Aakash
+ BYJU'S

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Time: 3 hrs.

CHEMISTRY
Class-XII
(CBSE 2022-23)
Answers & Solutions

Max. Marks: 70

GENERAL INSTRUCTIONS

Read the following instructions very carefully and follow them:

(i) This question paper contains **35** questions. **All** questions are compulsory.

(ii) Question paper is divided into **FIVE** sections – Section **A**, **B**, **C**, **D** and **E**.

(iii) **In Section – A :** Question Numbers **1** to **18** are Multiple Choice (MCQ) type questions carrying **1** mark each.

(iv) **In Section – B :** Question Numbers **19** to **25** are Very Short Answer (VSA) type Questions carrying **2** marks each.

(v) **In Section – C :** Question Numbers **26** to **30** are Short Answer (SA) type questions carrying **3** marks each.

(vi) **In Section – D :** Question Numbers **31** and **32** are case based questions carrying **4** marks each.

(vii) **In Section – E :** Question Numbers **33** to **35** are Long Answer (LA) type questions carrying **5** marks each.

(viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section – B, 2 questions in Section – C, 2 questions in Section – D and 2 questions in Section – E.

(ix) Use of calculators is **NOT** allowed.

SECTION-A

1. Which one of the following has lowest pK_a value? [1]

(a) $CH_3 - COOH$

(b) $O_2N - CH_2 - COOH$

(c) $Cl - CH_2 - COOH$

(d) $HCOOH$

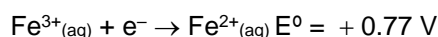**Answer (b)**

Sol. Lowest pK_a means most acidic

$NO_2 - CH_2 - COOH$ is most acidic due to $-I$ effect of NO_2

2. Which of the following cell was used in Apollo space programme? [1]

(a) Mercury cell

(b) Daniel cell

(c) H_2-O_2 Fuel cell

(d) Dry cell

Answer (c)

Sol. Alkaline fuel cell or H_2-O_2 fuel cell is used in Apollo space programme.

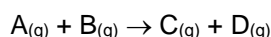**3.** Consider the following standard electrode potential values: [1]

$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ $E^0 = +0.77$ V

$MnO_4^-{}_{(aq)} + 8H^+ + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$ $E^0 = +1.51$ V

What is the cell potential for the redox reaction?

(a) -2.28 V

(b) -0.74 V

(c) $+0.74$ V

(d) $+2.28$ V

Answer (c)

Sol. $E^o_{cell} = \left(E^o_{MnO_4^-/Mn^{2+}}\right) - \left(E^o_{Fe^{3+}/Fe^{2+}}\right)$

$= 1.51 - 0.77$

$= 0.74$ V

4. The following experimental rate data were obtained for a reaction carried out at 25 °C: [1]

$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$

Initial $[A_{(g)}]$/mol dm^{-3}	Initial $[B_{(g)}]$/mol dm^{-3}	Initial rate/mol dm^{-3}s^{-1}
3.0×10^{-2}	2.0×10^{-2}	1.89×10^{-4}
3.0×10^{-2}	4.0×10^{-2}	1.89×10^{-4}
6.0×10^{-2}	4.0×10^{-2}	7.56×10^{-4}

What are the orders with respect to $A_{(g)}$ and $B_{(g)}$?

	Order with respect to $A_{(g)}$	Order with respect to $B_{(g)}$
(a)	Zero	Second
(b)	First	Zero
(c)	Second	Zero
(d)	Second	First

Answer (c)

Sol. · rate is independent of conc. of B

$$r \propto [B]^0$$

· rate becomes 4 times if we double the conc. of A

$$r \propto [A]^2$$

$\Rightarrow$ Second order w.r.t. A

$\Rightarrow$ Zero order w.r.t. B

5. The magnetic moment of $[NiCl_4]^{2-}$ [1]

    (a) 1.82 BM   (b) 2.82 BM

    (c) 4.42 BM   (d) 5.46 BM

    [Atomic number: Ni = 28]

Answer (b)

Sol. $Ni^{2+} = 4s^0\ 3d^8$

$n = 2 \Rightarrow \mu = \sqrt{(2)(2+2)} = \sqrt{8} = 2.82$ BM

6. Which of the following ions has the electronic configuration $3d^6$? (Atomic number: Mn = 25, Co = 27, Ni = 28)

                                                                          [1]

    (a) Ni^{3+} (b) Co^{3+}

    (c) Mn^{2+} (d) Mn^{3+}

Answer (b)

Sol. $Co_{27} = 4s^2\ 3d^7$

    $Co^{3+} = 4s^0\ 3d^6$

7. Which of the following aqueous solution will have highest boiling point?   [1]

    (a) 1.0 M KCl   (b) 1.0 M K_2SO_4
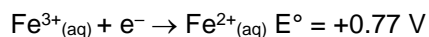
    (c) 2.0 M KCl   (d) 2.0 M K_2SO_4

Answer (d)

Sol. $\Delta T_b \propto (i)(m)$

    Value of (i) = 3 for K_2SO_4

    Value of (i)(m) is maximum for 2 M K_2SO_4

8. A voltaic cell is made by connecting two half cells represented by half equations below: [1]

    $Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E° = -0.14$ V

    $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ $E° = +0.77$ V

    Which statement is correct about this voltaic cell?
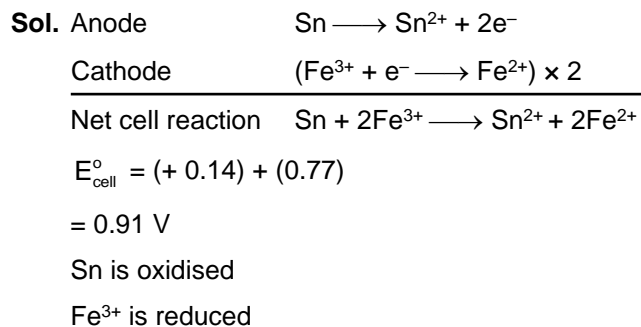
    (a) Fe^{2+} is oxidised and the voltage of the cell is -0.91 V

    (b) Sn is oxidised and the voltage of the cell is 0.91 V

    (c) Fe^{2+} is oxidised and the voltage of the cell is 0.91 V

    (d) Sn is oxidised and the voltage of the cell is 0.63 V
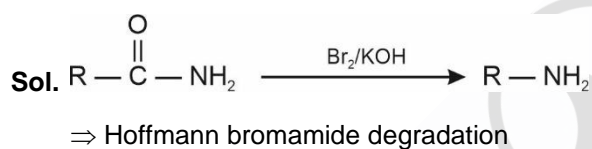
Answer (b)

Sol. Anode $\qquad$ $Sn \longrightarrow Sn^{2+} + 2e^-$

Cathode $\qquad$ $(Fe^{3+} + e^- \longrightarrow Fe^{2+}) \times 2$

_____

Net cell reaction $\qquad$ $Sn + 2Fe^{3+} \longrightarrow Sn^{2+} + 2Fe^{2+}$

$E^o_{cell} = (+ 0.14) + (0.77)$

$= 0.91\ V$

Sn is oxidised

Fe^{3+} is reduced

9. Amides can be converted into amines by the reaction named [1]

(a) Hoffmann degradation

(b) Ammonolysis

(c) Carbylamine

(d) Diazotisation

Answer (a)

Sol.
$$R - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - NH_2 \xrightarrow{Br_2/KOH} R - NH_2$$

$\Rightarrow$ Hoffmann bromamide degradation

10. Which of the following statements is not true about glucose? [1]

(a) It is an aldohexose

(b) On heating with HI it forms n-hexane

(c) It is present in pyranose form

(d) It gives 2, 4 DNP test

Answer (d)

Sol. Glucose doesn't give 2, 4 – DNP test because glucose exists in cyclic hemiacetal form with only a small amount of the open chain form in equilibrium.

