



# സഹായി

**SFI GEC PALAKKAD**

**B**

**NSA192009**

Reg No.: \_\_\_\_\_

Name: \_\_\_\_\_



**APJ ABDUL KALAM TECHNOLOGICAL UNIVERSITY**  
FIRST SEMESTER B.TECH DEGREE EXAMINATION(2019 SCHEME), DECEMBER 2019

**Course Code: CYT100**

**Course Name: ENGINEERING CHEMISTRY**  
**(2019-Scheme)**



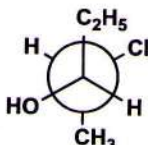
Max. Marks: 100

Duration: 3 Hours

**PART A**

*Answer all questions, each carries 3 marks.*

- 1 Calculate the equilibrium constant for the following reaction at 25°C:-  

$$\text{Fe}_{(s)} + \text{Cu}^{2+}_{(aq)} = \text{Fe}^{2+}_{(aq)} + \text{Cu}_{(s)}$$
 Given  $E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ ,  $E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$  (3)
- 2 Give the electrochemical reaction taking place when an iron nail is dipped in dil.HCl.  $E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ ,  $E^0_{\text{Fe}^{3+}/\text{Fe}} = -0.04 \text{ V}$ ,  $E^0_{\text{H}^+/\text{H}_2} = 0 \text{ V}$ . (3)
- 3 State and explain the law governing absorption of electromagnetic radiation by matter. Give any one limitation of this law. (3)
- 4 Which molecule will absorb at longest wavelength in UV? Explain.  
 a)  b)  (3)
- 5 What are the classifications of chromatography based on physical state of mobile and stationary phases? (3)
- 6 Explain the synthesis of nanoparticles by chemical reduction. (3)
- 7 Write the IUPAC name and assign R/S notation.  
 (3)
- 8 Write the different types of copolymers formed by the monomers A and B. (3)
- 9 Calculate the hardness of (i) 0.05 M  $\text{AlCl}_3$  and (ii) 0.04 N  $\text{MgCl}_2$ . (3)
- 10 What is the significance of measuring BOD of waste water? (3)

**PART B**

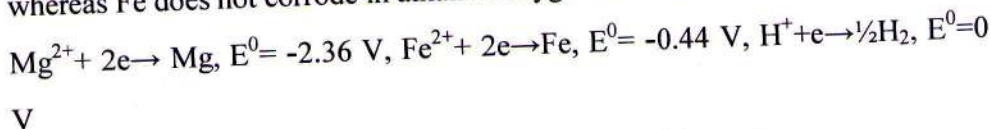
*Answer one full question from each module, each question carries 14 marks*

**Module-I**

- 11 a) Explain the construction and working of a calomel electrode as a reference electrode. What is the variation in the potential of a calomel electrode with change in chloride ion concentration? (8)

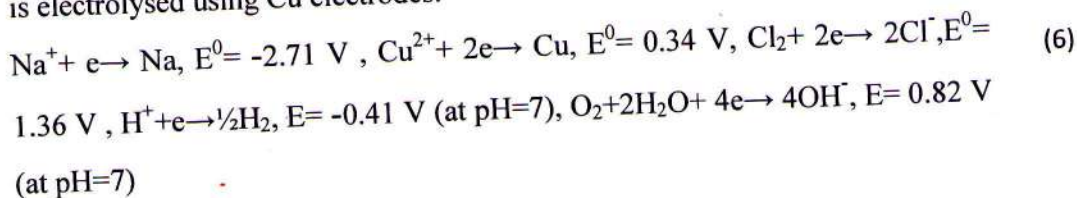
B

- b) Why Mg corrodes in both acidic and alkaline oxygen deficient conditions, whereas Fe does not corrode in alkaline oxygen deficient condition? (6)



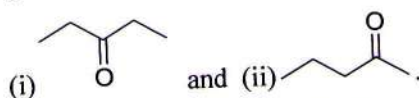
- 12 a) Write the construction, working and advantages of Li-ion cell. (8)

- b) What are the products of electrolysis at cathode and anode when NaCl solution is electrolysed using Cu electrodes.



### Module-II

- 13 a) Predict the number of signals, their relative positions and splitting pattern in the nmr spectrum of the following. (8)



- b) Compare the strengths of C-H bond and C=O bond if the absorption frequencies are  $3000\text{cm}^{-1}$  and  $1700\text{cm}^{-1}$  respectively. (6)

- 14 a) Give the instrumentation of UV spectrophotometer and explain the components in it. Comment on the role of conjugation in the wavelength of absorption with the help of examples. (8)

- b) Briefly explain the principle involved in MRI. Mention any two applications. (6)

### Module-III

- 15 a) Discuss in detail the Instrumentation of TG and DTA with neat sketch. (8)

- b) Discuss the various detectors used in GC and HPLC. (6)

- 16 a) Briefly explain the principle, instrumentation and applications of SEM. (8)

- b) Differentiate between TGA and DTA. (6)

### Module-IV

- 17 a) Draw and explain the conformational isomerism in ethane and butane. Draw the energy profile diagram. Which conformer is more stable in each case? (10)

- b) Explain the classification of conducting polymers. (4)

- 18 a) What is meant by conformational isomerism? Draw the *cis* and *trans* isomers of 1,4-dimethyl cyclohexane. In each case, mention the more stable conformer. (8)

- b) Brief out the basic principle, construction and working of OLED. (6)

### Module-V

**B****NSA192009****Pages: 3**

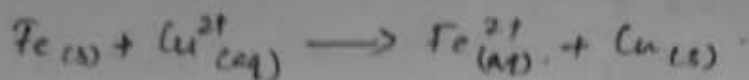
- 19 a) Describe the various steps involved in sewage treatment. (10)  
b) Write any four disadvantages of hard water. (4)
- 20 a) Write the principle and procedure of estimation of permanent and temporary hardness of water by complexometric titration. (8)
- b) 50 mL sewage water sample after reaction with 20 mL of  $K_2Cr_2O_7$  required 12.4 mL of 0.2 N ferrous ammonium sulphate solution. For blank titration 20 mL  $K_2Cr_2O_7$  required 20.4 mL of 0.2 N ferrous ammonium sulphate solution. (6)  
Calculate the COD of the sample.

\*\*\*\*

SFI GECP

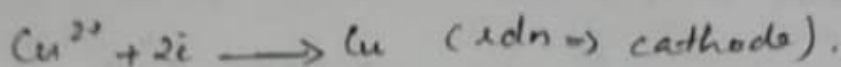
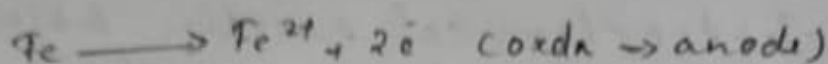


1. Calculate the equilibrium constant for the following reaction at  $25^\circ\text{C}$ .



Given  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$ ,  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$ .

soln



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

$$= E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Fe}^{2+}/\text{Fe}}$$

$$= 0.34 - (-0.44)$$

$$= 0.34 + 0.44$$

$$= 0.78\text{V}$$

By Nernst eqn. SFI GEC

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log k. \quad \text{--- (1)}$$

We have

$$\Delta G = -nF E_{\text{cell}}$$

At eqb  $\Delta G = 0$

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

$$\therefore \text{(1)} \Rightarrow 0 = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log k$$

$$= 0.78 - \frac{0.0591}{2} \log k$$

$$0.78 = \frac{0.0591}{2} \log k$$

$$\log k = \frac{0.78 \times 2}{0.0591}$$

$$= 26.4$$

$$k = \underline{2.5 \times 10^{26}}$$

2. Give the electrochemical reaction taking place when an iron nail is dipped in dil HCl.

$$E_{Fe^{2+}/Fe}^{\circ} = 0.44V \quad E_{Fe^{3+}/Fe}^{\circ} = -0.04V \quad E_{H^+/H_2}^{\circ} = 0V.$$

soln



S F I G E C

Here,

$Fe^{2+}$  is formed, not  $Fe^{3+}$  because,  
 $E_{cell}^{\circ}$  for  $Fe^{2+}$  is ::

$$E^{\circ} = E_c - E_a$$

$$= 0 + 0.44$$

$$= \underline{0.44V}$$

and  $E_{cell}^{\circ}$  for  $Fe^{3+}$  is

$$E^{\circ} = E_c - E_a$$

$$= 0 + 0.04$$

$$= 0.04V$$

We have

$$\Delta G = -nFE_{cell}$$

If  $E_{cell} \uparrow$   $\Delta G$  becomes more negative and reaction will be more spontaneous. Here

$E_{cell}$  of  $Fe^{2+}$  is greater than  $E_{cell}$  of  $Fe^{3+}$ .

$\therefore$  formation of  $Fe^{2+}$  is more spontaneous than  $Fe^{3+}$ .

$\therefore$  When an iron nail is dipped in a dil.  $HCl$ , the salt of the corresponding metal will be formed, here  $FeCl_2$  (ferrous chloride not ferric chloride due to spontaneity reason) along with liberation of hydrogen gas.

### 3. Beer-Lambert's Law

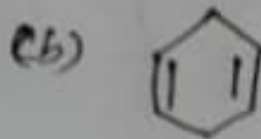
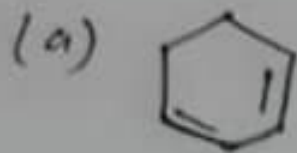
When a parallel beam of monochromatic electromagnetic radiation is passed through an absorbing solution of given concentration ( $c$ ), the rate of decrease of intensity ( $-di$ ) of radiation with thickness of the solution ( $dx$ ) is proportional to the intensity of incident radiation ( $i$ ) at that point and also to the concentration ( $c$ ) of the solution

$$-\frac{di}{dx} \propto ic$$

Limitation:-

• Light shouldn't be scattered.

4. Which molecule will absorb at longest wavelength in UV? explain. (4) (5)



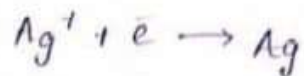
Soln

Molecule (a) absorb longest wavelength in UV radiation due to the presence of conjugated double bonds. In case of molecule (b), due to the absence of conjugated double bond, it will absorb low wave length radiation. @

In molecule (a)  $\pi$  to  $\pi^*$  transition takes place from HOMO to LUMO.



