

Additional Practice Question Paper

(2023 -24)

CHEMISTRY THEORY (043)

Max. Marks: 70

Time: 3 hours

General Instructions:

Read the following instructions carefully.

- (a) There are **33** questions in this question paper with internal choice.
- (b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
- (c) SECTION B consists of 5 short answer questions carrying 2 marks each.
- (d) SECTION C consists of 7 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 calculators is 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. What would be the major product formed when $(\text{CH}_3)_3\text{C}-\text{OH}$ is heated at 358 K in the presence of H_3PO_4 :
 - (a) $(\text{CH}_3)_3\text{COOH}$
 - (b) $(\text{CH}_3)_3\text{CHO}$
 - (c) $(\text{CH}_3)_2\text{CH}=\text{CH}_2$
 - (d) $(\text{CH}_3)_3\text{C}-\text{O}-\text{C}-(\text{CH}_3)_3$
2. The complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ is obtained in yellow and red coloured forms. The difference in colour is attributed to the following type of isomerism:
 - (a) Coordination Isomerism
 - (b) Facial isomerism
 - (c) Linkage isomerism
 - (d) Solvate isomerism
3. Which of the following purines (nitrogenous bases with two-ring structure) are common to RNA and DNA?
 - (a) Adenine, Thymine
 - (b) Guanine, Thymine
 - (c) Thymine, Cytosine
 - (d) Adenine, Guanine
4. India's first pipeline was laid to transport crude oil in Digboi, Assam. The rusting of these iron pipelines was a cause of concern for the authorities. Which of the following methods would have been used to prevent corrosion of these pipelines?
 - (a) Barrier protection
 - (b) Alloying
 - (c) Cathodic protection
 - (d) Anodising the material
5. Which of the following alkyl iodide cannot be produced by the reaction of HI with an appropriate ether:
 - (a) $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{I}$
 - (b) $(\text{CH}_3)_2\text{CH}-\text{I}$
 - (c) $\text{C}_6\text{H}_5\text{CH}_2-\text{I}$
 - (d) $\text{C}_6\text{H}_5-\text{I}$
6. What is the order and molecularity of hydrolysis of sucrose if the rate law is $\text{Rate} = k'[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$?

- (a) Order is zero, molecularity is one (b) Order is two, molecularity is two
(c) Order is two, molecularity is one (d) Order is one, molecularity is two
7. The electronic configuration of Ni in complex $\text{Ni}(\text{CO})_4$ would be:
(a) $t_2^6 e^4$ (b) $t_2^6 e^2$ (c) $e^4 t_2^6$ (d) $e^4 t_2^4$
8. Ankit has been given four organic compounds: a primary amine, a secondary amine, a secondary alcohol and a tertiary alcohol. Which of the following can Ankit use to identify all the compounds?
(a) Tollen's reagent and bromine water (b) 2,4 DNP and Lucas reagent
(c) Hinsberg's reagent and Lucas reagent (d) Sodium metal and Hinsberg's reagent
9. Which of the following is not true about enzymes?
(a) All enzymes are fibrous proteins
(b) Enzymes are needed in small quantities
(c) Enzymes reduce the magnitude of activation energy.
(d) They are specific for a reaction and the substrate.
10. Identify the products (1) and (2) in the following reactions:
 $\text{C}_2\text{H}_5\text{Cl} + \text{KCN} \longrightarrow (1)$ and $\text{C}_2\text{H}_5\text{Cl} + \text{KNO}_2 \longrightarrow (2)$
(a) (1) $\text{C}_2\text{H}_5\text{CN}$ (2) $\text{C}_2\text{H}_5\text{NO}_2$ (b) (1) $\text{C}_2\text{H}_5\text{NC}$ (2) $\text{C}_2\text{H}_5\text{NO}_2$
(c) (1) $\text{C}_2\text{H}_5\text{CN}$ (2) $\text{C}_2\text{H}_5\text{ONO}$ (d) (1) $\text{C}_2\text{H}_5\text{NC}$ (2) $\text{C}_2\text{H}_5\text{ONO}$
11. "Greater number of electrons from (n-1)d in addition to the ns electrons are involved in the interatomic metallic bonding." Which of the following case is result of the above statement:
(a) Vanadium forms complexes.
(b) Platinum acts as catalyst
(c) Chromium is having higher melting point than Vanadium and Manganese .
(d) Manganese show oxidation states ranging from +2 to +7 .
12. Which of the following reactions can be used to obtain benzaldehyde from benzene?
(a) Rosenmund's Reduction (b) Stephen's Reaction
(c) Etard's Reaction (d) Gatterman-Koch Reaction
13. Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion (A): Phenol on treatment with Br_2 in CS_2 gives ortho and para bromophenol.
Reason (R): Carbon disulphide is a solvent of low polarity, hence leads to monobromination of phenols
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.
14. Given below are two statements labeled as Assertion (A) and Reason (R)
Assertion: At high pressure, decomposition of ammonia on the catalyst surface is a first order reaction.
Reason: At high pressure, on changing the reaction conditions, the concentration of ammonia on the surface of the catalyst does not change.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.

- (c) A is true but R is false.
 (d) A is false but R is true.
15. Given below are two statements labeled as Assertion (A) and Reason (R)
Assertion (A): Ionisation enthalpy of Fe^{2+} is lower than the Mn^{2+}
Reason (R): Fe^{2+} has $3d^5 4s^1$ configuration, making the state highly stable
 Select the most appropriate answer from the options given below:
 (a) Both A and R are true and R is the correct explanation of A
 (b) Both A and R are true but R is not the correct explanation of A.
 (c) A is true but R is false.
 (d) A is false but R is true.
16. Given below are two statements labeled as Assertion (A) and Reason (R)
Assertion (A): Halogens are ortho and para-directing groups
Reason (R): Halogens are electron-withdrawing groups
 Select the most appropriate answer from the options given below:
 (a) Both A and R are true and R is the correct explanation of A
 (b) Both A and R are true but R is not the correct explanation of A.
 (c) A is true but R is false.
 (d) A is false but R is true.

SECTION B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. Answer the following questions:
 (a) Out of Co^{3+} and Cr^{2+} , which one liberates hydrogen from dilute acid and why?
 $[E_0\text{Co}^{3+}/\text{Co}^{2+} = +1.97 \text{ V}, E_0\text{Cr}^{3+}/\text{Cr}^{2+} = -0.41 \text{ V}]$
 (b) The transition metals and their compounds are known for their catalytic activity. Give a reason for their effectiveness as catalysts and name the transition element used as a catalyst in Haber's Process.
18. In metal carbonyls, metal-ligand bonds possess both sigma and pi character. Comment, whether the given statement is correct. Give reason for your answer.
19. Give an example of:
 (a) an amine each with basic strength greater than and less than N-Methylmethanamine in gaseous state
 (b) an isomeric amine each with boiling point less than and more than N-Ethyl ethanamine.
20. Consider the following reaction:
 (1) $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$
 (2) $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$
 In the above reaction, the rate of formation of the intermediate is slow.
 (a) Write the rate law.
 (b) How will the rate of the reaction be affected if the concentration of peroxide is doubled?

