PHYSICAL CHEMISTRY PAPER - VI
(Chapter wise question and answers)

1. Electrochemistry-I 10 hours- *26 marks*

1. Define Molar conductance. How is it related to conductivity?(2m)

Ans: It is the conductance of all the ions produced by one gram mole of an electrolyte in the given solution. Molar conductance = specific conductance/concentration OR $\mu = \kappa/C$ where μ is the molar conductance, κ-conductivity or specific conductance, C-molar concentration.

2. Give the SI units of specific conductance and molar conductance.(2m)

Ans: κ = S/m or $ohm^{-1}.m^{-1}$. $\mu = S.m^2/mol$. or $ohm^{-1}.m^2 \, mol^{-1}$.

3. Describe the determination of molar conductance of an electrolyte($NaNO_3$ or KCl) using Wheatstone's bridge.(4m)

Ans. 1. The following circuit is set up using a conductivity cell dipped in a solution of 0.1 N KCl. The balancing length is determined by unplugging a suitable resistance in the resistance box such that the balancing point is obtained at the centre of the bridge.

R_b Cell
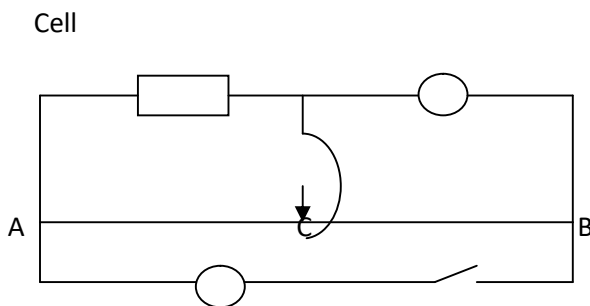
2. Resistance of KCl solution =(length BC/length AC) x resistance unplugged in the resistance box. Cell constant= specific conductance of 0.1N KCl solution x R_{KCl}

3. In a similar manner the balancing length for uni-univalent electrolyte solution is determined and resistance of the 0.1 M ($0.1x10^3 mol/m^3$) electrolyte solution is calculated.

4. Specific conductance of electrolyte solution, K = Cell constant/R

Molar conductance, $\mu = K /(0.1x10^3) \, Sm^2 mol^{-1}$.

4. What are conductometric titrations? Give the principles involved in it.(2m)

Ans: Titrations involving conductance changes as the tool to estimate the concentration of unknown solutions. Estimating the concentration of solutions using conductance changes at the end points which are obtained graphically.

5. What are the advantages of conductometric titrations over other conventional titrations(3m).

Ans: i) Suitable for coloured solutions which cannot be so accurate from other methods.
    ii) Accurate endpoint of titrations involving very dilute solutions can be obtained.

iii) use of indicators are not required.

iv) suitable for weak acid and weak base titrations and precipitation titrations.

v) conductometric titrations are more accurate as the results are obtained graphically

6) Explain or discuss the principles involved in the conductometric titration of a strong acid vs strong base graphically(4m).

Ans: A known volume of a strong acid solution (HCl) is taken in a beaker and the strong base solution (NaOH) is added from the burette. The conductance is measured after each addition of 0.5 ml of the base and a graph of conductance versus volume of base is plotted. A 'V' shaped graph is obtained from which the end point is determined as the volume corresponding to the minimum conductance.The reaction is: $H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$

As shown here initially the conductance will be maximum because of the presence of strongly conducting H^+ ions. After the addition of NaOH the conductance decreases as the strongly conducting H^+ ions are replaced by less conducting Na^+ ions. After the end point the conductance begins to increase as the added NaOH introduces strongly conducting OH^- ions
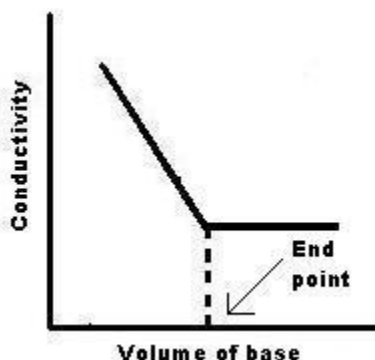
Graph:

anc

Conduct

end point

Volume of NaOH→
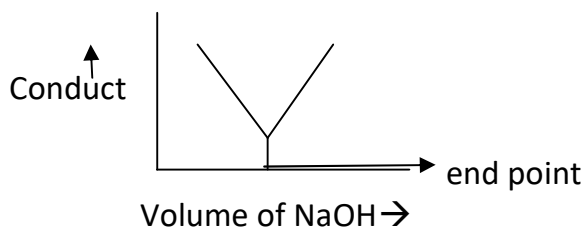
7) Explain or discuss the principles involved in the conductometric titration of a strong acid vs weak base graphically(4m)

Ans: In the case of titration of Strong acid Vs Weak Base HCl Vs NH_4OH; the equation is

E.g.: $[H^+ + Cl^-] + [NH_4^+ + OH^-] ---> [NH_4^+ + Cl^-] + H_2O$

In this case, initially the conductance will be more because of H^+ ions.But if once the NH_4^+ OH is added, H^+ ions will be replaced by NH_4^+ ions and so the conductivity decreases. As NH_4OH is a weak base, it do not dissociate and so after neutralization the conductivity do not increase.

Conductivity
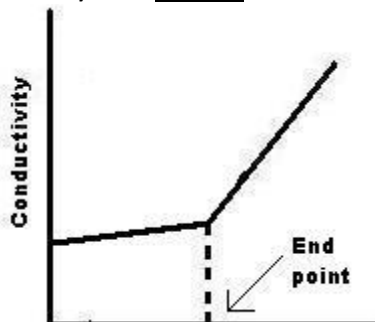
End point

Volume of base

8) Explain or discuss the principles involved in the conductometric titration of a Weak acid vs Strong base graphically(4m)

Ans: In the case of titration of Strong acid Vs Weak Base HCl Vs NH_4OH; the equation is

E.g.: $[CH_3COO^- + H^+] + [Na^+ + OH^-] \longrightarrow [CH_3COO^- + Na^+] + H_2O$

When a weak acid, CH_3COOH and is titrated with strong base NaOH. Once we add NaOH, the conductivity will increase. And after neutralization, because of highly mobile strong OH- ions, the conductivity again increases continuously. **Graph**

9) Explain or discuss the principles involved in theconductometric titration of a Weak acid vs Weak base graphically(4m)

Ans: In the case of titration of Strong acid Vs Weak Base HCl Vs NH_4OH; the equation is

E.g.: $[CH_3COO^- + H^+] + [Na^+ + OH^-] \longrightarrow [CH_3COO^- + Na^+] + H_2O$
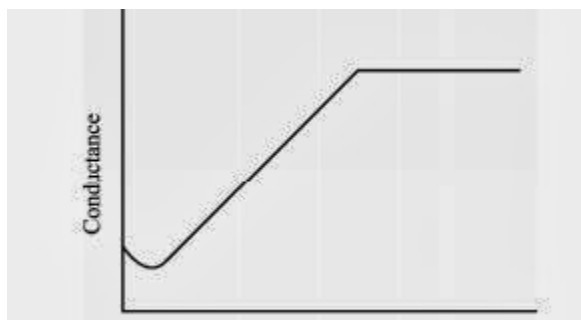
Volume of NH₄OH added

The conductivity in the beginning decreases due to the formation of the strong salt which decreases the dissociation of the weak acid further. With further addition of the weakbase, the conductance increases due to the increased concentration of the salt, which is highly ionized . This continues until at the end point, later the conductance remains constant because the salt hydrolysis is suppressed by the excessive base added.

10. Define i)transport number of an ion, ii) Ionic mobility iii) Absolute ionic mobility.
(2m each)

Ans: **i)Transport number of an ion:** Fraction of the total amount of electricity carried by an ion
That is, transport number of anion = current carried by anion/total amount of current carried by both the ions, similarly t_c= current carried by cation/total amount of current carried by both the ions.

ii) Ionic mobility(u_a or u_c): Distance travelled by an ion per second under a potential gradiant of 1Volt/cm. It is represented as u.

iii) Absolute ionic mobility: Absolute ionic mobility is defined as the mobility with which the ion moves under unit potential gradient. It's unit is cm sec^{-1}.Absolute ionic mobility = Ionic mobility/96,500.

12. How transport number of an ion and ionic mobilities are related to each other?(2m)

Ans:t_a (transport number of anion)=u_a/u_a+u_c ; $t_c = u_c/u_a+u_c$; and $t_a + t_c = 1$

similarly, $t_a = u_aF$, $t_c = u_cF$; 1F=96500C.

13)Describe the determination of transport number of H$^+$ ion in HCl by moving boundarymethod.(4m)

Ans: The principal electrolyte, HCl is placed over the indicator electrolyte, $CdCl_2$ such that a sharp boundary AB separates them in a glass tube as shown in the figure. On passing current the boundary moves to CD because of the migration of H$^+$ ions to the cathode.

 The transport number of H$^+$ ions is calculated using the formula, $t_{H+} = laC/(1000Q)$

 where 'l' cm is the distance moved by the boundary, 'a' cm^2 is the cross sectional area of the glass tube, C g.eqts./dm^3 is the concentration of HCl, Q is the number of Faradays of electricity passed through the solution measured using coulometer.

Transport number of chloride ions is given by, $t_{Cl-} = 1-t_{H+}$

HCl

Batt

A   B

C   D

Graphite cathode

$CdCl_2$

Cadmium anode
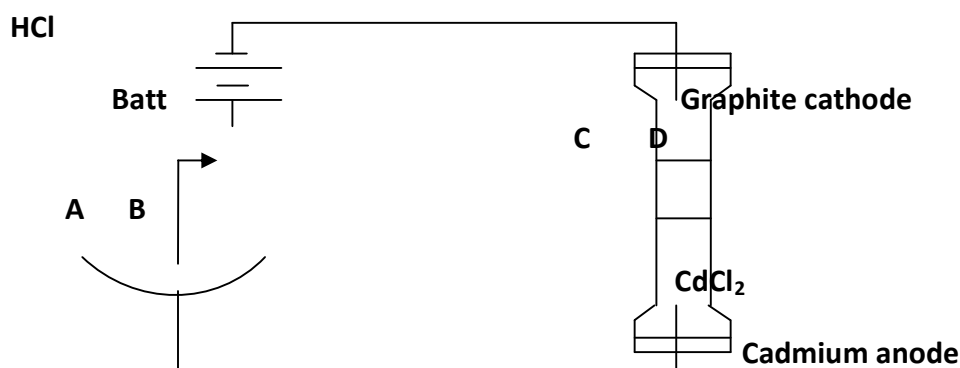
14. What is meant by abnormal transport number of an ion? Give an example.(2m)

Ans: Abnormal Transport Numbers. — It is evident that the transport number must lie between 0 to 1, for otherwise the positive ion would be travelling against the current or the negative ion with the current, and this is inconceivable. Such type of difference in the normal value of transport number of an ion is called abnormal transport numbers.

Ex: The transport number of Cd^{2+} apparently becomes negative as the concentration exceeds 0.5N instead of positive value.

15. Why is the transport number of cadmium ion in cadmium iodide abnormal at high concentrations?

Ans: In highly concentrated solutions cadmium ion forms complex CdI_4^{2-} ion ($CdI_2 + 2I^- \rightarrow CdI_4^{2-}$) which moves towards the anode. Therefore with increase in concentration of cadmium iodide solution the number of cadmium ions moving towards cathode starts to decrease thus

decreasing the transport number of cadmium ion. The transport number of cadmium ion may even take negative values in highly concentrated solutions.

16. Transport number of Cl⁻ ion is not the same in aqueous solutions of KCl and HCl. Give reason.(2)

Ans. We know that $t_+ + t_- = 1$. It means that the transport number of an ion depends on the other ion with which it is associated. As the mobility of H^+ ion is very high compared to that of K^+ ion, H^+ ion in HCl carries greater fraction of the current passed than K^+ of KCl. Hence transport number of Cl- ion is less in HCl and more in KCl.

17. State Kohlraush law of independent migration of ions and indicate the terms(2m).

Ans: ' The molar conductance or equivalent conductance at infinite dilution of an electrolyte is the sum of the ionic conductances of cation and anion of the respective electrolyte'.

$$\Lambda_0^{electrolyte} = \lambda_0^+ + \lambda_0^-$$

Where λ_0^+ and λ_0^- are the limiting equivalent conductivities of cation and anion respectively.

However the Kohlrausch law can also be stated in terms of molar conductivities as: 'The limiting molar conductivity of an electrolyte is the sum of individual contributions of limiting molar conductivities of its constituent ions.' i.e., The molar equivalent conductivity of an electrolyte, $\mu_0$electrolyte

$$\mu_0^{electrolyte} = n_+ \mu_0^+ + n_- \mu_0^-$$

Where μ_0^+ and μ_0^- are the limiting molar conductivities of cation and anion respectively and n_+ and n_- are the stoichiometric numbers of positive and negative ions formed during the dissociation of electrolyte.

18. Give the applications of Kohlrausch law.

Ans: 1. Used to calculate the limiting molar or equivalent conductivity of weak electrolytes.
2. Used in the determination of solubility of sparingly soluble salts
3. Used to determine the degree of dissociation and dissociation constants of weak acids/weak bases.
4. Used to determine and calculate the ionic product of water and absolute ionic mobility of ions.

18. Explain the application of Kohlrausch law in the determination of molar conductivity at infinite dilution of acetic acid and ammonium hydroxide(4m)

Ans: i) By determining the limiting molar conductivities of strong electrolytes like sodium acetate, HCl, and NaCl, λ_∞ of acetic acid can be calculated by Kohlraush law
$$\lambda_\infty \text{ of acetic acid} = \lambda_{\infty(CH3COONa)} + \lambda_{\infty HCl} - \lambda_{\infty NaCl} = \lambda_{\infty(CH3COO-)} + \lambda_{\infty H+}$$
ii) By determining the limiting molar conductivities of strong electrolytes like sodium hydroxide, ammonium chloride and sodium chloride λ_∞ of NH_4OH can be calculated by using Kohlraush law as follows: λ_∞ of NH_4OH = $\lambda_{\infty NH4Cl}$ + $\lambda_{\infty NaOH}$ - $\lambda_{\infty NaCl}$ = $\lambda_{\infty(NH4+)}$ + $\lambda_{\infty OH-}$

19. How is the solubility of a sparingly soluble salt determined by conductance measurements?(4m)/Explain the application of Kohlrausch law in the determination of solubility of silver chloride in water.

Ans. (i) A solution of 0.1N KCl is prepared and its conductance is determined by the meter bridge method. Cell constant is calculated using the formula, cell constant = specific conductance of 0.1N KCl solution/conductance.

(ii) A saturated solution of the sparingly soluble salt (Ex. AgCl) is prepared in conductivity water and its conductance (C_1) is determined. Also the conductivity of the water (C_2) used for preparing the solution is determined. Specific conductance of the salt solution is calculated using the formula, K = (C_1-C_2) x cell constant.

(iii) The molar conductance of the salt at infinite dilution (Λ^0) is calculated as the sum of ionic conductivities of the cation and anion (Λ^0_{AgCl} = Λ^0_{Ag+} + Λ^0_{Cl-}).