**Reduction:** Nano particles of gold and silver can be prepared by the reduction of their respective solutions using reducing agents, such as sodium borohydride, ascorbic acid, glucose etc. along with a protective agent like thiol, glucose etc. This method can be divided into two, reduction using reducing agents and electro reduction.



(a) **Reduction using reducing agents:** Silver nanoparticles can be prepared by the following method. 60 mL of 1 mM  $\text{AgNO}_3$  solution is taken in a beaker, covered with a watch glass and heated on hot plate. The solution is then stirred using a magnetic stirrer. On boiling the solution, 6 mL of 10 mM of trisodium citrate is added dropwise, about one drop per second. The beaker is then closed and kept for some time till the colour of the solution changed to a light golden colour. Then it is allowed to cool. The solvent can be removed by freeze-drying.

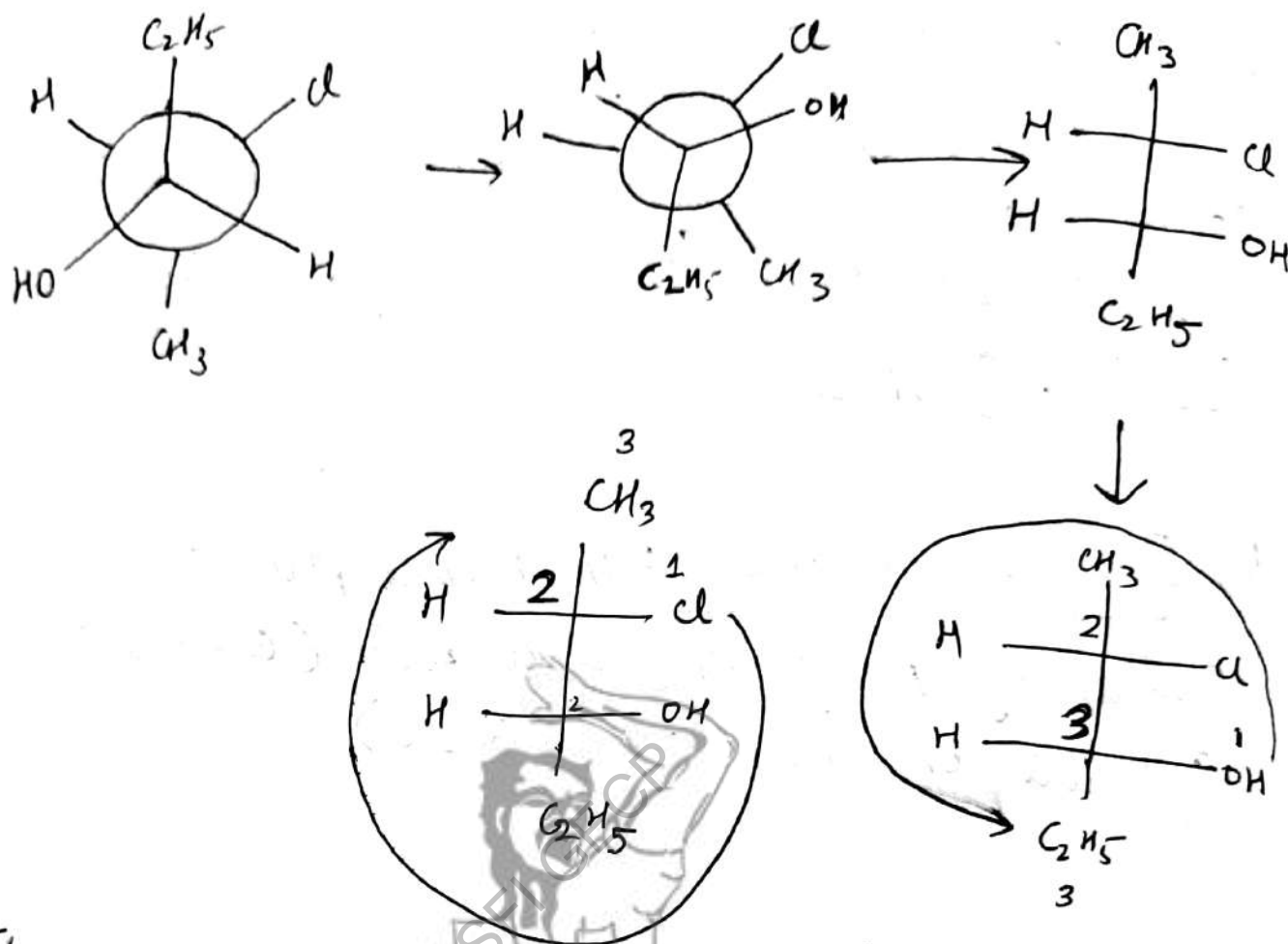
(b) **Electro reduction:** Copper nanoparticles have been prepared by electro-reduction process using copper plating bath containing homogeneously acidified copper sulphate solution. The nanoparticles are formed as spongy black coloured layers of ball structures at the cathode. The spongy layers of copper can be easily separated to give the particles.

5a) Based on the physical state of mobile and stationary phase, it can be classified as.

a) Liquid Chromatography: The mobile phase and stationary phase can be solid (LSC) or liquid supported on inert (LLC). Eg HPLC.

b) Gas Chromatography: The mobile phase is a gas and stationary phase can be a solid (GSC) or liquid supported on inert solid (GLC).

7A)

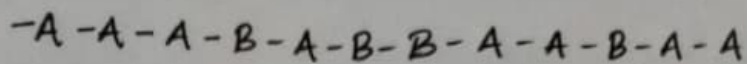


The wedged lines are represented in the right hand side of Newman's projections. Similarly, the groups coming in the left side of Newman projection is dashed bonds. The other bonds in the Newman projection should come plane bond.

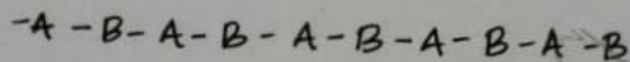
The given structure is converted into wedgedashed structure. Then IUPAC name =  $(2S, 3R)$ -2-chloropentan-3-ol

8. Write the different types of copolymers formed by monomers A and B.

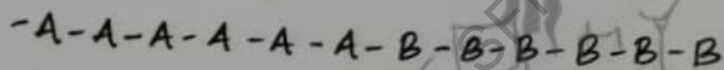
Ans: Random copolymer: The monomer species are located randomly in polymer molecule



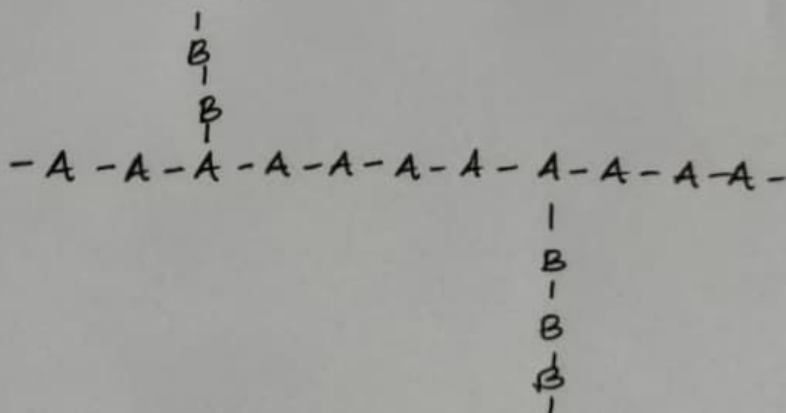
Alternating copolymer: Two species of monomer units distributed in alternating sequence



Block copolymer: Two or more homopolymer subunits linked by covalent bonds



Graft copolymer: The main chain is formed from one type of monomer and branches are formed from another type of monomer





Q. (i) 0.05M  $AlCl_3$

$$\begin{aligned}\text{Normality of } AlCl_3 &= M \times \text{charge of the ion} \\ &= 0.05 \times 3 \\ &= 0.15\end{aligned}$$

$$\begin{aligned}\text{Hardness} &= N \times \text{eq. wt of } CaCO_3 \\ &= 0.15 \times 50 \\ &= 7.5 \text{ g/L} \\ &= 7500 \text{ mg/L} \\ &= \underline{\underline{7500 \text{ ppm}}}\end{aligned}$$

(ii) 0.04 N  $MgCl_2$

$$\begin{aligned}\text{Hardness} &= 0.04 \times 50 \\ &= 2 \text{ g/L} = 2000 \text{ mg/L} \\ &= 2000 \text{ ppm}\end{aligned}$$

10. Significance of BOD: Dissolved oxygen is an important factor that determines the quality of water. Presence of biologically oxidisable substance like carbohydrate, proteins etc. increases the biological oxygen demand of water. During the oxidation of these materials by aerobic micro-organisms, the dissolved oxygen present in water is consumed. In lakes, rivers or aquaculture ponds the presence of these substances will be a threat to aquatic life and water gets polluted. Thus by knowing the value of BOD, the extent of pollution can be determined.

## PART B

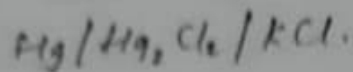
11. a) Explain the construction and working of a calomel electrode as a reference electrode. What is the variation in the potential of a calomel electrode with change in chloride ion concentration?

Soln.

Calomel electrode is a secondary reference electrode. This is commonly used reference electrode since it is difficult to set up and maintain SHE. This is an example of metal-metal insoluble metal salt electrode and a solution of its common ion (mercury-mercurous chloride electrode, KCl). It consists of a glass tube at the bottom of which a small amount of Hg is placed. This is covered with a paste of solid mercurous

chloride ( $\text{Hg}_2\text{Cl}_2$ /calomel) which is further in contact with a solution of  $\text{KCl}$ . A Pt wire dipped into the  $\text{Hg}$  layer is used for making electrical contact. The side tube is used for making contact with a salt bridge.

The electrode is represented as,



Electrode reaction:-



$$E^\circ = +0.2810 \text{ V}.$$

- The calomel electrode can act as anode or cathode depending on the electrode potential of the coupled electrode.
- If the electrode potential of the coupled electrode is lower than calomel electrode, then calomel electrode undergoes reduction and act as cathode.
- If the potential of the coupled electrode is greater, calomel electrode will undergo oxidation and act as anode.

