Maximum Marks:70 Time Allowed: 3 hours

General Instructions:

- a. All questions are compulsory.
- b. Section A: Q.no. 1 to 16 are very short answer questions (objective type) and carry 1 mark each.
- c. Section B: Q.no. 17 to 23 are short answer questions and carry 2 marks each.
- d. Section C: Q.no. 24 to 30 are long answer questions and carry 3 marks each.
- e. Section D: Q.no. 31 to 33 are also long answer questions and carry 5 marks each.
- f. There is no overall choice. However an internal choice has been provided in two questions of two marks, two questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
- g. Use log tables if necessary, use of calculators is not allowed.

Section A

1. The solutions which boil at a constant temperature like a pure liquid and possess the same composition in liquid, as well as vapour state are called azeotropes. The components of azeotropes cannot be separated by fractional distillation. Only non-ideal solutions form azeotropes. Solutions with negative deviation form maximum boiling azeotrope and the solutions with positive deviation form minimum boiling azeotrope. The boiling point of azeotrope is never equal to the boiling points of any of the components of the azeotrope.

Answer the following questions:

i. The azeotropic solutions of two miscible liquids show what type of deviation from Raoult's law?

- ii. The solutions which distil without a change in composition or temperature are called _____.
- iii. The azeotropic mixture of water & HCI boils at $108.5^{\circ}C$. What type of deviation is shown by the solution? Does this solution behave as ideal or non-ideal?
- iv. Do ideal solutions form azeotropes?
- v. Out of pure liquid and azeotrope showing positive deviation, Which one has a higher boiling point?
- 2. Name two metals which occur in nature as oxides.
- 3. Draw the structure of the monomer for the following polymer : Polypropene
- 4. Define native state in reference to proteins.
- 5. Are proteins natural or synthetic polymers?
- 6. Name the following compound according to IUPAC system of nomenclature.

or p-CHOC₆H₄CHO

- 7. Methyl bromide is converted into ethane by heating it in ether medium with
 - a. Na
 - b. Cu
 - c. Al
 - d. Zn
- 8. In the extraction of nickel by Mond's process, the metal is obtained by
 - a. Chemical reduction
 - b. Thermal decomposition
 - c. Electrochemical reduction
 - d. Electrolytic reduction

- 9. Which is called chromic acid?
 - a. CrO
 - b. H_2CrO_4
 - c. Cr_3O_4
 - d. Cr_2O_3
- 10. Which of the following complex species involves d^2sp^3 hybridization?
 - a. $[Cr(NH_3)_6]^{3+}$
 - b. [Fe(CN)₆]³⁻
 - c. $[Co(N{H_3})_6]^{3+}$
 - d. [CoF₆]³⁻
- 11. Which of the following is not correct regarding terylene?
 - a. Condensation polymer
 - b. Synthetic fibre
 - c. Step-growth polymer
 - d. Thermosetting plastic
- 12. Assertion: Except glycine, all naturally occurring α -amino acids are optically active. Reason: All α -amino acids occurring naturally except glycine has at least one asymmetric carbon.
 - a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 - b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT

explanation of the assertion.

- c. Assertion is CORRECT but, reason is INCORRECT.
- d. Assertion is INCORRECT but, reason is CORRECT.
- 13. Assertion: Addition of Br_2 to trans-2-butene yields meso-2,3-dibromobutane. Reason: Bromine addition to an alkene is an electrophilic addition reaction.
 - a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 - b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
 - c. Assertion is CORRECT but, reason is INCORRECT.
 - d. Assertion is INCORRECT but, reason is CORRECT.
- 14. **Assertion:** P_4 is more reactive than N_2 .

Reason: P - P single bond in P is much weaker than $N \equiv N$ in N_2 molecule.