(iv) As the solution of the salt is very dilute its molar conductance can be taken as equal to the molar conductance at infinite dilution. The solubility is calculated using the formula, Solubility in mol/m^3 = K/Λ^0

(Bariumsulphate the same explantion except the name of the salt and Λ^0_{BaSO4} = Λ^0_{Ba2+} + Λ^0_{SO4-})

20. Desribe the application of Kohlraushc law in the determination of the dissociation constant of monochloroacetic acid(4m)

Ans.i) Determination of conductance of the prepared concentrated monochloroacetic acid and the cell constant of the given conductivity cell by preparing 0.1N KCl solution and using wheatstones bridge or conductivity meter. ii) Calculation of conductivity or specific conductance and molar conductivity, K= cell constant x conductance, Molar conductivity λ_c = specific conductance/concentration.

iii) Kohlrausch law is used to calculate λ_o of monochloroacetic acid and the calculation of degree of dissociation of the acid.ɑ = λ_c/ λ_o,

iv) K_a of the acid is calculated using Ostwald's dilution law; K_a= ɑ^{2}C/(1- ɑ)

21, Give the Limitations of Arrhenius theory.(2m)

Ans: 1.This theory based law Ostwald's law is applicable only to weak electrolytes but fails for strong electrolytes.

2. The degree of dissociation calculated from conductivity measurements differs for a strong electrolytes determined from colligative property mesasurements.

3. Solvent medium that is aqueous medium is not a necessary requirement for dissociation since molten electrolytes also conducts the current.

4. Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

22. Explain or discuss the theory of strong electrolytes Or Explain: i) Asymmetric effect and ii) Electrophoretic effect in strong electrolytes(4m).

Ans: In the case of a strong electrolyte the molar conductance in aqueous solution increases upon dilution but there decrease in mobility of ions. The decrease in mobility is due to increase in interionic forces which can be explained through two effects.

(i) Asymmetry effect/Relaxation effect: In an electrolyte solution each ion is symmetrically surrounded by oppositely charged ions in absence of electric field. When an electric field is

applied the central ion moves in one direction whereas the ions around it in the opposite direction. This destroys the symmetry and an ion near the electrode experiences a backward pull from the more number of oppositely charged ions behind it.
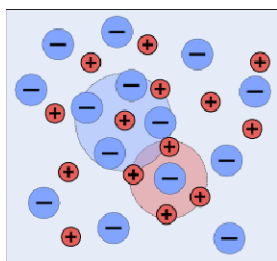
In absence of electric field   In an electric field

(ii) Electrophoretic effect: Each ion in a solution is hydrated. When an ion moves towards the electrode it has to carry the water molecules bound to it. When the ion at the centre moves in one direction along with the water molecules it has to make way through the water molecules moving in the opposite direction. This reduces its mobility.

OR

i)Asymmetric effect— Spherical symmetry before application of the current with diagram Asymmetry or dispersal of symmetry after application of the electrical field that decreases the conductivity with diagram

ii) Electrophoretic effect—Frictional drag of the solvent on mobility of the ions causes decrease in the conductance of the ions due to solvation to swim against the applied field.

23. Explain the significance and write the Debye Huckelonsager equation.

Ans: In addition it was assumed that the electric field causes the charge cloud to be distorted away from spherical symmetry. After taking this into account, together with the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to derive a theoretical expression to account for the empirical relation known as Kohlrausch's Law, for the molar conductivity, Λm. $\lambda_m = \lambda_m^o - k\sqrt{c}$, λ_m^o is known as the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. Limiting here means "at the limit of the infinite dilution". Onsager's expression is $\lambda_m = \lambda_m^o - (A + B \lambda_m^o) \sqrt{C}$, where A and B are constants that depend only

on known quantities such as temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. This is known as the Debye-Hückel-Onsager equation. However, this equation only applies to very dilute solutions. where $A = 8.24/(DT)^{1/2}\eta$

$B = 8.2 \times 10^5/(DT)^{1/2}$, Where D is the dielectric constant of the solvent and T is the temperature in kelvin scale, η= coefficient of viscosity, C= concentration in mole/lt.

Limitations: If the solution approaches infinite dilution, c is almost zero, then $\lambda_m = \lambda_m^o$. Plot of λ_m Vs C for a number of uni-univalent electrolytes is found to be linear up to 0.02M concentration. This shows it is applicable to dilute solutions. At higher concentrations deviations are observed.

24. Define Electrode potential and standard electrode potential of a metal(2M).

Ans: Potential difference between the metal and its solution containing its own ions of definite concentration and temperature is called electrode potential of the metal. it is represented as E. Potential difference between the metal and its solution containing its own ions of 1M concentration or a pressure of 1bar for gas electrodes and temperature of 298K is called electrode the standard electrode potential of the metal. it is represented as E^o.

25. What are Galvanic cells? Give an example.

Ans: A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cellthat derives electrical energy from spontaneous redox reactions taking place within the cell. Ex: Daniel cell.

26. Explain Reversible and Irreversible cells with examples.(4m)

Ans: **Reversible cells**: A cell works reversibly in the thermodynamic conditions. Ex. Daniel cell, Secondary batteries, Rechargeable batteries. The cell is reversible if it satisfies all the following conditions: i) If applied emf is equal to derived emf then the net reaction is zero ii) If applied emf is infinitesimally smaller than the derived emf then the cell should act as electrochemical cell (forward reaction) iii) If applied emf is infinitesimally greater than the derived emf then the cell should act as electrolytic cell (reverse reaction)Ex: Daniel cell.

Irreversible cells: Cells which do not obey the (above) conditions of thermodynamic reversibility are called irreversible cells. If one of the products escapes from the cell then that cell cannot be made reversible by applying an external current.

Ex. Zinc-Silver cell, Primary cells: Zn –Ag Cell: Zn / H_2SO_4 (aq) / Ag

Cell reaction:

$$\text{Anode: } Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$
$$\text{Cathode: } 2Ag^+ + 2e- \longrightarrow 2Ag$$
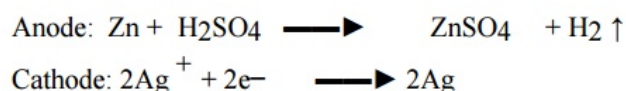
When two electrodes are connected from outside, zinc dissolves liberating hydrogen gas. Since one of the product hydrogen escapes, the cell reaction cannot be reversed when connected to an external EMF. The cell does not obey the conditions of reversibility and is called irreversible cell.

27. Describe the construction and working of a Daniel cell.(4m)

Ans: Daniell cell is the simplest voltaic or galvanic cell. It converts chemical energy into electrical energy spontaneously.

Construction: In Daniel cellcopper and zinc electrodes are immersed in a solution of copper(II) sulphate and zinc sulphate respectively. At the anode, zinc is oxidized as per the following half reaction:
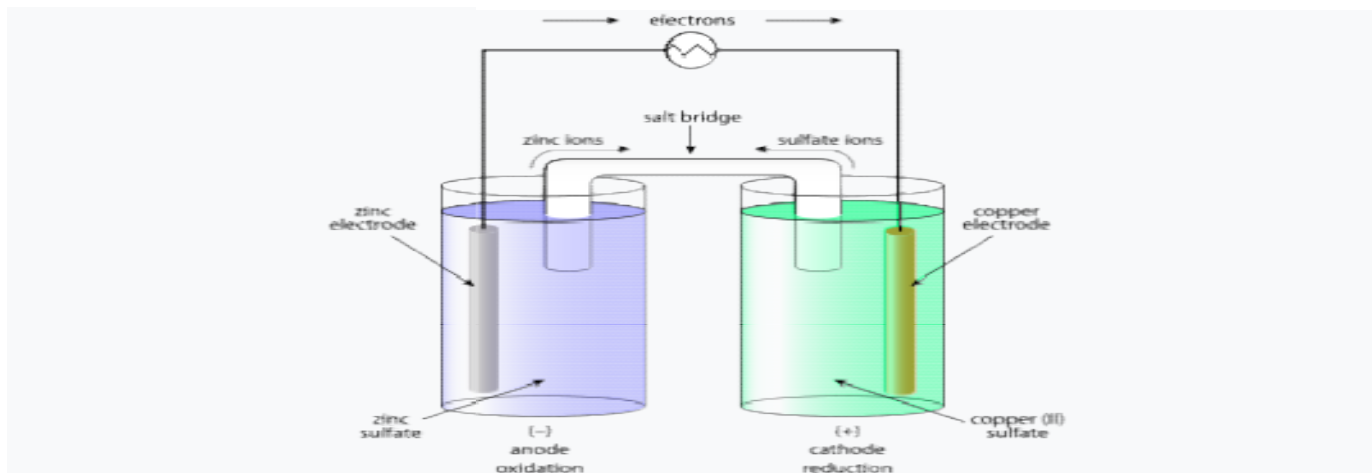
At the <u>anode</u>, zinc is <u>oxidized</u> as per the following half reaction:$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

(<u>Standard electrode potential</u> +0.7618 V)

At the <u>cathode</u>, copper is reduced as per the following reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

(<u>Standard electrode potential</u> +0.340 V)

The total reaction or Net cell reaction is:<u>Zn</u>(s) + <u>Cu</u>$^{2+}$(aq) $\rightarrow Zn^{2+}$(aq) + Cu(s)

(<u>Open-circuit voltage</u> 1.1018 V)

When the half cells are placed in two entirely different and separate containers, a <u>salt bridge</u> is often used to connect the two cells. The salt bridge typically contains a high concentration of potassium nitrate (a salt that will not interfere chemically with the reaction in either half-cell). In the above wet-cell during discharge, nitrate anions in the salt bridge move into the zinc half-cell in order to balance the increase in Zn^{2+} ions. At the same time, potassium ions from the salt bridge move into the copper half-cell in order to replace the Cu^{2+} ions being discharged. In the Daniell cell, the porous barrier cannot prevent the flow of copper ions into the zinc half-cell. Hence, recharging (reversing the current flow by an external source of <u>EMF</u>) is impossible because, if the zinc electrode is made to become the cathode, copper ions, rather than zinc ions, will be discharged on account of their lower potential.

28. Derive Nernst equation of electrode potential thermodynamically.

Ans: Consider a reversible reaction of the type taking place in an electrochemical cell,

$$A+ B \Leftrightarrow C+D.$$

The free energy change for the reaction is given by, $\Delta G = \Delta G^0 + RT\ln[(aCxaD)/(aAxaB)]$ …..(1), where ΔG^0 is the standard free energy change, aA, aB, aC and aD represent activities of substances A, B, C and D respectively.

The free energy change for the cell reaction is given by, $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$ where 'n' represents the number of electrons transferred, 'F' the Faraday's constant, 'E' emf of the cell at temperature T and E^0 emf of the cell under standard conditions.

Substituting in equation (1), $-nFE = -nFE^0 + RT\ln[(aCxaD)/(aAxaB)]$

Dividing by $-nF$, $E = E^0 - 2.303RT/(nF) \log[(aCxaD)/(aAxaB)]$ …(2).

This equation called Nernst equation to calculate emf of a cell.

Consider the reduction reaction taking place at an electrode, $M^{n+} + ne^- \Leftrightarrow M$.

Applying equation (2) for the electrode reaction, the electrode potential is given by,

$$E = E^0 - 2.303RT/(nF) \log (a_M /a_{Mn+})....(3)$$

where E^0 represents the standard electrode potential. Substituting molar concentration in place of activity as the two physical quantities are nearly equal,

$$E = E^0 +2.303RT/(nF) \log \{[Oxidised]/[Reduced]\}....(4)$$

is Nernst equation for single electrode potential.

29. How molar conductance varies with dilution. Account for your answer(2m).
Ans: Molar conductance increases with increase in dilution because the number of ions per unit volume decreases. Specific conductance or conductivity decrease and the molar conductance increases.

30. Write a note on abnormal transport numbers.(2m).
Ans: Variation in the transport numbers of ions due to complex formation. Example: Cadmium in higher concetrations, the transport number of cadmium ions rapidly decreased due to the formation of the complex ion $[CdI_4]^{2-}$ and transported to the anode.

31. The ionic conductances of H^+ and OH^- ions are abnormally high. Why?(2m)
Ans**:** The H^+ and OH^- ions are highly solvated and the protons are exchanged between neigh bouring solvent molecules showing high ionic conductances.

32. Define the following and give their SI units: i) Cell constant   ii) Conductivity(4m)
Ans: **i) Cell constant**: The Ratio of the length and area of cross section of electrodes is called the cell constant of the conductivity cell. Its SI unit is $m^{-1.}$.
ii) Conductivity or specific conductance of an electrolyte is defined as the conductance of the electrolyte solution when placed between the two electrodes of a conductivity cell of unit length and unit area of cross section. Its unit is S/m.

33. What the conductivity of 0.1N KCl solution? Mention its use.
Ans: Its value is 1.285 S/m. **It is used to determine the cell constant of the given conductivity cell.**

34. Platinized platinum electrodes are used in conductivity cells. Why?
Ans: The catalytic properties of platinum black ensures the electrode reactions occur rapidly and stay in phase with the rapid applied alternating voltage and avoids the polarization of the electrodes and electrolysis.

2.Electrochemistry-II5 Hours --14 marks

1. Define EMF of a cell, Name the cell is used as a standard to determine the emf of a test cell(2m).

Ans:The potential difference between the two electrodes in a galvanic cell is called a cell potential or emf of the cell. It is measured in volts. Emf of the cell = Potential of the half cell on the right hand side (Cathode) - Potential of the half cell on the left hand side (Anode)

Weston cadmium cell is used as a standard to determine the emf of cells.

2. What is Weston cell. Represent the Weston cell symbolically(2).

Ans: A primary cell used as a standard of emf, producing 1.018 volts consists of a cadmiumamalgam anode and the cathode consisting of pool of mercury in mercuric sulphate in an electrolyte of saturated cadmium sulphate.

$$Pt:Cd(Hg)/CdSO_4\ 8/3H_2O/CdSO_4(aq)\ /Hg_2SO_4(s)/Hg;Pt$$
$$\text{(-)A} \qquad\qquad\qquad\qquad \text{(+)C}$$
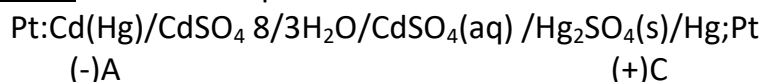
3. What is a standard cell. Mention its requirements. Give an example.(2) Or Weston is used as a standard cell. Why?

Ans: A standard cells are used as a reference or standard to determine the emf of cells . A cell is said to be standard if it satisfies the following conditions: i) Its potential is known and standard and reproducible.ii) Its temperature co-efficient dE/dT should be low iii) It should be a reversible cell. iv) There should be no permanent damage to the cell on passing current.
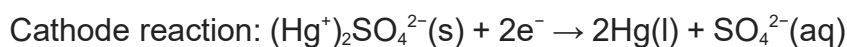
Ex: Weston cadmium cell.

