CMR INSTITUTE OF TECHNOLOGY



Sub:	Engineering Chemistry								15CHE12
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Date:	4/11/2016	Duration:	mins	Marks:	50	Sem:	(J,K,L,M,N,O)	Branch:	EC/EE/TE/CV

<u>Internal Assessment Test II – November 2016</u>

Answer any five sets completely

Q1. a) What is electroless-plating process? Explain the process of electroless plating of copper on PCB with relevant reaction.

Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating.

Metal ions + Reducing agent _____ catalytically active surface _____ Metal atom + Oxidised product

Constituents	Amount	Purpose		
CuSO ₄	12 g/L	Provides metal ions		
Н-СНО	8 g/L	Reducing reagent		
Rochelle salt	14 g/L	Complexing agent		
NaOH	15 g/L	Provides alkaline medium		
EDTA	20 g/L	Exaltant & complexing agent		
pН	11.0			
Temperature	25°C			

Reactions:

Oxidation of reducing reagent : $2HCHO + 4OH^{-} \longrightarrow 2HCOO^{-} + 2H_{2}O + H_{2} + 2e^{-}$

Reduction of metal ion over object surface $: Cu^{2+} + 2e^{-} \longrightarrow Cu$

Making of double sided PCBs with through-hole connections:

- A coating of copper on both sides a glass reinforced plastic (GRP) sheet/board is accomplished by cladding two thin foils of copper.
 Necessary circuits will be drawn (or printed) on either sides using etch-resistant ink. The
 - board is etched in acidified solution of FeCl3. Only the circuit parts will be left and rest other copper is etched away.
- Holes are drilled wherever, contact between
 After drilling
 the two circuits is necessary.

 Hele professores are estimated by two two treatment with
- Hole surfaces are activated by treatment with
 acidified SnCl₂ and then with acidified

 PdCl₂. Electroless plating of copper is activation of holes & electroless plating

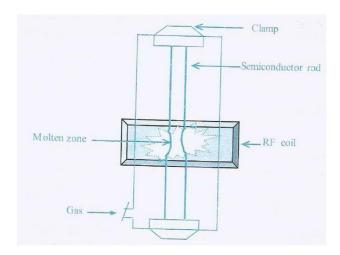
 carried out in a suitable bath as mentioned

 electrolessplating

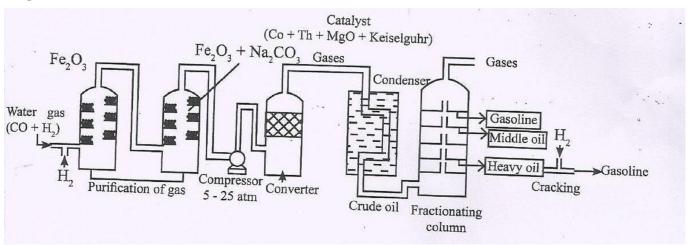
above to establish the contact between two circuits through the holes.

b) Explain Zone refining method for the purification of solar silicon rods.

Zone refining: Silicon of 99.9999 % of purity can be obtained by zone refining. It is based on the principle that impurities are more soluble in molten material than in the solid material. A vertical zone refiner is used in the purification of silicon. A rod of silicon to be purified is clamped and is heated by a RF coil to the melting point of silicon. The heater is moved very slowly from top to bottom. This is said to be one zone pass. Impurities move with the molten part of the material as the RF coil moves down. Pure silicon solidifies at the upper portion. The process is repeated number of times to get ultrapure silicon. When the process is complete, the bottom portion where the impurities are concentrated is removed.



Q2. a) Explain Fischer-Tropsch process for preparation of synthetic petrol with the help of a neat diagram.



- Synthetic petrol refers to a laboratory manufactured petroleum substitute (Prepared from nonpetroleum resourses).
- This process is a catalysed chemical reaction in which coke is converted into hydrocarbon.
- Water gas is produced by passing steam over red hot coke.

$$C + H_2O$$

1200 °C

 $CO + H_2$

Water gas

Water gas is mixed with H₂ to get synthetic gas.

