KSU CET

S1 & S2 Notes

2019 Scheme

Manifest the leadership in you

Reg No.:_____ Name:_____

APJ ABDUL KALAM TECHNOLOGICAL UNIVERSITY

First Semester B.Tech Degree Examination December 2021 (2019 scheme)

Course Code: CYT100

Course Name: ENGINEERING CHEMISTRY

(2019-Scheme)

Max. Marks: 100 Duration: 3 Hours

PART A

Answer all questions, each carries 3 marks. Marks

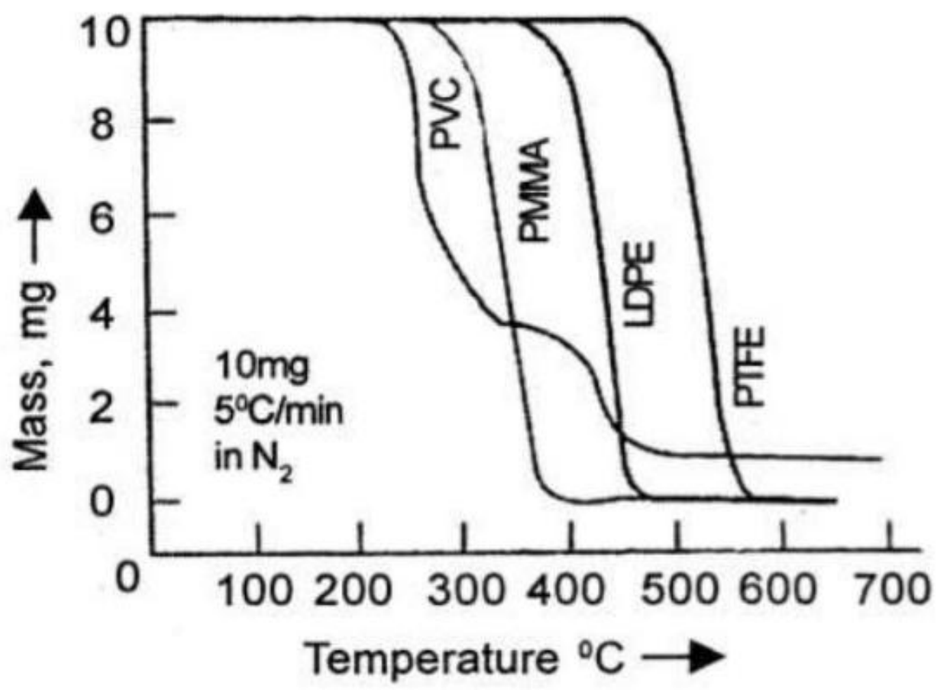
1 How is Helmholtz electrical double layer formed? (3)

2 Calculate the single electrode potential of dichromate electrode at 25^0C when $[Cr_2O7^{2-}]$ is 0.3M, $[Cr^{3+}]$ is 0.02M and $[H^+]$ is 1M. Given: $Cr_2O7^{2-} + 14\ H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$; $E^0 = 1.33$ V (3)

3 Recognize the atoms showing NMR phenomenon among the following. Give reason. a) ${}^{1}_{1}H$ b) ${}^{2}_{1}H$ c) ${}^{3}_{1}H$ d) ${}^{16}_{8}O$ e) ${}^{18}_{8}O$ f) ${}^{14}_{7}N$ (3)

4 IR spectroscopy can be used to differentiate intra molecular and inter molecular hydrogen bonds. Explain with an example. (3)

5 Compare the thermal stability of PVC, PMMA, LDPE and PTFE using TG given below. Justify your answer. (3)



6 Give the principle of TLC. Mention two applications of TLC. (3)

7 Assign the R/S notation to the following compounds. (3)

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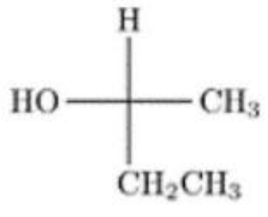
i.



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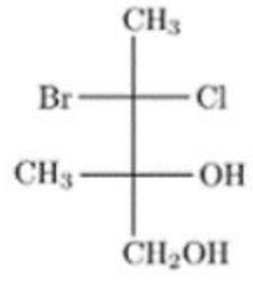

8 Explain doping in conducting polymers. (3)

9 A sample of water on analysis gives the following results. Ca^{2+} = 200 mg/L, Mg^{2+} = 180 mg/L, HCO_3^- = 360 mg/L, Cl^- = 200 mg/L and Na^+ = 80 mg/L. Calculate temporary and permanent hardness. (3)

10 Differentiate between aerobic and anaerobic oxidation. (3)

PART B

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

Module-I

11 a) How is glass electrode used in determining the pH of a solution? What are the advantages and limitations of a glass electrode? (8)

b) Describe the principle and applications of Electroless copper plating. (6)

12 a) Write the principle and procedure for the estimation of ferrous ion using dichromate solution potentiometrically. $E^0_{Fe3+/Fe2+}$= 0.77 V (8)

b) Emf of an electrochemical cell is 1.5175 V at 20^0C and 1.5213 V at 35^0C.If the cell reaction involve 2 electrons, find the standard emf of the cell and the reaction quotient. (6)

Module-II

13 a) What are the various types of electronic transitions possible in organic molecules? Give examples of each. Also give the instrumentation of UV Visible spectrophotometer. (8)

b) Suggest structural formula for the following compounds such that they give a single signal in proton NMR spectroscopy. a) $C_9H_{18}O$ and b) $C_{12}H_{18}$ (6)

14 a) Write the various modes of vibration possible for HCl, CO_2 and H_2O and state which of these modes are IR active. Write reason for their IR activity. (8)

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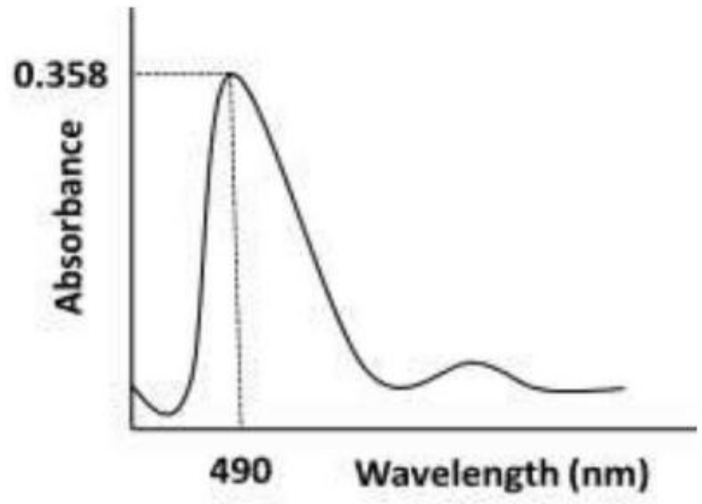
b) State Beer- Lambert's law and explain the term molar extinction co-efficient. (6)
Given is the absorption spectrum of a compound **A** of 2.5 x 10^{-6} M concentration, when measured using 1 cm cuvette in a UV-Vis spectrometer. Calculate the unknown concentration of a test sample of compound **A** if the absorbance is 0.518, when measured in the same condition.



Module-III

15 a) Sketch the instrumentation of DTA and explain the principle. Explain the DTA of $CaC_2O_4.H_2O$. (8)

b) Briefly explain the principle and instrumentation of SEM with the help of a diagram. (6)

16 a) Describe the principle and steps to be followed in column chromatography. (10)

b) How are nanomaterials classified on the basis of dimension? (4)

Module-IV

17 a) How many isomers (both structural and stereo) are possible for $C_4H_{10}O$? Draw the structure of each. (8)

b) What are OLEDs? Explain the construction and working of OLEDs. (6)

18 a) Draw the cis and trans isomers of 1, 3-dimethyl cyclohexane. Which will be optically active? Draw all the conformers. Which conformer is more stable and why? (8)

b) How is polyaniline synthesized? List any two properties and applications. (6)

Module-V

19 a) Explain the EDTA method for the estimation of hardness of water with calculation steps. (10)

b) Write the procedure for estimating COD of a sample of waste water. (4)

20 a) Discuss the action of chlorine as a disinfectant. How is it applied? What is break point chlorination? Write any two advantages of breakpoint chlorination. (10)

b) A pure water sample is added with 90 mg carbohydrate (CH_2O) per litre find the maximum BOD possible for the water sample. (4)

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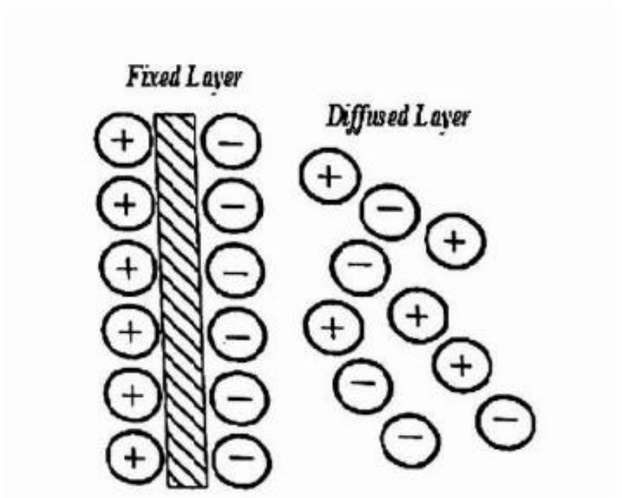
ANSWERS

PART- A

1- When an electrode is immersed in a solution of its own ions an electrical double layer is produced. It is the double layer of both positive and negative charges. Electrical double layer corresponds to an electrical capacitor. Electrical properties can be explained qualitatively by using the concept of electrical double layer at the solid liquid interphase. This concept was proposed by the scientist, Helmholtz. He considered that electrical double layer is produced at the surface of separation between the two phases, i.e. the solid electrode and liquid electrolyte.

Electrical double layer consists of two parts. 1) Fixed part 2) Diffused part



2- Given cell reaction

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

$$\therefore E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$E_{cell} = 1.33 - \frac{0.0591}{6} \log \frac{[0.02]^2}{[0.3][1]^{14}}$$

$$E_{cell} = 1.358V$$

3- ${}^{A}_{Z}X$

▷ For a Nuclei to be a NMR Active , It should have a net spin.

▷ When both atomic (Z) and mass number (A) are even numbers , net nuclear spin ' I ' becomes equal to zero and it will be NMR inactive.

Thus ${}^{16}_{8}O\ (d)$ & ${}^{18}_{8}O\ (e)$ are NMR inactive

${}^{1}_{1}H\ (a)$, ${}^{2}_{1}H\ (b)$, ${}^{3}_{1}H\ (c)$ & ${}^{14}_{7}N\ (f)$ are NMR active.

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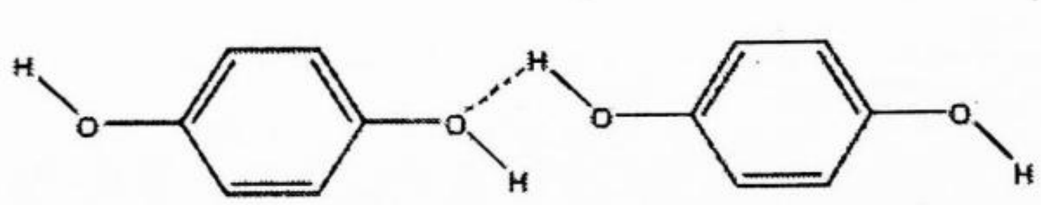
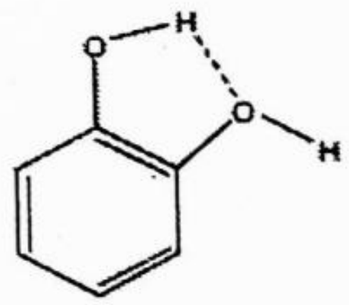
4- IR Spectroscopy can be used to distinguish between intra molecular and intermolecular hydrogen bonding. The -OH stretching frequency(3300-3500 cm-1) does not change on dilution in the case of intramolecular H-bonding. Eg. ortho-hydroxy phenol, and para-hydroxy phenol. In p-hydroxy phenol there exists inter molecular hydrogen bonding. The molecules get separated on dilution and intermolecular hydrogen bonding weakens and there is shift of absorption frequency with dilution. In o-hydroxy phenol the hydrogen bonding type is intramolecular which is not affected by dilution.