11. Which of the following alcohols will not undergo oxidation? [1]

(a) Butanol

(b) Butan-2-ol

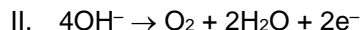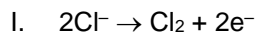(c) 2-Methylbutan-2-ol

(d) 3-Methylbutan-2-ol

Answer (c)

Sol. 3° alcohols do not undergo oxidation, 2-methyl butan-2-ol is

$$CH_3 - \overset{\overset{\displaystyle OH}{\displaystyle |}}{\underset{\underset{\displaystyle CH_3}{\displaystyle |}}{C}} - CH_2 - CH_3$$
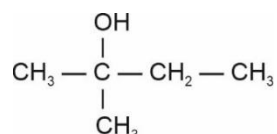
which is 3° alcohol

12. Four half reactions I to IV are shown below: [1]

I. $2Cl^- \rightarrow Cl_2 + 2e^-$

II. $4OH^- \rightarrow O_2 + 2H_2O + 2e^-$

III. $Na^+ + e^- \rightarrow Na$

IV. $2H^+ + 2e^- \rightarrow H_2$
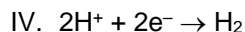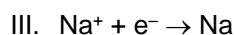
Which two of these reactions are most likely to occur when concentrated brine is electrolysed?

(a) I and III

(b) I and IV

(c) II and III

(d) II and IV

Answer (b)

Sol. Anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode $2H^+ + 2e^- \longrightarrow H_2$
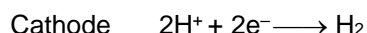
$E°$ for $Na^+ + e^- \longrightarrow Na$ is Highly –ve and hence doesn't occur on cathode so I & IV occurs.

13. Which property of transition metals enables them to behave as catalysts ? [1]

(a) High melting point

(b) High ionisation enthalpy

(c) Alloy formation

(d) Variable oxidation states

Answer (d)

Sol. Due to variable oxidation state, transition elements can act as catalysts.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$
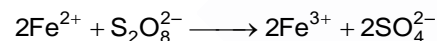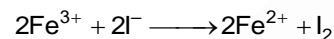
14. Which of the following would not be a good choice for reducing nitrobenzene to aniline ? [1]
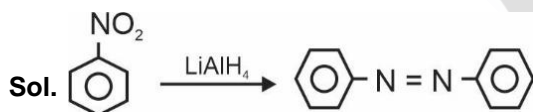
(a) LiAlH$_4$

(b) H$_2$/Ni

(c) Fe and HCl

(d) Sn and HCl

Answer (a)

Sol.

For questions number **15** to **18**, two statements are given – one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below :

(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is true, but Reason (R) is false.

(d) Assertion (A) is false, but Reason (R) is true.

15. Assertion (A) : Vitamin C cannot be stored in our body. [1]

Reason (R) : Vitamin C is fat soluble and is excreted from the body in urine,.

Answer (c)

Sol. Vitamin C is water soluble and hence is excreted from body in urine.

$\Rightarrow$ Assertion is true

$\Rightarrow$ Reason is false

16. **Assertion (A) :** The half life of a reaction is the time in which the concentration of the reactant is reduced to one half of its initial concentration. [1]

    Reason (R) : In first order kinetics when concentration of reactant is doubled, its half life is doubled.

Answer (c)

Sol. For first order reaction

$t_{1/2} = \dfrac{.693}{K}$ (Independent of Co)

$\Rightarrow$ Assertion is true

$\Rightarrow$ Reason is false

17. **Assertion (A) :** Bromination of benzoic acid gives m-bromobenzoic acid. [1]

    Reason (R) : Carboxyl group increases the electron density at the meta position.

Answer (c)

Sol. Carboxyl group decreases electron density from ortho/para position and hence electrophile attacks on meta position

$\Rightarrow$ Assertion is true

$\Rightarrow$ Reason is false

18. **Assertion (A) :** EDTA is a hexadentate ligand. [1]

    Reason (R) : EDTA has 2 nitrogen and 4 oxygen donor atoms.

Answer (a)

Sol. EDTA =
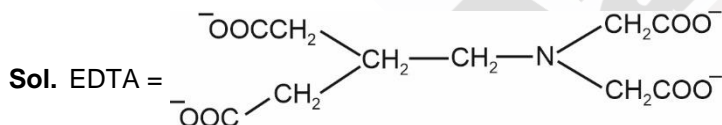
EDTA is hexadentate due to 2N and 4O atoms

$\Rightarrow$ Assertion and Reason are true and Reason is correct explanation of Assertion

SECTION-B

19. **(a)** Which of the following species cannot act as a ligand? Given reason. [2 × 1 = 2]

    $OH^-, NH_4^+, CH_3NH_2, H_2O$
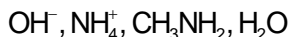
    (b) The complex $[Co(NH_3)_5(NO_2)]Cl_2$ is red in colour. Give IUPAC name of its linkage isomer.

Sol. (a) NH_4^+ cannot act as ligand because of the unavailability of lone pair of electrons.

   (b) Linkage isomer of $[Co(NH_3)_5(NO_2)]Cl_2$ is $[Co(NH_3)_5(ONO)]Cl_2$.
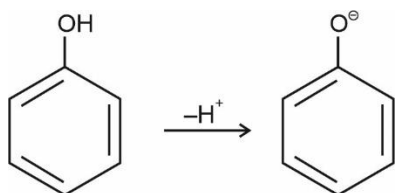
   Oxidation sate of Co = +3

   IUPAC: Triamminenitrito-O-cobalt (III) chloride.

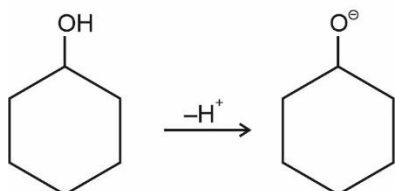**20.** For the pair phenol and cyclohexanol, answer the following: [2 × 1 = 2]

   (a) Why is phenol more acidic than cyclohexanol?

