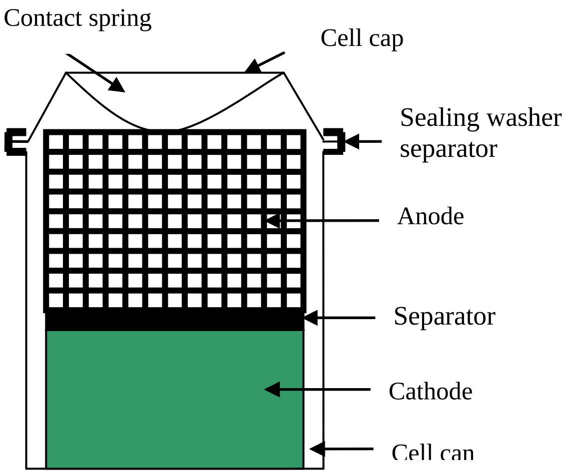
4 a) Explain the following battery characteristics

i) Cycle Life ii) Energy density iii) Capacity (06M)

Ans) jan 2013

b) Explain the construction & working of Ni-Cd (05M)

Ans) Construction: In these batteries, electrodes are made of porous nickel foil or nickel grid, into which the active material is packed. The active material for the anode is a mixture of a Cd .The active material for cathode is nickel trihydroxide, $NiO(OH)_3$. An aqueous solution of KOH acts as the electrolyte. Polypropylene is used as the separator



Cd + 2 Ni(OH)3 ---------- 2Ni(OH)2 + Cd(OH)2

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

c) Explain the construction & working of Me-O_2 fuel cell (05M)

Ans)JAN 2013

Dec.2014/Jan.2015

5 a)What are batteries? Explain the following battery characteristics.

i) Capacity ii) cyele life. (05M)

Ans) Capacity :It is the total amount of a electric current involved in the electro chemical reaction and expressed in a term of coulombs or ampere hour(Ah). It depends on a size of a battery and given

C=WnF/M where W is the mass& M is the molar mass of active materials

CYCLE LIFE: It is the number of charge or discharge process that are possible before failure occurs . Primary batteries are designed for single discharge but secondary batteries is chargeable. The cycle life of a storage must be high.

It depends on chemical composition, morphological changes and distribution of active materials in the cell

b) Describe the construction and working of nickel metal hydride battery . (05M)

Ans)JAN 2013

c) Define fuel cell. Explain the construction and working of methanol oxygen fuel cell. (05M)

Ans) DEC 2013

d) Explain the construction and working of lithium ion battery. (05M)

Ans) Lithium-ion battery (Li-ion Battery)

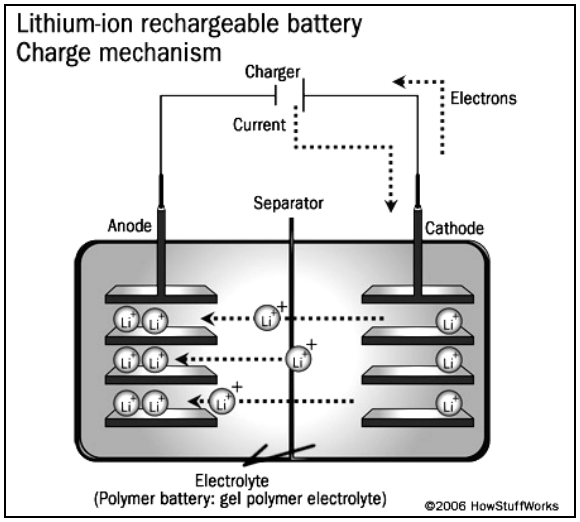
1.Li-ion batteries are secondary batteries.

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 ($LiMn_2O_4$)
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:

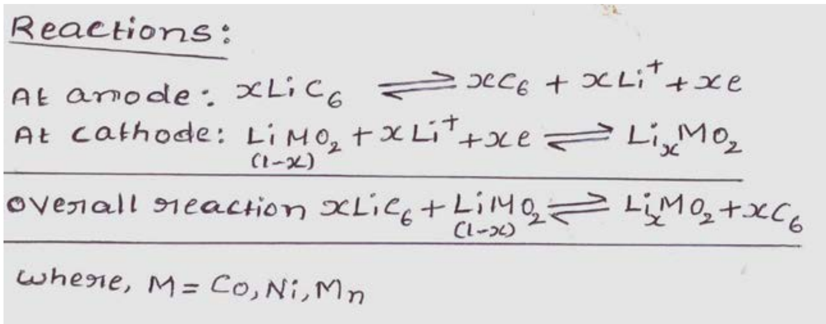
1. Li-ion cell has a four-layer structure.
2. A positive electrode made with Lithium Cobalt Oxide has a current collector made of thin aluminum foil – cathode.
3. A negative electrode made with specialty carbon has a current collector of thin copper foil – anode.
4. A separator is a fine porous polymer 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

June/July2015

6a) Discuss the construction and working of Li-MnO_2 battery. (05M)

Ans) JAN 2013

b)What are fuel cells? How is it different from galvanic cell? Mention any two advantages of fuel cell. (05M)

Ans)

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.

c)Discuss the construction and working of Zn-air battery. (05M)
Ans) June/July13
d)Explain the construction and working of methanol- oxygen fuel cell. Mention any two applications. (05M)
Ans) Dec.2013/Jan.2014

MODULE -2

METAL FINISHING & ELECTROLESS PLATING

January 2013

1 a) Define the term metal finishing . Mention any three technological importance ofmetalfinishing. (05M)

Ans) **Definition:** It is defined as a process carried out in order to modify the surface properties of a metal by deposition of a layer of another metal, polymer or by formation of oxide layer.

Technological importance of metal finishing:

It is the addition of certain properties to the materials to increase the utility of the material.

These include

☐ to increase corrosion resistance
☐ to improved wear resistance
☐ to impart electrical and thermal conducting surface
☐ imparting thermal resistance
☐ imparting hardness
☐ to offer the surface thermal or optical reflectivity
☐ manufacture of electrical and electronic components such as PCBs,capacitors,contacts
☐ electroforming process
☐ electropolishing,electrochemical etching

b) Explain the process of electroplating of chromium. (05M)

Ans) Bath : Cr_2O_3 250 g + 2.5 g H_2SO_4(100:1)
Temperature : 45-55 ^OC
Current density : 100-200 mA/Cm^2.
Current efficiency: 10-15%
Anode : Insoluble anode Pb-Sb or Pb-Sn coated with PbO_2
Cathode : Object to be plated.

At anode: $CrO_3 + H_2O \longrightarrow H_2CrO_4$

$$2\,H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O \longrightarrow Cr_2O_7^{-2} + 2H^+ + H_2O$$

$$Cr_2O_7^{-2} + 14\,H^+ + 6e \longrightarrow 2Cr^{+3} + 7\,H_2O$$

$$Cr^{+3} + 3e \longrightarrow Cr$$

At Cathode: $2\,H_2O \longrightarrow O_2 + 4H^+ + 4e$

Sulphuric acids acts as catalyst in converting Cr(VI) to Cr(III) by complex anodic reaction. To maintain the concentration of Cr(III) ions insoluble anodes like Pb-Sb, Pb-Sn, alloys are used covered PbO_2 which oxidize Cr(III) to Cr(VI)& controls the concentration of Cr(III) ions.

1) Cr metal passivates strongly in acid sulphate medium.
2) It gives Cr(III)ions on dissolution.In presence large Cr(III) ions a block Cr deposit is

obtained .

3)Difference in efficiency of anode and cathode(anode -100% cathode -20%).

c) What is electrolessplating ? Explain the electroless plating of nickel. (06M)

Ans) It is defined as deposition of metal or alloy from metal salt solution on to a electrilytically active surface by controlled chemical reduction of M^{n+} ions by suitable reducing agents without using electrical energy The metal is cleaned to remove impurities. Non metallic impurities are sensitized in stannous chloride solution followed by dipping in palladium chloride. The surface is dried.

Bath : $NiCl_2$(20g)
Red.agent : Sodium hypo phosphite(20g)
Buffer : Sodium acetate(10g/lt)
Complexing agent: Sodium succuinate(15g/lt)
Temp : 90°C
pH :4.5
Reactions
At anode $H_2PO_2 + H_2O \longrightarrow H_2PO_3 + 2H^+ + 2e$
At Cathode $Ni^{2+} + 2e \longrightarrow Ni$

<u>Uses</u>:

Because of hardness and abrasion resistance used in pumps and valves, piston and shafts,gears ,reaction vessels etc.

Used in instruments and computers because of good magnetic properties

<u>June/July13</u>

2 a) Explain the process of electroplating of Cu(06M)

Ans)) **<u>Electroless plating of copper</u>**

Pretreatment and activation of surface:The surface is treated to remove grease and other impurities.In case of insulators ,the surface is activated by dipping in stannous chloride and then in palladium chloride.The surface is dried.

Plating bath:
Bath :Copper sulphate 12 g per litre
Reducing agent :Formaldehyde 8 g per litre
Buffer :NaOH 15 g/litre & Rochelle salt 14 g/litre
Complexing agent :EDTA 20 g /litre
pH : 11
Temoerature :25^0 C
Reactions
At anode $2\,HCHO + 4\,OH \longrightarrow 2\,HCOO + 2\,H_2O + H_2 + 2e$
At cathode $Cu^{2+} + 2e \longrightarrow Cu$

b) Mention difference b/w electroplating & electroless plating(04M)

Ans) Distinction between Electro-plating and electro less-plating

reaction M Cathode reaction	$M^{n+} \longrightarrow ne$ R Or $H_2O \longrightarrow O_2 + H^+ + e$ $M^{n+} + ne \longrightarrow M$	Oxidized product+ ne $M^{n+} + ne \longrightarrow M$
Site of anode reaction	separate anode	article to be plated
Site of cathode reaction	article to be plated	article to be plated with
surface		Catalytically active
Nature of deposit Driving force	pure metal or definite alloy Electro-plating power supply	Metal contaminated with Eelectro less -plating auto-catalytic redox reaction
		Anode O/R species
Throwing power	not satisfactory	good
Application	applicable only to conductors	applicable both for
conductors		and non Conductors

c**) Discss the role of following factors on the nature of electrodeposit**
i) Metal ion conc.ii) Wetting agents (06M)

Ans) <u>Wetting agents</u>:In electroplating hydrogen gas evolved at cathode and these gas bubbles adhere to the cathode surface.The gas may try to escape when the plating is over and makes the deposit porous and brittle.Wetting agents added detach adsorbed hydrogen gas on the cathode surface and improve the adhesion of the deposit.

Ex.Sodium lauryl sulphate.

Metal salt and electrolyte concentration:The metal salt concentration is kept high to decrease the mass transfer otherwise the quality of plating is adversely affected.Electrolytes are also added to increase the conductivity of the plating bath.They also have the role of controlling the pH of bath solution particularly if the evolution of H_2 or O_2 at cathode or anode.H_2SO_4 is added to prevent hydrolysis of salt.Boric acid is used as buffering agent.

Dec.2013/Jan.2014

3 a) Explain how the following plating variables affect the nature of deposit:
i) Current densityii) P^Hiii) Complexing agent. (05M)

Ans) Current density : It is the current per unit area of the electreode surface(mA/cm^2)

- At low current densities surface diffusion is fast compared to electron transfer and adatoms find most favorable position resulting in well formed deposit.

As the current density increased surface diffusion is slowed down compared to electron transfer and adatom may not reach most favorable position resulting in less ordered deposit.

- At very high current density (below limiting value) mass transport predominates in solution resulting in bad deposit with rough and powdery texture which is poorly adherent to surface.
- When current density is increased beyond limiting current burnt and spongy appearance

of deposit takes place.This is due to depletion of H^+ ions at the cathode and formation of metal hydroxide also takes place. There fore optimum current density should be applied to get good deposit.

P^H: At low pH value , hydrogen gas evolution takes place causing deposit brittle and burnt. At higher pH deposits of insoluble metal hydroxides takes place.Hence optimum pH is maintained by using suitable buffers.

Complexing agents : These are added to convert free metal ions in to complexing ions to get fine grained and more adherent deposit.They are also added for the following reasons

- To prevent the reaction of cathode metal and plating ions
- To prevent passivation of anode and increase in current efficiency
- To improve throwing power of plating bath
- To increase the stability of slightly soluble metal salts
- To make potential of plating M^{n+} more -ve to carry out plating at lower potential

b) What is electroless plating? Explain electroless plating of copper? (06M)

Ans)JUN 2013

June/July 2014

4 a) Explain Decomposition potential & over voltage.Why practical is greater than theoretical E(05M)

Ans) Polarisation:It is defined as the departure of the electrode potential (increase or decrease) due to inadequate supply of species from the bulk of solution to the electrode surface.

The electrode potential is given by the Nernst equation

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

Where E-electrode potential, E^o standard electrode potential and $[M^{n+}]$ is the metal ion concentration.In presence of electric current metal ion concentration decreases due to deposition of metal.When the diffusion rate of metal ion is slow the variation in electrode potential is observed.At that stage the electrode is said to be polarized.

Factors depending on polarisation are

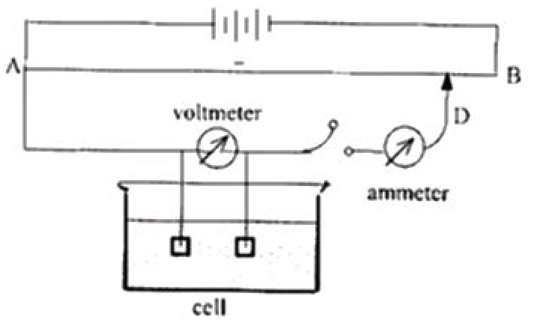
i.Nature of electrode (size&shape) ii.Concentration of electrolyte and its conductance

iii.Temperature iv.Products formed at electrode v.Rate of stirring of the electrolyte.

