Solutions

CMR
INSTITUTE OF
TECHNOLOGY

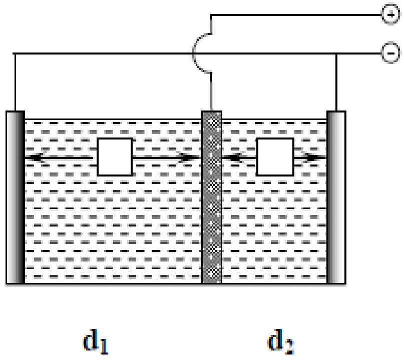
Sub:	**Engineering Chemistry**									Code:	17CHE22
Date:	16/04/2018	Duration:	90 mins	Max Marks:	50	Sem:	II			Branch:	All

Internal Assessment Test II

1. (a) Discuss the following factors influencing the nature of electrodeposit (a) Current density (b) Throwing power. (04 Marks) (CO1, L2)

Solution: (a) Current density: Current density is the current per unit area expressed as A cm^{-2} (or mA cm^{-2} or A m^{-2} or A ft^{-2}). Rise in current density, increases electrodeposition rate till a limiting value. At low current densities, surface diffusion is faster compared to electron transfer to metal ions resulting in coarse-grained deposits (fewer nuclei are formed). When current density is increased, opposite phenomena is observed and leads to fine grained deposits (with more of nuclei). However, at very high current densities, bad deposits with rough and powdery texture (or burnt deposits) are formed, which are poorly adherent to object surface. Fast depletion of metal ions may represent hydrogen evolution and presence of oppositely charged hydroxide ions, result in deposition of hydroxides or oxides of the metal. Therefore, optimum current densities are employed.

(b) Throwing Power: Ability of the plating bath to give uniform deposits on the object surface irrespective of its size or shape is called throwing power. Throwing power is particularly important for objects with intricate shapes.



Throwing power is determined by use of Haring-Blum cell. The cell is a rectangular box made of PVC (polyvinyl chloride) with a provision to place two plate type cathodes at distances, d1 & d2 (d1 >d2) from the active anode kept in between the two as shown in the figure. Electroplating is carried out for certain length of time, anode gets dissolved and deposits on to two cathode surfaces facing the anode (opposite sides will be blocked for such deposition). Let the mass of metal deposited be m1 & m2 on cathodes which are at distances, d1 and d2 respectively.

mass of metal deposited = **m1, m2.** Suppose, D =d1/d2, M=m2/m1. Percentage throwing power is calculated as % Throwing Power =(D-M)/D-M+2)*100. Throwing power of 100% represents uniform electrodeposition on to object surfaces, whereas, lower values represent as much uneven deposits.

(b) Explain electroless plating of copper on double sided PCB with suitable reactions . (06 Marks) (CO1, L4)

Solution: 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.

Treatment with $SnCl_2$ leaves a thin layer of $SnCl_2$ and later treatment with acidified $PdCl_2$ leads to deposition of Pd.

$$SnCl_2 + PdCl_2 \longrightarrow Pd + SnCl_4$$

Electroless-plating of Copper:

Substrate surface needs to be cleaned by suitable cleansing methods (solvent degreasing, acid pickling, alkali pickling, mechanical polishing, etc.). However, when the object is non-conducting or insulator material such as, plastics, PCBs, glass, etc. it needs to be activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$. Following bath compositions are used for plating.

Constituents	**Amount**	**Purpose**
$CuSO_4$	12 g/L	Provides metal ions
H-CHO	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
pH	11.0	
Temperature	25^oC	

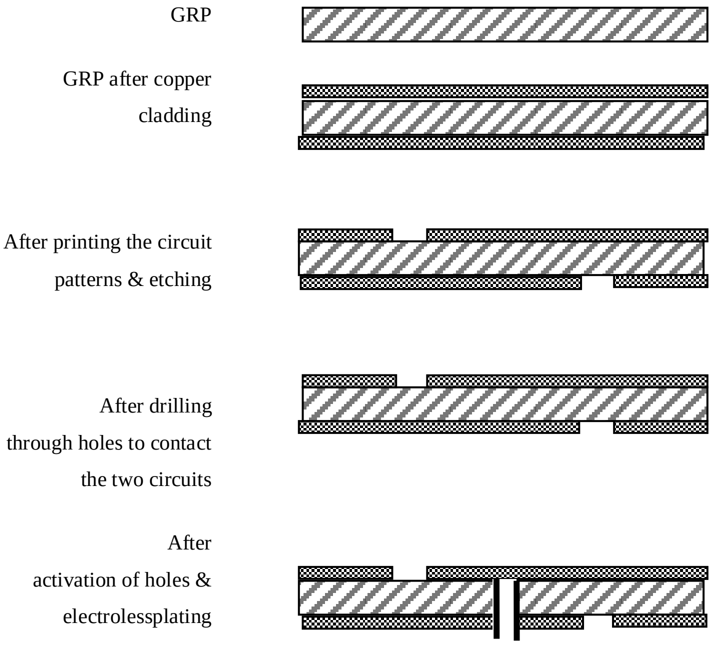
Reactions:

Oxidation of reducing reagent: $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

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

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

- 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 $FeCl_3$. Only the circuit parts will be left and rest other copper is etched away.
- Holes are drilled wherever, contact between the two circuits is necessary.
- Hole surfaces are activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$. Electroless plating of copper is carried out in a suitable bath as mentioned above to establish the contact between two circuits through the holes.



2. (a) Describe the process of electroplating of hard chromium. Mention its applications. (05 Marks) (CO1, L3)

Solution: Electroplating of Chromium:

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

- Active chromium anode is not used because, the anode efficiency is nearly 100% and that of the cathode is only around 20% at the best. There will be increase in concentration of Cr^{3+} ions which results in poor quality electrodeposits (black deposits).
- A thin coating of chromium is porous and thicker coating leads to cracking. Therefore, Cr-plating over steel is applied with an undercoat of copper and nickel. Copper is known to offer better finishing. Coverage of nickel and hence chromium is better with copper below. Also, lower thickness of nickel can be opted with an undercoat of copper. Chromium gives decorative & pleasing finish, nickel offers corrosion resistance and copper extends good coverage and better adhesion.
- 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+}.

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

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

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{sulfateion(SO_4^{2-})} 2Cr^{3+} + 7H_2O$$

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

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

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)

(b) Write short note on (a) Polarization and (b) Decomposition Potential. (05 Marks) (CO1, L3)

Solution: **(a) Polarization**: A process of variation in electrode potential due to change in concentration of ionic species at electrode surface by

(i) slow diffusion of ions from the bulk of the electrolyte to the electrode or from the electrode towards the bulk (known as concentration polarization)

(ii) one or more of elementary steps of discharge (or evolution) of gases being slow at electrode surface (known as overvoltage polarization).

Electrode potential is a function of active mass or molar concentration of ionic species in the solution given by the Nernst equation:

$$E = E^\circ + \frac{2.303\,RT}{nF}\log[M^{n+}]$$

For a reduction reaction at the cathodic surface, there is depletion in concentration of M^{n+} ions in the vicinity of cathodic surface. Until that time, ions diffuse from the bulk and re-establish the equilibrium, lower concentration of ionic species alters the electrode potential. Similar such phenomena can be seen at the anodic surface. This effect is known as concentration polarization. Polarization of electrodes depends upon :

(i) current densities applied

(ii) nature of the electrode (i.e., composition, size, shape, etc.)

(iii) nature of electrolyte, its concentration and conductivity

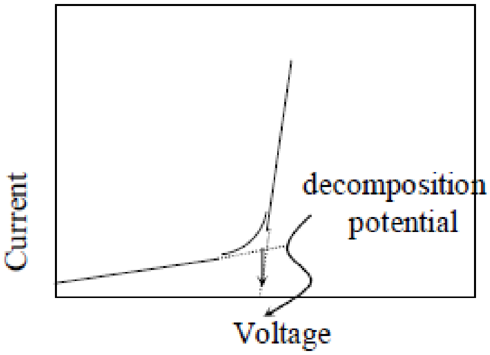
(iv) agitation / temperature of the electrolyte

(v) nature of the products formed at the electrode surfaces.

(b) Decomposition Potential: Decomposition potential is the experimentally determined minimum external potential that needs to 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 cathode and oxygen at the anode. Thus, 1.68 V is the decomposition potential of water.

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.



3. (a) Define Gross and Net calorific value of a fuel. Calculate the gross and net calorific value of a coal sample from the following data: Weight of coal=0.96g, Weight of water=2500g, Water equivalent of calorimeter=0.4Kg, Rise in temperature=3K, Specific heat of water=4.187J/g/K, latent heat of steam=2454J/g/K, % of Hydrogen in coal=6 (06 Marks) (CO2, L4)

Solution: **<u>Gross Calorific value</u>**: It is the amount of heat energy released when unit quantity of fuel is burnt completely in air or oxygen and the products of combustion are cooled to room temperature. All fuels invariably contain C & H. On combustion it gets converted into CO2 and steam. On cooling the combustion product, steam gets condensed to water and liberates its latent heat. Thus the measured gross calorific value includes latent heat of steam. Therefore it is always higher than the net calorific value.