- a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
- b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
- c. Assertion is CORRECT but, reason is INCORRECT.
- d. Assertion is INCORRECT but, reason is CORRECT.
- 15. Assertion: The boiling point of diethyl ether is much less than that of ethanol.Reason: In ethanol, the molecules are associated by the formation of intermolecular hydrogen bonding whereas in diethyl ether, it is not possible.
 - a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

- b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
- c. Assertion is CORRECT but, reason is INCORRECT.
- d. Assertion is INCORRECT but, reason is CORRECT.
- 16. Assertion: Small quantity of soap is required to prepare a stable emulsion.Reason: Soaps lowers the interfacial tension between oil and water.
 - a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 - b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
 - c. Assertion is CORRECT but, reason is INCORRECT.
 - d. Assertion is INCORRECT but, reason is CORRECT.

Section B

- 17. Arrange the following polymers in increasing order of their intermolecular forces.
 - i. Nylon 6, 6, Buna-S, polythene
 - ii. Nylon 6, Neoprene, polyvinyl chloride.
- 18. Give the units of specific reaction rate constant for a zero order reaction.
- 19. What are primary cell?
- 20. Give an example of industrial application of forming coordination complex.
- 21. Name the following complex using IUPAC norms: [Co(en)₂(ONO)Cl]Cl.

OR

Write the name and draw the structure of each of the following complex compounds:

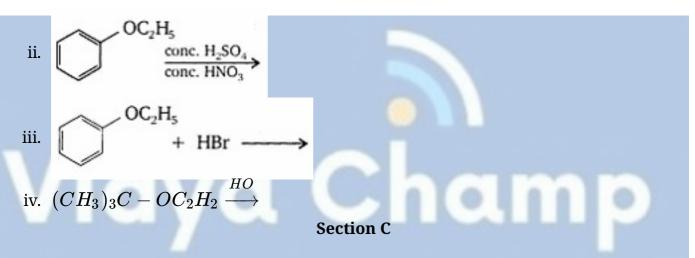
i. $[Co(NH_3)_4(H_2O)_2]Cl_3$

- ii. [Pt(NH₃)₄][NiCl₄]
- 22. How is leaching carried out in case of low grade copper ores?

OR

Name one example each of

- i. Acidic flux
- ii. Basic flux
- 23. Predict the products of the following reactions:
 - i. $CH_3 CH_2 CH_2 O CH_3 + HBr$



- 24. State Kohlrausch's law of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data?
- 25. Hydrogen peroxide, $H_2O_2(aq)$ decomposes to H_2O and O_2 in a reaction which is first order in H_2O_2 and has a rate constant, $k = 1.06 \times 10^{-3} min^{-1}$. Then:
 - i. How long will it take 15% of a sample of H_2O_2 to decompose?
 - ii. How long will it take 85% of a sample of H_2O_2 to decompose?

OR

Hydrogen peroxide, $H_2O_2(aq)$ decomposes to H_2O and O_2 in a reaction which is first order in H_2O_2 and has a rate constant, $k=1.06 imes 10^{-3}min^{-1}$. Then:

i. How long will it take 15% of a sample of H_2O_2 to decompose?

- ii. How long will it take 85% of a sample of H_2O_2 to decompose?
- 26. Calculate the equilibrium constant for the reaction.

- 27. Describe the following about halogen family (Group 17 elements):
 - i. Relative oxidising power.
 - ii. Relative strength of their hydrides.
 - iii. Oxyacids and their related oxidising ability.
- 28. A compound 'A' contains carbon and hydrogen only and has molecular mass of 72. Its photo chlorination gives a mixture containing only one monochloro and two dichloro hydrocarbons. Deduce the structure of A and the chlorinated products.
- 29. Give reasons for the following:
 - a. Carboxylic acids do not give characteristic reactions of carbonyl group.
 - b. Treatment of benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation.
 - c. Sodium bisulphite is used for the purification of aldehydes and ketones.

OR

How are the following conversions carried out.

- i. Ethanol to 1, 2-Ethanediol
- ii. Phenol to Acetophenone
- 30. Why are cimetidine and ranitidine better antacids than sodium hydrogen carbonate or magnesium or aluminium hydroxide?

Section D

- 31. Write short notes on:
 - i. Brownian movement

ii. Hardy and Schultz rule.