To decrease the polarisation effect the electrode surface must be large and low concentration of electrolyte with high conductance.

Decompositon potential: The minimum external voltage applied in order to cause continuous electrolysis of an electrolyte is called decomposition potential.

It is measured using an electrolytic cell as shown in the fig.



Determination of decomposition potential

The cell consists of two platinum electrodes immersed in the electrolyte.The voltage is varied by moving the contact C along the wire AB and the current passing through the cell is measured with ammeter.When dilute solution of acid or base is taken in the cell,at low voltage i.e. Less than 1.7 V no reaction is found to occur because the inert platinum electrodes are converted in to active hydrogen and oxygen gas electrodes.The secondary cell formed produces back emf opposing the applied emf.When the voltage is increased above 1.7V sudden evolution of H_2 and O_2 gas takes place at the respective electrodes.The abrupt increase in current also observed at this point.The decomposition potential is calculated by plotting current versus applied voltage as shown in the graph.

b) Explain electrolessplating of Ni & its applicatio(05M)
Ans)JAN 2013
c)Explain electroless plating of Cu(05M)

Ans) JUN 2013

Dec.2014/Jan.2015

5 a) What is electro less plating? Write the diff between electroplating & plating. (05M)
Ans)JUN 2014
b) Discuss the electroplating of gold using Acidic Cyanide bath . (05M)
Ans) Electro plating of gold (acidic cyanide bath) :
Gold plating baths are divided in to three types based on pH range
i.Alkaline cyanide bath(pH 10 to 13)
ii.Neutral cyanide bath(pH 6 to 9)
iii.Acid cyanide bath (pH 3.5to 5.0)
The alkaline cyanide bath composition is
Bath : pot. Gold cyanide 12-15gL^{-1}, Citric acid, Cobalt
PH :3.6-4.5
Temperature :40-65^{o}C
Current density : 86-252 mAcm^{-2}
Additives : Citrate Buffer , Sodium allyl sulphonate as leveler
Anode :Platimised titanium , gold,or graphite
Cathode : object to be plated

Chemcal asorption of $[Au(CN_2)]^-$ Complex
$[Au(CN_2)]^- \longrightarrow (AuCN)_{(ad)} + CN^-$
The chemical desorption and crystallization make up the final step
$(AuCN)_{(ad)} + e^- \longrightarrow (Au^0CN)^-_{(ad)}$
$(Au^0CN)^-_{(ad)} \longleftrightarrow \text{Au lattice} + CN^-$
The equilibrium depend on the crystal orientation of the substrate and presence of impurities such as nickel that can affect the nucleation rate and hardness of the gold.

c) Explain the cffect of any two the nature of electro deposit. (05M)

Ans)JUN2014

d) Explain the process of electroless plating of copper with relevant reactions. (05M)

Ans)JUN2014

June/July2015

6a) Explain the following factors influencing rate of electro-deposit. i) current density ii) metal ion concentration iii) throwing power. (05M)

Ans) Metal salt and electrolyte concentration:The metal salt concentration is kept high to decrease the mass transfer otherwise the quality of plating is adversely affected.Electrolytes are also added to increase the conductivity of the plating bath.They also have the role of controlling the pH of bath solution particularly if the evolution of H_2 or O_2 at cathode or anode.H_2SO_4 is added to prevent hydrolysis of salt.Boric acid is used as buffering agent.

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Throwingpower:Theabilityoftheplatingbathtogiveuniformandevendepositontheentiresurfaceofcathodeofirregularshape.

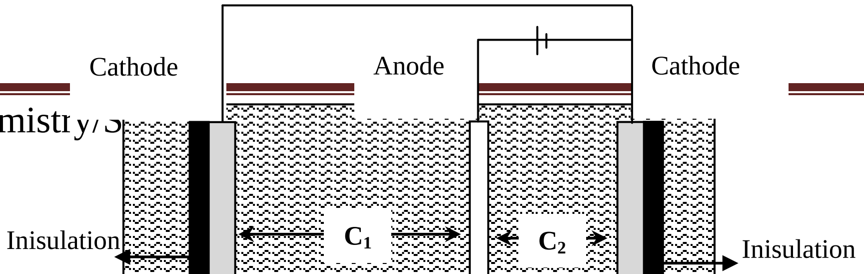
ItisdeterminedbyHaringblumcell.Itconsistsofinsulatingcontainerfilledwithelectrolytewhosethrowingpoweristobedetermined.Anodeisplacedatthecenterandtwocathodes(C_1&C_2)areplacedatdifferentdistancesd$_1$&d$_2$($d_1>d_2$)asshowninthefig.

Electroplatingiscarriedoutforsufficienttimeandweightsw$_1$&w$_2$depositedoncathodesC$_1$&C$_2$aredetermined.

Theweightofdeposit(w_1)oncathodeC$_1$islessbecauseofitsloweroverpotential.Itiscalculatedbytheequation

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

wherex= d_1/d_2&y=w_2/w_1



Determinationofthrowingpower

b)Explain the process of electroplating of chromium for engineering applications. Indicate the reasons for not employing chromium as anode. (05M)
Ans)Jan 2013
c)Write a short note on i) polarization ii) Decomposition potential (05M)
Ans) JUN2014
d)Explain the process of electroless plating of copper on PCB. (05M)
Ans)JUN2014

CORROSION SCIENCE & CORROSION CONTROL

January 2013

1 a)Define the term corrosion .Explain the electro chemical theory of corrosion wrt iron.(7M)

Ans) Definition of corrosion: Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions.

Example: When iron is exposed to air in the presence of moisture, hydrated ferric oxide (rust) is formed.

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

$2Fe(OH)_2 + 11/2\ O_2 + H_2O \longrightarrow Fe_2O_3.3H_2O$ rust(brown colour)

Electrochemical theory of corrosion: According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur.
A large number of tiny galvanic cells with anodic and cathodic regions are formed.

1.Oxidation of metal takes place at the anodic region. e.g. $Fe \rightarrow Fe^{2+} + 2e^-$

The Fe^{2+} ions dissolve, so corrosion takes place at the anodic region.

1. The electrons travel through the metal from the anodic region to cathodic region.
2. Reduction of O_2 or H^+ takes place at the cathodic region.

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

The metal is unaffected at the cathodic region.

4. Fe^{2+} and OH^- ions travel through the aqueous medium and form corrosion product.

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

5 The corrosion product may undergo further oxidation to form rust.

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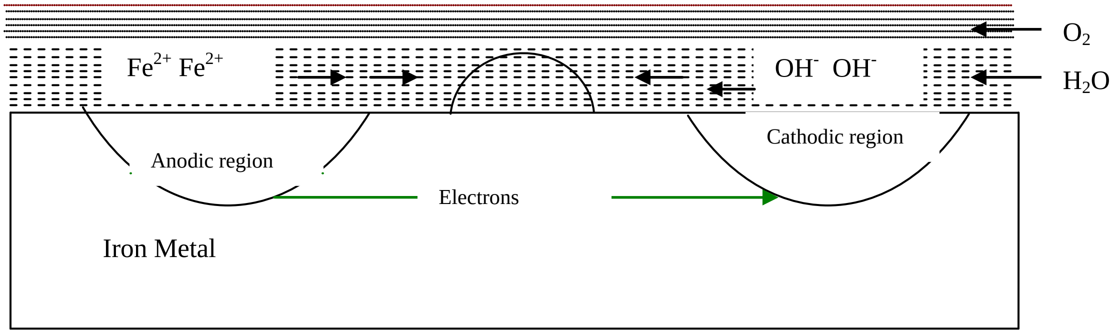


$$2Fe(OH)_2 + 11/2\ O_2 + H_2O \longrightarrow Fe_2O_3.3H_2O$$

Reactions:

Reaction at anodic region: As mentioned above, oxidation of metal takes place at anode.

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

Reactions at cathodic region: At cathode, the reaction is either a) liberation of hydrogen or b) absorption of oxygen.

a) Liberation of hydrogen (in the absence of oxygen)

In acidic medium the reaction is.

$$2H^+ + 2e^- \longrightarrow H_2\uparrow$$

In neutral or alkaline medium, the reaction is

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

b) Absorption of oxygen (in the presence of oxygen)

In acidic medium, the reaction is

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

In neutral or alkaline medium, the reaction is

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

Overall reaction:

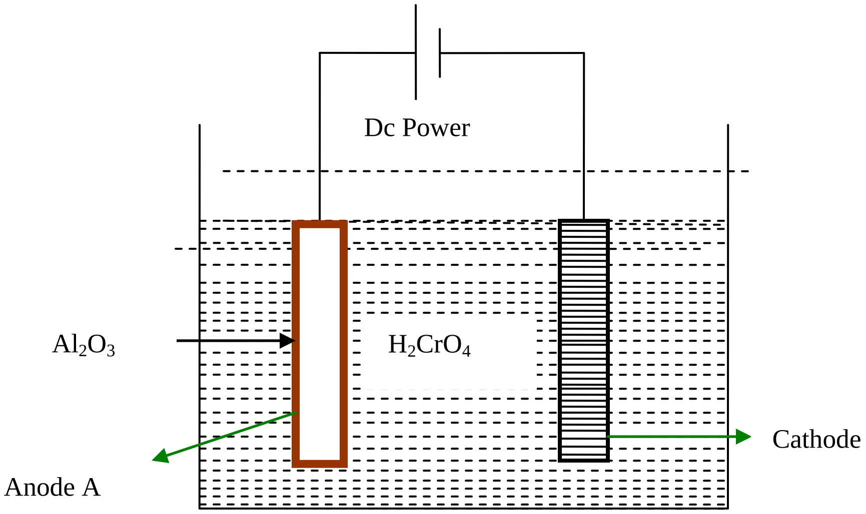
$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2\downarrow$$

$$2Fe(OH)_2 + 11/2\ O_2 + H_2O \longrightarrow Fe_2O_3.3H_2O$$

b) Write a note on galvanization (03M)

1. **Ans)<u>Galvanizing</u>:** Galvanizing is the process of coating a metal surface such as iron with zinc metal. Galvanizing of iron is an example of anodic metal coating on the surface of a cathodic metal. Galvanization is carried out by hot dipping method. It involves the following steps

.



1. The metal surface is washed with organic solvents to remove organic matter on the surface.
2. Rust is removed by washing with dilute sulphuric acid.
3. Finally, the article is washed with water and air-dried.
4. The article is then dipped in a bath of molten zinc. (Molten zinc is covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.)
5. The excess zinc on the surface is removed by passing through a pair of hot rollers.

<u>June/July13</u>

2 a) Explain the following types of corrosion i)galvanic corrosion ii)stress corrosion (06M)

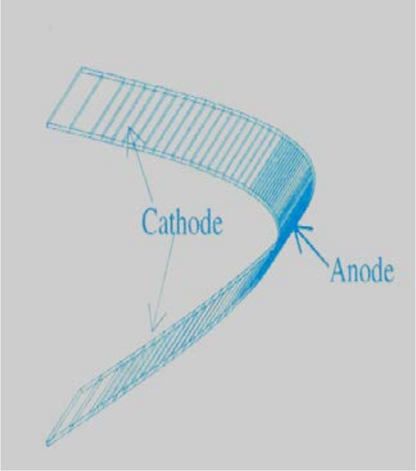
Ans) Stress corrosion

It is observed in metals under stress due to the mechanical operations such as welding ,bending ,pressing, riveting etc.In this case corrosive agents are specific and selective such as KOH or NaOH for mild steel, traces of ammonia for brass, solution of metal chlorides for stainless steel.

Stress corrosion is explained on the basis of electrochemical theory. In a corrosive environment the stressed portion act as anode under goes corrosion and stress free part become cathode.

The metal which is bended as shown in figure has a stress at the bent region.At the stressed part the metal atoms are always at higher energy levels as compare to the one free from stress.The stressed part of the metal therefore become more reactive and undergoes corrosion

Example of stress corrosion:



Caustic embrittlement

It is observed in mild steel boilers.The boiler water contains small portion of sodium carbonate added during softening purpose.In boilers this breaks up to give sodium hydroxide and carbon dioxide and makes water alkaline.

$$Na_2CO_3 + H_2O \longrightarrow 2\,NaOH + CO_2$$

Due to crack developed at stressed portion the alkaline boiler water enters in to minute hair cracks by capillary action.The water get evaporated leaving behind NaOH at cracks.As the concentration of NaOH increases it attacks the mild steel and dissolves the iron as sodium ferrate which decomposes to magnetite.

$$3\,Na_2FeO_2 + 4\,H_2O \longrightarrow 6\,NaOH + Fe_3O_4 + H_2$$

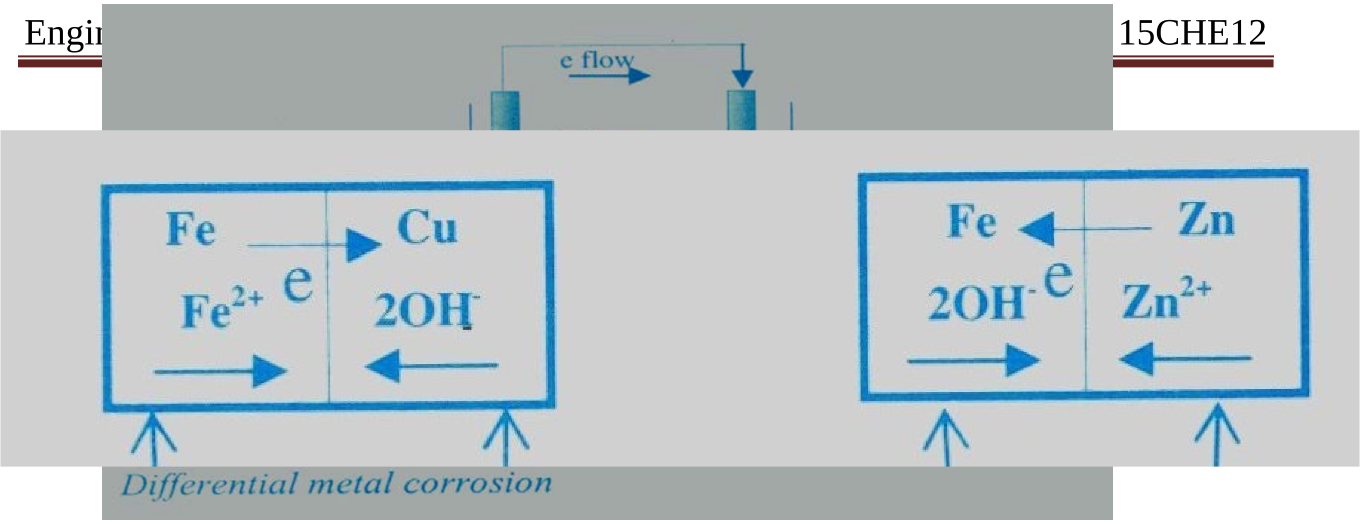
The regenerated NaOH further enhances the corrosion.It is prevented by adding sodium sulphate, tannin, lignin etc. which blocks the cracks and prevents the infiltration of alkali.