Nernst equation of this electrode:-

$$E_{\text{calomel}} = E_{\text{calomel}}^\circ - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2$$

$$E_{\text{calomel}} = E_{\text{calomel}}^\circ - \frac{2.303RT}{F} \log [\text{Cl}^-]$$

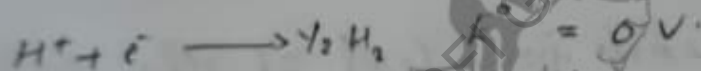
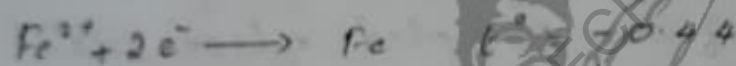
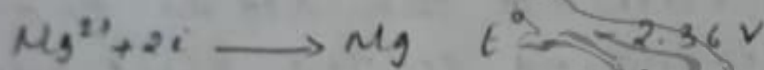
For saturated calomel electrode electrode potential =  $0.2422 \text{ V}$ .



From the above equation it is seen that the potential of the calomel electrode varies with the concentration of the KCl solution (or  $\text{Cl}^-$  ion concentration).

i.e. potential of calomel electrode decreases with increase in the concentration of  $\text{Cl}^-$  ion.

- b) Why Mg corrodes in both acidic and alkaline oxygen deficient conditions, whereas Fe does not corrode in alkaline oxygen deficient condition?



Soln.

In acidic medium, electrode potentials are.

$$E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2} = 0 \text{ V}$$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

$$E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.36 \text{ V}$$

Here the electrode potential of both Fe & Mg is less than hydrogen  $\therefore$  they get have a tendency to get oxidised. Therefore in acidic medium both Fe & Mg get corroded.

But in the case of alkaline medium, the electrode potential of Hydrogen is different. It is  $-0.828 \text{ V}$

The electrode potentials are:

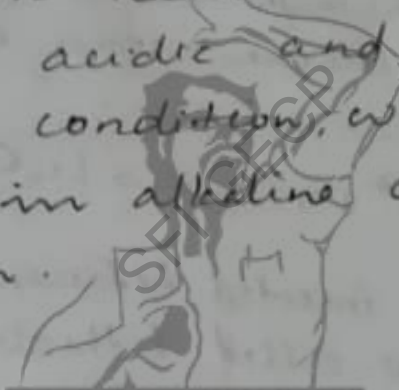
$$E_{H^+/H_2} = -0.828 V$$

$$E_{Fe^{2+}/Fe} = -0.44 V$$

$$E_{Mg^{2+}/Mg} = -2.36 V$$

Here the reduction potential of Mg is greater than hydrogen so it has a tendency to get reduced & hence corrodes. But in the case of Fe, the electrode potential is greater than Hydrogen <sup>so</sup> and it has less chance to get corroded.

∴ This is the reason why Mg corrodes in both acidic and alkaline oxygen deficient condition, whereas Fe does not corrode in alkaline oxygen deficient condition.



12. a) Write the construction working and advantages of Li-ion cell.

#### Construction

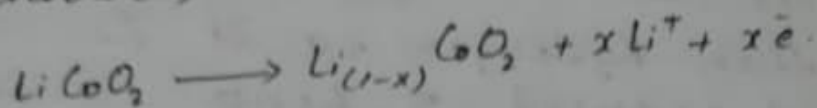
Li-ion cell is a rechargeable battery in which Li-ion moves between anode and cathode during charging and discharging. In typical lithium ion cell, the positive electrode is made by using a crystalline mixed oxide  $Li_2O \cdot Co_2O_3$  or  $LiCoO_2$ . The negative terminal is made of graphite. The electrolyte is a solution of Li-salt ( $LiPF_6$ ,  $LiBF_4$  or  $LiClO_4$ ), in an organic solvent such as ether or a solid phase polymer electrolyte which can transport  $Li^+$  ion.

## Working

### charging:-

- During charging the cell act as an electrolytic cell, the electrical energy is converted into chemical energy.

At anode (+):-



Here  $x < 1$ .

At cathode (-):-

The  $\text{Li}^+$  ion produced at the anode get migrated through the electrolyte and get reduced to lithium atoms at the graphite electrode.

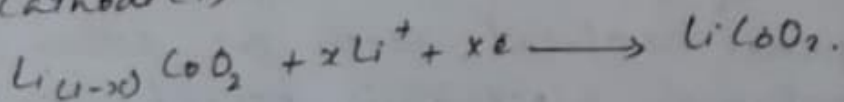


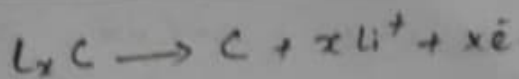
- Li atoms are inserted between the layers of carbon atoms. This so called lithiated graphite is written as  $\text{Li}_x\text{C}_6$ , containing no Li metal as such. This why Li-ion battery is not called as Li battery.

### Discharging:-

- During discharging, the cell act as an electrochemical cell, the chemical energy is converted to electrical energy. When the cell act as an electrochemical cell,  $\text{LiCoO}_2$  act as cathode while graphite act as anode.

At cathode (+) :-



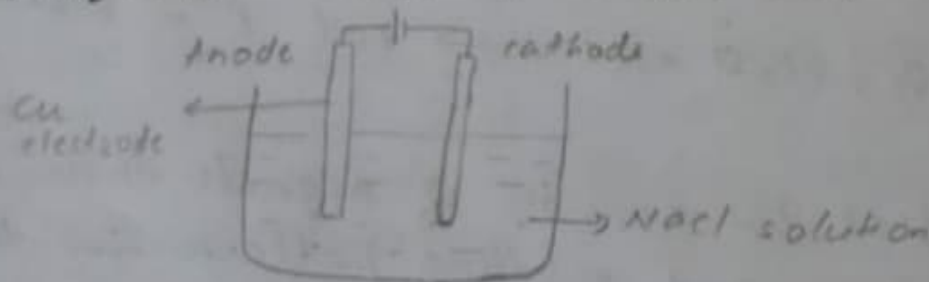
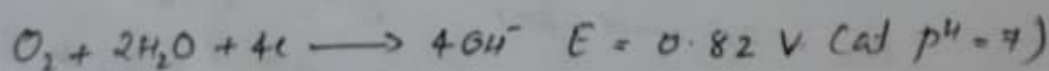
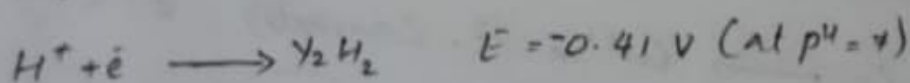
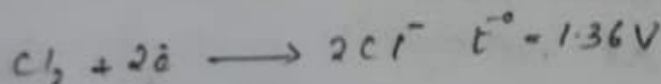
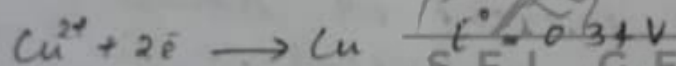
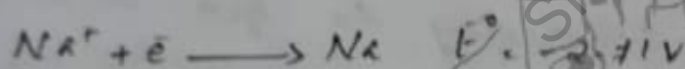


Lithium-ion cell based on  $LiCoO_2$  has an emf of 3.7 V.

### Advantages

- It is more popular than other batteries because of the various characteristics of Lithium. Li has a higher negative value for reduction potential and a lower atomic mass than any other metal. Only 6.94 g of Li is needed to provide 1 mole of electrons.
- The cell is having high energy to weight ratio.

6) What are the products of electrolysis at cathode and anode when NaCl solution is electrolysed using Cu electrodes.



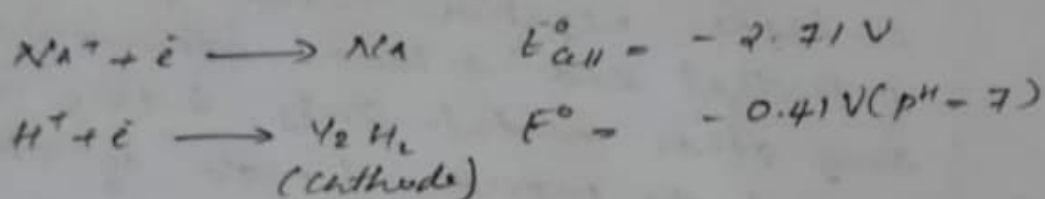
The ions formed in the solution are  $Na^+$ ,  $Cl^-$ ,  $H^+$ ,  $OH^-$



### At cathode (-)

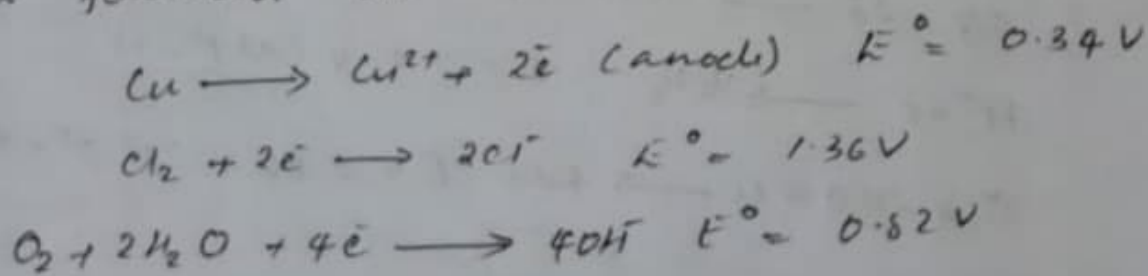
(10)

- Reduction takes place in cathode. Since cathode is negative the ions occupies near cathode are  $H^+$  &  $Na^+$ .
- But  $H^+$  has more electrode potential than  $Na^+$ ,  $\therefore H^+$  has more tendency to get reduced,  $\therefore$  Hydrogen gas is liberated at cathode.

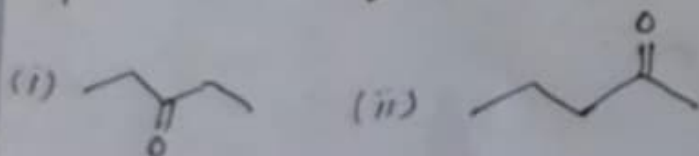


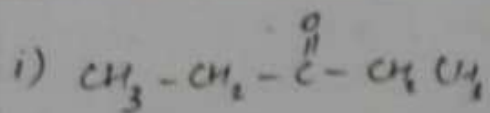
### At anode (+)

- Oxidation takes place at anode. Since anode is positive, the ions occupies near anode are  $OH^-$  &  $Cl^-$ .
- Since the anode is Cu electrode, & Cu also have a tendency to get reduced.
- Among the ions present at anode Cu has lowest electrode potential  $\therefore Cu^{2+}$  ion is formed at anode.