Net Calorific Value: It is the amount of heat energy released when unit quantity of fuel is burnt completely in air or oxygen and the products of combustion are let off into the surrounding i.e. they are not cooled to room temperature.

Given,

Mass of the fuel, m= 0.96g=0.96*10^{-3}Kg

Weight of water, W=2500g=2500*10^{-3}Kg

Water equivalent, w=0.4Kg

Specific heat of water, S=4.187J/g/K=4.187*10^{3} J/Kg/K

Rise in Temperature, (T2-T1)°C=3K=3°C

Latent heat of steam, L=2454J/g/K=2454*10^{3} J/Kg/K

% of Hydrogen= 6%

GCV=(W+w)*S*(T2-T1)/m

= (2500*10^{-3}+0.4)* 4.187*10^{3}*3/0.96*10^{-3}

=37944.68kJ/kg

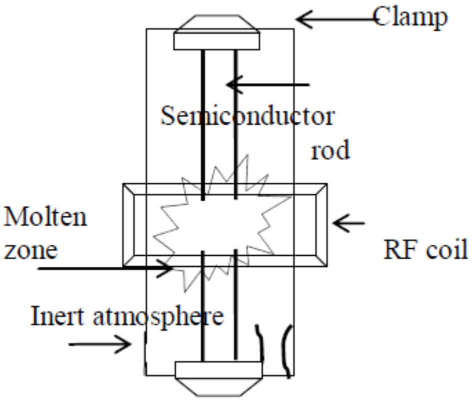
NCV=GCV- (0.09*% of Hydrogen*Latent heat)

=37944.68-(0.09*6*2454*10^{3})

=36619.52 kJ/kg

(b) Illustrate zone refining method for purifying Si to semiconductor grade quality. (03 Marks) (CO4, L2)

Solution: Silicon of 99.999999% 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.



4. (a) Explain the production of solar grade silicon by Union Carbide process. (06 Marks) (CO4, L3)

Solution:

I. Preparation of Metallurgical Grade Silicon from Naturally Occurring Quartz:

A mixture of quartz (SiO_2) and carbon (from coke or coal) is struck by electric arc in a furnace using carbon electrodes.

$$\underset{(s)}{SiO_2} + \underset{(s)}{2C} \longrightarrow \underset{(l)}{Si} + \underset{(g)}{2CO}$$

CO is oxidized to CO_2 and escapes into the atmosphere.
Silicon is obtained in the molten state and is contaminated with aluminium, calcium and magnesium. The impurities could be removed as slag by the addition of silica. Following reactions take place there.

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

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

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

The oxides of aluminium, calcium and magnesium combine with additional silica to form the corresponding silicates and are removed as slag. The silicon left behind is called *metallurgical grade silicon* (98.5 %).

II. Synthesis of Silane (Silicon Hydride- SiH_4) from Silicon:

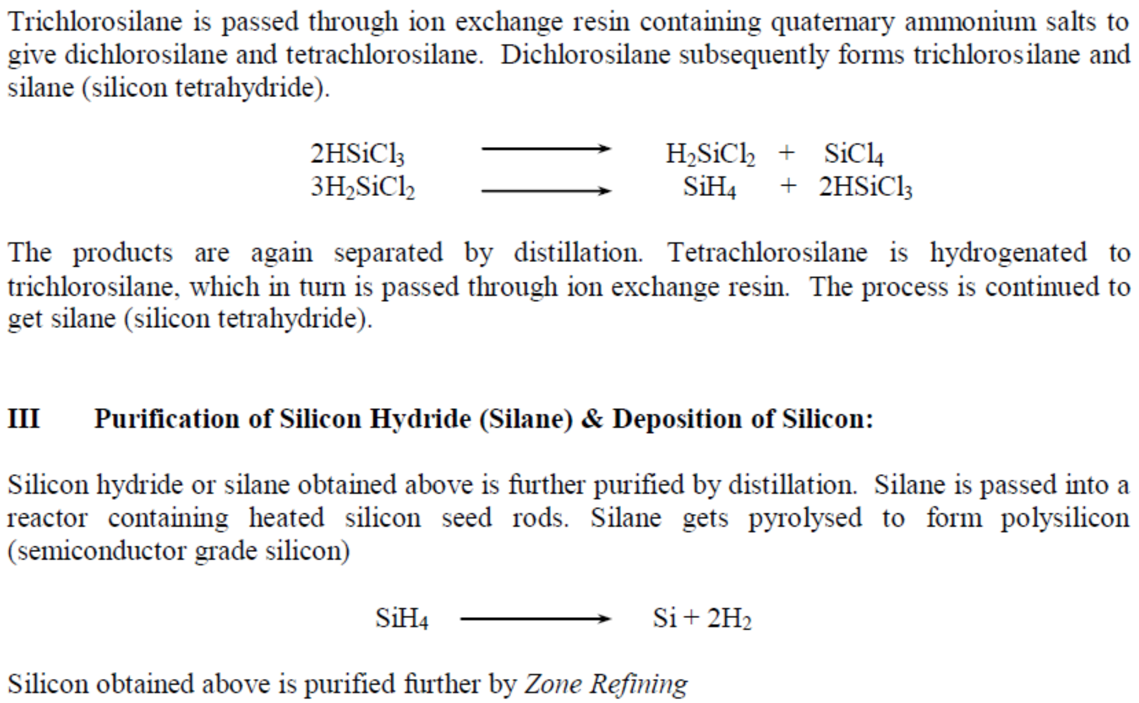
Metallurgical grade silicon is heated to 300-350°C and dry hydrogen chloride is passed. Trichlorosilane and a small amount of tetrachlorosilane are formed as given below

