Class-XII Session 2022-23
Subject - Chemistry
Sample Question Paper - 23
With Solution

BLUE PRINT

S. No.	Chapter Name	Section-A (MCQs & A/R) 1 Mark		Section-B (VSA) 2 Marks		Section-C (SA) 3 Marks		Section-D (Case Study) 4 Marks		Section-E (LA) 5 Marks		Total Marks
		Q. No.	Marks	Q. No.	Marks	Q. No.	Marks	Q. No.	Marks	Q. No.	Marks	
1	Solutions	3, 16	2	23	2	27	3					7
2	Electrochemistry	4, 15, 18	3	25	2	29	3					8
3	Chemical Kinetics	9, 12	2							33	5	7
4	d -and f -Block Elements	5	1	22	2					35	5	8
5	Coordination Compounds	2	1	20	2	30	3					6
6	Haloalkanes and Haloarenes	6	1	19	2			32	4			7
7	Alcohols, Phenols and Ethers	7, 13	2	21	2	26. a, b	2					6
8	Aldehydes, Ketones and Carboxylic Acids	1, 11	2			26. c	1			34	5	8
9	Amines	8, 14	2					31	4			6
10	Biomolecules	10, 17	2	24	2	28	3					7
	Total Marks (Total Questions)	18	18	7	14	5	15	2	8	3	15	70

Time : 3 Hours **Max. Marks : 70**

General Instructions

Read the following instructions carefully

(a) *There are 35 questions in this question paper with internal choice.*

(b) *SECTION A consists of 18 multiple-choice questions carrying 1 mark each.*

(c) *SECTION B consists of 7 very short answer questions carrying 2 marks each.*

(d) *SECTION C consists of 5 short answer questions carrying 3 marks each.*

(e) *SECTION D consists of 2 case- based questions carrying 4 marks each.*

(f) *SECTION E consists of 3 long answer questions carrying 5 marks each.*

(g) ***All questions are compulsory.***

(h) ***Use of log tables and calculator are not allowed.***

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Which produces ketone on treatment with Grignard reagent?
(a) methyl cyanide (b) acetaldehyde (c) methyl alcohol (d) acetic acid

2. For an octahedral complex, which of the following *d*-electron configuration will give maximum CFSE?
(a) High spin with d^6 configuration (b) Low spin with d^4 configuration
(c) Low spin with d^5 configuration (d) High spin with d^7 configuration

3. The decrease in the vapour pressure of solvent depends on the
(a) quantity of non-volatile solute present in the solution
(b) nature of non-volatile solute present in the solution
(c) molar mass of non-volatile solute present in the solution
(d) physical state of non-volatile solute present in the solution

4. On the basis of the following E° values, the strongest oxidizing agent is :
$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$; $E° = -0.35$ V
$Fe^{2+} \rightarrow Fe^{3+} + e^-$; $E° = -0.77$ V
(a) $[Fe(CN)_6]^{4-}$ (b) Fe^{2+} (c) Fe^{3+} (d) $[Fe(CN)_6]^{3-}$

5. Which one of the following statements concerning lanthanide elements is false?
(a) Lanthanides are separated from one another by ion exchange method.
(b) The ionic radii of trivalent lanthanides steadily increase with increase in atomic number.
(c) All lanthanides are highly dense metals.
(d) Most characteristic oxidation state of lanthanides is +3.

6. Among the following which one can have a *meso* form?
(a) $CH_3CH(OH)CH(Cl)C_2H_5$ (b) $CH_3CH(OH)CH(OH)CH_3$
(c) $C_2H_5CH(OH)CH(OH)CH_3$ (d) $HOCH_2CH(Cl)CH_3$

7. What is the correct order of reactivity of alcohols in the following reaction? $R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$
(a) 1° > 2° > 3° (b) 1° < 2° < 3° (c) 3° > 2° > 1° (d) 3° > 1° > 2°

8. In an acidic medium, ... behaves as the strongest base
(a) nitrobenzene (b) aniline (c) phenol (d) cresol

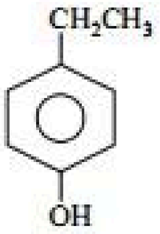
9. The order of a reaction with rate equal to $k[A]^{3/2}[B]^{-1/2}$ is :
(a) 1 (b) $-\frac{1}{2}$ (c) $-\frac{3}{2}$ (d) 2

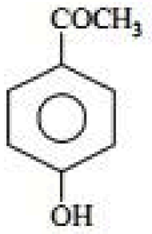
10. The function of DNA in an organism is
(a) to assist in the synthesis of RNA molecule
(b) to store information of heredity characteristics
(c) to assist in the synthesis of proteins and polypeptides
(d) all of these.