4. Describe the construction and working of Weston cell(4m).

Ans: The cell consists of H shaped glass vessel with a platinum wire sealed through the
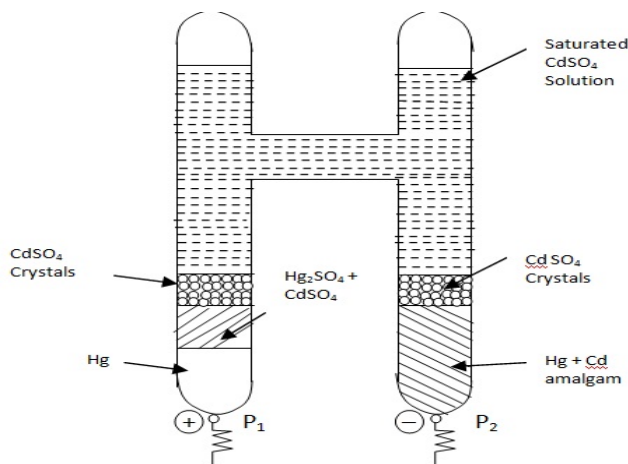
bottom of each limb. The anode limb consists of a layer of solid cadmium amalgam containing 12.5% cadmium and the cathode limb consists of a pool of mercury layered with a thick paste of mercuric sulphate Hg_2SO_4. The electrolyte is a solution which is kept saturated by the crystals of hydrated $CdSO_4 .8/3 H_2O$ crystals. The electrolyte is cadmium sulphate solution. The ends are sealed using paraffin or wax.
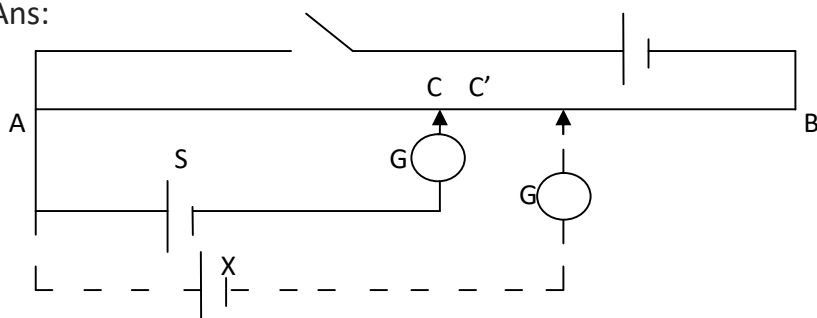
$$\text{Anode reaction: } Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$$
$$\text{Cathode reaction: } (Hg^+)_2SO_4{}^{2-}(s) + 2e^- \rightarrow 2Hg(l) + SO_4{}^{2-}(aq)$$

The net cell reaction is: $Cd(s) + (Hg^+)_2SO_4^{2-}(s) \rightarrow Cd^{2+}(aq) + 2Hg(l) + SO_4^{2-}(aq)$

If the current is passed through the cell, the above cell reaction is reversed. The emf of the above cell is 1.018V at 298K.

5. (a) How is EMF of a cell experimentally measured by Poggendorff's compensation method?(4)

Ans:

The end terminals A and B on a Potentiometer bridge are connected to a DC source. The point A is also connected to a standard cell (S) such that the positive of the battery and positive of the standard cell are at the same point A. The negative terminal from the standard cell is connected to a jaw key through a galvanometer. The jaw key is moved over the potentiometer wire so as to determine the balancing length when the galvanometer shows zero deflection. The length AC is measured. Length AC α E_s ...(1) , $E_s$emf of the standard cell.

The standard cell is now replaced by the cell (X) whose EMF is to be measured and as explained above the balancing length, AC' is determined. Length AC' α E_{cell} .....(2)

From (1) and (2), AC/AC' = E_s/E_{cell} ......(3) Knowing the value of E_s , E_{cell} can be calculated.

6. How the standard electrode potential of a metal is determined? Explain with examples4m)

Ans: It is impossible to determine the absolute potentials of single electrodes. For that the electrode is to be coupled with a standard hydrogen electrode whose potential is arbitrarily fixed as zero, the emf of the cell is determined using a potentiometer. Since E^0 of SHE is zero, the E^o of the metal can be calculated.

Ex: i) Determination of E^o of zinc: The zinc electrode is coupled with NHE and the cell is constructed as follows and emf is determined using a potentiometer.

$Zn/Zn^{2+}(a=1) // (a=1)H^+/H_2(1atm);Pt.$ then EMF = $E_{cathode} - E_{anode}$; EMF = $E^o_{SHE} - E^o_{Zn/Zn2+}$

EMF = $0 - E^o_{Zn/Zn2+}$, Hence $E^o_{Zn/Zn2+}$= -EMF Volts. = -0.76V(since emf of the cell is -0.76V.

The half cell reaction is $Zn + 2H^+ \rightarrow Zn^{2+}$ - H_2

ii) Determination of E^o of Copper: The Copper electrode is coupled with NHE and the cell is constructed as follows and emf is determined using a potentiometer.

$Pt; H_2(1atm)H^+(a=1)// Cu^{2+}(a=1)/Cu$ then EMF = $E_{cathode} - E_{anode}$; EMF = $E^o_{Cu2+/Cu} - E^o_{SHE}$

EMF = $E^o_{Cu2+/Cu} - 0$, Hence E^o = EMF Volts. = 0.34V(since emf of the cell is 0.34V)

The half cell reaction is: $Cu^{2+} + H_2 \rightarrow Cu + 2H^+$

7. Give the relationship between the change in Gibb's free energy and the emf of a Galvanic cell.(2m)

Ans: ΔG^o = -nFΔE^o, WhereΔG^o = Standard free energy change of the electrode reaction, n= No. of electrons involved in the reaction F = Number of faradays of current generated.

ΔE^o = Standard electrode potential of the electrode or standard EMF of the cell.

8. What is meant by liquid junction potential? Mention its significance and how can it be minimized?(2m)

Ans: **Liquid junction potential** occurs when two electrolytic solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. Thus at the point of junction,a potential difference will develop because of the ionic transfer.This potential is called liquid junction potential whose magnitude depends on the relative speeds of the ions' movement.

The liquid junction potential interferes with the exact measurement of EMF of a chemical cell. So it should be eliminated or at least its effect should be minimized. The general practice to eliminate the liquid junction potential is to place a salt bridge consisting of usually a saturated solution of Potassium chloride (KCl) and Ammonium nitrate (NH_4NO_3) with Lithium acetate (CH_3COOLi) between the two solutions constituting the junction. When such a bridge is used, the ions in the bridge are present in large excess at the junction and they carry almost the whole of the current across the boundary. The efficiency of KCl/NH_4NO_3 is connected with the fact that in these salts, the transport numbers of anion and cation are the same.

9. Write a note on different types of electrodes?(4m)

Ans: In an electrochemical cell, there are two electrodes, positive and negative. Each electrode constitutes a half cell or a single electrode. Although a number of electrodes are possible but the more important of these electrodes are grouped into the following types:

(*i*) Metal-metal ion electrodes
(*ii*) Metal-metal insoluble salt electrodes
(*iii*) Metal-amalgam electrodes
(*iv*) Gas-ion electrodes
(*v*) Oxidation-reduction or redox electrodes.

(*i*) ***Metal-metal ion electrodes*** : These electrodes consist of a pure metal (M) in contact with a solution of its cation (M^{n+}). For example, a silver rod immersed in a solution of Ag^+ ions or copper rod in copper sulphate solution. The electrode is represented as M^{n+} and the electrode reaction can be written as : $Mn^+ (a) + ne^- \rightarrow M$

Since the electrode is reversible to the metal cation, its electrode potential depends on the activity/concentration of the metal cation in the solution.

(*ii*) ***Metal-metal insoluble salt electrodes***: Such electrodes are important and are frequently used in electrochemical works. These consist of a metal (M) covered by a layer of sparingly soluble salt (MX) immersed in a solution containing a common anion (X^-). Examples of such electrodes are **mercury-mercuroussulphate in contact with a solution of potassium sulphate** or a **silver wire coated with silver chloride immersed in potassium chloride solution**. These electrodes are reversible to the anion of the sparingly soluble salt, X–.

(*iii*) ***Gas-ion electrodes***: A gas electrode consists of an inert metal usually gold or platinum immersed in a solution containing ions to which the gas is reversible. A current of pure gas is continuously bubbled through the solution. The inert metal electrode does not participate in the electrode reaction but simply helps in making electrical contact.

The gas (X_2) electrode is denoted as : $X^-(a)/X_2(P = x\,atm)/Pt$: Ex: Chlorine electrode.

(*v*) ***Oxidation-reduction or redox electrodes***: These are electrodes in which the emf arises from the presence of ions of a substance in two different oxidation states. These electrodes are set up by dipping an inert metal like gold or platinum into a solution containing ions in two different oxidation states of the substance. For example, a platinum wire immersed in a

solution of ferrous and ferric ions or stannous and stannic ions constitutes a redox electrode. These electrodes are represented as : $Pt|M^{n_1+}(a_1), M^{n_2+}(a_2)$ where M^{n_1+} is the higher oxidation state and M^{n_2+} is the lower oxidation state. Ex: Pt; $Fe^{2+}/Fe^{3+}(a)$'

10. What are reference and indicator electrodes? Give examples(4m)

Ans: Reference Electrodes: The electrode whose potential is arbitrarily fixed to a certain value is exactly known is called a reference electrode. Commonly used reference electrodes are: 1. Standard Hydrogen electrode(SHE) - Primary reference electrode
2. Standard calomel electrode(SCE)- Secondary reference electrode
- Advantages of Standard Hydrogen Electrode (S.H.E.): Small potential is developed on the hydrogen electrode, hence it can be taken as zero.
- In determining the single electrode potential, using S.H.E. as a reference, the potential of the unknown potential will be equal to the e.m.f. of the cell.

Limitations of Standard Hydrogen Electrode (S.H.E.):
1. It is not convenient to assemble the apparatus.
2. It is difficult to maintain the pressure of hydrogen gas and concentration of HCl.
3. It is difficult to get pure, dry hydrogen gas and prepare ideal platinised platinum plate.
The impurities present in H_2 and HCl poison the Pt, and affect the equilibrium at the electrode.
2. Standard calomel electrode(SCE)- Secondary reference electrode: Electrode potential depends upon concentration of KClsolution.Pt, Hg (l) | Hg_2 Cl_2 (s) | KCl (aq) (a = x) At 298K, oxidation potentials are: 1N KCl or 1M KCl: - 0.280V,
2. Indicator Electrodes: The electrode system which is used to determine the concentration of the solution used as an electrolyte in the half cell is known as indicator electrode.

Example:$Zn_{(s)} | Zn^{2+}_{(aq)} (1M)$

11. Mention the factors affecting the electrode potential of a metal.(2m)

Ans: The electrode potential of a metal depends on the following factors: i)Nature of the metal ii) Concentration of the electrolyte/solution iii) Temperature iv) Valency of the ion.

12. What is standard hydrogen electrode? Describe the construction, working and limitations of standard hydrogen electrode.(4m)

Ans: This is a gas electrode. It consists of a thin rectangular platinum foil which is coated with fresh platinum black to increase the adsorption capacity of the metal. This is welded and the end of it is fused into the inner tube through the base. In the inner tube, little mercury is taken and a Cu wire is introduced to make the external electrical contact. The inner tube is enclosed in an outer jacket having an inlet tube for sending in H_2 gas and has a perforated wider base for the escape of excess of H_2. This unit is dipped in 1M HCl taken in a beaker such that the metal foil remains in the solution.
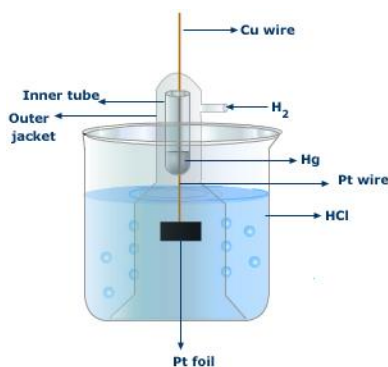
Working:
When pure and dry H_2 gas is passed through the inlet tube, a part of the gas gets adsorbed and the excess bubbles out through the perforations. Between the H_2 gas absorbed on the surface of the metal and H+ of the solution, an equilibrium is established and an electrical double layer of opposite charges is formed. The potential developed is called H_2 electrode potential. In the above system, when the H_2 gas at a pressure of 1atm is bubbled through 1M HCl, the electrode (constructed) or formed is called STANDARD HYDROGEN ELECTRODE (SHE) or Normal H_2 electrode (NHE).
Electrode/Half cell representation: Pt, ½ H_2 (760 mm of Hg or 1 atm) / H^+(IM)
The standard H_2 electrode potential is defined as the potential that is developed between the H_2 gas adsorbed on the pt metal and H^+ of the solution when the H_2 gas at a pressure of 760 mm of Hg is in equilibrium with H^+ of unit concentration
The magnitude of SHE **potential is considered to be zero**. It is used-
1) For the determination of electrode potential of metal electrode system.
2) For the determination of pH of the solution.
Limitations:1) It is rather difficult to regulate the pressure of the H_2 gas to be at exactly 1atm throughout the experiment.
2) Excess of H_2 bubbling out carries little HCl with it and hence the H^+ concentration decreases. In such a system, it is difficult to maintain the concentration of HCl at 1M.
3) Platinum foil gets easily poisoned by the impurities present in the gas and HCl. In fact, the attainment of equilibrium is ensured by trial and error.
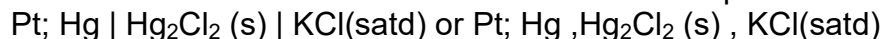4) If the solution contains any oxidizing agent, the H_2 electrode cannot be used.

13. Describe the construction and working of calomel electrode.Give its advantages.
Ans: Calomel Electrode (Mercury-Mercurous electrode)- Secondary Reference Electrode
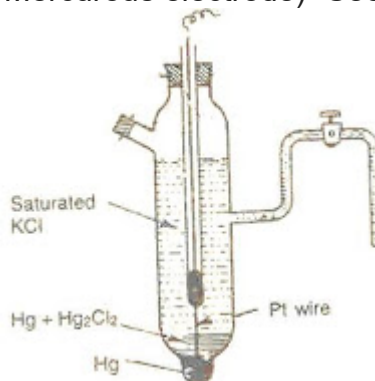
Standard Hydrogen electrode is a primary reference electrode, the usage is difficult as it has many disadvantages. Other electrodes with constant electrode potential are called as second-dary reference electrodes. Calomel electrode and Silver-Silver chloride electrodes are the examples for such reference electrodes.Calomel electrode cell is represented as
Pt; Hg | Hg_2Cl_2 (s) | KCl(satd) or Pt; Hg ,Hg_2Cl_2 (s) , KCl(satd)
Calomel electrode acts as an anode or cathode electrode depending on the nature of the other electrode. Electrode reaction/Half cell reaction as cathode: $Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + Cl^-$
Electrode reaction/Half cell reaction as anode: $2Hg + Cl^- \rightleftharpoons Hg_2Cl_2 + 2e^-$,
The expression of electrode potential is $E = E^o - 0.0591 \log[Cl^-]$, hence the electrode potential depends on the concetration of chloride ions in the solution

Concentration of KCl	Reduction Potential		
		1.0NKCl	0.2800 V
		0.1NKCl	0.3338 V
Saturated KCl	0.2415 V		

Advantages of calomel electrode: -secondary reference electrode:
1. It is very simple in construction. 2, The potential is stable and reproducible.3. The temperature coefficient is minimum.
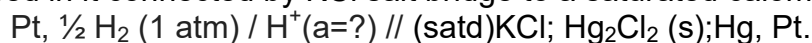
14. What are pH indicator electrodes? Give examples(2m).
Ans: The electrode potential of the electrodes are reversible with respect to concentration of hydrogen ions and depends on the concentration of hydrogen ions, such electrodes are called pH indicator electrodes. Ex: Hydrogen electrode, Quinhydrone electrode, Glass electrode.