$$Si + 3\,HCl \longrightarrow \underset{\text{Trichlorosilane}}{HSiCl_3} + H_2$$

$$Si + 4\,HCl \longrightarrow \underset{\text{Tetrachlorosilane}}{SiCl_4} + 2H_2$$

The compounds can be separated by simple distillation. Then, tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C in a reactor.

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



Trichlorosilane is passed through ion exchange resin containing quaternary ammonium salts to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms trichlorosilane and silane (silicon tetrahydride).

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$
$$3H_2SiCl_2 \longrightarrow SiH_4 + 2HSiCl_3$$

The products are again separated by distillation. Tetrachlorosilane is hydrogenated to trichlorosilane, which in turn is passed through ion exchange resin. The process is continued to get silane (silicon tetrahydride).

III Purification of Silicon Hydride (Silane) & Deposition of Silicon:

Silicon hydride or silane obtained above is further purified by distillation. Silane is passed into a reactor containing heated silicon seed rods. Silane gets pyrolysed to form polysilicon (semiconductor grade silicon)

$$SiH_4 \longrightarrow Si + 2H_2$$

Silicon obtained above is purified further by *Zone Refining*

(b) What is reforming of petrol? Describe catalytic reformation with reactions. (04 Marks) (CO4, L2, L3)

Solution: 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. Structural modifications refer to linear hydrocarbons being converted into more compact branched hydrocarbons or into cyclic hydrocarbons or into alkenes or into aromatics.

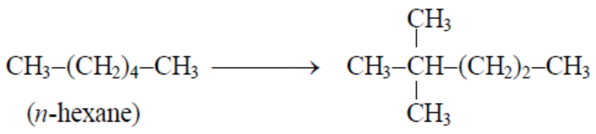
Process conditions-

Feed stock: Virgin gasoline

Catalyst: Pt supported on alumina or silica base, Temperature: 475-525°C, Pressure: 15-50 atm.

Description- Feed stock vapor, free from sulphur and nitrogen content (which otherwise would poison the catalyst) is mixed with hydrogen, preheated, compressed and passed over catalyst in a series of reformers and the products are fractionated to get **stabilized gasoline**. Reforming reactions are as follows:

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

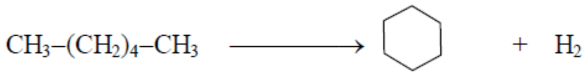


$$CH_3{-}(CH_2)_4{-}CH_3 \longrightarrow CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}H{-}(CH_2)_2{-}CH_3$$

(*n*-hexane)

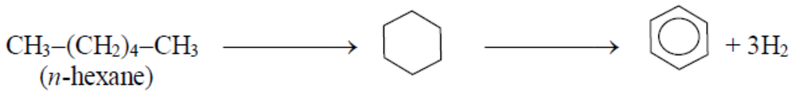
(2-methyl pentane)

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



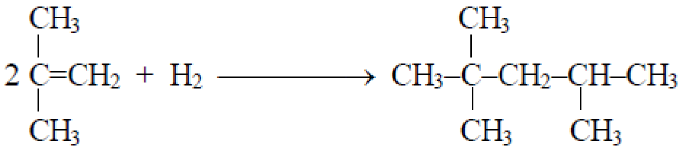
(*n*-hexane) (cyclohexane)

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



(cyclohexane) (Benzene)