11. Reduction of benzoyl chloride with Pd and $BaSO_4$ gives :
(a) benzyl chloride
(b) benzaldehyde
(c) benzoic acid
(d) benzene sulphonyl chloride

12. In a chemical reaction $X \rightarrow Y$, it is found that the rate of reaction doubles when the concentration of X is increased four times. The order of the reaction with respect to X is
(a) 1
(b) 0
(c) 2
(d) $\frac{1}{2}$

13. Which of the following is the correct order of the acidity of the three compounds ?


I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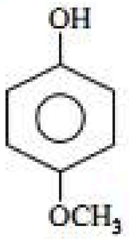

III

(a) II > III > I
(b) III > II > I
(c) II > I > III
(d) III > I > II

14. Out of the following, the strongest base in aqueous solution is
(a) Methylamine
(b) Dimethylamine
(c) Trimethylamine
(d) Aniline

In the following questions (15-18) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
(c) Assertion is correct, but reason is wrong statement.
(d) Assertion is wrong, but reason is correct statement.

15. **Assertion:** If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation :

$\Lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$

Reason: This is according to Kohlrausch law of independent migration of ions.

16. **Assertion :** The vapour pressure of a liquid decreases if some non-volatile solute is dissolved in it.
Reason : The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

17. **Assertion :** Disruption of the natural structure of a protein is called denaturation.
Reason : During denaturation secondary and tertiary structures are destroyed but primary structure remains intact.

18. **Assertion:** When 1M $CuSO_4$ (aq) solution is electrolysed using copper electrodes, copper is dissolved at anode and copper gets deposited at cathode.
Reason: The standard oxidation potential of copper is less than the standard oxidation potential of water and standard reduction potential of copper is greater than the standard reduction potential of water.

SECTION-B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

19. What precautions are taken in preservation of chloroform?

20. Some complexes of Ni (II) are diamagnetic while some of others are paramagnetic. Justify.

21. How will you convert :

(a) Ethyl alcohol to n-propyl amine, (b) Phenol to benzoic acid, and

OR

Write the equation for the reaction of HI with the following:

(a) 1-Propoxypropane (b) Methoxybenzene

22. What happens when:

(a) $S_2O_3^{2-}$ is oxidised by MnO_4^- in neutral aqueous medium.

(b) Fe^{2+} is oxidised by $Cr_2O_7^{2-}$ in acidic medium.

23. (a) Why vapour pressure of a liquid is constant at constant temperature?

(b) 2 g each of the solutes A and B (mol. mass of A > B) are dissolved separately in 20 g each of the same solvent C. Which will show greater lowering of vapour pressure and why?

24. What are nucleotides? Name two classes of nitrogen containing bases found in nucleotide.

25. The conductivity of 0.02 M $AgNO_3$ at 25 °C is $2.428 \times 10^{-3}\ \Omega^{-1}cm^{-1}$. What is its molar conductivity?

OR

Conductivity of a solution is $6.23 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and its resistance is 13710 Ω. If the electrodes are 0.7 cm apart, calculate the cross-sectional area of the electrode.

SECTION-C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

26. Account for the following:

(a) Alcohols act as weak bases. (b) Ethanol has higher b.p. than methoxymethane.

(c) Explain why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid.

27. The density of 10% by mass of KCl solution is 1.06 g cm^{-3}. Calculate the molarity of the solution.

OR

If 2g each of solutes A and B (Molecular mass of A > B) are dissolved separately in 20 g each of the same solvent C. Which will show greater lowering of vapour pressure and why?

28. (a) Give the appropriate term to describe the following:

(i) A molecule with a full positive charge and a full negative charge on different parts of the same molecule.

(ii) A compound formed by condensing together a number of amino acid molecules.

(iii) The change which occurs when a solution of a protein is heated.

(iv) The class of proteins to which keratin belongs.

(b) What does the letter 'D' before the name of a monosaccharide indicate?

29. Consider a cell composed of two half-cells:

(i) Cu(s), Cu^{2+} (aq), and (ii) Ag(s) / Ag^+ (aq).

Calculate

(a) the standard cell potential, and

(b) the cell potential when concentration of Cu^{2+} is 2M and concentration of Ag^+ is 0·05 M, at 298 K.

(Given: $E^\circ_{Cu^{2+}/Cu} = +0.34V$, $E^\circ_{Ag^+/Ag} = 0{\cdot}80 V$, $R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$, $F = 96500\ C\ mol^{-1}$)

30. A metal complex having composition $Cr(NH_3)_4\ Cl_2\ Br$ has been isolated in two forms 'A' and 'B'. The form 'A' reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas 'B' gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of 'A' and 'B' and state the hybridization of chromium in each. Calculate their magnetic moments (spin only value).

OR

The oxidation state of Fe in both $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ is +2 and they are expected to exhibit same magnetic character. However the former has been found to be paramagnetic while the later has been found to be diamagnetic. Why?