3. a) Predict the number of signals, their relative positions and splitting pattern in the nmr spectrum of the following





Here no. of types of proton = 2

$\therefore$  no. of signals = 2.

Type a ( $\text{CH}_3$ ) = 6 protons

Type b ( $\text{CH}_2$ ) = 4 protons

$\therefore$  ratio = 6:4 = 3:2



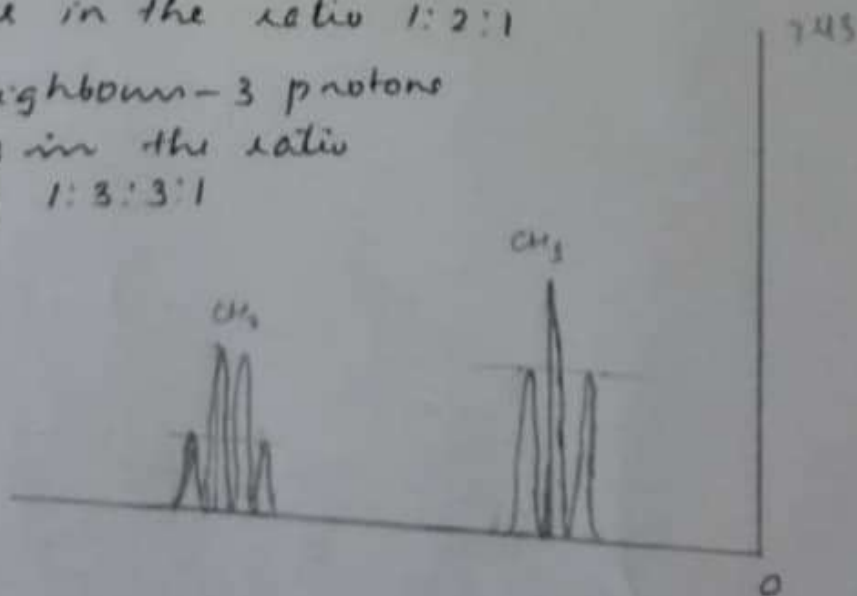
splitting

a  $\rightarrow$  neighbours - 2 proton

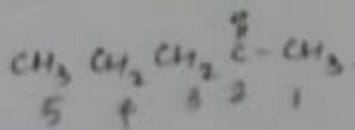
$\therefore$  split in the ratio 1:2:1

b  $\rightarrow$  neighbours - 3 protons

split in the ratio  
of 1:3:3:1



ii)



Here the no. of types of proton = 4.

$\therefore$  no. of signal = 4.

ratio = 3:2:3:2



splitting

5  $\rightarrow$  neighbouring protons = 2

$\therefore$  splits in the ratio of 1:2:1

4  $\rightarrow$  neighbouring protons = 5

splits into 6.

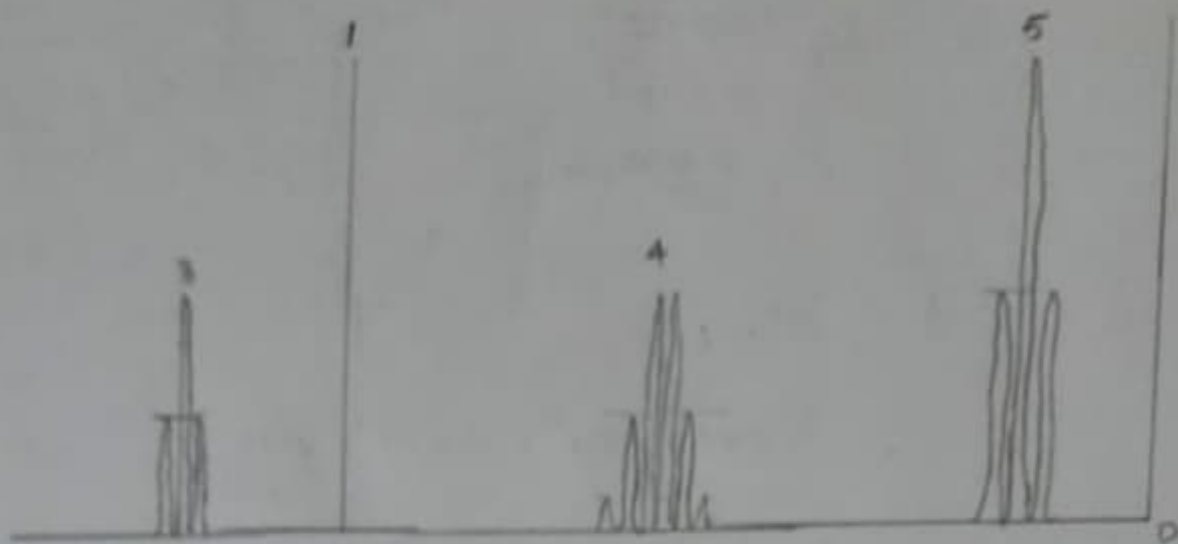
1:5:10:10:5:1

3  $\rightarrow$  neighbouring protons 2

splits in the ratio 1:2:1

1  $\rightarrow$  0 neighbouring proton

$\therefore$  no splitting.



- 6) Compare the strength of C-H bond C=O bond of the absorption frequencies are 3000  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$  respectively

soln

In case of CH bond.

$$k = 4\pi^2 \nu_0^2 \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$k = \frac{4\pi^2 \nu_0^2 \mu}{2\pi}$$

$$\nu = \bar{\nu} c \quad k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

here  $\bar{\nu} = 3000 \text{ cm}^{-1} = 3 \times 10^5 \text{ m}^{-1}$

$$\mu = \frac{12 \times 1}{13}$$

$$= \frac{12}{13}$$

$$k = 4\pi^2 \times 9 \times 10^{16} \times 9 \times 10^{10} \times \frac{12}{13}$$

$$= \underline{\underline{2990 \times 10^{26} \text{ N/m}}}$$



In the case of  $c=O$

$$m = \frac{16 \times 12}{21} = \frac{192}{21}$$

$$\begin{aligned}\bar{L} &= 1700 \times 10^2 \\ &= 1.7 \times 10^5\end{aligned}$$

$$K = 4\pi^2 \bar{\nu}^2 m c^2$$

$$= 4\pi^2 \times 16 \times 10^2 \times (1.7 \times 10^5)^2 \times \frac{192}{21}$$

$$= 7134.2 \times 10^{26} \text{ N/m}$$

SFI GEC

$K_{c=O} > K_{C-H}$

$c=O$  bond is stronger than  $c-H$  bond

14. a) Give the instrumentation of UV spectrometer and explain the components in it. Comment on the role of conjugation in the wavelength of absorption with the help of examples.

The UV spectrometer consists of a light source, monochromator (prism or grating), sample, reference, detector and recorder. The most suitable light sources are Tungsten Filament lamp and H-discharge lamp. In modern instruments xenon flash lamps are used. Most of the spectrometers are double beam instruments. A beam of light is split into two equal beams and one is passed through sample (sample beam  $I$ ) and the other through reference (reference beam  $I_0$ ). A very dilute solution of the sample is prepared using a suitable solvent and is taken in transparent cuvette. The pure solvent is taken as reference in another simple cuvette. The most commonly used solvents are water, ethanol, hexane and cyclohexane. The intensities of these light beams are then measured by electronic detectors and compared. If the sample doesn't absorb light of a given wavelength then,  $I = I_0$ . However if the sample absorbs light then  $I$  is less than  $I_0$  and this difference is detected and recorded. The graph obtained is a plot of absorbance  $V_s$  wavelength.

## - Effect of conjugation -

The greater the number of conjugated double bonds the lower the energy jump and higher the wavelength of the UV-visible peak.

eg:



$\lambda_{\text{max}}$

nm

165

16,000

217

21,000



eg: In ethylene molecule  $\text{CH}_2 = \text{CH}_2$  the absorption peak is at 169 nm.

But in the case of 1,3-butadiene the absorption peak is at 217 nm.

SFI GEC



### 15(a) Thermogravimetric analysis (TGA):

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature, as the sample is heated from room temperature to temperature as high as  $1200^{\circ}\text{C}$  in a controlled atmosphere.

#### Instrumentation:

The main components of TGA apparatus are the following:

1. Sample holder
2. Furnace with temperature programming facility.
3. Thermobalance.
4. Temperature sensor.
5. Environment control Equipment.
6. Detector and recorder.



The sample to be analyzed (3mg) is taken in the sample holder. The sample holder is surrounded by a furnace with temperature programming facility. i.e., the heating rate can be adjusted according to the requirement of the experiment. Eg.  $5^{\circ}\text{C}/\text{min}$  or  $10^{\circ}\text{C}/\text{min}$  etc. The environment control equipment provides suitable atmosphere for analysis such as, air,  $\text{N}_2$ , He, etc. The sample holder is attached to a thermobalance which is highly temperature sensitive.



ie, whenever the temperature changes, it automatically measures the mass of the sample. The temperature sensor records the sample temperature. The signals are amplified and recorded. The graph obtained is a plot of mass vs temperature.

### Differential Thermal Analysis (DTA):

Differential Thermal Analysis is a thermoanalytic technique. In DTA, the material under study and an inert reference material (usually alumina, silicon carbide or glass beads) are heated under identical conditions at a constant rate.

SFI GEC

### Instrumentation:

In DTA, the material under study and an inert reference material are heated under identical conditions at a constant rate. Two thermocouples  $T_1$  and  $T_2$  record the ~~thermo~~ temperature in sample and reference. The data is amplified and processed in a computer.