(iv) Polymerization & hydrogenation:

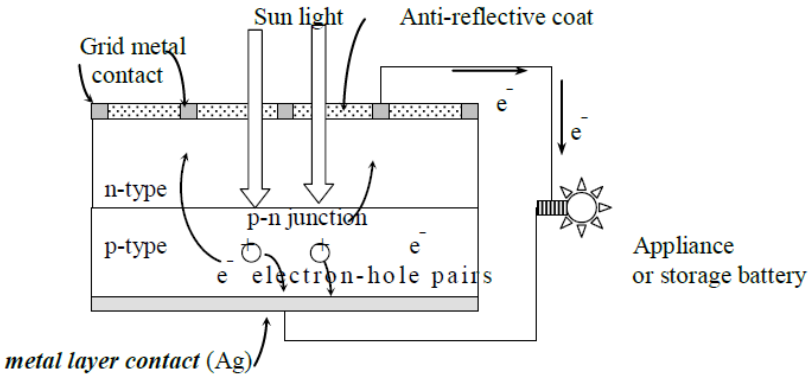


$$2\ \underset{CH_3}{\overset{CH_3}{C}}{=}CH_2 + H_2 \longrightarrow CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{CH}{-}CH_3$$

(Isobutene) (*iso*-octane or 2,2,4-trimethyl pentane)

5. (a) Explain the construction and working of PV cell. **(05 Marks) (CO4, L4)**

Solution:



Photovoltaic cell is made of a semiconductor diode (p-n junction). The diode has two electrical contacts. A metallic grid is used on one side and on the other side; a layer of noble metal such as Ag is used. Ag is nobler than the Si-semiconductor and this contact is called as back contact.

The metal grid permits the light to fall on the diode between the grid lines. An antireflective coating is used to enhance the light trapping (absorption) by p-n junction.

$$E = \frac{hc}{\lambda},$$

where E is the energy of photon absorbed; h is the Planck's constant, c is the velocity of the light and λ is the wavelength of the light.

When electromagnetic radiation (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 now and holes move towards p-region as it is negatively charged now.

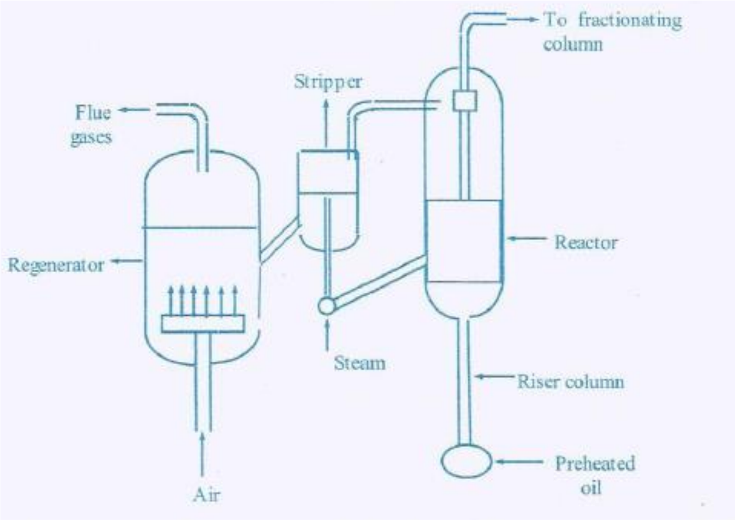
The electrons are driven into the external circuit and an appliance can be run using it or the energy can be stored in a battery. The stored energy could later be used for various applications such as lighting purposes, telecommunication, etc.

(b) Define cracking. Explain the process of fluidized bed catalytic cracking. (05 Marks) (CO4, L1, L4)

Solution:

Cracking is defined as the process of breaking of less useful, higher molecular weight hydrocarbons into more useful lower molecular weight hydrocarbons like kerosene, petrol etc. It involves rupture of C-C & C-H bond and produces low boiling alkanes & alkenes. The main objective of cracking to increase the quantity of useful fuel.

$$\underset{\text{Decane}}{C_{10}H_{22}} \longrightarrow \underset{\text{Octane}}{C_8H_{18}} + C_2H_4$$



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.

Advantages of fluidised bed catalytic cracking:

- The process is continuous unlike fixed bed cracking. Catalyst usage and regeneration are separate and simultaneous.
- Cracking efficiency is higher because, **feed in the vapour form and catalyst in the fluid form come in good contact with each-other.** Thermal cracking efficiency is lesser.
- Octane rating of fuel is higher (80-85) than in thermal cracking (66-68).

6. (a) Describe the synthesis of petrol by Fischer Tropsch process. (06 Marks) (CO4, L3).