OR

- 20 The half-life of a sample A ($t_{1/2} = 100$ days) did not change with concentration of A. The half-life of

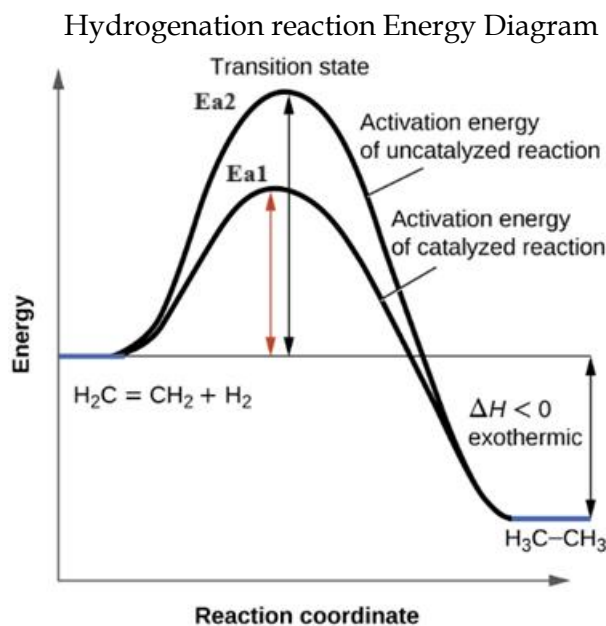
another sample B ($t_{1/2} = 120$ days) decreases with decrease in concentration of B. If the initial concentration of both the samples were 1M, what will be their rate constants?

21. Arrange the following as indicated
- n-Butane, Propan-1-ol, Propanal, Acetone, Methoxymethane (increasing order of boiling point)
 - Acetaldehyde, Acetone, Acetophenone, (increasing order of reactivity towards nucleophilic addition)

SECTION C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. Observe the potential energy diagram for the hydrogenation of ethene to give ethane.



- For the same process, predict why there is a difference in E_{a1} and E_{a2} ?
- Assuming both the reaction are reversible then in which case the backward reaction will be faster?
- Will the ΔG value of this reaction be different in the above two paths? Explain.

(for visually challenged learners)

- What will be the effect on E_a and ΔG for a given reaction in the presence of a catalyst. Justify your answer.
- According to the collision theory, what are the criteria to determine effective collision?

23. Answer the following questions:

- Give an example of the liquids which when mixed result in an endothermic process, What will be the change in volume when the liquids are mixed?
- At 300K, what is the relation between the osmotic pressure of two equimolar solutions, one whose Van't Hoff factor is 2 and for the other is $\frac{1}{2}$?
- Which of the two aqueous solutions has a higher melting point: 2molal glucose solution or 3 molal sucrose solution? Why?

24. Give reason for the following:

- The complex formed by Ca^{2+} with EDTA is more stable than the complex formed by Ca^{2+} with ethylene diamine.

- (b) In d^4 complexes, ligands for which $\Delta_o < P$ form high spin complexes.
- (c) On removal of water from $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating, it becomes colourless.

OR

24. (a) What will be the colour of precipitate obtained when ionization isomer of compound $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ reacts with AgNO_3 ?
- (b) An element M forms complex 'A' with ligand-ethane-1,2-diamine and complex 'B' with chlorido having coordination number six.
- (i) Out of the two complexes which one will be more stable and why?
- (ii) If metal forms d^4 ion, which complex will have higher magnetic moment?
25. An organic compound 'A' is having a molecular formula $\text{C}_7\text{H}_8\text{O}$. On oxidation with acidified KMnO_4 it forms compound 'B'. Compound 'B' can also be obtained from compound C, on its reaction with NaOH and then with CO_2 followed by hydrolysis. Compound C can be easily formed when butylphenylether is made to react with HI . Identify the compound A, B and C. Write the chemical reactions involved.
26. Rohan was carrying out the reaction of potassium iodide with Potassium permanganate in the acidic medium. The Iodine gas was liberated from potassium iodide, during the reaction. When he repeated the reaction for further study, he forgot to add acid. He observed, the products released during the second case were different from the previous.
- (i) Give the possible chemical reactions in both the cases.
- (ii) Give reason for the difference in observation.
- (iii) Give the structure of MnO_4^-
27. Answer the following questions:
On passing current type 'X' through aqueous CuSO_4 solution, electrolysis was observed. When current type 'Y' was used, the conductivity of the solution could be measured.
- (a) Identify 'X' and 'Y' type of current used.
- (b) Write the electrolysis products of aqueous CuSO_4 solution on passing 'X'.
28. Convert Propanamide to the following compounds in not more than two steps:
- (a) N-Ethylpropanamine
- (b) Ethanol
- (c) N-Propylethanamide

SECTION D

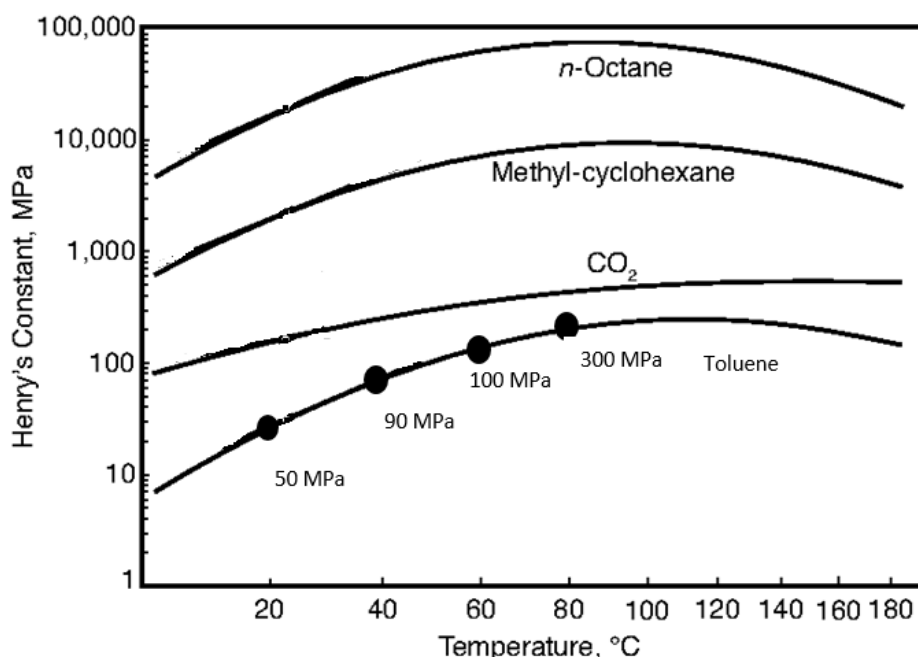
The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. Temperature dependence of Henry's law constant

Henry's law and Henry's law constant are widely used in chemical and environmental engineering. Unfortunately, many people do not appreciate that Henry's constant is not a true constant but has a significant non-linear temperature dependence. Figure 1 illustrates some typical behavior of *Henry's constant vs temperature* for several solutes in water.