Diffrential metal corrosion(Galvanic corrosion)

When two dissimilar metals are electrically connected and exposed to corrosive environment the metal with lower electrode potential (higher up in electrochemical series) undergoes corrosion.For example when zinc and copper are electrically connected in presence of electrolyte the zinc metal with low electrode potential acts as anodic area; gets corroded as shown in figure,where as copper which is higher electrode potential become cathode.

The rate of this type of corrosion depends on difference in potential. Higher the difference in potential faster is the rate of corrosion.

Ex.:1)Steel pipe connected to copper
2)Tin coating on copper vessel 3) Zinc coating on mild steel



Differential metal corrosion

b)What is anodizing ?Explain the anodizing of Al. (05M)

Ans) Anodizing of Al:

The process of formation of a film of metal oxide on the surface of a metal by electrochemical oxidation is known as anodizing.

The aluminium article to be anodized is degreased followed by electropolishing to remove impurities present on the metal surface.It is connected to positive terminal i.e. made as anode and steel or copper is made as cathode.

Bath composition:

Electrolyte: 5-10 % Chromic acid/10% H_2SO_4/Oxalic acid

Temperature: 35^0 C

Current density: 10-20 mA/cm^2

Electrode reaction:

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

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

Finally the object is treated with nickel or cobalt acetate followed by boiling water treatment to improve corrosion resistance.

Uses:Used for soap boxes, Tiffin carriers ,window frames etc.

Dec.2013/Jan.2014

3 a) What is metallic corrosion? Explain electrochemical theory of corrosion by taking iron as example. (06M)

Ans)JAN 2013

b) explain the corrosion control technique by cathodic protection. (05M)

Ans)JAN 2013

c) Explain galvanization process. (05M)

Ans) JUL 2013

June/July 2014

4 a) Discuss the electrochemical theory of corrosion taking iron as corroding metal. (05M)

Ans)JAN 2013

b) Explain the following types of corrosion i) differential metal ii) stress iii)

water line corrosion(06M)

Ans) Water-line corrosion

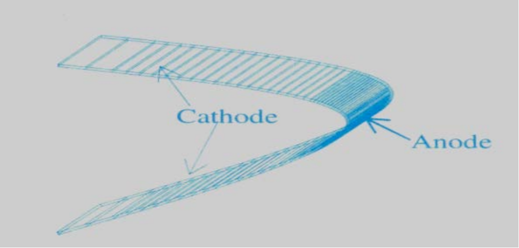
It is observed in water storage tanks,ship water lifting pipes etc. For example in water storage tank the metal Tank part inside water level exposed only to dissolved oxygen get orroded(anode) while the part above water line is exposed to higher oxygen concentration is protected(cathode).

Stress corrosion

It is observed in metals under stress due to the mechanical operations such as welding ,bending ,pressing, riveting etc.In this case corrosive agents are specific and selective such as KOH or NaOH for mild steel, traces of ammonia for brass, solution of metal chlorides for stainless steel.

Stress corrosion is explained on the basis of electrochemical theory. In a corrosive environment the stressed portion act as anode under goes corrosion and stress free part become cathode.

The metal which is bended as shown in figure has a stress at the bent region.At the stressed part the metal atoms are always at higher energy levels as compare to the one free from stress.The stressed part of the metal therefore become more reactive and undergoes corrosion



It occurs when a metal surface is exposed todifferent air / oxygen concentration. The metal part exposed to less oxygen concentration acts as anodic area and corrodes where as the higher oxygenated area is protected from corrosion(Cathode).For example when an iron strip is partiallyimmersed in aerated solution of sodium chloride as shown in figure.The metal part inside electrolyte get corroded due to anodic reaction and the more oxygenated area of the metal(cathode) is protectedEx.:Nail inside the wall corrodes, Window frame inside wall corrodes

c) Discuss the sacrificial anode & impressed current methods of corrosion control (05M)

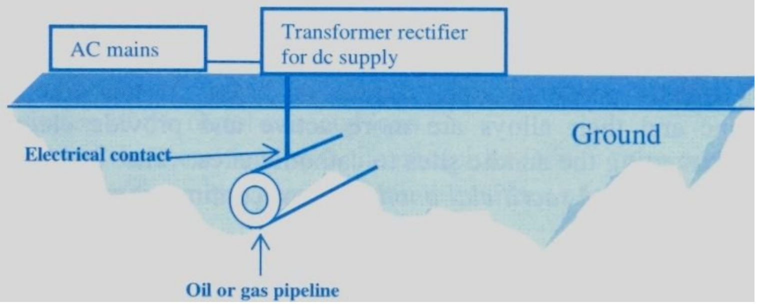
Ans) In this method the more reactive metals(sacrificial anodes) like Zn, Mg which provide electrons connected to the metal structure to be protected.The base metal will become cathodic &more reactive metal become anode, preferentiallycorrosion occurs at anode.

The sacrificial anode which gets corroded, has to be replaced to protect base metal continuously.

Example: A Mg block connected to a buried oil storage tank.

IMPRESSED CURRENT METHOD:

In this method the electrons for cathodic protection are supplied by a source of direct current .The specimen to be protected should be made –ve otherwise it corrodes. This is used in buried oil pipe lines, water storage tanks.



Dec.2014/Jan.2015

5a) Explain the clectrochemical theory of corrosion by taking iron as an exampie.(05M)
Ans)jan 2013
b) What is corrosion ? explan the following factors affectin the rate of corrosion : i) Nature of corrosion product ii) Anodic and cathodic area .(05M)
Ans) Jun 2013
c) What is Anodisin? Explain the anodizing of aluminium. .(05M)
Ans)JAN 2013
d)What is Cathodic protection ? Explain sacrificial anodic method and impressed method. (05M)
Ans)JUN 2014

June/July2015

6a) What is stress corrosion? Explain stress corrosion in boilers due to alkali with chemical reactions. (05M)
Ans) July 2013
b)How does the following factor affect the rate of corrosion? (05M)
Ans) Jun 2013
c)What is cathodic protecton? Explain sacrificial anodic method and impressed current method. (05M)
Ans) Jun2014
d)Explain the electro chemical theory of corrosion by taking iron as an example. (05M)
Ans)Jan 2015

MODULE-3

CHEMICAL ENERGY SOURCES & SOLAR ENER

January 2013

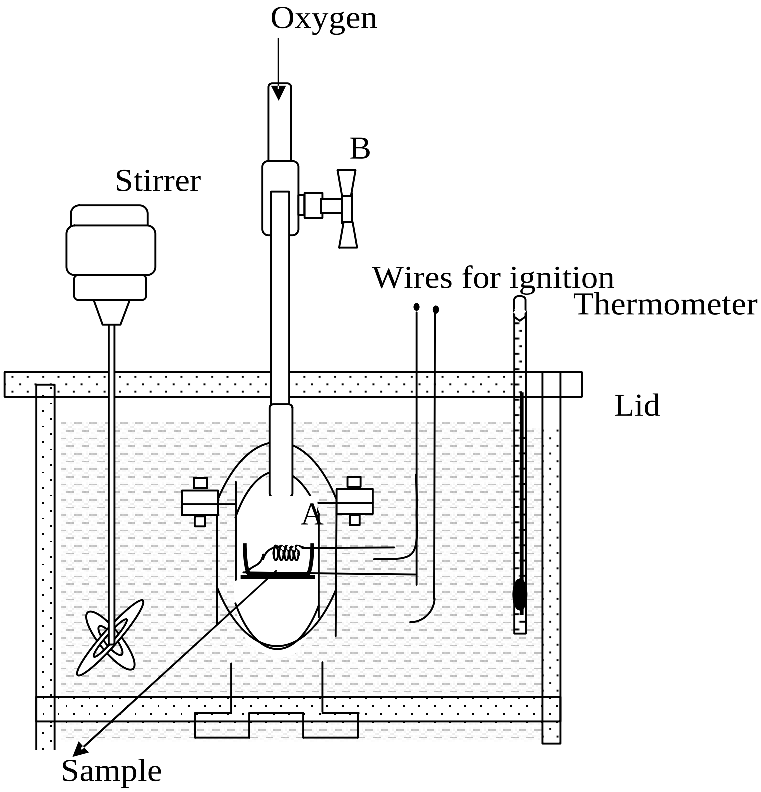
1 a)Define the term fuel. Explain the determination of calorific value of solidfuel.(06M)

Ans) A chemical fuel is a substance, which produces a significant amount of heat enegy and light energy when burnt in air or oxygen .

Principle: A known mass of the solid sample is burnt in excess oxygen. The surroundin water and the calorimeter absorbs the heat liberated. Thus the heat liberated by the fuel is equal to the heat absorbed by the water and the calorimeter.

Construction: The bomb calorimeter consists of a stainless steel vessel with an airtight lid. This vessel is called bomb. The bomb has an inlet valve for providing oxygen atmosphere inside the bomb and an electrical ignition coil for starting of combustion of fuel. The bomb is placed in an insulated copper calorimeter. The calorimeter has a mechanical stirrer for dissipation of heat and a thermometer for reading the temperature.

Working: A known mass of the solid fuel is placed in a crucible. The crucible is placed inside the bomb. The lid is closed tightly. The bomb is placed inside a copper calorimeter. A known mass of water is taken in the calorimeter. The bomb is filled with oxygen at a pressure of 25-30 atm



Observation and calculations:

Gross calorific value $= \dfrac{(w_1 + w_2)\ s\ \Delta t}{m}$ J kg^{-1}

where

$w = w_1 + w_2$

= mass of water in the calorimeter, in kg + water equivalent of the calorimeter, in kg

s = specific heat of water, in J kg^{-1} $^oC^{-1}$

$\Delta t = t_2 - t_1$ = rise in temperature, in ^oC

m = mass of the fuel, in kg

(Note: If the mass of fuel is given in grams, convert that into kg. For example, 0.2 g = 0.2 $\times 10^{-3}$ kg. If specific heat of water is given in J kg^{-1} $^oC^{-1}$, calorific value will be in J kg^{-1}. If the specific heat is given in kJ kg^{-1} $^oC^{-1}$, then the calorific value will be in kJ kg^{-1}.)

(Note: Specific heat of water is the amount of heat energy required to increase the temperature of one kg of water by one degree C.)

Problem 1. Calculate the calorific value of a sample of coal from the following data:

Mass of Coal = 0.6 g

Mass of water + water equivalent of calorimeter = 2200 g

b)Define term ocane number. Describe two methods of improving ocane number. (03M) Octane Number

Ans)

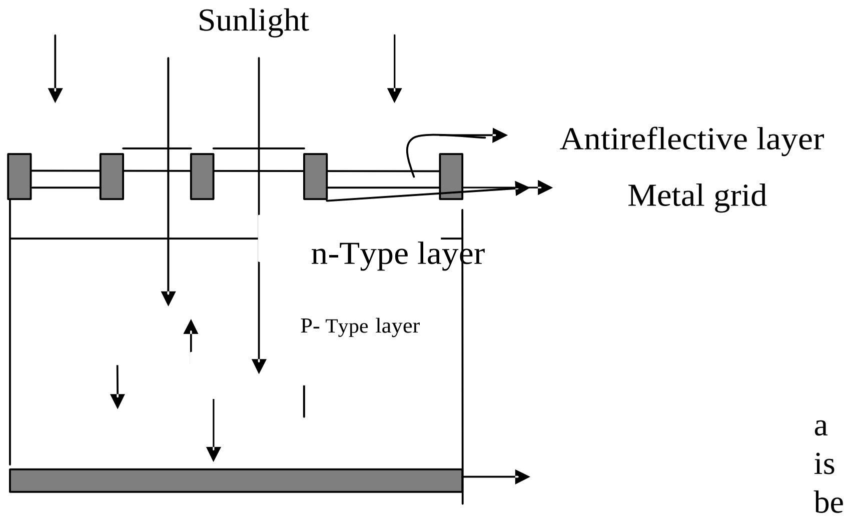
- The resistance to knocking offered by petrols is expressed in terms of an arbitrary scale called *octane number*

- Octane number is the percentage by volume of isooctane present in a mixture of isooctane and n – heptane which has the same knocking characteristic as the petrol under test.