15. Describe the determination of pH of a solution using a hydrogen electrode(4m).
Ans: **Theory**: The potential of a hydrogen electrode in contact with $[H^+]$ ions constitutes the equilibrium: $H^+ + e^- \leftrightarrows \frac{1}{2} H_2$, Whose potential expression from Nernst equation is
$E = E^° + 0.0591 \log[H^+]$; since $E^°$ of SHE is zero, then we can write $E = 0.0591 \log[H^+]$;
or $E = -0.0591$ pH; Hence it can be used as a pH indicating electrode.
Procedure: The following cell is constructed using unknown pH taken in a beaker, hydrogen electrode is immersed in it connected by KCl salt bridge to a saturated calomel electrode as
$$Pt, \frac{1}{2} H_2 \text{ (1 atm) } / H^+(a=?) // \text{ (satd)KCl; } Hg_2Cl_2 \text{ (s);Hg, Pt.}$$
EMF of the constructed cell is determined using a potentiometer
$E = E_r - E_l = E_{SCE} - E_{HE} = E^°_{cal} - (-0.0591 \text{ pH })$
rearranging, we get 0.0591 pH $= E_{cell} - E^°_{cal}$, $\therefore pH = \dfrac{E_{cell} - E^°_{cal}}{0.0591}$

$\boxed{pH = \dfrac{E_{cell} - E^°_{cal}}{0.0591 \quad 0.0591}}$

Note: If SHE is used as reference electrode instead of calomel electrode, then the expression
is: $pH = \dfrac{E_{cell}}{0.0591}$

16. What is quinhydrone electrode? Explain the principle involved in the use of the electrode as a pH indicating electrode.
Ans: The quinhydrone electrode is a type of <u>redox</u> <u>electrode</u> which can be used to measure the hydrogen ion concentration (<u>pH</u>) of a solution in a chemical experiment. The electrode consists of an inert metal electrode (usually a <u>platinum</u> wire) in contact with <u>quinhydrone</u> crystals and a water-based solution. Quinhydrone is slightly soluble in water, dissolving to form a mixture of two substances, quinone and hydroquinone, with the two substances present at equal concentration. Each one of the two substances can easily be oxidised or reduced to the other. The potential at the inert electrode depends on the ratio of the <u>activity</u> of two substances.
$$\text{Quinone} + 2H^+ + 2e^- \leftrightarrows \text{Hydroquinone}$$
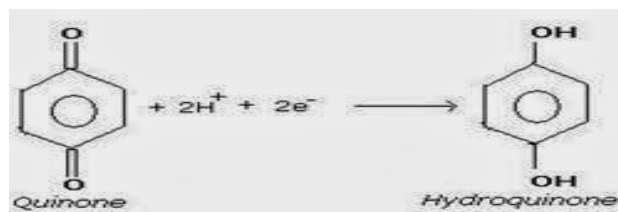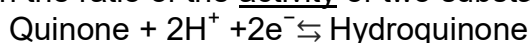
Because the electrode <u>half-reaction</u> involves hydrogen ions, the <u>electrode potential</u> depends on the activity of hydrogen ions. From the <u>Nernst equation</u>:
$$E = E^° + 2.303RT/2F \log \{[Q][H^+]^2/[QH_2]\}$$
At 298K, $2.303RT/F = 0.0591$, hence $E = E^° + 0.0591/2 \times 2 \log \{[Q][H^+]/[QH_2]\}$
  At equilibria, the concentrations of Q and QH_2 are in equal proportions, hence $[Q] = [QH_2]$
The above equation simplifies to $E_{Q,QH2} = E_{Q,QH2}^° + 0.0591 \log [H^+]$;

simplifying we get; $E_{Q,QH2} = E_{Q,QH2}^{o} - 0.0591$ pH, Hence the electrode potential depends on the hydrogen ion concentration of the solution, it can be used as a pH indicating electrode.

17. Give the limitations of quinhydrone electrode(2m).

Ans: 1. The quinhydrone electrode is not reliable above pH 8.
2. It is also unreliable in the presence of strong oxidising or reducing agents, which would disturb the equilibrium between hydroquinone and quinone.
3. It is also subject to errors in solutions containing proteins or high concentrations of salts.

18. Describe the determination of pH of a solution using a quinhydrone electrode (4m).

Ans: Theory: Quinhydrone electrode acts a pH indicator electrode based on the equation
$E_{Q,QH2} = E_{Q,QH2}^{o} - 0.0591$ pH, since $E_{Q,QH2}^{o} = 0.6996$, $E_{Q,QH2} = 0.6996 - 0.0591$ pH
Procedure: The solution whose pH is to be determined is taken in a beaker, a pinch quinhydrone powder is added to it, a bright platinum or carbon electrode is dipped in it and connected to a potentiometer using a saturated calomel electrode as a reference electrode.
The following cell is constructed: Pt; $Hg,HgCl_2$(satd) KCl // (a=?)H^+; Q,QH_2;Pt
EMF of the constructed cell is determined using a potentiometer.
EMF(E_{cell}) = $E_r - E_l$ = $E_{QH} - E^{o}_{Cal}$; Hence $E_{cell} = E_{Q,QH2}^{o} - 0.0591$ pH - E^{o}_{Cal}
$E_{Q,QH2}^{o} - E_{cell} - E^{o}_{Cal} = 0.0591$ pH; $\therefore$ pH $= \dfrac{E_{Q,QH2}^{o} - E_{cell} - E^{o}_{Cal}}{0.0591}$

Since $E_{Q,QH2}^{o} = 0.6996$ and $E^{o}_{Cal} = 0.2515$ if saturated calomel electrode is used
the pH $= \dfrac{0.6996 - E_{cell} - 0.2415}{0.0591}$; pH $= \dfrac{0.4581 - E_{cell}}{0.0591}$

pH $= \dfrac{0.6996 - E_{cell} - 0.2415}{0.0591}$

pH $= \dfrac{0.4581 - Ecell}{0.0591}$ Hence pH can be calculated.

19, Describe the construction, working and determination of pH of a solution using a glass electrode.(4m)
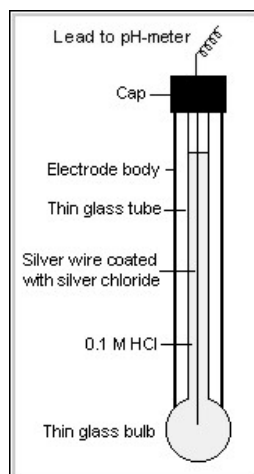
Ans: The glass electrode is constructed based on the experimental fact that, there exists a potential difference at the interface between glass and a solution containing hydrogen ions. glass electrode is made up of a special type of glass which is having relatively low melting point and high electrical conductivity. The glass tube is blown into a bulb at the one end and sealed at the bottom. A solution of 0.1M HCl solution, which gives a constant hydrogen ion concentration,

is placed inside the cell. A silver-silver chloride electrode or a platinum wire is inserted into the tube for electrical contact. The reference electrode used is calomel electrode. The cell may be represented as   **Pt,0.1M HCl/glass/experimental solution/KCl (salt sol),Hg$_2$Cl$_2$(s), Hg**
The emf of such a cell can be measured conveniently as the emf of calomel electrodeis known.

20. Give the merits and demerits of a glass electrode.(2m)
Ans: Merits: 1. It can be used in both oxidizing and reducing solutions. 2. It is immune to poisoning. 3. It is simple to operate 4. It can be used for the determination of pH values from 0-9 using ordinary electrodes, spcial glasses are used up to pH 12.
Limitations/demerits: 1. Gives good results in pH range 1-9. special lithium glasses are used for pH>9. 2. Special electronic tube potentiometers can only be used. otherwise asymmetric effect results.

21. What are concentration cells? Describe the determination of solubility of silver chloride is determined using concentration cells(4m)
Ans: Concentration cells are the electrochemical cells in the emf is generated due to the concentration difference between electrode or electrolyte by transference of material from one part to the other.
Determination of solubility of AgCl: 1.   Construction of the concentration cell: Ag/AgCl(s)(0.01N KCl) // (0.01N) AgNO$_3$, Ag. Two solutions are prepared they are 0.01N KCl and 0.01N Silver nitrate solution, taken separately in two different beakers. A silver wire is placed in each of the two beakers
2. To the solution of 0.01N KCl, few drops of AgNO$_3$ is added, a white ppt. of AgCl is formed. Ag electrode is dipped and coupled with Ag$^+$/Ag electrode, this is a concentration cell w.r.t Ag$^+$ ion, emf of the constructed cell is determined using a potentiometer

$$EMF = 0.0591 \log 0.01/ C_{Ag+}, \quad Ksp = [Ag^+][Cl^-] \; ;$$
$$Ksp = C_{Ag^+} \times 0.01, \quad \text{then the solubility is } s = \sqrt{Ksp}$$

22. Give the principle of potentiometric titrations.(2m)
Ans: Potentiometric titration is a volumetric method in which the potential between two electrodes is measured (referent and indicator electrode) as a function of the added reagent volume. The part of the curve that has the maximum change marks the equivalence point of the titration.

23, What are the advantages of potentiometric titrations? (2m)
Ans: 1. The process also measures oxidation or corrosion against the amount of titrant added, making it suitable for measuring acid concentration.
2. The process uses a minimal amount of substance, making it an inexpensive method.
3. The automotive, pharmaceutical, food, beverage and environmental companies are examples of industries using the process.
4. No indicators are required for the process of titration
5. It can be used for weak acid and weak base titrations.
6. Gives accurate results even in coloured solution.
7. pH of solutions can be determined.

24. What are red-ox electrodes? Give examples, and emf of such electrodes.(2m)
Ans: Red ox electrodes are the inert electrodes like Pt or carbon dipped in the solution containing both oxidized and reduced state of a system. Ex. Pt; dipped in a solution ofa red ox system containing both oxidizing and reducing components. Pt dipped in a solution containing ferrous and ferric system. EMF of such cells = $E_r - E_l$ =$E^o_{red} + E^o_{ox}$.
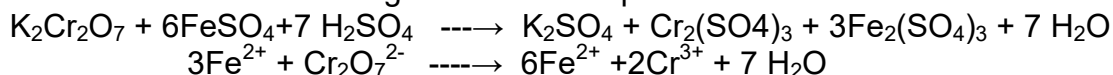
25. Write a note on potentiometric titrations applicable to redox systems(4m)

Ans: Potentiometric titrations can be used to perform titrations involving red-ox systems like potassium dichromate vs. ferrous ammonium sulphate systems in acidic medium. Both end point as well as formal red-ox potentials can be determined by titration method.

Illustration of potentiometric titration of ferrous ammonium sulphate vs potassium dichromate.

Aim: To determine the strength of ferrous ion present in one litre of the given ferrous ammonium sulphate solution potentiometrically .

Principle:Potentiometric titration depends on measurement of emf between reference electrode and an indicator electrode . When ferrous sulphate solution is titrated against standard potassium dichromate the following reaction taken place.

$$K_2Cr_2O_7 + 6FeSO_4 + 7\ H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO4)_3 + 3Fe_2(SO_4)_3 + 7\ H_2O$$
$$3Fe^{2+} + Cr_2O_7^{2-} \longrightarrow 6Fe^{2+} + 2Cr^{3+} + 7\ H_2O$$

During this titration ,Fe^{2+} is converted into Fe^{3+} (oxidation) whose concentration increases as well as $K_2Cr_2O_7$ is reduced to $Cr_2(SO4)_3$ (Chromic sulphate) . At the end point , there will be a sharp change due to removal of all Fe^{3+} ions

Procedure: There are two steps involved in the titration,

1. Titration: I - Preliminary titration: A known strength of potassium dichromate solution is filled in a cleaned and rinsed burette.10 ml of the estimated ferrous ammonium sulphate solution is pipetted out into a clean 100ml beaker. Then10ml of dil. H_2SO_4 is added to the beaker solution. The electrodes-(Platinum electrode and Calomal electrode)are placed into the beaker and two terminals are connected with potentiometer. Initially the emf increases gradually by the addition of $K_2Cr_2O_7$ solution. When all the Fe^{2+}ions are converted to Fe^{3+} ions, there is sudden jump occurs (sharp increases) in the emf value. This titration is called as preliminary titration. This is used to find the end point .finally graph is drawn between volume of $K_2Cr_2O_7$ Vs Emf.(Graph-1).
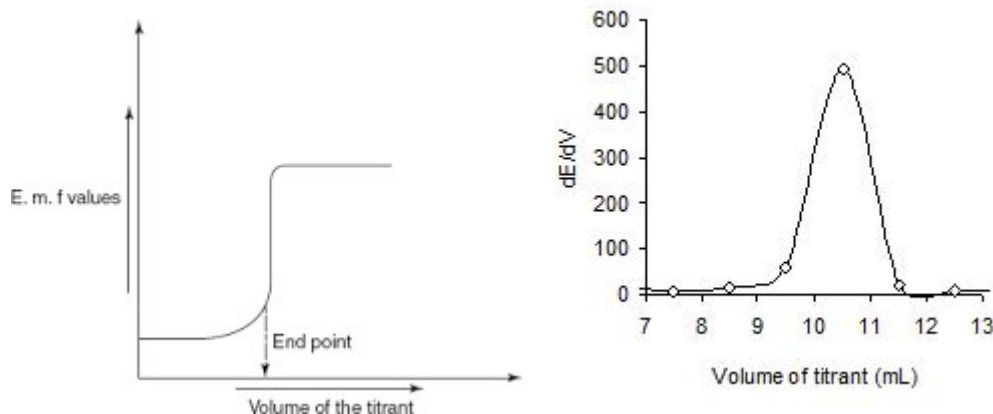
2. Titration: II – Final titration: The burette is again filled with Std. $K_2Cr_2O_7$upto zero level.
Again 10ml of ferrous ammonium sulphate is pipetted out in to a 100ml beaker, Then10ml of dil. H_2SO_4 is added to the beaker solution. The electrodes-(Platinum electrode and Calomal electrode)are placed into the beaker and two terminals are connected with potentiometer.
The two terminals of the electrode are connected with potentiometer. Now titration is carried out by adding 0.1 ml of Std. $K_2Cr_2O_7$ to the Fe^{2+} ion taken in the beaker, just before the 2ml from end point and emf of the solution is noted after the each addition. At the equivalence point there is a sharp increase in the emf value is noted. After this end point 5 to 6 more readings are taken , Thus, the accurate end point is noted. Thus the strength of Fe^{2+} ion can be calculated.

I: Preliminary titration   **II: Final(neat)-titration**

S.NO	Volume of $K_2Cr_2O_7$ (ml)	Emf (Volts)	Sl. NO	Volume of $K_2Cr_2O_7$ (ml)	Emf (Volts)	ΔE/ΔV

The following graphs are plotted to get the end point of the titration

Calculation: Normality(strength) of ferrous ion = N_1 = $\dfrac{V_2 \times N_2}{V_1}$ = $\dfrac{V_2 \times 0.1}{10}$ = ...N

Where V_2 – volume of pot.dichromate run down from the burette, V_1= Volume of FAS = 10ml

N_2 = Normality of pot.dichromate solution = 0.1N

Hence Amount of ferrous iron solution present in 1litre of the given Solution = N_1 x 55.85 = ------gms

26. (a) Write a short note on potentiometric titrations.(2)

Ans. In a potentiometric titration the end point is determined by plotting a graph of emf versus the volume the titrant solution added. It is observed that the change in emf till the end point is small and at the end point a sudden jump is observed. For the measurement of emf an electrochemical cell is set up by combining an indicator electrode which is sensitive to the changing concentration of an ion in the solution with a reference electrode. In a red-ox titration of ferrous ammonium sulphate versus potassium dichromate the indicator electrode used is platinum electrode and the reference electrode is calomel electrode. Platinum electrode is sensitive to the change in red-ox potential of ferrous-ferric system.