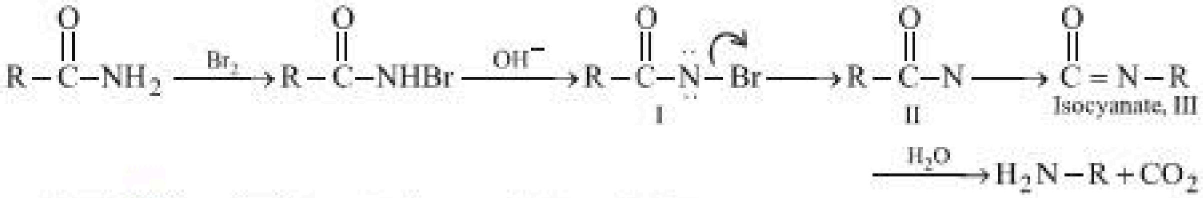
SECTION-D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. The conversion of an amide to an amine with one carbon atom less by the action of alkaline hypohalite is known as Hoffmann degradation.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2$$

The most important feature of the reaction is the rearrangement of N-bromamide anion to isocyanate :



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2} R-\overset{\overset{O}{\|}}{C}-NHBr \xrightarrow{OH^-} \underset{I}{R-\overset{\overset{O}{\|}}{C}-\ddot{\underset{..}{N}}-Br} \longrightarrow \underset{II}{R-\overset{\overset{O}{\|}}{C}-N} \longrightarrow \underset{\text{Isocyanate, III}}{\overset{\overset{O}{\|}}{C}=N-R}$$

$$\xrightarrow{H_2O} H_2N-R+CO_2$$

Hoffmann reaction is accelerated if the migrating group is more electron-releasing.

Answer the following questions :

(a) What is the change in carbon chain during Hoffman reaction?

(b) Which type of amine is produced by Hoffman reaction?

(c) Mention the gas evolved along with amine in Hoffman reaction.

OR

Name one migrating group which will not accelerate Hoffman reaction.

32. Isopropyl bromide was treated separately with sodium tert-butoxide and sodium ethoxide under two different conditions.

Reaction I : Treatment of isopropyl bromide with sodium tert-butoxide at 40°C gave almost exclusively compound A.

Reaction - II : Treatement of isopropyl bromide with sodium ethoxide at 30°C yielded compound A along with small amount of an ether B ($C_5H_{12}O$).

Compound A was readily oxidized by a neutral solution of cold dilute potassium permangnate to give a brown precipitate.

Answer the following questions :

(a) Which type of reaction can be used to explain the formation of A.

(b) Compound A is

(c) What happened when product A is treated with cold and alkaline $KMnO_4$.

OR

What is the IUPAC name of the compound B.

SECTION-E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

33. (a) Consider the following data for the reaction :

$$A + B \longrightarrow \text{Products}$$

S.No	Initial concentration [A]	Initial concentration [B]	Initial rate (mol $L^{-1}s^{-1}$)
1	0.10 M	1.0 M	2.1×10^{-3}
2	0.20 M	1.0 M	8.4×10^{-3}
3	0.20 M	2.0 M	8.4×10^{-3}

Determine the order of reaction with respect to A and with respect to B and the overall order of the reaction.

(b) What is the rate of reaction and the order of reaction, if the mechanism is

$2NO + H_2 \longrightarrow N_2 + H_2O_2$ (Slow) $\qquad H_2O_2 + H_2 \longrightarrow 2\,H_2O$ (Fast)

OR

(a) A first order reaction is 20% complete in 20 minutes. Calculate the time it will take the reaction to complete 80%.

(b) What are pseudo unimolecular reactions? Give two examples.

34. (a) Explain Why?

(i) During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled.

(ii) Carboxylic acids do not form oximes.

(b) Write chemical equations to illustrate each of the following reactions:

(i) Gatterman – Koch reaction

(ii) Cannizzaro reaction

OR

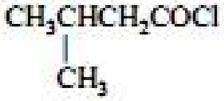
(a) Formic acid reduces Tollen's reagent while other carboxylic acids do not. Justify.

(b) Why are boiling points of aldehydes and ketones lower than those of the corresponding acids?

(c) Why is benzoic acid a stronger acid than acetic acid?

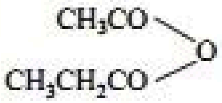
(d) Give IUPAC names of the following:

(i)



$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COCl$

(ii)



$(CH_3CO)(CH_3CH_2CO)O$

35. (a) Complete the following :

(i) Why do *d*-block elements have greater tendency to form complexes that *f*-block elements?

(ii) Name the element which finds use in X-ray tube.

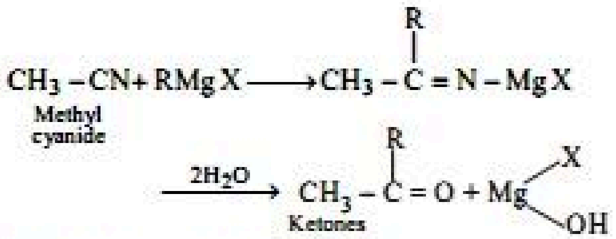
(b) Explain why ?