- The octane value of isooctane is arbitrarily taken as 100 and that of n – heptane as zero.
- Different standard mixtures (90:10; 80:20, 75:25 etc) of isooctane and n–heptane are prepared and the compression ratio of each of these is determined under standard conditions.
- The compression ratio of the fuel under test is determined under the same conditions.
- Suppose the compression ratio of the fuel is same as that of 80 :20 mixture, the octane number of the fuel is 80.

c)What are photovoltaic cells? List out its advantages. (04M)

Ans) A typical silicon photovoltaic cell is composed of a thin water consisting of an ultra thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon.



a p-n junction is formed between the two.

- A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines.
- An antireflective layer between the grid lines increase the amount of light transmitted to the semiconductor.
- The cell's other electrical contact is formed by a metallic layer on the back of the solar cell.
- When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation
- The electrons are drifted to and collected at the n- type end and the holes are drifted to 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.

Photovoltaic cell provides enormous amount of energy from sun which is unlimited, inexhaustible and renewable.

- Photovoltaic cells can serve for both off grid and on grid application.
- Photovoltaic cell produces no pollution so it is environment friendly.

June/July13

2 a) Discuss the following
i)Power alcohol ii) Biodisel(06M)

Ans) POWER ALCOHOL

- This is alcohol-blended petrol.

- Gasohol is a blend of 10 – 85% of absolute ethanol and 90 – 15% of petrol by volume and is used as a fuel in the United States. Absolute alcohol is used in the preparation of Power alcohol to prevent phase separation.
- Alcohol contains higher percentage of oxygen than MTBE and hence brings about complete oxidation of petrol more effectively.
- Therefore power alcohol has better antiknocking characteristics than unleaded petrol.

Advantages of power alcohol

- power output is high
- does not release CO, causes less pollution.
- alcohol is obtained from molasses, a agricultural product and hence renewable.
- biodegradable.
-

Biodiesel

It is an alternative fuel to diesel > It is ecofriendly fuel obtained from renewable sources like vegetables oils and animal fuels . Vegetable oils like soyabean oil, palm oil,peanut oil are used to obtain biodiesel.
The triglycerides are needed to converted into biodiesel by a process caleed transesterfication .During trans esterification,the triglyceride is treated with methanol or ethanol in the presence of base to form methyl or ethyl ester of fatty acids
Triglyceride +3CH30H--------□R_1COOCH3+R_2COOCH3+ R_3COOCH3+ Glycerol
Before subjecting the oil for trans esterification process, free fatty acid of oils are to be esterfied in the presence of an acid catalyst otherwise a semisolid soap will form and it affects the performance of the engine as well as separation of glycerol from diesel layer Where R1 ,R2, R3 are long chain fatty acids , Transesterification is carried above the BP of alcohol around 55 -60.C for a period of 1 to 8 hours.The upper layer of methyl ester is washed with water and is purified further to remove excess of alcohol.
b) On burning 0.85g of a solid fuel in a bomb calorimeter the temperature of 2.1kg of water is increased from 24^0C to 27.6^0C the water equivalent of calorimeter and latent heat of steam are 1.1 Kg and 2454KJ/Kg, specific heat of water is 4.2KJ/Kg/^{0}C (It contain 2.5% of H_2)(04M)

Ans) Given m = 0.85 g = 0.85×10^{-3} kg
w_{1+W2} = (2.1+1.1) kg = kg
$\Delta t = t_2 - t_1 = 24 - 27.6 = {}^oC$
s = 4.2 kJ $kg^{-1}\ {}^oC^{-1} = 4.2 \times 10^3$ J $kg^{-1}\ {}^oC^{-1}$
L = 2457 kJ kg^{-1} = 2457 $\times 10^3$ J kg^{-1}

a) Gross C.V. = $$\frac{(w_1 + w_2)\, s\ \Delta t}{m} = \frac{2.986\ X\ 3X\ 4.2\ X\ 10^3}{0.756X\ 10^{-3}}\ J/Kg = 56920\ k\ J/Kg$$

NCV = [GCV-Latent heat of steam] = [56290 – 2.5X0.09 X2457]K J/ Kg
= 55737.2KJ/Kg

Dec.2013/Jan.2014

3 a) Define calorific value. Explain how calorific value of solid fuel is determined by bomb calorimeter. (06M)

Ans)JAN 2013

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/0 C, latent heat of steam 2457kJ/Kg. (05M)

Ans) Given $m = 0.78\ g = 0.78 \times 10^{-3}\ kg$

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

$\Delta t = t_2 - t_1 = 2.5^{o}C$

$s = 4.2\ kJ\ kg^{-1}\ {}^{o}C^{-1} = 4.2 \times 10^{3}\ J\ kg^{-1}\ {}^{o}C^{-1}$

$L = 2457\ kJ\ kg^{-1} = 2457 \times 10^{3}\ J\ kg^{-1}$

$$\text{Gross C.V.} = \frac{(w_1 + w_2)\ s\ \Delta t}{m} = \frac{3.986\ X\ 2.5X\ 4.2\ X\ 10^{3}}{0.78X\ 10^{-3}}\ J/Kg = 5365.5\ k\ J/Kg$$

NCV = [GCV-Latent heat of steam] = [5365.5 – 2.5X0.09 X2457]K J/ Kg

= 48126.2KJ/Kg

c) Explain the purification of silicon by zone refining process. (05M)

Ans) Purification of Si (Zone refining) The liquid zones are formed by heating (and by cooling the adjacent solids). Many practical heating methods have been used: electrical resistance coils, induction heating, electric arc, and electron beam, radiant energy, plasmas (ionized gases), solar heating, lasers, and peltier heating and cooling (produced by an electric current flowing across the junction between two different materials). For organic compounds resistance-heated coils of wire are most common, although radiant heating has been used. If a compound or element is liquid at room temperature, the operation is conventionally done in a refrigerator.

The usual container is one that will not contaminate the material. Glass, Vycor (heat- and chemical-resistant glass), fused silica, molybdenum, tantalum, and graphite have all been used. If zone refining is done vertically, a transparent container is helpful, but good work has been done using opaque containers such as stainless steel. If the container is a horizontal, semicircular cross-section boat, it can be opaque, because the liquid zone is readily distinguished from the solid. If a filled container, horizontal or vertical, is used, care must be taken to prevent cracking either by change in volume during freezing (or melting) or by differential thermal contraction (if the charge sticks to the containing wall). Various solutions have been found for these problems.

Contamination of the charge by the container is a problem in all purification work, but a unique solution was found for zone refining, namely,float zoning, invented by a U.S. scientist to produce ultrapureSi. This semiconducting element is even more useful than germanium for most transistor applications. In float zoning, a vertical silicon rod is held by end clamps, and a short molten zone is produced by induction heating (producing heat from electric currents induced by an alternative magnetic field) and moved along the rod. The liquid is held in place by its surface tension, which theoretically limits the stable zone height. Various ingenious induction-heating procedures have been devised for stabilizing zones of greater height. Nearly perfect single crystals of ultrapure silicon have been produced commercially by such means.

Substances that melt at high temperatures also have high surface tension, enabling them to be ultrapurified by float zoning. Examples are tungsten, molybdenum, tantalum, and Be. A half-inch bar of beryllium, normally a very hard and brittle metal, has been easily bent 360° by hand after float zoning in a high vacuum using an electron beam to produce the molten zone. Other important factors, however, must be considered in applying zone-melting techniques. These include stirring, natural convection, and the handling of vaporous substances.

June/July 2014

4 a)What is meant by cracking? Explain fluidized bed catalytic cracking(06M)

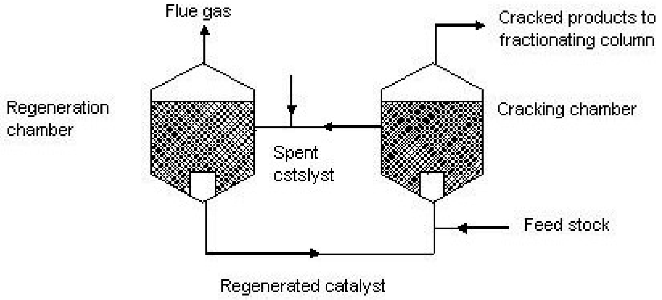
Ans) Definition of cracking: Cracking is defined as the process of converting high molecular weight hydrocarbons into lower molecular weight hydrocarbons.

$$C_{14}H_{30} \longrightarrow C_7H_{16} + C_7H_{14}$$

Fluidized bed catalytic cracking:

Principle: In fluidized bed catalytic cracking, the powder catalyst is kept agitated by gas streams (cracking fuel) so that the catalyst can be handled like a fluid system. This also results in a good contact between the catalyst surface and the reactant.

Construction: A schematic diagram of fluidized bed catalytic cracking method is shown in the following figure.



Optimum conditions:

Catalyst used: y- type zeolite activated with a rare earth oxide(Al_2O_3+ SiO_2)

Temperature: 550^0 C

Working: The feed stock vapours are passed into cracking chamber. The reactants undergo cracking in the presence of catalyst. The products are passed to a fractionating column. Spent catalyst from the cracking chamber is continuously transported into the regeneration chamber through an air stream. The carbon deposited on catalyst particles is burnt off in regeneration Chamber. The regenerated catalyst is transported back into the cracking chamber together with feed stock.

b) What is knocking?What are ill effects?Give the mechanism of knocking (05M)

Ans) Knocking in IC Engines

- The power output and efficiency of an IC engine depends on the *Compression ratio* which is the ratio of the volume of the cylinder at the end of the suction stroke to the volume of the cylinder at the end of the compression stroke.

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

- Under ideal conditions, in an IC engine the petrol-air mixture drawn into the cylinder of the engine undergoes compression and then ignited.
- The hydrocarbons in petrol undergo complete combustion and the flame propagates smoothly.
- Sometimes, due to deposits of carbon on the walls of the cylinder the hydrocarbons in petrol form peroxy compounds.
- The accumulated peroxides decompose suddenly and burst into flames producing shock waves.
- The shock wave hits the walls of the engine and the piston with a rattling sound.
- This is knocking.
- The reactions that take place in an IC engine are given below (taking ethane as an example for the hydrocarbon present in petrol):

Under ideal conditions

$$C_2H_6 + 7/2\,O_2 \rightarrow 2\,CO_2 + 3H_2O$$

Under knocking conditions

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

(Dimethyl peroxide)

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

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

$$HCHO + O_2 \rightarrow H_2O + CO_2$$

- Note that the overall reaction is the same under both the conditions. One molecule of ethane reacts with 7/2 molecules of oxygen forming carbon dioxide and water with the release of energy.
- Under ideal conditions, the energy is released at a uniform rate.

- Under knocking conditions, the energy is released slowly at first followed by a lag (formation of peroxides) and finally the energy is released at a very fast rate (decomposition of peroxides) Ill effects of knocking

1. Decreases life of engine
2. Causes Piston wrap
3. Consumption of fuel is more

c) What are chemical fuels.Give the classification of fuels with example (05M)

Ans) A chemical fuel is a substance, which produces a significant amount of heat enegy and light energy when burnt in air or oxygen

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

Dec.2014/Jan.2015

5 a) What is Cracking ? Explain the fluidized cracking process.(05M)

Ans) June/July 2014

b) 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 28^0C.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 (05M)

Ans) Given m = 0.75 g = 0.76 × 10^{-3} kg

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

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

$s = 4.2\ kJ\ kg^{-1}\ ^oC^{-1} = 4.2 \times 10^3\ J\ kg^{-1}\ ^oC^{-1}$

$L = 2457\ kJ\ kg^{-1} = 2457 \times 10^3\ J\ kg^{-1}$

$$\text{a) Gross C.V.} = \frac{(w_1 + w_2)\ s\ \Delta t}{m} = \frac{2.986\ X\ 3X\ 4.2\ X\ 10^3}{0.756X\ 10^{-3}}\ J/Kg = 49351.5\ k\ J/Kg$$

NCV = [GCV-Latent heat of steam] = [49351.5 – 2.5X0.09 X2457]K J/ Kg

= 48798.2KJ/Kg

c)Discuss the production of solsr grade silicon by Union –Carbide process. (05M)

Ans) Solar grade silicon has impurities in the ppb level is required for polysilicon used in semiconductor industry. It can be prepared by using two methods.

Essential silicon is made by the reduction of silica with carbon.At high temperature silica is reduced to elemental silica. SiO_2+ 2C-----------□Si+2CO

CO is further oxidized to CO_2 & reduced to atmosphere the silica is in molten state.

Refining:

O2 is passed through molten silicon mixed with a flux of silica.Al, Ca, Mg are oxidized to respective oxides. These oxides combines with silica forming a slag of silicates.The slag is removed and refined melt is poured into moulds where silica is solidifies.This is called Metallurgical grade silica.

$4Al+3SiO_2$---------□$3Si+2Al_2O_3$

$2Ca+ SiO_2$-------□$Si +2 CaO$

$2Mg+ SiO_2$-----□$Si +2MgO$

To get semiconductors grade silicon metallurgical grade Si is treated with dry HCl gas at 300^0C .

$$Si + 3HCl \longrightarrow SiHCl_3 + H_2$$

Tri chloro silane

$Si + 4HCl$---------□$SiCl_4+ 2Cl_2$

Tetra chloro silane

The mix is treated to get pure tri chloro silane

$SiCl_4+ H_2$----------□$HSiCl_3+ HCl$

The Union Carbide process:

This process involves the following steps:

The hydrogenation of tetrachlorosilane through a bed of metallurgical silicon is carried out in a fluidized bed reactor

$$3SiCl_4 + 2H_2 + Si \longrightarrow 4SiHCl_3$$

The trichlorosilane is separated by distillation while the unreacted tetrachlorosilane is recycled back to the hydrogenation reactor.