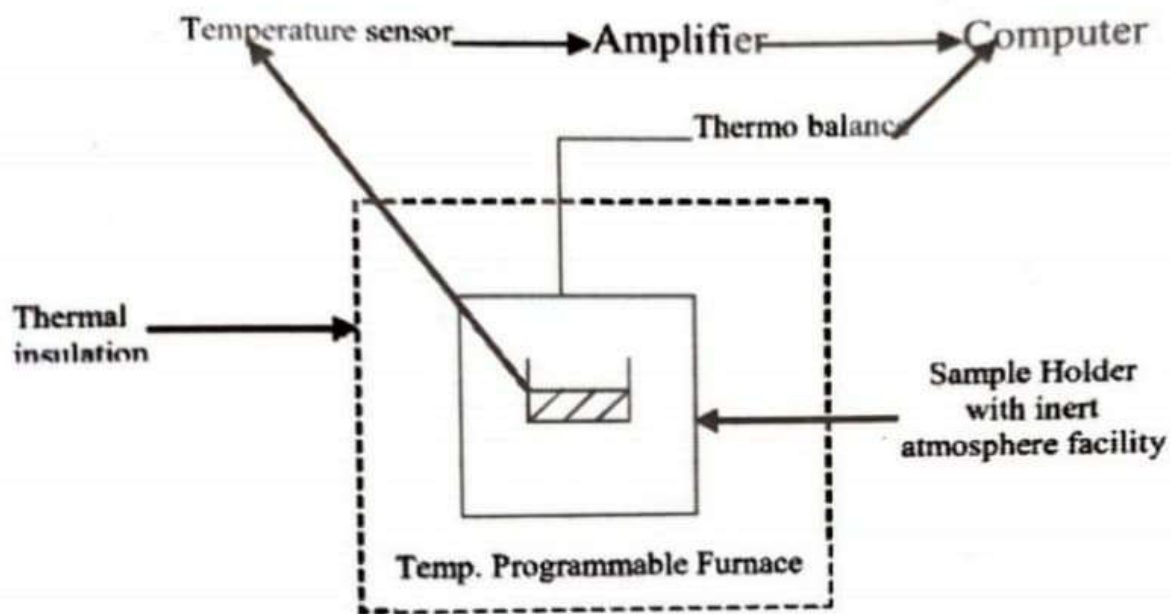


Figure 3.2: Block diagram of TGA apparatus

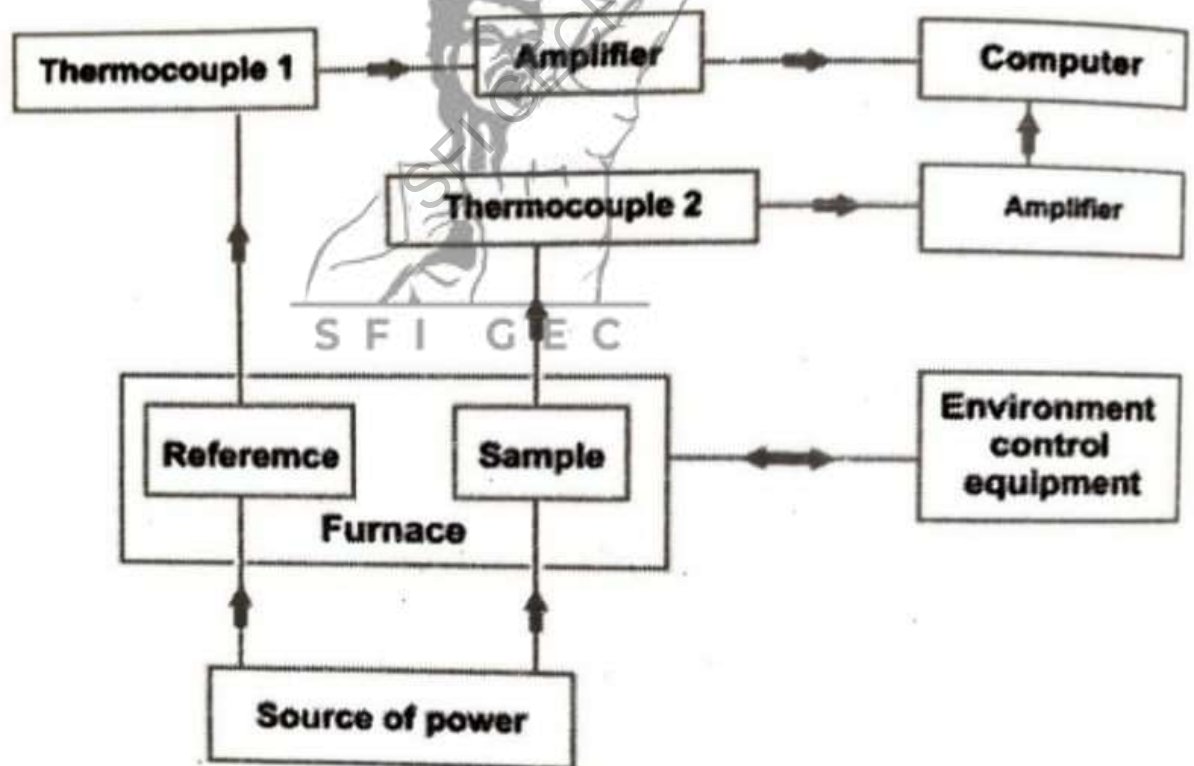


Figure 3.7: Block diagram of DTA apparatus



(b) In GC,

**Detectors:** Any physical property, which varies widely from one gas to another and which can be easily monitored from the basis of the detector. Based on these physical properties, detectors are of various types. These include Thermal conductivity Detector (TCD), Flame ionisation detector (FID), Electron capture detector (ECD) etc. The FID and TCD are considered as universal detectors while ECD is a specific detector.

(i) Thermal conductivity detector (TCD) or Katharometer (KCD) : The thermal conductivity detector responds to all types of organic and inorganic compounds including those not detected by FID. Further, it doesn't destroy the eluted components and therefore it is suitable for preparative work. It is however less sensitive than the FID with a minimum detection limit



of  $10^{-5}$  g. The principle is based on the rate of heat loss from a heated wire placed in a gas stream (made of Pt or W), which depends on the thermal conductivity of the gas, so the temperature of the wire changes, consequently the resistance.

(ii) Flame Ionisation Detectors (FID): The ionization detectors are based on the electrical conductivity of gases. So the flame ionization detector is the most widely used and generally applicable detector for gas chromatography. With a burner ( $H_2$ -air flame), the effluent from the column is mixed with  $H_2$  and air and then ignited electrically. Most organic compounds, when pyrolysed at the temperature of a  $H_2$ /air flame, produce ions and electrons that can conduct electricity through the flame. The resulting current ( $10^{-12}$  A) is then directed into a high impedance operational amplifier for measurement.

In HPLC,

Detectors used are of 2 types:

- (i) Bulk property detector: Bulk property detectors respond to bulk properties like refractive index, dielectric constant, density etc., of the mobile phase. When a particular species are eluted out, these properties will change and detector gives the signal. After detection, the component is collected in the sampling tube along with solvent. The qualitative analysis can be done by spectral studies.
- (ii) Solute property detectors: They respond to solute properties such as UV absorbance, fluorescence properties of the solute molecules which are not possessed by mobile phase. For eg. paracetamol can be detected using UV-detector since it gives an absorption at 255 nm due to the presence of a benzene ring in the molecule.



16. a) Briefly explain the principle, instrumentation and applications of SEM

b) Differentiate between TGA and DTA

Ans: Principle: SEM produce images of a sample by scanning the surface with a focused beam of electrons. The interaction of electron beam with the atoms near the surface of the sample results in production of secondary electrons (SE), back scattered electrons (BSE) and x-rays. The signals are then detected by appropriate detectors and can be used to obtain information about the surface topography and composition. The high resolution, three-dimensional images produced by SEM makes them invaluable in a variety of science and industry applications.

Instrumentation:

1. Electron Source: Generates beam of energetic electrons. They are of 2 types:

① Thermionic gun (produces electron beam at high temperature, eg:- W filament, La B<sub>6</sub> etc)

② Field emission gun (produces electron beam under strong electric field)

2. Anode: Accelerates the electron beam. As the velocity of electron increases wavelength decreases (according to the De Broglie relation,  $\lambda = h/mv$ ) and thus enhances the resolution power.

3. Vacuum chamber: High vacuum minimises the scattering of electron beam.

4. Condenser lens: It is the electromagnetic lens used to focus the electron beam into small, thin and coherent beam. Generally tubes wrapped in coils, known as solenoids, are used as condenser lenses.

5. Objective lens: It is also an electromagnetic lens. Electron beam passes through the scanning coils of objective lens that deflect the beam in raster fashion over a rectangular area of sample surface.
6. Sample chamber: The sample is kept in sample chamber.
7. Detectors: There are suitable detectors to detect SE, BSE and X-rays.
8. PC control: To provide the SEM image.

### Applications:

1. SEM helps in characterization of solid materials
2. It can detect and analyze surface features, surface contamination and provide information in microstructure.
3. It helps to reveal spatial variations in chemical compositions and to identify crystalline structures.
4. It is used as an essential ~~research~~ research tool in fields such as life science, nano-science, gemology, medical and forensic science.

⑥ ~~Diff~~

Thermogravimetric Analysis (TGA)	Differential Thermal Analysis (DTA)
Mass vs temperature is plotted	$T_s - T_R = \Delta T$ vs $T_s$ is plotted
Type of molecule is lost during a decomposition can be determined	No such information
Rate of evaporation of a liquid can be determined	No such information
composition of binary mixtures can be determined	No such information

No information regarding  
Melting point phase transition  
temperature of a solid.

No information regarding  
glass transition ( $T_g$ ) temperature  
of a polymer.

No information regarding  
enthalpy change ( $\Delta H$ ) of a  
process.

Melting point phase transition  
temperature of a solid can  
be measured

Glass transition ( $T_g$ ) temp.  
of a polymer can be  
determined.

Enthalpy change ( $\Delta H$ ) of a  
process can be determined  
from peak area.

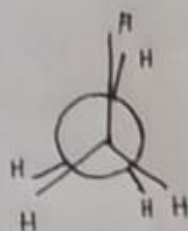




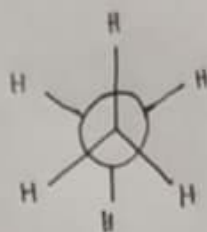
17 a

- Conformational isomerism is a form of stereo isomerism where interconversion of isomers are possible by rotations referring to single bond.

