CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-4-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

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

(iii) **Section A** – question number **1** to **16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – question number **17** to **21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – question number **22** to **28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – question number **29** and **30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – question number **31** to **33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the Sections except Section –**A**.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculator is NOT allowed.

Section A (16 marks)

*Question No. **1** to **16** are Multiple Choice type questions carrying 1 mark each.*

1. The molar ionic conductivities of Al^{3+} and SO_4^{2-} are 189 S cm^2 mol^{-1} and 160 S cm^2 mol^{-1} respectively. The value of limiting molar conductivity of $Al_2(SO_4)_3$ will be : [1 mark]

(A) 198 S cm^2 mol^{-1}

(B) 858 S cm^2 mol^{-1}

(C) 588 S cm^2 mol^{-1}

(D) 891 S cm^2 mol^{-1}

Correct Answer: (B) 858 S cm^2 mol^{-1}

Solution:

Concept:

- Kohlrausch's law states that the limiting molar conductivity of an electrolyte is the sum of the limiting ionic molar conductivities, each multiplied by its stoichiometric coefficient.
- For $Al_2(SO_4)_3$, the coefficients are two for Al^{3+} and three for SO_4^{2-}; ionic charge is not an extra multiplier.

Step 1: Write the ionic contribution At infinite dilution, one mole of $Al_2(SO_4)_3$ produces two moles of aluminium ions and three moles of sulphate ions. Hence

$$\Lambda_m^\circ = 2\lambda_{Al^{3+}}^\circ + 3\lambda_{SO_4^{2-}}^\circ.$$

Step 2: Substitute and compare the options Using the given ionic conductivities,

$$\Lambda_m^\circ = 2(189) + 3(160) = 378 + 480 = 858\,\text{S cm}^2\,\text{mol}^{-1}.$$

Option (B) matches this sum. Options (A), (C) and (D) do not equal the stoichiometrically weighted total; simply adding the two ionic values would also ignore the formula coefficients.

Step 3: Conclusion The limiting molar conductivity is $858\,\text{S cm}^2\,\text{mol}^{-1}$. Hence, the correct option is (B).

Quick Tip to Solve: Read the subscripts in the electrolyte formula before multiplying each ionic conductivity.

2. Which of the following acids represents Vitamin C ? [1 mark]

(A) Saccharic acid

(B) Gluconic acid

(C) Ascorbic acid

(D) Benzoic acid

Correct Answer: (C) Ascorbic acid

Solution:

Concept:

- Vitamin C is ascorbic acid, a water-soluble vitamin required in the diet.
- The name of the vitamin is a specific chemical identity; an acid obtained from glucose is not automatically vitamin C.

Step 1: Identify vitamin C The chemical name associated with vitamin C is ascorbic acid. It acts as an antioxidant, and its deficiency causes scurvy. Thus the acid in option (C) has the required vitamin identity.

Step 2: Check the remaining acids Saccharic acid, option (A), is a glucose oxidation product in which both terminal groups are oxidised. Gluconic acid, option (B), results from oxidation of the aldehyde group of glucose. Benzoic acid, option (D), is an aromatic carboxylic acid. None of these three acids represents vitamin C.

Step 3: Conclusion Vitamin C is ascorbic acid. Hence, the correct option is (C).

Quick Tip to Solve: Remember the direct identity vitamin C = ascorbic acid; do not confuse it with glucose oxidation products.

3. Rosenmund reduction is used for the preparation of Aldehydes. The catalyst used in this reaction is : [1 mark]

(A) Pd-$BaSO_4$

(B) Anhydrous $AlCl_3$

(C) Iron (III) oxide

(D) $HgSO_4$

Correct Answer: (A) Pd-$BaSO_4$

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into an aldehyde by catalytic hydrogenation.
- Palladium supported on barium sulphate, $Pd/BaSO_4$, is the catalyst; the controlled catalyst activity limits further reduction.

Step 1: Write the selective reduction An acyl chloride reacts with hydrogen in the presence of

Quick Tip to Solve: Link Rosenmund to acyl chloride plus hydrogen over palladium supported on barium sulphate.

palladium on barium sulphate:

$$\mathrm{RCOCl} + \mathrm{H_2} \xrightarrow{\mathrm{Pd/BaSO_4}} \mathrm{RCHO} + \mathrm{HCl}.$$

The catalyst is made less active so that the aldehyde product is not readily reduced further to the corresponding alcohol.

Step 2: Compare the catalysts offered Option (A), $\mathrm{Pd} - \mathrm{BaSO_4}$, supplies the Rosenmund catalyst. Anhydrous $\mathrm{AlCl_3}$, option (B), is a Lewis-acid catalyst used in Friedel–Crafts reactions. Iron(III) oxide, option (C), is not the Rosenmund catalyst. $\mathrm{HgSO_4}$, option (D), is used in acid-catalysed hydration of alkynes, rather than this selective hydrogenation.

Step 3: Conclusion The catalyst is $\mathrm{Pd/BaSO_4}$. Hence, the correct option is (A).

Quick Tip to Solve: Link Rosenmund to acyl chloride plus hydrogen over palladium supported on barium sulphate.

4. From the elements of 3d series given below, which element shows the maximum number of oxidation states ? [1 mark]

(A) Scandium

(B) Manganese

(C) Chromium

(D) Titanium

Correct Answer: (B) Manganese

Solution:

Concept:

- Transition elements show variable oxidation states because both their $4s$ and $3d$ electrons can participate in bonding.
- Manganese has the configuration $[\mathrm{Ar}]\,3d^5 4s^2$, providing seven outer electrons and a wide range of oxidation states.

Step 1: Compare the electronic configurations Scandium, titanium, chromium and manganese lie in the first transition series. Manganese has five $3d$ electrons and two $4s$ electrons. The participation of these electrons allows manganese to attain several positive oxidation states, including its highest value of $+7$.

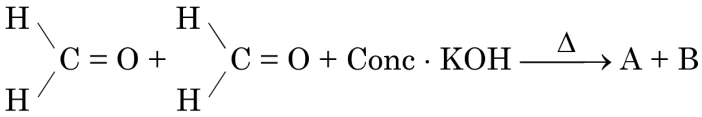
Step 2: Compare the usual oxidation-state ranges Manganese exhibits oxidation states from $+2$ to $+7$, for example $+2$ in $\mathrm{MnCl_2}$, $+4$ in $\mathrm{MnO_2}$ and $+7$ in $\mathrm{KMnO_4}$. Scandium mainly shows $+3$, titanium commonly shows $+2, +3, +4$, and chromium has fewer commonly encountered states than manganese. Hence options (A), (C) and (D) do not give the maximum number in this comparison.

Step 3: Conclusion Manganese shows the maximum number of oxidation states among the given elements. Hence, the correct option is (B).

Quick Tip to Solve: For the first transition series, associate the widest oxidation-state range with manganese, not just a high single state.

5. Consider the following reaction :

Identify A and B from the given options : [1 mark]



(A) A – Methanol, B – Potassium formate

(B) A – Ethanol, B – Potassium formate

(C) A – Methanal, B – Ethanol

(D) A – Methanol, B – Potassium acetate

Correct Answer: (A) A – Methanol, B – Potassium formate

Solution:

Concept:

- Aldehydes without an α-hydrogen undergo the Cannizzaro reaction in concentrated alkali.
- In this disproportionation, one aldehyde molecule is reduced to an alcohol while another is oxidised to a carboxylate salt.

Step 1: Identify the reaction of methanal The starting aldehyde is methanal, HCHO. It has no α-carbon and therefore no α-hydrogen. With concentrated potassium hydroxide and heating, it undergoes Cannizzaro disproportionation rather than aldol condensation.