The purified trichlorosilane is passed through a fixed bed column filled with quaternary ammonium ion exchange resin acting as catalyst. Trichlorosilane gets converted into dichlorosilane.

$$2SiHCl_3 \longrightarrow SiH_2Cl_2 + SiCl_4$$

The products are separated by distillation, tetrachlorosilane is recycled to the hydrogen reactor and dichlorosilane is passed through a second fixed bed column filled with quaternary ammonium ion exchange resin. Dichlorosilane is converted into silane.

$$3SiH_2Cl_2 \longrightarrow SiH_4 + 2SiHCl_3$$

The above products are separated by distillation and trichlorosilane is recycled to the first bed column. Silane is further purified by distillation and then pyrolized to produce polysilicon onto heated silicon seed rods mounted in a metal bell-jar reactor

$$SiH_4 \longrightarrow 2H_2 + Si$$

d)what are the advantages and disadvantages of PV –Cells? (05M)

Ans) Advantages of PV cells :

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

Disadvantages of PV cells:

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

e) Explain the determimation of calorific value of a solid fuel using calorimeter.

Ans)JAN 2013

f) Define the following term i)Chemical fuel ii) Calorific value iii) biodiesel iv) octane number v) Reforming of petrol (05M)

Ans) chemical fuel: A chemical fuel is a substance, which produces a significant amount of heat enegy and light energy when burnt in air or oxygen.

Biodiesel :

It is an alternative fuel to diesel > It is ecofriendly fuel obtained from renewable sources like vegetables oils and animal fuels . Vegetable oils like soyabean oil, palm oil,peanut oil are used to obtain biodiesel.

The triglycerides are needed to converted into biodiesel by a process caleed transesterfication .During trans esterification,the triglyceride is treated with methanol or ethanol in the presence of base to form methyl or ethyl ester of fatty acids

Triglyceride +3CH30H--------□R_1COOCH3+R_2COOCH3+ R_3COOCH3+ Glycerol

Before subjecting the oil for trans esterification process, free fatty acid of oils are to be esterfied in the presence of an acid catalyst otherwise a semisolid soap will form and it affects the performance of the engine as well as separation of glycerol from diesel layer Where R1 ,R2, R3 are long chain fatty acids .

calorific value: It is defined as the amount of heat released when unit quantity of a fuel is completely burnt in air or oxygen and the products of combustion are let off into the atmosphere.

Octane Number

- The resistance to knocking offered by petrols is expressed in terms of an arbitrary scale called *octane number*

- Octane number is the percentage by volume of isooctane present in a mixture of isooctane and n – heptane which has the same knocking characteristic as the petrol under test.

- The octane value of isooctane is arbitrarily taken as 100 and that of n – heptane as zero.
- Different standard mixtures (90:10; 80:20, 75:25 etc) of isooctane and n–heptane are prepared and the compression ratio of each of these is determined under standard conditions.

The compression ratio of the fuel under test is determined under the same conditions.

reformation of petrol: Conversion of straight chain hydrocarbons in petrol into branched chain, cyclic and aromatic hydrocarbons, resulting in upgradation of petrol is known as reformation.

g) Discuss the construcrtion and working of a PV –Cell. (05M)

Ans)JUN 2013

h)What is doping ? Discuss the purification of silicon of zone –refining. (05M)

Ans)JUN2014

June/July2015

6a) On burning 1.15g of a coal sample in a bomb calorimeter, the temperature of 3.5kg of water in the calorimeter increased from 26.5^0 C.to 28.5^0 C. water equivalent of calorimeter is 325g. Specific heat of water 4.187kJ/kg/^{0}C. Latent heat of steam =587 Cal/g. If the fuel contains 4% hydrogen, Calculate gross and net calorific values. (05M)

Ans) Given $m = 0.75\text{ g} = 0.76 \times 10^{-3}\text{ kg}$

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

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

$s = 4.2\text{ kJ kg}^{-1}\ ^oC^{-1} = 4.2 \times 10^3\text{ J kg}^{-1}\ ^oC^{-1}$

$L = 2457\text{ kJ kg}^{-1} = 2457 \times 10^3\text{ J kg}^{-1}$

a) Gross C.V. $= \frac{(w_1 + w_2)\, s\, \Delta t}{m} = \frac{2.986\ X\ 3X\ 4.2\ X\ 10^3}{0.756X\ 10^{-3}}\ J/Kg = 49351.5\ k\ J/Kg$

NCV = [GCV-Latent heat of steam] = [49351.5 – 2.5X0.09 X2457]K J/ Kg
= 48798.2KJ/Kg

b)Explain synthesis of petrol by Fischer Tropseh process. (05M)

Ans) 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.

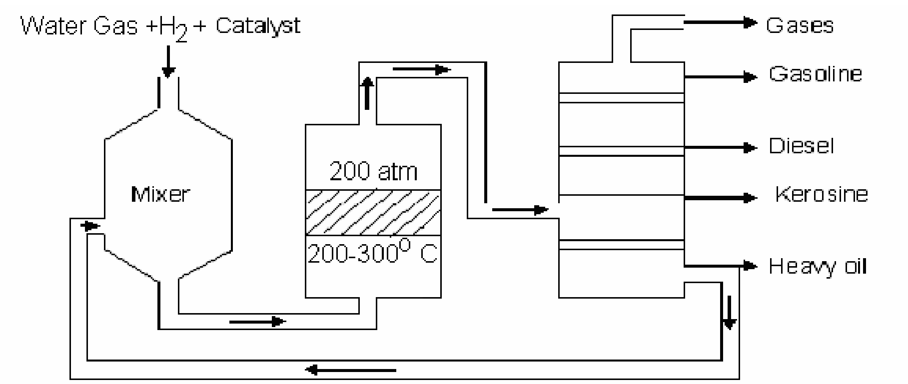
$C + H_2O \longrightarrow CO + H_2$ (water gas)

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.

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

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



c)Define octane number. Explain reformation of petrol with equations. (05M)

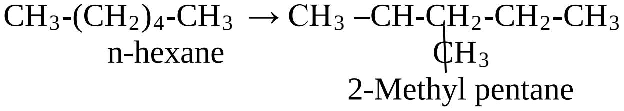
Ans) Reforming of petrol:

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.



$$CH_3\text{-}(CH_2)_4\text{-}CH_3 \rightarrow CH_3\text{–}CH\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H_2\text{-}CH_2\text{-}CH_3$$

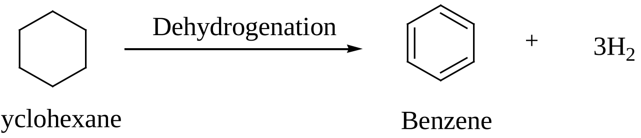
n-hexane

2-Methyl pentane

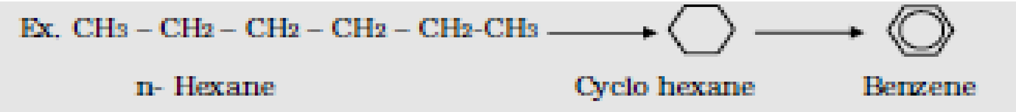
Dehydrogenation: This process involves the conversion of cycloalkanes into aromatic compounds.

$$C_6H_{12} \longrightarrow C_6H_6 + 3H_2$$

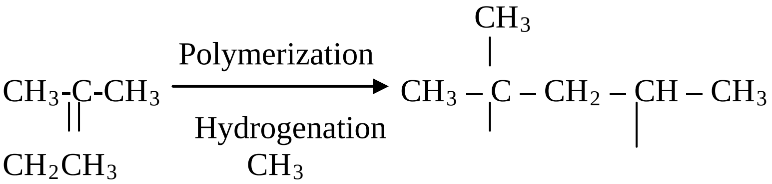
Cyclohexane Benzene



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



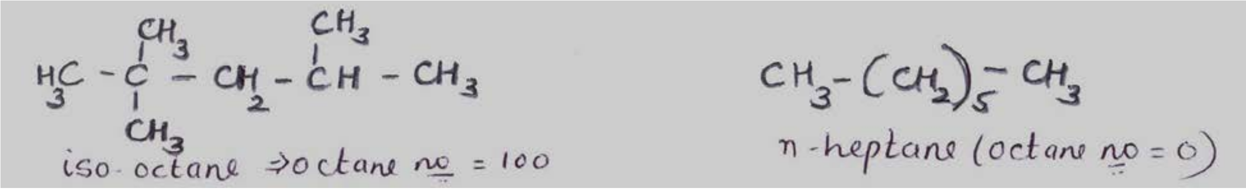
Polymerization: This process involves the formation of high molecular mass followed by hydrogenation.



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

CH3

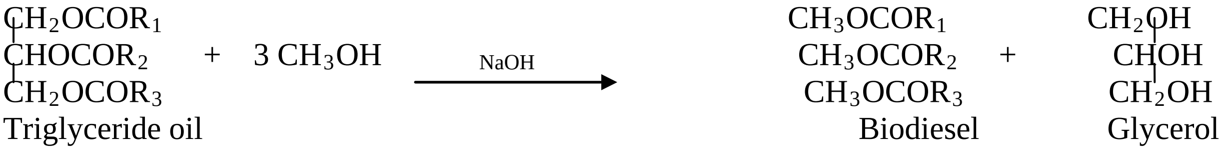
Octane number: The knocking characteristics of petrol sample are described by the octane number. Higher the octane number lower is the tendency to knock and better is the quality of the petrol.Isooctane (2,2,4-trimethyl-pentane) has least knocking tendency and its octane number is arbitrarily fixed as 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.



d)What is biodiesel? How is it prepared ? What are the advantages? (05M)

Ans) **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:



$$\underset{\text{Triglyceride oil}}{\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array}} + 3\,CH_3OH \xrightarrow{NaOH} \underset{\text{Biodiesel}}{\begin{array}{l} CH_3OCOR_1 \\ CH_3OCOR_2 \\ CH_3OCOR_3 \end{array}} + \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}}$$

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.

e)Discuss the construction and working of a photovoltaic cell. (05M)

Ans) JUN 2013

f)Explain the production of solar grade silicon by Union- Carbide process. (05M)

Ans) Dec14/Jan15

g)What is doping? Explain doping of Si by diffusion Technique. (05M)

Ans) **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 B Br_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.

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

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.

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

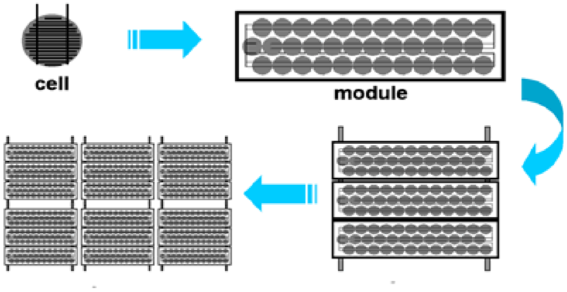
A n-type silicon can be obtained by heating a silicon walfer below its melting point in an atmosphere of n-type impurity such as Phosphorus. The valency of silicon is 4.

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.

h) Explain the designing of PV cells- Module, panel and Array. (05M)

Ans) 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.



MODULE-4
HIGH POLYMERS

January 2013

1 a)Explain the mechanism of addition polymerization with respect to ethylene. (06M)

- **Ans)** 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' ex. Azo compounds ,Peroxides ,Peracids

Initiation:

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

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

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

$$C_6H_5^{\bullet} + CH_2 = CH_2 \rightarrow R - CH_2 - C^{\bullet}H_2$$

Propagation:

- In this step, the radical site at the first monomer uint 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

2

$$R - CH_2 - C^{\bullet}H_2 + CH_2 = CH_2 \rightarrow R - CH_2 - CH_2 - CH_2 - C^{\bullet}H_2$$

- 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

$$R - CH_2 - CH_2 - CH_2 - C^{\bullet}H_2 + CH_2 = CH_2 \rightarrow R - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - C^{\bullet}H_2$$

$$R - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - C^{\bullet}H_2 + CH_2 = CH_2 \rightarrow R - [CH_2 - CH_2]_3 - CH_2 - C^{\bullet}H_2$$

$$R - [CH_2 - CH_2]_{n-1} - CH_2 - C^{\bullet}H_2 + CH_2 = CH_2 \rightarrow R - [CH_2 - CH_2]_n - CH_2 - C^{\bullet}H_2$$

Termination:

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:

$$R – [CH_2 – CH_2]_m – CH_2 – C^{\bullet} H_2 \;+\; R – [CH_2 – CH_2]_n – CH_2 – C^{\bullet} H_2 \rightarrow$$

$$R – [CH_2 – CH_2]_m – CH_2 – CH_2 – CH_2 – CH_2 – [CH_2 – CH_2]_n – R$$

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.:

$$R – [CH_2 – CH_2]_m – CH_2 – C^{\bullet} H_2 \;+\; R – [CH_2 – CH_2]_n – CH_2 – C^{\bullet} H_2 \rightarrow$$

$$R – [CH_2 – CH_2]_m – CH_2 – CH_3 \;+\; R – [CH_2 – CH_2]_n – CH = CH_2$$

- This type of termination results in formation of two molecules of shorter chain length, while a single molecule of longer chain length is obtained in the first method of termination.

b) Explain the term glass transition temperature. Mention the factors that influence Tg. (05M)

Ans) Glass transition temparature(Tg)

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

Factors influencing glass transition temparature.

i.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 aromatic or bulky side group hinder the freedom of rotation and restricts the chain mobility thereby increases Tg value.

ii.Presence of plasticizers:Addition of low molecular compound called plasticizer to the polymer reduces the Tg,since plasticizer imparts flexibility to the polymer.

iii.Molecular mass:Tg decreases as the molecular weight of a polymer decreases. This is because there are more chain

5

ends in low molecular weight polymer. It is not significantly affected if the degree of polymerization is above250.

c)Describe the manufacture of the following polymers: i]Teflon; (05M)

Ans) Monomer : Tetra fluro Ethylene($CF_2 = CF_2$)

Pressure : High pressure

Initiator : Oxygen or Hydrogen peroxide

Polymerisation process:

$$n\,[CF_2 = CF_2] \rightarrow -CF_2 - CF_2\text{-}CF_2 -[\,CF_2\text{-}CF_2]_n - CF_2 - CF_2\text{-}CF_2 -$$

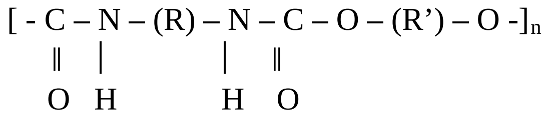
Dec.2013/Jan.2014.