Solution:

- 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.

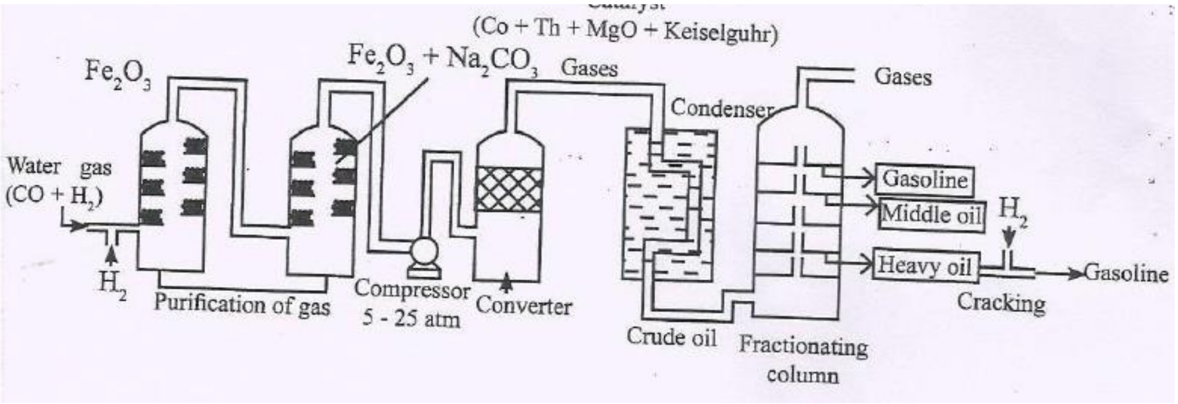
$$C + H_2O \xrightarrow{1200\ ^{\circ}C} \underset{\text{Water gas}}{CO + H_2}$$

- Water gas is mixed with H_2 to get synthetic gas.

$$CO + H_2 + H_2 \longrightarrow \underset{\text{Synthetic gas}}{CO + 2H_2}$$

- The gas is purified by passing through Fe_2O_3 (to remove H_2S) and then into a mix of Fe_2O_3. Na_2CO_3 (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.

Advantage:

1. No nitrogenous compound.
2. No sulphur compounds

Disadvantage:
1. Gasoline formed is rich in straight chain hydrocarbon and hence has low octane no.
2. Feed stock is coal which will compete with electrical power generation.
3. By product is CO_2, a green house gas associated with global warming.

(b) Explain Module, Panel, and Arrays of Photovoltaic cell. (04 Marks) (CO4, L2)

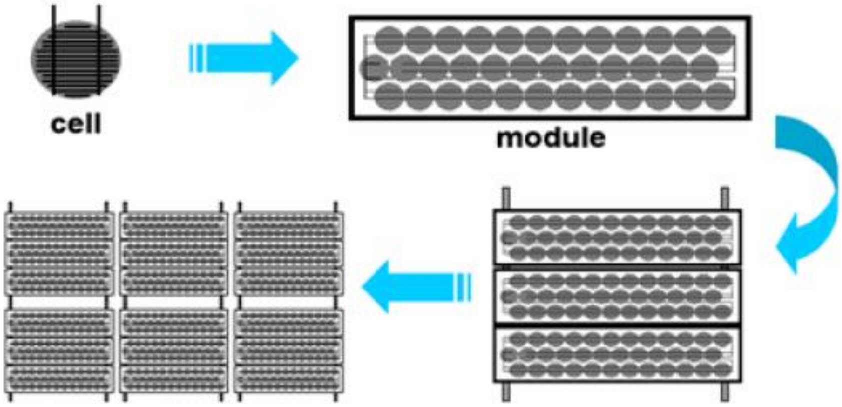
Solution:

Module: A single solar cell produces only 0.5 volts and hence cannot be used for power generation. At least 36 cells are connected to form a module. The module is the basic building block of systems for power generation. The cells in a module are connected in series provided with a protective back surface. This is called encapsulation and involves lamination of the cells between a polymer and a thin film of aluminium or stainless steel. Encapsulation protects the module from moisture and contaminants and pollutants in the atmosphere and thus prevent failure of the solar module. Though this should produce 18 volts, it produces only 12 -14 volts because the cells get heated in the sun.

Panel: If higher energy is needed, the modules may be connected in series or in parallel The group of modules that are packaged and connected with wires for installation is called a panel. A set of four or more modules are framed or attached together by wire connections panel. This panel is typically around 1.85 -3.25 square meter in area for ease of handling on a roof.

Array: An array consists of two or more panels and forms the power generating unit.