Inter molecular H-bonding in p-hydroxy phenol



intramolecular H-bonding in o-hydroxy phenol

5- The curves clearly indicate that PVC is the least thermally stable and PTFE is the most thermally stable.And it is seen that PVC starts decomposing at low temperature compared to Low Density Poly Ethylene (LDPE). This is due to the fact that elimination of HCI takes place in PVC. Also it is seen that PTFE (Poly Tetra Fluoro Ethane) is having high thermal stability, owing to strong C-F bond than C-H bond in other polymers.ie, The order of Thermal Stability of PVC, PMMA, LDPE, PTFE is in the order of ,

PVC<PMMA<LDPE<PTFE

6- **Thin-layer chromatography (TLC)** is a very commonly used technique in synthetic chemistry for identifying compounds, determining their purity and following the progress of a reaction. It also permits the optimization of the solvent system for a given separation problem. In comparison with column chromatography, it only requires small quantities of the compound and is much faster as well.

Thin layer chromatography is another type adsorption chromatography, which involves separation of substances of a mixture over a thin layer of adsorbent. This technique is based on the principle of adsorption as well as partition chromatography..

Applications of TLC :-

1. To check the purity of a sample.
2. For monitoring the progress of a chemical reaction.
3. To determine the appropriate solvent for a column-chromatographic separation.

7- (i) S

(ii) 2R,3R

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8- Conductivity of intrinsically conducting polymers can be increased by creating a positive charge or negative charge by oxidation or reduction. This process is called doping. Conducting polymers obtained by this process is called doped conducting polymers. Doping is of two types.ie, p-doping & n-doping

P-Doping	N-Doping
⚫Done by Oxidation	⚫Done by reduction
⚫ Positive charge is created during the process	⚫ Negative charge is created during the process.
⚫ Polorons are produced	⚫ Polorons and bipolorons are produced.
⚫ Single step process.	⚫ Two step process.
⚫ Lewis acid like FeCl3 is used as the reagent.	⚫Lewis base like sodium naphthalide is used as reagent.

9- Given ,

$\mathrm{Ca^{2+}} = 200\ \mathrm{mg/L}$, $\mathrm{Mg^{2+}} = 180\ \mathrm{mg/L}$, $\mathrm{HCO_3^-} = 360\ \mathrm{mg/L}$, $\mathrm{Cl^-} = 200\ \mathrm{mg/L}$, $\mathrm{Na^+} = 80\ \mathrm{mg/L}$

By the equation,

$$\mathrm{CaCO_3\ equivalent\ hardness} = \mathrm{Quantity} \times \frac{100}{\mathrm{M_{HPS}}}$$

$\left(where\ M_{HPS}\ \mathrm{Mass\ of\ Hardness\ Producing\ Substance}\right)$

$$\mathrm{For\ Ca^{2+}} = 200 \times \frac{100}{40} = 500\ \mathrm{ppm}$$

$$\mathrm{For\ Mg^{2+}} = 180 \times \frac{100}{24} = 750\ \mathrm{ppm}$$

$$\mathrm{For\ HCO_3^-} = 360 \times \frac{100}{(2\times 61)} = 295\ \mathrm{ppm}$$

$\therefore$ Total Hardness $= 500 + 750 = 1250$ ppm

Temporary Hardness $= 295$ ppm

Permanent Hardness $= 1250 - 295 = 955$ ppm

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10-

Aerobic Oxidation	Anaerobic Oxidation
⚫ It occurs in presence of excess oxygen, ⚫ Oxidation by aerobic bacteria. ⚫ The products of oxidation are CO_2.nitrates, phosphates, sulphates.	⚫ It occurs in presence of limited quantity oxygen. ⚫ Oxidation by anaerobic bacteria. ⚫ The products of oxidation are acetic acid,methane, H_2S, NH_3,. phosphine.

PART- B

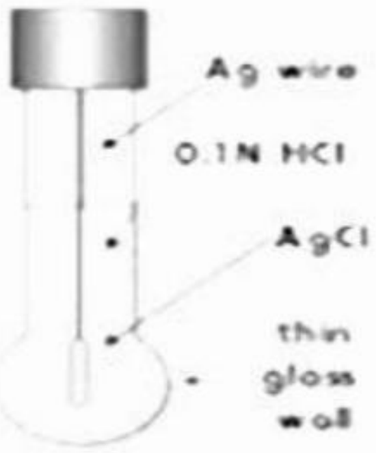
MODULE - I

11- (a) **GLASS ELECTRODE**

Glass electrode is a secondary reference electrode. Corning 015glass has been used for making glass electrode. It is a special type of glass with low melting point and high electrical conductivity. It consists of 72% SiO2, 6% CaO & 22% Na_2O.

Construction :-

It consists of a thin glass bulb in which Ag wire coated AgCl is used as an internal reference electrode. It is then filled with 0.IN HCl solution.



Ag,AgCl(s)/HCl(0.1N)/Glass//

Glass electrode works on the principle that potential difference between thesurface of the glass membrane and a solution is a linear function of P^H. Here the glass membrane acts as an ion selective membrane sensitive to $[H^+]$. So an ion exchange reaction occurs between singly charged cations of glass (Na^+) & H^+ ions of solution.Finally an equilibrium is established between (Na^+) ions of glass & H^+ ions of solution.

$$H^+_{(solution)} + Na^+Gl^- \rightarrow Na^+_{(solution)} + H^+Gl^-$$

$$E_G = E^0_G + 0.0591 \log [H^+] = E^0_G - 0.0591\ P^H$$

The potential of glass electrode varies with concentration of H^+ ions. E^0_G is constant and it depends on the nature of the glass and also the P^H of the solution taken inside the glass bulb.

E^0_G= 0.6990 V

The concentration of H^+ ion inside the glass is constant,i.e. P^H is constant. But when it is dipped into a solution of unknown P^H, concentration of H^+ ion inside the glass bulb changes. As a result, P^H changes. This results in the development of a potential difference.

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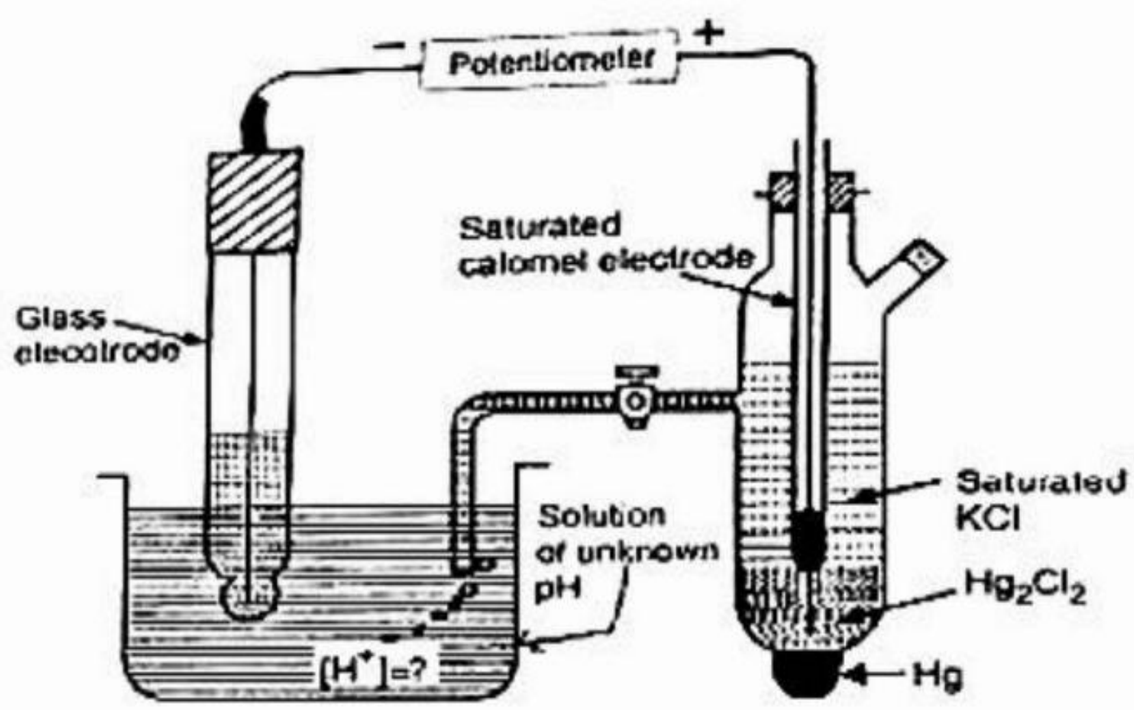
Determination of PH using glass electrode

Glass electrode is used as an internal reference electrode. In order to determine the unknown PH of a solution, glass electrode is coupled with SCE and the resultant cell can be represented like this, $Ag,AgCl_{(s)}/0.1N\ HCl/Glass/Solution\ of\ Unknown\ P^H//\ KCl_{(sat)}/Hg_2Cl_{2(s)}/Hg_{(l)}/Pt$



$$E_{cell} = E_R - E_L = E_{SCE} - E_G$$
$$= 0.2422 - (E^0_G - 0.0591\ P^H)$$
$$= 0.2422 - E^0_G + 0.0591\ P^H$$

E^0_G of glass electrode can be determined by using a solution of known P^H.

$$0.0591\ P^H = E_{cell} + E^0_G - 0.2422$$

$$P^H = \frac{E_{Cell} + E^0G - 0.2422}{0.0591}$$

Advantages of glass electrode :-

1. It is very simple to operate.
2. It can be use to find the pH of oxidising, reducing and even coloured solutions
3. Glass electrode works effectively in the pH range of 1-9 and is unaffected by oxidising, reducing and poisoning agents.
4. Electrodes made of special glasses can be used upto a pH of 12.

Limitations of glass electrode :-

1. It cannot be used as a reference electrode for solutions having pH greater than 12.
2. Glass membrane has very high resistance. So ordinary potentiometers cannot be used for determining potential of electrode instead special electronic potentiometers has to be used.

(b) **ELECTROLESS COPPER PLATING**

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In this method, article to be plated is immersed in a plating bath containing CuSO4 (As a source of Cu), formaldehyde (Reducing Agent), buffer solution of NaOH and Rochelle salt and a complexing reagent. Air is bubbled slowly through the medium to control the formation of cuprous oxide. Electroless plating of Cu takes place as follows.

Oxidation,

$2HCHO+4OH^- \rightarrow H_2$ (Gas) $+ 2HCOO^- + 2H_2O + 2e^-$

Reduction,

$Cu^{2+} + 2e^- \rightarrow Cu$

Net reaction,

$2HCHO+4OH^- + Cu^{2+} \rightarrow H_2$ (Gas) $+ 2HCOO^- + 2H2O + Cu$

Applications of electroless Cu plating :-

- Widely used for metalizing printed circuit boards.
- Used for plating on non-conductors.
- It is also used for making decorative plating on plastics.

12- (a) **Potentiometric titrations** Titrations which involve the measurement of potential of an indicator electrode with the addition of a titrant is called potentiometric titrations.

Merits of potentiometric titrations:-

- No external indicator is required.
- Titrations of weak acids & bases can be carried out potentiometrically.

Principle :-

The potential of an electrode dipping into the solution of an electrolyte depends upon the concentration of ions with which it is in equilibrium. Potentiometric titrations are based on the fact that potential of suitable indicator electrode is measured relative to that of a reference electrode and is related to the concentration changes in the solution being titrated. Near the end point, there is a sharp change in the potential of indicator electrode.

Types of potentiometric titrations :-

Three types of potentiometric titrations are

1. Acid-base titrations
2. Redox titrations
3. Precipitation titrations

Potentiometric redox titrations :-

In order to explain the potentiometric titration, let us consider the oxidation of Fe^{2+} to Fe^{3+} by Ce^{4+} in acid medium.The Ce+ ions having greater reduction potential (1.60V) will undergo reduction & Fe^{2+} ions (0.77V)get oxidized to Fe^{3+}.

