Class-XII Session 2022-23
Subject - Chemistry
Sample Question Paper - 26
With Solution

BLUE PRINT

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

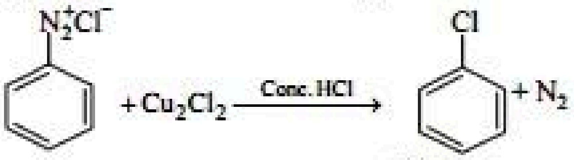
(a) $P_{total} = \overset{\circ}{P}_A + (\overset{\circ}{P}_A - \overset{\circ}{P}_B)x_B$ (b) $P_{total} = \overset{\circ}{P}_B + (\overset{\circ}{P}_A - \overset{\circ}{P}_B)x_A$

(c) $P_{total} = \overset{\circ}{P}_B + (\overset{\circ}{P}_B - \overset{\circ}{P}_A)x_A$ (d) $P_{total} = \overset{\circ}{P}_B + (\overset{\circ}{P}_B - \overset{\circ}{P}_A)x_B$

2. The compound which reacts fastest with Lucas reagent at room temperature is

(a) butan-1-ol (b) butan-2-ol (c) 2-methylpropan-1-ol (d) 2-methylpropan-2-ol

3.

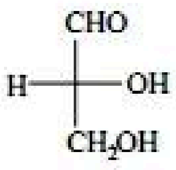


Chlorobenzene

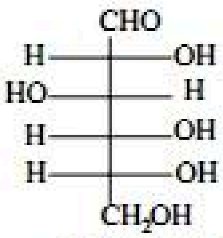
Above reaction is known as:

(a) Strecker's reaction (b) Sandmeyer's reaction (c) Wohl-Ziegler reaction (d) Stephen's reaction

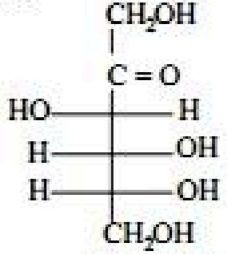
4. Optical rotations of some compounds alongwith their structures are given below which of them have D configuration.



(+) rotation
(I)



(+) rotation
(II)



(–) rotation
(III)

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

*** FOR VISUALLY CHALLENGED LEARNERS**

***4.** Glycosidic linkage is actually an :

(a) Carbonyl bond (b) Ether bond (c) Ester bond (d) Amide bond

5. The rate of the reaction $2NO + Cl_2 \longrightarrow 2NOCl$ is given by the rate equation, rate = $k[NO]^2[Cl_2]$

The value of the rate constant can be increased by:

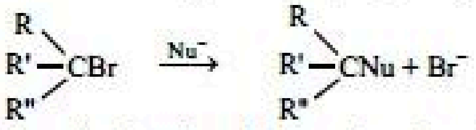
(a) increasing the concentration of NO.
(b) increasing the temperature.
(c) increasing the concentration of the Cl_2
(d) doing all of the above

6. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?
(a) Cl^- (b) Cl^+ (c) $AlCl_3$ (d) $[AlCl_4]^-$

7. A solution is prepared by dissolving 10 g NaOH in 1250 mL of a solvent of density 0.8 g/mL. The molality of the solution in mol kg^{-1} is
(a) 0.25 (b) 0.2 (c) 0.008 (d) 0.0064

8. The complex that can show *fac*- and *mer*- isomers is:
(a) $[Co(NH_3)_4Cl_2]^+$ (b) $[Pt(NH_3)_2Cl_2]$ (c) $[CoCl_2(en)_2]$ (d) $[Co(NH_3)_3(NO_2)_3]$

9. Which of the statement(s) is/are true, regarding following reaction?



(i) The reaction involves the formation of transition state.
(ii) Higher the nucleophilic character of the nucleophile, faster will be the reaction.
(iii) The product is always optically inactive.
(a) (ii) only (b) (ii) and (iii) (c) All the three (d) None of the three

10. *tert*-Butyl ethyl ether can't be prepared by which reaction?
(a) *tert* – Butanol + ethanol $\xrightarrow{H^+}$
(b) *tert*-Butyl bromide + sodium ethoxide →
(c) Sodium *tert*-butoxide + ethyl bromide →
(d) Isobutene + ethanol $\xrightarrow{H^+}$

11. Standard reduction potentials of the half reactions are given below :
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$; $E^\circ = +2.85$ V
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$; $E^\circ = +1.36$ V
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$; $E^\circ = +1.06$ V
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$; $E^\circ = +0.53$ V
The strongest oxidising and reducing agents respectively are
(a) F_2 and I^- (b) Br_2 and Cl^- (c) Cl_2 and Br^- (d) Cl_2 and I_2

12. Which of the following transition element shows the highest oxidation state?
(a) Mn (b) Fe (c) V (d) Cr

13. A compound does not react with 2, 4 dinitrophenyl-hydrazine, the compound is :
(a) Acetone (b) Acetaldehdye (c) CH_3OH (d) $CH_3CH_2COCH_3$

14. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as follows:
$O_3 \xrightarrow{\text{Fast}} O_2 + O$; $O + O_3 \xrightarrow{\text{Slow}} 2O_2$ the rate law expression should be
(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2[O_2]^{-1}$ (c) $r = k^3[O_3][O_2]^2$ (d) $r = [O_3][O_2]^2$

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 :** The molecular weight of acetic acid determined by depression in freezing point method in benzene and water was found to be different.
Reason : Water is polar and benzene is non-polar.

16. **Assertion:** Reduction of *m*-dinitrobenzene with ammonium sulphide gives *m*-nitroaniline.
Reason: *m*-Nitroaniline formed gets precipitated and hence further reduction is prevented.

17. **Assertion :** Oxidation of glucose by Br_2 water gives saccharic acid.
Reason : Br_2 water oxidizes –CHO but not alcohol.