OR

- 1. Account for the following:
 - i. Alkaline medium inhibits the rusting of iron.
 - ii. Iron does not react even if the zinc coating is broken in a galvanized iron pipe.
- 2. Construct the galvanic cell using the following data:-

For what concentration Ag⁺ ions will the emf of the cell be zero at 25°C if the

concentration of Cu^{2+} is 0.01 M? [log 3.919 = 0.593]

- 32. i. Illustrate the following reactions giving suitable example in each case:
 - a. Ammonolysis
 - b. Coupling reaction
 - c. Acetylation of amines
 - ii. Describe Hinsberg method for the identification of primary, secondary and tertiary amines. Also, write the chemical equations of the reactions involved.

OR

How will you convert

- i. Ethanoic acid into methanamine
- ii. Hexanenitrile into 1-aminopentane
- iii. Ethanamine into methanamine
- iv. Nitromethane into dimethylamine
- v. Propanoic acid into ethanoic acid
- 33. Explain giving reasons:
 - i. Transition metals and many of their compounds show paramagnetic behaviour.
 - ii. The melting point of transition metals are high.
 - iii. The transition metals generally form coloured compounds.
 - iv. Transition metals and their many compounds act as good catalyst.

- OR
- a. Complete the following chemical reaction equations:

a.
$$Fe^{2+}(aq)+MnO_{4}^{-}\left(aq
ight) +H^{+}\left(aq
ight)
ightarrow$$

b.
$$Cr_2O_7^{2-}(aq)+I^-(aq)+H^+(aq)
ightarrow$$

- b. Explain the following observations:
 - i. Transition elements are known to form many interstitial compounds.
 - ii. With the same d⁴ d-orbital configuration Cr²⁺ ion is reducing while Mn³⁺ ion is oxidizing.
 - iii. The enthalpies of atomization of transition elements are quite high.



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Solution Section A

- 1. i. The azeotropic solutions of two miscible liquids may show positive or negative deviation from Raoult's law.
 - ii. Azeotrope.
 - iii. The solution is non-ideal and shows a negative deviation.
 - iv. No, ideal solutions don't form azeotropes. Only the non-ideal solution form azeotrope.
 - v. The boiling point of a pure liquid is higher as compared to azeotrope showing positive deviation.
- 2. Iron as Haematite [Fe_2O_3] and Copper as Cuprite [Cu_2O]
- 3. $CH_2 = CH CH_3$ (Propene) is the monomer of the polymer polypropene.
- 4. Native state of protein is the sequence in which the amino acids are linked together with the help of peptide bond.
- 5. Proteins are natural polymers.
- 6. Benzene-1,4-dicarbaldehyde
- 7. (a) Na

Explanation: The Wurtz reaction, named after Charles-Adolphe Wurtz, is a coupling reaction in organic chemistry, organometallic chemistry and recently inorganic main group polymers, whereby two alkyl halides are reacted with sodium metal in dry ether solution to form a higher alkane: $2R-X + 2Na \rightarrow R-R + 2NaX$.

- (b) Thermal decomposition
 Explanation: Ni is first reacted with CO to form Nickel tetracarbonyl which is volatile which decomposes to give Nickel.
- 9. (b) H₂CrO₄

Explanation: H_2CrO_4 is chromic acid. It is actually formed by mixing concentrated sulphuric acid to a dichromate like sodium dichromate. It is a strong acid as it completely dissociates into H^+ ions.

10. (b) $[Fe(CN)_6]^{3-1}$

Explanation: In this complex there are 6 CN⁻ ligands means a total of -6 charge on ligands. There is a charge of -3 on the complex so oxidation state of Fe is +3. Atomic number of Fe is 26. So the electronic configuration of Fe⁺³ is 1s²2s²2p⁶3s²3p⁶3d³.Coordination number of the metal is 6 so the complex has octahedral geometry and since CN⁻ is a strong field ligand so it causes pairing and hence inner orbital complex is formed. So the hybridization is d² sp 3

- 11. (c) Step-growth polymerExplanation: Step-growth polymer
- 12. (a) Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

Explanation: Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

13. (b) Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.