Step 2: Obtain the alcohol and salt The balanced reaction is

$$2\mathrm{HCHO} + \mathrm{KOH} \xrightarrow{\Delta} \mathrm{CH_3OH} + \mathrm{HCOOK}.$$

Reduction gives methanol, and oxidation gives potassium formate. Option (A) contains both products. Options (B) and (C) incorrectly introduce ethanol, while option (D) incorrectly gives potassium acetate. The products retain the one-carbon skeleton of methanal.

Step 3: Conclusion A is methanol and B is potassium formate. Hence, the correct option is (A).

Quick Tip to Solve: With HCHO and concentrated KOH, pair methanol with formate; both products must keep one carbon.

6. Which alkyl halide from the given options will undergo S_N1 reaction faster ? [1 mark]

(A) $(CH_3)_3C–Br$

(B) $(CH_3)_2CH–Br$

(C) $CH_3–CH_2–Br$

(D) $(CH_3)_3C–CH_2–Br$

Correct Answer: (A) $(CH_3)_3C–Br$

Solution:

Concept:

- In an S_N1 reaction, the slow step is ionisation of the alkyl halide to form a carbocation and a halide ion.
- For ordinary alkyl carbocations, stability follows tertiary $>$ secondary $>$ primary owing to the electron-releasing effect and hyperconjugation of alkyl groups.

Step 1: Identify the carbocation formed in each case Option (A), $(CH_3)_3CBr$, forms a tertiary tert-butyl carbocation. Option (B) forms a secondary isopropyl carbocation, whereas option (C) forms a primary ethyl carbocation. In option (D), the bromine-bearing carbon is CH_2, so initial ionisation produces a primary neopentyl carbocation.

Step 2: Apply the rate-determining step All four substrates have the same leaving group, bromide. The major comparison is therefore the ease of forming the initial carbocation. The tertiary carbocation from (A) is most stable, so its formation is fastest under comparable S_N1 conditions. The secondary and primary carbocations in (B), (C) and (D) form less readily. The tertiary carbon adjacent to CH_2Br in (D) does not make the halogen-bearing carbon tertiary.

Step 3: Conclusion $(CH_3)_3C - Br$ undergoes the fastest S_N1 reaction. Hence, the correct option is (A).

Quick Tip to Solve: Classify the carbon directly bonded to Br; a neighbouring tertiary carbon does not make CH2Br tertiary.

7. The fraction of molecules having energy equal to or greater than activation energy is : [1 mark]

(A) A

(B) $e^{-E_a/RT}$

(C) K

(D) $A\,e^{-E_a/RT}$

Correct Answer: (B) $e^{-E_a/RT}$

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the pre-exponential factor and E_a the molar activation energy.
- Here R is the gas constant and T the absolute temperature. The exponential factor gives the

Quick Tip to Solve: In the Arrhenius equation, remove the pre-exponential factor when asked only for the energetic fraction.

fraction with sufficient energy in the standard Arrhenius treatment.

Step 1: Separate the energetic fraction Molecules must have energy at least equal to the activation-energy barrier to be energetically capable of reaction. The fraction satisfying this energy requirement is represented by

$$f = e^{-E_a/(RT)}.$$

The exponent is dimensionless because E_a and RT both have units of energy per mole.

Step 2: Distinguish the fraction from the rate constant Option (B) is this exponential fraction. Option (A), A, is the pre-exponential factor, not a fraction. Option (C), printed as K, does not give the energetic fraction. Option (D), $Ae^{-E_a/(RT)}$, is the full Arrhenius expression for the rate constant. A fraction is dimensionless and lies between zero and one for positive E_a and T, whereas a rate constant has units determined by the reaction order.

Step 3: Conclusion The required fraction is $e^{-E_a/(RT)}$. Hence, the correct option is (B).

Quick Tip to Solve: In the Arrhenius equation, remove the pre-exponential factor when asked only for the energetic fraction.

8. Identify the primary amine from the given options : [1 mark]

(A) $(C_2H_5)_3N$

(B) $(C_2H_5)_2NH$

(C) $C_2H_5NH_2$

(D) $(CH_3)_3N$

Correct Answer: (C) $C_2H_5NH_2$

Solution:

Concept:

- Amines are classified by the number of carbon groups bonded directly to the nitrogen atom.
- A primary amine has the general formula RNH_2, a secondary amine R_2NH, and a tertiary amine R_3N, where R is an alkyl or aryl group.

Step 1: Count the groups on nitrogen In $C_2H_5NH_2$, nitrogen is bonded to one ethyl group and two hydrogen atoms. Thus only one hydrogen of ammonia has been replaced by an alkyl group.

Step 2: Classify the other options $(C_2H_5)_2NH$ has two ethyl groups on nitrogen and is secondary. Both $(C_2H_5)_3N$ and $(CH_3)_3N$ have three alkyl groups on nitrogen and are tertiary. The length of each carbon chain does not determine the class of an amine.

Step 3: Conclusion $C_2H_5NH_2$, ethylamine, is the primary amine. Hence, the correct option is (C).

Quick Tip to Solve: Count carbon groups attached directly to N: one group with two N-H bonds identifies a primary amine.

9. The general electronic configuration of d-block elements is : [1 mark]

(A) $(n-1)d^{1-10}ns^{1-2}$

(B) $(n-1)d^{10}ns^{1-2}$

(C) $(n-1)d^{10}ns^{2-3}$

(D) $(n-1)d^{0}ns^{1-2}$

Correct Answer: (A) $(n-1)d^{1-10}ns^{1-2}$

Solution:

Concept:

- In d-block elements, the differentiating electron enters the d subshell of the penultimate shell, written as $(n-1)d$.
- A d subshell can accommodate up to ten electrons; the outermost s subshell can accommodate up to two electrons. Here n is the principal quantum number of the outermost shell.

Step 1: Identify the subshell being filled Across a d-block series, electrons progressively occupy the $(n-1)d$ subshell. Its occupancy is therefore expressed by the range 1 to 10, while the printed general form gives 1 to 2 electrons in ns.

Step 2: Compare the printed alternatives Options (B) and (C) restrict every element to a completely filled d^{10} subshell, so they cannot describe the whole block. Option (C) also allows three electrons in an s subshell, exceeding its capacity. Option (D) gives d^{0}, omitting the characteristic occupation of the d subshell. Exceptional individual configurations do not make these restricted alternatives the general pattern.

Step 3: Conclusion The required general configuration is $(n-1)d^{1-10}ns^{1-2}$. Hence, the correct option is (A).

Quick Tip to Solve: For the printed general configuration, check the d-occupancy range and remember that an s subshell holds at most two electrons.

10. Match the reagents required for the given reactions :

I. Oxidation of primary alcohols to aldehydes (p) $NaBH_4$

II. Butan-2-one to Butan-2-ol (q) 85% phosphoric acid at 440 K

III. Bromination of Phenol to 2, 4, 6-Tribromophenol (r) PCC

IV. Dehydration of propan-2-ol to propene (s) Bromine water [1 mark]

(A) I-(r), II-(p), III-(s), IV-(q)

(B) I-(q), II-(r), III-(p), IV-(s)

(C) I-(s), II-(q), III-(p), IV-(r)

(D) I-(p), II-(s), III-(r), IV-(q)

Correct Answer: (A) I-(r), II-(p), III-(s), IV-(q)

Solution:

Concept:

- The reagent must match the reaction type: controlled oxidation, carbonyl reduction, electrophilic substitution or dehydration.
- PCC is pyridinium chlorochromate, a mild oxidising agent; $NaBH_4$ is a reducing agent for aldehydes and ketones.