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3.Ionic Equilibria3Hours -*8marks*

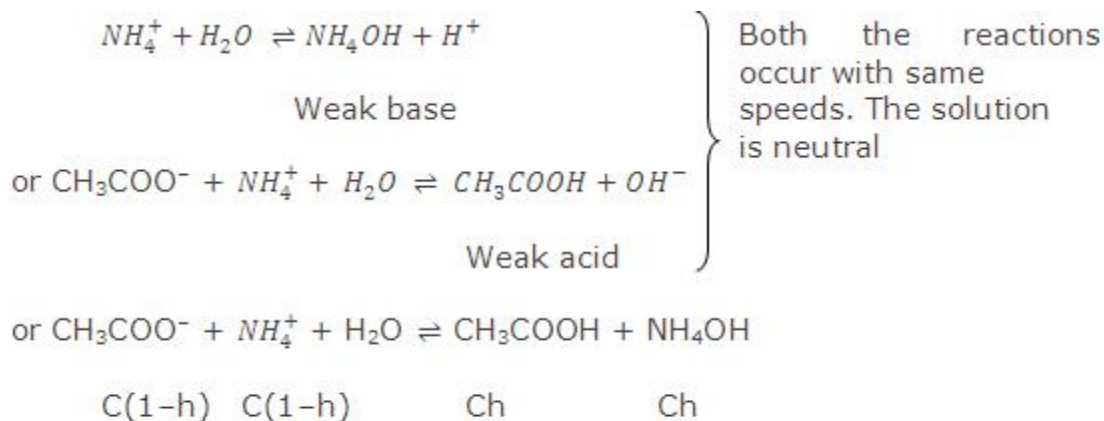1. **Define i) Hydrolysis ii) Degree of hydrolysis of salts iii) Ionic product of water**

Ans: i) Hydrolysis: The process of interaction of ions of the salt with oppositely charged ions of water that is H^+ and OH^- ions to give acidic or basic solution is called hydrolysis.

ii) **Degree of hydrolysis:** The extent to which **hydrolysis** proceeds are expressed as the degree of **hydrolysis**and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as *h* or *x*.

iii) **Ionic product of water:** The product of molar concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. It is found to be constant, its value is 10^{-14} at 298K. It is expressed as K_w.

2. **Derive a relation between hydrolysis constant(K_h), ionic product of water K_w and dissociation constants of acid and bases in the hydrolysis of the salt formed from weak acid vs. weak base($K_a$and K_b), and an expression for the degree of hydrolysis.**

Ans:Salt of a Weak Acid and a Weak Base: Maximum hydrolysis occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H^+ and OH^- ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt CH_3COONH_4. It gives CH_3COO^- and ions in solution. Both react with water.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Weak base

Both the reactions occur with same speeds. The solution is neutral

$$or\ CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Weak acid

$$or\ CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$C(1-h) \quad C(1-h) \qquad Ch \qquad\qquad Ch$$

$$Kh = \frac{[VH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

Other equilibria which exist in solution are for weak acid: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$,

$K_a = [CH_3COO^-][H^+]/[CH_3COOH]$ ..... (i)

Similarly for weak base: $NH_4OH \rightleftharpoons NH^{+4} + OH^-$,

$$K_b = [NH_4^+] [OH^-]/[NH_4OH] \qquad\qquad ..... (ii)$$

For the dissociation of water: $H_2O \rightleftharpoons H^+ + OH^-$, ionic product of water: $K_w = [H^+][OH^-]$ ......(iii)

From Eqs. (i), (ii) and (iii), $K_h = K_w/K_a.K_b = [CH_3COOH][NH_4OH]/[CH_3COO^-][NH^{+4}]$ ...... (iv)

Let C be the concentration and h be the degree of hydrolysis $K_h = h^2/(1-h)^2$, When h is small,

$$(1-h) \rightarrow 1., \text{ hence } K_h = h^2; \quad h = \sqrt{Kh} = \sqrt{K_w/K_a K_b}; \quad [H+] K_a \times h$$

$$h = K_a \times \sqrt{K_w/K_a{}^*K_b} = \sqrt{K_w} \times K_a/K_b$$

3. Derive the relation: pH = 7 + 1/2 pK$_a$ + 1/2 pK$_b$ in the case of salt hydrolysis of weak acid and weak base.(4)

Ans: We know that h = $\sqrt{Kh}$ = $\sqrt{K_w/K_a K_b}$; we know that: $K_a = [H^+][CH_3COO^-] / [CH_3COOH]$

hence; $[H^+] = K_a x [CH_3COOH]/ CH_3COO^-$, Since $[CH_3COOH]/ CH_3COO^- = \sqrt{K_h}$

∴ $[H^+] = K_a x \sqrt{K_h}$, substituting we get, $[H^+] = K_a \times \sqrt{K_w/K_a K_b}$; or $[H^+] = \sqrt{K_w/K_a K_b} \times K_a{}^2$

$$\therefore [H^+] = \sqrt{K_w K_a / K_b}; \text{ taking log on both sides we get}$$

$$-\log [H+] = -\tfrac{1}{2} \log K_a - \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log K_b$$

$$pH = \tfrac{1}{2} pK_a + \tfrac{1}{2} pK_w - \tfrac{1}{2} pK_b$$

$$= 7 + \tfrac{1}{2} pK_a - \tfrac{1}{2} pK_b$$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}logC$$

When pK$_a$ = pK$_b$, pH = 7, i.e., solution will be neutral in nature.
When pK$_a$ >pK$_b$. The solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7.In case pK$_a$ <pK$_b$, the solution will be acidic as the acid is relatively stronger than base andpH will be less than 7.

4. Account for the following: i) Aqueous solution of sodium chloride is neutral to litmus. ii) Aqueous solution of sodium acetate is basic to litmus.(2m)

Ans: i) **NaCl i**s a salt of strong acid and strong base. It does not undergo hydrolysis in water. Hence there is not change in concentration of hydrogen and hydroxyl ions and the solution remains neutral.

ii) **Sodium acetate** on hydrolysis in water produces weak acid acetic acid and strong base sodium hydroxide. The formation of strong base increases OH$^-$ ions due to ionization, hence it is basic to litmus.

5. What is the effect of dilution and temperature on the degree of hydrolysis the salt formed from weak acid and weak base? oron the hydrolysis of ammonium acetate(2m)

Ans: Dilution has no effect on the degree of hydrolysis of the salt. Where as increase in temp-erature increases the degree of hydrolysis.

6. State and explain common ion effect with an example.(2m)

Ans: The phenomenon of suppression of the degree of dissociation of a weak acid or a weak base by the addition of a strong electrolyte containing a common ion is known as common ion effect. For example: let us consider the ionization of a weak base ammonium hydroxide i.e. NH_4OH as: NH_4OH (aq) ⇌ NH_4^+ (aq) + OH^- (aq)The ionization constant for the base will be:$K_b = [NH_4+] [OH^-] / [NH_4OH]$. If solid NH_4Cl is added to the solution, the concentration of NH_4^+ ions increases. According to Le-Chatelier's principle, the equilibrium shifts to the left. As a result, the concentration of OH^- is considerably decreased and the weak base NH_4OH becomes even weaker in the presence of its salt. NH_4OH ⇌ $NH_4^+ + OH^-$ (Equilibrium shifts to left side) $NH_4Cl \rightarrow NH_4^+ + Cl^-$; This phenomenon is known as common ion effect.

7. Define solubility product and ionic product or Give the differences between solubility product and ionic product(3m)

Ans: The main differences between solubility product and ionic product are given below:

Solubility product	Ionic product
1. Solubility product is the concentration of ions of electrolyte, each raised to the power of their coefficients in the balanced chemical equation in a saturated solution.	1. It is the product of concentration of ions of the electrolyte, each raised to the power of their coefficients in the balanced chemical equation in solution at any concentration.
2. Applicable only to saturated solutions.	2. Applicable to all types of solutions of any concentration.
3. At constant temperature, its value is constant for a given electrolyte.	3 The value keeps changing with concentration.

8. Based on the magnitudes of K_{sp} and Ionic product values of a salt solution, how the prediction of saturated, supersaturated and undersaturated solution can be made?(2)

Ans: On mixing the two solutions of different concentrations if,

i) K_{sp}> Ionic product, the solution is undersaturated, it will be a clear solution.

ii) K_{sp}< Ionic product, the solution is super saturated, there will be a precipitation.

iii) K_{sp} = Ionic product, the solution is saturated, there will no precipitation.

9. Why is ammonium chloride added in excess prior to ammonium hydroxide during the detection of third group basic radicals in the inorganic qualitative analysis?(2)

Ans. Due to common ion effect caused by excess ammonium ion the dissociation of ammonium hydroxide is suppressed or the concentration of hydroxyl ion is decreased. This helps in the precipitation of only those hydroxides with lesser K_{sp} values (Al^{3+}, Cr^{3+}, etc.) and prevent the precipitation of those with higher K_{sp}values (Zn^{2+}, Mn^{2+}, etc.).

10. Account for the following: i) Silver and lead are precipited by hydrogen sulphide gas in acid medium where as Zinc and manganese is precipitated in basic medium with the same hydrogen sulphide gas. ii) Ammonium chloride and ammonium hydroxide are added before passing hydrogen sulphide to the salt solutions of IV group basic radicals.(4m)

Ans: i) H_2S is a weak acid that ionizes partially as follows $H_2S \rightleftharpoons 2H^+ + S^{2-}$, to exceed the ionic products of II group basic radicals sulphides like Silver and lead sulphides S^{2-} concentrations are to be decreased, in order to facilitate it, common ion is created by adding dil.HCl, which favours their precipitation. In that condition IV group metallic sulphides ionic products are less so that they are not precipitated.

ii) Ammonium chloride and ammonium hydroxide are added before passing hydrogen sulphide to the salt solutions of IV group basic radicals because common ion effect is created by the addition of ammonium chloride to ammonium hydroxide to decrease the concentration of OH^-ions so that it shifts the equilibrium of hydrogen sulphide towards RHS,to release sufficient concentration of sulphide ions to exceed the solubility products of IV group metallic sulphides and precipitation occurs.

11. What are buffer solutions? Give an example each for an acidic, basic and a neutral buffers.(4m)

Ans: A solution whose pH remains unaltered by the addition of small quantities of a strong acid or strong base. It usually consists of a weak acid and its salt with a strong base, a weak base and its salt with a strong acid, conjugate acid base mixture.

Buffers are of three types: **a) Acidic buffer**(pH<7): Ex: i) CH_3COOH +CH_3COONa,
ii) HCN + NaCN, iii) HCOOH + HCOOK **b) Basic buffer**(pH >7) Ex: i) NH_4OH + NH_4Cl
ii) $Mg(OH)_2$ + Mg Cl_2 iii) NH_4OH + NH_4NO_3. **c) Neutral buffer**(pH = 7) Ex: i)Ammoninium acetate, ii) Ammonium citrate

12. What is meant by Buffer action? Explain the buffer action of an acidic buffer.

Ans: The ability of the buffer solution to resist the changes in pH value on the addition of small amount of an acid or a base is known as buffer action.

For example: Consider an acidic buffer such as a solution containing an equimolar amounts of acetic acid and sodium acetate, the solution contains a large number of sodium ions (Na+), acetate ions (CH_3COO^-) and also a large number of un-dissociated acetic acid molecules.

$$CH_3COONa \text{ (aq)} \rightarrow CH_3COO^- \text{ (aq)} + Na^+ \text{ (aq)}$$

Suppose, a few drops of HCl are added to this buffer solution. This would provide hydrogen (H^+) ions. These additional H^+ ions would combine with the large reserve of CH_3COO^- ions to form undissociated acetic acid molecules. $CH_3COO^- \text{ (aq)} + H^+ \text{ (aq)} \rightleftharpoons CH_3COOH$

The additional H^+ ions are neutralized by CH_3COO^- ions in the solution, hence there will be no change in its pH value. The reserve basicity of the solution is due to acetate ions.
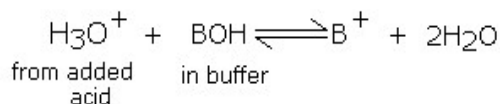
A few drops of strong base NaOH is added added to this buffer solution, the added OH^- ion
OH^- + $CH_3COOH \rightarrow CH_3COO^-$ + H_2O

reacts with the weak acid acetic acid forming sodium acetate and water. Formation of acetate ions(sodium acetate) suppresses the ionization of the weak acid-(common ion effect), hence pH is not altered.
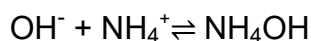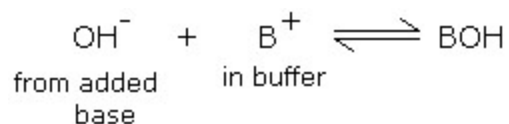
13. Explain the buffer action of a basic buffer- NH_4OH + NH_4Cl .

Ans: **Action of basic buffer :** A basic buffer contains a weak base (BOH - NH_4OH), and its salt with strong acid (BX - NH_4Cl). The buffer solution thus contains large amounts of the weak base BOH - NH_4OH, and the cation B^+- NH_4^+ (coming from the dissociation of the salt BX - NH_4Cl), in addition to H_3O^+ and OH^-.

The addition of an acid or a base to the basic buffer causes the following reactions:

$$\underset{\substack{\text{from added} \\ \text{acid}}}{H_3O^+} + \underset{\text{in buffer}}{BOH} \rightleftharpoons B^+ + 2H_2O$$

$$H_3O^+ + NH_4OH \rightleftharpoons NH_4^+ + 2H_2O$$

Hence addition of an acid forms the salt and water, presence of common ion suppresses the dissociation of the weak acid ammonium hydroxide, hence pH remains constant.

$$\underset{\substack{\text{from added} \\ \text{base}}}{OH^-} + \underset{\text{in buffer}}{B^+} \rightleftharpoons BOH$$

$$OH^- + NH_4^+ \rightleftharpoons NH_4OH$$

proceeds in the forward direction. It is clear that the addition of an acid or a base to any buffer solution does cause a change in the concentrations of the buffer acid (or base) and the salt. The weak base dissociation is less, pH remains constant.

14. Derive Henderson's equation for an acidic buffer(4m)

Ans: Consider an acidic buffer solution, containg a weak acid HA and its salt of a strong base MA.The weak acid dissociates partially as   HA $\leftrightarrows$ $H^+ + A^-$;

and the salt dissociates completely as MA $\rightarrow$ $M^+ + A^-$

The dissociation constant of the weak acid is given by Ka $= \dfrac{[H+][A-]}{[HA]}$ ----(1)

$$\text{Rearranging, } [H^+] = \dfrac{[HA]}{[A-]} \text{Ka} = \dfrac{[acid]}{[salt]} \text{Ka} -----(2)$$
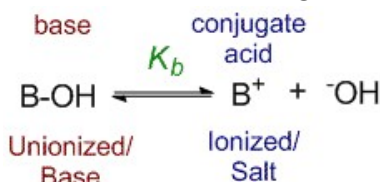
Taking log on both sides and multiplying by -1, we get,

$$-\log[H^+] = -\log\text{Ka} + \left\{ -\log \dfrac{[acid]}{[salt]} \right\} \text{ OR}$$

$$\text{pH} = \text{pKa} + \log \dfrac{[salt]}{[acid]}$$

This equation is called Henderson equation for an acidic buffer.

15. Derive Henderson's equation for an basic buffer(4m)

Ans: Consider a basic buffer consists of a weak base BOH and its salt B^+

According to the law of dissociation, the base dissociation constant K_b can be defined by the equation:K_b = $[OH^-][B^+]$ / [BOH]where $[B^+]$ and $[OH^-]$ are the concentrations of the ionized form of the base, while [BOH] is the concentration of the unionized form.

Taking log on both sides you get: log K_b = log ($[OH^-][B^+]$ / [BOH])

Splitting the log terms into separate components gives you:

log K_b = log $[OH^-]$ + log ($[B^+]$ / [BOH])

Since pK_b = $-\log_{10} K_b$ and pOH = $-\log_{10} [OH^-]$, therefore:

$$-pK_b = - pOH + \log ([B^+]/[BOH])$$

Rearranging the terms we get the Henderson-Hasselbalch equation for bases:

pOH = pK_b + log ($[B+]$/[BOH])

This equation can also be written as: pOH = pK_b + log [(salt)/(base)]

16. Write a note on Analytical and biological applications of buffers(4m)

Ans:Importance of Buffers: Chemistry plays an important role in our surrounding environment, daily lives and biological systems. So buffers being an integral part of inorganic chemistry also prove the importance of applied chemistry in environment and other sectors.