$Ce^{4+} + e^- \rightarrow Ce^{3+}$

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$Fe^{2+} \rightarrow Fe^{3+} + e^-$

Over all reaction;

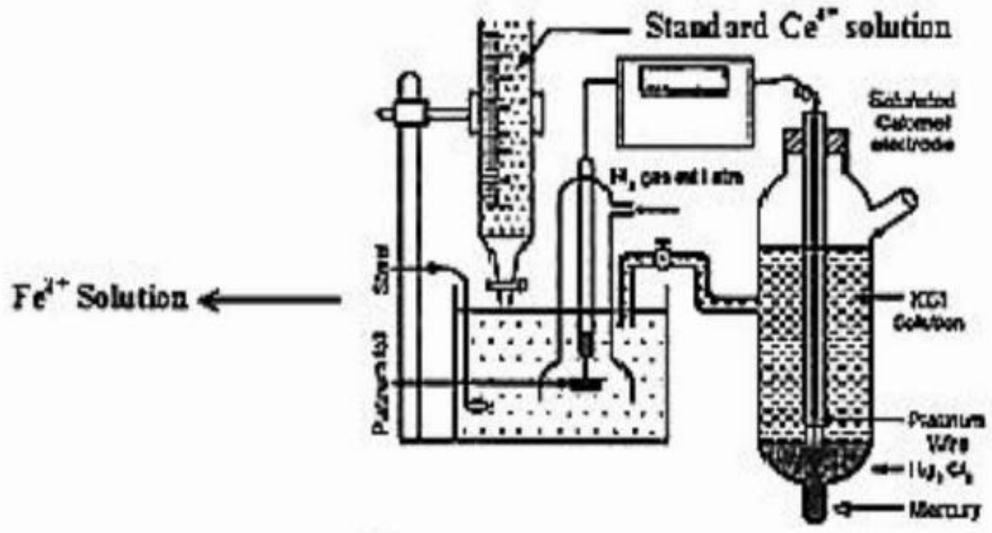
$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

The potential of indicator electrode is

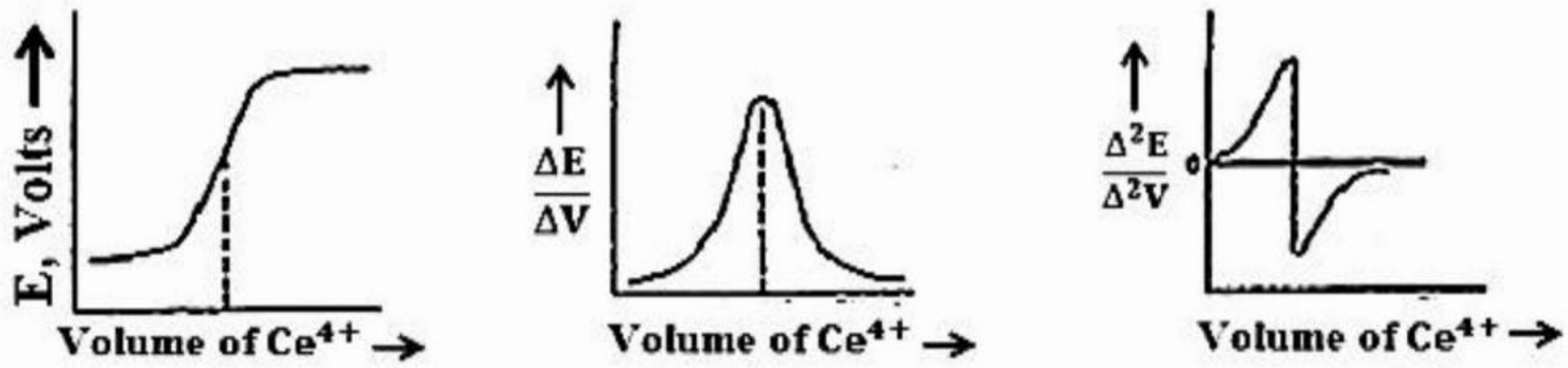
$$\mathbf{E = E_0 + \frac{0.0591}{n} \log \frac{[Oxidised\ state]}{[Reduced\ state]}}$$

$$\mathbf{= E_0 + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}}$$

20 ml ferrous sulphate solution is mixed with 20ml 4N H_2SO4, in a beaker. A platinum electrode is then inserted into it. It is then coupled with SCE. The electrodes are then connected using a potentiometer. Then standard ceric ammonium sulphate solution is added from the burette. After each addition emf is noted. Emf is then plotted against volume of ceric solution. Emf initially increases with the addition of titrant due to the oxidation of Fe^{2+}. Near the end point potential changes sharply. After the end point emf changes very slowly.



Emf is then plotted against volume of Ce^{4+} solution, we get an 'S' shaped curve. More and most accurate results are obtained by plotting $\frac{\Delta E}{\Delta V}$ against volume of Ce^{4+} solution and $\frac{\Delta^2 E}{\Delta^2 V}$ against volume of Ce^{4+} solution, the following curves are obtained.



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(b) $$1.5175 = \mathbf{E^0_{cell}} - \frac{2.303\mathbf{RT}}{\mathbf{nF}} \log \mathbf{Q}$$

$$1.5175 = \mathbf{A} + \mathbf{B} \times 293 \ldots\ldots (1)$$

$$1.5213 = \mathbf{A} + \mathbf{B} \times 308 \ldots\ldots (2)$$

on solving $\Rightarrow$

$$\mathbf{B} = 2.5333 \times 10^{-4}$$

$$\mathbf{A} = 1.4432\ \mathbf{V} = \mathbf{E^0_{cell}}$$

$$\mathbf{B} = -\frac{2.303\mathbf{R}}{\mathbf{nF}} \log \mathbf{Q}$$

$$2.5333 \times 10^{-4} = -\frac{2.303 \times 8.314}{2 \times 96500} \log \mathbf{Q}$$

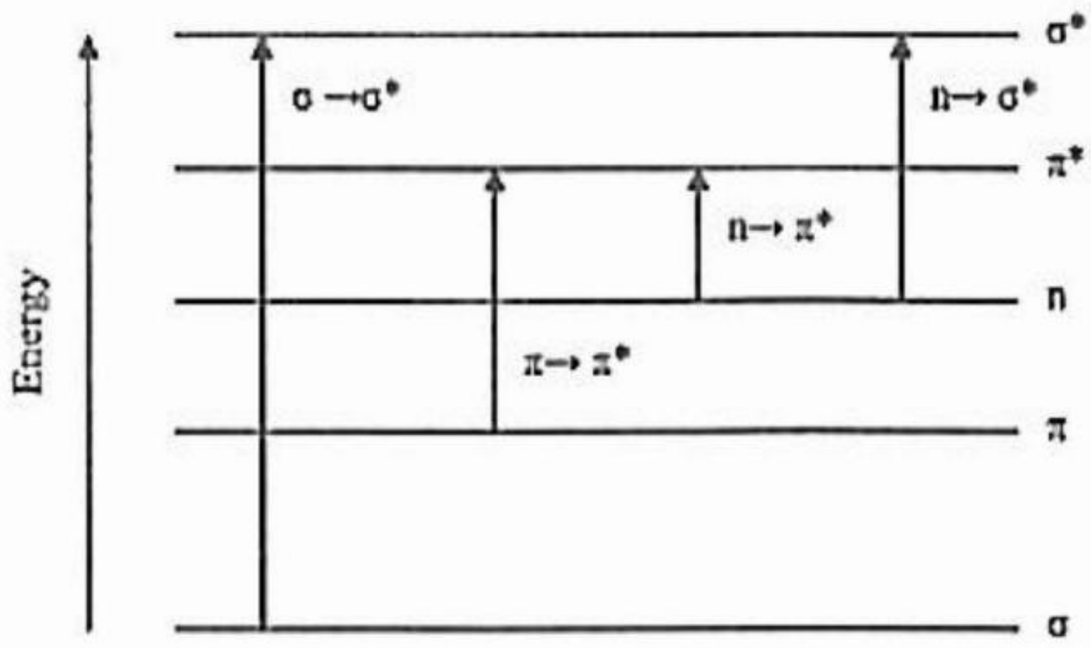
$$\log \mathbf{Q} = -2.5535$$

$$\Rightarrow \mathbf{Q} = 2.795 \times 10^{-3}$$

MODULE - II

13- (a) **Electronic spectrum of polyatomic molecules**

In the case of polyatomic molecules, electronic transitions give rise to absorption spectra in the UV-Visible region. From the investigations of UV-Visible spectra we get information about various energy levels in the molecule depending on the energy of the molecular orbitals. The electronic transitions are $\sigma - \sigma^*$, $\boldsymbol{\pi} - \boldsymbol{\pi}^*$, $n - \boldsymbol{\pi}^*$ & $n - \sigma^*$ respectively.



Electronic transitions in molecules

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(i) σ – σ* transition :-

The energy required for this transition is very high. Since the σ electrons are held more strongly in the molecule and are highly energetic. Hence the absorption band occurs in far UV region. All saturated hydrocarbons will undergo this transition. These types of transitions occur only below 150 nm. The ordinary UV spectrometers can take spectra only from 200 – 780nm. Hence saturated hydrocarbons cannot be detected using UV-Visible spectra.

(ii) *π* – *π transition :-**

Unsaturated hydrocarbons containing ***π*** bonds can produce this type of transition. But C=C of CH2=CH2 molecule gives absorption maxima at 169nm.So it cannot be detected using ordinary UV spectrometer .But in compounds containing conjugated double bonds, due to the presence of conjugated double bonds absorption occurs in visible region. In such molecules ***π*** – ***π**** transition produces absorption bands in the UV-Visible region. (eg.1,3- Butadiene, absorption occurs at 217 nm). Due to this transition high intensity absorption bands are produced in the near UV region. Benzene also produces these transitions, due to the presence of three conjugated double bonds. In the case of lycopene red coloured of tomato, there are eleven double bonds in conjugation, its λmax is 505 nm. For every double bond in conjugation, there is an increment of 30 nm.

(iii) n - π* transition :-

Unsaturated compounds containing atoms such as O, N, S, X etc, containing lone pair of electrons produces absorption band due to nr transition and the absorption bands are observed in the visible region. (eg., aldehydes and ketones containing C-C and C=C bonds).

(iv) n - σ* transition :-

Saturated compounds containing atoms such as O, N, S. X etc, containing lone pair of electrons produces absorption band due to n-σ* transition and the absorption bands are observed in the near UV region. Generally absorption takes place below 200 nm. (eg., CH3OH, CH3NH2 & (CH3)2NH etc.)