Explanation: Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.

14. (a) Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

Explanation: Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

15. (a) Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

Explanation: Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

16. (a) Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

Explanation: Both assertion and reason are CORRECT and reason is the

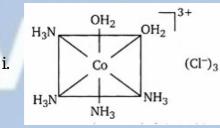
CORRECT explanation of the assertion.

Section B

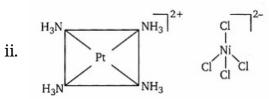
- 17. i. Buna-S < polythene < Nylon 6 6ii. Neoprene < polyvinyl chloride < Nylon 6
- 18. Unit of k for zero order reaction is mol $L^{-1} s^{-1}$.
- 19. Primary cell are those cells which are not rechargeable and cell reaction occurs only once and then cell become dead.

The most common example of dry cell is Leclanche cell.

- 20. Silver and gold are extracted by treating zinc with their cyanide complexes. K[Ag(CN)₂]is used for electroplating of silver, K[Au(CN)₂]is used for gold plating.
- 21. Chlorobis (ethylene diammine) nitro cobalt (III) chloride
 - OR



Tetraamminediaquacobalt (III) chloride



Tetraamineplatinum (II) tetrachloronickelate (II)

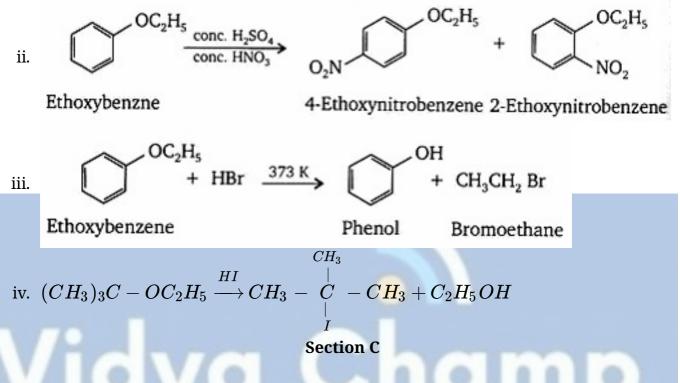
22. The leaching of the low grade copper ores is carried out with acids in presence of air, when copper goes into solution as Cu^{2+} ions. The following reaction is involved: $2Cu(s) + 2H_2SO_4(aq) + O_2(g) \rightarrow 2CuSO_4(aq) + 2H_2O(l)$

or

$$Cu(s) + 2H^+(aq) + rac{1}{2}O_2(g) o Cu^{2+}(aq) + H_2O(l)$$

OR

- i. Acidic flux : SiO_2
- ii. Basic flux : CaO, MgO
- 23. i. $CH_3CH_2CH_2OCH_3 + HBr \rightarrow CH_3CH_2CH_2OH + CH_3Br$



24. Kohlrausch law of independent migration of ions: It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. If $\lambda^o N a^+$ and $\lambda^o C l^-$ are limiting molar conductivity for sodium chloride is given by $\lambda_m^0 (NaCl) = \lambda^o Na + \lambda^0 C l^-$

Calculation of degree of dissociation of weak electrolyte like acetic acid. The degree of dissociation α is given by:

$$lpha=rac{\lambda_m}{\lambda_m^0}$$

where λ_m be molar conductivity and λ_m^0 be the limiting molar conductivity.

25. i. For 15% decomposition of $H_2 0_2$ [R]₀ = 100 M, [R] = 100 - 15 = 85 M k = 1.06 × 10⁻³ min⁻¹ For first order reaction

$$egin{aligned} t &= rac{2.303}{k} \log rac{[R_0]}{[R]} \ t &= rac{2.303}{1.06 imes 10^{-3}} imes \log \Big[rac{100}{85} \Big] \ t &= rac{2.303}{1.06 imes 10^{-3}} imes [\log 100 - \log 85] \ t &= rac{2.303}{1.06 imes 10^{-3}} imes \log (2 - 1.9292) \ t &= rac{2.303}{1.06 imes 10^{-3}} imes (0.0706) \ t &= 153.38 \, \mathrm{min.} \end{aligned}$$

ii. Similarly, for 85% decomposition of reaction

$$t = \left(\frac{2.303}{1.06 \times 10^{-3}}\right) \log\left(\frac{100}{15}\right)$$

t = 1790.325 min.