(i) *d*-Block elements have greater tendency to form complexes than *f*-block elements.

(ii) As compared to other transition elements Zn, Cd and Hg have very low melting point.

Solutions

SAMPLE PAPER-4

1. (a) 

$$CH_3-CN + RMgX \longrightarrow CH_3-\overset{R}{\overset{|}{C}}=N-MgX$$

Methyl cyanide

$$\xrightarrow{2H_2O} CH_3-\overset{R}{\overset{|}{C}}=O + Mg\begin{matrix}X\\OH\end{matrix}$$

Ketones

2. (c) (a) High spin with d^6 configuration

t_{2g}^4 and e_g^2 CFSE $= -0.4\Delta_0$

(b) Low spin with d^4 configuration

t_{2g}^4 and e_g^0 CFSE $= -1.6\Delta_0$

(c) Low spin with d^5 configuration

t_{2g}^5 and e_g^0 CFSE $= -2.0\Delta_0$

(d) High spin with d^7 configuration

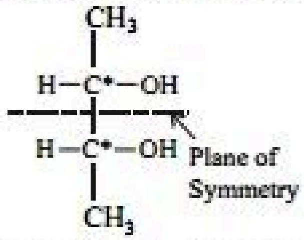
t_{2g}^5 and e_g^2 CFSE $= -0.8\Delta_0$

3. (a) For example, decrease in the vapour pressure of water by adding 1.0 mol of sucrose to one kg of water is nearly similar to that produced by adding 1.0 mol of urea to the same quantity of water at the same temperature.

4. (c) The given data explains that Fe^{3+} is the strongest oxidising agent. More the positive value of E°, more will be the tendency to get oxidized.

5. (b) The ionic radii of trivalent lanthanides decreases progressively with increase in atomic number which is also termed as lanthanide contraction.

6. (b) A molecule having a plane of symmetry but having chiral carbons will have *meso* form.



7. (c) HCl + An. $ZnCl_2$ is known as lucas reagent. It is used to determine degree of an alcohol.
The reaction follow nucleophilic substitution reaction in which — OH group is replaced by — Cl. In this reaction carbocation is formed as intermediate. Higher the stability of intermediate carbocation higher will be the reactivity of reactant molecule. Since 3° carbocation is more stable than 2° carbocation as well as 1° carbocation, so the order of reactivity of alcohols is 3° > 2° > 1°.

8. (b) aniline.

9. (a) Given $r = k[A]^{3/2}[B]^{-1/2}$

Order $= 3/2 - 1/2 = \frac{3-1}{2} = \frac{2}{2} = 1$

10. (d)

11. (b) This reaction is known as Rosenmund's reduction.

$$C_6H_5COCl \xrightarrow{Pd/BaSO_4} C_6H_5CHO$$

12. (d) $\frac{1}{2}$

$X \longrightarrow Y$

$r_1 = R \propto [X]^n$

$r_2 = 2R \propto [4X]^n \Rightarrow \frac{2R}{R} = \frac{[4X]^n}{[X]^n} \Rightarrow 2 = 4^n \Rightarrow n = \frac{1}{2}$

13. (c)

14. (b) Order of basicity in aqueous solution for amines :

$2° > 1° > 3° > NH_3$

15. (a) According to Kohlrausch law, "limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte." That is,

$\Lambda°_{NaCl} = \lambda°_{Na^+} + \lambda°_{Cl^-}$

16. (b) On adding a non-volatile solute in a liquid the vapour pressure decreases. The solution has more randomness (entropy) than the pure liquid and hence has lesser tendency to evaporate.

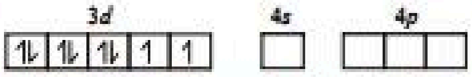
17. (b) Due to denaturation, a protein molecule uncoils and, form a more random conformation and ultimately precipitates from the solution. Also, during denaturation protein molecule loses its biological activity.
Thus, reason is correct but it is not the correct explanation of assertion.

18. (c) Assertion is true and reason is false.

19. The following precautions must be taken in preservation of $CHCl_3$:

(i) It must be stored in dark coloured bottles to protect it from sunlight; the bottles must be filled up to brim and stoppered properly to keep out air. (1 mark)

(ii) A small amount of ethyl alcohol (0·6 to 1%) must be added to the bottle of chloroform. It converts the poisonous phosgene, if formed, to non-toxic and harmless diethyl carbonate. (1 mark)