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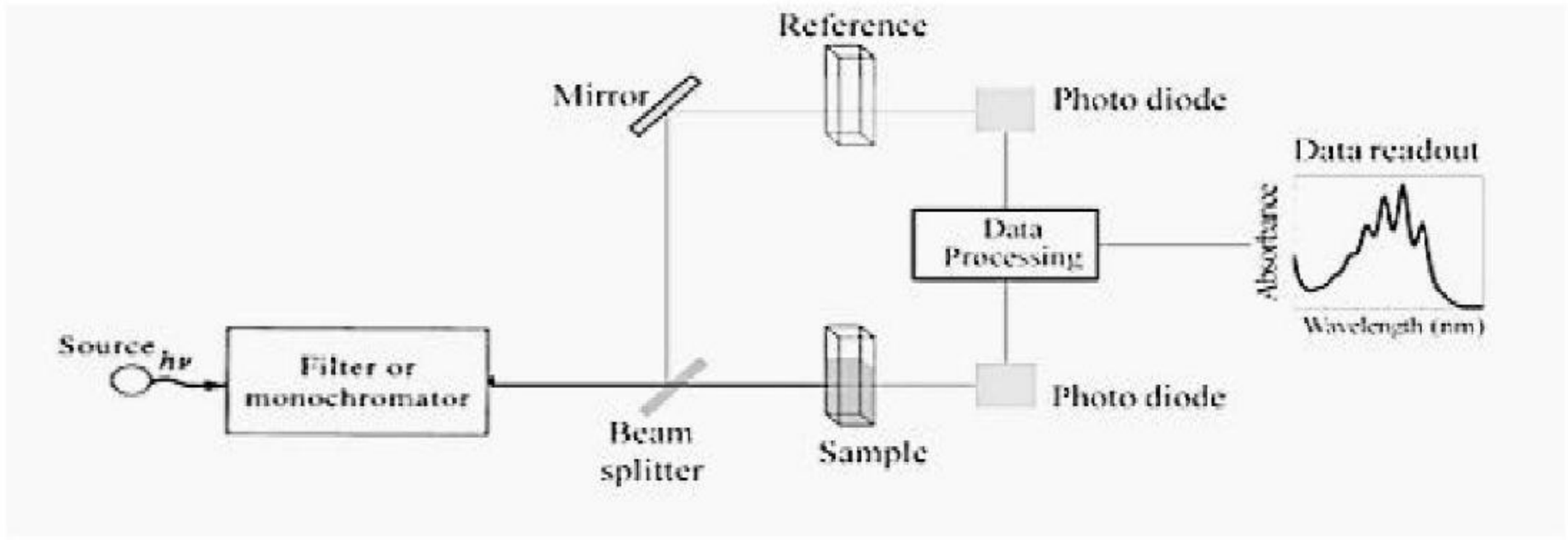
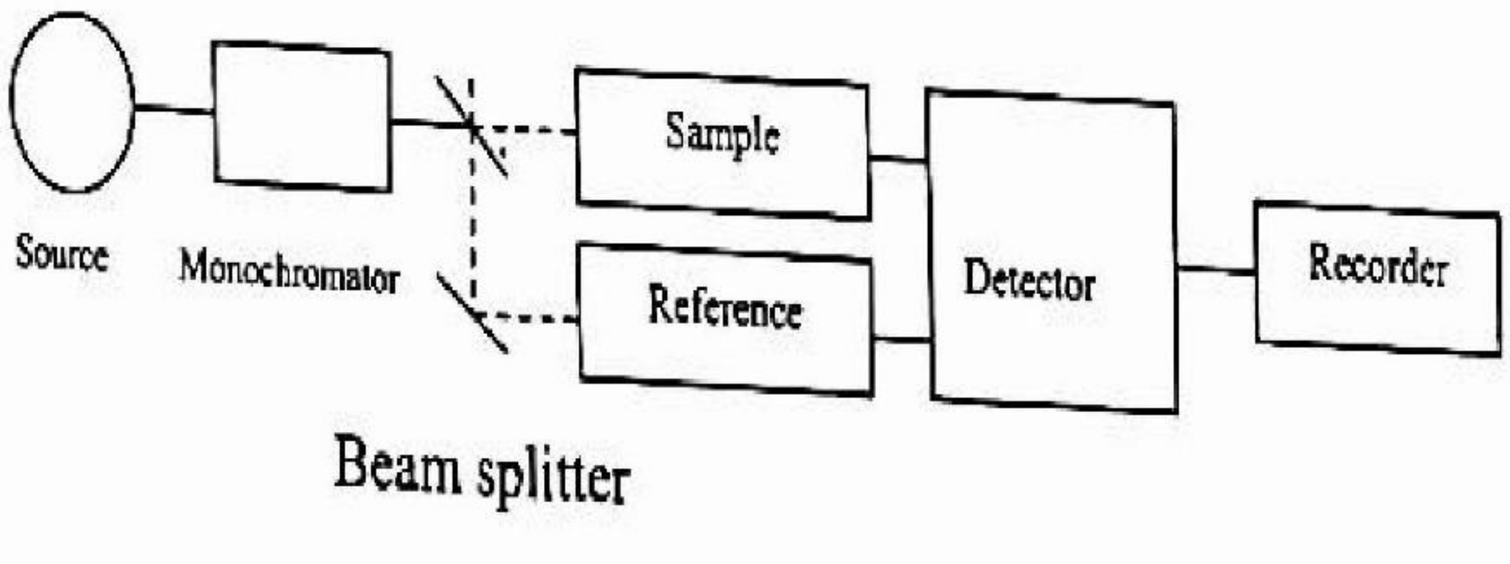
ELECTRONIC (UV –VISIBLE) SPECTROSCOPY

Instrumentation of UV –Visible) Spectrometer :-





UV-Visible spectrometers have components similar to those of other spectrometer using electromagnetic radiation. The essential parts of aUV-Visible spectro- photometer are as follows,

(i) Radiation source :-

The UV-Visible spectrophotometers usually covers the UV and visible regions. Their wavelength range extends from 200 nm to about 780 nm both high and low voltage hydrogen lamps give rise to continuous spectrum in the region between 200-370 nm, and a tungsten filament lamp for the region 325-750 nm.

(ii) Monochromator/filter :-

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The filter unit consists of an entrance slit, a dispersing element and an exit slit. The dispersing element is generally a prism or grating. The function of the wavelength controller/ filter is to isolate a narrow band of wavelength from the radiation source.

(iii)Sample holder/Cells :-

Modern instruments are double-beam recording spectrophotometers in which the light beam from the source is divided in to two identical parallel beams of equal intensity.These beams are allowed to pass through the sample cell and reference cell containing the solvent. Cells used in UV-Visible spectroscopy are made entirely of quartz.

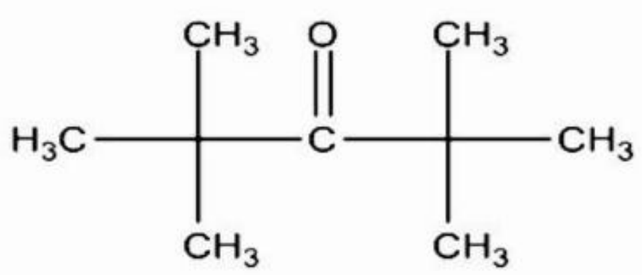
(iv) Detectors :-

The two beams, one emerging from the sample cell and the other from the reference cell, are then led to the detector system. The detectors convert the transmitted radiation in to electrical energy.

(v) Recording system :-

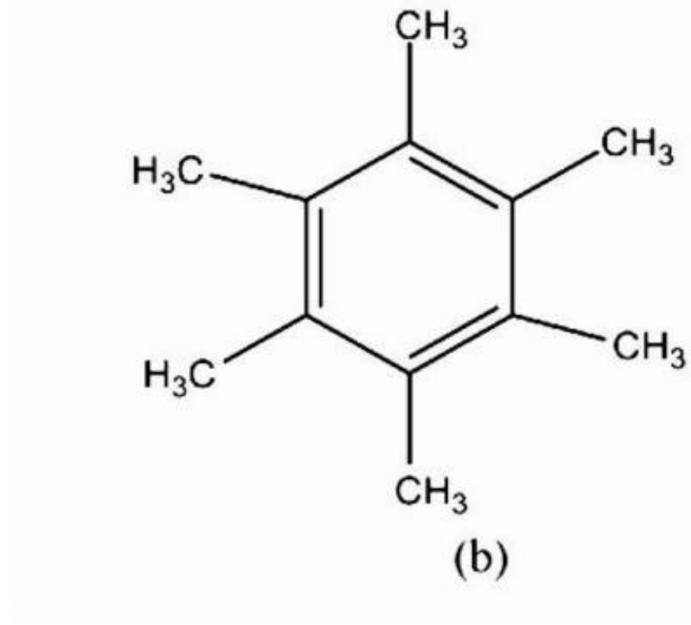
The detector transmits the signals to a recorder which gives the output displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each wavelength.

(b) (a) DBE= (20-18)/2=1



(a)

(b) DBE = (26-18)/2=4



(b)

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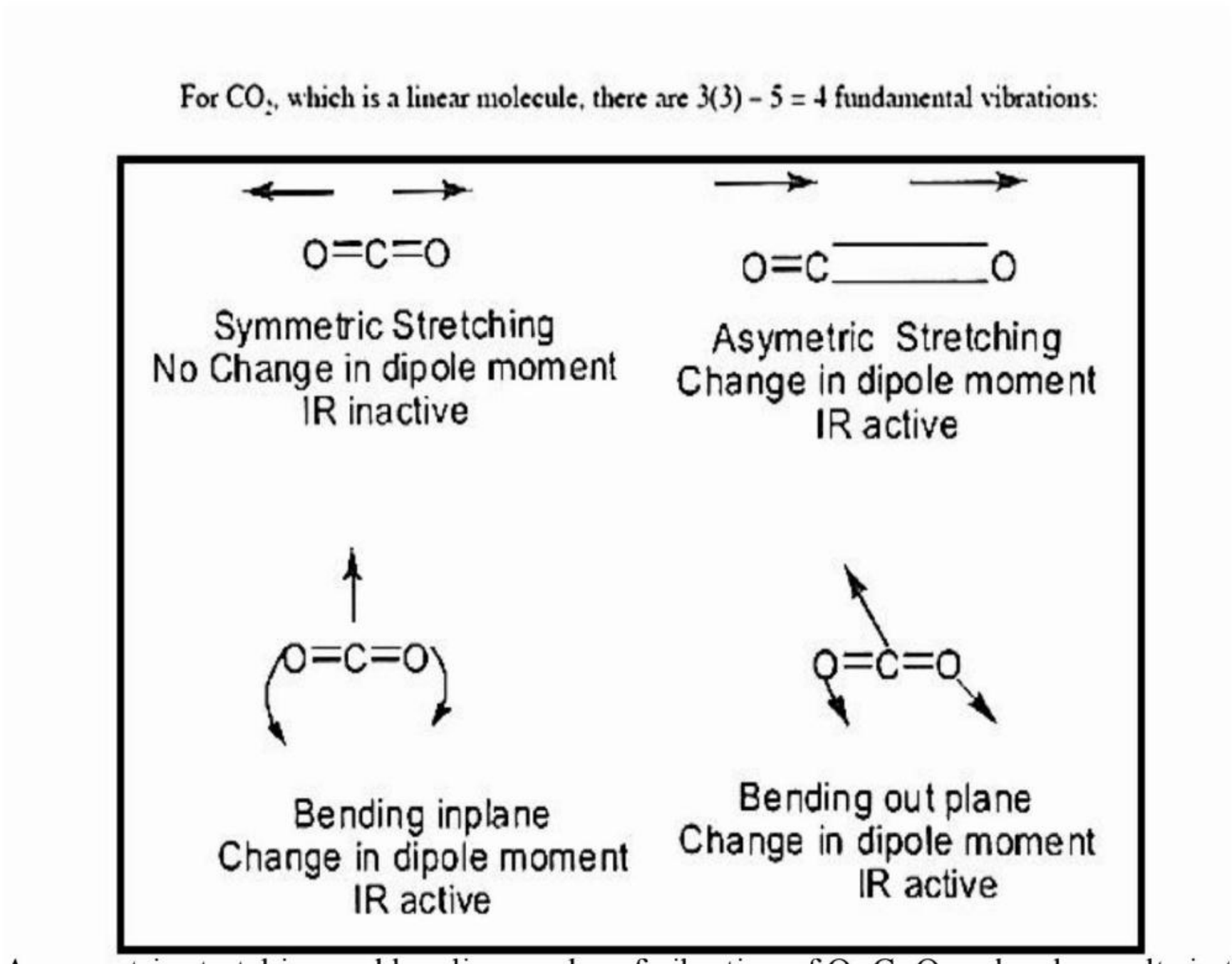
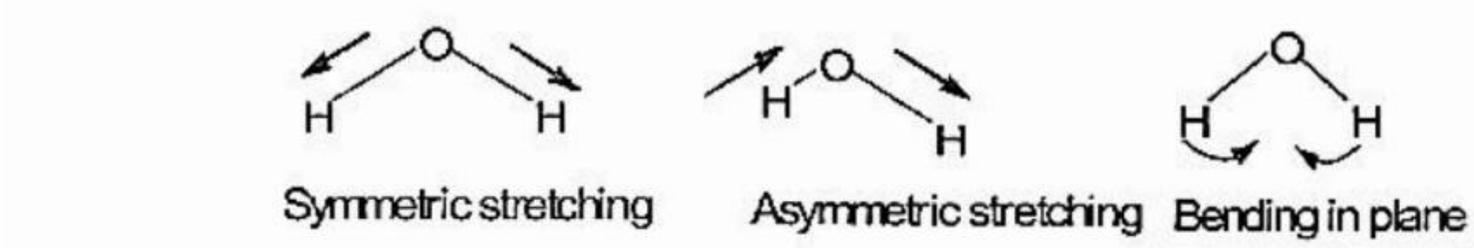
14- (a) In the case of polyatomic molecules, IR spectrum depends on the number of vibrational modes. But the number of vibrational modes depends upon the structure.

→ For linear molecules (**CO2**), number of vibrational modes = 3n-5 and for non-linear molecules (H2O, SO2), number of vibrational modes = 3n-6. CO2 has four vibrational modes symmetric stretching, asymmetric stretching and two bending vibrations in two mutually perpendicular planes. Out of the four vibrational modes only three are IR active. The symmetric stretching does not involve the change of di-pole moment and is not IR active.