18. **Assertion:** The major products formed by heating $C_6H_5CH_2OCH_3$ with HI are $C_6H_5CH_2I$ and CH_3OH.
Reason: Benzyl cation is more stable than methyl cation.

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. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S $cm^2 mol^{-1}$.
Given $\lambda^\circ(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^\circ(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

20. $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. Explain why.

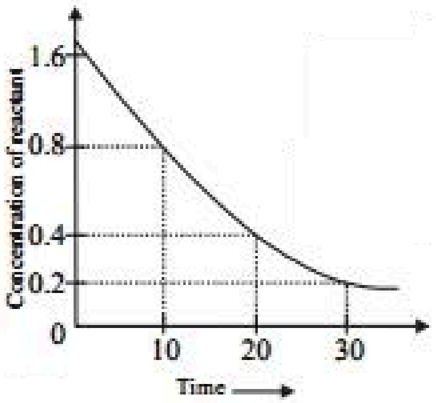
OR

State reason for each of the following
(i) CO is stronger complexing reagent than NH_3.
(ii) The molecular shape of $Ni(CO)_4$ is not the same as that of $[Ni(CN)_4]^{2-}$.

21. Identify X, Y and Z in the following sequence of reactions?

$$CH_3CH_2CH_2Br \xrightarrow{\text{Alk. KOH}} (X) \xrightarrow{H_2O/H^+} (Y) \xrightarrow{PCl_5} (Z)$$

22. Analyse the given graph, drawn between concentration of reactant vs. time.



(a) Predict the order of reaction.
(b) Theoretically, can the concentration of the reactant reduce to zero after infinite time? Explain

OR

For a reaction

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

the proposed mechanism is as given below:
(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ (fast)
    (a) Write rate law for the reaction.
    (b) Write the overall order of reaction.
    (c) Out of steps (1) and (2), which one is rate determining step?

23. (a) Mention the name of the bases produced on hydrolysis of DNA.
(b) What is an invert sugar?

24. (a) What is the composition of Fehling's reagent?
(b) Draw structure of the semicarbazone of Ethanal.

25. (a) Which metal in the first transition series (3*d* series) exhibits +1 oxidation state most frequently and why?
(b) Which of the following cations are coloured in aqueous solutions and why?
Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}
(At. nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

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. (a) Anhydrous $CaCl_2$ is not recommended as a drying agent for alcohols and amines.

(b) Why are Grignard reagents soluble in ether but not in benzene?

(c) Explain why the cleavage of aryl ethers with hydrogen halides always yield phenol and a molecule of halide and not aryl halide and alcohol.

OR

Draw the structure and name the product formed if the following alcohols are oxidised. Assume that an excess of oxidising agent is used.

(a) $CH_3CH_2CH_2CH_2OH$ (b) 2-butanol (c) 2-methyl-1-propanol

27. The following rate data were obtained at 300 K for the reaction :

$2A + B \longrightarrow C + D$

Exp. No.	[A] (mol/L)	[B] (mol/L)	Rate of formation of D (mol / L / min)
1	0.1	0.1	6×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

Determine the rate law, order and rate constant for reaction.

28. Among $Ag(NH_3)_2Cl$, $[Ni(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$, which

(a) has square planar geometry?

(b) remains colourless in aqueous solution and why?

[Ag (Z = 47), Ni (Z = 28), Cu (Z = 29)].

29. Give the plausible explanation for the following (any 3):

(a) Glucose doesn't give 2,4-DNP test.

(b) The two strands in DNA are not identical but are complementary.

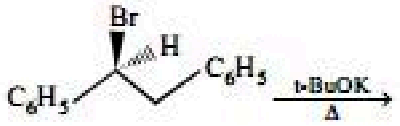
(c) Starch and cellulose both contain glucose unit as monomer, yet they are structurally different.

(d) Coagulation of protein is known as denaturing.

30. (a) Out of $(CH_3)_3C-Br$ and $(CH_3)_3C-I$, which one is more reactive towards S_N1 and why?

(b) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(c) The major product obtained in the following reaction is :



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 word "colligative" has been adapted or taken from the Latin word "colligatus" which translates to "bound together". A colligative property is a property of a solution that is dependent on the ratio between the total number of solute particles (in the solution) to the total number of solvent particles. Colligative properties are not dependent on the chemical nature of the solution's components. Dilute solution containing non-volatile solute exhibit some properties which depend only on the number of solute particles present and not on the type of solute present. These properties are called colligative properties. These properties are mostly seen in dilute solutions. There are different types of colligative properties of a solution. These include, vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure.

Answer the following questions :

(a) Name the colligative property which is used for determining the molecular weight of macromolecules. Why?

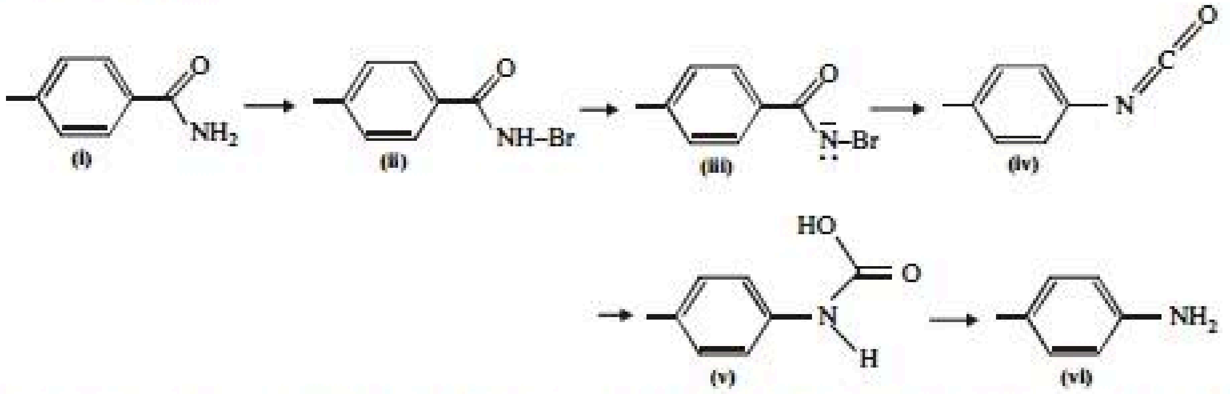
(b) What will happen to colligative properties if the solute is an electrolyte?