1. Importance of Buffers in Biological Systems: a) Processes that take place in living organisms are called physiological processes. Like blood circulatory system, respiration etc. The internal pH of most living cells is close to 7.0. The pH of human blood is 7.4. A blood pH of below 7 or above 7.8 can cause death within minutes. So buffering of blood pH is very

important to stabilize it around 7.4. pH plays an important role in almost all biological processes. Small change in pH i.e. deceased or high pH can cause metabolic implications in human body like acidosis and alkalosis. Where metabolism is involved there would be definitely a need of buffer as within cells metabolism is associated with the release of protons (H^+) i.e. decrease in pH or uptake of protons (H^+) i.e. increase in pH. Important buffers that are dominant in human body are   Bicarbonate buffers, Phosphate buffers and Protein buffers

2. Proportion of carbonic acid and hydrogen carbonate is also very much important in blood. Carbonic acid concentration is controlled by respiration through lungs while hydrogen carbonate concentration is controlled by urination through kidneys.

3) Phosphate buffer (Buffering of internal cell fluids)

The phosphate buffer system works in the internal fluid of all cells. This buffer system consists of dihydrogen phosphate ions ($H_2PO_4^-$) as a weak acid and hydrogen phosphate ions (HPO_4^{2-}) as a conjugate base of weak acid. In the absence of phosphate buffer from cell fluid, sharp changes in pH of cell fluids may cause cell death or improper working of different proteins and cell organelles present within the cell.

4. Protein buffer in Buffering in Cells and Tissues): As all cells and tissues are composed of proteins mainly so in the absence of protein buffer the sharp changes in pH may cause cell death or tissue damage of a living organisms.

Importance of buffers in industries: Buffers are of prime importance in different kind of industrial processes especially in pharmaceuticals, fermentation/food and textile dyeing industries. It also finds its role in many other industries as described below.

1. Pharmaceuticals Industries:
i)Maintain some drug or medicine in ionized form as ionized forms are more soluble in aqueous solutions. ii) Maintain some drug or medicine in un-ionized form as un-ionized forms are more soluble in lipids

2. Fermentation and food industry:
Each fermentation process requires a specific pH for the best results. The pH during a fermentation process changes by itself due to fermentation process so to control this pH change buffers play an important role. Buffers are also used in foods to maintain the acidity of the food in order to preserve the flavor and appearance of food.

3. Miscellaneous industries:
Buffers of different types are majorly used in above explained three types of industries. However, buffers also play an important role in:

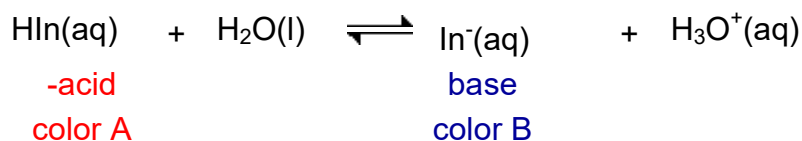i)Printing industries as pH of paper and inks must be controlled to assure proper penetration and drying of the ink.

ii)Electroplating industries as some alloys can be plated if very strict pH control is maintained.

iii)Leather industries as narrow range of pH control of tanning and dyeing baths determine the texture and color of the finished product.

 iv)Glue and gelatin manufacturing industries as properties of gelatin and glue vary rapidly with a very slight change in pH during manufacture.

17. What are Indicators. Explain acid base theory of indicators with phenolphthalein as example.

Ans: Indicators are the substances indicates the completion of the reaction by means of a sharp colour change at the end point of the titration.Acid - base indicators (also known as pH indicators) are substances which change color with pH.They are usually weak acids or bases.Consider an indicator which is a weak acid, with the formula HIn. At equilibrium, the following chemical equation is established.

$$\text{HIn(aq)} \quad + \quad \text{H}_2\text{O(l)} \quad \rightleftharpoons \quad \text{In}^-\text{(aq)} \quad + \quad \text{H}_3\text{O}^+\text{(aq)}$$

-acid   base

color A   color B

The acid and its conjugate base have different colors. At low pH, the concentration of H_3O^+ is high and so the equilibrium position lies to the left. The equilibrium solution has the color A. At high pH, the concentration of H_3O^+ is low and so the equilibrium position thus lies to the right and the equilibrium solution has color B.

Ex: Phenolphthalein is an example of an indicator which establishes this type of equilibrium in

aqueous solution. $\text{HPh} \rightleftharpoons \quad H^+ \quad + \qquad \text{Ph}^-$

Colourless(acid medium)   Pink(basic medium)
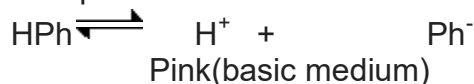
 Phenolphthalein is a colorless, weak acid which dissociates in water forming magenta anions. Under acidic conditions, the equilibrium is to the left,and the concentration of the anions is too low for the magenta color to be observed. However, under alkaline conditions, the equilibrium is to the right, and the concentration of the anion becomes sufficient for the magenta color to be observed.

(OPTIONAL)

colorless (acid)   magenta (base)

****
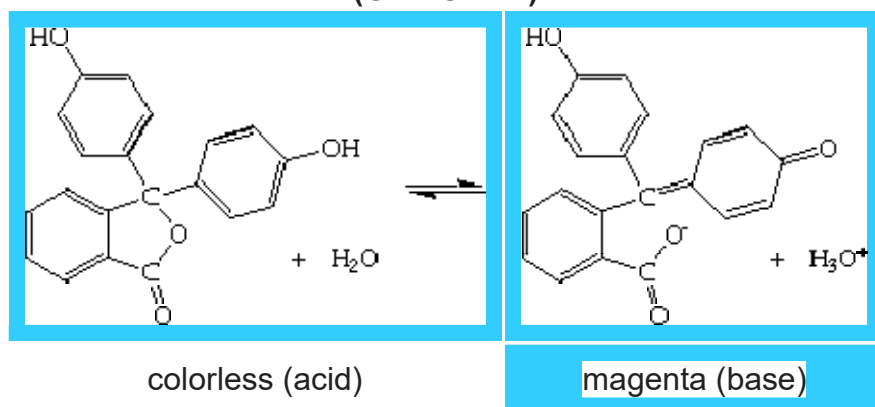
4. Physical Properties and Molecular Structure 5 Hours --- *12 marks*

1. Define polarization.
Ans: The Phenomenon of distortion of electrostatic field of a molecule causing the changes in equilibrium positions of the nuclei, separating the centres of positive and negative charges is called polarization of the molecule. Then the positively charged nuclei is attracted towards negative plate and vice versa.

2. What are polar and non-polar molecules? Give two examples for each.
Ans: The polarity exists in heteronuclear molecules, where the shared electron pairs are displaced towards the electronegative atom, as a result a slight positive charge($\delta+$) and a slight negative charge($\delta-$) is acquired and the molecule is known as polar or dipole.
Ex; HCl, HCN
No polarity exists in homo nuclear molecules where the shared electron pair lies exactly at the centre of the two atoms are called non polar molecules. Ex: H_2, Cl_2

3. Define dipole moment.
Ans: The dipole moment of a polar molecule is defined as the product of the charge on each end of the molecule and the average distance between the centers of their nuclei. $\mu = q \times d$.

4. The dipole moment of HF, HCl, HBr and HI are 2,1.3, 0.8 and 0.4 Debye. Arrange them in the increasing order of polar character.
Ans: HF >HCl>HBr> HI - Increasing order of polar character.

5. p-dichlorobenzene has a zero dipole moment where p-dihydroxy benzene has a net dipole moment of 1.64D. Give reason.
Ans: In p-dichlorobenzene, the two chlorine atoms are present in para or opposite positions, the net dipole moment is zero as the bond moments gets cancels each other. where as the dipole moment of 1,4-dihydroxybenzene is not zero because <u>resonance</u> locks the C-OH groups in the plane of the ring.

6. Chloroform has a permanent dipole moment while carbon tetrachloride does not have. Explain
Ans: In chloroform molecule definite polarity exists between C-H and C-Cl, hence it has permanent dipole moment. In the case of carbon tetrachloride molecule, the different bond moments of C-Cl cancels out each other, hence the net dipole moment is zero.

7. Explain why CO_2 has a zero dipole moment and SO_2 has a positive dipole-moment(2)
Ans: CO_2 is a linear molecule, so the dipoles are symmetrical; the dipoles are equal in magnitude but point in opposite directions. Generally, when dipole distribution is symmetrical, there is no dipole moment.
The SO_2 molecule has a bent shape like H_2O with C2v symmetry. It has a net dipole moment, which is the resultant vector of the two S-O moments. Therefore, it is polar.

8. Write the structure of dichloroethene which has zero dipole moment.
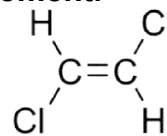
Ans: Trans dichloroethene which has zero dipole moment: Structure:

9. Maleic acid possesses a permanent dipole moment but not fumaric acid. Explain.
Ans**:** Fumaric acid(trans form) has a symmetry about it. the acids on either side of the alkene pull with equal and opposite force, thus eliminating the dipole moment of the molecule. Fumaric acid's isomer, maleic acid, does have a dipole as the acids are on the same side of the double bond, creating a net electric pull upwards on the molecule.

10. Write a note on applications of dipole moment.
Ans: 1. Used to predict the shapes of molecules   2. Differentiates between cis and trans isomers,   3) Differentiates o, p and m isomers   4) Supports the possibility of resonating structures.

11. What is meant by induced dipolemoment?
Ans: The phenomenon involved in the introduction of dipole moment for a non polar molecule due to the application of electric field is called induced dipole moment, the molecule gets polarized only under the applied electric field.

12. Write Clausius-Mosotti equation and indicate the terms involved
Ans: $P_m = (\epsilon_r-1/ \epsilon_r+2) \times V_m = 4\pi/3 \, N_A \, \alpha_d$ OR $P_m = (\epsilon_r-1/ \epsilon_r+2) \times V_m = [N_A /3\epsilon_0] \, \alpha_d$
        ϵ_r = Dielectric constant/relative permittivity of medium, V_m= molar volume
   N_A=Avagadro's Number.α_d= distortion polarizability, P_m= molar polarization,
    ϵ_0=Permittivity of the free space.

13. Explain the term Magnetic susceptibility.
Ans**:** The intensity of magnetization produced per unit strength of the applied magnetic field is called specific magnetic susceptibility. The product of magnetic susceptibility and molar volume of the material is called the magnetic susceptibility of the substance.

**14.What is paramagnetism? What are the factors contributing to paramagnetism in a
   substance?**
Ans: The phenomenon exhibited by certain substances which are weakly attracted towards magnetic lines of force, which lises their magnetism in the absence of magnetic field is called paramagnetism.   The paramagnetism is affected by the following factors: i) Number of unpaired electrons ii) Temperature iii) magnetic susceptibility iv) magnetic permeability

15. What are paramagnetic and diamagnetic substances? Give two example each.
Ans: The substances when placed in a magnetic field, the lines of force deflect towards the substance,they are weakly attracted by magnetic lines of force , its magnetic susceptibility is positive and its magnetic permeability is greater than one are called paramagnetic substances.
Ex: Al, Pt, Mg, Mo, Li
The substances when placed in a magnetic field, the lines of force deflect away from the substance , its magnetic susceptibility is negative and its magnetic permeability is less than one are called diamagnetic substances. Ex: Cu,Sb,Bi, Au Graphite.

16. What are ferro magnetic substances? Mention their characteristics.
Ans: Substances which are attracted by the magnets and can be magnetized are called ferro-magnetic substances: Ex: Fe,Co, Ni

Characteristics: i) Shows all the properties of paramagnetic substances to a much a greater degree ii) The susceptibility decreases as the temperature increases.iii) Magnetic suscepti-bility is very high.

17. Give the characteristics of paramagnetic and diamagnetic substances.

Sl.No.	Paramagnetic(Al, Mn,Pt, O_2)	Diamagnetic(Cu, Bi, Sb H_2)
1.	Attracted by magnets when placed in a magnetic field	Repelled by magnets when placed in a magnetic field
2.	They move from weaker to stronger parts of the field	They move from stronger to weaker to parts of the field
3.	The lines of force tend to close towards a material.	The lines of force move away from a material
4.	Susceptibility of this material is positive and it is inversely proportional to the temperature	Susceptibility of this material has small value do not depend on temperature

18. What are ferro magnetic substances? Mention their characteristics.
Ans: Substances which are attracted by the magnets and can be magnetized are called ferro-magnetic substances: Ex: Fe,Co, Ni
Characteristics: i) Shows all the properties of paramagnetic substances to a much a greater degree ii) The susceptibility decreases as the temperature increases.iii) Magnetic suscepti-bility is very high.

19. What is peltier effect?
Ans: The Peltier effect is a temperature difference created by applying a voltage between two electrodes connected to a sample of semiconductor material. This phenomenon can be useful when it is necessary to transfer heat from one medium to another on a small scale. The Peltier effect is one of three types of thermoelectric effect.

20. Explain Seebeck effect and Thomson effect with examples?(4m)
Ans: The Seebeck effect is a phenomenon in which a temperature difference between two dissimilar electrical conductors or semiconductors produces a voltage difference between the two substances.The Seebeck effect is responsible for the behavior of thermocouples, which are used to approximately measure temperature differences or to actuate electronic switches that can turn large systems on and off. This capability is employed in thermoelectric coolingtechnology. Commonly used thermocouple metal combinations include constantan/copper, constantan/iron, constantan/chromel and constantan/alumel.
The evolution or absorption of heat when electric current passes through a circuit composed of a single material that has a temperature difference along its length is called Thomson effect. This transfer of heat is superimposed on the common production of heat associated with the electrical resistance to currents in conductors. If a copper wire carrying a steady electric current is subjected to external heating at a short section while the rest remains cooler, heat is absorbed from the copper as the conventional current approaches the hot point, and heat is transferred to the copper just beyond the hot point.

21. What are semi conductors? Give examples(4)
Ans: semiconductor is a material that is neither a good conductor of electricity nor a good insulator, but has properties of electrical conductivity somewhere between the two.
Silicon and germanium are good semiconductor materials.

22. Explain the following with examples: i) Piezo electricity, ii) Inverse Piezo electricity

Ans: **Piezoelectric Effect** is the ability of certain materials to generate an electric charge in response to applied mechanical stress. The word Piezoelectric is derived from the Greek piezein, which means to squeeze or press, and piezo, which is Greek for "push".

For example, lead zirconatetitanate crystals will generate measurable piezoelectricity when their static structure is deformed by about 0.1% of the original dimension. The directpiezoelectric effect allows piezoelectric materials to be used for acoustic sensing, for example, in microphones, hydrophones, and even pick-ups for acoustic-electric guitar

The **inverse piezoelectriceffect** refers to a deformation of these materials that results from the application of an electric field. The deformation could lead to either tensile or compressive strains and stresses in the material depending upon the direction of the electric field, the preferred direction of polarization in the material, and how the material is connected to other adjacent structures.An example of the use of the inverse effect is found in buzzers. Piezoelectric actuators, which can be used for micro-positioning, also rely on the inverse piezoelectric effect.

23. Write a note on: i) Ferroelectricity and ii) Pyroelectricity

Ans: **Ferroelectricity** is a property of certain materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ex: Rochelle salt $BaTiO_3$ $PbTiO_3$, Lead ZirconateTitanate.

Applications: Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines.

Pyroelectricity is the property of certain cystals which are naturally electrically polarized and as a result contain large electric fields. Itis the ability of certain materials to generate a temporary voltage when they are heated or cooled. The change in temperature modifies the positions of the atoms slightly within the crystal structure, such that the polarization of the material changes. This polarization change gives rise to a voltage across the crystal.