OR

- i. For 15% decomposition of $H_2 0_2$ $[R]_0 = 100 \text{ M}, [R] = 100 - 15 = 85 \text{ M}$ $k = 1.06 \times 10^{-3} \text{ min}^{-1}$ For first order reaction $t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$ $t = \frac{2.303}{1.06 \times 10^{-3}} \times \log \left[\frac{100}{85}\right]$ $t = \frac{2.303}{1.06 \times 10^{-3}} \times [\log 100 - \log 85]$ $t = \frac{2.303}{1.06 \times 10^{-3}} \times \log(2 - 1.9292)$ $t = \frac{2.303}{1.06 \times 10^{-3}} \times (0.0706)$ t = 153.38 min.
- ii. Similarly, for 85% decomposition of reaction

$$t = \left(\frac{2.303}{1.06 \times 10^{-3}}\right) \log\left(\frac{100}{15}\right)$$

t = 1790.325 min.

26.
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
 $\mathbf{E_{cell}} = \mathbf{E^{0}_{Cu^{+2}/Cu}} - \mathbf{E^{0}_{Zn^{+2}/Zn}}$
 $= + 0.34\text{V} - (-0.763\text{V})$

= 1.103 V $\log K = \frac{nE^0}{0.0591}$ $= \frac{2 \times 1.103}{0.0591}$ $\log K = \frac{2.206}{0.0591} = 37.326$ k = Antilog 37.326 $= 2.118 \times 10^{37}$

- 27. The decreasing order of the property for the elements of Group 17 is given below:
 - i. $F_2 > Cl_2 > Br_2 > I_2$ is decreasing order to oxidising power.
 - ii. HI > HBr > HCl > HF is decreasing order of strength of an acid.
 - iii. The order of oxidising power of different oxyacids is given below:

HClO >HClO₂ >HClO₃ >HClO₄

also; HOI > HOBr > HOCl

HOF does not exist at room temperature.

28. A is C_5H_{12} (mol. wt. 72) Since its gives one mono chloro and two dichloro derivatives on photochemical chlorination, it is

$$CH_3 - egin{pmatrix} CH_3 \ dots \ CH_3 - CH_3 \ dots \ CH_3 \ CH_3 \ CH_3 \ \end{pmatrix}$$

neo-pentane

The reactions are

monochloro derivative

$$CH_3 - egin{array}{ccc} CH_3 & CH_3 \ ert \ CH_3 - egin{array}{ccc} CH_3 & CH_3 \ ert \ CH_3 \ ect \ CH_3 \$$

dichloro derivatives

$$CH_3 - egin{array}{c} CH_3 & CH_2Cl & CH_2Cl \ ec{l} & ec{l} & ec{l} \ ec{l}$$

29. a. This is due to the lone pairs on oxygen atom attached to the hydrogen atom in the -COOH group, are involved in resonance and hence making the carbon atom less electrophilic. Hence, carboxylic acids do not give their action of carbonyl groups

$$\begin{array}{c} 0 & O^{\ominus} \\ R - C - \overset{H}{\odot} H \longleftrightarrow R - C = \overset{H}{O} H \end{array}$$

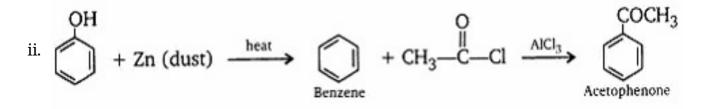
b. C_6H_5CHO reacts with HCN to form isomeric benzaldehyde cyanohydrins because an asymmetric carbon atom is introduced

These two isomers are enantiomers and therefore, cannot be separated by physical methods like fractional distillation.