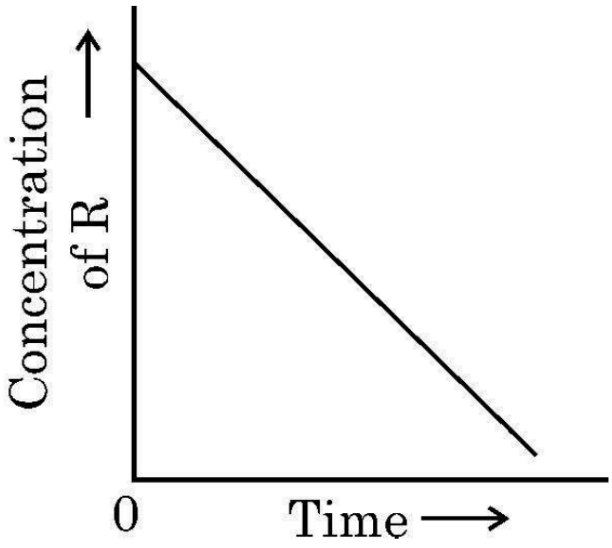
Step 1: Match oxidation and reduction PCC oxidises a primary alcohol to an aldehyde under controlled, anhydrous conditions without proceeding to the carboxylic acid: I-(r). Sodium borohydride reduces the ketone group of butan-2-one to the secondary alcohol group of butan-2-ol: II-(p). Interchanging these two reagents would interchange oxidation and reduction.

Step 2: Match substitution and elimination The strongly activating hydroxyl group of phenol directs bromination to the ortho and para positions. Bromine water gives 2,4,6-tribromophenol: III-(s). Heating propan-2-ol with 85% phosphoric acid at $440\,K$ eliminates water to produce propene: IV-(q). Options (B), (C) and (D) do not give this complete set of reagent functions.

Step 3: Conclusion The matching is I-(r), II-(p), III-(s), IV-(q). Hence, the correct option is (A).

Quick Tip to Solve: Anchor the matching with PCC for controlled oxidation and sodium borohydride for ketone reduction, then match bromine water and hot acid.

11. In a given graph of zero order reaction, the slope and intercept are : [1 mark]



(A) Slope = k, Intercept = $[R]_0$

(B) Slope = –k, Intercept = $[R]_0$

(C) Slope = k/2.303, Intercept = $\ln[R]_0$

(D) Slope = –k/2.303, Intercept = ln A

Correct Answer: (B) Slope = –k, Intercept = $[R]_0$

Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$, where k is the positive rate constant.
- The integrated equation is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration and t is time.

Step 1: Compare with the straight-line equation The graph plots concentration $[R]$ vertically against time t horizontally. Comparing $[R] = -kt + [R]_0$ with $y = mx + c$ identifies the coefficient of time as the slope and the constant term as the vertical intercept.

Step 2: Check the sign and the intercept Concentration falls with time, so the line has a negative slope, $-k$, rather than $+k$. At $t = 0$, the concentration is $[R]_0$. The factors involving 2.303 and logarithmic intercepts in options (C) and (D) do not belong to this concentration-versus-time equation for a zero-order reaction.

Step 3: Conclusion Slope $= -k$ and intercept $= [R]_0$. Hence, the correct option is (B).

Quick Tip to Solve: Write the integrated rate law as y = mx + c using the graph's actual axes; a falling concentration line must have a negative slope.

12. Nucleophilic addition of Grignard reagent to ketones followed by hydrolysis with dilute acids forms : [1 mark]

(A) Alkene

(B) Primary alcohol

(C) Tertiary alcohol

(D) Secondary alcohol

Correct Answer: (C) Tertiary alcohol

Solution:

Concept:

- A Grignard reagent, $RMgX$, supplies a nucleophilic carbon group R that adds to the electrophilic carbon of a carbonyl group.
- Hydrolysis protonates the resulting alkoxide to form an alcohol. The alcohol class depends on the number of carbon groups attached to the carbon bearing OH.

Step 1: Count the carbon groups after addition A ketone already has two carbon groups attached to its carbonyl carbon. Addition of the carbon group from the Grignard reagent gives that carbon a third carbon group and converts the carbonyl oxygen into an alkoxide oxygen.

Step 2: Identify the hydrolysis product Dilute acid supplies a proton to the alkoxide oxygen, producing OH without removing any of the three carbon groups on that carbon. Thus hydrolysis gives a tertiary alcohol. Formaldehyde gives a primary alcohol, while other aldehydes give secondary alcohols with Grignard reagents; these are not ketones. An alkene would require elimination rather than the stated addition and hydrolysis.

Step 3: Conclusion A ketone reacts with a Grignard reagent and undergoes acidic hydrolysis to give a tertiary alcohol. Hence, the correct option is (C).

Quick Tip to Solve: Count two carbon groups on the ketone carbon, then add one from the Grignard reagent: three groups make the product a tertiary alcohol.

13. Two statements are given - one labelled Assertion (A) and the other labelled Reason (R).

Assertion (A) : Phenols are stronger acids than alcohols.

Reason (R) : Alkoxide ion is more stable than phenoxide ion. [1 mark]

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

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

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

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

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- Acid strength depends on the ease of releasing a proton and the stability of the conjugate base formed.
- Phenol gives a phenoxide ion on losing a proton, whereas an alcohol gives an alkoxide ion. Resonance stabilisation favours formation of the conjugate base.

Step 1: Evaluate the assertion Phenoxide ion is resonance stabilised: its negative charge is delocalised through the oxygen and the aromatic ring. This makes proton loss from phenol more favourable than proton loss from an ordinary alcohol. Therefore the assertion that phenols are stronger acids than alcohols is true.

Step 2: Evaluate the reason An alkoxide ion has no comparable resonance delocalisation of its negative charge into an aromatic ring. Its alkyl group also has an electron-releasing inductive effect, which does not stabilise the negative charge. The reason reverses the stability comparison: phenoxide, rather than alkoxide, is the more stable conjugate base. Hence the reason is false.

Step 3: Check the explanatory relation The true explanation for the assertion is the greater resonance stabilisation of phenoxide ion. The printed reason states the opposite and therefore cannot explain the assertion. Options (A) and (B) incorrectly call the reason true, and (D) incorrectly calls the assertion false.

Step 4: Conclusion The assertion is true, but the reason is false. Hence, the correct option is (C).

Quick Tip to Solve: For an acidity comparison, remove H from each OH group and compare conjugate-base stability; resonance favours the phenoxide ion.

14. Assertion (A) : For a Daniell cell, $Zn/Zn^{2+}(1M)$ || $Cu^{2+}(1M)/Cu$ with E°_{cell} = 1.1 V, if the external opposing potential is more than 1.1 V, the electrons flow from Cu to Zn.

Reason (R) : Cell acts like a galvanic cell. [1 mark]

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

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

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

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

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- A Daniell cell spontaneously oxidises zinc and reduces copper ions, with electrons flowing externally from zinc to copper.
- An opposing external potential greater than the cell emf forces the reverse, non-spontaneous reaction; the arrangement then operates as an electrolytic cell.

Step 1: Evaluate the assertion At the stated concentrations, the Daniell cell emf is $1.1\,\text{V}$. If the opposing external potential exceeds this value, it overcomes the spontaneous direction. Copper is oxidised and zinc ions are reduced:

$$\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\,\text{e}^{-}, \qquad \text{Zn}^{2+} + 2\,\text{e}^{-} \longrightarrow \text{Zn}.$$

Electrons therefore flow through the external circuit from Cu to Zn, as stated in the assertion. The assertion is true.