The Henry's constant typically increases with temperature at low temperatures, reaches a maximum, and then decreases at higher temperatures. The temperature at which the maximum occurs depends on the specific solute-solvent pair.

Clearly, the use of a Henry's constant that was derived at 25°C at a different temperature could lead to serious errors during manufacturing. Even a variation as small as 10 K can cause the Henry's constant to change by a factor of two, which could have a serious impact on many process designs.



Temperature dependence of Henry's constant for several solutes in water.

- (a) Which of the following is not a true constant like Henry's constant
- speed of light (c)
 - Planck's constant (h)
 - rate constant (k)
 - gas constant (R)
- (b) How will the solubility of n-octane vary with a change in temperature, provided the pressure is kept constant?

OR

Rishita works in an aerated drinks factory. To increase the fizz in the drink, she proposes to bottle the aerated drinks at 40°C instead of 20°C. Do you support her proposal? Why or why not?

- (c) Find the ratio of solubility of toluene in water at 20°C and 60°C.

(for visually challenged learners)

Henry's law and Henry's law constant are widely used in chemical and environmental engineering. Unfortunately, many people do not appreciate that Henry's constant is not a true constant but has a significant non-linear temperature dependence. The Henry's constant typically increases with temperature at low temperatures, reaches a maximum, and then decreases at higher temperatures. The temperature at which the maximum occurs depends on the specific solute-solvent pair. For example, the temperature at which maxima occurs for n-octane-water pair is nearly 90°C.

- (a) Which of the following is not a true constant like Henry's constant
- speed of light (c)
 - Planck's constant (h)
 - rate constant (k)
 - gas constant (R)
- i. (b) How will the solubility of n-octane vary with a change in temperature, provided the pressure is kept constant?

OR

Rishita works in an aerated drinks factory. She is aware that the temperature at which maxima occurs for carbon dioxide-water pair is above 80°C.

Rishita proposes to bottle the aerated drinks at 40°C instead of 20°C, this will increase the fizz in the drink. Do you support her proposal? Why or why not?

- (c) If the pressure is constant, the ratio of solubility of n-octane in water at 20°C and 60°C will be:
(i) greater than 1 (ii) less than 1 (iii) equal to 1? Give reason for your choice.

30. Nucleophilic Substitution Reactions

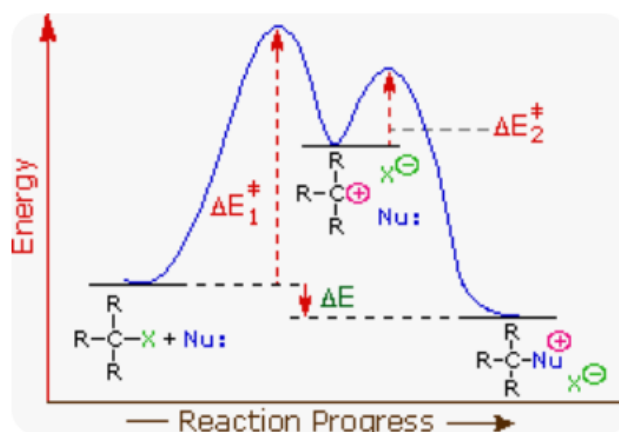
In nucleophilic substitution reactions, a bond between carbon and a leaving group (C-LG) is broken, and a new bond between carbon and a nucleophile (C-Nu) is formed. Nucleophilic substitution reactions of alkyl halides occur through two main pathways: S_N1 and S_N2 .

One way to visualize the differences between these two mechanisms is to sketch out their reaction coordinate diagrams, where we plot changes in potential energy (vertical axis), the starting materials pass along the "reaction coordinate" toward their conversion into products (horizontal axis) In these diagrams the "peaks" (local maxima) represent transition states whereas "valleys" (local minima) represent intermediates.

The reaction coordinate diagram of the S_N1 reaction has two peaks, representing the two transition states (Step 1 and Step 2, respectively) flanking a single "valley" representing the carbocation intermediate.

Each step of the process has an activation energy represented by the difference in energy between the reactant and the transition state.

The rate-determining step of a reaction is the step requiring the highest activation energy, that is, the largest change in potential energy from reactant to transition state.



(Source: James Ashenurst, Comparing the S_N1 and S_N2 Reactions, Master Organic Chemistry)

- (a) On the basis of the activation energies for step 1 and step 2 for S_N1 reaction, identify the rate-determining step and justify your answer.
- (b) If the alkyl group in the alkyl halide used as an example in figure 1 is the same but the halogen bromine is replaced by chlorine, which of the following is correct and why?
- (i) E_a for step 2 will be more than shown in the figure 1
(ii) E_a for step 2 will be less than shown in the figure 1
(iii) E_a for step 2 will be same as shown in the figure 1

OR

Plot rate of reaction vs. concentration of nucleophile for S_N1 reaction.

(c) Draw the reaction coordinate diagram for S_N^2 reaction.

(For visually challenged candidates)

30. Nucleophilic Substitution Reactions

In nucleophilic substitution reactions, a bond between carbon and a leaving group (C-LG) is broken, and a new bond between carbon and a nucleophile (C-Nu) is formed. Nucleophilic substitution reactions of alkyl halides occur through two main pathways: S_N^1 and S_N^2 .

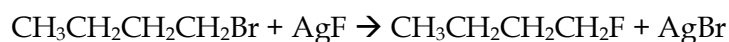
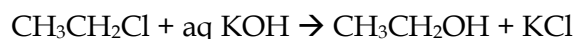
S_N^1 occurs in two steps. Each step of the process has an activation energy represented by the difference in energy between the reactant and the transition state. The rate-determining step of a reaction is the step requiring the highest activation energy.

- (a) What is the difference in energy of the reactants and that of the transition state called?
- (b) A reaction occurs in two steps. If step 1 of the reaction has a greater activation energy than step 2, which will be the rate-determining step and why?

OR

The slowest step in a complex reaction requires the highest activation energy. Account for the above statement on the basis of the information provided about the nucleophilic substitution reactions.