c. Aldehydes and ketones form addition compounds with NaHSO₃ whereas impurities do not. On hydrolysis, we get pure aldehydes and ketones back.

$$CH_3 - \overset{O}{C} - H + NaHSO_3
ightarrow CH_3 - \overset{O}{CH} - SO_3Na \xrightarrow{H_2O/H} CH_3 - \overset{O}{O} - H_3$$

i.
$$\begin{array}{c} CH_{3}CH_{2}OH \xrightarrow{\text{conc } H_{2}SO_{4}} \\ \xrightarrow{\text{Ethanol}} \end{array} \xrightarrow{\text{Ch}_{2}SO_{4}} CH_{2} = CH_{2} + H_{2}O + [O] \xrightarrow{\text{Cold alkaline}} CH_{2}OH \\ \xrightarrow{\text{KMnO}_{4}} CH_{2}OH \end{array}$$



30. Sodium hydrogen carbonate or magnesium or aluminium hydroxide neutralize the excess HCl and raise the pH to an appropriate level in stomach. Therefore, these antacids controls only the symptoms and not the cause. In contrast, cimetidine and ranitidine are better antacids because they prevent the interaction of histamine with the receptors present in the stomach wall and thus release lesser amount of HCl.

Section D

- 31. i. Brownian movement: When colloidal solution are viewed under the powerful microscope, the colloidal particles are seen to be in constant motion in zig-zag path. This zig-zag motion of dispersed phase particles is known as Brownian movement. This zig-zag movement is supposed to be due to the unequal bombardment of the colloidal particles by the molecules of dispersion medium. Importance:
 - a. With the help of Brownian movement Avogadro's number can be calculated.
 - b. It gives the direct demonstration of ceaseless motion of molecules as shown by kinetic theory.
 - c. Due to Brownian movement, colloidal particle do not settle down under the influence of gravity, hence it is responsible for the stability of colloidal solution.
 - ii. Hardy and Schultz rule: For the coagulation of sol, different electrolytes may be added to the colloidal solution. Different electrolytes have different coagulation values. Hardy and Schultz rule tells us about the effectiveness of an electrolyte which is used for coagulation. According to it, greater the valency of the active ion, greater will be the power to cause coagulation.

Active ion is responsible for coagulation, it has the charge opposite to the charge present on sol. Thus, in case of the coagulation of positively charged sol, the coagulation power of anion in the order of as:

 $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

OR

1. (i) H^+ ions are required for rusting to take place. Alkaline medium will react with

H⁺, therefore inhibit rusting.

(ii) It is because zinc acts as anode because it is more reactive. (

 $E^{\ominus}_{(Zn^{2+}/Zn)}=~-0.76~V$ and $E^{\ominus}_{(Fe^{2+}/Fe)}=~-0.44~V$) $Zn
ightarrow Zn^{2+}+2e^{-}$

Even if any Fe^{2+} is formed it will gain electrons and change into Fe and thus corrosion will be prevented.

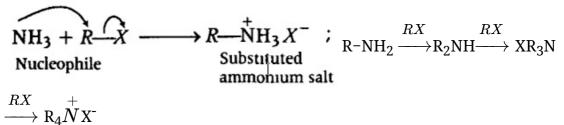
 $Fe^{2+} + 2e^- \to Fe$

2. From the data, it is found that standard emf of the Copper is less than Silver, therefore Copper is oxidized and Silver is reduced.