(c) Why colligative properties do not depend on the chemical nature of solution's components?

OR

Someone has added a non electrolyte solid to the pure liquid but forgot that among which of the two beakers he has added that solid. How can this problem be solved?

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



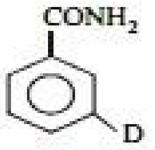
In this reaction, RCONHBr is formed from which the reaction has derived its name. Hoffmann reaction is accelerated if the migrating group is more electron-releasing. Hoffmann degradation reaction is an intramolecular reaction.

Answer the following questions :

(a) Which is the rate determining step in Hofmann bromamide degradation?

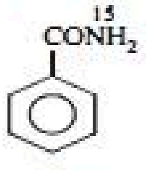
(b) Which amide can give propanamine by Hoffmann bromamide reaction?

(c) What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?



(i)

and



(ii)

OR

Which one is more basic among structure (i), (vi), (ii)?

SECTION-E

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

33. (a) Which of the following solutions has larger molar conductance?

(i) 0.10 M solution which has resistivity equal to 58 Ω cm.

(ii) 0.08 M solution having conductivity equal to $2.0 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$.

(b) Knowing that :

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s);\ E^\circ = +0.34\ V$$

$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s);\ E^\circ = +0.80\ V$$

reason out whether, 1M silver nitrate solution can be stored in copper vessel or 1M copper sulphate solution in silver vessel.

(c) How does molar conductivity of KCl vary with concentration?

OR

The following chemical reaction is occurring in an electrochemical cell.

$$Mg(s) + 2Ag^+(0.0001\ M) \longrightarrow Mg^{2+}(0.10\ M) + 2Ag(s)$$

The E$^\circ$ electrode values are:

$Mg^+/Mg = -2.36\ V$; $Ag^+/Ag = 0.81\ V$

For this cell,

(a) (i) Calculate E$^\circ$ value for the $2\ Ag^+/2\ Ag$.

(ii) Calculate standard cell potential E°_{cell}.

(b) Calculate cell potential E_{cell}.

(c) (i) Give symbolic representation of the above cell.

(ii) Will the above cell reaction be spontaneous?

34. (a) An alkene 'A' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C.

(b) Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have the same solubility in water.

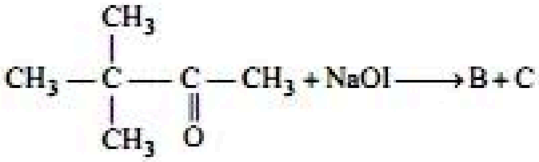
(c) There are two $-NH_2$ group in semicarbazide. However, only one is involved in the formation of semi carbazones. Give reason.

OR

(a) A compound (A), molecular formula $C_5H_{10}O$ gives a positive 2, 4-DNP test but a negative Tollen's test. It can be oxidised to carboxylic acid (B), of molecular formula $C_3H_6O_2$, when treated with alkaline $KMnO_4$ under vigorous conditions. The salt of B gives a hydrocarbon C on Kolbe's electrolytic decarboxylation. Identify A, B and C and write chemical equations of the reactions.

(b) Complete the following reactions by identifying A, B and C.

(i) $A + H_2(g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CHCHO$ (ii)



$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-CH_3 + NaOI \longrightarrow B + C$

35. (a) Which one is more basic $La(OH)_2$ or $La(OH)_3$, and why?

(b) Explain why,

(i) As we move from V to Zn in 3*d*- series we find that there is no regular variation of reduction potentials $E^\circ(M^{2+}/M)$.

(ii) Zn, Cd, Hg have low m.pt and b.pt compared to other members of transition elements.

(iii) The element chromium is very hard but mercury is a liquid.

(iv) $HgCl_2$ and $SnCl_2$ cannot exist together. Explain why.

Solutions

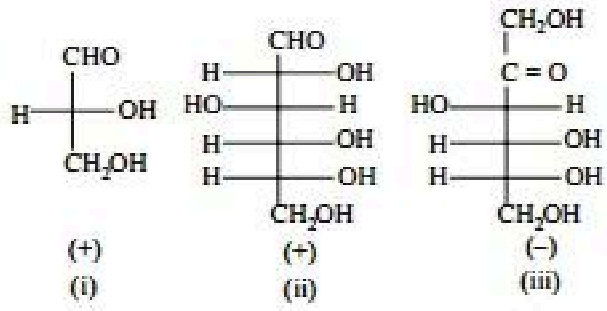
SAMPLE PAPER-9

1. **(b)** $P = P_A^\circ x_A + P_B^\circ x_B = P_B^\circ + x_A\left(P_A^\circ - P_B^\circ\right)$ $[\because x_B = 1 - x_A]$

2. **(d)** The order of reactivity of alcohol with Lucas reagent is *tert.* > *sec.* > *pri.*

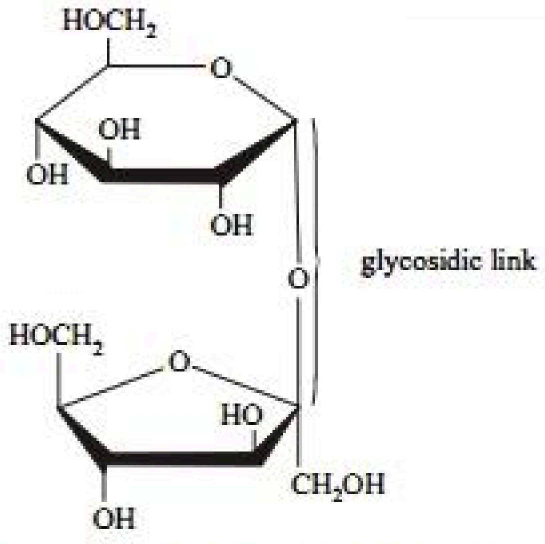
3. **(b)** The given reaction is known as Sandmeyer's reaction.