A photovoltaic system typically includes a panel or an array of solar modules, an inverter, and sometimes a battery and/or solar tracker and interconnection wiring.



7. (a) What are polymers? Explain the mechanism of free radical based addition polymerization taking vinyl chloride as an example. (07 Marks) (CO5, L4)

Solution: Polymers are macromolecules formed by the covalent linkage of a large number of monomer units. Eg. Polyethylene. The fundamental chemical process by which the monomer units are converted into a polymer is called **polymerization**.

Mechanism of addition polymerization by Free Radical mechanism

(Case study: Polyvinyl chloride)

This mechanism explains the addition polymerization. It involves three steps

1. Initiation. 3. Propagation 4.Termination

Initiation: Initiation of an addition polymerization reaction happens with the help of initiators which are thermally unstable compounds that decompose into products called free radicals. The decomposition takes place on supplying energy in the form of heat or light and the molecule splits into two symmetrical free radicals. For addition polymerization reaction of vinyl chloride, the initiator is dibenzoyl peroxide.

$$\underset{\text{vinyl chloride}}{nCH_2 = CHCl} \xrightarrow[h\upsilon\ /\Delta]{(C_6H_5COO)_2} \underset{\text{polyvinyl chloride}}{(\text{-}CH_2\text{-}CHCl\text{-}CH_2\text{-}CHCl\text{-})n}$$

The free radical here is generated as:

$$\underset{\text{Dibenzoyl peroxide}}{(C_6H_5COO)_2} \longrightarrow 2C_6H_5COO^{\cdot} \longrightarrow CO_2 + \underset{\text{phenyl radical}}{2C_6H_5^{\cdot}\ (\text{or } R_{.})}$$

Free radical having a lone pair electron, is very reactive, and can attack any molecule which has a lone electron or a double bond monomer molecule. The free radical R reacts with the double bond in the monomer resulting in a new free radical .

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

Propagation: In this step, the new free-radical attacks another monomer molecule to produce yet another new free radical. Many repetitions of this step lead to polymer chain growth and formation of the addition polymer. This continues until termination occurs.

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

Or in general,

$$CH_2 = CHCl + R\text{-}[CH2\text{-}CHCl]_{x\text{-}1}\text{-}CH_2\text{-}CHCl^{\cdot} \longrightarrow R\text{-}(CH_2\text{-}CHCl)_x\text{-}CH_2\text{-}CHCl^{\cdot}$$

$$CH_2 = CHCl + R\text{-}[CH2\text{-}CHCl]_{y\text{-}1}\text{-}CH_2\text{-}CHCl^{\cdot} \longrightarrow R\text{-}(CH_2\text{-}CHCl)_y\text{-}CH_2\text{-}CHCl^{\cdot}$$

Termination: The termination occurs when the growing polymer chain (free radical) is transformed into a stable polymer molecule. This may take place in two different ways.

(a) Termination by coupling:- Here, two growing chains combined by the coupling of one polymer free radical chain with another to form a dead polymer. As this process involves the coupling of the two lone electrons the termination step is known as" Termination by coupling".

Termination by coupling (by the combination of two radicals)

$$R\text{-}[CH_2\text{-}CHCl]_x\text{-}CH_2\text{-}CHCl^{\cdot} + {}^{\cdot}CHCl\text{-}CH_2\text{-}(CH_2\text{-}CHCl)_y\text{-}R \xrightarrow{\text{coupling}} R\text{-}(CH_2\text{-}CHCl)_x\text{-}CH_2\text{-}CHCl\text{-}CHCl\text{-}CH_2\text{-}(CH_2\text{-}CHCl)_y\text{-}R$$

Dead polymer

(b) Termination by dis-proportionation:- Here, one H from a growing chain is shifted to the other growing chain and as a result two dead polymer molecules are formed. One saturated and another unsaturated. Termination process result is the formation of two polymer molecules shorter chain length.