2 a) What is glass transition temperature? Explain any three factors that influence the glass transition temperature. (05M)

Ans) JAN 2013

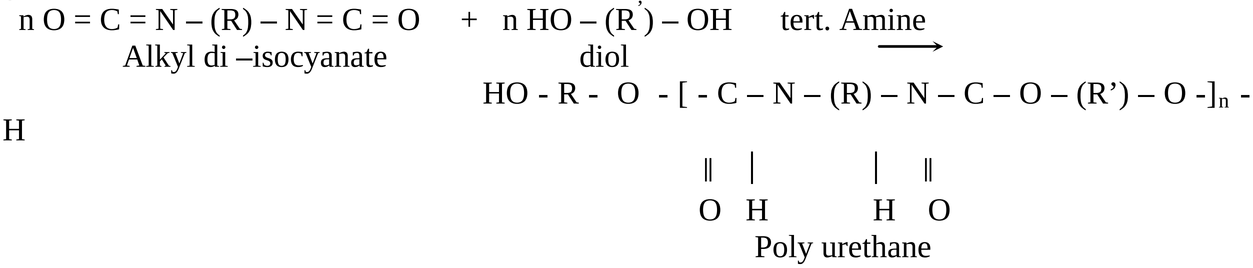
b) Explain the manufacture of plastic by compression moulding and injection moulding technique. (05M)

Ans) 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:



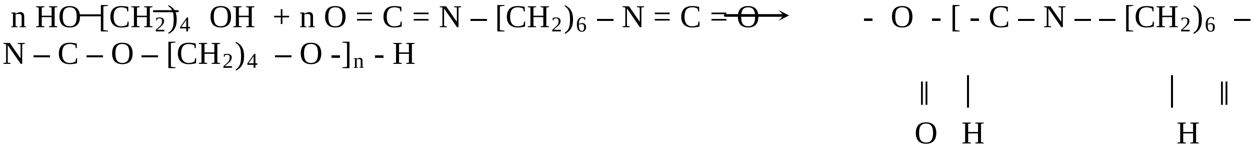
$$[-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(R)-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-O-(R')-O-]_n$$

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:



$$\underset{\text{Alkyl di –isocyanate}}{n\,O=C=N-(R)-N=C=O} + \underset{\text{diol}}{n\,HO-(R')-OH} \xrightarrow{\text{tert. Amine}} \underset{\text{Poly urethane}}{HO-R-O-[-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(R)-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-O-(R')-O-]_n-H}$$

Ex.Perlon urethane



$$n\,HO-[CH_2)_4\,OH + n\,O=C=N-[CH_2)_6-N=C=O \rightarrow -O-[-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}--[CH_2)_6-\underset{\underset{H}{|}}{N}-\underset{\|}{C}-O-[CH_2)_4-O-]_n-H$$

c)Give the synthesis of i) Teflon (06M)

Ans)JAN 2013

June/July 2014

3 a) What is meant by cracking? Explain fluidized bed catalytic cracking (06M)

Ans) JUN 2013

b)What is knocking?What are ill effects?Give the mechanism of knocking(05M)

Ans)JAN 2013

c) What are chemical fuels.Give the classification of fuels with example (05M)

Ans)JUN2014

Dec.2014/Jan.2015

4 a)Explain the free radical mechanism of addition polymerization by taking Vinyl chloride as a monomer.

Ans) Initiation:

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

$$[C_6H_5COO]_2 \xrightarrow{\qquad} 2\ C_6H_5COO^\bullet \xrightarrow{\qquad} 2\ C_6H_5^\bullet + CO_2$$

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

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

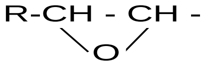
$$R - [CH_2 - CHCl]_m - CH_2 - CH_2Cl \ + \ R - [CH_2 - CHCl]_n - CH = CHCl$$

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

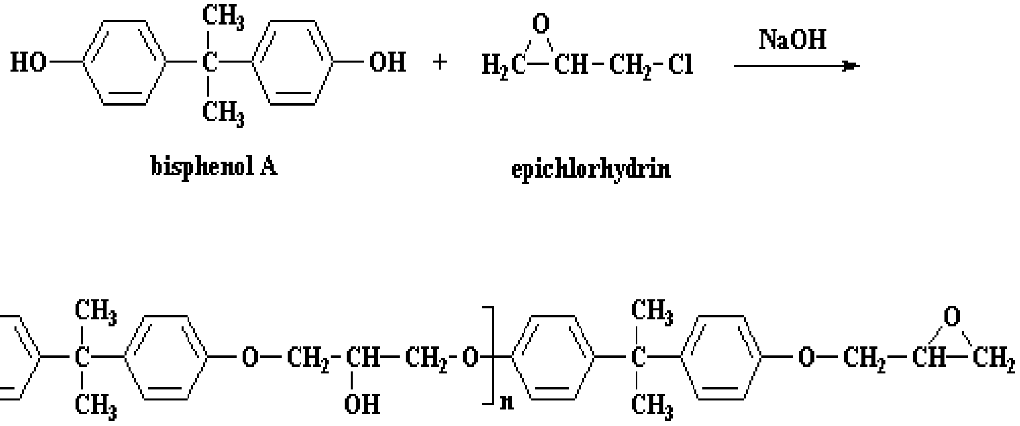
b) what are adhesives?explain the synthesis and applications of epoxy resin.

Ans) 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.

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.

c) write the syathesis and applications of the following polymers :

i) polymethyl methacrylate ii) Teflon.

Ans) Poly Tetra Fluro Ethylene (PTFE)or Teflon

Monomer : Tetra fluro Ethylene($CF_2 = CF_2$)

Pressure : High pressure

Initiator : Oxygen or Hydrogen peroxide

Polymerisation process:

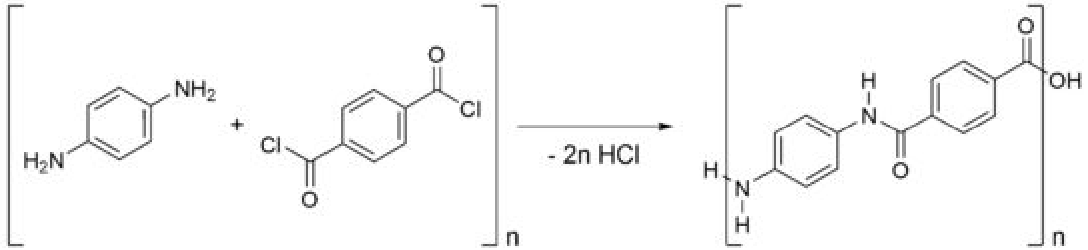
$$n\ [CF_2 = CF_2] \quad \rightarrow \quad -CF_2 - CF_2\text{-}CF_2 - [\ CF_2\text{-}CF_2]_n - CF_2 - CF_2\text{-}CF_2 -$$

Properties:

Linear and no branches, presence of highly electronegative F atoms and regular configuration results strong attractive forces. Because of these strong attractive forces it is extreme toughness, high softening point(about 360^0C)and high chemical resistance except molten alkali and hot fluorine solution. Mechanical properties unchanged over wide temperature range. Resistant to strong acids.

d)what are polymer composites ? explain the preparation and uses of Kevlar fiber.

Ans) 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.



The reaction of 1,4-phenylene-diamine (*para*-phenylenediamine) with terephthaloyl chloride yielding kevlar. Kevlar (poly paraphenylene terephthalamide) production is expensive because of the difficulties arising from using concentrated sulfuric acid, needed to keep the water-insoluble polymer in solution during its synthesis and spinning.[*citation needed*]

e) calculate the number average and weight average molecular mass of a polymer with the following composition

Cl cl–CH_2 –CH– is 40% ; –CH_2–CH– is 30% ;
200 400
Cl
–CH $_2$–CH – is 30% Given At Wt . of C= 12 . Atomic weight of h= 1 ; and Atomic
500
Weight of ct= 35.5

Ans)

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

=40x12500+30x25000+30x31250/40+30+30

=21875

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

=$40x(12500)^2+30x(25000)^2+30x(31250)^2$/40x12500+30x25000+30x31250

=24821.42

f)What is glass transition temperature?how is it affected by

i) Intermolecular forces ii) flexibility

Ans) 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.

Glassy state $\longrightarrow$ Viscoelastic state $\longrightarrow$ Viscofluid State
(Hard and brittle) Tg (Rubbery) Tm (Polymer melt)

***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.

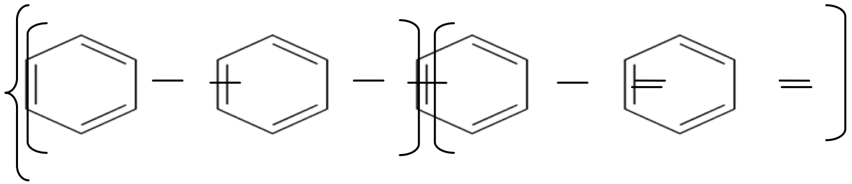
Intermolecular forces: Due to presence of large number of polar groups in the polymer chain leads to strong intermolecular forces of attraction which restrict the chain mobility. This leads to increase in Tg. For example polypropylene is -18^0C and nylon 66 is 57^0C. In nylon 66 the hydrogen bonding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

g)What is conducting polymer? Explain the mechanism of conduction in polyaniline

Ans)

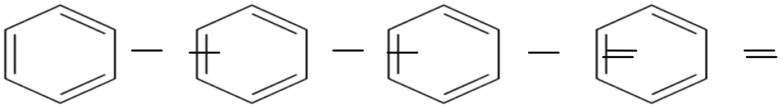
<u>Polyaniline:</u> Distilled 0.2M aniline dissolved in pre cooled 1M HCl solution and maintained at 5^0C. Calculated amount of 0.5M$(NH_4)_2S_2O_8$(oxidizing dopant) dissolved in 1M HCl is added slowly to above prepared solution. Since the polymerization reaction is exothermic, to maintain temperature 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.

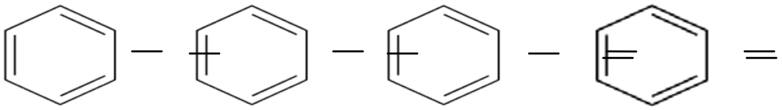
Different oxidation states of polyaniline are



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.



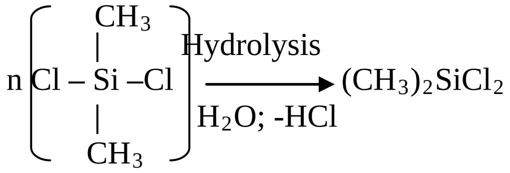


h)Give the synthesis and uses of the following polymers :

i) Silicon rubber ii) Polycarbonates.

Ans) 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

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



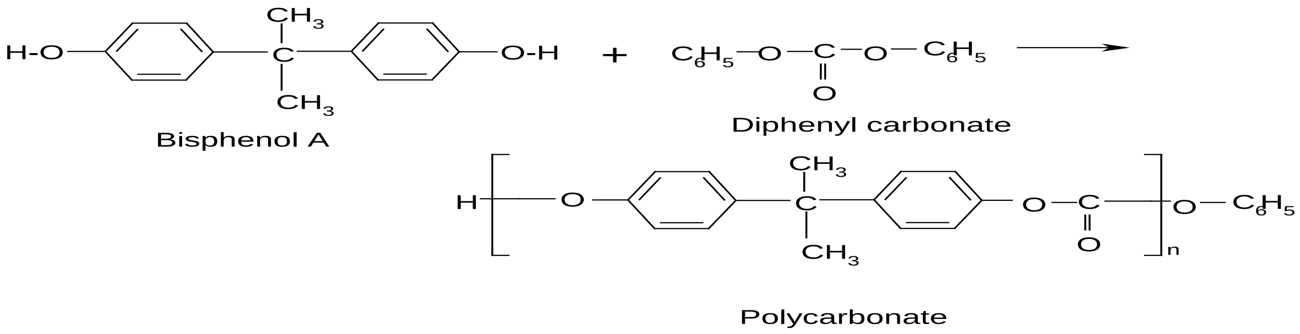
$$n\left[\begin{array}{c} CH_3 \\ | \\ Cl - Si - Cl \\ | \\ CH_3 \end{array}\right] \xrightarrow[H_2O;\ -HCl]{Hydrolysis} (CH_3)_2SiCl_2$$

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 silicon

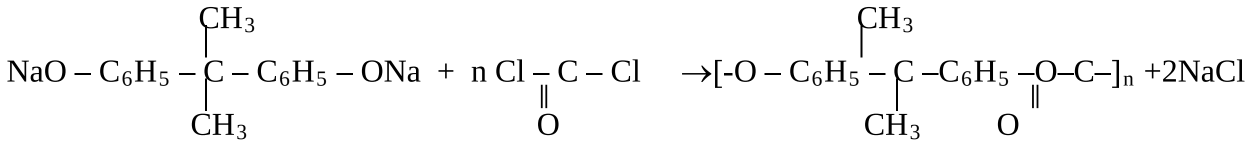
Polycarbonates are condensation polymers - polyesters of phenols and carbonic acid, HO – CO – OH. They contain [- O – CO – O -] linkage.