4. **(a)**



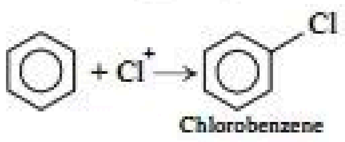
When OH on lowest asymmetric carbon is written at right hand side, it is represented as D configuration and when OH is written on left hand side, it is represented as L configuration.

*4. **(b)** Glycosidic linkage is actually an ether bond as the linkage forming the rings in an oligosaccharide or polysaccharide is not just one bond, but the two bonds sharing an oxygen atom e.g. sucrose



5. **(b)** The value of rate constant can be increased only by increasing the temperature.

6. **(b)** $AlCl_3 + Cl_2 \longrightarrow [AlCl_4]^- + Cl^+$



7. **(a)** Given: w = 10 g; Mol. mass = 40
Weight of solvent = 1250 × 0.8 g = 1000 g = 1 kg

$\therefore$ Molality $= \dfrac{10}{40 \times 1} = 0.25$

8. **(d)** $[Ma_3b_3]$ type complex shows facial and meridional isomerism.
So, the complex $[CO(NH_3)_3(NO_2)_3]$ will show fac and mer-isomers.

9. **(d)** *tert*-Alkyl halides undergo S_N1 reactions, hence they involve the formation of quite stable carbocations, and not the transition state. In S_N1 reactions, the nucleophile is not involved in rate determining (first) step, hence its stronger or weaker nature does not influence the reaction rate. In S_N1, the product has more percentage of the inverted configuration than the retained configuration, i.e. only partial racemization takes place, hence the product will be having some optical activity.

10. **(b)** $(CH_3)_3CBr + NaOC_2H_5$ can't be applied for synthesising the ether because sod. ethoxide, being a strong base, will preferentially cause elimination reaction.

$$(CH_3)_3CBr \xrightarrow{^-OC_2H_5} (CH_3)_2C = CH_2 + HBr$$

In isobutene + ethanol, isobutene will form *tert*-butyl cation which reacts with ethanol, a nucleophile to form ether.

$$(CH_3)_2C = CH_2 \xrightarrow{H^+} (CH_3)_2\overset{+}{C}CH_3$$

$$\xrightarrow[\text{(ii) } -H^+]{\text{(i) } CH_3CH_2OH} (CH_3)_3COCH_2CH_3$$

11. **(a)** Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.

12. **(a)** Highest O.S. by Mn (+7)

13. **(c)** Only aldehydes and ketones react with 2, 4-dinitrophenylhydrazine.

14. **(b)** $O_3 \xrightarrow{\text{Fast}} O_2 + O;\ O + O_3 \xrightarrow{\text{Slow}} 2O_2$

$k = \dfrac{[O_2][O]}{[O_3]}$ (I) Rate = $k'[O_3][O]$ put [O] from (I)

$$r = \frac{k'[O_3]K[O_3]}{[O_2]} = k[O_3]^2[O_2]^{-1}$$

Intermediates are never represented in rate law equation.

15. **(a)** In polar solvents, acetic acid will dissociate which loads to greater depression in freezing point. (1 mark)

16. **(c)** The correct reason is : The overall electron deficiency in *m*-nitroaniline is much less (due to –R effect of NO_2 group and +R effect of NH_2 group) than in *m*-dinitrobenzene (–R effect of the two NO_2 groups) and hence does not accept additional electrons from a weak reducing agent such as $(NH_4)_2S$ and thus further reduction is prevented. (1 mark)

17. **(d)** Br_2 water oxidized only –CHO not alcohol. Oxidation of glucose with Br_2 water produces gluconic acid. (1 mark)

18. **(a)** Benzyl cation $(C_6H_5\overset{+}{C}H_2)$ is more stable than methyl cation $(\overset{+}{C}H_3)$, so the products formed are $C_6H_5CH_2I$ and CH_3OH. (1 mark)

19. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$\Lambda^\circ_{(CH_3COOH)} = \lambda^\circ_{(CH_3COO^-)} + \lambda^\circ_{(H^+)}$$

$= 40.9 + 349.6 = 390.5$

Now degree of dissociation (α)

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ} = \frac{39.05}{390.5} = 0.1 \quad \text{(1 mark)}$$

The degree of dissociation of acitic acid is 0.1.

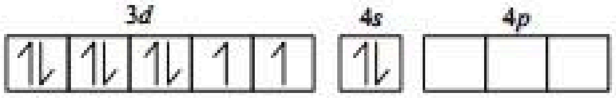
20. In $[Co(NH_3)_6]^{3+}$, Co is in + 3 oxidation state, with the configuration $3d^6$. In the presence of NH_3, 3*d* electrons pair up leaving two *d*-orbitals empty. Hence, the hybridisation is d^2sp^3 forming an inner orbital complex. (1 mark)

In $[Ni(NH_3)_6]^{2+}$, Ni is in + 2 oxidation state with the configuration $3d^8$. In presence of NH_3, the 3*d* electrons do not pair up. The hybridisation involved is sp^3d^2 forming an outer orbital complex. (1 mark)

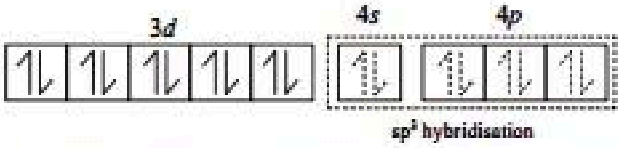
OR

(i) Since CO can form σ as well as π bond, whereas NH_3 has lone pair of electrons and can form σ bond only. Therefore, CO is better complexing reagent than NH_3. (1 mark)

(ii) Electronic configuraton of Ni in $Ni(CO)_4$:
$[Ar]\,4s^2, 3d^8$

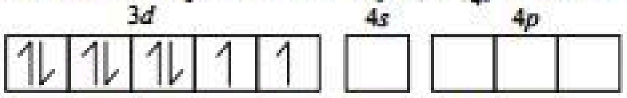


CO is a strong field ligand.