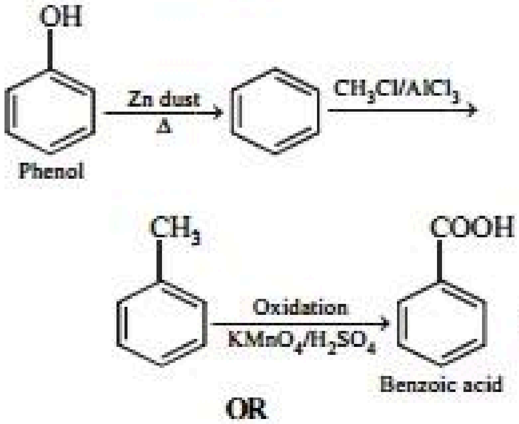
20. (a) Ni^{2+} 

In some complexes, the two unpaired 3*d* electrons pair up and the hybridisation is *dsp*^{2}. Thus, no unpaired electron is left. The nature of complex depends on the type of hybridisation of the central metal atom (Ni). dsp^2 hybridisation gives square planar complexes and sp^3 hybridisation gives tetrahedral complexes i.e., diamagnetic or paramagnetic complexes respectively. Strong ligands like NH_3, CN^-, CO forms diamagnetic complexes while paramagnetic complexes are formed by weak field ligands like Cl^-, Br^-. (2 marks)

21. (a) $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[NaBr + H_2SO_4]{HBr} CH_3CH_2Br$

$\xrightarrow[\text{Step-up reaction}]{KCN} CH_3CH_2CN \xrightarrow{4H\ (LiAlH_4)} \underset{\text{n-Propyl amine}}{CH_3CH_2CH_2NH_2}$ (1 mark)

(b)



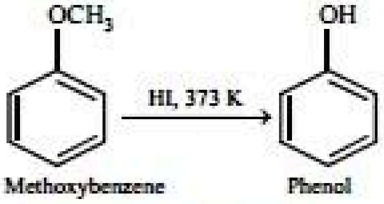
(1 mark)

OR

(a) $\underset{\text{1–Propoxy propane}}{CH_3CH_2CH_2 — O — CH_2CH_2CH_3} \xrightarrow[373K]{HI}$

$\underset{\text{Propanol}}{CH_3CH_2CH_2 — OH} + \underset{\text{Iodopropane}}{CH_3CH_2CH_2I}$ (1 mark)

(b)



$+ CH_3 — I$ (1 mark)

22. (a) $8MnO_4^- + 3S_2O_3^{2-} + 2H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$ (1 mark)

(b) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ (1 mark)

23. (a) Vapour pressure of a liquid is constant at constant temperature. This is beacuse it reaches a state of equilibrium where rate of evaporation becomes equal to rate of condensation. (1 mark)

(b) B will show greater lowering of vapour pressure because $\dfrac{p^\circ - p_s}{p^\circ} = \dfrac{w_2 \times M_1}{w_1 \times M_2}$ (1 mark)

24. Nucleotides are monomers of nucleic acids. A nucleotide is made of three components a nitrogen containing heterocyclic base, five carbon pentose sugar and a phosphoric acid residue. (1 mark)

The two classes of nitrogen containing bases found in nucleotides are:

(i) Purine (ii) Pyrimidine (1 mark)

25. Given : $C = 0.02$ M, $\kappa = 2.428 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$

To find : Molar conductivity

Formula : Molar conductivity $= \dfrac{1000\kappa}{C}$ (½ mark)

Calculation :

Molar conductivity $= \dfrac{1000\,\kappa}{C} = \dfrac{1000 \times 2.428 \times 10^{-3}}{0.02}$

$= 121.4\,\Omega^{-1}\,cm^2\,mol^{-1}$ (1 mark)

Molar conductivity of 0.02 M $AgNO_3$ solution at 25 °C is $121.4\,\Omega^{-1}\,cm^2\,mol^{-1}$. (½ mark)

OR

Given : Conductivity (κ) $= 6.23 \times 10^{-5}\,\Omega^{-1}\,cm^{-1}$

Resistance (R) = 13710 Ω

Distance between electrodes (l) = 0.7 cm

To find: Area of cross-section of the electrode (a)

Formula: $\kappa \times R = \dfrac{l}{a}$ (½ mark)

Calculation : From formula,

$a = \dfrac{l}{\kappa \times R} = \dfrac{0.7}{6.23 \times 10^{-5} \times 13710} = 0.82\ cm^2$ (1 mark)

The cross-sectional area of the given electrode is 0.82 cm^2. (½ mark)

26. (a) Due to presence of lone pair of electrons on oxygen, alcohols behave as Bronsted base (proton acceptors). (1 mark)

(b) Alcohol molecules are capable of forming H–bonds with each other. On the other hand ether molecules do not form H–bonds and thus they do not exhibit association, hence their boiling point are lower than the isomeric alcohols. (1 mark)

(c) In *ortho*-hydroxy benzaldehyde, intramolecular H-bonding takes place due to which it exists as a liquid, whereas, in para-hydroxy benzaldehyde, intermolecular H-bonding takes place. Due to intermolecular H-bonding, the molecules of *p*-hydroxy benzaldehyde associate and hence, it is a high melting solid. In the *ortho* isomer due to intramolecular H-bonding, melting point is low, so it is liquid. (1 mark)

27. **Step I.** Calculation of volume of the solution.