Ethane -

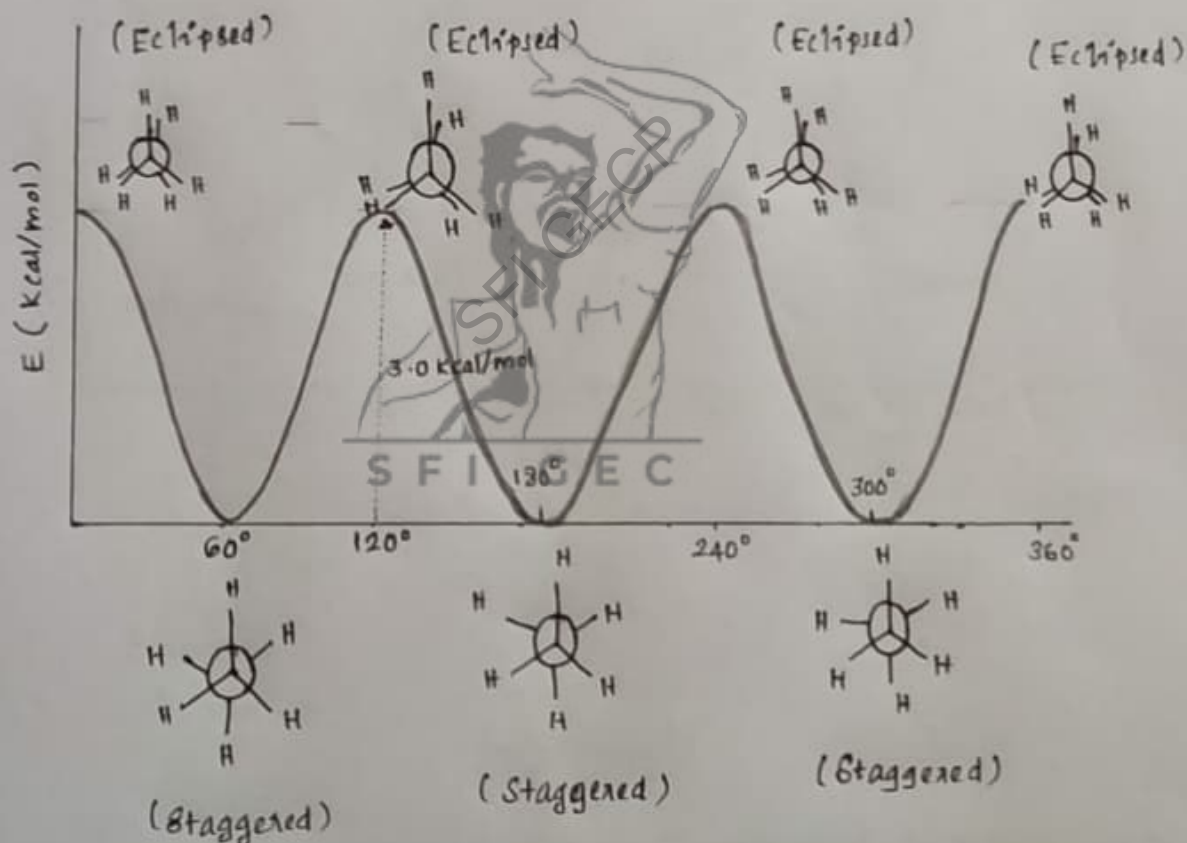


Eclipsed Ethane



Staggered ethane

Energy profile diagram



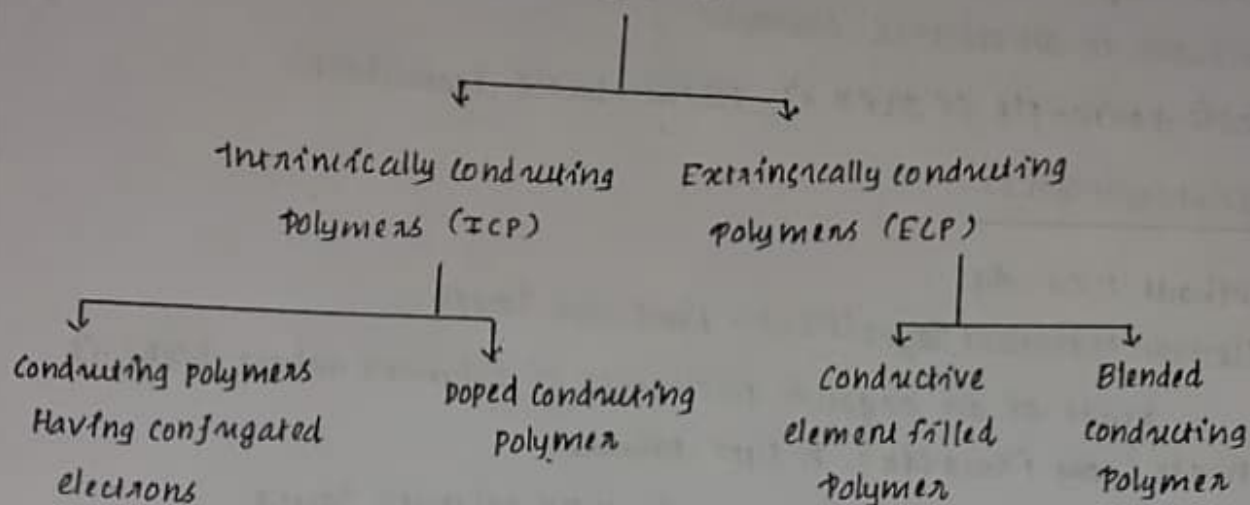
From the energy profile diagram it is clear that in ethane staggered form have less energy  $\therefore$  they are more stable



17 b

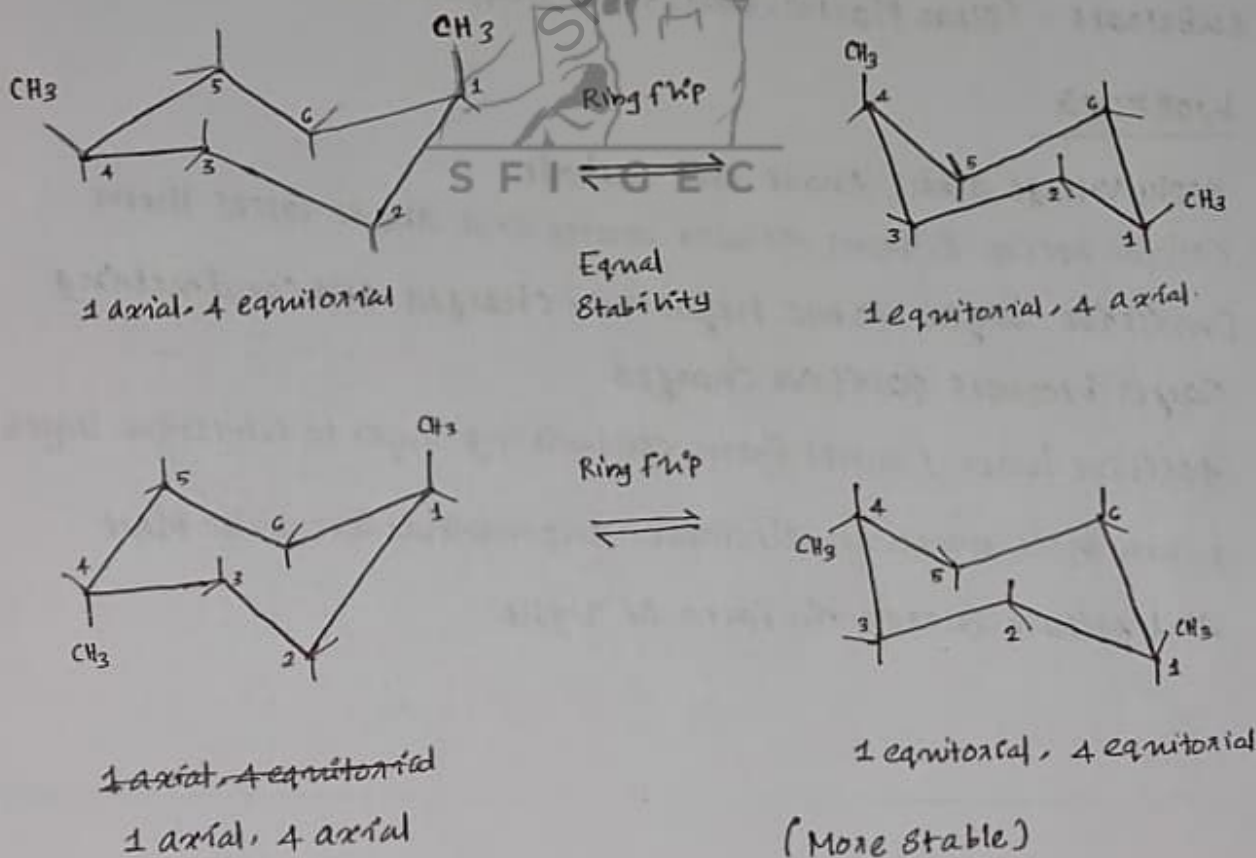
A polymer which can conduct electricity is termed as conducting polymer.

### Conducting Polymers



18 a

Conformational isomerism is a form of stereo isomerism where interconversion of isomers are possible by rotations referring to single bond.



OLED is a Light emitting diode in which the emissive electroluminescence layer is a film of compound which emit light in response to an electric current

- Basic principle of OLED is HOMO-LUMO transition.

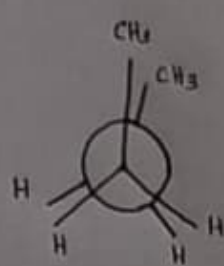
### Construction:

- Cathode : Ca, Ag
- Electron transport layer (ETL) - Emissive layer  
made of an organic molecule of polymer where light is made (poly Fluoride) n-type polymer
- Hole transport layer (HTL) conductive polymer layer  
that transport hole from anode  
(Poly aniline or poly paraphenylene vinylene PPV)  
P-type Polymer
- Anode - ITO, LiF
- Substrate - (clear plastic, glass, foil) supports the OLED

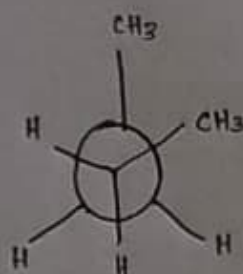
### WORKING

- Apply voltage across Anode and Cathode
- Cathode receive  $e^-$ s from power source and anode losses them
- Emissive layer become negatively charged and conducting layer becomes positive charged
- positive holes jumps from conducting layer to emissive layer
- When hole meets an electron, recombination take place and release energy in form of light.