- (a) In the following reaction, identify the leaving group and the nucleophile:



SECTION E

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

31. Answer the following questions:

- (a) Draw the structure of the ethylene ketal of hexan-3-one.
- (b) Between Benzoic acid and acetic acid which is more acidic and why?
- (c) An optically active organic compound 'A', with molecular formula, $\text{C}_5\text{H}_{10}\text{O}_2$ when treated with Chlorine in the presence of Red Phosphorous forms compound 'B', $\text{C}_5\text{H}_9\text{O}_2\text{Cl}$, whereas when it is treated with thionyl chloride forms compound 'C', $\text{C}_5\text{H}_9\text{OCl}$. Compound C, on further hydrogenation with palladium on BaSO_4 in the presence of S, forms compound D, $\text{C}_5\text{H}_{10}\text{O}$. Compound D gives positive Tollen's test and regenerates A. A can also be obtained by base hydrolysis and further acidification of C. Write the reaction for the formation of 'A' from 'C' and Identify A, B, C, D.

OR

Answer the following questions:

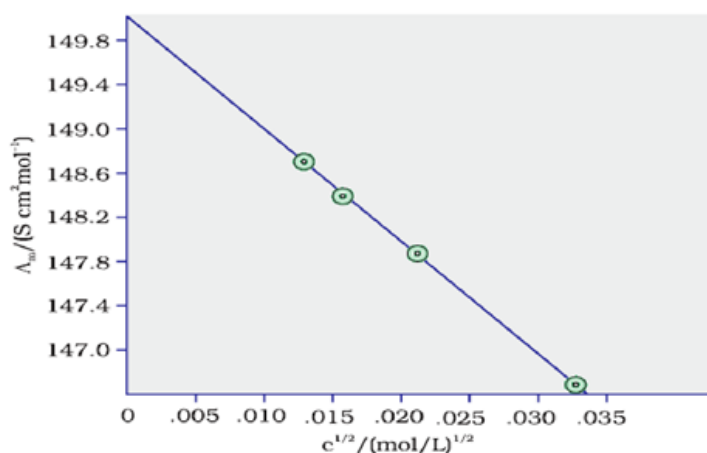
31. (a) Bring about the following conversions:
- (i) Propanal to 2-methyl pentanol
- (ii) Iodobenzene to benzoic acid
- (b) Though Carboxylic acids have $>\text{C}=\text{O}$ group in their structure, but they are not prone to nucleophilic addition reactions. Why?
- (c) An organic compound A, with molecular formulae C_9H_{12} is oxidized to monocarboxylic acid B, $\text{C}_7\text{H}_6\text{O}_2$ on vigorous oxidation with Potassium permanganate, whereas when oxidized in presence of air and further treated with dilute acid forms phenol. Sodium salt of B finds use as a food preservative and esters of B are used in perfumery. Identify A and B and write the

reactions involved.

32. (a) Calculate the current and the thickness of the coating if the current was passed for 1hr. to deposit 2g silver on metal object of area 1 cm². (Ag = 108, 1 Faraday = 96500 coulombs, density of silver = 10.5g/cc).
- (b) Calculate the electrode potential of Cr³⁺/Cr electrode at [Cr³⁺] = 0.001 M.
Given: Cr³⁺ + 3e⁻ → Cr E° = - 0.74 V

OR

32. (a) The half-cell reactions of an electrochemical cell are given below:
- $$\text{Mn}^{3+} (0.1 \text{ M}) + \text{e}^{-} \longrightarrow \text{Mn}^{2+} (0.01 \text{ M}) \quad E^{\circ} = 1.50 \text{ V}$$
- $$\text{Ag}^{+} (0.001 \text{ M}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s}) \quad E^{\circ} = 0.80 \text{ V}$$
- (i) Formulate a galvanic cell using the above data.
- (ii) Calculate the emf of the cell at 25°C.
- (b) The graph represents the variation of molar conductivity of an electrolyte with respect to concentration. Identify the type of electrolyte and also determine the value for A.



(for visually challenged learners)

32. (a) Calculate the current and the thickness of the coating if the current was passed for 1hr. to deposit 2g silver on metal object of area 1 cm². (Ag = 108, 1 Faraday = 96500 coulombs, density of silver = 10.5g/cc).
- (b) Calculate the electrode potential of Cr³⁺/Cr electrode at [Cr³⁺] = 0.001 M.
Given: Cr³⁺ + 3e⁻ → Cr E° = - 0.74

OR

- (a) The half-cell reactions of an electrochemical cell are given below:
- $$\text{Mn}^{3+} (0.1 \text{ M}) + \text{e}^{-} \longrightarrow \text{Mn}^{2+} (0.01 \text{ M}) \quad E^{\circ} = 1.50 \text{ V}$$
- $$\text{Ag}^{+} (0.001 \text{ M}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s}) \quad E^{\circ} = 0.80 \text{ V}$$
- (i) Formulate a galvanic cell using the above data.
- (ii) Calculate the emf of the cell at 25°C.
- (b) The molar conductivity of an electrolyte decreases slowly with increase in concentration.
- (i) Identify the type of electrolyte and give the equation with which we can represent this change in molar conductivity.
- (ii) Calculate the slope of the electrolyte if the intercept on the y axis and x axis at 150 and 0.034 respectively.

33. Answer the following questions:

- (a) (i) Name an important carbohydrate which makes the cell wall of bacteria and plants. What is the basic unit of this carbohydrate?
- (ii) How are these basic units linked to each other, name the linkage.
- (iii) Draw the Haworth structure of the basic unit.
- (b) Identify the disaccharide with molecular formulae, $C_{12}H_{22}O_{11}$, which produces 2 moles of α -D(+) Glucose on hydrolysis. What will be the observation when Tollen's reagent is added to such a disaccharide.
- (c) Change in optical rotation is observed when sucrose is hydrolysed. What is the reason for the inversion of configuration observed?

OR

33. Answer the following questions:

- (a) (i) A polynucleotide chain is seen to produce pentose sugar, phosphoric acid, Adenine, Guanine, Cytosine and Thymine on complete hydrolysis. Name the nucleic acid having such a polynucleotide chain. How are the bases paired in this polynucleotide?
- (ii) What links these nucleotides together in a polynucleotide?
- (iii) Give one important function and one application of the above nucleic acid.
- (b) Keratin is a hair protein. What kind of tertiary protein is this? Describe the structure and links present in this protein. Comment on its solubility in water?