Step 2: Evaluate the reason A galvanic cell supplies electrical energy from a spontaneous reaction. Here an external source supplies energy to drive the reverse reaction. Under the specified opposing potential, the cell acts as an electrolytic cell, so the reason claiming galvanic operation is false.

Step 3: Check the explanatory relation The reversed electron flow follows from the applied opposing potential exceeding the emf, rather than from galvanic operation. Options (A) and (B) would require a true reason; option (D) would require a false assertion. Neither condition fits the stated case.

Step 4: Conclusion The assertion is true, but the reason is false. Hence, the correct option is (C).

Quick Tip to Solve: Compare the opposing potential with the cell emf: above 1.1 V, the Daniell reaction reverses and the cell becomes electrolytic.

15. Assertion (A) : Benzoic acid does not undergo Friedel - Crafts reaction.

Reason (R) : Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to the carboxyl group. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Friedel–Crafts alkylation and acylation are electrophilic aromatic substitution reactions requiring a sufficiently reactive benzene ring.
- The $-COOH$ group withdraws electron density through inductive and resonance effects, while its oxygen atoms can bind the Lewis acid catalyst $AlCl_3$.

Step 1: Judge the assertion Benzoic acid does not undergo the usual Friedel–Crafts reaction. Its $-COOH$ group strongly deactivates the aromatic ring towards electrophilic attack. Thus Assertion (A) is true.

Step 2: Judge the reason The carboxyl group is electron withdrawing and hence deactivating. In addition, it forms a complex with aluminium chloride through an oxygen atom, binding the catalyst. Both statements in Reason (R) are true.

Step 3: Relate the reason to the assertion Ring deactivation suppresses electrophilic substitution and complex formation with $AlCl_3$ further prevents the usual Friedel–Crafts conditions from working. These effects directly explain the assertion. Option (B) incorrectly denies this explanatory link; options (C) and (D) incorrectly classify one of the statements as false.

Step 4: Conclusion Both A and R are true, and R is the correct explanation of A. Hence, the correct option is (A).

Quick Tip to Solve: For Friedel–Crafts questions, check both strong ring deactivation and whether a functional group binds the Lewis acid catalyst.

16. Assertion (A) : Fructose is a reducing sugar.

Reason (R) : Fructose does not reduce Fehling solution and Tollen's reagent. [1 mark]

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

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

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

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

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- A reducing sugar reduces mild oxidising agents such as Fehling's solution and Tollens' reagent.
- In an alkaline medium, fructose undergoes enediol rearrangement to the aldoses glucose and mannose, which have reducing behaviour.

Step 1: Judge the assertion Fructose is a reducing sugar, even though its open-chain form contains a ketone group. In alkaline solution it rearranges through an enediol intermediate to glucose and mannose. These aldoses reduce the test reagents, so Assertion (A) is true.

Step 2: Judge the reason Fructose does reduce both Fehling's solution and Tollens' reagent under their alkaline test conditions. The former gives a brick-red precipitate of Cu_2O, while the latter deposits metallic silver. Therefore the claim that fructose does not reduce them is false.

Step 3: Check the assertion–reason relationship Because R is false, it cannot explain the true assertion. Options (A) and (B) incorrectly regard R as true, and option (D) incorrectly regards A as false. The correct combination is A true and R false.

Step 4: Conclusion Assertion A is true, but Reason R is false. Hence, the correct option is (C).

Quick Tip to Solve: Do not classify fructose as non-reducing merely because it is a ketose: alkaline test reagents permit conversion into aldoses.

Section B (10 marks)

17. Define the following terms :

(a) Half life period ($t_{1/2}$)

(b) Effective collisions [2 marks]

Solution:

Concept:

- Reaction progress can be described by the decrease in the concentration of a reactant with time.
- Collision theory requires sufficient collision energy and suitable orientation for colliding reactant species to form products.

Step 1: Define the half-life period (a) The half-life period, $t_{1/2}$, is the time required for the concentration (or amount) of a reactant to decrease to one-half of its initial value. If its initial concentration is

Quick Tip to Solve: For half-life, specify half of the initial reactant concentration; for effective collisions, state both energy and orientation requirements.

$[A]_0$, then at this time

$$[A]_{t_{1/2}} = \frac{[A]_0}{2}.$$

It is a time interval, expressed in a unit such as seconds. This definition applies regardless of the reaction order; the formula for calculating it depends on the order.

Step 2: Define effective collisions (b) Effective collisions are collisions between reactant particles that actually lead to formation of products. The colliding particles must possess energy equal to or greater than the activation-energy threshold and must collide with a suitable orientation. Adequate energy allows the activated complex to form, while correct orientation permits the necessary bonds to break and form. A collision failing either requirement is ineffective.

Step 3: Conclusion Half-life is the time for a reactant to fall to half its initial concentration; effective collisions are suitably oriented, sufficiently energetic collisions that form products.

Quick Tip to Solve: For half-life, specify half of the initial reactant concentration; for effective collisions, state both energy and orientation requirements.

18. A solution containing 60 g of a non-volatile solute in 250 g of water freezes at 270.67 K. Calculate the molar mass of the solute. (K_f of water = $1.86\,\text{K kg mol}^{-1}$) [2 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile solute, freezing-point depression is $\Delta T_f = K_f m$, where K_f is the cryoscopic constant and m is molality.
- Molality is moles of solute per kilogram of solvent: $m = (w_2/M_2)/(w_1/1000)$, where w_1, w_2 are masses in grams and M_2 is the solute molar mass.

Step 1: Calculate the freezing-point depression Pure water freezes at $273.15\,\text{K}$. The solution freezes at $270.67\,\text{K}$, so the decrease in freezing temperature is

$$\Delta T_f = 273.15 - 270.67 = 2.48\,\text{K}.$$

Use the positive depression, rather than the solution's absolute temperature, in the colligative-property equation. No dissociation or association is specified, so use the ordinary molecular-solute relation.

Step 2: Find molality and molar mass The solvent mass is $250\,\text{g} = 0.250\,\text{kg}$. Substituting $K_f = 1.86\,\text{K kg mol}^{-1}$ gives

$$m = \frac{\Delta T_f}{K_f} = \frac{2.48}{1.86} = \frac{4}{3}\,\text{mol kg}^{-1}.$$

Thus the moles of solute dissolved are $n = (4/3)(0.250) = 1/3\,\text{mol}$. Using the given solute mass,

$$M_2 = \frac{w_2}{n} = \frac{60\,\text{g}}{(1/3)\,\text{mol}} = 180\,\text{g mol}^{-1}.$$

Step 3: Conclusion The molar mass of the non-volatile solute is $\boxed{180\,\text{g mol}^{-1}}$.

Quick Tip to Solve: First subtract the solution freezing point from 273.15 K, then convert only the solvent mass to kilograms when calculating molality.

19. (a) Which of the following compounds will react more rapidly by S_N1 reaction and why?

$(CH_3)_3C-Br$ **or** CH_3CH_2Br

(b) Arrange the following compounds in the increasing order of their boiling points:

Bromoform, Dibromomethane, Chloromethane, Bromomethane [2 marks]

Solution:

Concept:

- In an S_N1 reaction, slow ionisation forms a carbocation; a more stable carbocation forms more readily and gives a faster reaction under comparable conditions.
- Alkyl groups stabilise carbocations through the positive inductive effect and hyperconjugation. The usual stability order is tertiary greater than secondary greater than primary.
- Boiling point generally rises with molecular mass and polarizability for the closely related halomethanes, because stronger intermolecular dispersion forces require more energy to overcome.