Asymmetric stretching and bending modes of vibration of O=C=O molecule results in the variations of dipole moment. Hence these vibrational modes are IR active

→ **H2O** is a non –linear molecule. So number of vibrational modes = 3n -6 =3X3 – 6 =3. They are symmetric stretching, asymmetric stretching and bending in plane vibrational modes. In all these cases there is a change in dipole moment. So all are IR active.



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→ In **HCl**: N = 2,Molecule is linea r ∴ number of modes = 3×2 – 5 = 6 – 5 = 1
ie, Stretching Vibration and is IR active(because,it is a hetero nuclear polar molecule).

(b) **BEER – LAMBERT'S LAW**

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in concentration of absorbing solution as well as thickness of the medium.

$$\log \frac{I_O}{I} \alpha\, ct$$

$$\log \frac{I_O}{I} = \varepsilon ct$$

Io = Intensity of incident radiation

I = Intensity of light transmitted radiation.

c =concentration of the solution in mols/liter

t = thickness of the medium

ε = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation.It depends on the nature of medium and also the extent of absorption.

$$\log \frac{I_O}{I} = A \text{ absorbance}$$

The above relation is known as the Beer-Lambert's Law which is the fundamental equation for colorimetry and spectrophotometry.

→ $A = \varepsilon ct$

$\Rightarrow A \alpha c$

$$\therefore \frac{A_1}{A_2} = \frac{c_1}{c_2}$$

$$\frac{0.358}{0.518} = \frac{2.5 \times 10^{-6}}{c_2}$$

$$\Rightarrow \quad c_2 = \frac{(2.5 \times 10^{-6}) \times 0.518}{0.358}$$

$$= 3.62 \times 10^{-6}\ M$$

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MODULE - III

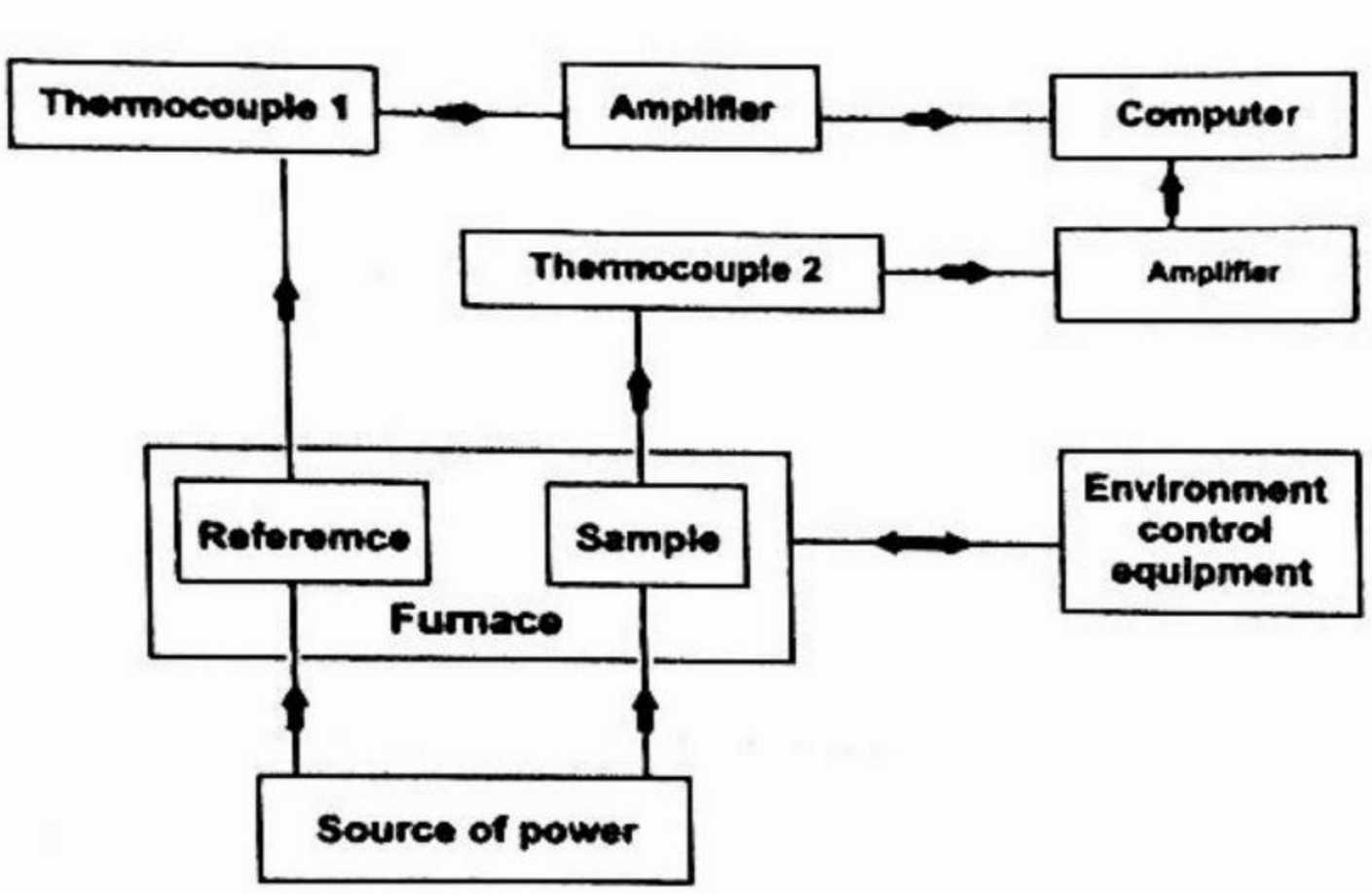
15- (a) DIFFERENTIAL THERMAL ANALYSIS (DTA)

DTA is a thermal method of analysis in which difference in temperature between the sample and inert reference compound is measured as a function of sample temperature as the sample and the reference compound are heated uniformly in a constant rate. Usually used reference compounds are alumina and silicon carbide. In DTA, difference in temperature between the sample and the reference compound is
monitored continuously and is plotted against sample temperature to obtain differential thermogram.

Instrumentation :-

DTA instrument is similar to the one for TGA. It consists of,

1. A sample holder, sample containers and a ceramic or metallic block- furnace.
2. A temperature programmer, comprising of thermocouples.
3. Recorder



Block diagram of DTA apparatus

The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple is placed in an inert material such as Al2O3, while the other is placed in 1 sample of the material under study. As the temperature is increased, there will be a brief deflection of the voltmeter if the sample is undergoing a phase transition. This occurs because the input of heat will raise the temperature of the inert substance, but it will be incorporated

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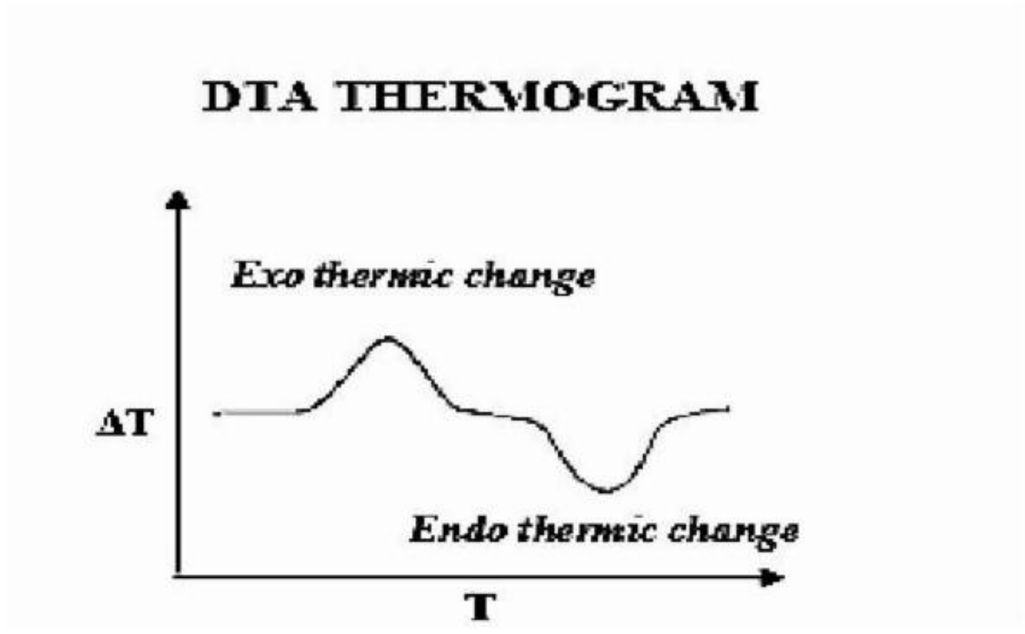
as latent heat in the material changing phase. The thermogram obtained is a plot of ΔT versus reference temperature TR. It is known as differential thermogram.

Principle and method :-

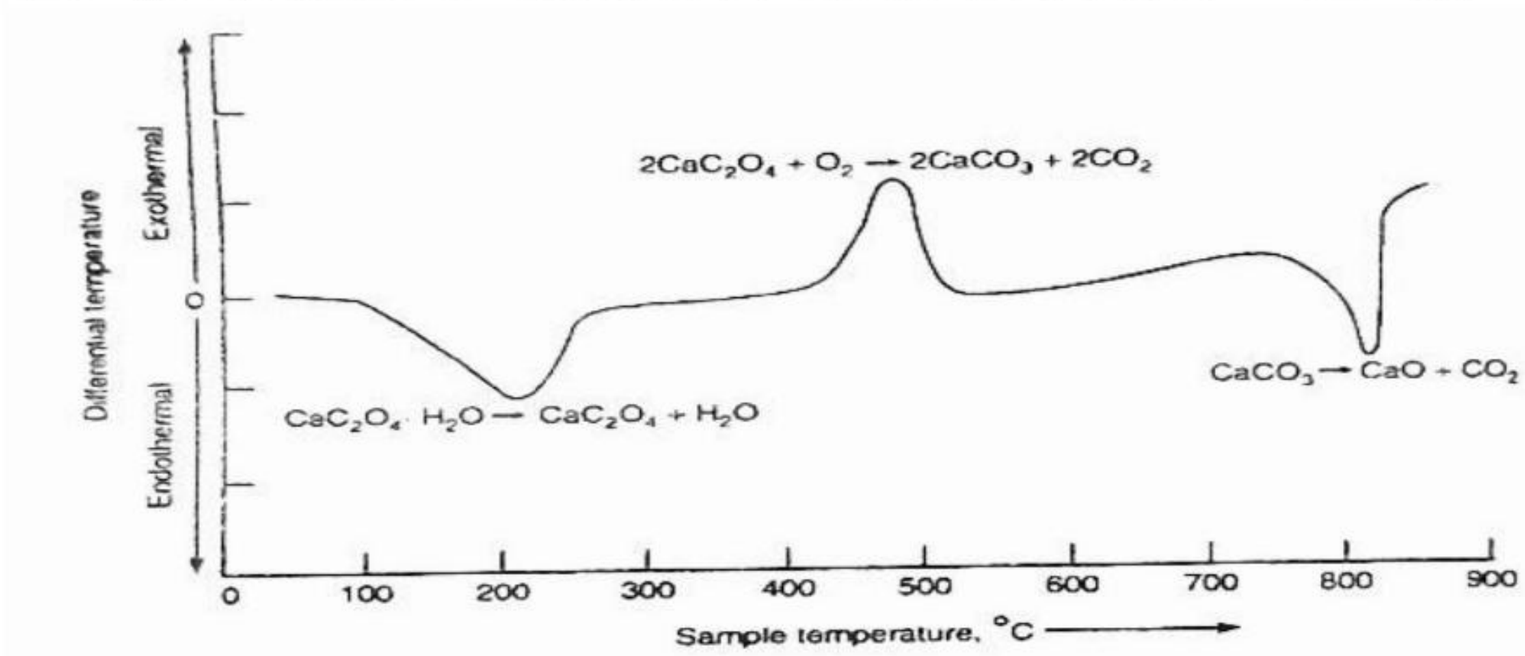
In DTA, peaks are obtained due to the physical and chemical changes undergone by the substance on heating. Physical changes are endothermic or exothermic. Physical changes like fusion, evaporation, sublimation, absorption, desorption etc. are endothermic. But adsorption and crystallisation are exothermic physical changes. Chemical changes are also endothermic or exothermic. Reduction in inert atmosphere, dehydration and decomposition are usual endothermic chemical changes. Oxidation in air, polymerisation are exothermic chemical changes.