Additional Practice Question Paper

(2023 -24)

CHEMISTRY THEORY (043)

MARKING SCHEME

SECTION-A

(Q1 to 16, 1 mark allotted for the correct option)

- (c) $(\text{CH}_3)_2\text{CH} = \text{CH}_2$, Tertiary alcohol undergoes intramolecular dehydration reaction in the presence of H_3PO_4
- (c) Linkage isomerism, NO_2^- is an ambidentate ligand .
- (d)
- (c) Cathodic protection
Iron pipes are connected to more reactive metal like Magnesium, zinc so that an electrochemical cell is set up between the two. Iron behaves like cathode and doesn't corrode.
- (d) $\text{C}_6\text{H}_5-\text{I}$, ether having an aryl part will lead to the formation of phenol rather than iodobenzene. Formation of phenyl cation will not be favoured , partial double bond character of $\text{C}-\text{O}$ will make it less stable.
- (d) Order is one, molecularity is two
- (c) $\text{e}_g^4 \text{t}_{2g}^6$
- (c) Hinsberg reagent helps in identifying primary, secondary and tertiary amines and Lucas reagent helps in identification of primary, secondary and tertiary alcohols.
- (a) Enzymes are majorly globular proteins. So this statement mentioning enzymes as fibrous protein is false. Rest all are true statements.
- (c) Both CN^- and $\bar{\text{O}}\text{NO}$ are ambident nucleophiles and KCN and KNO_2 are ionic in nature
- (c) Chromium is having higher melting point than Vanadium and Manganese .This statement shows that melting point is higher because of involvement of $(n-1)d$ electrons in addition to the s electrons in the interatomic metallic bonding.
- (d) Gattermann-Koch reaction involves the conversion of benzene to benzaldehyde on reaction with CO and HCl . Rest of the named reactions involve preparation of benzaldehyde from the different starting material.
- (a) Both A and R are true and R is the correct explanation of A
- (d) A is false but R is true. Decomposition of ammonia follows zero order kinetics.
- (c) A is true but R is false. Reason is false, as there is no loss of exchange energy in d^6 configuration.
- (b) Halogens withdraw electrons through an inductive effect $(-I)$ and release electrons through resonance $(+R)$. Through inductive effect, halogens destabilize the intermediate carbocation formed during the electrophilic substitution. Through resonance, halogen tends to stabilize the carbocation and the effect is more pronounced at ortho- and para- positions. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

SECTION-B

- (a) E_0 values $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative shows that Cr^{2+} whereas positive value of $E^\circ\text{Co}^{3+}/\text{Co}^{2+}$, shows Co^{3+} it will not displace hydrogen from dilute acid.
(b) The ability of transition metals to adopt multiple oxidation states and to form complexes using empty atomic orbitals make them suitable to act as catalyst. Finely divided iron is used in Haber's Process. Catalytic property can be attributed to their large surface area. (1)
- The metal-carbon bond in metal carbonyls possess both σ and π character. The $\text{M}-\text{C}$ σ bond is formed by the donation of lone pair of electrons from $\sigma 2p_z$ on the carbonyl carbon into a d_z^2 vacant

orbital of the metal. The M-C π bond is formed by the donation of a pair of electrons from a filled d orbital d_{xy} of metal into the vacant antibonding $\pi^* 2p_x$ orbital of carbon monoxide. (1+1)

19. (a) An amine with basic strength greater is N, N-Dimethylethanamine and less is methanamine (or any other correct option) (1/2+1/2)
- (b) An isomeric amine with boiling point less than the N-Ethyl ethanamine is N,N-Dimethylethanamine and more is Butanamine (1/2+1/2)
20. (a) Since the formation of intermediate is slow, the first step is the slowest step. Hence the rate will depend on the first step.
- Therefore,
- $$\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-] \quad (1/2+1/2)$$
- (b) If the concentration of peroxide is doubled, the rate of the reaction also doubles. (1)

OR

20. Since $t_{1/2}$ for sample A did not change with change in concentration, it follows first order kinetics. Therefore, the rate constant is
- $$t_{1/2} = 0.693/k \quad (1/2)$$
- $$k = 0.693/100 = 0.00693/\text{day} \quad (1/2)$$
- Since $t_{1/2}$ for sample B decreases with decrease in concentration, it follows zero order kinetics.
- $$t_{1/2} = [A_0]/2k \quad (1/2)$$
- $$k = 1/2 \times 120$$
- $$k = 1/240 = 0.0041 \text{ M/day} \quad (1/2)$$
21. (a) n-Butane < Methoxymethane < Propanal < Acetone < Propan-1-ol
- The boiling points of aldehydes, ketone, ethers are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. (1)
- (b) Acetophenone < Acetone < Acetaldehyde
- Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Among the ketones, in acetophenone the positive charge over carbonyl carbon is delocalized, involved in resonance, so its reactivity decreases in comparison to aliphatic ketones. (1)

SECTION-C

22. (a) There is a difference in activation energy because the process with E_{a1} is a catalysed reaction which lowers the threshold energy for the formation of intermediate activated complex while. (1)
- E_{a2} path is uncatalyzed and has higher threshold energy. (1/2)
- (b) In a reversible catalysed reaction, the rate of both forward and backward reactions are faster than an uncatalyzed reaction. (1/2)
- (c) ΔG value is independent of the path taken as Gibbs free energy is a state function and not a path function. (1)

(for visually challenged learners)

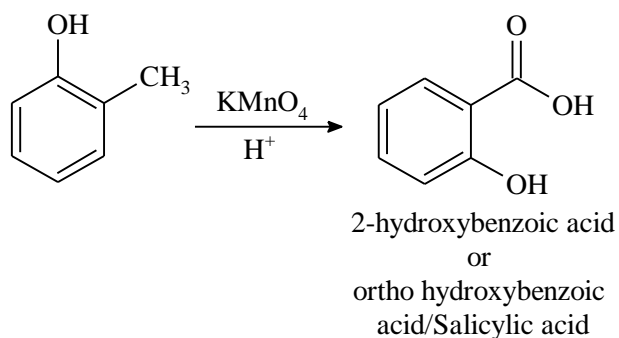
- (a) The value of E_a will be lower as the threshold energy for the formation of intermediate activated complex is less. (1/2+1/2)
- A catalyst does not alter Gibbs energy, ΔG of a reaction. ΔG value is independent of the path taken as Gibbs free energy is a state function and not a path function. (1/2+1/2)
- (b) Activation energy and proper orientation of the molecules (1/2+ 1/2)

- 23 (a) Ethanol and acetone, or any other example, the volume will increase (The liquids show positive deviation from Raoult's law) ($\frac{1}{2} + \frac{1}{2}$)
 (b) $\pi_1/\pi_2 = 4$ (1)
 (c) 2 molal glucose because it will have lower depression in freezing point, higher melting point. (1)
- 24 (a) EDTA is a hexadentate ligand while ethylene diamine is bidentate, the chelating effect of EDTA is more therefore EDTA- Ca^{2+} complex is more stable. (1)
 (b) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$ (1)
 (c) On heating water molecule which is acting as ligand is lost. In the absence of ligand, crystal field splitting does not occur so there is no d-d transition and hence the substance is colourless (1)