Mass of solution = 100 g ; Density of solution = 1.06 g cm^{-3}

Volume of solution $= \dfrac{\text{Mass of solution}}{\text{Density}}$ (½ mark)

$= \dfrac{(100\ g)}{(1.06\ g\ cm^{-3})} = 94.34\ cm^3$ (½ mark)

Step II. Calculation of molarity of the solution

Molarity of solution (M) =

$\dfrac{\text{Mass of KCl/Molar mass of KCl}}{\text{Volume of solution in } dm^3}$ (½ mark)

Mass of KCl = 10 g ; Molar mass of KCl = 39 + 35.5 = 74.5 gmol^{-1} (½ mark)

Volume of solution = $94.34\ \text{cm}^3 = \frac{94.34}{1000} = 0.0943\ \text{dm}^3$

$$\text{Molarity (M)} = \frac{10\ \text{g} / (74.5\ \text{g mol}^{-1})}{(0.0943\ \text{dm}^3)} = 1.42\ \text{mol dm}^{-3}$$

(1 mark)

= 1.42 M

Alternative:

Molarity of solution can also be obtained by applying the formula :

Molarity =

$$\frac{\%\ \text{Strength of solution} \times \text{Density of solution} \times 10}{\text{Molar mass of KCl}}$$

$$\text{Molarity} = \frac{10 \times 1.06 \times 10}{74.5} = 1.42\ \text{M}$$

OR

For dilute solutions, $\frac{P^\circ - P_s}{P^\circ} = \frac{W_2 M_1}{W_1 M_2}$ (1 mark)

$$\frac{\Delta P}{P^\circ} = \frac{W_2 M_1}{W_1 M_2}$$

For same P°, *i.e.*, P° constant and M_1 is also constant.

$W_2 = W_A = W_B = 2$ g

$W_1 = W_C = 20$ g (1 mark)

Hence $\frac{\Delta P_A}{\Delta P_B} = \frac{M_B}{M_A}$.

As $M_A > M_B$, therefore, $\Delta P_B > \Delta P_A$. (1 mark)

It means B will show greater lowering of vapour pressure.

28. (a) (i) Zwitter ion (½ mark)

(ii) Polypeptide (½ mark)

(iii) Denaturation (½ mark)

(iv) Fibrous proteins. (½ mark)

(b) It indicates that the –OH group at carbon next to the terminal (or penultimate) carbon atom is towards right.

(1 mark)

29. In this cell, Cu/Cu^{2+} electrode acts as anode, and Ag^+/Ag electrode acts as cathode. (¼ + ¼ = ½ mark)

(a) Standard electrode potential,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0{\cdot}80\ \text{V} - 0{\cdot}34\ \text{V} = 0{\cdot}46\ \text{V}.$$

(½ mark)

(b) The net cell reaction is $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

(½ mark)

Here n = 2.

By Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{2{\cdot}303\,RT}{nF} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$ (½ mark)

$$\therefore E_{cell} = 0{\cdot}46\ \text{V} - \frac{2{\cdot}303 \times 8{\cdot}314 \times 298}{2 \times 96500} \log \frac{2}{(0{\cdot}05)^2}$$

$$= 0{\cdot}46 - \frac{0{\cdot}0591}{2} \log \frac{2 \times 10^4}{25}$$

$$= 0{\cdot}46 - 0{\cdot}086 = 0{\cdot}37\ \text{V}.$$ (1 mark)

30. Since 'A' gives a white precipitate with $AgNO_3$ and this precipitate is soluble in NH_3, so in 'A' Cl is present in the ionisation sphere.

Since 'B' gives a pale yellow precipitate with $AgNO_3$ and this precipitate is soluble in concentrated NH_3, so in 'B' Br is present in the ionisation sphere.

The formula of these two isomers can be written as

$$\underset{\text{'A'}}{\left[Cr(NH_3)_4ClBr\right]Cl} \quad \text{and} \quad \underset{\text{'B'}}{\left[Cr(NH_3)_4Cl_2\right]Br}$$

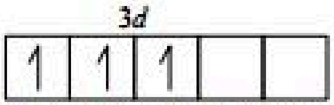
(1 mark)

Hybridisation of chromium in both the isomers is d^2sp^3 (the C.N. of chromium in both isomers is 6) (1 mark)

Calculation of Magnetic moment

In both the isomers chromium is present in +3 oxidation state.

Cr^{3+}



Thus, it has three unpaired electrons in +3 state.

Hence magnetic moment $= \sqrt{n(n+2)}$ B.M.

(n = number of unpaired electrons)

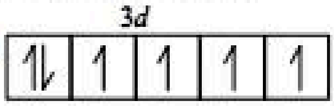
$= \sqrt{3(3+2)}$ B.M. $= \sqrt{15}$ B.M.

= 3.87 B.M. (1 mark)

OR

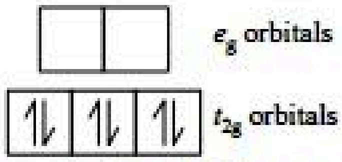
In Fe^{2+} ion all the 3*d*-orbitals have same energy because of their degenerate nature.