Step 1: Compare the carbocations in part (a) Ionisation of tert-butyl bromide, $(CH_3)_3C-Br$, gives the tertiary tert-butyl carbocation, $(CH_3)_3C^+$. Ethyl bromide, CH_3CH_2Br, would give the primary ethyl carbocation, $CH_3CH_2{}^+$. Three methyl groups stabilise the tertiary carbocation by electron donation and hyperconjugation. Therefore tert-butyl bromide reacts more rapidly by the S_N1 pathway; the primary carbocation is much less favourable.

Step 2: Arrange the halomethanes in part (b) Chloromethane is CH_3Cl, bromomethane is CH_3Br, dibromomethane is CH_2Br_2, and bromoform is $CHBr_3$. Replacing chlorine with the heavier, more polarizable bromine and then increasing the number of bromine atoms increases intermolecular attractions. The increasing boiling-point order is

$$CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3.$$

Step 3: Conclusion (a) $(CH_3)_3C-Br$ reacts faster because it forms a more stable tertiary carbocation. (b) Chloromethane $<$ Bromomethane $<$ Dibromomethane $<$ Bromoform.

Quick Tip to Solve: For part (a), compare the carbocations after bromide leaves; for part (b), count bromine atoms and compare mass and polarizability.

20(a). Write the stepwise mechanism of nucleophilic addition reactions in the carbonyl compounds. [2 marks]

Solution:

Concept:

- The carbonyl bond is polar: oxygen bears a partial negative charge and the carbonyl carbon a partial positive charge. Hence an electron-rich nucleophile attacks the carbon atom.
- Nucleophilic addition converts the planar carbonyl group into a tetrahedral addition product. Let Nu^- represent a nucleophile and R, R^1 represent hydrogen or alkyl groups.

Quick Tip to Solve: Direct the nucleophile to the carbonyl carbon, move the pi-bond pair onto oxygen, and protonate oxygen only after forming the alkoxide intermediate.

Step 1: Attack the carbonyl carbon The nucleophile donates an electron pair to the electrophilic carbonyl carbon. Simultaneously, the carbon-oxygen pi-bond electron pair moves onto oxygen, forming a tetrahedral alkoxide intermediate:

$$\mathrm{R{-}C(=O){-}R^1 + Nu^- \longrightarrow R{-}C(O^-)(Nu){-}R^1.}$$

Thus, carbon forms a new bond to the nucleophile, while oxygen acquires a negative charge. The carbonyl carbon changes from sp^2 to sp^3 hybridisation.

Step 2: Protonate the alkoxide intermediate The negatively charged oxygen accepts a proton from an available proton donor, such as water or an acid, to form the alcohol addition product:

$$\mathrm{R{-}C(O^-)(Nu){-}R^1 + H^+ \longrightarrow R{-}C(OH)(Nu){-}R^1.}$$

This proton-transfer step neutralises the alkoxide. The original carbon-oxygen double bond has become a single bond, with hydroxyl and nucleophile groups attached to the same carbon.

Step 3: Conclusion The stepwise mechanism consists of nucleophilic attack on the carbonyl carbon to form a tetrahedral alkoxide, followed by protonation of oxygen to give $\mathrm{R{-}C(OH)(Nu){-}R^1}$.

Quick Tip to Solve: Direct the nucleophile to the carbonyl carbon, move the pi-bond pair onto oxygen, and protonate oxygen only after forming the alkoxide intermediate.

OR

20(b). How will you convert the following :

(i) Toluene to benzoic acid.

(ii) Ethanol to 3-Hydroxybutanal [2 marks]

Solution:

Concept:

- Hot alkaline potassium permanganate oxidises an alkyl side chain on benzene to a carboxylate group; acidification then gives the carboxylic acid.
- Ethanol first gives ethanal by dehydrogenation. Ethanal has alpha-hydrogen atoms and undergoes aldol addition with dilute alkali to form a beta-hydroxy aldehyde.

Step 1: Convert toluene to benzoic acid Heat toluene with alkaline $\mathrm{KMnO_4}$, then acidify the benzoate formed with dilute acid. The methyl side chain is oxidised while the benzene ring is retained:

$$\mathrm{C_6H_5CH_3 \xrightarrow{KMnO_4/OH^-,\,heat} C_6H_5COO^- \xrightarrow{H^+} C_6H_5COOH.}$$

The overall oxidation can be represented as

$$\mathrm{C_6H_5CH_3 + 3\,[O] \longrightarrow C_6H_5COOH + H_2O.}$$

Step 2: Convert ethanol to 3-hydroxybutanal Pass ethanol vapour over heated copper at $573\,\mathrm{K}$ to

Quick Tip to Solve: For the second conversion, first make ethanal, then double its carbon skeleton by aldol addition; keep the product cool to retain the hydroxyl group.

obtain ethanal:

$$CH_3CH_2OH \xrightarrow{Cu,\,573\,K} CH_3CHO + H_2.$$

Treat ethanal with dilute $NaOH$ at low temperature. Two ethanal molecules undergo aldol addition:

$$2\,CH_3CHO \xrightarrow{dil\cdot\,NaOH} CH_3CH(OH)CH_2CHO.$$

Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Avoid heating the aldol product, since dehydration would instead produce but-2-enal.

Step 3: Conclusion (i) Toluene gives benzoic acid by hot alkaline permanganate oxidation followed by acidification. (ii) Ethanol gives ethanal over heated copper, then 3-hydroxybutanal by aldol addition with dilute alkali.

Quick Tip to Solve: For the second conversion, first make ethanal, then double its carbon skeleton by aldol addition; keep the product cool to retain the hydroxyl group.

21. (a) What happens when Glucose reacts with Nitric acid ? Write chemical equation.
(b) Write one structural difference between DNA and RNA. [2 marks]

Solution:

Concept:

- Nitric acid is a strong oxidising agent. In the open-chain structure of glucose it oxidises both the aldehyde group and the terminal primary alcohol group to carboxyl groups.
- DNA and RNA differ structurally in their pentose sugars: DNA contains 2-deoxyribose, whereas RNA contains ribose.

Step 1: Write the oxidation of glucose On oxidation with nitric acid, glucose forms saccharic acid, also called glucaric acid. Its two terminal carbon atoms become carboxyl groups:

$$CHO{-}(CHOH)_4{-}CH_2OH + 3\,[O] \xrightarrow{HNO_3} HOOC{-}(CHOH)_4{-}COOH + H_2O.$$

Here $[O]$ denotes an oxidising oxygen equivalent supplied by nitric acid. Oxidation of the aldehyde group requires one such equivalent, and oxidation of the primary alcohol group requires two. Hence the product is a dicarboxylic acid, rather than gluconic acid, which contains only one carboxyl group.

Step 2: State the structural difference between DNA and RNA The sugar in DNA is 2-deoxyribose, while the sugar in RNA is ribose. At the $2'$-carbon of the sugar, DNA has a hydrogen atom in place of the hydroxyl group present in RNA. This is a structural difference within the nucleotide units forming the two nucleic acids.

Step 3: Conclusion (a) Nitric acid oxidises glucose to saccharic acid, $HOOC{-}(CHOH)_4{-}COOH$, as shown in the equation. (b) DNA contains 2-deoxyribose, while RNA contains ribose, differing by the hydroxyl group at the sugar's $2'$-carbon.

Quick Tip to Solve: Strong nitric acid oxidises both ends of glucose. To distinguish the sugars, remember that DNA lacks the hydroxyl group at carbon 2 of ribose.

Section C (21 marks)

22. (a) Draw the geometrical isomers of the given complex :

$[Pt(NH_3)_2Cl_2]^{2+}$

(b) Write the electronic configuration of d^5 ion if $\Delta_0 < P$.