Synthetic gas

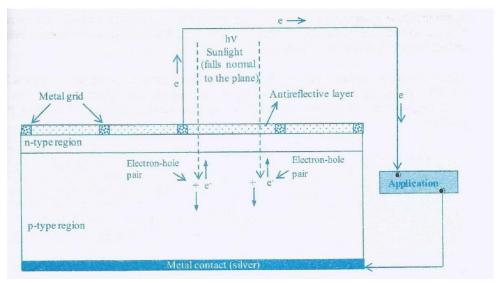
- The gas is purified by passing through Fe₂O₃ (to remove H₂S) and then into a mix of Fe₂O₃.
 Na₂CO₃ (to remove organic s compounds).
- The purified gas is compressed to 5 25 atm and then led through a converter which is maintained at 200 - 300 °C and contain mixture of 100 parts Co, 5 parts Thoria, 8 parts magnesia and 200 parts Keiselguhar earth.

The Reactions are-

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

- The outcoming gaseous mixture is led to a condenser or cooler where the liquid crude oil is obtained.
- The crude oil is fractionated to yield gasoline and heavy oil.
- The heavy oil is used for cracking to get more gasoline.
- b) Describe the construction and working of Photo voltaic cell with a neat sketch.



Construction:

Si is used as starting material. Si is cut into the form of disc and then disc is converted to wafer.

Boron is used for p-doping and P is used for n-doping of the wafer.

Anti reflecting coating of TiO₂ / Ag-nitride is applied in the form of thin film

Metallic grid is screen printed by Al paste on the front side of the wafer.

Ag paste is used to prepare metallic layer.

Working:

- Photovoltaic cell is made of a semiconductor diode (p-n junction).
- The diode has two electrical contacts: on one of its sides, a metallic grid is used and on the other side, a layer of noble metal (such as, silver-Ag) is used. Ag is nobler than the Si-semiconductor.
- The metal grid permits the light to fall on the diode between the grid lines.
- When electromagnetic radiation (example: sunlight) having energy sufficient to overcome the barrier potential falls normal to the surface of the p-n junction, electron hole pairs are created.
- The electrons move towards the n-region (as it is positively charged) and holes move towards p-region (as it is negatively charged).
- The electrons are driven into the external circuit and an appliance can be run or the energy can stored in a battery. The stored energy could later be used for various applications such as lighting purposes, telecommunication, etc.

Q3. a) On burning of 0.85 gm of a solid fuel in a bomb calorimeter, the temperature of 2.1 Kg water is raised from 24 °C to 27.6 °C. The water equivalent of calorimeter & latent heat of steam are 1100 gm and 2454 KJ/Kg respectively. Specific heat of water is 4.187 KJ/Kg. If the fuel contains 2% hydrogen, calculate its gross and net calorific values?

Given,

 $m = 0.85~gm = 0.85~X~10^{\text{-}3}~Kg$, W1 = 2.1~Kg , W2 = 1100g = 1.1~kg , T2 = (24 + 273) = 297~K , ~T1 = (27.6 + 273) = 300.6~K , s = 4.187~kJ/Kg

GCV =
$$\frac{(W_1 + W_2)(T_2 - T_1) s}{m} kJ kg^{-1}$$

= $(2.1 + 1.1) (300.6 - 297) \times 4.187 / 0.85 \times 10^{-3}$
= 56746.16Kj/kg

NCV =
$$GCV - 0.09 \times H \times L_v \text{ kJ kg}^{-1}$$

= $56746.16 - 0.09 \times 2 \times 2454 = 56304.4 \text{kj/kg}$

b) Give synthesis reactions and applications of following polymers:

i) PMMA

Preparation of polymer (plexi glass):

APPLICATIONS:

- (i)For making lenses, air craft windows, artificial eyes, TV screens, attractive sign boards etc.
- (ii)It is also used for making transparent bottles, tubes etc.

ii) Polyurethane

Applications:

- (i) They are used as coatings, films foams adhesives and elastomers etc.
- (ii) They are resistant to water, they are used in light weight water repellent garments like swim suites.

Q4. a) Describe the method of production of solar grade silicon by Union Carbide method.

(i) <u>Preparation of Metallurgical Grade Silicon from Naturally Occurring</u> <u>Ouartz:</u>

Pure silicon is not available on earth. It comes in form of quartz sand, which is heated with carbon (coke) in an electric arc furnace heated at 1500-2000 °C. Silica is reduced to elemental silicon.

$$SiO_{2(s)} + 2C_{(s)} \longrightarrow 2CO + Si$$

Si thus obtained is in molten state. CO is further oxidized to CO₂ and released into atmosphere.