Fe^{2+}



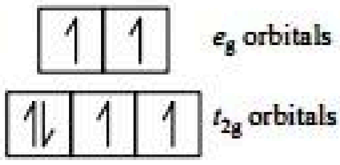
When CN^- ion approach these *d*-orbitals, the five *d*-orbitals split up into two groups (i.e. e_g and t_{2g}). The t_{2g} group containing three *d*-orbitals d_{xy}, d_{yz} d_{zx} has lower energy than those of e_g group containing two orbitals (d_{z^2}, $d_{x^2-y^2}$). This splitting is caused by CN^- ions in an octahedral field and as a result the rearrangement occurs in electronic structure of Fe^{2+} when it forms complex with CN^-. The six 3*d*-electrons of Fe^{2+} will tend to pair in three lower energy levels in violation of Hund's rule.

Fe^{2+} in $[Fe(CN)_6]^{4-}$



In $[Fe(H_2O)_6]^{2+}$ the separation is smaller because neutral H_2O molecule repels electrons less than negatively charged CN^- ions. In this case the electron distribution in Fe^{2+} is retained.

Fe^{2+} in $[Fe(H_2O)_6]^{2+}$



Since, $[Fe(H_2O)_6]^{2+}$ has unpaired electrons so it is paramagnetic, whereas in $[Fe(CN)_6]^{4-}$ there is no unpaired electron so it is diamagnetic. (3 marks)

31. (a) Carbon chain decreases by one carbon atom. (1 mark)

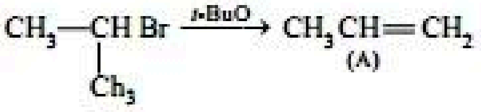
(b) 1° Amine or primary amine. (1 mark)

(c) CO_2 (2 marks)

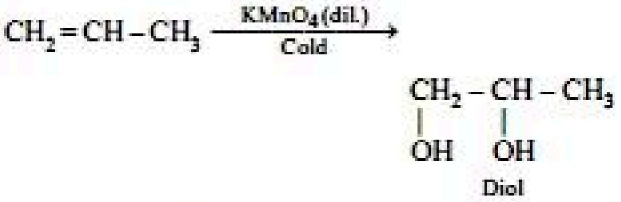
OR

$-NO_2$ (electron withdrawing group) (2 marks)

32. (a) The *tert*-butoxide ion, being large in size faces difficulty in attacking the carbon atom of isopropyl cation, which thus loses proton to form propene (A), E2 reaction. (1 mark)

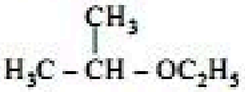
(b) 

$$CH_3-\underset{\underset{Ch_3}{|}}{C}H\,Br \xrightarrow{t\text{-}BuO^-} \underset{(A)}{CH_3CH=CH_2}$$ (1 mark)

(c) 

$$CH_2=CH-CH_3 \xrightarrow[\text{Cold}]{KMnO_4(\text{dil.})} \underset{\text{Diol}}{\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-CH_3}$$

OR

2-Ethoxypropane : 

$$H_3C-\overset{\overset{CH_3}{|}}{C}H-OC_2H_5$$ (2 marks)

33. (a) The rate law may be expressed as :

Rate $= k\,[A]^p\,[B]^q$

$(\text{Rate})_1 = k\,[0.1]^p[1.0]^q = 2.1 \times 10^3$ .... (i) (½ mark)

$(\text{Rate})_2 = k\,[0.2]^p\,[1.0]^q = 8.4 \times 10^{-3}$ .... (ii) (½ mark)

$(\text{Rate})_3 = k\,[0.2]^p\,[2.0]^q = 8.4 \times 10^{-3}$ .... (iii) (½ mark)

Dividing equation (iii) by (ii),

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.2]^p[2.0]^q}{k[0.2]^p[1.0]^q} = \frac{8.4\times10^{-3}}{8.4\times10^{-3}}$$ (½ mark)

$[2]^q = [2]^0$; $q = 0$

Dividing equation (ii) by (i),

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[0.20]^p[1.0]^q}{k[0.10]^p[1.0]^q} = \frac{8.4\times10^{-3}}{2.1\times10^{-3}} = 4$$

$[2]^p = [2]^2$; $p = 2$ (½ mark)

Order w.r.t. A = 2 ; B = 0 ; Overall order = 2. (½ mark)

(b) Rate of reaction $= k\,[NO]^2\,[H_2]$ (1 mark)

Order of reaction = 2 + 1 = 3. (1 mark)

OR

(a) Use the equation for first order.