Termination by disproportionation

$$R\text{-}[CH_2\text{-}CHCl]_x\text{-}CH_2\text{-}CHCl^{\cdot} + {}^{\cdot}CHCl\text{-}CH_2\text{-}(CH_2\text{-}CHCl)_y\text{-}R \xrightarrow{\text{coupling}} R\text{-}(CH_2\text{-}CHCl)_x\text{-}CH_2\text{-}CH_2Cl + R\text{-}(CH_2\text{-}CHCl)_y\text{-}\ CH = CHCl$$

(b) Write short note on (a) Biodiesel or (b) Power alcohol. (03 Marks) (CO4, L2)

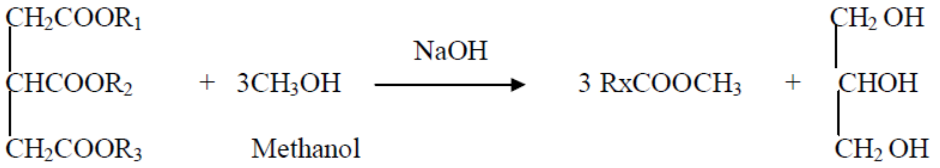
Solution: (a) Biodiesel

Biodiesel

1. Biodiesel is an alternative fuel which can be produced by a simple chemical process from waste vegetable oil.
2. Biodiesel refers to a vegetable oil or animal fat based diesel fuel consisting of long chain alkyl esters. It is a mixture of mono alkyl ester of long chain fatty acid.
3. Biodiesel is produced from

(a) Vegetable oil such as soyabean, corn, sunflower, cottonseed, coconut oil, palm oiletc.
(b) Waste vegetable oil (WVO)
(c) Animal fat – tallow, lard, chicken fat etc.

4. Biodiesel is produced by **'*Trans* – esterification' of vegetable oil or animal fat.** It involves reaction of vegetable or animal oil (triglycerides) with an excess of alcohol in presence of a catalyst to give monoalkyl ester of long chain fatty acid and glycerol. Commonly methanol is used to produce methyl esters (Fatty acid methyl ester – FAME). Ethanol is used to produce ethyl ester (Fatty acid ethyl ester – FAEE) biodiesel.



$$\begin{array}{l} CH_2COOR_1 \\ | \\ CHCOOR_2 \\ | \\ CH_2COOR_3 \end{array} + \underset{\text{Methanol}}{3CH_3OH} \xrightarrow{NaOH} 3\ RxCOOCH_3 + \begin{array}{l} CH_2\,OH \\ | \\ CHOH \\ | \\ CH_2\,OH \end{array}$$

Oil (Triglyceride oil) Bio diesel Glycerol

R_1, R_2, R_3 are long chain fatty acids in oil.
X – 1,2 & 3

The mixture is allowed to settle down at the bottom of tank, after that byproduct glycerol is simply drawn off from the bottom of the vessel. Excess methanol is removed through distillation. The upper layer is purified further and used. It has characteristics of diesel fuel.

Advantages –

1. It is renewable as it is derived from vegetable oil which is essentially grown – a sustainable resource.
2. It is carbon neutral. As vegetable from which Biodiesel is extracted utilizes atmospheric CO_2 during photosynthesis, while when Biodiesel is burnt CO_2 is liberated back to atmosphere.
3. It lacks unpleasant odour of petroleum diesel.
4. It is non – toxic.
5. It is biodegradable.
6. It is simple to produce.
7. It is non – hazardous and is safe to store.

Disadvantages-

1. Lower fuel economy and power
2. More expensive
3. More nitrogen oxide emission

Applications-

1. Used in conventional power generation.
2. Used as a heating fuel in boilers.
3. It can be used in most diesel engines.
4. It can be used to remove paints, adhesive etc.

Or

(b) Power Alcohol:

A blend containing **10 to 85% of ethanol and 15-90% of gasoline**, used as fuel is known as power alcohol. The addition of alcohol to petrol increases its octane no.. Power alcohol is used as a fuel by blending with petrol in IC engine. It is also blended with diesel to form E-diesel. Power alcohol has calorific value of about 7000 cal/g and its octane no. is 90.

Advantages:

- Addition of alcohol to petrol increases octane number (octane number of ethanol is 112) and reduces knocking.
- Because of increased O.N., it can be used in engine with high CR, thus better power output is achieved.
- Because, alcohol contains oxygen, it is referred as oxygenate which assist better combustion efficiency. Also, VOC (volatile organic content) emissions are reduced or pollution is lessened.
- Alcohol can be synthesised from plants. Thus, especially, with higher proportion of alcohol, one has a sustainable fuel [an alternative to fast depleting fossil fuels].
- When synthesised, helps in improved economy of a country because imports are avoided.

Disadvantages:

- Lowers the calorific value of the fuel (two third that of gasoline).
- Atomization is difficult because of high surface tension of alcohol.
- Alcohol gets oxidised to acids and may corrode concerned engine equipment.
- Modification of CR of the engine is required otherwise, power out put is reduced.
  (Gasoline engines generally have a CR of around 8 which need be increased to around 12).
- Alcohol as such has good affinity for water and as a result separation of alcohol and petrol layers takes place especially at low temperature. To avoid this blending agent such as benzene or toluene are used.