   (b) Give one chemical test to distinguish between the two.

Sol. (a)

Phenol

In case of phenol, after loss of H⁺ phenoxide ion is formed which is resonance stabilised. Whereas is case of cyclohexanol, the O⁻ formed is not stabilised by resonance.

   (b) $FeCl_3$ can be used to distinguish the two. Phenol forms a violet colour complex with $FeCl_3$ whereas cyclohexanol doesn't.

21. (a) (i) Draw the zwitter ion structure for sulphanilic acid. [2 × 1 = 2]

   (ii) How can the activating effect of –NH_2 group in aniline be controlled?

OR

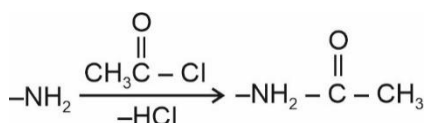   **(b) (i)** Complete the reaction with the main product formed: [2 × 1 = 2]
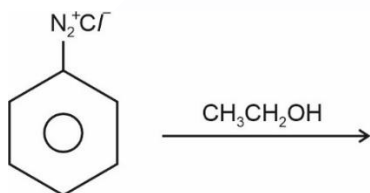
   (ii) Convert Bromoethane to Propanamine.
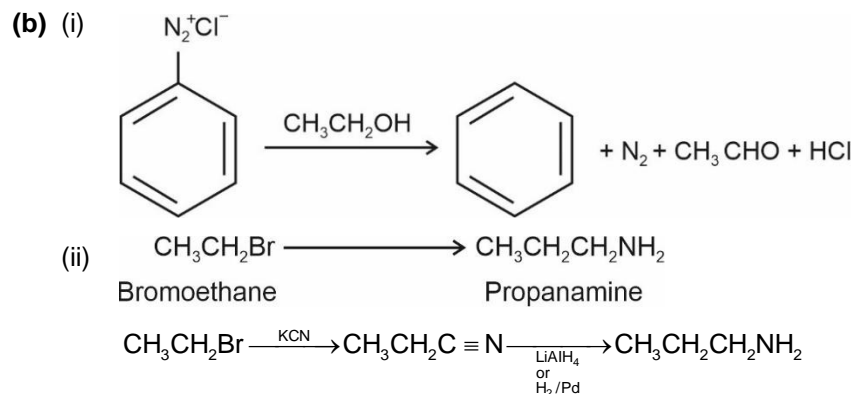
Sol. (a) (i)
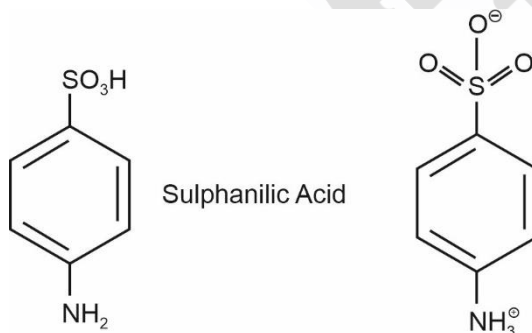
Sulphanilic Acid

The Zwitter ion form of sulphanilic acid is containing equal number of negative and positive charges

   (ii) –NH_2 has strong activating effect. To control the effect, acetylation of the group is done to convert it from a strong activating group to a moderate activating group.
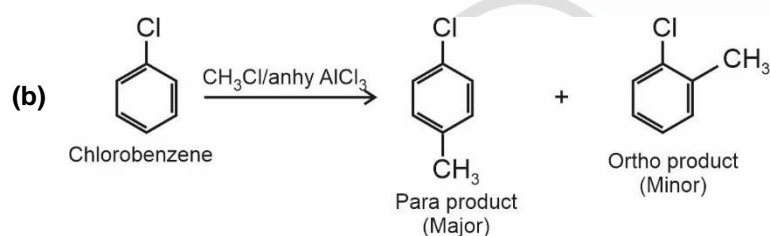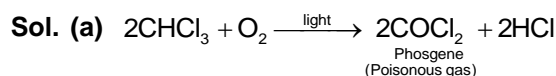
OR

(b) (i)

(ii) $CH_3CH_2Br \longrightarrow CH_3CH_2CH_2NH_2$

      Bromoethane   Propanamine

$$CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2C \equiv N \xrightarrow[\substack{or \\ H_2/Pd}]{LiAlH_4} CH_3CH_2CH_2NH_2$$

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22. Write equations for the following :   [2 × 1 = 2]

    (a) Oxidation of chloroform by air and light

    (b) Reaction of chlorobenzene with CH_3Cl/anhyd. $AlCl_3$

Sol. (a) $2CHCl_3 + O_2 \xrightarrow{light} 2COCl_2 + 2HCl$

                              Phosgene
                         (Poisonous gas)

(b)

23. What happens to the rate constant k and activation energy E_a as the temperature of a chemical reaction is increased? Justify.   [2]

Sol. Temperature dependence of rate constants is described by Arrhenius Equation.

$k = Ae^{-E_a/RT}$

E_a corresponds to activation energy, A corresponds to collision frequency

Rate = k[Conc]^x

Rate of reaction increases 2 to 3 times for every 10° rise in temperature.

The reason being that on increasing the temperature the fraction of molecules crossing the energy barrier increases.
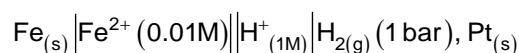
So, k increases as temperature increases.

    E_a remains constant as temperature increases.

24. (a) (i) What should be the signs (positive/negative) for E^o_{Cell} and ΔG^o for a spontaneous redox reaction occurring under standard conditions?

        (ii) State Faraday's first law of electrolysis.   [2 × 1 = 2]

OR

    (b) Calculate the emf of the following cell at 298 K: [2]

        $Fe_{(s)} \mid Fe^{2+}(0.01M) \parallel H^+_{(1M)} \mid H_{2(g)}(1\,bar), Pt_{(s)}$

        Given $E^o_{Cell} = 0.44\,V$.

Sol. (a) (i) For spontaneous redox reaction, ΔG^o is negative.