20% complete means $[A] = 0.8\,[A]_0$

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{20}\log\frac{[A]_0}{0.8[A]_0}$$ (½ mark)

or $$k = \frac{2.303}{20}\log\frac{5}{4} = \frac{2.303}{20}(\log 5 - \log 4)$$

$$k = \frac{2.303}{20}(0.6990 - 0.6021) = \frac{2.303}{20}\times 0.0969\ \text{min}^{-1}$$ (1 mark)

80% complete means $[A] = 0.2\,[A]_0$

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{k}\log\frac{[A]_0}{0.2[A]_0}$$ (½ mark)

or $$t = \frac{2.303}{2.303}\times\frac{20}{0.0969}\log 5$$

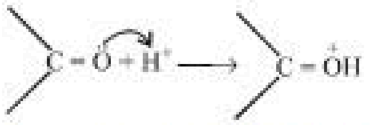
$$= \frac{20}{0.0969}\times 0.6990 = 144.2\ \text{min}.$$ (1 mark)

(b) Those reactions which are bimolecular but their order is found to be one are called pseudo unimolecular reactions. (1 mark)

(i) $CH_3COOC_2H_5 \xrightarrow{H^+} CH_3COOH + C_2H_5OH + H_2O$ (½ mark)

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ (½ mark)

34. (a) (i) Formation of ammonia derivatives (oximes, hydrazone, semi-carbazone, etc.) proceeds via the attack of carbonyl carbon with proton to form the conjugate acid.



Therefore, presence of an acid is must for preparing these derivatives. However, in strongly acidic medium, the proton attacks the unshared pair of electrons on nitrogen to form the species $R\overset{+}{N}H_3$ which cannot attack the carbonyl carbon.

$$H^+ + :NH_2R \longrightarrow \overset{+}{N}H_3R$$

In basic medium, there is no protonation of carbonyl group, and hence no reaction.

$>C=O \xrightarrow{\text{Basic medium}}$ No protonation (No reaction)

Therefore, preparation of ammonia derivatives requires slightly acidic medium (pH ≃ 3·5) and its careful control is essential. (2 marks)

(ii) Due to resonance between lone pairs of electrons on the O-atom of the OH group and C = O, the carboxyl carbon is less electrophilic than carbonyl carbon in aldehyde and ketones. Therefore, nucleophilic addition of NH_2OH to the C = O group of carboxylic acids does not occur and hence carboxylic acids do not form oximes. (1 mark)

(b) (i) $C_6H_6 \xrightarrow[\text{Anhy. }AlCl_3/CuCl]{CO/\,HCl} C_6H_5CHO$ (1 mark)

(ii) $2C_6H_5CHO \xrightarrow{\text{Conc. NaOH}} C_6H_5CH_2OH + C_6H_5COONa$ (1 mark)

OR

(a) HCOOH has an aldehydic (CHO) group in addition to carboxyl group (COOH). Therefore, it is expected to behave as reducing agent and also reduces Tollen's reagent to form a shining mirror.

$$\underset{\text{Formic acid}}{\mathrm{HCOOH}} + \underset{\text{Tollen's reagent}}{2[\mathrm{Ag(NH_3)_2}]^+\mathrm{OH}^-} \longrightarrow$$

$$\underset{\text{Silver mirror}}{2\mathrm{Ag}} + 2\mathrm{H_2O} + \mathrm{CO_2} + 4\mathrm{NH_3}$$ (1 mark)

(b) In the carboxylic acids, the carboxylic groups are involved in the intermolecular hydrogen bonding resulting in the formation of dimer. However, it is absent in the aldehydes and ketones. Therefore, aldehydes and ketones have lower boiling point than the corresponding acids of comparable molecular mass. (1 mark)

(c) The K_a value of benzoic acid (6.3×10^{-5}) is more than that of acetic acid (1.75×10^{-5}). Actually, C_6H_5 group with –I effect facilitates the release of H^+ from benzoic acid while CH_3 group with +I effect tends to retard it. Therefore, benzoic acid is stronger acid than acetic acid. (1 mark)

(d) (i) 3-Methylbutanoyl chloride (1 mark)
(ii) Ethanoic propanoic anhydride (1 mark)

35. (a) (i) *d*-orbitals are influenced more by ligands as they can project out and so they have greater tendency to form complexes. Comparatively, *f*-orbitals lie deep inside the atom and thus, *f*-electrons do not come in contact with ligands. Therefore, *f*-block elements form lesser complexes. (2 marks)

(ii) Molybdenum, Mo. (1 mark)

(b) (i) *d*-orbitals are influenced more by ligands as they can project out and so they have greater tendency to form complexes. Comparatively, *f*-orbitals lie deep inside the atom and thus, *f*-electrons do not come in contact with ligands. Therefore, *f*-block elements form lesser complexes. (1 mark)

(ii) The strength of metallic bond in transition metals depend upon number of unpaired electrons in valence shell, *i.e.*, $(n-1)d$ and ns orbitals. As there are no unpaired electrons in these metals, the bond strength is quite weak and thus they are soft and have very low melting points. Hg is liquid at ordinary temperature. (1 mark)