Upward peak or maxima corresponds to exothermic change, whereas downward peak or minima correspond to endothermic change. Peak areas in differential thermo grams depend upon the mass of the sample (m), enthalpy change (ΔH) of the physical or chemical changes and certain geometric and conductivity factors. Peak Area (A) = $-kGm\Delta H$ A is the peak area, G is the calibration factor which depends upon the sample geometry and k is a constant related to the thermal conductivity of the sample.

DTA of $CaC_2O_4.H_2O$:-

The thermogram contains two minima representing endothermic regions The first minima indicates the dehydration of $CaC_2O_4.H_2O$. The middle maxima indicate the decomposition of anhydrous calcium oxalate to calcium carbonate and carbon monoxide.



DTA of Calcium Oxalate ($CaC_2O_4.H_2O$) in a current of air

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In general

1. For exothermic changes like oxidation, crystallization, adsorption etc. the peak appear above zero in the differential thermogram (maxima).
2. For endothermic changes like vapourization, sublimation, desorption, fusion etc., the peaks appear below zero in the differential thermogram (minima),

(b) SCANNING ELECTRON MICROSCOPY (SEM)

SEM is an important surface characterisation technique used in nanotechnology. It is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. This can provide information about topography (surface features), morphology (shape and size of the particles), composition and crystallographic information.

Principle :-

SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can give information about the surface topography and composition. Electrons from the top of the column is accelerated down and passed through a combination of lenses to produce a focused beam of electrons which hits the surface of the sample. As a result of the electron sample interaction, signals are produced. These signals are then detected by appropriate detectors. Thus high resolution three dimensional images are produced.

Instrumentation of SEM :-

A schematic representation of an SEM is shown below with all essential components and features.

1. Electron gun: Located at the top of the column where free electrons are generated by thermionic emission from a tungsten filament at ~2700K. The filament is inside the Wehnelt which controls the number of electrons leaving the gun. Electrons are primarily accelerated towards an anode that is adjustable from 200 an anode that is adjustable from 200V to 30 kV.

2. Condensing Lens: All the electrons are negatively charged and hence the electrons in a beam will repel each other. This will increase the beam diameter and will adversely affect the resolution of the image. Hence electrical coils are used to squeeze the beam to a diameter of 5 nm or less. These are called condensing lens coils.

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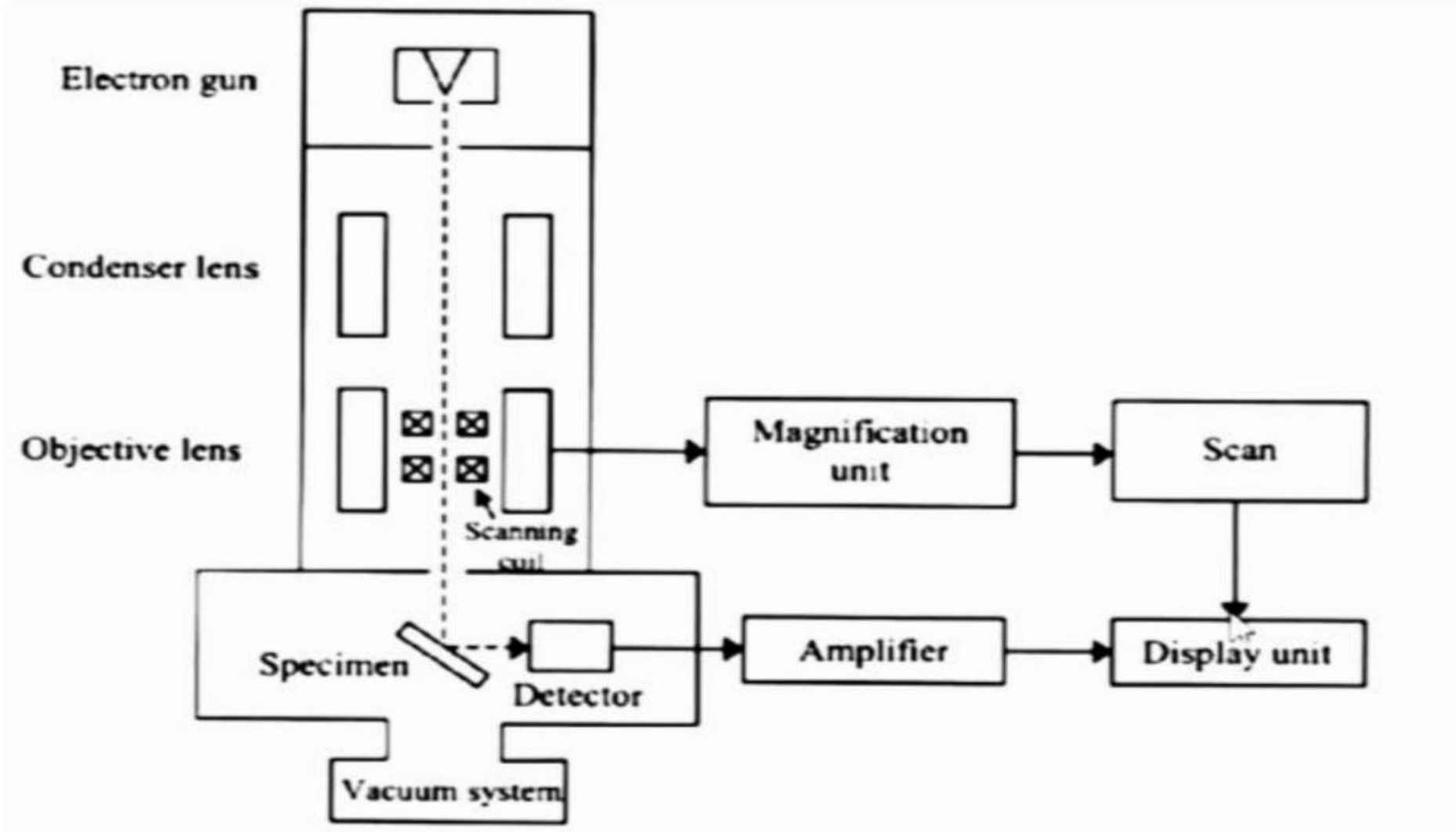

3. Deflection coils: There are many differences between the SEM and optical microscopes, in terms of the techniques used. An electron beam is not used in the same way as light in optical microscope. In light microscope, the entire sample (or the region of interest) is illuminated simultaneously. In SEM, only one tiny spot is 'illuminated' with the beam. Then the beam is moved in small steps(usually in nm) by a process called 'rastering". This is similar to moving electron beam in a cathode ray tube (CRT). By applying suitable electric field, the beam can be made to "walk' in the X and Y direction. The entire sample is analyzed by scanning the electron beam. Hence the instrument is called scanning electron microscope. The coils used for moving the electron beam are called deflection coils.

4. Objective Lens: After the deflection coil, there is another electromagnetic lens called objective lens which can focus the electron beam down to the sample.

5. Sample Chamber: After passing through the objective lens, the electron beam passes in to the sample chamber. This chamber holds the sample under vacuum to eliminate interference of unwanted particles.

6. Detectors: Finally there are detectors. These are used to produce magnified images, and collect other data. They will detect various signals given off by the sample as it is struck by electrons from the beam scanning over it. These signals include secondary electrons, back scattered electrons and X-rays among others The display monitor can be used for the display of images.

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16- (a) **COLUMN CHROMATOGRAPHY**

When a column of solid is used as the adsorbent, it is called adsorption column chromatography. On the other hand, when the solid column is acting only as a support to the liquid adsorbent, it is called partition column chromatography. The common adsorbent used in column chromatography are silica, calcium carbonate,calcium phosphate, magnesia, starch etc. selection of the solvent is based on the nature of components in the mixture. Adsorption depends upon the nature of both the solvent and the adsorbent.

The rate of separation of the mixture depends up on the activity of the adsorbent and the polarity of the solvent. If the activity of the adsorbent is very high and the polarity of the solvent is low, then the separation is very slow with good separation. On the other hand, if the activity of the adsorbent is low and the polarity of the solvent is high, the separation is rapid and gives poor separation.

Procedure :-

A proper adsorbent is selected and made slurry with a suitable liquid and placed in a tube which is plugged at the bottom with glass wool or porous disc. The mixture which is to be separated is dissolved in a suitable solvent and introduced at the top of the column and is allowed to pass through the column. The components are adsorbed at different regions depending on their ability for adsorption. The component with greater adsorption power will be adsorbed at the top and the one with lower adsorption power will be adsorbed at the bottom. The banded column of adsorbed constituents is called chromatogram. In order to separate or estimate the various constituents, the chromatogram after development is pushed out of the glass tube and various zones are cut with a knife at the boundaries.

The colored components are dissolved in suitable solvents, which on evaporation give the pure components. The different components in the chromatogram can be adsorbed and collected separately by adding more solvent at the top and this process is known as elution. The process of dissolving out of the components from the adsorbent is called elution and the solvent is called elutent or eluent. The different fractions are collected separately. Distillation or evaporation of the solvent from the different fractions gives the pure components.

Solvents Used: Selection of a solvent depend on the dissolving power and boiling point (60-85°C) of the solvent. For most purposes light petroleum with a boiling point of around 85°C is recommended. The other solvents used are benzene, cyclohexane, chloroform, carbon tetra chloride, carbon disulphide, ethyl alcohol, acetic acid and ethyl acetate. Basically a solvent has to perform three important functions:

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1. They dissolve the mixture of various components. Usually non polar solvents like benzene and petroleum ether are used, so the adsorption takes place more readily. 2. They are passes in to the column for the development of chromatogram. The solvent used for this purpose is known as developers. The developer is generally a solvent in which the components of the mixture are not highly soluble.

3. They are also used for removing the various constituents of the mixture from the chromatogram after it is properly developed, and are called elutent.
→ Thin Layer Chromatography (TLC) is used for monitoring column chromatographic separation and to determine appropriate solvent for column chromatographic separation.

(b) **Classification based on dimension :-**
This is the classification based on the number of dimensions which are not confined to the nanoscale range(<100 nm)

1. Zero dimension (0-D) Here all the three dimensions are in the nanometric range. Eg. Nano particles

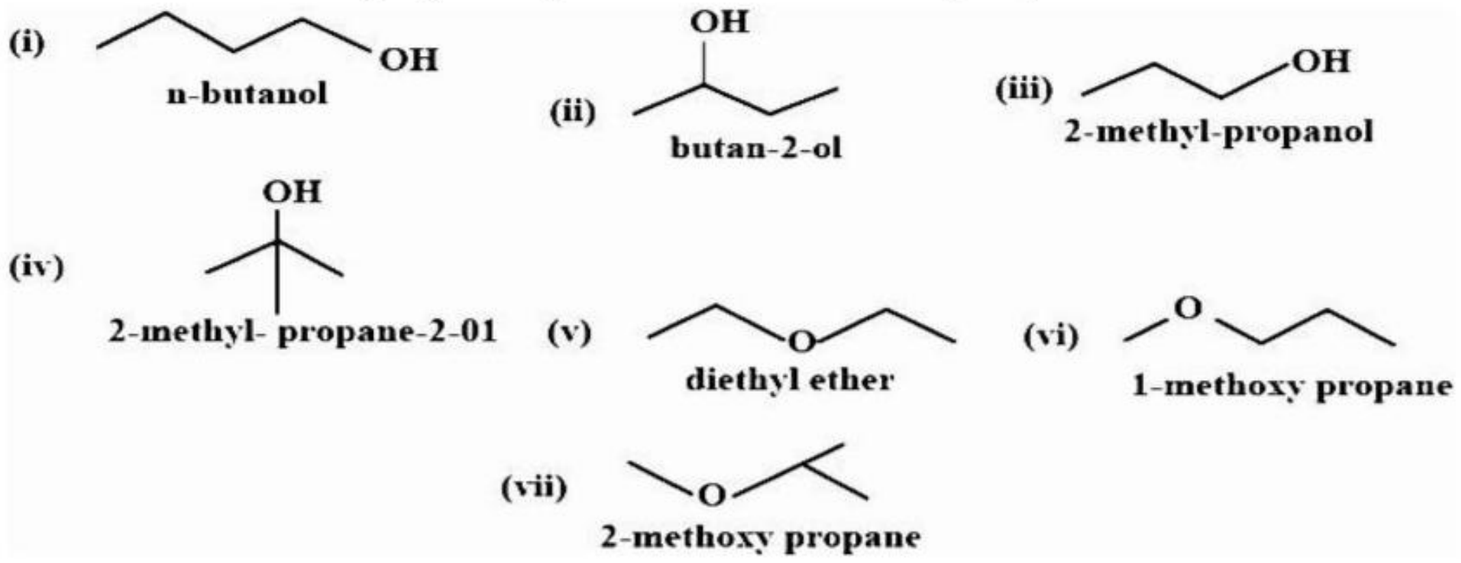
2. One dimension (1-D) Here one of the dimensions is outside the nanometric range and the other two are within the
range. Eg. Nano wires, fibres and tubes.