$\Delta G^o = -nFE^o_{Cell}$

∴ E^o_{Cell} for the spontaneous redox reaction is positive.
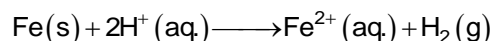
(ii) <u>Faraday's first law of Electrolysis</u>

The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt)

OR

(b) $Fe_{(s)}\left|Fe^{2+}(0.01M)\right|\left|H^+_{(1M)}\right|H_{2(g)}(1\,bar), Pt_{(s)}$

$E^o_{Cell} = 0.44$ V

$Fe(s) + 2H^+(aq.) \longrightarrow Fe^{2+}(aq.) + H_2(g)$

$E_{Cell} = E^o_{Cell} - \dfrac{RT}{nF}\ln\dfrac{\left[Fe^{2+}\right]P_{H_2}}{\left[H^+\right]^2}$

$= 0.44 - \dfrac{2.303 \times 8.314 \times 298}{2 \times 96485}\log\dfrac{\left(10^{-2}\right)(1)}{1^2}$

$= 0.44 - 0.03(-2)\log 10$

$= 0.44 + 0.06$

$= 0.50$ V

25. Give the reaction of glucose with acetic anhydride. Presence of which group is confirmed by this reaction? [2]

Sol.
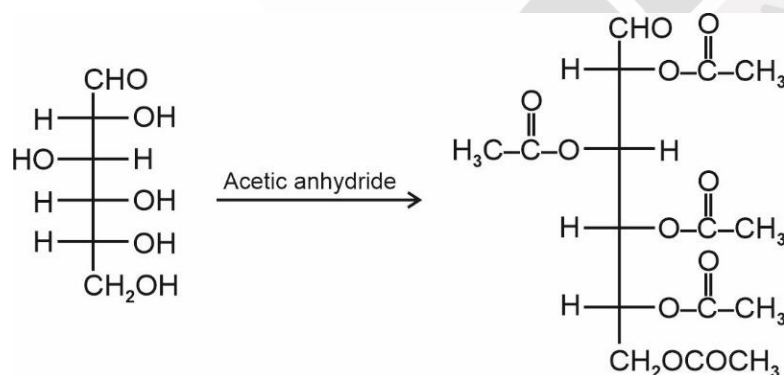
In above reaction, glucose pentaacetate is formed which confirms the presence of five –OH groups. Since the formed compound is stable, it means the five –OH groups should be attached with different carbons atoms.

SECTION-C

26. (a) (i) Why is the C – O bond length in phenols less than that in methanol? [3 × 1 = 3]

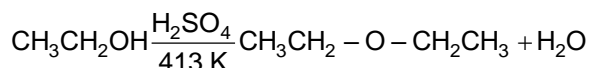**(ii)** Arrange the following in order of increasing boiling point :

Ethoxyethane, Butanal, Butanol, n-butane

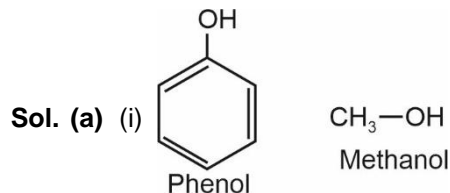**(iii)** How can phenol be prepared from anisole? Give reaction.

OR

(b) (i) Give mechanism of the following reaction: [2 + 1 = 3]

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} CH_3CH_2 - O - CH_2CH_3 + H_2O$$

(ii) Illustrate hydroboration-oxidation reaction with an example.

Sol. (a) (i)
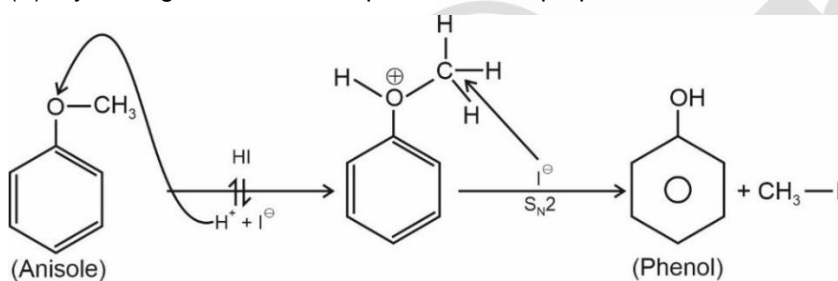
OH

Phenol

$CH_3 - OH$

Methanol

In phenol oxygen shows resonance with benzene ring so it acquires double bond character.

∴ It's bond length decreases, whereas in methanol C – O bond is perfect single bond
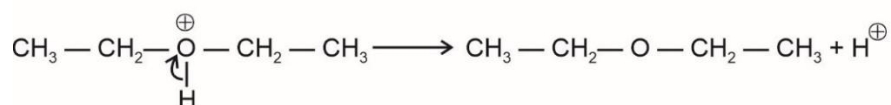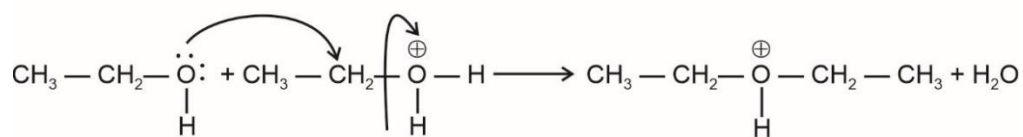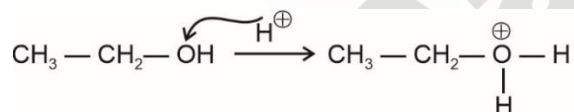
(ii) Correct decreasing order of boiling point is

Butanol > Butanal > Ethoxyethane > n-butane

(iii) By adding HI into anisole, phenol can be prepared as:

(Anisole)   (Phenol) $+ CH_3 - I$
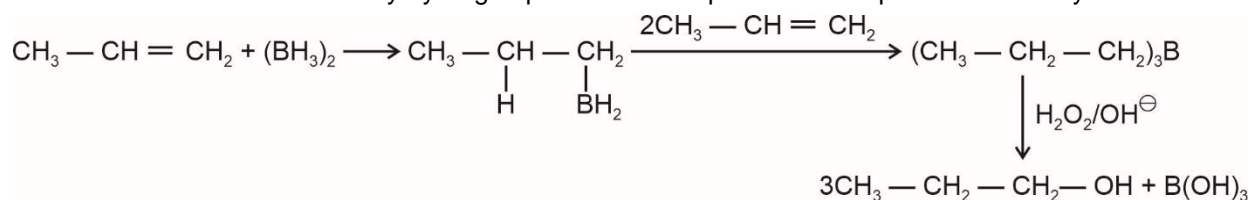
OR

(b) (i) The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as below

(ii) Hydroboration-oxidation: Diborane $(BH_3)_2$ reacts with alkenes to give trialkylboranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

27. (a) On the basis of crystal field theory write the electronic configuration for d^5 ion with a weak ligand for which $\Delta_0 < P$. [1 + 2 = 3]

(b) Explain $[Fe(CN)_6]^{3-}$ is an inner orbital complex whereas $[FeF_6]^{3-}$ is an outer orbital complex.
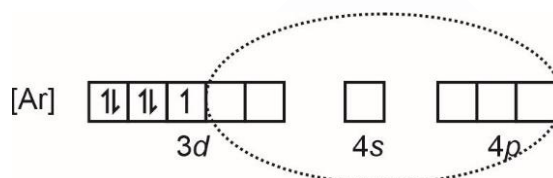
[Atomic number : Fe = 26]