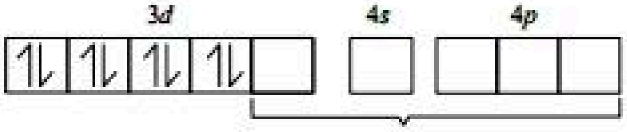
Thus $[Ni(CO)_4]$ has sp^3 hybridisation and has tetrahedral shape.

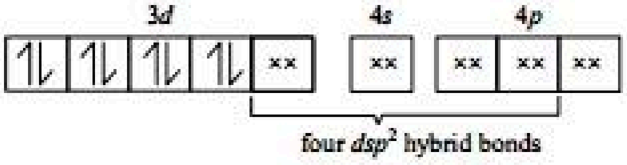
Electronic configuration of Ni in $[Ni(CN)_4]^{2-} = 3d^8\,4s^0$



the ligand involved here is strong i.e., CN^- ion.

Ni^{++} (after rearrangement)





$[Ni(CN)_4]^{2-}$ has dsp^2 hybridisation and has square planar shape. (1 mark)

21. X is $CH_3-CH=CH_2$

Y is $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$, Z is $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$

22. (a) Half-life calculation from the given graph: Concentration of reactant reduces from 0.8 to 0.4 in (20 – 10) = 10 seconds.

Again the concentration reduces to half (0.4 to 0.2) in (30 – 20) = 10 seconds.

Thus, the half-life of reaction remains constant or we can say that order of reaction is one.

(b) For a first order reaction, concentration never reduces to zero. For first order reaction $ln\,[A] = [A]_0\,e^{-kt}$ where $[A]_0$ is the initial concentration of the reactant. Mathematically, $[A] > 0$ for all $t < \infty$ (1 mark)

OR

(a) Rate law for the reaction (1 mark)
Rate $= k[H_2O_2]\,[I^-]$

(b) Order of reaction is 2. (½ mark)

(c) Step 1 is rate determining step because it is the slowest step. (½ mark)

23. (a) DNA, on hydrolysis, gives four nitrogenous bases, namely adenine, guanine, cytosine and thymine. (1 mark)

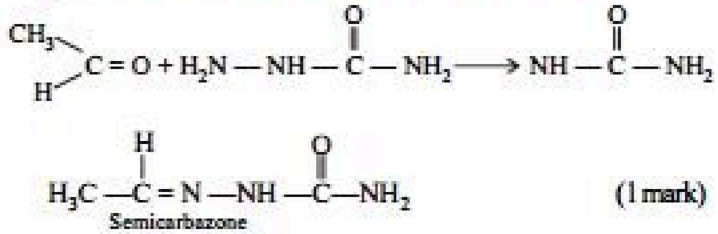
(b) An equimolar mixture of glucose and fructose is called an invert sugar. (1 mark)

24. (a) Fehling's reagent is composed by Fehling A and Fehling B. Fehling A is a blue-coloured aqueous solution of $CuSO_4$. Fehling B is colorless aqueous solution of potassium sodium tartrate ($KNaC_4H_4O_6.4H_2O$). (1 mark)

Note

Fehling reagent is used to test aldehydes. Ketones and aromatic aldehyde do not respond to Fehling's test.

(b) Structure of semicarbazone of ethanal



$$CH_3(H)C=O + H_2N-NH-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow NH-\overset{O}{\overset{\|}{C}}-NH_2$$

$$H_3C-\overset{H}{\overset{|}{C}}=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$$

Semicarbazone

(1 mark)

25. (a) Copper exhibits + 1 O.S. because after loss of one electron, it acquire $3d^{10}$ configuration and becomes fully filled and hence stable.

(b) V^{3+} ($3d^2$), Mn^{2+} ($3d^5$) ions are coloured in aqueous solution because they have unpaired electrons in *d*-subshell.

26. (a) Alcohols and amines combine with anhydrous $CaCl_2$ to form complexes. For example, with C_2H_5OH it gives a complex of molecular formula, $CaCl_2.3C_2H_5OH$. Therefore, it cannot be used as a drying agent. (1 mark)

(b) Grignard reagents form coordination complexes with ethers but not with benzene since the former has lone pairs of electrons but the latter does not. Grignard reagent and ether form a complex where Mg acts as a Lewis acid and ether act as a Lewis base. This makes Grignard reagent soluble in ether. (1 mark)

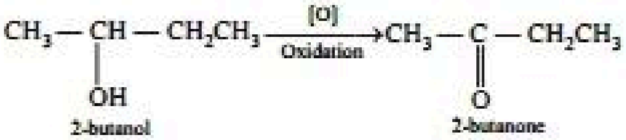
(c) This is because the nucleophile attack by the halide ion on the carbon of the benzene ring does not occur. Oxygen of ether is in resonance with ring. Also the C of ring is sterically more hindered. (1 mark)

OR

(a) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Oxidation}]{[O]} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$

(1 mark)