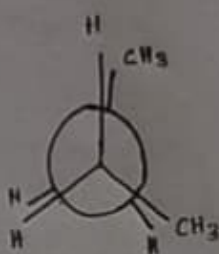
## Butane :



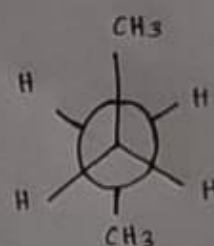
Eclipsed



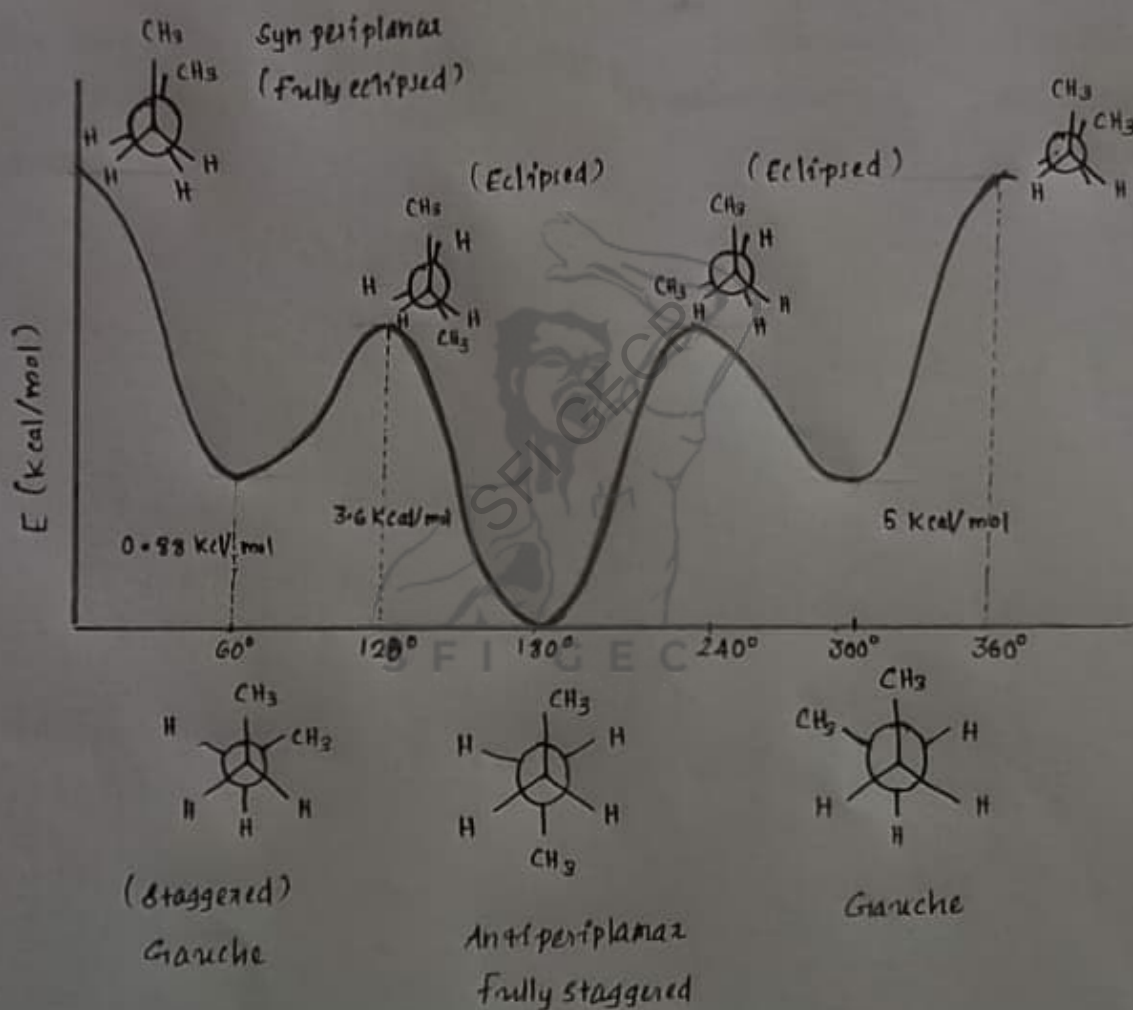
Gauche



Partially Eclipsed



Staggered

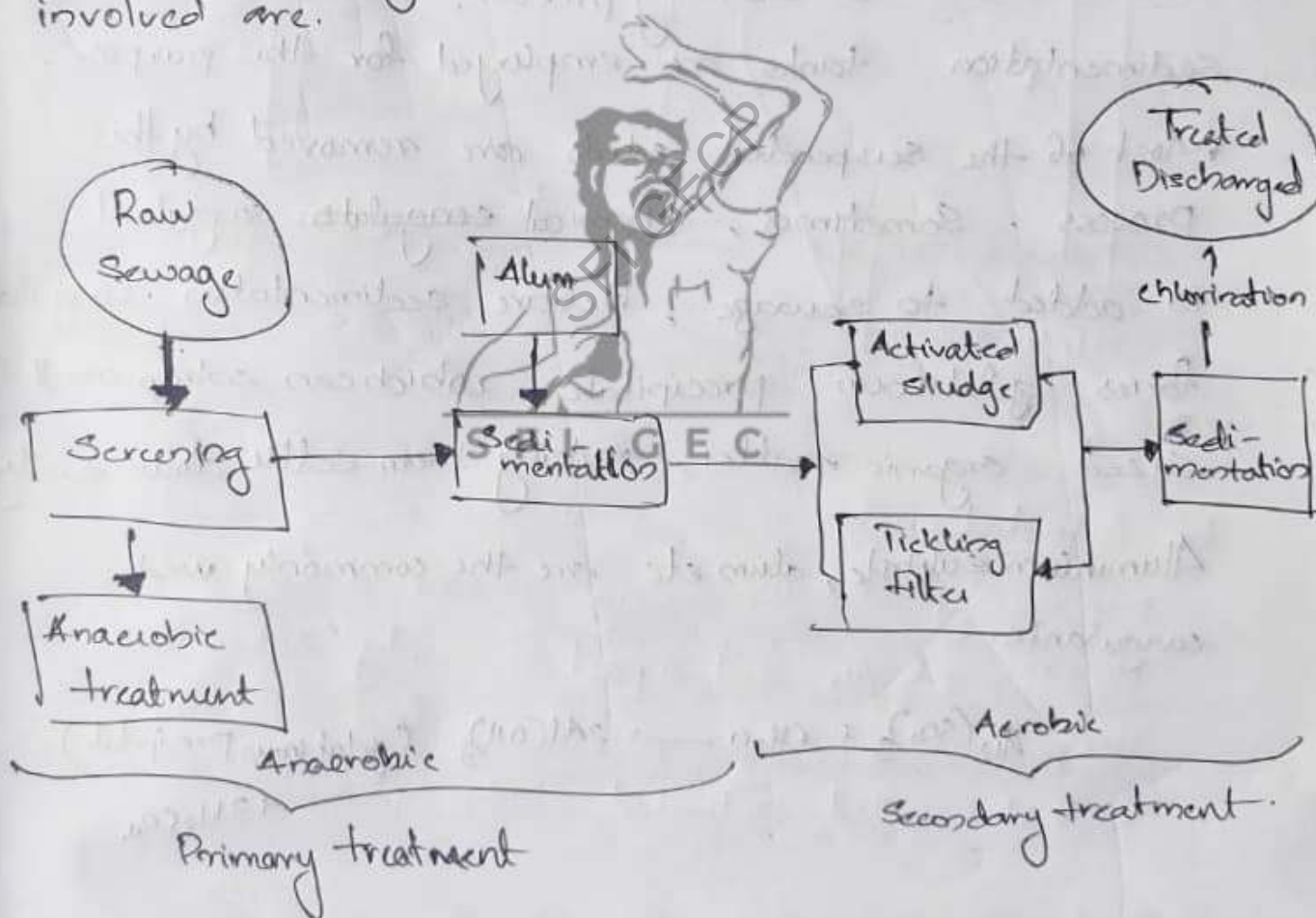


From the energy profile diagram it is clear that Anti periplanar (Fully staggered) structures have lesser energy. Therefore it is more stable.



19)

Sewage water has to be treated before sending it into running streams. Presence of biologically oxidisable matter (carbohydrates, proteins etc) in water increases the BOD of the water. The sewage treatment is carried out to reduce BOD of water. If high BOD water is sent to running streams, due to lack of dissolved oxygen aquatic life get extinct, Sewage treatment is carried out using an artificial process. The various steps involved are.



### ① Primary Process:

- a) ~~Sewage~~ Screening: In this process, large solids and inorganic matter, which are suspended in the sewage, are removed. Sewage is passed

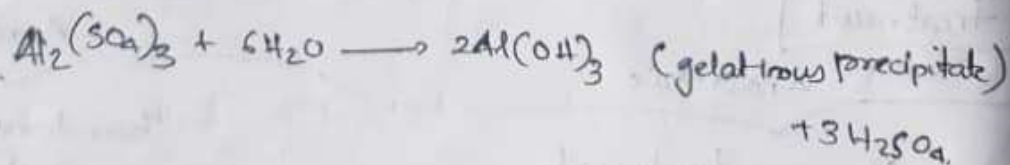


in upward direction through bar and mesh screens to remove suspended and coarse solids. The residue obtained is subjected to anaerobic treatment such as USAB process and the filtrate is subjected to sedimentation followed by aerobic treatment such as trickling filter process.

b) Sedimentation or settling process: Continuous flow-type sedimentation tanks are employed for this purpose.

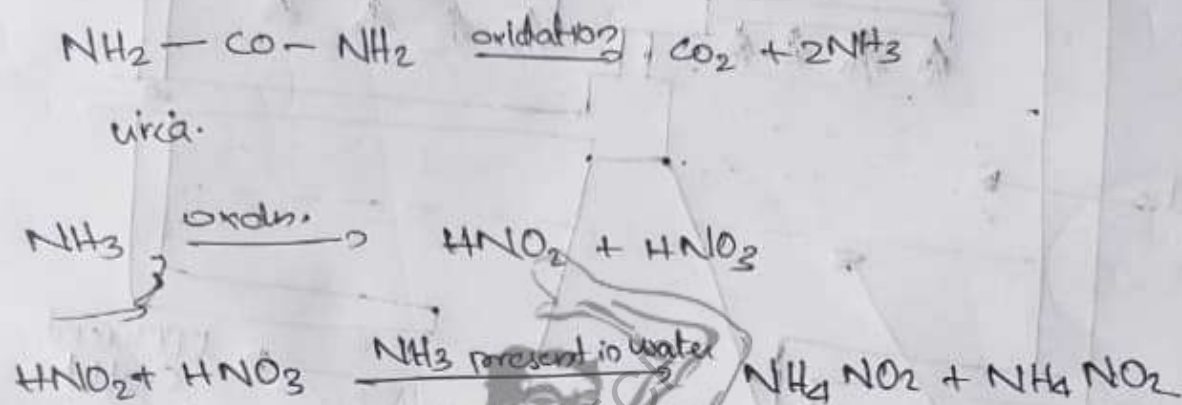
Most of the suspended solids are removed by this process. Sometimes, chemical ~~coagulation~~ coagulant is added to sewage before sedimentation. Coagulant forms gelatinous precipitate, which can entrap small sized organic matter, making them settle down easily.