Sol. (a) The electronic configuration for d^5 in weak field ligand will be:

$$t_{2g}^3 , eg^2$$

Because of less energy gap there will be no pairing of electrons

or we can say : $\underbrace{3d_{xy}{}^1, 3d_{xz}{}^1, 3d_{y^2}{}^1}_{t_{2g}}, \underbrace{\lambda_{x^2y^2}{}^1, 3d_{z^2}{}^1}_{eg}$

(b) In complex $[Fe(CN)_6]^{3-}$, Fe has +3 oxidation state and $[Ar]3d^5$ electronic configuration and CN^- are strong field ligand so pairing will takes place

∴ It will form d^2sp^3 hybridisation and inner-orbital complex

In complex $[FeF_6]^{3-}$, F^- are weak field ligands therefore they can not pair up the electrons.
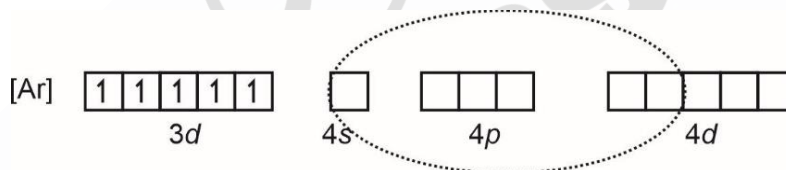
So, here outer d-orbitals are involved in hybridisation (sp^3d^2)

Therefore, it will be the outer orbital complex.

28. Give reasons for any 3 of the following observation: [3 × 1 = 3]

(a) Penta-acetate of glucose does not react with hydroxylamine.

(b) Amino acids behave like salts.

(c) Water soluble vitamins must be taken regularly in diet.

(d) The two strands in DNA are complimentary to each other.

Sol. (a) The penta-acetate of glucose does not react with hydroxylamine because it does not contain free –CHO group.

(b) Amino acids has both acidic and basic part into it. So because of proton transfer from acidic site to basic site it acquires anionic and cationic part and behaves as salts.

(c) Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored in our body.

(d) The two strands in DNA are complementary to each other because the hydrogen bonds are formed between specific pairs of base. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.
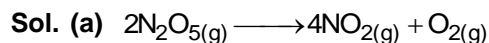
29. **(a)** For the reaction   [1 + 2 = 3]

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)} \text{ at } 318K$$
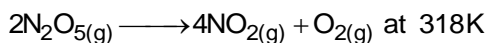
calculate the rate of reaction if rate of disappearance of $N_2O_5(g)$ is 1.4×10^{-3} m s^{-1}

(b) For a first order reaction derive the relationship $t_{99\%} = 2t_{90\%}$

Sol. (a) $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

Rate of disappearance of N_2O_5 is = 1.4×10^{-3} m s^{-1}

The relation between rate of reaction and rate of disappearance of N_2O_5 is

$$ROR = \frac{(ROD)_{N_2O_5}}{2}$$

$\therefore$ Rate of reaction (ROR) = $\dfrac{1.4 \times 10^{-3}}{2} = 7 \times 10^{-4}$ m s^{-1}

(b) For 1st order reaction $k.t = \ln\left(\dfrac{a_0}{a_t}\right)$

For t_{99}, if $a_0 = 100$ then $a_t = 1$

$\therefore \quad t_{99} = \dfrac{1}{k}\ln\left(\dfrac{100}{1}\right)$ ...(1)

For t_{90}, if $a_0 = 100$ then $a_t = 10$

$\therefore \quad t_{90} = \dfrac{1}{k}\ln\left(\dfrac{100}{10}\right)$ ...(2)

On dividing (1) ÷ (2)

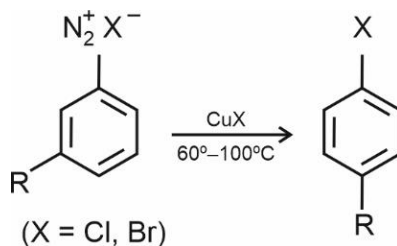$$\frac{t_{99}}{t_{90}} = 2$$

$\therefore \quad t_{99} = 2t_{90}$

30. **(a)** Illustrate Sandmeyer's reaction with an equation.   [1 + 2 = 3]

(b) Explain, why $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in aqueous solution.

Sol. (a) Sandmeyer's reaction:- Sandmeyer reaction is a type of substitution reaction that is widely used in the production of aryl halides from aryl diazonium salts.
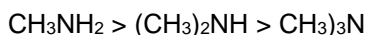

(X = Cl, Br)

**(b)** Basicity of 1º, 2º and 3º amines is decided by the factors which are given as:

(1) **+I effect of alkyl group:** Due to +I effect of alkyl groups, the basicity order of amines will be

$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
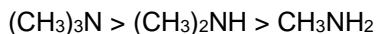
(2) **Solvation effect:** Due to solvation effect the order of basic strength will be

$CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

(3) **Steric factor:** More the steric hindrance, less will be the basicity of amine in general. Therefore the order will be

1º > 2º > 3º amines.
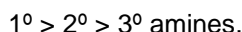
Since two factors favours 2º amines for making it more basic than 3º amine

Hence $(CH_3)_2NH$ will be more basic than $(CH_3)_3N$.

SECTION-D

The following questions are case-based questions. Read the passage carefully and answer the questions that follow:

31. Rahul set-up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity K and molar conductivity $\wedge_m$ and recorded his readings in tabular form.

S. No.	Conc. (M)	k S cm^{-1}	$\wedge_m$ S cm^2 mol^{-1}
1.	1.00	111.3×10^{-3}	111.3
2.	0.10	12.9×10^{-3}	129.0
3.	0.01	1.41×10^{-3}	141.0

Answer the following questions :

(a) Why does conductivity decrease with dilution? [1]

(b) If $\wedge_m°$ of KCl is 150.0 S cm^2 mol^{-1}, calculate the degree of dissociation of 0.01 M KCl. [1]

(c) If Rahul had used HCl instead of KCl then would you expect the $\wedge_m$ values to be more or less than those per KCl for a given concentration. Justify. [2 × 1]

OR

(c) Amit a classmate of Rahul repeated the same experiment with CH_3COOH solution instead of KCl solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul. [2 × 1]

Sol. (a) Conductivity of a solution is defined as the conductance of ions present in a unit volume of the solution.

When the solution is diluted, the no. of ions (responsible for carrying current) decreases in unit volume. Hence, conductivity decreases with dilution.

(b) As, $\alpha = \dfrac{\Lambda}{\Lambda°}$

$\Lambda_m = 141.0$ S cm^2 mol^{-1} $\Lambda° = 150$ S cm^2 mol^{-1}

$\therefore \ \alpha = \dfrac{141}{150} = 0.94 = 94\%$

(c) If Rahul had used HCl instead of KCl, we would expect $\wedge_m$ values to be more than those from KCl solution. Because mobility of H^+ ions is very high as compared to K^+ ions

OR

(c) For CH_3COOH and KCl solution

Similar – • Cell constant for cell

• Concentration of electrolyte

Different – • Resistance

• Resistivity

• Conductivity

• Molar conductivity

32. Nucleophilic Substitution

Nucleophilic Substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. S_N1 is a two step reaction while S_N2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent.