Refining-

The crude silicon rod is taken in large bundles and treated with silica sand (SiO₂) and O₂. Aluminium, calcium and magnesium present as impurities are oxidized to the corresponding oxides.

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

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

The oxides of Al, Mg and Ca react with excess of SiO_2 to form insoluble slag. The slag is removed and the refined melt is poured into the moulds where silicon solidifies. This is called **metallurgical grade silicon** (98.5%).

The metallurgical grade silicon obtained above is further processed to get semi-conductor grade silicon or polysilicon.

(ii) Union Carbide Process for Production of Semiconductor Grade silicon

This process was developed by Union Carbide Chemicals in the United States of America. It involves the following steps:-

Metallurgical grade silicon is treated with HCl gas at 500°C, pressure of 40-50 bar in boiled bed reactor to form trichlorosilane and some amount of tetrachlorosilanes.

$$Si + 3HC1$$
 \longrightarrow $HSiCl_3 + H_2$
 $Si + 4HC1$ \longrightarrow $SiCl_4 + 2H_2$

Tetrachlorosilane is reduced to trichlorosilane by passing through a hydrogenation reactor.

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

The trichlorosilane still has some impurity and is further purified by distillation.

The pure trichlorosilane is passed through fixed bed column containing quaternary ammonium ion exchange resin (catalyst) which converts it into dichlorosilane and further into silane.

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$

$$3H_2SiCl_2 \longrightarrow SiH_4 + 2HSiCl_3$$

The silane obtained is purified by distillation and trichlorosilane and tetrachlorosilane is recycled to the exchange resin and hydrogenation reactor respectively.

Pure silane obtained in the above step is subjected to pyrolysis in a reactor at high temperature. In pyrolysis reactor, pure Si rods are used for heating. Si formed by decomposition of silane gets deposited over these pure Si rods.

$$SiH_4 \longrightarrow Si + 2H_2$$

b) Explain the following factors affecting rate of electroplating:

(i) temperature

Good deposits are obtained at slightly higher temperatures. Higher temperature increases the solubility of metal-salt, its dissociation, mobility of ions and lowers the viscosity of plating solution. This in turn, improves the conductivity of plating bath and relatively higher current densities can be opted and deposit coat is rapidly established. However, increased temperature may boost (i) the competing cathodic reaction, H₂ evolution over object surface, (ii) corrosion of plating equipment and (iii) decomposition of additives, etc. with overall lowered performance of plating quality. Therefore, moderate temperatures of the order of 35 to 60°C are preferred.

(ii) metal ion concentration

In general, low metal ion concentration decreases the crystal size and results in a fine-grained adherent coating. This is achieved either by common ion effect or by the formation of complex ions or compounds.

For example,

(i) Sulphuric acid is used in electrodeposition of copper (acid bath).

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

cupric ion concentration is reduced (to about 10% of total salt concentration) due to common ion effect of SO_4^{2-} ions.

(ii) Sodium cyanide is used in electroplating of copper (cyanide bath)

Q5. a) Explain the free radical mechanism of addition polymerization by taking Vinyl chloride as a monomer.

$$nCH_2$$
 CHCl $(C_6H_5COO)_2$ (-CH₂-CH₂-CH₂-CH₂-)n
Ethylene Polyethylene

Generation of free radicals

$$(C_6H_5COO)_2$$
 \longrightarrow $2C_6H_5COO$ \longrightarrow $CO_2 + 2C_6H_5$ (or R.)

Dibenzoyl peroxide

Initiation

Or in general,

$$CH_2 = CHCl + R-[CH2-CHCl]_{x-1}-CH_2-CHCl'$$

$$R-(CH_2-CHCl)_x-CH_2-CHCl'$$

$$CH_2 = CHCl + R-[CH2-CHCl]_{y-1}-CH_2-CHCl'$$

$$R-(CH_2-CHCl)_y-CH_2-CHCl'$$

Termination by coupling (by the combination of two radicals)

Termination by disproportionation

$$R-[CH2-CHCl]x-CH2-CHCl' + CHCl-CH2-(CH2-CHCl)y-R \xrightarrow{coupling}$$

$$R-(CH2-CHCl)x-CH2-CH2-CH2-CHCl)y-CH = CHCl$$

b) Explain the process of electroplating of Cr. Indicate the reason for coating anode with PbO₂.