OR

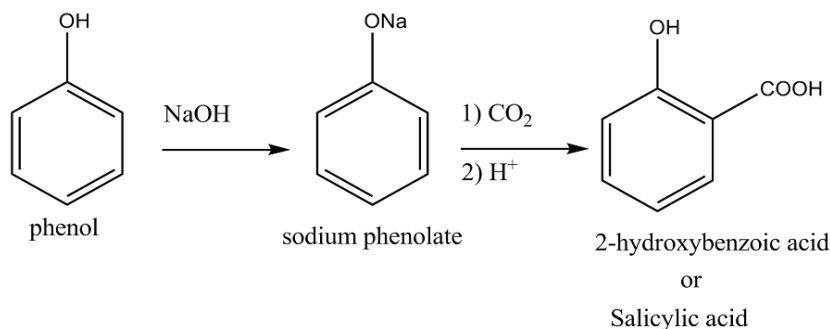
24. (a) The colour of precipitate obtained when ionization isomer of compound $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$, i.e. $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (1)
 reacts with AgNO_3 will be pale yellow. The pale yellow precipitate of AgBr will be obtained.
 (b) (i) The complex A with ligand ethane-1,2-diamine will be more stable as it is didentate ligand leading to the formation of chelate and hence increasing the stability. (1)
 (ii) The higher magnetic moment will be in the case of Complex B, with ligand chlorido as no pairing up of electrons will take place. (1)
25. Compound - A is ortho methylphenol, ($\frac{1}{2}$)
 Compound- B is ortho hydroxybenzoic acid. ($\frac{1}{2}$)
 Compound - C is Phenol. ($\frac{1}{2}$)
 The chemical reaction involved are :

- (a) Formation of B from compound A using KMnO_4



($\frac{1}{2}$)

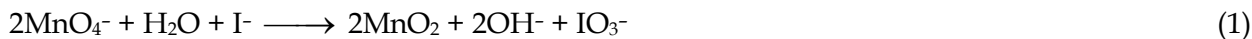
- (b) Formation of B from C i.e Phenol



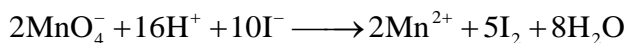
($\frac{1}{2}$)

- (c) $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{HI}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{OH}$ ($\frac{1}{2}$)

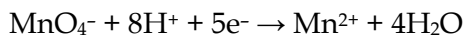
- 26 (i) A notable reaction is the oxidation of iodide to iodate, when no acid present



When the acid was present



- (ii) In case of oxidising action of KMnO_4 , the hydrogen ion concentration plays an important part in influencing the reaction. In the presence of acid medium, oxidation number of Mn changes from +7 to +2 and in basic medium from +7 to +4 (1)



(iii)



27.(a) Since electrolysis (decomposition) happens with current type 'X', it is a DC (Direct current).

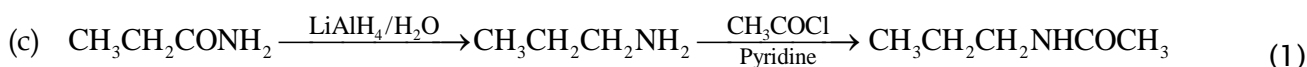
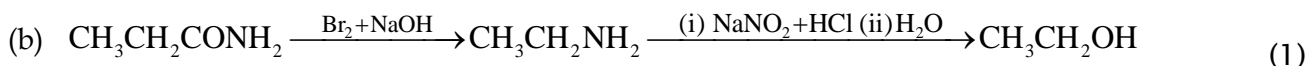
Current type 'Y' is AC (Alternating current) and is used to measure conductivity of solutions. (1+1)

(b) When CuSO_4 is electrolysed, copper gets deposited at cathode and oxygen gas is released at anode.

At cathode reduction of Cu^{2+} occurs (as it requires lesser electrode potential than H^+)



At anode oxidation of water occurs (as it requires lesser electrode potential to get oxidized than SO_4^{2-})



SECTION D

29 (a) (iii) Rate constant (k), it changes with temperature (1)

- (b) The solubility will decrease with temperature at low temperatures, reach a minimum value and then increase at higher temperatures because the Henry's constant typically increases with temperature at low temperatures, reaches a maximum, the temperature at which maxima occurs for n-octane-water pair is nearly 90°C and then decreases at higher temperatures. (1)

OR

It is not a good proposal.

K_H for CO_2 is higher at 40°C ,

so the solubility of CO_2 will be lower, thus fizz be less.

- (c) Ratio of solubility will be greater than 1 because

$$p = K_H X$$

At 20°C $K_H = 50\text{MPa}$, and at 60°C $K_H = 100\text{MPa}$

$$K_H(60) / K_H(20) = X(20) / X(60)$$

$$100/50 = 2 = X(20) / X(60) \quad (2)$$

For Visually impaired

- (a) (iii) Rate constant (k), it changes with temperature. (1)

- (b) The solubility will decrease with temperature at low temperatures, reach a minimum value and

then increase at higher temperatures because the Henry's constant typically increases with temperature at low temperatures, reaches a maximum, and then decreases at higher temperatures. (1)

OR

It is not a good proposal.

K_H for CO_2 will be higher at 40°C , because maxima is obtained above 80°C

So, the solubility of CO_2 will be lower, thus fizz be less.

- (c) Ratio of solubility greater than 1 because

$$p = K_H X$$

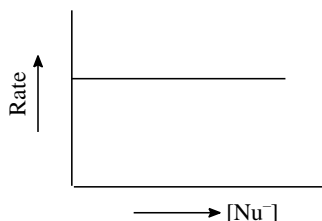
At 20°C K_H will be less than K_H at 60°C

So solubility at 20°C will be more than at 60°C (2)

- 30 (a) The activation energy for step 1 is larger than step 2, so step 1 is the slowest step and the rate determining step. (1)

- (b) (i) E_a for step 2 will be more than shown in figure 1, because Br^- is a better-leaving group than Cl^- . (1)

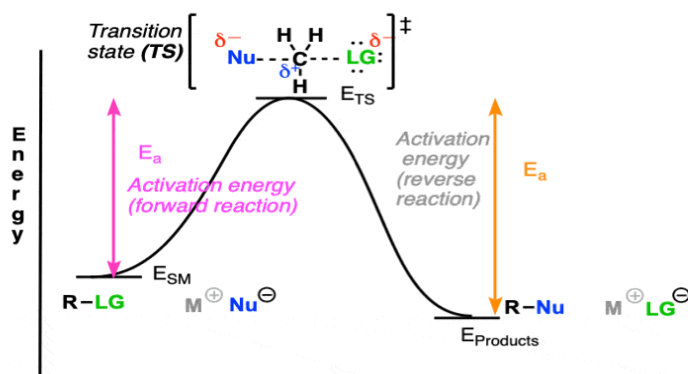
OR



- (c)

Reaction Energy Diagram for the $\text{S}_{\text{N}}2$ Reaction

The reaction coordinate for a typical $\text{S}_{\text{N}}2$ reaction shows a single transition state and no intermediates.