Influences of solvent polarity : In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane at 25°C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both S_N1 and S_N2 reaction, but with different results. Generally speaking weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1. Generally speaking the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example ethanol containing water).

Answer the following questions :

(a) Why racemisation occurs in S_N1 ? [1]

(b) Why is ethanol less polar than water ? [1]

(c) Which one of the following in each pair is more reactive towards S_N2 reaction ?

(i) $CH_3 — CH_2 — I$ or $CH_3CH_2 — Cl$

(II)   [2 x 1]

OR

**(c)** Arrange the following in the increasing order of their reactivity towards S_N1 reactions :
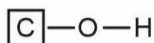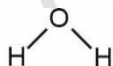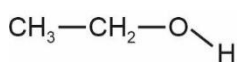
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane [2 x 1]

Sol. (a) In S_N1 reaction, carbocation intermediate formed is a planar specie (sp^2 hybridised). Therefore, attack of nucleophile can occur from both front and back side with same ease, giving racemic mixture

Example:
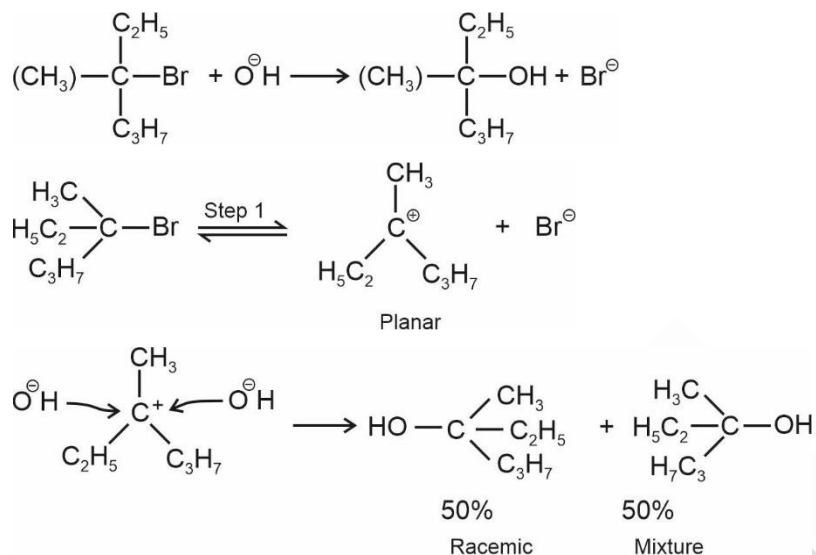
(b) Ethanol is less polar than water as O is attached to two hydrogen atoms in case of water and O is attached to one hydrogen atom and one carbon atom. Electronegativity of carbon atom is more than that of hydrogen atom making it less polar.
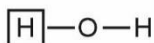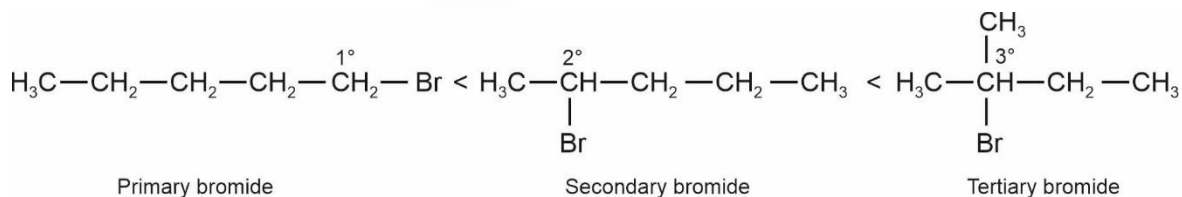

(c) (i) $CH_3 — CH_2 — I$ is more reactive than $CH_3 — CH_2 — Cl$ towards S_N2 reaction because $I^\ominus$ is a good leaving group as compared to Cl^- because of its large size.

(ii)

 is more reactive than towards S_N2 reaction because it is primary halide (less sterically hindered)

OR

(c) (i) Order of reactivity towards S_N1 reaction is 1-Bromopentane < 2-Bromopentane < 2-Bromo-2-methylbutane

Carbocation intermediate formed during S_N1 in case of 2-Bromo-2-methyl butane is more stable (3° carbocation formed) than 2-Bromopentane in which 2° carbonation is formed and 1-bromopentane is least reactive due to formation of less stable 1° carbocation.
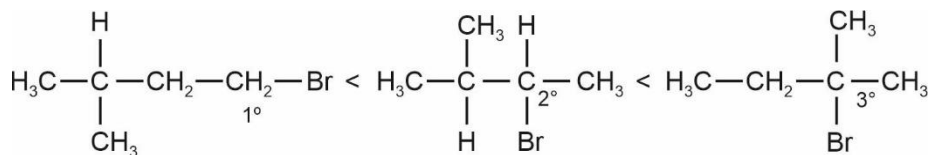
(ii) Order of reactivity is governed by stability of carbocation formed is step 1 in S_N1 reaction.

Stability of alkyl carbocations is

3° > 2° > 1°
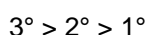
∴ Order of reactivity is

1-Bromo-3-methylbutane < 2-Bromo-3-methylbutane < 2-Bromo-2-methylbutane

SECTION-E

33. (a) (i) Write the reaction involved in Cannizzaro's reaction. [1 + 1 + 3 = 5]

(ii) Why are the boiling point of aldehydes and ketones lower than that of corresponding carboxylic acids?

(iii) An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to n-pentane with hydrazine followed by heating with NaOH and Glycol. 'A' forms a dioxime with hydroxylamine and gives a positive Iodoform and Tollen's test. Identify 'A' and give its reaction for Iodoform and Tollen's test.

OR

(b) (i) Give a chemical test to distinguish between ethanal and ethanoic acid. [1 + 1 + 3 = 5]

(ii) Why is the α-hydrogens of aldehydes and ketones are acidic in nature?

(iii) An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of 'C' with acidified potassium permanganate also produces 'B'. Sodium salt of 'B' on heating with soda lime gives methane.

(1) Identify 'A', 'B' and 'C'.

(2) Out of 'B' and 'C', which will have higher boiling point?

Give reason.