Chromium is employed for either decorative purposes (as a thinner coat) or engineering purposes (as a thicker hard coat). Mentioned below are coating specifications.

Bath composition	CrO_3 (chromic acid): $H_2SO_4 = 100$: 1 ratio
Temperature	45 - 60 °C
Current density	$100 - 200 \text{ mA/cm}^2$
Current efficiency	17 – 21 %
Anode material	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)
Cathode material	Surface cleaned object metal
Reaction at anode	$H_2O \longrightarrow \frac{1}{2} O_2 \uparrow + 2H^+ + 2e^-$
Reaction at cathode	$Cr^{3+} + 3e^{-} \longrightarrow Cr$

$$CrO_3 + H_2O \longrightarrow H_2CrO_4 \longrightarrow 2H^+ + CrO_4^{2-}$$

 $2H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O \longrightarrow 2H^+ + Cr_2O_7^{2-} + H_2O$
 $Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{sulfate ion(SO_4^{2-})} 2Cr^{3+} + 7H_2O$

Chromium plating is a hard, attractive coating, with low coefficient of friction exhibiting wear resistance, abrasion resistance and also good corrosion resistance (with an undercoat of nickel and copper)

• There is a complex sequence of reactions which control the concentration of Cr^{3+} in the plating bath. Sulfate ion is said to catalyse the conversion of Cr^{6+} into Cr^{3+} and PbO_2 catalyses the conversion of Cr^{3+} into Cr^{6+} .

$$Cr^{3+} + 3O_2 \xrightarrow{lead\ oxide(PbO_2)} 2CrO_3 + 6e^{-}$$

Q6. a) What is catalytic cracking? Describe how the fluidized bed catalytic cracking process enhances the calorific value of a particular petroleum fraction.

Decomoposition of larger hydrocarbon into smaller one in presence of catalyst is known as catalytic cracking.

Fluidised bed catalytic cracking:

Process conditions:

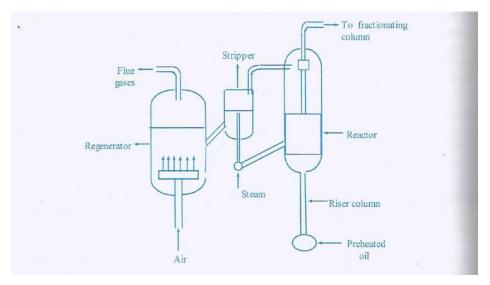
Feed stock: light gas oil or heavy gas oil

Catalyst: Y-type of zeolite activated with rare earth oxide

+ ZSM-5 type of zeolite (to increases O.N.) into a matrix of aluminium silicate

Temperature: 500-550°C

Pressure: slightly above ambient pressure



Description:

- Oil preheated to about 300 °C is sprayed into the reactor through riser column.
- The reactor contains the finely powdered catalyst at 700 °C.
- Cracking takes place in fluidized state with in contact time of 3 seconds.
- Temperature in the reactor falls to about 530 °C.
- Cracked hydrocarbons are removed from top, condensed and fractionated to get gasoline. Heavy
 residues are taken for second stage cracking to improve the cracking efficiency.
- After some time due to accumulation of oil and deposition of carbon, catalyst gets inactivated.
- Thus it is sent to oil stripper where, oil is removed using a blast of steam.
- Then, it is sent into regeneration chamber to remove C. Carbon is burnt off in presence of hot air and flue gases escape from a vent.
- Regenerated catalyst is mixed with fresh feed stock and returned to cracking chamber

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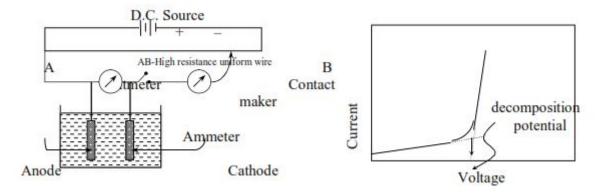
b) Define electro deposition. Write in detail the significance of Decomposition potential following with reference to electro deposition.

The process of deposition of metal on the surface of another metal with the help of electrolysis is known as electro deposition.