Ex: Gallium nitride semiconductor.

Applications: The large electric fields in this material are unwanted for light emitting diodes (LEDs), but are very helpful for the fabrication of power transistors. A pyroelectric material can be repeatedly heated and cooled to generate usable electrical power.\

24. What is the effect of temperature on the paramagnetic property of a substance?

Ans: Paramagneticpropertyof a substance is inversely proportional to their temperature, i.e. that materials become more magnetic at lower temperatures.

25, Explain the significance of curie temperature.

Ans: Below the Curie **temperature**, the atoms are aligned and parallel, causing spontaneous magnetism; the material is **ferromagnetic**. Above the Curie temperature the material is paramagnetic, as the atoms lose their ordered magnetic moments when the material undergoes a phase transition.

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# 5. Chemical Spectroscopy-I and IIand Raman Spectroscopy
12 Hours --- *30 marks*

1. Bring out the differences between line spectra and band spectra.(2m)
Ans: 1. *Line spectrum*: Line spectra are sharp lines of definite wavelengths. It is the charact-eristic of the emitting substance. It is used to identify the gas. Atoms in the gaseous state, i.e. free excited atoms emit line spectrum.
2.*Band Spectrum* It consists of a number of bright bands with a sharp edge at one end but fading out at the other end. Band spectra are obtained from molecules. It is the characteristic of the molecule. each band is found to be made of a large number of fine lines, very close to each other at the sharp edge but spaced out at the other end. Using band spectra the molecular structure of the substance can be studied.

2. Derive the relationship between moment of inertia and bond length of diatomic mole-cules.(4)
Ans:Consider a diatomic molecule, with m_1 and m_2 as the atomic masses of two atoms at a distance r_1 and r_2 respectively from the centre of gravity C. r_0 is the total distance between them This distance is called intermolecular distance or bond length.Let us imagine the diatomic molecule as a system of two tiny spheres at either end of a thin weightless rod.

$$\text{C}$$
$$m_1 \qquad\qquad m_2$$
$$|\leftarrow \quad r_1 \quad \rightarrow|\leftarrow \quad r_2 \quad \rightarrow|$$
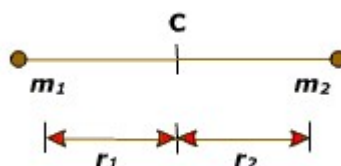
Now, $r_1 + r_2 = r_0$ ---------- (1)and $m_1 r_1 = m_2 r_2$ ---------- (2)
where m_1 and m_2 are the masses of the two atoms.
   From equation (1); $r_2 = r_0 - r_1$ and From equation (2)$m_1 r_1 = m_2 (r_0 - r_1)$ or $m_1 r_1 = m_2 r_0 - m_2 r_1$

$$r_1 (m_1 + m_2) = m_2 r_0 \text{ or } r_1 = \frac{m_2}{m_1 + m_2} r_0 \qquad \text{Similarly } r_2 = \frac{m_1}{m_1 + m_2} r_0$$

Let I be the moment of inertia of the diatomic molecule about an axis passing through the centre of mass of the molecule and perpendicular to bond length.;

$$\text{Then, } I = m_1 r_1^2 + m_2 r_2^2 \text{ or } I = m_1 \left[\frac{m_2}{m_1 + m_2} r_0\right]^2 + m_2 \left[\frac{m_1}{m_1 + m_2} r_0\right]^2$$

$$\text{or } I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} r_0^2$$

$$\text{or } I = \frac{m_1 m_2 (m_2 + m_1)}{(m_1 + m_2)^2} r_0^2 \text{ or } I = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

But $\frac{m_1 m_2}{m_1 + m_2} = \mu$ (reduced mass of molecule)

Hence $\therefore I = \mu r_0^2$

Therefore, moment of inertia of a diatomic molecule about an axis passing through the centre of the diatomic molecule and perpendicular to bond length, is the product of reduced mass of the molecule and the square of bond length.

3. Mention the regions of electromagnetic spectrum where rotational and vibrational spectra areobserved(2).
Ans: Rotational Spectra ---- Microwave region and vibrational spectra---Infra red region.

4. Name the different types of molecular spectra. Mention the regions of the electromag-neticspectrum in which they appear.(4)
Ans: The different types of molecular spectra are:
i) Rotational Spectra ---- Microwave region
ii) Vibration- Rotational spectra and Vibrationa spectra --Infra red region and
iii) Electronic spectra in the Ultra violet region of the electromagnetic radiation.

5. State Born-Oppenheimer approximation(2).
 Ans: Born–Oppenheimer approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. The energy of the molecule may be considered as the sum of the electronic,vibrational,rotational and translational energies. $E= E_{rot}+ E_{vib}+ E_{ele} + E_{Tr}$neglecting the translational energy, which is relatively small and negligible.
$$.E= E_{rot}+ E_{vib}+ E_{ele}$$

6. Write the expression for the rotational constant(B) of a diatomic molecule. Indicate the terms involved.
Ans: The rotational constant $B = h/ 8\pi^2 Ic$, where h= Planck's constant, I=Moment of inertia of the molecule, c= velocity of light.

7. Write the expression for the rotational energy of a diatomic molecule. Indicate the terms involved.
Ans:$E_{rot}= \dfrac{h^2}{8\pi^2 I}J(J+1)$ Joules or$E_{rot}= \dfrac{h}{8\pi^2 Ic}J(J+1)$ m^{-1} or
where h= Planck's constant, I=Moment of inertia of the molecule, c= velocity of light and J=Rotational quantum number = 1,2…………

8. In a typical rotational spectrum of a diatomic molecule, the lines are equi-spaced. Justify.(2)
Ans. The energy difference for a rotational transition from a level J to J+1 is given by $\Delta E = 2B(J+1)$ m-1. For values of J = 0,1,2,3 etc. rotational spectral lines are observed at $\Delta E = 2B, 4B, 6B, 8B$, etc. m^{-1}, such that the spacing between any two rotational lines is 2B m^{-1}. Hence rotational spectrum of a diatomic molecule consists of equi-spaced lines.

9. Explain why H_2 does not show rotation spectrum while HCl shows rotation spectrum.2
Ans: The important criteria for a molecule to exhibit rotational spectra is, the molecule should posses permanent dipole moment, H_2 molecule lacks dipolemoment or dipole moment=0,where as HCl possess permanent dipolemoment, hence it shows rotation spectrum.

10. CO is microwave active but O_2 is microwave inactive. Give reason.(2).
Ans: The important criteria for a molecule to be microwave active is, the molecule should posses permanent dipole moment, O_2 molecule lacks dipole moment or dipole moment=0,where as CO possess permanent dipolemoment, hence it is microwave inactive.

11. Nitrogen molecule fails to exhibit rotational spectra but carbon monoxide exhibits. Why ?

Ans: The important criteria for a molecule to exhibit rotational spectra is, the molecule should posses permanent dipole moment, N_2 molecule lacks dipole moment or dipole moment=0,where as CO possess permanent dipolemoment, hence it shows rotation spectrum.

12. Explain how is the rotational spectra used to determine the bond length in HClmolecule.(3)

Ans:i) HCl gas is subjected to rotational spectal analysis in which 2B value is recorded from its first rotational spectral line. ii) We know that $2B = h/4\pi^2 Ic$; $I = h/4\pi^2(2B)c$; hence moment of inertia can be calculated. iii) $I = \mu r_o^2$ or $r_o = I/\mu$, where $\mu = m_1 m_2/(m_1+m_2) N$ where $m_1 m_2$ are the atomic masses and N is the Avagadro's number, hence r_0 can be calculated.

13. State Hooke's law.Give the expression for the frequency and wave number of a simple harmonic oscillator(4)

Ans: Hooke's law states that the force (F) needed to extend or compress a spring by some distance X is proportional to that distance. That is: F = - kx, where k is the force constant which is the measure of the stiffness of the bond and x is the displacement.
Expression for the frequency $\omega_{osc} = 1/2\pi \sqrt{k/\mu}$ Hz.
Expression for the wave number:$v' = 1/2\pi c \sqrt{k/\mu}$ m^{-1}. where ω_{osc}oscillation frequency of the vibrating molecule in Hz, c = velocity of light.k is the force constant, μ is the reduced mass $\mu = m_1 m_2/(m_1+m_2) N$ where $m_1 m_2$ are the atomic masses and N is the Avagadro's number

14. Give an equation relating force constant with vibrational frequency(2)

Ans: $\omega_{osc} = 1/2\pi \sqrt{k/\mu}$, or $k = 4\pi^2 \omega^2_{osc}\mu$, where ω_{osc}oscillation frequency of the vibrating molecule in Hz, c = velocity of light.k is the force constant, μ is the reduced mass $\mu = m_1 m_2/(m_1+m_2) N$ where $m_1 m_2$ are the atomic masses and N is the Avagadro's number

15.Write vibrational energy expression for a diatomic molecule, indicate the terms.

Ans:Vibrational energy expression for a diatomic molecule = $E_v = (v + \frac{1}{2})hc\omega_{osc}$, v=vibrational quantum number = 0,1,2……, h= Planck's constant, c = velocity of light, ω_{osc}= oscillating frequency.

16.Write vibrational energy expression for a diatomic molecule at zero level / lowest level.(2).

Ans:Vibrational energy expression for a diatomic molecule = $E_0 = \frac{1}{2} hc\omega_{osc}$kJ
h= Planck's constant, c = velocity of light, ω_{osc}= oscillating frequency.

17. Calculate the total number of modes of vibrations for i) CO_2 and ii) H_2O molecules(2):

Ans: 1. The degrees of vibrational modes for linear molecules can be calculated using the formula: (3n−5). CO_2 is a linear triatomic moleucule. Hence n=3, 3x3-5=4 modes of vibration.2. The degrees of freedom for nonlinear molecules can be calculated using the formula = 3n−6,
H_2O is a non-linear triatomic molecule, hence n=3, 3x3-6= 3 modes of vibration.

18. Two absorption bands are observed in the IR spectrum of CO_2 instead of four. Explain.(2)

Ans: This is because the "bend" (let's start by placing the molecule along the x-axis) can occur in the y direction and the z direction. But these two motions are the same, just deforming in differrent directions, the bend is said to be degenerate, accounting for the "fourth" vibration.

19. Sketch the normal modes of vibration in CO_2 molecule. Which of these are I.R active?
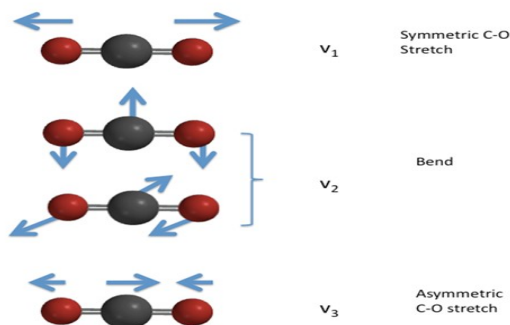**Ans:**

Fig. 1 Vibrational modes of CO_2

(4)

The symmetric stretch does not result in a change (of the initially zero dipole moment), so it is IR -inactive.---v_1
The asymmetric stretch does result in a change in dipole moment so it is IR-active. ---v_2
The bending type also results in a change in dipole moment, so it is also IR-active. ---v_3

20. Explain why only two absorption bands are observed in IR spectrum of CO_2(2350 cm^{-1} and 667 cm^{-1})(2)
Ans**:** The symmetric vibration causes no change in dipole. Thus, the symmetric vibration is infrared inactive. The asymmetric vibration produce a change in dipole moments, so absorption at 2350 cm^{-1} results. The remaining two vibrational modes of carbon dioxide involve scissoring. The two bending vibrations are the resolved components at 90 deg to one another of the bending motion in all possible planes around the bond axis. The two vibrations are identical in energy and thus produce a single peak at 667 cm^{-1}.

21. Define the terms: i) Force constant ii) Zero point energy, mention their significances. (4)
Ans: **i) Force constant** :is defined as force needed to deform a specific covalent bond divided by the deformation produced by that force k_1 for stretching and k_2 for bending.It is the restoring force per unit area, It is indicated as k. It is the measure of the stiffness or rigidity of the bond or bond strength.
ii) Zero point energy: The energy of the vibrating moleculeat the lowest vibrational quantum level is called zero point energy. The significance of zero point energy is even at absolute zero translational and rotational energies are zero but vibrational energy of a molecule is not zero that is the atoms of a diatomic molecule can never be completely at rest relative to each other.

22. Give the selection rules for pure rotational and vibrational transitions.(2)
Ans: Pure Rotational: $\Delta J = \pm 1$, vibrational transitions = $\Delta V = \pm 1$,

23. Explain the terms: Fundamental bands and overtones?(2)
Ans: The selection rules for a simple harmonic oscillator is $\Delta V = \pm 1$, A single line is observed in vibration absorption spectrum for the transition V=0 to V =1, $\Delta V = +1$ transitions are called **fundamental absorptions** and are intense.
The molecules showing anharmonicity that is $\Delta V = +2$, $\Delta V = +3$ are also observed and these transitions are known as first and second overtones respectively and these are not intense.

24. What is Raman Shift?(2)
Ans: Difference in frequency between incident and the scattered monochromatic radiation is called Raman shift. $\Delta v = (v_i - v_s)$

25. Give any four general characteristics of Raman lines.(4)
Ans:**Characteristics of Raman lines:** 1. Raman lines indicates the change in the frequency of lightdue to interaction with matter. 2. Raman signals is 10^{-5} times weaker than incident light(v_0)3. Photons are not absorbed 4. The criteria of Raman scattering is the molecule must be polarizable. 5. Raman lines are having higher or lower frequencies than the incident radiation, the lower frequency lines are stokes lines and that of the higher frequency lines are anti-stokes lines.

26. What are stokes and anti-stokes lines? How are they different from Raleigh lines?(3)
Ans: The scattered radiation have a lower frequency than the incident light when viewed perpendicular to the direction incident light, the corresponding lines observed are **Stoke'slines.** **$v_s < v_i$** --The scattered radiation have a higher frequency than the incident light when viewed perpendicular to the direction incident light, the lines resulted are **Anti-Stoke'slines.$v_i < v_s$**
In Raleigh lines there is no difference in frequencies of incident and scattered radiations **$v_i = v_s$.**

27. Bring out the differences between Raman spectra and IR spectra. (4)
Ans: Differences between IR and Raman spectra.

Sl. No.	Raman spectra	I.R spectra
1.	It is due to the scattering of light by the vibrating molecules.	It is the result of absorption of light by vibrating molecules
2.	The vibration is Raman active if it causes a change in polarizability	Vibration is IR active if there is change in dipole moment.
3.	Cost of instrumentation is very high	Comparatively inexpensive.
4.	Water can be used as a solvent.	Water cannot be used due to its intense absorption of IR.
5.	Sample preparation is not very elaborate, it can be in any state	Sample preparation is elaborate Gaseous samples can rarely be used.
6.	Gives an indication of covalent character in the molecule	Gives an indication of ionic character in the molecule
7.	In Raman spectral studies visible or UV radiation is used	IR radiation is used in IR spectra
8.	Method is very accurate but not very sensitive	Method is very accurate and sensitive

28. Give the selection rules for Raman rotational spectrum.
Ans:For linear molecules $\Delta J = 0, \pm 2$. For non linearmoleucules $\Delta J = 0, \pm 1, \pm 2$

29. Give any two advantages of Raman spectroscopy over Infra-red spectroscopy.(2)
Ans:Advantages of Raman spectroscopy over Infra-red spectroscopy:
1) Simple experimental set up 2) Homonuclear diatomic molecules can be studied 3) Water can be used as solvent 4) Micrograms of the substance are sufficient 5) Analysis of mixture of cis and trans isomers can be studied.