Sol. (a) (i) Cannizzaro's reaction :
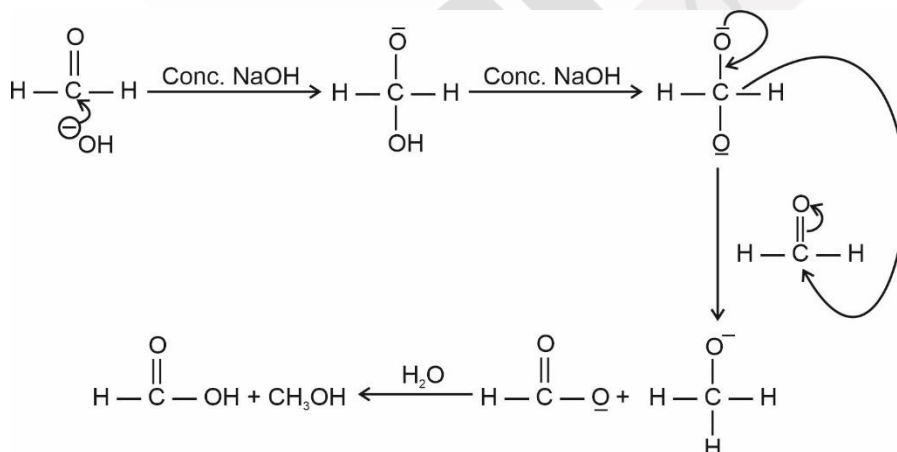
(ii) Aldehydes and ketones and corresponding carboxylic acids all are polar compounds but due to intermolecular hydrogen bonding in carboxylic acids, their boiling points are relatively higher than aldehydes and ketones.

(iii) DBE for the given compound with molecular formula $C_5H_8O_2$ will be 2 as per the following formula.

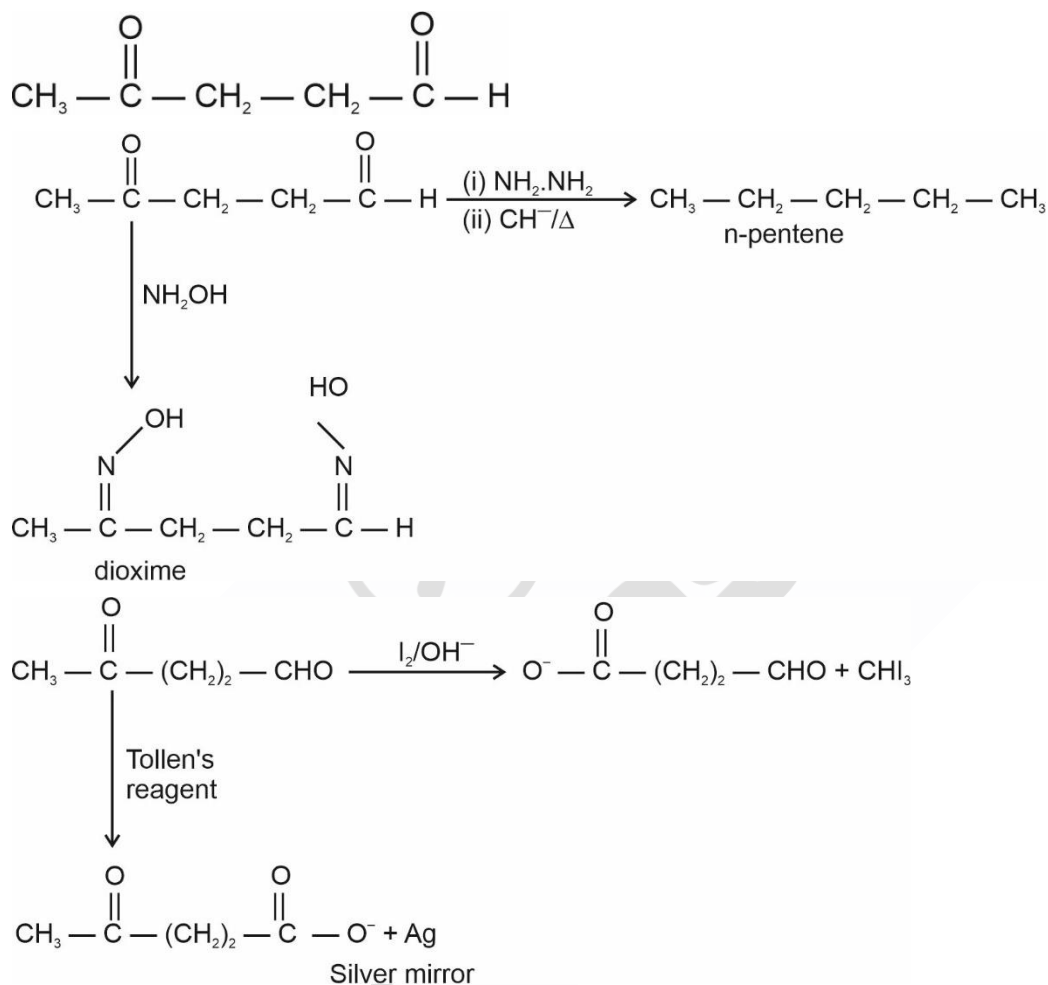DBE (Double bond equivalent) = $C - \dfrac{H}{2} + 1 = 5 - \dfrac{8}{2} + 1 = 2$

Since DBE of the given compound is 2, it will have either two double bonds or one triple bond.

Now, the given compound is reduced to n-pentane with hydrazine followed by heating with NaOH and Glycol, it means it is having carbonyl group.
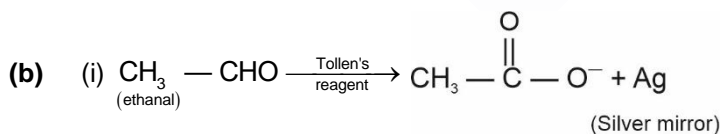
Also the given compound forms a dioxime with hydroxyl amine, it will have two carbonyl group.

Since the compound gives positive iodoform test and tollen's test, it must have one keto group and another aldehyde group.
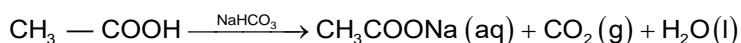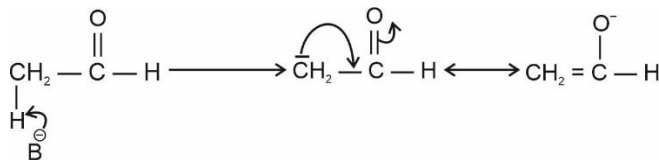
The given compound should have the structure

OR

(b) (i) $CH_3 - CHO \xrightarrow[\text{reagent}]{\text{Tollen's}} CH_3 - \overset{\overset{O}{\|}}{C} - O^- + Ag$ (Silver mirror)

(ethanal)

Carboxylic acids give briskeffervescence with sodium bicarbonate.

$CH_3 - COOH \xrightarrow{NaHCO_3} CH_3COONa\,(aq) + CO_2\,(g) + H_2O\,(l)$
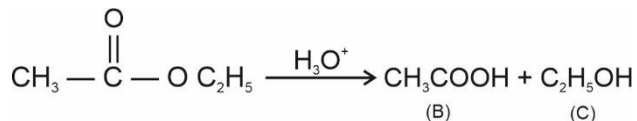
(ii) Aldehydes and ketones are acidic in nature because their conjugate base are resonance stabilized.