(2)

(For visually impaired)

- (a) Activation energy (1)
 (b) step 1 The rate-determining step of a reaction is the step requiring the highest activation energy. (1)

OR

slowest step is the rate determining step so it requires highest activation energy The rate-determining step of a reaction is the step requiring the highest activation energy.

- (c) (i) leaving group is Cl^- and nucleophile is OH^- (1)
 (ii) leaving group Br^- and nucleophile is F^- (1)

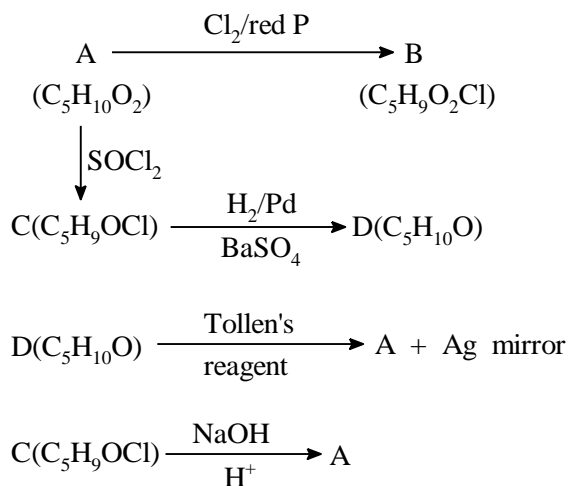
SECTION E

31. (a)



(b) Benzoic acid is more acidic. This is because of greater electronegativity of sp^2 hybridized carbon to which carboxyl carbon is attached, whereby phenyl group acts as an electron withdrawing group and stabilizes the intermediate carboxylate ion. (1)

(c)

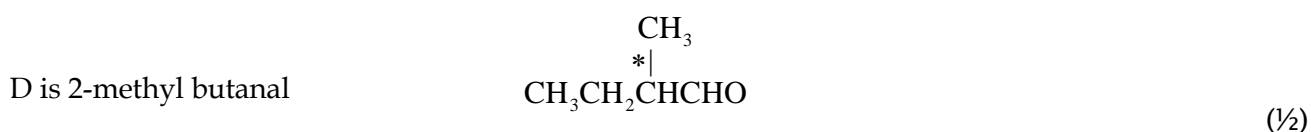
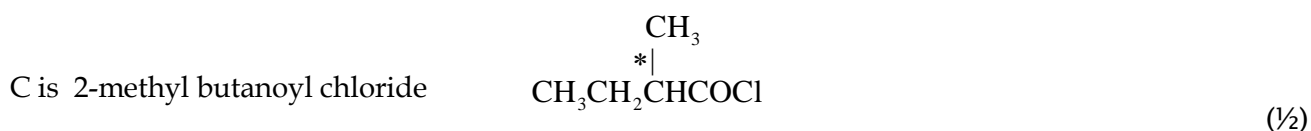
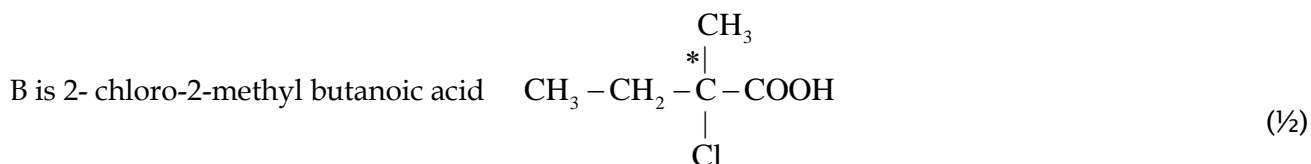
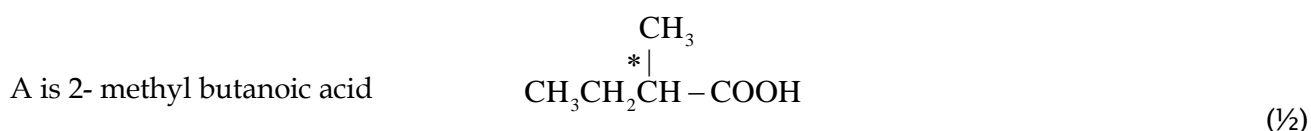


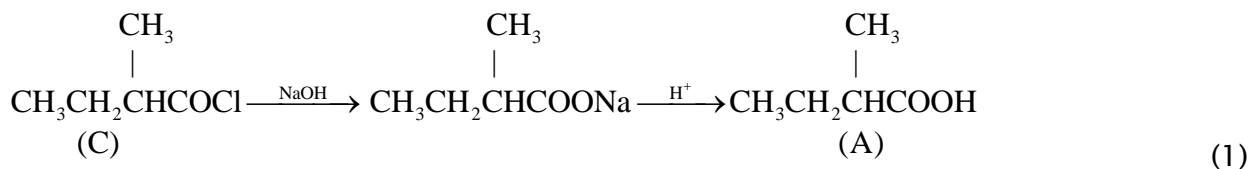
Since D, $\text{C}_5\text{H}_{10}\text{O}$ gives a positive Tollen's test, it is an aldehyde. D is also obtained from C by controlled catalytic hydrogenation, so C is an acid halide.

C is obtained by treatment of thionyl chloride on A, so A is an acid.

A when reacted with halogen in Red phosphorus produces B, So B is α -halocarboxylic acid and A is an acid with α -hydrogen.