30. Using a suitable diagram indicate Raman transitions. Write the characteristics of Raman lines.

Ans:
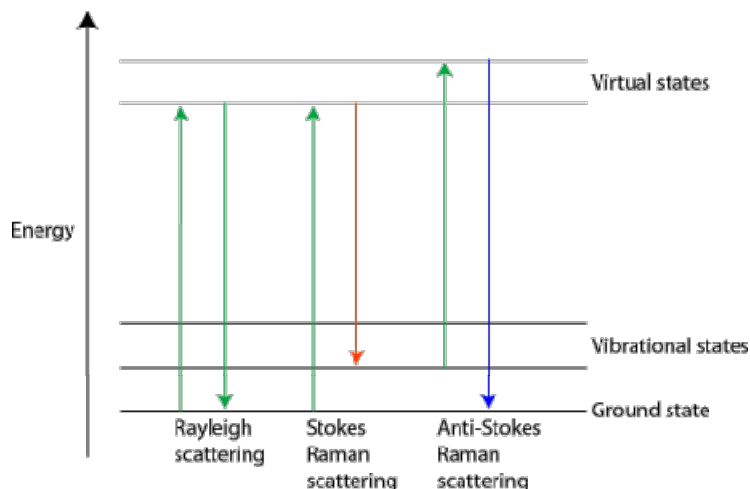
Characteristics of Raman lines: 1. Raman lines indicates the change in the frequency of light due to interaction with matter. 2. Raman signals is 10^{-5} times weaker than incident light(v_0) 3. Photons are not absorbed 4. The criteria of Raman scattering is the molecule must be polarizable.5. Raman lines are having higher or lower frequencies than the incident radiation the lower frequency lines are stokes lines and that of the higher frequency lines are anti-stokes lines.

31. Mention any two applications of Raman spectra.(2)

Ans:1. Useful in counterfeit drug identification 2. In forensic analysis 3. Finds used in food and agriculture industry applications 4. Quality control incoming raw material identification can be made up to 100% 5. Useful in biomedical analysis 6. Finds applications in Geology and geminology

32. Mention the different types of electronic transitions and arrange them in the increasing order of energies(3)

Ans: The different types of electronic transitions possible are from the molecular orbitals containingσ,π, π*-delocalized and lone pair(n) of elecrons to the excited state. The relative energies of these molecular orbitals in the ground state are n >   π-delocalized >π >σ. Hence to promote an electron from ground state to excited state the maximum energy is required for σ.less for π still less **for** π*-delocalized and minimum for n.

33. What are singlet and triplet states? (2)

Ans:Singlet state is the state of the electron attained when the spin multiplicity is one, that arises when all the electrons are paired up. The total spin becomes zero, then the spin multiplicity is one. Spin multiplicity = 2s+1 = 0+1=1 so s=0.

Triplet states is the state attained when the spin multiplicity is three. This arises when there are two unpaired electrons with parallel spins. Then the total spin is one and Spin multiplicity is 3. Spin multiplicity = 2s+1 = 2x1+1=3.

34. State Frank-Condon principle.(2)

Ans: Franck – Condon principle states that the electronic transition takes place so rapidly in a molecule such that the inter-nuclear distance almost remains unchanged.

35. What are the allowed transitions that occur in molecules during electronic spectra?(4).

Ans:The allowed electronic transitions that occur in molecule during electronic spectra are
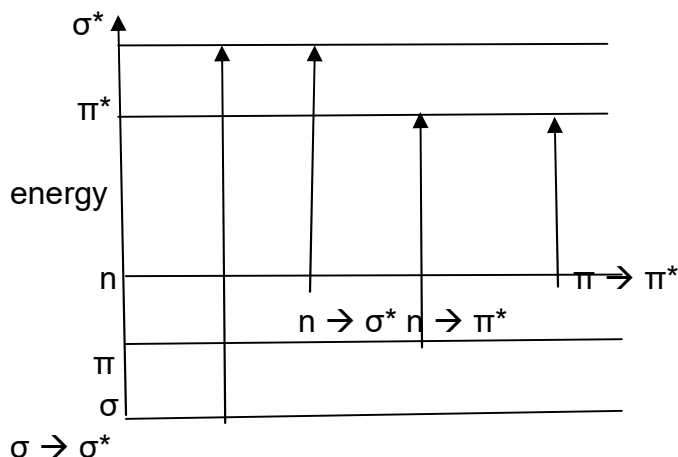
The types of transitions are, (i) $\sigma - \sigma^*$; Ex. Ethane (ii) $\pi - \pi^*$; Ex. Ethene (iii) $n - \pi^*$; Ex. Acetone (iv) $n - \sigma^*$; Ex. Acetone

36. (a). Draw the potential energy curves for bonding and anti-bonding molecular orbitals in a diatomic molecule and indicate the electronic transition. What are non-bonding orbitals?(4)

Ans.
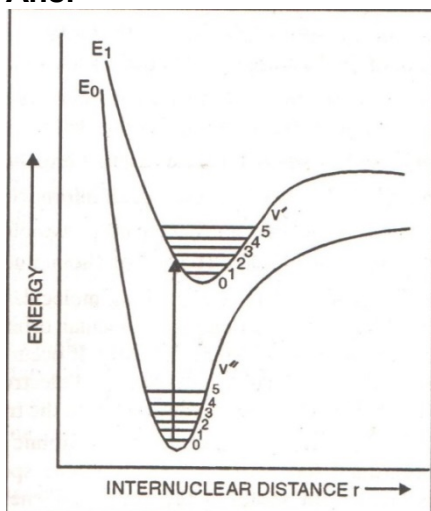
E_0 is the bonding molecular orbital (ground state) and E_1 is the antibonding molecular orbital (first excited state).The most intense transition line is obtained for $v''=0$ to $v'=2$ electronic transition.

Non-bonding orbitals are the molecular orbitals containing the lone pair of electrons which are not bonded. Organic compounds containing O (carbonyl compounds), N (amines), etc. have non-bonding orbitals.

6.ElectroanalyticalMethods5Hours --- *12 marks*

1. How is a dropping mercury electrode set up?
Ans. The **dropping mercury electrode** is set up by allowing drops of mercury to form at the end of a capillary tube as a result of gravity. The mercury drop of a DME grows continuously as mercury flows from a reservoir under the influence of gravity and has a finite lifetime of several seconds. At the end of its lifetime the mercury drop is dislodged, either manually or on its own, and replaced by a new drop.

2. Mention the advantages of a dropping mercury electrode in polarography.(2)
Ans. (i) DME is highly sensitive & the measurements are reproducible.
(ii) This is very important due to high over voltage of liquid mercury to hydrogen, which enables the determination of heavy metals (zinc, nickel and cobalt, etc.) and other species with highly negative half wave potentials.
(iii) The actual potential window is extending.

3. Give the limitations of a dropping mercury electrode.(2)
Ans. Disadvantages of using Dropping Mercury Electrode:
(i) Hg is highly toxic.
(ii) Handling of drop system is complicated.

4. Write Ilkovic equation and explain the terms.
Ans. The Ilkovic equation is $i_d = k\ n\ D^{1/3}M^{2/3}t^{1/6}c$
Where k is a constant which includes Faraday constant, π and the density of mercury, and has been evaluated at 708 for max current and 607 for average current, D is the diffusion coefficient of the depolarizer in the medium (cm^2/s), n is the number of electrons exchanged in the electrode reaction, m is the mass flow rate of Hg through the capillary (mg/sec), and t is the drop lifetime of Hg in seconds, and c is depolarizer concentration in mol/cm^3.

5. Give the significance of Ilkovicequation(2).
Ans: Ilkovic equation is a relation used in polarography relating the diffusion current (i_d) and the concentration of the depolarizer (c), which is the substance reduced or oxidized at the dropping mercury electrode

6. What is half wave potential in a polarography experiment? Mention its significance.(2)
Ans. Half Wave Potential ($E_{1/2}$): Half wave potential is defined as the middle point voltage of the sharp rise in current-potential plot. For a given species in a given medium, red-ox system has a unique $E_{1/2}$.
Significance of Half wave potential: Chemical, thermodynamic and structural information may be obtained from the measurements of the half-wave potentials of reversible and irreversible waves under varying experimental conditions.

7. Draw the current - potential curve in a polarographic experiment. Explain the different types of currents observed in a polarogram. (4)
Ans. Three types of current are involved in a polarogram: (i) Limiting current, (ii) Residual current and (iii) Diffusion current.
The limiting current is defined as the limiting value of a faradaic current that is approached as the rate of charge-transfer to an electrode is increased. The limiting current can be approached,

for example, by increasing the electric potential or decreasing the rate of mass transfer to the electrode. The constant current beyond the steep rise is called the limiting current. It is limited by the rate at which the reactant can be brought to the surface of electrode by mass- transport processes.

Residual Current: Even in the absence of analyte, a small, measurable current flows through an electrochemical cell this current is called residual current. This **residual current** has two components: a faradaic current due to the oxidation or reduction of trace impurities and the charging current that is non-faradaic current. An example of a non-faradic current is the current that charges a condenser.

Diffusion Current (I_d): Diffusion current is defined as the limiting current observed in polarography when the magnitude of the current is limited only by the rate of diffusion of the reactant to the electrode surface.

SHAPE OF THE POLAROGRAM
A graph of current versus potential in a polarographic experiment is called a polarogram.
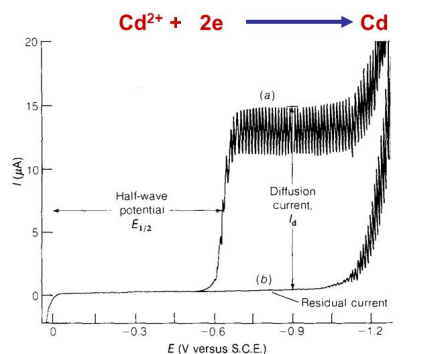
8. (a) What is cyclic voltammetry? Describe the experimental set up required for this technique.(4)

Ans. Cyclic voltammetry is a versatile electroanalytical technique for the study of electroactive species. CV monitors redox behavior of chemical species within a wide potential range. During a CV experiment, the current which flows between two electrodes (the working and counter electrodes) is plotted on the y-axis, and the potential of the electrode of interest, vs a reference electrode potential, is plotted on the x-axis. The resulting plot is called a cyclic voltammogram.

In the CV technique, three electrodes are employed. The main electrode at which the desired redox reaction of the analyte is made to occur is called the working electrode (WE), usually consisting of a noble metal (Pt or Au), various forms of carbon, or Hg. The WE can take the shape of a wire, a plate, or a disc, and can range in surface area from 1 cm2 to as small as 1 µm2 (the special domain of 'microelectrodes'). As current flows at the WE during oxidation (electron loss from the analyte to the WE) or reduction (electron is transferred to the analyte from the WE), electrons flow to or from the counter electrode (CE), usually a high area inert Pt gauze electrode. Therefore, when the W.E is the anode, the CE is the cathode, and vice versa. The reason that current flows at the WE is because its potential is changed vs. a reference electrode (RE) by the controlling instrumentation, the potentiostat. The reference electrode can be a saturated calomel electrode, SCE (Eo= 0.245 V vs. SHE), an Ag/AgCl electrode (Eo = 0.222 V vs. SHE) or others. If the potential of the WE, sometimes called the excitation signal, is

made positive of Eo, a net oxidation reaction occurs. If the WE potential is made negative of the equilibrium potential, reduction of the analyte occurs. In CV, the potential of the WE vs the RE is scanned linearly in time between two potential limits, sometimes referred to as the switching potentials, E+ and E-, at a certain sweep rate, usually between 1 and 100 mV/s,
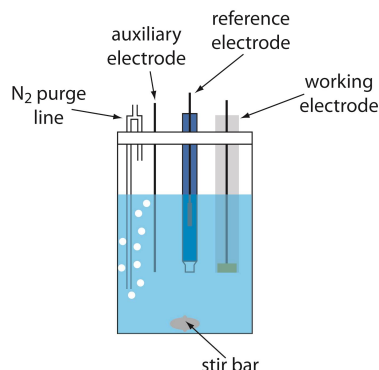
9. Mention any two applications of cyclic voltammetry.
Ans. 1. Cyclic voltammetry is widely employed for the analysis of trace metals in the alloys including ultra-pure metals, minerals/metallurgy, environmental analysis, foodstuffs, beverages and body-fluids, toxicology and clinical analysis.
2. In the biological systems it is used to determine vitamins, alkaloids, hormones, terpenoids and so on.

10. Give the applications of polarography(3)
Ans: 1. Polarography is used widely employed for the analysis of trace metals in the alloys including ultra-pure metals, minerals/metallurgy, environmental analysis, foodstuffs, beverages and body-fluids, toxicology and clinical analysis.

2. In the biological systems it is used to determine vitamins, alkaloids, hormones, terpenoid substances and so on.

3. In medical field polarography is used to analyze natural colouring substance of drugs and Pharmaceutical preparations, determining pesticide or herbicide residues in food stuffs and in the structure determination of many organic compounds.Since a fresh, smooth, reproducible drop is produced at regular intervals of time contamination or surface poisoning will be limited.

## 11. How diffusion coefficient is calculated for an analyte system?
Ans: Determination of diffusion coefficient: Diffusion coefficient of the system is calculatedusing the eqution$I_d = (7.08 \times 10^4) \, nCD^{1/2}m^{2/3}t^{1/6}$Where,id = average diffusion current during the life of the drop(μA).D= Diffusion coefficient of the analyte in the medium (cm^2/s).n = Number of electrons transferred per mole of analyte.m = mass flow rate of Hg through the capillary (mg/sec).t = drop lifetime(s).c = analyte concentration (mol/cm^3).

$$E = E_{1/2} + \frac{0.0591}{n}\log\frac{i_d - i}{i}$$

where E= applied voltage.i= current

12. What is a cyclic voltammogram? Explain with an example.(4)

Ans: A cyclic voltammogram is a graphical representation of the variation of current at the working electrode during the potential scans.The following cyclic voltammogramc is for a single electron electron reduction and oxidation for a reversible reaction : A typical cyclic voltammogram(50 mV/s) of K3Fe(CN)6 in 0.2 is shown in the above Figure for the case of a platinum working electrode immersed in a non-stirred solution containing $K_3Fe(CN)_6$ as the electroactive species in 0.2 M KCl in water. The potential axis is versus a Ag/AgCl reference electrode. The relevant redox reaction is given in reaction

$$[Fe_{(III)}(CN)_6]^{3-} + e^- \leftrightarrow [Fe_{(II)}(CN)_6]^4$$
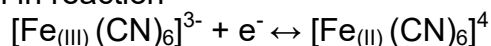
13. Write a note on polarographic analysis of organic compounds

Ans: Polarographic Analysis of Organic Compounds:Polarography technique is employed in organic chemistry for qualitative and quantitative analysis and structure determinations of organic compounds. Since the organic compounds are insoluble in pure aqueous medium the solvent in which the organic compound and its electrode product is soluble is added to the supporting electrolyte. Examples of solvents include various alcohols or ketones, dimethyl formamide, acetonitrile, ethylene diamine and so on. The widely employed supporting electrolytes which are easily mixed with organic solvents are various quaternary ammonium salts such as tetra-butyl ammonium-iodide.

14. Define diffusion coefficient and give its significance.(2)

Ans: Diffusion coefficient implies that the mass of the substance diffuses through a unit surface in a unit time at a concentration gradient of unity. The dimension of D in the SI system is a square meter per second.

The diffusion coefficient is a physical constant dependent on molecule size and other properties of the diffusing substance as well as on temperature and pressure

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