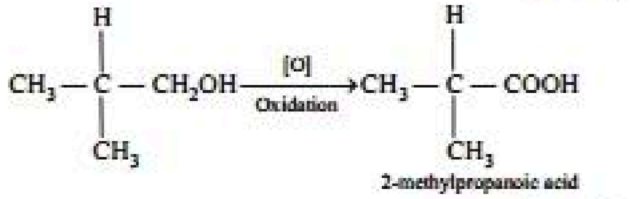
(b)



$$\underset{\text{2-butanol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_2CH_3} \xrightarrow[\text{Oxidation}]{[O]} \underset{\text{2-butanone}}{CH_3-\underset{O}{\underset{\|}{C}}-CH_2CH_3}$$

(1 mark)

(c)



$$CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH \xrightarrow[\text{Oxidation}]{[O]} \underset{\text{2-methylpropanoic acid}}{CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COOH}$$

(1 mark)

27. Rate = $k[A]^\alpha [B]^\beta$

Divide $(Rate)_1$, and $(Rate)_4$

$$\frac{(Rate)_1}{(Rate)_4} = \frac{k(0.1)^\alpha (0.1)^\beta}{k(0.4)^\alpha (0.1)^\beta}; \frac{6\times10^{-3}}{2.40\times10^{-2}} = \left(\frac{0.1}{0.4}\right)^\alpha$$

$$\frac{1}{4} = \left(\frac{1}{4}\right)^\alpha; \alpha = 1$$ (½ mark)

$$\frac{(Rate)_2}{(Rate)_3} = \frac{k(0.3)^\alpha (0.2)^\beta}{k(0.3)^\alpha (0.4)^\beta} \Rightarrow \frac{7.2\times10^{-2}}{2.88\times10^{-1}} = \left(\frac{0.2}{0.4}\right)^\beta$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^\beta; \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^\beta; \beta = 2$$ (½ mark)

Rate = $k[A]^1 [B]^2$

Order : $1 + 2 = 3$ (1 mark)

From experiment 1 :

$6 \times 10^{-3} = k(0.1)^1 (0.1)^2$

$k = 6 \times 10^{-3} / 1 \times 10^{-3} = 6\ mol^{-2}\ L^2\ min^{-1}$ (1 mark)

28. (a) $[Ni(CN)_4]^{2-}$ has square planar geometry on account of dsp^2 hybridisation. (1 mark)

(b) $[Ag(NH_3)_2]^+ Cl^-$ remains colourless in aqueous solution. The complex does not have unpaired electron in central cation, Ag^+ and thus d-d transition is not possible. Ag in + 1 oxidation state which has following electronic configuration:

The electronic configuration of $[Ag]^+$ is $[Kr]_{36}\ 4d^{10}\ 5s^0$. (2 marks)

29. (a) Aldehyde group is not free in glucose, it is involved in the formation of cyclic structure in glucose. Thus, it does not react with 2, 4-dinitrophenylhydrazine. (1 mark)

(b) The two strands in DNA are held together by hydrogen bonds between specific pair of bases (cytosine with guanine and adenine with thymine).

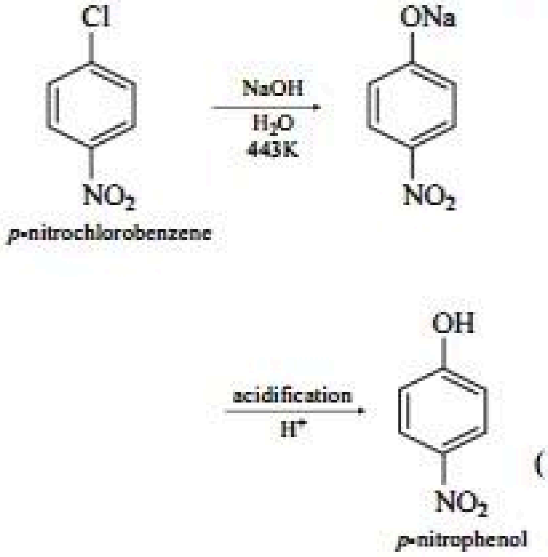
Thus, the two strands are complementary to each other. (1 mark)

(c) Starch contains α-D-glucose, while cellulose contains β-D-glucose as their monomers. (1 mark)

(d) When a protein, in its native form, is subjected to a physical change like change in temperature, or a chemical change like change in pH, the native conformation of the molecule is disrupted and proteins so formed are called **denaturated proteins**. (1 mark)

30. (a) $(CH_3)_3C—I$ is more reactive towards S_N1 than $(CH_3)_3C—Br$ because I^- is a better leaving group than Br^-. (1 mark)

(b)



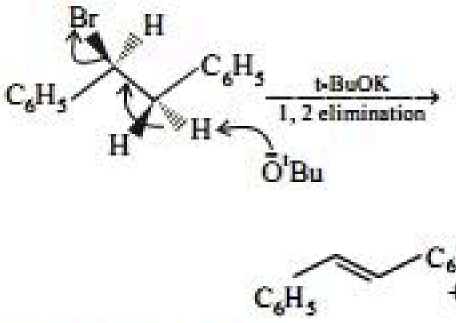
(1 mark)

(c) Elimination reaction is highly favoured if

(i) Bulkier base is used

(ii) Higher temperature is used

Hence in given reaction, biomolecular elimination reaction provides major product.



31. (a) Osmotic pressure.

Measurement of osmotic pressure is performed at room temperature and the concentration of the solution is taken in molarity. Biomolecules such as proteins are not stable at higher temperature. Therefore, osmotic pressure determination is the best method of finding out the molecular weight of macromolecules. (1 mark)

(b) Colligative properties depend on the number of solute particles. If the solute is an electrolyte then it will produce more number of particles in the solution and the magnitude of colligative property will be high. (1 mark)

(c) The rules of colligative properties obey in ideal or very dilute solutions. In these conditions, there is no interaction between particles. Hence, chemical properties do not depend on the chemical nature of solute particles. (2 marks)

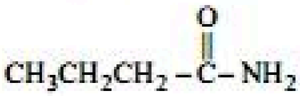
OR

By measuring the relative lowering in vapour pressure, the elevation in boiling point, the depression in freezing point, the osmotic pressure.