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.



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

Sodium salt of Bisphenol A Phosgene Polycarbonate

June/July2015

6a) Explain the free radical mechanism of polymerization taking vinay Chloride As monomer. (06M)

Ans) Dec.2014/Jan.2015

b)Differentiate addition and condensation polymerization. (04M)

Ans) 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’

$$n\,[CH_2 = CH_2] \rightarrow \ -CH_2 - CH_2\text{-}CH_2 -[CH_2\text{-}CH_2]_n - CH_2 - CH_2\text{-}CH_2 -$$

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

c)Give the synthesis reaction of Teflon and polycarbonate. (04M)

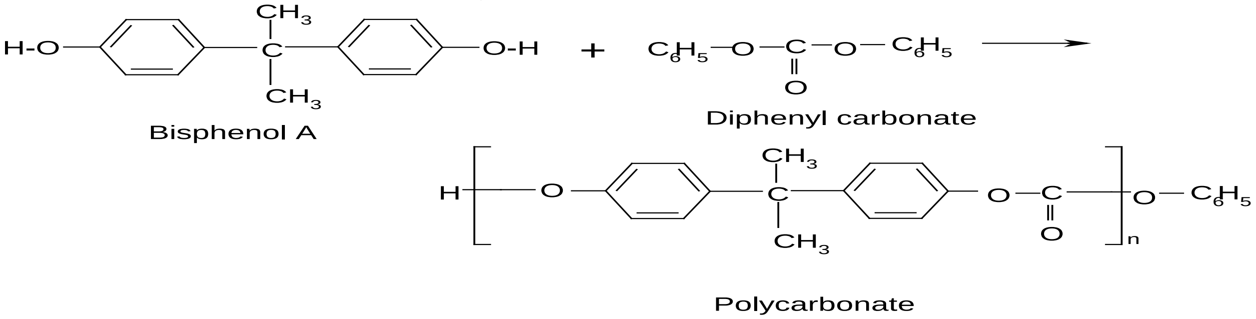
Ans) Dec.2014/Jan.2015

Polycarbonates:

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

Preparation:

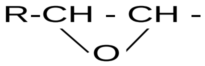
They are prepared by condensing Bisphenol A with diphenyl carbonate involving elimination of phenol in presence of tert.amine catalyst



d) Discuss the synthesis, properties and applications of epoxy resin. (06M)

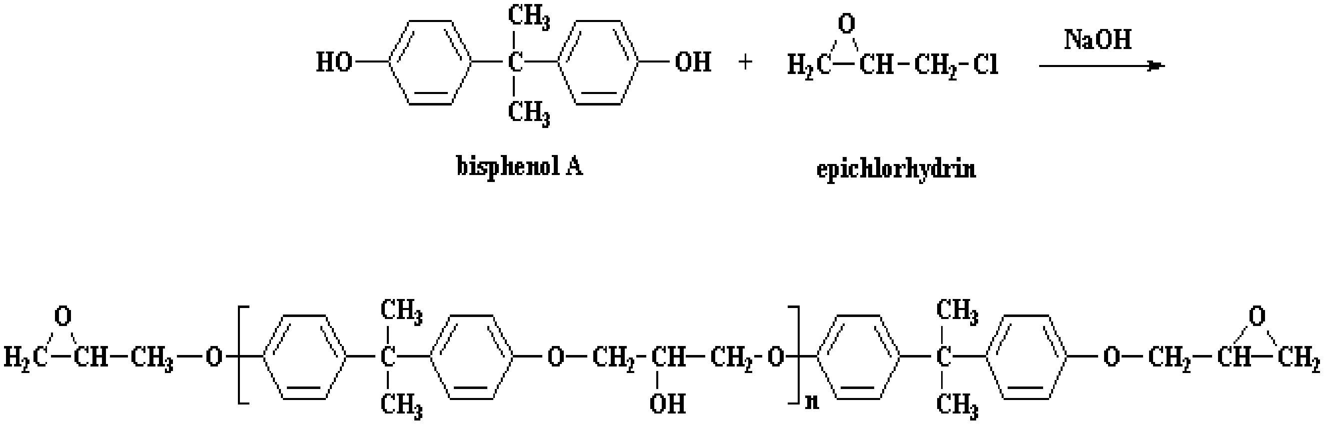
Ans) **Epoxy Resins [Araldite]**

Epoxy resins are basically poly ethers and containing epoxy group:



$\underset{\diagdown O \diagup}{R\text{-}CH - CH -}$

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 $145\text{-}155^oC$.

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.

e)Explain the following structure property relationships of polymers.
i) Crystalinity ii) Elasticity iii) Plastic deformation. (06M)

Ans)_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.

- **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.

f)Explain the following factors influencing the Tg.
i) Flexibilityii) Branching and cross linking (04M)

Ans)_ 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

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.

g)what is conducting polymer? Explain the mechanism of conduction in polyaniline and give the applications. (06M)

Ans)_ Dec.2014/Jan.2015

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

January 2013

1 a)Define BOD and COD.why COD is always greater than BOD. (05M)

Ans) "BOD is defined as the amount oxygen required by microorganism to oxidize all organic matter present in one litre of waste water at 20^{o}C over a period of 5 days"

It is defined as the amount of oxygen consumed in the

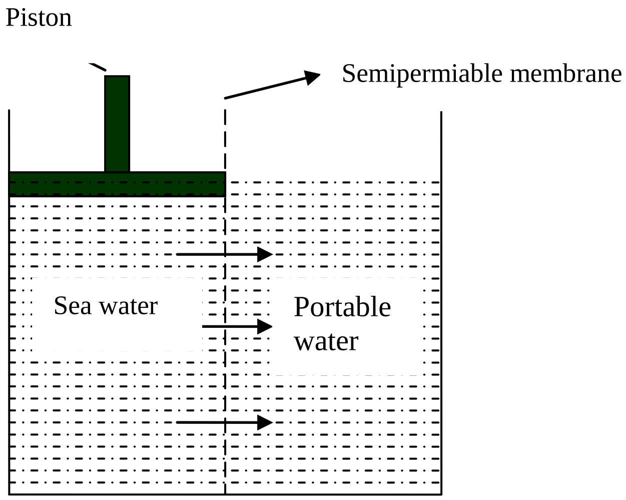
chemical oxidation of organic and inorganic impurities present in one litre of waste water by using acidified $K_2Cr_2O_7$ solution in presence of silver sulphate and mercuric sulphate as catalyst.

b)Explain reverse Osmosis process. (05M)

Ans) Reverse osmosis:

The movement of solution molecule through semi permeable membrane from higher concentration to lower concentration **or** the process which reverse to the natural spontaneous osmosis is called reverse osmosis.

RO system tube contains a semi permeable membrane made up of polymethylacrylate and polyamide. Brackish water and fresh water is separated by semi permeable membrane. When the brackish water (1000ppm) supplied with high pressure, water flow from brackish water to fresh water, Fresh water is collect from fresh water outlet and brackish water (2000ppm) is discharged in to the environment.



June/July13

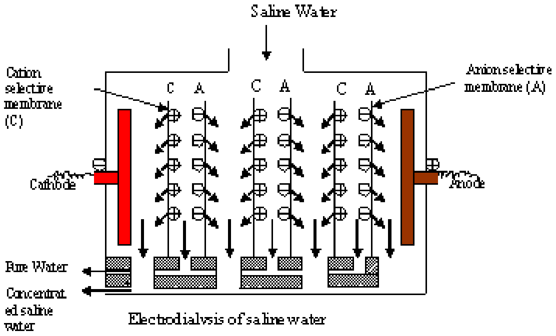
2 a) Describ the electrodialysis method of desalination of water. 06M)

Ans)) Electro dialysis:

The process of decreasing the concentration of salts in saline water using ion-selective membrane under the influence of an applied emf is called as electro dialysis.

Process: It apparatus consists of two electrodes and ion selective membrane. The anode is placed near the anode selective membrane and cathode is placed near the cathode selective membrane.

When the emf is applied across two electrodes, the cation present in salt water move towards the cathode through cation selective membrane and anion move towards the anode through anion selective membrane. As a result of this, there is a decrease in salt concentration in the CA compartment and increase in salt concentration in AC compartment.



Electrodialysis of saline water

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

b) 25cm3 of a sample of COD analysis was reacted with 15cm3 of .2N K2Cr2O7 & the unreacted K2Cr2O7 requires 8.2cm3 0f .2N FAS .25cm3 of same K2Cr2O7 & 25cm3 of distilled water under the same condition requires 16.4cm3 0f .1N FAS.What is COD of water

Ans) COD= Nx(V_2-V_1) of K2Cr2O7x8000/ V of effluent

=.2x6.8x8000/25

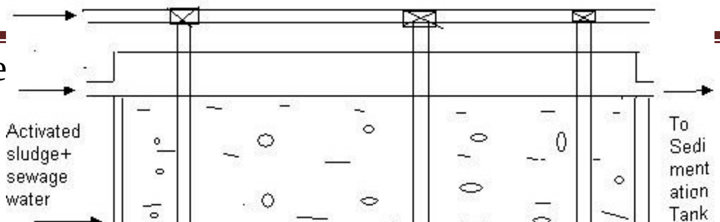
=435.2/dm3

Dec.2013/Jan.2014

3 a)Define COD. Explain the sewage treatment of activated sludge process. (04M)

Ans) It is defined as the amount of oxygen consumed in the chemical oxidation of organic and inorganic impurities present in one litre of waste water by using acidified $K_2Cr_2O_7$ solution in presence of silver sulphate and mercuric sulphate as catalyst.

Secondary treatment or activated sludge method: The waste water after primary treatment is allowed to flow into a large tank where biological treatment is carried out. Here the water is sprayed with activated sludge, the microorganism present in sludge form a thin layer on water and break down all organic impurities into simpler compounds. The air is passed from the centre of tank vigorously in order bring effective aerobic oxidation. The residual water is chlorinated to kill bacteria and then treated with potash alum to settle the impurities. The water is then filter and discharge into drainage.



June/July 2014

4 a) Define BOD & COD. Calculate the BOD when 1Ltr of effluent from sugar industry containing 150mgm of glucose was completely oxidized into CO_2 & H_2O (06M)

Ans) Biological Oxygen Demand:

The amount of oxygen required in milligrams by the microorganism to bring about oxidation of biological compounds present in 1 dm^3 waste water over a period of five days at 20^oC

Chemical oxygen demand:

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

$C_6H_{12}O_6 + 6O_2$ ----- $6CO_2 + 6H_2O$

Therefore 150mg of glucose requires 192 mg of O2

BOD=192ppm

b)Explain the desalination of water by reverse Osmosis.(04M)

Ans)JAN 2013

Dec.2014/Jan.2015

5 a**) What is boiler feed water ? explain the scale and sludge and sludge formation in boiler .mention their ill effects. (05M)**

Ans) Boiler feed water Boiler feedwater is water used to supply ("feed") a boiler to generate hot water. At tthermal power station the feedwater is usually stored, pre-heated and conditioned in a feed water tank and supplied to the boiler by a boiler feed pump.

Scale is caused by impurities being precipitated out of the water directly on heat transfer surfaces or by suspended matter in water settling out on the metal and becoming hard and adherent. Evaporation in a boiler causes impurities to concentrate. This interferes with heat transfers and may cause hot spots. Leading to local overheating. Scaling mechanism is the exceeding of the solubility limits of mineral substances due to elevated temperature and solids concentration at the tube/water interface. The deposition of crystalline precipitates on the walls of the boiler interferes with heat transfer and may cause hot spots, leading to local overheating. The less heat they conduct, the more dangerous they are.

Boiler sludge is a deposit that forms when suspended materials present in the boiler water settle on, or adhere to, hot boiler tubes or other surfaces. Sludge typically consists primarily of compounds such as hydroxyapatite (also known as calcium hydroxyl phosphate) or serpentine (magnesium silicate). Metal oxides are normally the result of condensate corrosion but may also come from the makeup water or feedwater system corrosion. Metal oxides can form a hard tenacious deposit on tube surfaces which restricts heat transfer. Metal oxides can also be absorbed onto sludge particles and become part of the sludge. Metal oxides are typically iron oxide but may include copper or other metallic components.ChemTreat’s boiler scale and deposition control treatment programs are designed to prevent and control crystallization resulting in deposit formation, as well as provide deposit dispersion and sludge conditioning.

Common feed water contaminants that can form boiler deposits include Ca,Mg,Fe and silica. Scale is formed by salts that have limited solubility but are not totally insoluble in boiler water. These salts reach the deposit site in a soluble form and precipitate.

b) What is desalination ? explain the desalination of saline water by electro dialysis. (05M)

Ans)DEC 2013

C) Define COD. Calculate the COD of the effluent sample sample when 25cm^3 of the effluent sample requires 8. 5cm^3 of 0.001 N $K^2 Cr^2 O_7$ Solution for complete oxidation. (05M)

Ans) COD= NxV of K2Cr2O7x48000/ V of effluent

=.001x8.5x8000/25

=2.72/dm3

d)Discuss in detail the softening of water by ion—exchange process. (05M)

Ans) **Softening of water by ion exchange process**

It is the process of reducing the dissolved salts of Ca,Mg,Fe in water ,there by reducing the Hardness.