Aluminium sulphate, alum etc are the commonly used coagulants.



## ② Secondary process or Biological Treatment:

This process is used for treating the filtrate obtained in primary process. This is aerobic the oxidation of sewage, during which the conversion of carbon to  $\text{CO}_2$ , nitrogen to  $\text{NH}_3$  and finally to nitrate and nitrates occur.



③ There are two types of aerobic process.

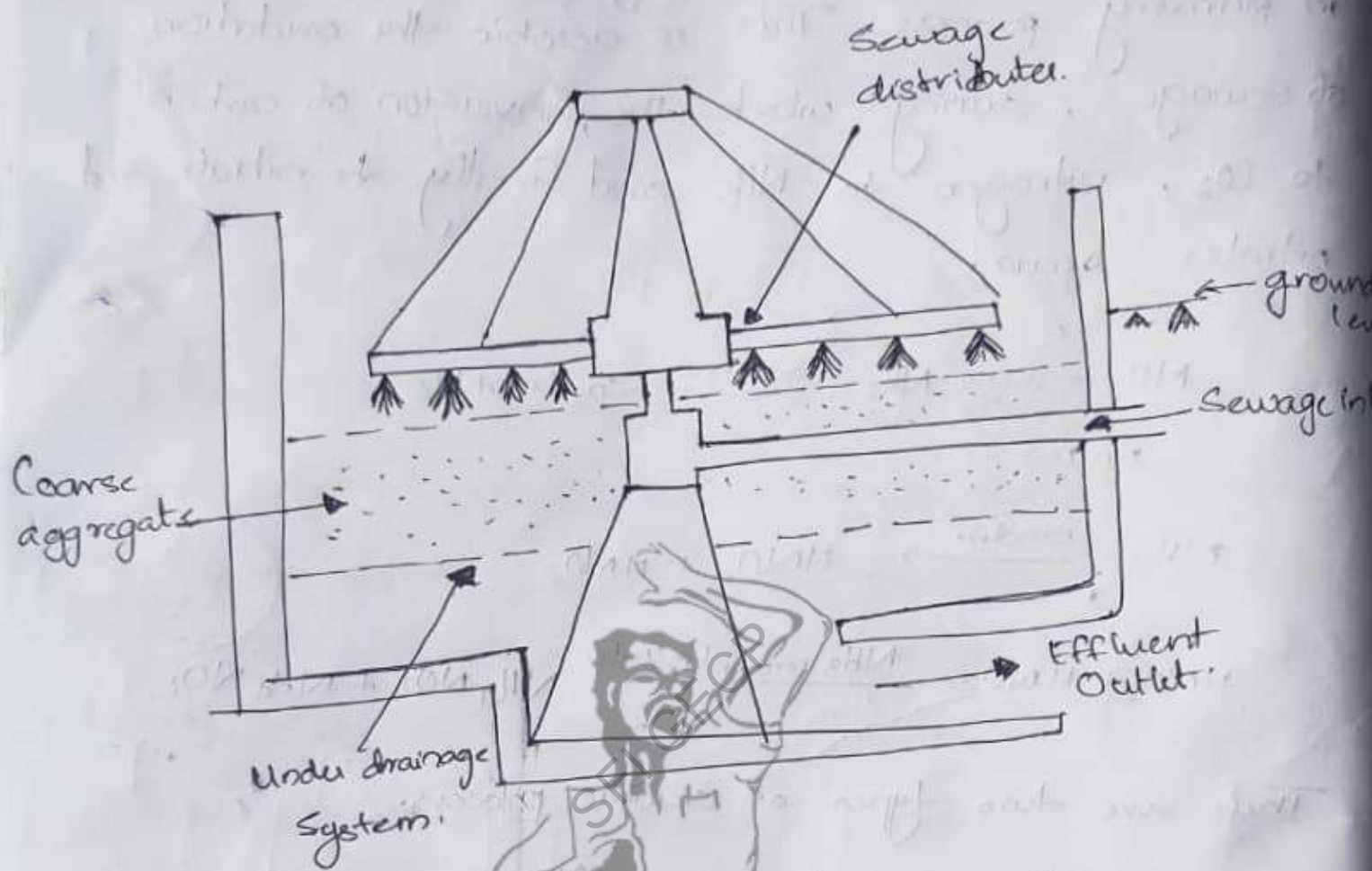
### a) Trickling filter method (Aerobic filtration method):

Biological treatment is carried out with the help of trickling filters. The filter is in rectangular in shape with about 2m depth. It is filled with material like broken bricks, crushed rock etc. and fitted with a rotating distributor.

The sewage trickles over the filter with the help of a rotating distributor then it moves down through the filtering medium and the aerobic micro-organisms start consuming the organic matter in the sewage matter in the sewage. They grow over the surface of the



agitates and more or less effluent is collected using under drive system.



b) **Activated sludge process:** In this process aerobic processing of the sewage is carried out in the presence of air and a part of sludge taken from the previous oxidation process is fast and this method is called activated sludge process.

③ **Tertiary treatment:** This is the advanced phase of sewage treatment. By the process, the amount of nitrogen and phosphorus compounds present in the effluent can be reduced. The three steps involved are

a) Precipitation: Effluent from the secondary process is treated with  $\text{CaO}$  so that calcium phosphate will be precipitated.

b) Nitrogen stripping: Ammonia gas is removed by passing the effluent through a series of baffle plate.

c) Chlorination: Disinfection of sewage is done by treating with chlorine, when pathogenic bacteria are killed.

After tertiary treatment the water can be sent to ponds or water bodies.





B. Disadvantages of using hard water for industrial purpose:

1. Scale and sludge formation in boilers:

During continuous evaporation of water in boilers the concentration of dissolved salts if present increase progressively finally the conc attain saturation and at this point the salts are driven out of water as precipitates, which stick to the inner walls of the boiler

2. Priming and foaming in boilers. - when a boiler produces steam rapidly, some particles of liq water will also be carried along with steam. This wet steam formation is called priming. Foaming is the process of formation of small, but persistent foam or bubbles at the surface of water in boilers

3. It causes boiler corrosion

4. Hard water is not good for dyeing clothes,

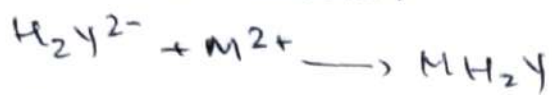
5.

5. It tastes bitter

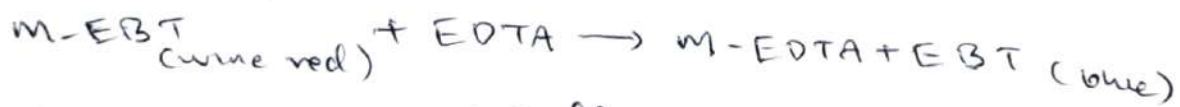
6. It produces stain in bathroom fittings

7. Cause wastage of soap in laundry

20) a) principle:- ethylene diamine tetra acetic acid can be represented as  $H_2Y$ , where H represents the acetic H-atoms and Y represents the remaining organic part. EDTA exist as divalent anion ( $H_2Y^{2-}$ ) at about pH 10 the anion complexes with metal ions ( $M^{2+}$ ) present in hard water.



The titration is conducted using an indicator Erichrome Black T (EBT). EBT forms wine red coloured complex M-EBT with the metal ions  $M^{2+}$  at pH around 10. As hard water is titrated against EDTA, it first gets complexed with free  $M^{2+}$  ions present in hard water. But towards the end point no free  $M^{2+}$  ions are available. Thus it takes metal ions from M-EBT complex. Since M-EBT complex is less stable than M-EDTA, M-EBT complex decomposes. Thus free indicator (blue color) is generated near the end point and the colour of the solution changes from wine red to blue.



Here  $NH_4OH-NH_4Cl$  Buffer Solution is used to maintain the pH around 10, since only at this pH EBT can form complex  $Ca^{2+}$  or  $Mg^{2+}$ .

Complexation takes place by the donation lone pairs of electrons by the two nitrogen atoms of the azo group and the two phenolic OH groups. The colour change in complexation is due to lack of  $n \rightarrow \pi^*$  transition in complex.



procedure : Preparation of standard hard water  
about 1g of pure, ~~ex~~ dry  $\text{CaCO}_3$  is weighted accurately  
and is dissolved in minimum quantity of dilute HCl and  
evaporated ~~dissolved~~ in ~~minimum quantity of~~ and to dryness  
in a china dish. The residue is dissolved in distilled  
water and made up to in a standard flask.

### Standardisation of EDTA Solution

20ml of standard hard water is pipetted out into a  
conical flask, 2ml of Buffer solution and 2-3 drops  
of EBT indicators are added. It is then titrated against  
EDTA solution taken in the burette till wine red  
colour changes to blue ~~to~~ colour. Let the volume of  
EDTA consumed be  $V_1$  ml.

### Estimation of total hardness of unknown hard water.

20ml of unknown hard water sample is pipetted out  
into a conical flask, 2ml of buffer solution and 2-3 drops  
of EBT indicators are added. It is then titrated against  
EDTA solution taken in the burette, till wine red  
colour changes to blue colour. Let the volume  
of EDTA consumed be  $V_2$  ml.

### Estimation of permanent hardness

250 ml of unknown water sample is boiled in a beaker  
till its volume is reduced to 50ml by this process,  
all the bicarbonates present will be decomposed to  
carbonates and hydroxides of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Then the  
water is filtered and this filtrate is made up to 250ml  
with distilled water. 20ml of this water is titrated  
against EDTA solution and let the volume of EDTA  
be  $V_2$  ml.