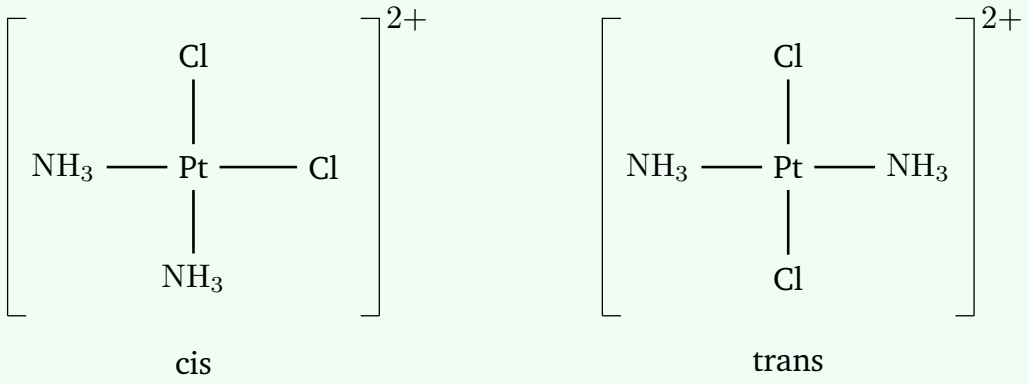
(c) What is an ambidentate ligand ? [3 marks]

Solution:

Concept:

- Geometrical isomers differ in relative ligand positions. In the four-coordinate planar arrangement, adjacent identical ligands give the cis form and opposite identical ligands give the trans form.
- In an octahedral crystal field, the three t_{2g} orbitals lie below the two e_g orbitals. When the splitting energy Δ_o is less than the pairing energy P, electrons occupy all five orbitals singly before pairing.
- An ambidentate ligand has two alternative donor atoms, but coordinates through only one of them at a time; it is different from a bidentate ligand, which attaches through two atoms simultaneously.

Step 1: (a) Arrange the ligands in the cis and trans forms The two chlorido ligands are adjacent in cis, with a 90° bond angle, and opposite in trans, with a 180° angle. Ammonia occupies the remaining positions; the drawings retain the printed $2+$ charge.



Cis and trans ligand arrangements of the given complex

Step 2: (b) Fill the orbitals of the high-spin d^5 ion Since $\Delta_o < P$, occupation of e_g costs less than pairing in t_{2g}. Hund's rule gives one electron in each of the three lower and two upper orbitals. The octahedral configuration is

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

with five unpaired electrons.

Step 3: (c) Define an ambidentate ligand with an example An ambidentate ligand can bind to a metal ion through either of two different donor atoms. For example, NO_2^- can coordinate through nitrogen (nitro) or through oxygen (nitrito). In either mode it uses only one donor atom to attach to a particular metal ion.

Step 4: Conclusion (a) The geometrical isomers are cis (adjacent chlorides) and trans (opposite chlorides), as drawn. (b) The configuration is $t_{2g}^3 e_g^2$. (c) An ambidentate ligand has two alternative

Quick Tip to Solve: Compare the positions of the two Cl ligands: adjacent means cis and opposite means trans; $\Delta_o < P$ means high spin.

donor atoms, for example NO_2^-.

Quick Tip to Solve: Compare the positions of the two Cl ligands: adjacent means cis and opposite means trans; $\Delta_o < P$ means high spin.

23. Write chemical equations for the following reactions (Do any three) :

(a) Hydroboration - oxidation reaction

(b) Williamson Synthesis

(c) Friedel-Crafts Alkylation of Anisole

(d) Reimer-Tiemann Reaction [3 marks]

Solution:

Concept:

- Hydroboration followed by oxidation converts an alkene into an alcohol with anti-Markovnikov orientation: the OH group attaches to the less substituted carbon.
- Williamson synthesis forms an ether by an S_N2 reaction of an alkoxide ion with a suitable primary alkyl halide.
- The methoxy group of anisole activates its benzene ring and directs electrophilic substitution to the ortho and para positions. Reimer–Tiemann reaction introduces a CHO group mainly ortho to the OH group of phenol.

Step 1: (a) Hydroboration–oxidation of propene Propene reacts with diborane in ether to form a trialkylborane. Oxidation with hydrogen peroxide in aqueous sodium hydroxide replaces the carbon–boron bond by a carbon–oxygen bond, giving propan-1-ol:

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2,\ NaOH]{1.\ B_2H_6,\ \text{ether}} CH_3CH_2CH_2OH.$$

The OH group is attached to the terminal carbon; propan-2-ol is not the hydroboration–oxidation product.

Step 2: (b) Williamson synthesis of ethoxyethane Sodium ethoxide displaces bromide from bromoethane. A primary alkyl halide is chosen to favour substitution rather than elimination:

$$C_2H_5ONa + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr.$$

The resulting ether is ethoxyethane, also called diethyl ether.

Step 3: (c) Friedel–Crafts alkylation of anisole Anisole reacts with chloromethane in the presence of anhydrous aluminium chloride to give ortho- and para-methylanisole. The para product predominates because it suffers less steric crowding:

$$C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} o\text{–}\ CH_3C_6H_4OCH_3 + HCl,$$

$$C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} p\text{–}\ CH_3C_6H_4OCH_3 + HCl.$$

Quick Tip to Solve: Recall each reagent pair: diborane then alkaline peroxide; alkoxide plus primary halide; alkyl chloride/$AlCl_3$; chloroform/aqueous alkali.

These are alternative product equations, not two products formed from a single molecule of anisole.

Step 4: (d) Reimer–Tiemann reaction of phenol Heating phenol with chloroform and aqueous sodium hydroxide, followed by acidification, gives mainly 2-hydroxybenzaldehyde (salicylaldehyde). A balanced net equation for the main product is

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{\Delta} \text{o–}\ HOC_6H_4CHO + 3NaCl + 2H_2O.$$

Acid work-up releases the phenolic product from its sodium salt. A small amount of the para isomer may also form.

Step 5: Conclusion The equations above give propan-1-ol, ethoxyethane, ortho-/para-methylanisole and salicylaldehyde, respectively. The question permits any three of these four reactions.

Quick Tip to Solve: Recall each reagent pair: diborane then alkaline peroxide; alkoxide plus primary halide; alkyl chloride/$AlCl_3$; chloroform/aqueous alkali.

24. (a) Give chemical tests to distinguish between the following pairs of compounds :

(i) Phenol and Benzoic acid

(ii) Propanal and Propanone

(b) Which one of the given compounds is a stronger acid and why ?

$CH_2FCH_2CH_2COOH$ or CH_3CHFCH_2COOH [3 marks]

Solution:

Concept:

- Carboxylic acids liberate carbon dioxide from sodium hydrogencarbonate; phenol is too weak an acid to do so. Gas evolution therefore distinguishes benzoic acid from phenol.
- Aldehydes reduce Tollens' reagent, containing $[Ag(NH_3)_2]^+$, to metallic silver. Ordinary ketones such as propanone do not give this test.
- Fluorine withdraws electron density by the negative inductive ($-I$) effect and stabilises a carboxylate ion. This effect decreases rapidly as the distance between fluorine and the COOH group increases.

Step 1: (a)(i) Distinguish phenol and benzoic acid with sodium hydrogencarbonate Add aqueous $NaHCO_3$ to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide, whereas phenol gives no effervescence under the same conditions:

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 \uparrow + H_2O.$$

The gas turns limewater milky. Benzoic acid can displace carbonic acid from its salt; phenol, being weaker than carbonic acid, cannot. Thus the sample evolving CO_2 is benzoic acid.