At Cathode (Reduction) : $2Aq^+(aq)+2e^ightarrow Aq(s)$ At Anode (Oxidation): $Cu(s)
ightarrow Cu^{2+}(aq) + 2e^{-}$ Cell representation of the cell is: $Cu(s)|Cu^{2+}(aq)||Aq^{+}(aq)|Aq(s)|$ Complete cell reaction is the summation of these two half cell reactions. $Cu(s)+2Ag^+(aq)
ightarrow Cu^{2+}(aq)+2Ag(s)$ for this reaction **n** = 2 moles of electrons Now standard emf of the cell is $E^{\ominus}_{cell} = E^{\ominus}{}_{(Ag^+/Ag)} - E^{\ominus}_{(cu^{2+}/cu)}$ = + 0.80 V - 0.34 V = + 0.46 VNernst equation is $E_{cell} = E^{\ominus}{}_{cell} - rac{2.303 RT}{nF} {
m log} rac{\left\lfloor Cu^{2+}
ight
ceil}{\left\lfloor Aa^{+}
ight
ceil}$ For this reaction, n=2 , F=96500 Cmol⁻¹ , T=298 K $egin{aligned} E_{cell} &= E_{cell}^{\ominus} \ - \ rac{0.0591}{2} \mathrm{log} \, rac{[Cu^{2+}]}{[Ag^+]^2} \ 0 &= 0.46 \ V \ - \ rac{0.0591}{2} \mathrm{log} \, rac{[Cu^{2+}]}{[Ag^+]^2} \ (ext{Given } E_{cell} = 0 \) \ \mathrm{log} \, rac{0.01}{[Ag^+]^2} &= rac{0.46V imes 2}{0.0591} = rac{0.92}{0.0591} \end{aligned}$ = 15.567 $egin{array}{lll} \log rac{0.01}{\left[Ag+
ight]^2} &=& 15.567 \ rac{0.01}{\left[Ag+
ight]^2} &=& anti\log(\ 15.567) \end{array}$ $= 3.690 imes 10^{15}$ $[Ag^+]^2 = rac{0.01}{3.688 imes 10^{15}} = 2.71 imes 10^{-18}$ $\therefore [Ag^+] = 1.65 imes 10^{-9} mol \; L^{-1}$

32. i.

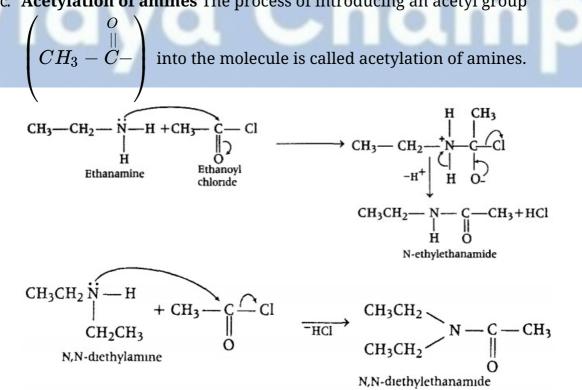
a. **Ammonolysis** The process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis. In this process, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which halogen atom is replaced by an amino (-NH₂) group. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines and further quaternary salts.



b. Coupling reaction Arenediazonium salts react with highly reactive (i.e. electron-rich) aromatic compounds such as aniline, phenols to form brightly coloured azo compounds, Ar-N =N-Ar. This reaction is called coupling reaction. e.g. Benzene diazonium chloride reacts with aniline in faintly acidic medium (pH 4- 5) at 273·278K, in which the molecule at its para-position is coupled with the diazonium salt to form p-aminoazobenzene. This is an example of coupling reaction.

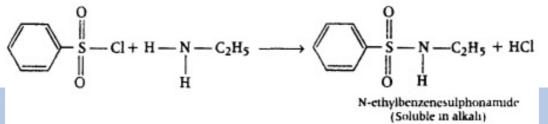
$$\bigvee$$
 N⁺₂Cl⁻+H \longrightarrow NH₂ $\xrightarrow{273 \text{ K}}$ \bigvee N=N \longrightarrow NH₂
(*p*-aminoazobenzene)

c. Acetylation of amines The process of introducing an acetyl group



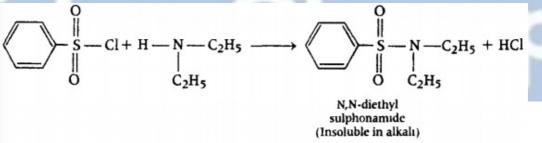
$$\underbrace{\bigcirc}_{NH_2 + CH_3 - C - Cl} \underbrace{\stackrel{Pyridine}{\frown}}_{N-phenylethanamide} \underbrace{\bigcirc}_{N-phenylethanamide} O \\ \underbrace{\bigcirc}_{NH_2 + CH_3 + HCl} O \\ \underbrace{\bigcirc}_{N-phenylethanamide} O$$

- ii. The reaction of primary and secondary amines with benzenesulphonyl chloride $(C_6H_5SO_2Cl, known as Hinsberg's reagent to form sulphonamides is known as Hinsberg's method (or reaction). This method (or reaction) is used for separating <math>1^{\circ}$, 2° and 3° amines.
 - a. The reaction of benzenesulphonyl chloride with primary amine yields Nethylbenzenesulphonamide.