All these phenomena are colligative properties of solution as they are dependent on the added solute particles in solution. (2 marks)

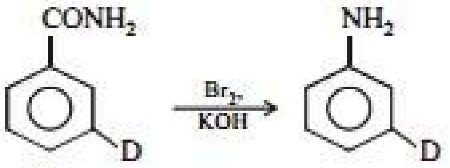
32. (a) Conversion of (iii) to (iv) involving rearrangement is the slowest step. Species (iii) is electron deficient (N has only 6 electrons), hence it has a tendency to get its octet completed by migration of alkyl group. (1 mark)

(b)

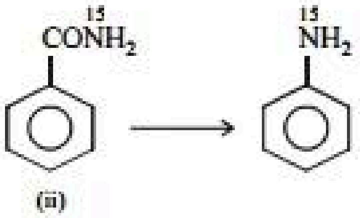


$CH_3CH_2CH_2-\overset{\overset{\large O}{\|}}{C}-NH_2$ (1 mark)

(c) Since the reaction is intramolecular, no cross product will be formed.



(i)



(ii)

OR

Amine (vi) is more basic than amide (i) because lone pair of electrons on nitrogen is in conjugation with C = O group in amides. (2 marks)

33. (a) (i) $\Lambda_m = \frac{1}{\rho}.\frac{1000}{C} = \frac{1}{58\ \Omega\ cm} \times \frac{1000\ cm^3\ L^{-1}}{0.1\ mol\ L^{-1}}$

$$= 172.4\ \Omega^{-1}\ cm^2\ mol^{-1}$$

(ii) $\Lambda_m = \kappa \dfrac{1000}{C} = \dfrac{2\times10^{-2}\,\Omega^{-1}\ \text{cm}^{-1}\times1000\,\text{cm}^3\text{L}^{-1}}{0.08\ \text{mol L}^{-1}}$

$= 250\ \Omega^{-1}\ \text{cm}^2\,\text{mol}^{-1}$ (1 mark)

Therefore, solution (ii) has larger molar conductance.

(b) A solution of an electrolyte can be stored in a particular vessel only in case there is no chemical reaction taking place with the material of the vessel.

Now if silver nitrate solution is to be kept in copper vessel, the probable reaction will be :

$$Cu\,(s) + 2\ Ag^{+}\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2Ag(s)$$

Since copper is placed below silver in the activity series, this means that it is a stronger reducing agent and can lose electrons to Ag^{+} ions and the chemical reaction will occur. Therefore, silver nitrate solution cannot be kept in copper vessel. Now, when copper sulphate solution is placed in silver vessel, the likely chemical reaction is :

$$2Ag\,(s) + Cu^{2+}\,(aq) \longrightarrow Cu\ (s) + 2Ag^{+}\,(aq)$$

Since Ag is placed above copper in the activity series, the chemical reaction will not take place. As a result, copper sulphate can be easily stored in silver vessel. (3 marks)

(c) Λ_m slightly decreases with increase in concentration of KCl. At higher concentration in strong electrolyte, there is large inter-ionic attraction. (1 mark)

OR

(a) (i) E° is an intensive property i.e., it does not depend on the amount of material in the system. Therefore, E° value for $2Ag^{+}/2Ag$ is the same as for Ag^{+}/Ag, i.e., 0.81V. (1 mark)

(ii) $E^\circ_{cell} = E_{right} - E_{left}$

$= 0.81\ V - (-2.36\ V)$

$= 3.17\ V$ (1 mark)

(b) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n}\log\dfrac{[Mg^{2+}]}{[Ag^{+}]^2}$

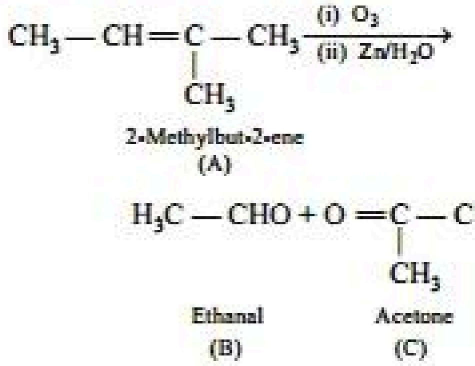
$= 3.17 - \dfrac{0.0591}{2}\log\dfrac{(0.1)}{(0.0001)^2} = 2.96\ V$

(2 marks)

(c) (i) $Mg(s)\,|\,Mg^{2+}\,(0.10\,M)\,||\,Ag^{+}\,(0.0001\,M)\,|\,Ag(s)$ (½ mark)

(ii) Yes (½ mark)

34. (a) Compound B is an aldehyde having α-H atom as it gives positive Fehling's test and also forms iodoform. Compound C should be a methyl ketone as it forms iodoform and does not give Fehling's test. The reactions involved are given as:

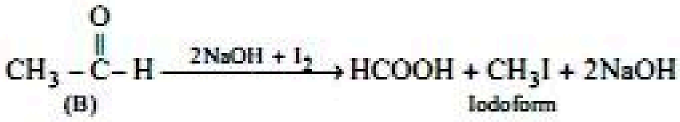


$$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} H_3C-CHO + O=\underset{\underset{CH_3}{|}}{C}-CH_3$$

2-Methylbut-2-ene (A)

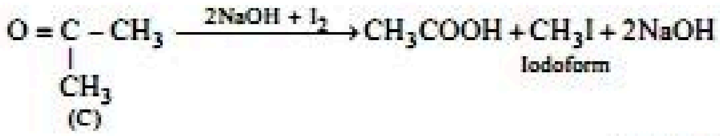
Ethanal (B) Acetone (C)

(2 marks)



$$\underset{(B)}{CH_3-\overset{\overset{O}{||}}{C}-H} \xrightarrow{2NaOH + I_2} HCOOH + \underset{\text{Iodoform}}{CH_3I} + 2NaOH$$

(½ mark)

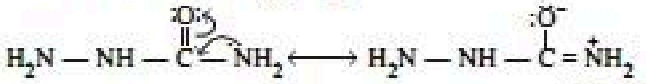


$$\underset{(C)}{O=\underset{\underset{CH_3}{|}}{C}-CH_3} \xrightarrow{2NaOH + I_2} CH_3COOH + \underset{\text{Iodoform}}{CH_3I} + 2NaOH$$

(½ mark)

(b) The boiling point of butanol is higher than that of butanal because butanol has stronger inter-molecular H-bonding while butanal has weak dipole - dipole attraction. However, both of them form H-bonds with water and hence are soluble. (1 mark)

(c) It is because the NH_2 – group closer to the carbonyl group is deactivated, i.e., resonance stabilised compared with the other end NH_2 group.