Step 2: (a)(ii) Distinguish propanal and propanone with Tollens' reagent Warm separate samples gently with freshly prepared Tollens' reagent. Propanal produces a silver mirror (or a grey deposit

Quick Tip to Solve: Count from COOH before comparing acidity: beta-fluorine exerts a stronger $-I$ effect than gamma-fluorine.

of silver), while propanone shows no silver deposition. Propanal is oxidised to propanoate in the alkaline reagent:

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O.$$

The aldehydic group is readily oxidised under these mild conditions, whereas the ketonic group in propanone is not.

Step 3: (b) Compare the positions of fluorine and the inductive effect Count carbon positions outward from the carboxyl carbon. In $CH_2FCH_2CH_2COOH$, fluorine is on the gamma carbon; in CH_3CHFCH_2COOH, it is on the beta carbon. Fluorine is therefore closer to the COOH group in the second compound.

Its stronger $-I$ effect at this shorter distance stabilises the negatively charged conjugate base more effectively, making release of H^+ more favourable. Consequently,

$$CH_3CHFCH_2COOH > CH_2FCH_2CH_2COOH \quad \text{in acid strength.}$$

Step 4: Conclusion Benzoic acid gives CO_2 effervescence with $NaHCO_3$, while phenol does not. Propanal gives a silver mirror with Tollens' reagent, while propanone does not. CH_3CHFCH_2COOH is the stronger acid because fluorine is nearer the COOH group.

Quick Tip to Solve: Count from COOH before comparing acidity: beta-fluorine exerts a stronger $-I$ effect than gamma-fluorine.

25. Show that the time required for 99.9% completion in a first order reaction is 10 times of half-life ($t_{1/2}$) of the reaction. [log 2 = 0.3010, log 10 = 1] [3 marks]

Solution:

Concept:

- For a first order reaction, the integrated rate equation is $t = \frac{2.303}{k}\log\frac{[A]_0}{[A]_t}$, where k is the rate constant, $[A]_0$ is the initial reactant concentration and $[A]_t$ is its concentration after time t.
- The half-life $t_{1/2}$ is the time at which half the initial reactant remains. For first order kinetics, it is independent of the initial concentration.

Step 1: Find the fraction remaining at 99.9 percent completion Completion refers to the reactant consumed, whereas the integrated rate equation uses the reactant remaining. When 99.9% has reacted, the amount remaining is $100 - 99.9 = 0.1\%$ of the initial amount. Therefore,

$$[A]_t = \frac{0.1}{100}[A]_0 = \frac{[A]_0}{1000}.$$

Substituting into the first order equation and using $\log 10 = 1$,

$$t_{99.9\%} = \frac{2.303}{k}\log 1000 = \frac{2.303}{k} \times 3.$$

Quick Tip to Solve: Use the fraction left, not the fraction reacted: 99.9 percent completion leaves one-thousandth of the initial reactant.

Step 2: Obtain the half-life and compare the two times At half-life, $[A]_t = [A]_0/2$. Hence, using the supplied value $\log 2 = 0.3010$,

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010.$$

Division cancels both the common numerical factor and the rate constant:

$$\frac{t_{99.9\%}}{t_{1/2}} = \frac{3}{0.3010} = 9.9668 \approx 10.$$

Thus the printed relation expresses the time ratio rounded to ten; the unrounded ratio from the supplied logarithm is about 9.97.

Step 3: Conclusion The time needed for 99.9% completion of a first order reaction is approximately ten half-lives: $\boxed{t_{99.9\%} \approx 10 t_{1/2}}$.

Quick Tip to Solve: Use the fraction left, not the fraction reacted: 99.9 percent completion leaves one-thousandth of the initial reactant.

26. Define the following terms :

(a) Glycosidic linkage

(b) Primary structure of protein

(c) Disaccharides [3 marks]

Solution:

Concept:

- Monosaccharide units combine through an oxygen bridge to form larger carbohydrates; amino acids combine through peptide bonds to form polypeptides.
- Hydrolysis breaks the linkage between constituent units by addition of water. The order of amino acids specifies a protein's primary structure.

Step 1: (a) Define glycosidic linkage A glycosidic linkage is the $\mathrm{C-O-C}$ linkage joining two monosaccharide units through an oxygen atom. It forms when hydroxyl groups of the participating sugar units undergo condensation with elimination of a water molecule. At least one participating carbon is an anomeric carbon. For example, the two glucose units in maltose are joined by an $\alpha(1 \to 4)$ glycosidic linkage: carbon 1 of one glucose unit is connected through oxygen to carbon 4 of the other.

Step 2: (b) Define the primary structure of a protein The primary structure of a protein is the specific sequence, or order, of amino acids in its polypeptide chain. The amino acids are joined by peptide bonds, $-\mathrm{CO-NH}-$, and the sequence is conventionally written from the amino-terminal end to the carboxyl-terminal end. A change in the identity or position of an amino acid changes the primary structure. This term describes the sequence itself; the coiling or folding of the chain belongs to higher levels of protein structure.

Step 3: (c) Define disaccharides Disaccharides are carbohydrates that give two monosaccharide units on hydrolysis. The two units, which may be identical or different, are joined by a glycosidic

Quick Tip to Solve: Keep the defining feature distinct: oxygen bridge for glycosidic linkage, amino acid sequence for primary structure, and two hydrolysis products for a disaccharide.

linkage. For example, maltose gives two glucose molecules, while sucrose gives one glucose and one fructose molecule. Formation of a disaccharide from two monosaccharides involves loss of water, and hydrolysis reverses this joining process:

$$\text{disaccharide} + H_2O \longrightarrow \text{two monosaccharide units.}$$

Step 4: Conclusion A glycosidic linkage joins sugar units through oxygen; primary structure specifies a protein's amino acid sequence; a disaccharide yields two monosaccharide units on hydrolysis.

Quick Tip to Solve: Keep the defining feature distinct: oxygen bridge for glycosidic linkage, amino acid sequence for primary structure, and two hydrolysis products for a disaccharide.

27. (a) Write the IUPAC name of the given compound :

$CH_2 = CH - CH_2 - CH_2 - Cl$

(b) Why is thionyl chloride preferred for preparing alkyl halides from alcohols ?

(c) What happens when Methyl bromide reacts with KCN ? [3 marks]

Solution:

Concept:

- In naming a haloalkene, choose the longest chain containing the double bond and number it to give the double bond the lowest locant. The halogen is named as a substituent.
- Thionyl chloride, $SOCl_2$, converts alcohols into alkyl chlorides. Cyanide, CN^-, is an ambident nucleophile; ionic KCN predominantly attacks through carbon to give a nitrile.

Step 1: (a) Name the given unsaturated chloro compound The structure $CH_2 = CH - CH_2 - CH_2 - Cl$ has a four-carbon parent chain. Numbering from the double-bond end places the double bond between carbons 1 and 2, and chlorine on carbon 4. The double bond receives priority for the lower locant, so the parent is but-1-ene and the substituent is 4-chloro. Numbering from the chlorine end would place the double bond at carbon 3 and is therefore unsuitable.

Step 2: (b) Explain the preference for thionyl chloride An alcohol reacts with thionyl chloride to give an alkyl chloride:

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 \uparrow + HCl \uparrow.$$

The by-products, sulphur dioxide and hydrogen chloride, are gases and escape from the reaction mixture. Their easy removal leaves the alkyl chloride relatively pure and makes its isolation convenient. Thus thionyl chloride is preferred for preparing alkyl chlorides from alcohols because no nonvolatile by-product needs to be separated from the desired product.