The hydrogen attached to N-atom in sulphonamide is strogly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

b. In the reaction with secondary amine, N, N-diethylbenzenes amide is formed.

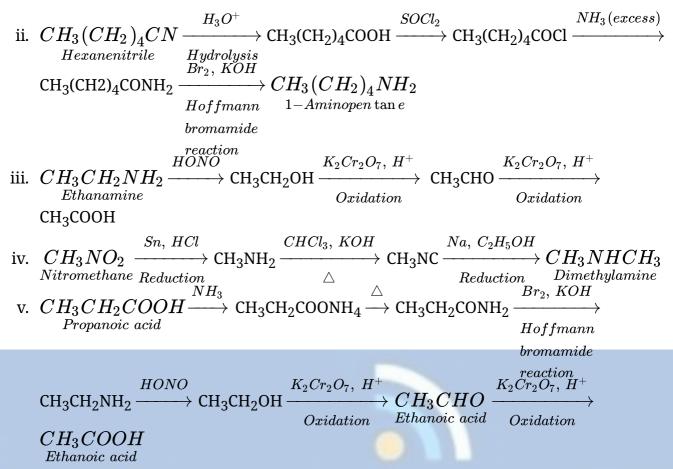


Since, N, N-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence, insoluble in alkali.

c. Tertiary amines do not react with benzenesulphonyl chloride. as it doesn't contain replaceable hydrogens.

OR

i.
$$\begin{array}{c} CH_{3}COOH \xrightarrow{SOCl_{2}} \operatorname{CH}_{3}\operatorname{COCl} \xrightarrow{NH_{3}(excess)} \operatorname{CH}_{3}\operatorname{CONH}_{2} \\ \xrightarrow{Ethanoic \ acid \ -SO_{2}, \ -HCl} \xrightarrow{SO_{2}, \ -HCl} \xrightarrow{CH_{3}\operatorname{COCl}} \xrightarrow{NH_{3}(excess)} \operatorname{CH}_{3}\operatorname{CONH}_{2} \\ \xrightarrow{Hoffmann \ Methanamine \ bromamide \ reaction}} \end{array}$$



- i. It is due to the presence of unpaired electrons due to which they are attracted by magnetic field and show paramagnetism.
 - ii. It is because of presence of unpaired electrons in them due to which they form strong metallic bonding and hence they have high lattice energy and consequently high melting point.
 - iii. It is due to the presence of unpaired electrons, they undergo d-d transitions by absorbing light from visible region and radiate complementary colour.
 - iv. It is due to variable oxidation states. They have large surface area and can form intermediate with reactants which readily changed into products.

OR

a. i. $5Fe^{2^+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2^+}(aq) + 4H_2O(l) + 5Fe^{3^+}(aq)$

ii. $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{I}^-(\text{aq}) + 14\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 3\text{I}_2(\text{g})$

b. i. The transition metals have voids in their crystal lattice into which small atoms like H, C, N are trapped inside resulting in the formation of interstitial compounds.

- ii. Cr^{2+} ion is reducing as its configuration changes from d^4 (in Cr^{+2}) to d^3 (in Cr^{+3}), the latter +3 oxidation state is stable because it has half filled t_{2g} configuration. While Mn^{+3} is oxidizing as its configuration changes from d^4 (in Mn^{+3}) to d^5 (in Mn^{+2}), the latter +2 oxidation state is stable due to half filled d^5 configuration.
- iii. Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomization.