An ion exchange resin is a cross linked Organic Polymer network with some ionisable group.Two types of ion exchange resins

1. Cation exchanger : Resins which have –SO_3H,-COOH,phenolic group as the ionisable group.Since these resins exchange the Cationic portion of minerals by their hydrogen.
2. Anion exchanger: Resins which have –NH_2,-$NHCH_3$, $N(CH_3)_2OH$ as the ionisable group.Since these resins exchange the Anionic portion of minerals by OH ion.

ion exchange Softening Process:

Water is 1st passed through a tank having cation exchanger which absorbs all the cations present in water and leaves behind the hydrogen.

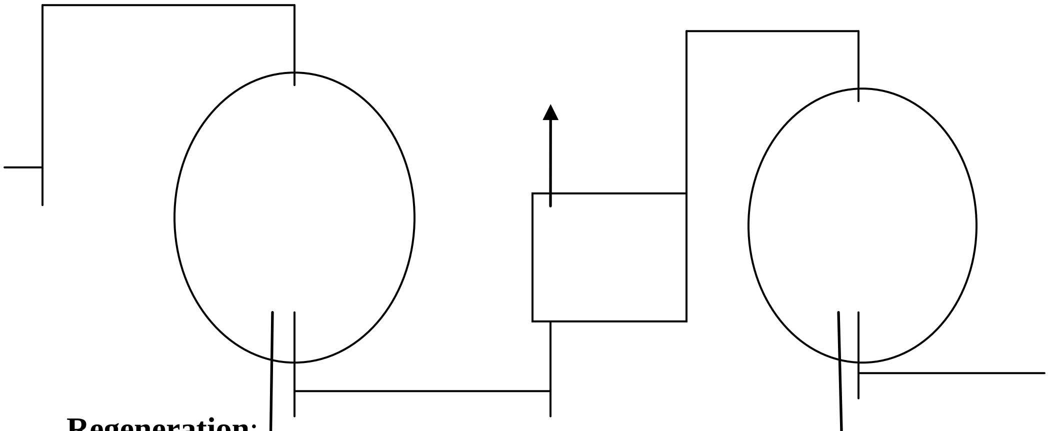
$CaSO_4 + Na_2R \longrightarrow CaR + Na_2SO_4$

$CaSO_4 + H_2R \longrightarrow CaR + H_2SO_4$

The cation free water is now passed through another tank having anion exchanger, which absorbs all the anions present in water and leaves behind water molecules.

$R^1(OH)_2 + H_2SO_4 \longrightarrow R^1 SO_4 + 2H_2O$

$R^1(OH)_2 + H_2CO_3 \longrightarrow R^1 CO_3 + 2H_2O$



Regeneration:

Ion exchange resins have a limited capacity and will eventually become exhausted. They can be regenerated by treating Cation exchange beds are regenerated with HCl or H_2SO_4

$CaR + H_2SO_4 \longrightarrow CaSO_4 + H_2R$ (C.E.R)

$MgR + H_2SO_4 \longrightarrow MgSO_4 + H_2R$

The Anion resin bed can be regenerated by treating with dil.NaOH

$R^1 SO_4 + NaOH \longrightarrow R^1(OH)_2 + Na_2SO_4$

$R^1Cl_2 + 2 NaOH \longrightarrow R^1(OH)_2 + 2NaCl$

Advantages:

1. The process can be used to soften highly acidic or alkaline waters.
2. Very low hardness water is obtained.
3. Demineralised water can be used for industrial as well as domestic purposes.

Dis advantages:

1. It is not economical.
2. Softening is reduced due to the presence of turbidity in water.

June/July2015

6a) what is boiler feed water? Expalin the priming and foaming in boilers. (05M)

Ans) 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.

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.

b)Define COD. Discuss the Experimental determination of COD of waste water. (05M)

Ans)

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,coolandtitrateagainstFASusingferroinindic atortilltogetreddishbrowncolour. Letthetitervaluebea cm^3.Performablanktitrationinsimilarwayexceptusingwastewatersample.Lettheblanktitervaluebeb cm^3.

CALCULATION

VolumeofK$_2$Cr$_2$O$_7$consumedforthesample=(b-a) cm^3
1000cm^{3}of1NFASsolution=1equivalentofoxygen=8gofoxygen(or8x10^{3}mgofO$_2$)

8x10^{3}x(b-a)xNofFAS
(b-a)cm^{3}of......NFASsolution==.........X.mgofoxygen/
1000x125cm^{3}ofwastewater

25cm^{3}ofwatersampleconsumedXmgofO$_2$
.Xx1000
1000cm^{3}ofwastewatersamplecontains= 25mgofoxygen/ dm^3

CODofwastewatersample=.......................................mgofO$_2$perdm^3

c)Explain the activated sludge treatment of sewage water. (05M)
Ans) **<u>Dec.2013/Jan.2014</u>**
d)Discuss the Desalination of sea water by reverse osmosis. (05M)
Ans) **<u>January 2013</u>**

NANO MATERIALS

Dec.2014/Jan.2015

1a) what are nano materials? Explain the synthesis of nano material by sol- gel method (05M)

Ans) 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.

Sol-gel process

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides

$M(OR)_z$ can be described as follows:

MOR + H_2O → MOH + ROH (hydrolysis)

MOH + ROM → M-O-M + ROH (condensation)

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

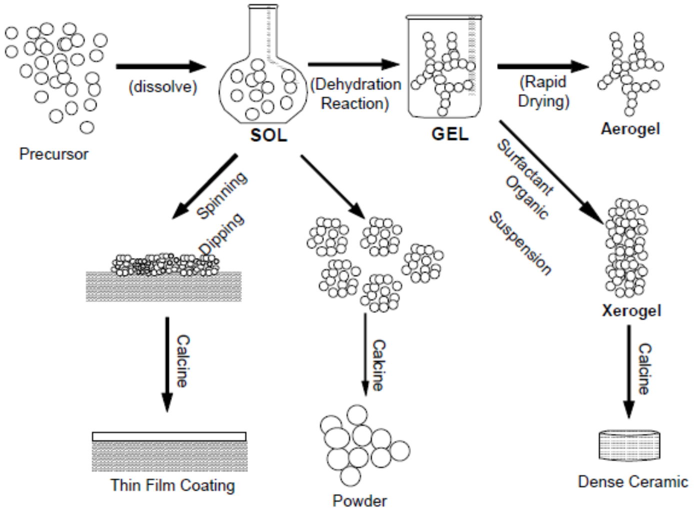


Fig. 7. Schematic representation of sol-gel process of synthesis of nanomaterials.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscocity of the solution.
3. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
4. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a xerogel. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an aerogel.
5. Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 8000C.

6. Densification and decomposition of the gels at high temperatures (T>8000C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics.

The major difficulties to overcome in developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process. Also production rates of nano powders are very low by this process. The main advantage is one can get mono sized nano particles by any bottom up approach.

Precipitation is the creation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When the reaction occurs in a liquid solution, the solid formed is called the **precipitate**. The chemical that causes the solid to form is called the **precipitant**. Without sufficient force of gravity (settling) to bring the solid particles together, the precipitate remains in suspension. After sedimentation, especially when using a centrifuge to press it into a compact mass, the precipitate may be referred to as a **pellet**.

The precipitate-free liquid remaining above the solid is called the **supernate** or **supernatant**. Powders derived from precipitation have also historically been known as **flowers**. Precipitation may occur if the concentration of a compound exceeds its solubility (such as when mixing solvents or changing their temperature).

Precipitation may occur rapidly from a supersaturated solution. In solids, precipitation occurs if the concentration of one solid is above the solubility limit in the host solid, due to e.g. rapid quenching or ion implantation, and the temperature is high enough that diffusion can lead to segregation into precipitates. Precipitation in solids is routinely used to synthesize nanoclusters.

An important stage of the precipitation process is the onset of nucleation. The creation of a hypothetical solid particle includes the formation of an interface, which requires some energy based on the relative surface energy of the solid and the solution. If this energy is not available, and no suitable nucleation surface is available, super saturation occurs.

b) Write a note on carbon nano tubes.(05M)

Ans) Carbon nanotubes (**CNTs**) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of upto 132,000,000:1significantly larger than for any other material. These cylindrical carbonmolecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. For instance, nanotubes form a tiny portion of the material(s) in some (primarily carbon fiber) baseball bats, golf clubs, or car parts.

Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled

nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking.
Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, similar to those of graphite. These bonds, which are stronger than the sp^3 bonds found in alkanes and diamond, provide nanotubes with their unique strength.

c)Explain the synthesis of nanomaterials by hydro thermal process.(05M)

Ans) Hydrothermal : **Hydrothermal synthesis** includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method".

The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the twentieth century. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.

Chemical reactions: Micro porous crystals, super ionic conductors, metal oxides, ceramics, zeolites, carbonaceous materials, magnetic materials, phosphers, plus nanoparticles, gels, thin films, helical/chiral structures.

Advantages

- Most material can be made soluble in a proper solvent by heating and pressurizing the system close to its critical point;
- Significant improvement in the chemical activity of the reactant, and in producing materials that cannot be obtained via solid-state reaction;
- Products of intermediate state, metastable state and specific phase may be easily produced > novel products of metastable state and other specific condensed state.

Disadvantages

- Expensive autoclaves;
- Safety issues during the reaction;
- Could not monitor and observe the reaction.
- Difficult to control morphology, size, size distribution
- Not for all materials

Mechanism

•Usually follows a liquid nucleation model;

•Different from solid-state reaction mechanism in terms of diffusion of atoms/ions among reactants

•Enhanced solubility –solubility of water increases with T, but alkaline solubility increases much greater with T –high pH.

USES : A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germanates etc. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals that have been efficiently grown are emeralds,rubies, quartz, alexandrite and others. The method has proved to be extremely efficient both in the search for new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multicomponent systems at elevated temperatures and pressures.

d) what are fullernces ? Explain the synthesis and uses of fullerence.(05M)

Ans) A **fullerene** is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, 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. The first fullerene molecule to be discovered, and the family's namesake, buckminsterfullerene (C_{60}).The structure was also identified some five years earlier by Sumio Iijima, from an electron microscope image, where it formed the core of a "bucky onion." Fullerenes have since been found to occur in nature. More recently, fullerenes have been detected in outer space. "It’s possible that buckyballs from outer space provided seeds for life on Earth."

The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphous carbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nano technology. Minute quantities of the fullerenes, in the form of C_{60}, C_{70}, C_{76}, C_{82} and C_{84} molecules, are produced in nature, hidden in soot and formed by lightning discharges in the atmosphere. Types of fullerene

Buckyball clusters: smallest member is C_{20} (unsaturated version of dodecahedrane) and the most common is C_{60};

Nanotubes: hollow tubes of very small dimensions, having single or multiple walls; potential applications in electronics industry;

Megatubes: larger in diameter than nanotubes and prepared with walls of different thickness; potentially used for the transport of a variety of molecules of different sizes;

polymers: chain, two-dimensional and three-dimensional polymers are formed under high-pressure high-temperature conditions; single-strand polymers are formed using the Atom Transfer Radical Addition Polymerization (ATRAP) route;

nano"onions": spherical particles based on multiple carbon layers surrounding a buckyball core; proposed for lubricants;

linked "ball-and-chain" dimers: two buckyballs linked by a carbon chain; **fullerene rings**.

June/July2015

2a) what is nano material? Discuss the synthesis of nano material by gas condensation and precipitation methods. (05M)

Ans) 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.

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.

b) write a note on carbon nano tubes. (05M)

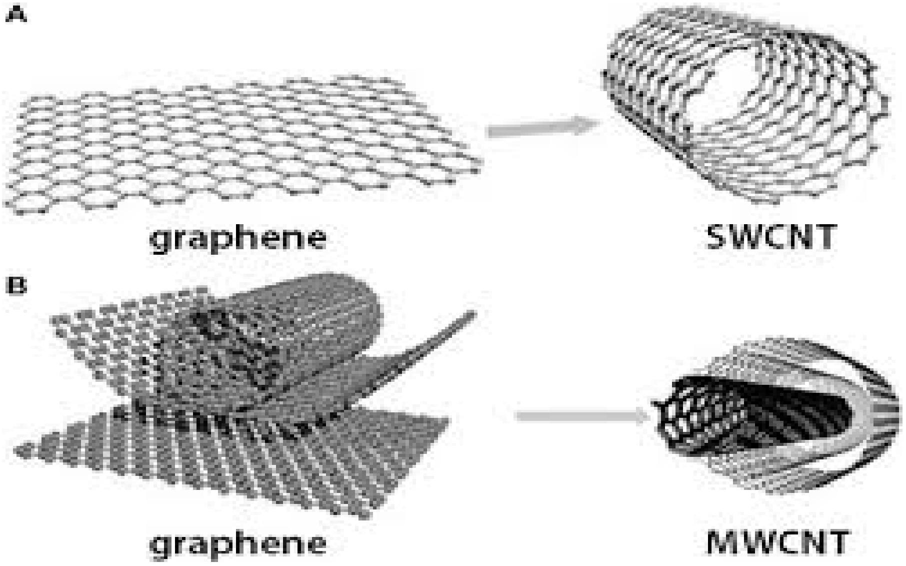
Ans) Carbon Nanotubes (CNTs): Carbon Nanotubes are cylindrical tubes with a central hollow core formed by rolling up of graphine sheets. Its ends are capped by hemisphere of fullerene sheets.The diameter of CNT is in the range of 1-50nm and the length can go up to few micrometers. The CNT is a one dimensional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

c)Explain the synthesis of nanomaterials by hydro thermal process. (05M)

Ans) **Dec.2014/Jan.2015**