Decomposition potential is the experimentally determined minimum external potential that needsto be applied in order to have continuous decomposition of the electrolyte. For example, in the decomposition of water, a dilute solution of either an acid or alkali is electrolysed using smooth platinum electrodes. For the applied potential less than 1.68 V, there is initial surge of current which will drop to zero in a while. When the applied potential is 1.68 V

or more, there is continuous decomposition of water with the liberation of hydrogen at cathodeand oxygen at the anode. Thus, 1.68 V is the decomposition potential of water.

Decomposition potential can be determined by the measurements of current for varying potentials (or voltages) applied across the electrodes immersed in electrolyte under investigation. Set-up as shown in the figure is used for such measurements. . A plot of current against potential (or voltage) helps in knowing the decomposition potential. For lower voltages, there is no significant rise in current till the reach of decomposition potential. Beyond this potential, it starts rising abruptly. Laws of electrolysis are applicable only in this region. Decomposition potential is obtained by the intersection of the two tangents drawn as shown in the figure.



Q7. a) What is reformation? Write the reactions involved in it.

Reformation: Reforming of petrol (or gasoline) is defined as the process of increasing the octane number of petrol by structural modifications or molecular rearrangements of hydrocarbons.

Process conditions-

Feed stock: Virgin gasoline

Catalyst: Pt supported on alumina or silica base

Temperature: $475-525\Box C$

Pressure: 15-50 atm.

Reforming reactions:

(i) Isomerization: Conversion of straight hydrocarbon into branched chain hydrocarbon.

$$CH_3$$
-(CH_2)₄- CH_3 \longrightarrow CH_3 - CH -(CH_2)₂- CH_3
(n -hexane) CH_3
(2 -methyl pentane)

(ii) Cyclization: Conversion of straight chain hydrocarbon into cyclic compounds.

$$CH_3-(CH_2)_4-CH_3$$
 \longrightarrow $+$ H_2 $(n\text{-hexane})$

(iii) Cyclization and dehydrogenation: Conversion of straight chain hydrocarbon into aromatic compounds.

$$CH_3-(CH_2)_4-CH_3$$
 \longrightarrow \longrightarrow \longrightarrow \longrightarrow \longrightarrow $+3H_2$ $(n\text{-hexane})$ $(cyclohexane)$ (Benzene)

(iv) Polymerization & hydrogenation:

$$\begin{array}{c} \text{CH}_3 & \text{CH}_3 \\ 2 \text{ C=CH}_2 + \text{H}_2 & \longrightarrow \text{CH}_3 - \text{C-CH}_2 - \text{CH-CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \end{array}$$

$$\begin{array}{c} \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \end{array}$$

$$\text{(Isobutene)} \qquad \qquad \text{(iso-octane or 2,2,4-trimethyl pentane)}$$

b) A polymer sample contains 100,120,300 and 400 molecules having molecular mass 1000, 2000, 3000 and 4000 respectively. Calculate the number average and weight average molecular masses of the polymer.

$$Given, \ n1 = 100 \ , \ n2 = 120 \ , \ n3 = 300 \ , \ n_4 = 400 \ , \ M1 = 1000, \ M2 = 2000 \ , \ M3 = 3000, \ M_4 = 4000 \ , \ M_{1} = 1000, \ M_{2} = 2000 \ , \ M_{3} = 3000, \ M_{4} = 4000 \ , \ M_{1} = 1000, \ M_{2} = 2000 \ , \ M_{3} = 3000, \ M_{4} = 4000 \ , \ M_{2} = 2000 \ , \ M_{3} = 3000, \ M_{4} = 4000 \ , \ M_{3} = 3000, \ M_{4} = 4000 \ , \ M_{5} = 1000, \ M_{5} = 10000, \ M_{5} = 10000, \ M_{5} = 10000, \ M_{$$

$$Mn = n1 M1 + n2 M2 + n3 M3 + + ni Mi / n1 + n2 + n3 + ... + ni$$

$$Mw = n1 M^2 1 + n2 M^2 2 + n3 M^2 3 + \dots + ni M^2 i / n1 M1 + n2 M2 + n3 M3 + \dots + ni Mi$$

$$=100\ x\ (1000)^2+200\ x\ (2000)^2+300\ x\ (3000)^2\ +400\ x\ (4000)^2/\ 100\ x\ 1000+200\ x\ 2000+300\ x\ 3000+400\ x\ 4000$$

= 3408.45