3. Two dimension (2-D) Here two of the dimensions is outside the nanometric range and one is within the range.
Eg. Nano films, layers and coatings

4. Three dimension (3-D) Here all the dimensions are outside the nano metric range and one is within the range.
Eg. Bundles of nano wires and tubes, multi nanolayers..

MODULE - IV

17- (a) 8 isomers including optically active enantiomer pair,



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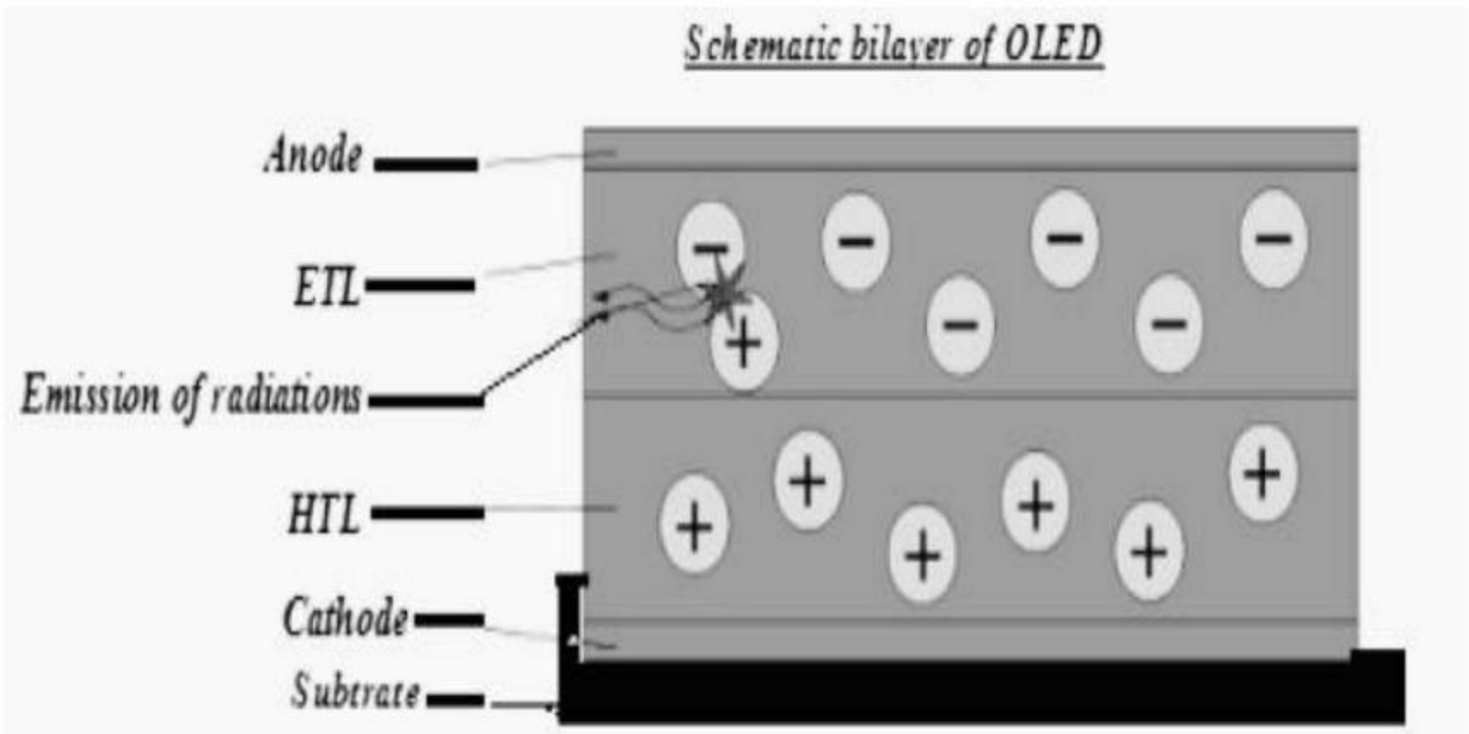
(b) **OLED (Organic Light Emitting Diode)**

OLED is an advanced form of LED and is made up of conducting polymer like polyaniline.Its thickness is 200 times smaller than human hair.

OLED STRUCTURE :-

Parts of OLED: 1. Substrate:
2. Anode
3. Hole Transport Layer (HTL)
4. Electron Transport Layer (ETL)
5. Cathode

→Substrate: A clear plastic or glass that supports OLED is called substrate.
→Anode: When current passes through the OLED, it removes electrons and adds holes. Usually used anode is ITO (Indium Titanium Oxide)
→HTL: It is the conducting layer made of conducting polymer like polyaniline. It helps for the transport of holes from the anode through the OLED.
→ETL: It is the emissive layer made of polyfluorene. Light is produced in the ETL. It helps for the
transport of electrons from the cathode through the OLED.
→ Cathode: It ejects electrons when current flows through the OLED. Al or Ca is used as cathode.



Working of OLED :-

When a voltage is applied across the OLED, a current of electrons flows from cathode to anode. During this current flow electron hole capture each other by electrostatic force of

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attraction. Recombination of electrons with holes produces light. The wave length of light produced depends on the band gap of the conducting polymer.

Properties :-

- It is considered as a cold lighting source. Since no heat is generated during its working.
- Its power consumption is very less.
- It is flexible, very thin and small.
- It generates good quality light.
- More efficient than incandescent lamps and halogen lamps.

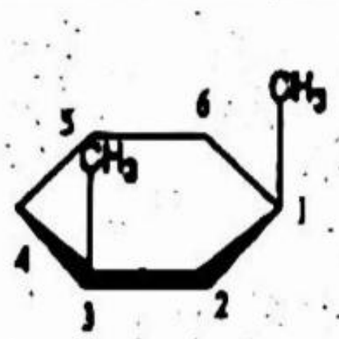
18- (a) The total number of isomers including stereoisomers for 1,3-dimethyl cyclohexane is 3, one cis and two optically active trans forms

1, 3-dimethyl cyclohexane

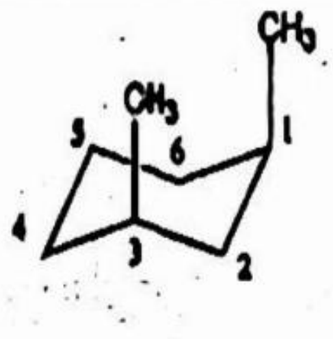
This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

a). (Cis) 1, 3-dimethyl cyclohexane

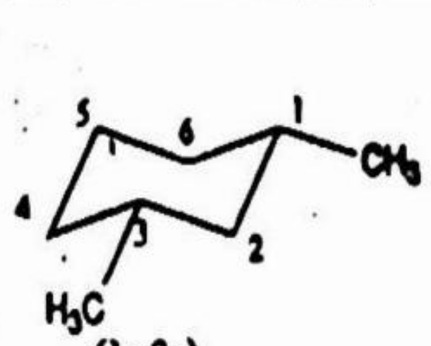
This compound has two conformers (1a, 3a) and (1e, 3e). They interconvert each other by flipping. (1a, 3a) has two Gauche interactions with the ring CH_2 groups whereas (1e, 3e) has no Gauche interaction. Thus (1e, 3e) conformer is more stable in (cis) 1, 3-dimethyl cyclohexane.



(cis)1,3-dimethyl cyclohexane



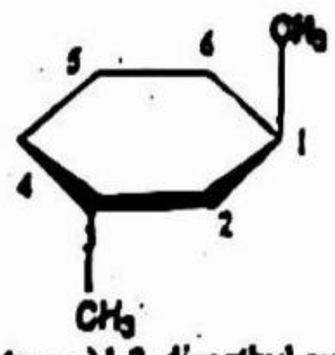
(1a,3a)



(1e,3e)

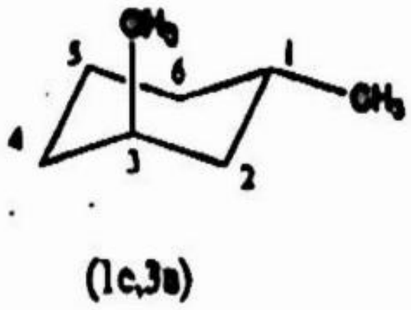
b). (Trans) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 3e) and (1e, 3a). Both are equally stable since they have equal number of gauche interactions. They interconvert each other by flipping. Both are equally stable since they have equal number of gauche interactions.



(trans)1,3-dimethyl cyclohexane

(1a,3e)



(1e,3a)

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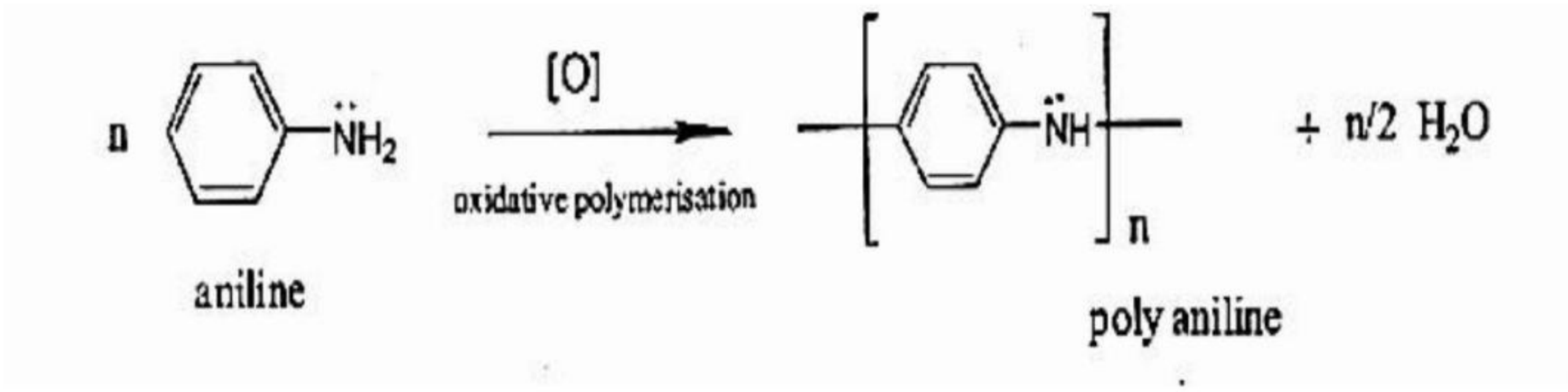
(b) **Poly aniline :-**

Polyaniline is one of the oldest conductive polymers known. It has been known as an electrically conductive polymer (ECP) for the past 35 years. Emeraldine (an oxidative form of polyaniline) is also known as "synthetic metal". It has conductivity like metals, metallic lustre and metallic sound. Although the compound itself was discovered over 150 years ago, only since the early 1980s has polyaniline captured the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity

Preparation :-

Polyaniline is made by the oxidative polymerization of aniline under acidic conditions. The most common oxidant is ammonium persulphate. The components are dissolved in 1 M HCl and the two solutions slowly combined. The reaction is very exothermic. The polymer precipitates as an unstable dispersion with micrometer-scale particulates.



Properties of polyaniline :-

- Polyaniline has light weight and mechanical flexibility.
- Poly anilines have three distinct oxidation states.

Applications of Polyaniline :-

- Can be used in chemical vapor sensors, super capacitors and biosensors.
- The different colors, charges and conformations of the multiple oxidation states make the material promising for applications such as actuators, super capacitors and electrochromics.