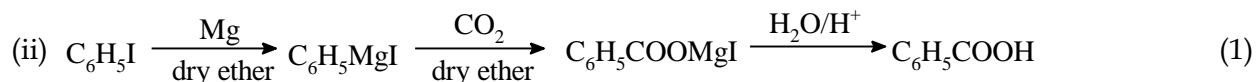
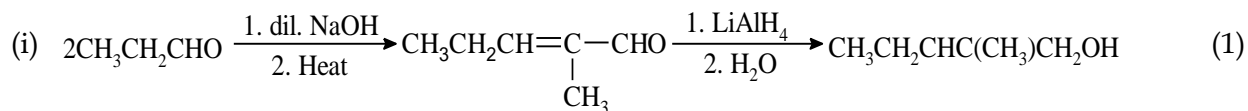
Since A is an optically active compound with 5 carbons, therefore



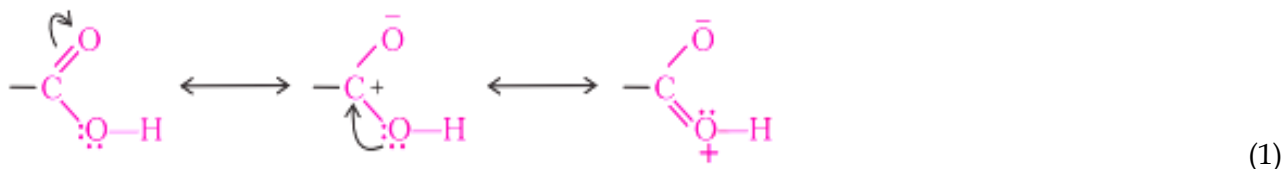


OR

31. (a)

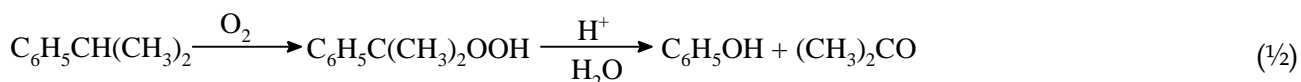


(b) This is so because the Carbon in $>\text{C}=\text{O}$ group in carboxylic group is less electrophilic due to the possible resonance as shown:



(c) A is oxidized to monocarboxylic acid, B indicates that the ring structure has only one side chain. Also, Phenol is formed when oxidized in the presence of air and further treatment with dil acid so A must be Cumene. (1/2)

Sodium salt of B is food preservative and esters of it is used in perfumery, confirms B to be benzoic acid. (1/2)

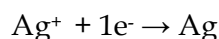


32. (a) Mass of Ag deposited = 2g

$$\begin{aligned} \text{Volume} &= \frac{\text{mass}}{\text{density}} = 2 \text{ g} / 10.5 \text{ gcm}^3 \\ &= 0.190 \text{ cm}^3 \end{aligned} \quad (1/2)$$

$$\begin{aligned} \text{Thickness} &= 0.190 \text{ cm}^3 / 1 \text{ cm}^2 \\ &= 0.190 \text{ cm} \end{aligned} \quad (1/2)$$

For current



108 g of Ag is deposited by 1F of charge

$$\begin{aligned} 2 \text{ g of Ag will be deposited by } &\frac{1 \times 2}{108} \text{ charge} \\ &= 0.0185 \text{ F} = 0.0185 \times 96500 \text{ C} \end{aligned} \quad (1)$$

$$t = 1 \text{ hr}$$

$$Q = Ixt$$

$$0.0185 \times 96500 = I \times 60 \times 60$$

$$I = \frac{0.0185 \times 96500}{3600} = 0.495 \text{ A} \quad (1)$$

$$(b) \quad E_{\text{Cr}^{3+}/\text{Cr}} = E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} - \frac{0.059}{3} \log \frac{1}{[\text{Cr}^{3+}]} \quad (1/2)$$

$$E_{\text{Cr}^{3+}/\text{Cr}} = -0.74 - \frac{0.059}{3} \log 10^3 \quad (1/2)$$

$$E_{\text{Cr}^{3+}/\text{Cr}} = -0.74 - 0.059 \quad (1/2)$$

$$E_{\text{Cr}^{3+}/\text{Cr}} = -0.799 \text{ V} \quad (1/2)$$

OR

$$32. (a) (i) \quad \text{Ag}_{(s)} | \text{Ag}^+ (0.001 \text{ M}) || \text{Mn}^{3+} (0.1 \text{ M}) | \text{Mn}^{2+} (0.01 \text{ M}) | \text{Pt} \quad (1)$$

$$(ii) \quad E_{\text{cell}}^{\circ} = +1.50 - 0.80 = +0.70 \text{ V} \quad (1/2)$$

$$Q = \frac{[\text{Ag}^+][\text{Mn}^{2+}]}{[\text{Mn}^{3+}]} \quad (1/2)$$

$$Q = \frac{10^{-3} \times 10^{-2}}{10^{-1}} = 10^{-4}$$

$$\log Q = -4$$

$$E = E^{\circ} - \frac{0.059}{n} \log Q \quad (1/2)$$

$$E = +0.70 - \frac{0.059}{1} \times (-4)$$

$$= +0.70 + 0.236 \quad (1/2)$$

$$E = +0.936 \text{ V}$$

(b) Strong Electrolyte

$$\Lambda = \Lambda^{\circ} - A\sqrt{C} \quad (1/2)$$

For a straight line equation,

$$y = c + mx$$

$$\text{Slope} = m = -A$$

Slope is also given by $\tan \theta$.

Slope = Perpendicular/base

$$= \frac{150}{0.034} \quad (1/2)$$

$$\text{Slope} = -A = -4411.76 \quad A = 4411.76 \quad (1)$$

(for visually challenged learners)

32. (a) and (b) Same as above

OR

(a) Same as above

(b) (i) Strong electrolyte

$$\Lambda = \Lambda^\circ - A\sqrt{C} \quad (1/2)$$

Slope = Perpendicular/base

$$= \frac{150}{0.034} \quad (1/2)$$

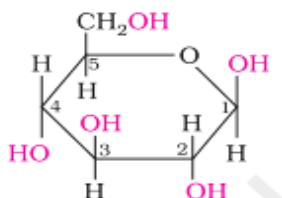
$$\text{Slope} = -A = -4411.76 \quad A = 4411.76 \quad (1)$$

33. (a) (i) **Cellulose** (1/2)

β -D(+) Glucose (1/2)

(ii) C-1 of one unit of glucose is linked to C-4 of another unit of glucose. These units are linked to each other by **glycosidic linkages**. (1)

iii) Haworth structure of β -D(+)-Glucose:



(1)

(b) Maltose (1/2)

Silver mirror will be observed as Tollen's reagent is reduced by maltose due to the presence of free aldehyde group. (1/2)

(c) Sucrose is dextrorotatory, but on hydrolysis it produces a mixture of α -D-(+) Glucose and β -D-(-) Fructose. Since the laevorotation of fructose is more than the dextrorotation of α -glucose, so overall mixture becomes laevorotatory, hence inversion is observed. (1)

OR

33. (a) (i) **DNA** (1/2)

Specific base pair sequence 1) Adenine with Thymine by two H- bonds and 2) Guanine with Cytosine by three H- bonds (1/2)

ii) **Phosphodiester linkages**. (1)

iii) **Function:** DNA is a reserve of genetic information and is responsible for identity of different species (1/2)

Application: DNA fingerprinting is used in forensic labs for identification of Criminals (1/2)

(b) **Fibrous protein** (1/2)

In the fibrous protein the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, resulting in a fibre-like structure. (1)

Fibrous proteins are insoluble in water (1/2)