(iii) Compound A should be

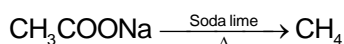$$CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - O + C_2H_5$$
(A)
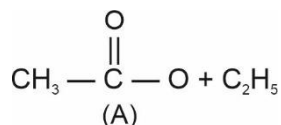
A undergoes acid hydrolysis to form acetic acid and ethanol as follows

$$CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - O\,C_2H_5 \xrightarrow{\;H_3O^+\;} \underset{(B)}{CH_3COOH} + \underset{(C)}{C_2H_5OH}$$

Ethanol on oxidation with acidified potassium permanganate gives acetic acid

$$C_2H_5OH \xrightarrow{\;KMnO_4/H^+\;} CH_3COOH$$
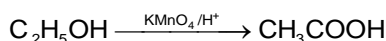
Sodium salt of B i.e. CH_3COONa gives methane on heating with soda lime as follows

$$CH_3COONa \xrightarrow[\Delta]{\;Soda\ lime\;} CH_4$$

Boiling point of acetic acid (B) is 118°C whereas that of ethanol (C) is 78°C. This is because acetic acid has intermolecular hydrogen bonding.

34. **(a)** (i) Why is boiling point of 1 M NaCl solution more than that of 1 M glucose solution? [1 + 2 + 2 = 5]

(ii) A non-volatile solute 'X' (molar mass = 50 g mol^{-1}) when dissolved in 78 g of benzene reduced its vapour pressure to 90%. Calculate the mass of X dissolved in the solution.

(iii) Calculate the boiling point elevation for a solution prepared by adding 10 g of $MgCl_2$ to 200 g of water assuming $MgCl_2$ is completely dissociated.

(K_b for Water = 0.512 K kg mol^{-1}, Molar mass $MgCl_2$ = 95 g mol^{-1})

OR

(b) (i) Why is the value of van't Hoff factor for ethanoic acid in benzene close to 0.5? [1 + 2 + 2 = 5]

(ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32×10^{-2} g of K_2SO_4 in 2 L of solution at 25°C, assuming that K_2SO_4 is completely dissociated.

(R = 0.082 L atm K^{-1} mol^{-1}, Molar mass K_2SO_4 = 174 g mol^{-1})

(iii) When 25.6 g of sulphur was dissolved in 1000 g of benzene, the freezing point lowered by 0.512 K. Calculate the formula of Sulphur (S_x).

(K_f for benzene 5.12 K kg mol^{-1}, Atomic mass of Sulphur = 32 g mol^{-1})

Sol. **(a)** (i) Boiling point of 1 M NaCl solution is more than that 1 M glucose solution because van't Hoff factor i = 1 for glucose and i = 2 for NaCl (assuming complete ionisation)

(ii) Let W gm of solute X is dissolved in 78 g of benzene.

Mole fraction of solute X = $\dfrac{\dfrac{W}{50}}{\dfrac{W}{50} + \dfrac{78}{78}} = \dfrac{W}{W + 50}$

Relative lowering of vapour pressure = $\dfrac{100 - 90}{100}$

$$= \dfrac{10}{100} = \dfrac{W}{W + 50}$$

∴ W = 5.55 gm

(iii) Number of moles of $MgCl_2 = \dfrac{10}{95}$

Mass of water = 200 gm

Molality of $MgCl_2$ solution $= \dfrac{10 \times 1000}{95 \times 200} = \dfrac{10}{19}$

i = 3 for $MgCl_2$

$\Delta T_b = iK_b m$

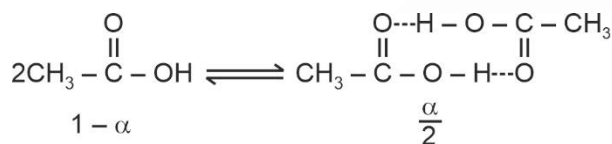$\quad = 3 \times 0.512 \times \dfrac{10}{19}$

$\quad = 0.81$ K

∴ Elevation in boiling point of $MgCl_2$ solution = 0.81 K

OR

(b) (i) Ethanoic acid is almost completely dimerised in benzene due to intermolecular H-bonding.

$$2CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - OH \rightleftharpoons CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - O - H \cdots \overset{\overset{\textstyle O \cdots H - O - \overset{\overset{\textstyle O}{\|}}{C} - CH_3}{}}{O}$$

$1 - \alpha \qquad\qquad\qquad\qquad \dfrac{\alpha}{2}$

$i = 1 - \dfrac{\alpha}{2} \simeq 0.5 \qquad\qquad\qquad\qquad (\because \; \alpha \simeq 1)$

(ii) Concentration of K_2SO_4 solution $= \dfrac{2.32 \times 10^{-2}}{174 \times 2} = 6.67 \times 10^{-5}$ M

van't Hoff factor, i = 3

Osmotic pressure, $\pi = icRT$

$\qquad\qquad\qquad = 3 \times 6.67 \times 10^{-5} \times 0.082 \times 298$

$\qquad\qquad\qquad = 4.89 \times 10^{-3}$ atm

(iii) Mass of sulphur (S_x) = 25.6 g

Number of moles of $S_x = \dfrac{25.6}{32x}$

Molality of solution of S_x in benzene $= \dfrac{25.6}{32x}$

$\Delta T_f = 0.512$ K and K_f (for benzene) = 5.12

$\Delta T_f = iK_f m$

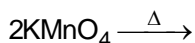$0.512 = 5.12 \times \dfrac{25.6}{32x} \qquad\qquad\qquad [\because \; i = 1]$

$x = \dfrac{5.12 \times 25.6}{0.512 \times 32} = 8$

∴ Formula of sulphur is S_8.

35. **(a)** A transition element X has electronic configuration [Ar] $4s^2 3d^8$. $\quad$ [1 + 1 + 3 = 5]

Predict its likely oxidation states.

(b) Complete the reaction mentioning all the products formed:

$2KMnO_4 \xrightarrow{\Delta}$

(c) Account for the following :

(i) In the 3d transition series, zinc has the lowest enthalpy of atomisation.

(ii) Cu^+ ion is unstable in aqueous solution.

(iii) Actinoids show more number of oxidation states than lanthanoids.

Sol. **(a)** Electronic configuration of (X) is [Ar] $4s^2 3d^8$.

Possible oxidation state of X are II, III, IV and V.

(b) $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

(c) (i) In 3d transition series, zinc has the lowest enthalpy of atomisation due to weak metallic bonding.

(ii) Cu^+ is unstable in aqueous solution as it disproportionates to Cu^{2+} and Cu due to higher enthalpy of hydration of Cu^{2+}.

$2Cu^+ \rightarrow Cu^{2+} + Cu$
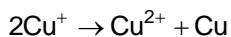
(iii) Actinoids show more number of oxidation states than lanthanoids because of the fact that 5f, 6d and 7s levels are of comparable energies.

❑ ❑ ❑