MODULE - V

19- (a) **Estimation of hardness by EDTA process**

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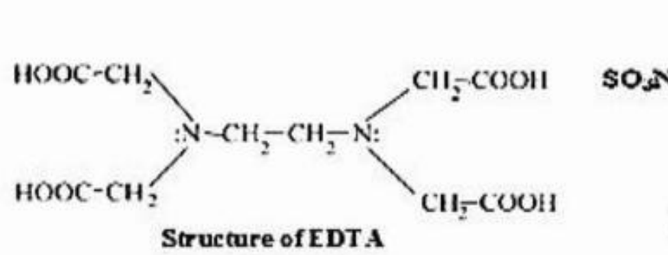
It is a complexometric method used for the determination of hardness of water sample. In this method, EDTA is used as titrant and EBT (Erio-chrome Black-T) is the titrant. It is blue in colour. It works effectively at the PH of 10. So a buffer solution is required to maintain the PH at 10. Usually used buffer is ammonium chloride- ammonium hydroxide buffer.

Principle and method of EDTA process:-

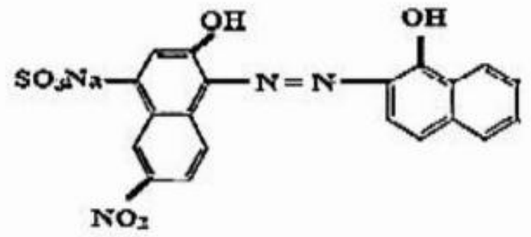
At a PH of 10, the Ca2+ & Mg2+ ions present in water forms a weak wine red coloured complex with EBT. When EDTA is added to this, weak EBT can be replaced by strong EDTA to form metal- EDTA complex. At the same time, wine red colour changes to blue due to the regeneration of EBT.

$$\mathbf{M^{2+} + EBT \rightarrow M{-}EBT\ (\boldsymbol{weak\ \&\ wine\ red})}$$
$$\mathbf{M{-}EBT + EDTA \rightarrow M{-}EDTA + EBT\ (\boldsymbol{blue})}$$

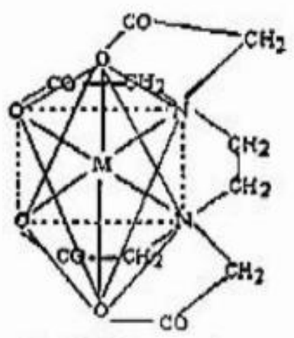
The PH is maintained around 10 using NH4Cl and NH4OH buffer, since indicator effective only at this PH. Initially M-EBT complex is formed, which is unstable. Then the addition of EDTA replaces EBT from the M-EBT complex produces M-EDTA complex and the colour changes from wine red to blue.



Structure of EDTA



Structure of Eriochrome Black-T



M-EDTA complex

Procedure :-

I. Preparation of solutions :-

a) Standard Hard Water (SHW) Dissolve 1g pure dry CaCO3 in minimum quantity dil.HCl and evaporate to dryness. The residue obtained is dissolved in distilled water and is made up to 1 litre. Each ml of this solution is equivalent to 1mg CaCO3 equivalent hardness.

b) EDTA solution Dissolve 4g EDTA crystals and 0.1g MgCl2 in 1 litre distilled water.

c) EBT indicator Dissolve 0.5g EBT powder in 100 ml alcohol.

d) Buffer solution 67.5g NH4Cl is added to 570 ml of liquor NH3 and is diluted to 1 litre using distilled
water.

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II. Standardisation of EDTA :-

50 ml SHW is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against EDTA till the wine red colour changes to blue. Let the volume of EDTA consumed be V1 ml & N1 be its normality. 50 ml SHW = V1 ml EDTA

(Each ml SHW contains 1mg $CaCO_3$ equivalent hardness.)

V1 ml EDTA = 50mg $CaCO_3$ equivalent hardness

1 ml EDTA (N1) =50/V1 mg $CaCO_3$ equivalent hardness

III. Determination of Total hardness :-

50 ml Unknown Hard Water (UHW) is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against standardized EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_2 ml

N_2 be the normality of UHW

$$50 \text{ ml UHW} = V_2 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$50N_2 = V_2 \times \frac{50}{V_1}$$

$$1 \text{ litre of UHW} = \frac{V_2}{V_1} \times 1000 \text{ mg } CaCO_3 \text{ equivalent hardness}$$

$$\text{Total Hardness} = \frac{V_2}{V_1} \times 1000 \text{ mg/L or ppm}$$

IV. Determination of permanent hardness :-

250 ml UHW is boiled to 50 ml. During boiling, soluble bicarbonates changes to insoluble CaCO3&Mg(OH)2. These are precipitates are filtered off and the filtrate is collected and is made upto 250 ml. It contains only permanent hardness causing ingredients.

50 ml of this Boiled Hard Water (BHW) is mixed with 10 ml buffer solution and add 3-4drops of EBT indicator. It is then titrated against standardized EDTA till the wine red colour changes to blue. Let the volume of EDTA consumed be V3 ml. N3 be the normality of BHW.

$$50 \text{ ml UHW} = V_2 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$50 N_3 = V_3 \times \frac{50}{V_1}$$

$$1 \text{ ml BHW } (N_3) = \frac{V_3}{V_1}$$

$$1 \text{ litre of BHW} = \frac{V_3}{V_1} \times 1000 \text{ mg } CaCO_3 \text{ equivalent hardness}$$

$$\text{Permanent Hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

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V. Determination of temporary hardness

$$\text{Temporary Hardness} = \text{Total Hardness} - \text{Permanent Hardness}$$
$$= \left(\frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000\right) \text{mg/L or ppm}$$
$$= \frac{V_2 - V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

(b) Chemical Oxygen Amount (COD) :-

It is the amount of oxygen required for the complete oxidation of biologically active and biologically inert materials present in sewage water using strong oxidizing agent like acidified K2Cr2O7 for a period of 3 hours. Only less time is required for the determination of COD. COD is always greater than BOD, since it causes the oxidation of both biologically active and biologically inert material.

Experimental determination of COD of water sample :-

A known volume of sewage is mixed with a fixed volume of K2Cr2O7 solution and dil. sulphuric acid and is refluxed for about 2-3 hours in presence of small amount of Ag2SO4 catalyst. The solution is then cooled and titrated with standard ferrous ammonium sulphates solution. Thus the unreacted K2Cr2O7 in the solution can be determined. A blank experiment is conducted with pure water. From the difference between the titre values of the blank and the test solution, COD can be calculated.

$$\text{COD} = \frac{(V_1 - V_2) \times N_2 \times B}{V_e} \times 1000$$

Where V1& V2 are the volumes of Mohr salt used by the blank and test samples respectively. Ve is the volume of effluent sample taken for test and N is the normality of Mohr's salt solution.

20- (a) **Chlorination :-**

Sterilization by chlorine is the most common sterilizing method in water treatment. Chlorine may be added directly as a gas or in the form of concentrated solution in water. When Chlorine is added to water, HOCI which acts as a powerful germicide is produced. It is believed that HOCI reacts with bacteria and inactivate the enzymes present in the cells of bacteria. These enzymes are responsible for the metabolic activities of microorganisms. Since these enzymes are inactivated, microorganisms become dead.

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$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

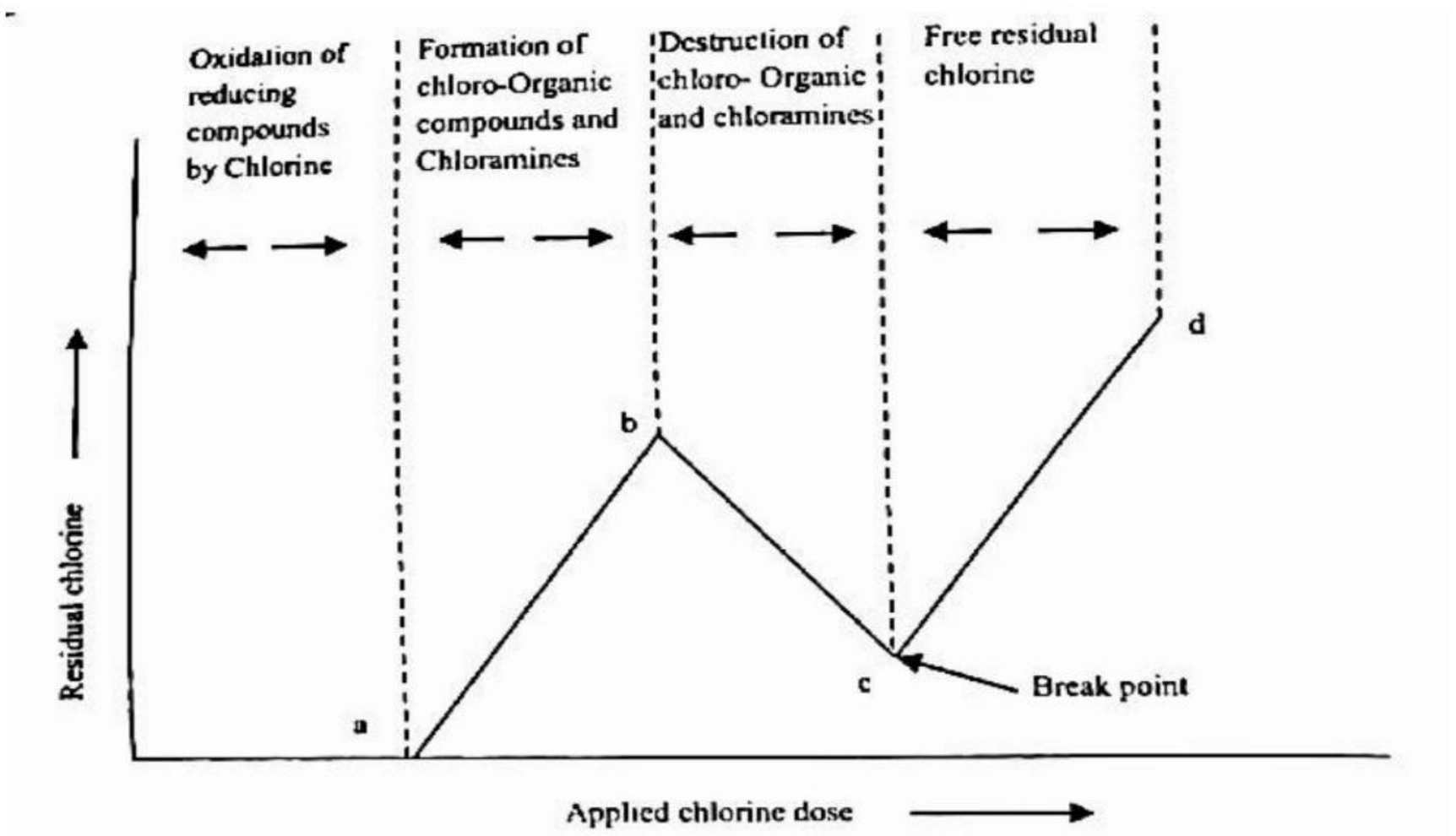
$$HCl + Bacteria \longrightarrow Dead\ Bacteria$$

Break point of chlorination :-

Break point of chlorination is defined as the addition of sufficient amount of chlorine to kill the microorganisms and to destroy them completely by the oxidation of reducing matter, organic matter, and free ammonia and leave behind free residual chlorine to continue the further disinfection.

If we plot, residual chlorine against applied chlorine, we get a curve. The dip in the curve 'C' shows the break point.

At the break point all the colour, odour, taste disappears and all the disease causing microorganisms get killed. It completely oxidises the organic compounds, ammonia and reducing compounds. After the break point, any further addition of chlorine appears to be present as free residual chlorine which will continue the further disinfection. The amount of free chlorine required for continuing further disinfection is 0.1-0.2 ppm. If over chlorination occurs, excess chlorine can be removed by passing the water through molecular sieve or by stirring it with activated carbon followed by filtration. Excess chlorine can be removed by adding dechlorinating agents like SO2, Na2SO3, sodium thiosulphate, etc



Break point of chlorination

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Advantages of Break Point of Chlorination :-

1. It ensures complete destruction of organic compound which imparts color, bad odour and unpleasant taste to water.
2. It completely destroys all disease causing bacteria.
3. It prevents the growth of any weeds in water.

(b) $CH_2O + O_2 \rightarrow CO_2 + H_2O$

$30\ g \quad 32\ g$

ie, $30\ g\ CH_2O$ reacts with $32\ g\ O_2$

$\therefore 90$ mg carbohydrates requires $90 \times \frac{32}{30} = 96$ mg Oxygen

Thus the BOD of the water sample $= 96$ mg/L $= 96$ ppm

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