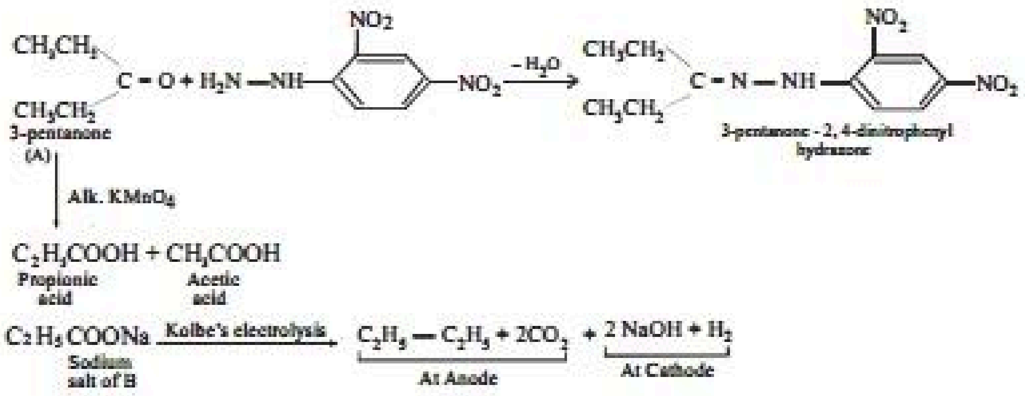


$$H_2N-NH-\overset{\overset{:\ddot{O}:}{||}}{C}-NH_2 \longleftrightarrow H_2N-NH-\overset{\overset{:\ddot{O}^-}{|}}{C}=\overset{+}{N}H_2$$

(1 mark)

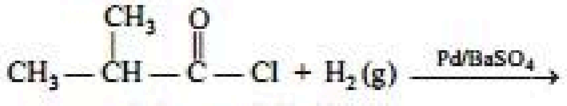
OR

(a) As the compound A gives negative Tollen's test but positive 2, 4-dinitrophenyl hydrazine test, it is a ketone (and not an aldehyde). It is further confirmed by the fact that it gives a carboxylic acid with lesser number of carbon atoms on vigorous oxidation. The sodium salt of acid (B) on electrolytic reduction gives a hydrocarbon. The reaction involved are:



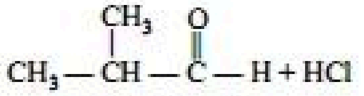
(3 marks)

(b) (i) The reaction is an example of Rosenmund's reduction in which the acid chloride is reduced to an aldehyde.



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\overset{O}{\overset{\|}{C}}-Cl + H_2(g) \xrightarrow{Pd/BaSO_4}$$

2-Methylpropanoyl chloride
[A]

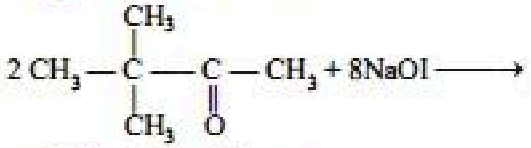


$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-H + HCl$$

2-Methylpropanal

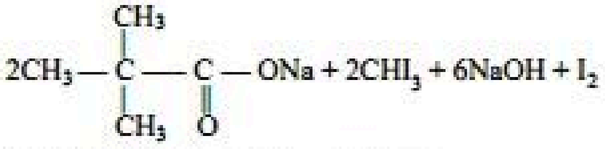
(1 mark)

(ii) This reaction is an example of iodoform reaction and proceeds as follows :



$$2\,CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-CH_3 + 8NaOI \longrightarrow$$

3,3-Dimethylbutan-2-one



$$2CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-ONa + 2CHI_3 + 6NaOH + I_2$$

Sodium-2,2-dimethylpropanoate
[B]

Iodoform
[C]

(1 mark)

35. (a) $La(OH)_2$ is more basic than $La(OH)_3$. La^{3+} has smaller size than La^{2+} and due to this $La(OH)_2$ is more ionic and so more basic than $La(OH)_3$. (1 mark)

(b) (i) Because ionisation energies ($I.E_1$ and $I.E_2$) and sublimation energies of transition metals of 3*d*-series do not exhibit any regular trend, therefore there is no regular variation of reduction potentials. (1 mark)

(ii) These metals have completely filled *d*-orbitals with no unpaired electron that may be available for covalent bonding amongst the atoms of these metals which is responsible for high m.pt and b.pt. (1 mark)

(iii) Due to six unpaired electron in *d*-orbitals ($[Ar]\,3d^5\,4s^1$) chromium possesses strong tendency of covalent bonding amongst its atoms whereas mercury has completely filled configuration ($[Xe]\,4f^{14}\,5d^{10}\,6s^2$) and have no scope for covalent bonding. (1 mark)

(iv) This is because $SnCl_2$ reduces $HgCl_2$ first to mercurous chloride (white) and then to mercury (block).

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{(White)}{Hg_2Cl_2} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{(Black)}{2Hg} + SnCl_4$$

(1 mark)