Step 3: (c) Describe the reaction of methyl bromide with KCN The cyanide ion supplied by KCN acts as a nucleophile. It attacks methyl bromide through its carbon end and displaces bromide by nucleophilic substitution:

$$CH_3Br + KCN \longrightarrow CH_3C \equiv N + KBr.$$

The organic product is ethanenitrile, also called acetonitrile or methyl cyanide. Its carbon chain has

Quick Tip to Solve: Give the double bond the lower locant before chlorine, and remember that KCN adds one carbon by forming a carbon-bonded nitrile.

two carbons because the carbon of the cyanide group becomes part of the product. KCN therefore gives a nitrile here; methyl isocyanide is associated with the different reagent AgCN.

Step 4: Conclusion (a) The IUPAC name is $\boxed{\text{4-chlorobut-1-ene}}$. (b) $SOCl_2$ is preferred because its gaseous by-products escape, leaving relatively pure alkyl chloride. (c) Methyl bromide with KCN forms $\boxed{CH_3CN}$, ethanenitrile, with KBr.

Quick Tip to Solve: Give the double bond the lower locant before chlorine, and remember that KCN adds one carbon by forming a carbon-bonded nitrile.

28. Calculate emf of the following cell at $25\,^\circ$C:

$$\mathrm{Sn/Sn^{2+}(0.001\,M)\,\|\,H^+(0.01\,M)\,|\,H_{2(g)}(1\,bar)\,|\,Pt_{(s)}}$$

Given: $E^\circ(\mathrm{Sn^{2+}/Sn}) = -0.14\,\mathbf{V}$, $E^\circ(\mathrm{H^+/H_2}) = 0.00\,\mathbf{V}$ **(**$\log 10 = 1$**).** [3 marks]

Solution:

Concept:

- For the cell as written, the left electrode is the anode and the right electrode is the cathode. Using reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At $298\,\mathrm{K}$, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solid activities are unity.

Step 1: Write the electrode reactions and the standard emf Tin is oxidised at the anode while hydrogen ions are reduced at the platinum cathode:

$$\mathrm{Sn}(s) \longrightarrow \mathrm{Sn^{2+}}(aq) + 2e^-,$$
$$2\mathrm{H^+}(aq) + 2e^- \longrightarrow \mathrm{H_2}(g).$$

Therefore, the balanced overall reaction is

$$\mathrm{Sn}(s) + 2\mathrm{H^+}(aq) \longrightarrow \mathrm{Sn^{2+}}(aq) + \mathrm{H_2}(g), \qquad n = 2.$$

From the given reduction potentials,

$$E^\circ_{\text{cell}} = 0.00 - (-0.14) = 0.14\,\mathrm{V}.$$

Step 2: Evaluate the reaction quotient and apply the Nernst equation Use the hydrogen pressure relative to its standard pressure of 1 bar, and concentrations relative to $1\,\mathrm{M}$. The solid tin and platinum do not enter the quotient:

$$Q = \frac{[\mathrm{Sn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

The exponent 2 on the hydrogen ion concentration comes from its coefficient in the balanced reaction.

Quick Tip to Solve: Balance the cell reaction first: the two hydrogen ions put a square on their concentration in Q, and two electrons give n = 2.

Hence, using $\log 10 = 1$,

$$E_{\text{cell}} = 0.14 - \frac{0.0591}{2} \log 10$$
$$= 0.14 - 0.02955 = 0.11045\,\text{V}.$$

Step 3: Conclusion The emf of the cell at 25 °C is $\boxed{E_{\text{cell}} \approx 0.110\,\text{V}}$.

Quick Tip to Solve: Balance the cell reaction first: the two hydrogen ions put a square on their concentration in Q, and two electrons give n = 2.

Section D (8 marks)

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

29. In a galvanic cell, chemical energy of a redox reaction is converted into electrical energy, whereas in an electrolytic cell the redox reaction occurs on passing electricity. The simplest galvanic cell is in which Zn rod is placed in a solution of $ZnSO_4$ and Cu rod is placed in a solution of $CuSO_4$. The two rods are connected by a metallic wire through a voltmeter. The two solutions are joined by a salt bridge. The difference between the two electrode potentials of the two electrodes is known as electromotive force. In the process of electrolysis, the decomposition of a substance takes place by passing an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

Answer the following questions : [4 marks]

29(a). What is the function of a salt bridge in a galvanic cell ? [1 mark]

Solution:

Concept:

- A galvanic cell requires both an external electron path and an internal ionic path to maintain a continuous current.
- The salt bridge contains an inert electrolyte whose ions maintain electrical neutrality in the two half-cells without reacting with the electrode solutions.

Step 1: Identify the charge imbalance produced by the reactions In the zinc half-cell, $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$ increases positive charge in solution. In the copper half-cell, $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$ removes positive ions, leaving excess negative charge.

Step 2: Explain the movement of ions through the bridge Anions from the salt bridge migrate towards the anode compartment and cations migrate towards the cathode compartment. This prevents charge accumulation and completes the internal circuit so the cell can keep supplying current. Electrons travel through the metallic wire; the bridge conducts by ions.

Step 3: Conclusion A salt bridge completes the internal circuit and maintains electrical neutrality in both half-cells by allowing ion migration.

Quick Tip to Solve: Remember anions to the anode and cations to the cathode: the bridge balances solution charges while the wire carries electrons.

29(b). When does galvanic cell behave like an electrolytic cell ? [1 mark]

Solution:

Concept:

- A galvanic cell generates current through a spontaneous redox reaction, whereas an electrolytic cell uses external electrical energy to drive a non-spontaneous reaction.
- An applied potential opposing a galvanic cell must exceed its emf to reverse the current and the cell reaction.

Step 1: Compare the opposing potential with the cell emf Let E_{ext} be an external potential applied in opposition to the cell emf E_{cell}. At $E_{\text{ext}} = E_{\text{cell}}$, there is no net driving potential and current stops; this condition alone does not cause electrolysis.

Step 2: Describe the reversal of the reaction When $E_{\text{ext}} > E_{\text{cell}}$, the external source forces current in the reverse direction. The previously spontaneous chemical reaction is reversed, and electrical energy is now consumed to drive the chemical change. The cell therefore operates in electrolytic mode.

Step 3: Conclusion A galvanic cell behaves like an electrolytic cell when an external opposing potential greater than its emf is applied.

Quick Tip to Solve: Equality of the opposing voltage and cell emf stops current; exceeding the emf reverses the reaction and produces electrolytic operation.

29(c). Can copper sulphate solution be stored in a pot made of zinc? Explain with the help of the value of E°_{cell}.

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34\,\text{V}, \qquad E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76\,\text{V}.$$

[2 marks]

Solution:

Concept:

- A metal container is unsuitable for a salt solution if the metal spontaneously reduces the salt's metal ions and is itself oxidised.
- Using standard reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. A positive value gives $\Delta G^\circ = -nFE^\circ_{\text{cell}} < 0$, indicating a spontaneous reaction under standard conditions; F is the Faraday constant.

Step 1: Write the possible displacement reaction Zinc from the pot can be oxidised while copper ions in solution can be reduced:

$$\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-,$$
$$\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s).$$

Adding these half-reactions gives

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s).$$

Quick Tip to Solve: For a metal pot in a salt solution, test whether the pot metal can reduce the solution's metal ion; subtract the anode reduction potential as given.

Sulphate ions are spectators, so the molecular equation is $\mathrm{Zn} + \mathrm{CuSO_4} \longrightarrow \mathrm{ZnSO_4} + \mathrm{Cu}$.

Step 2: Calculate the standard cell potential and assess storage Copper is the cathode and zinc is the anode for this reaction. Substitute the given reduction potentials without changing the sign of the zinc value beforehand:

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10\,\text{V}.$$

This positive standard potential shows that the displacement is spontaneous. Zinc dissolves from the walls of the pot and copper deposits, changing the stored solution and corroding the container.

Step 3: Conclusion No, copper sulphate solution cannot be stored in a zinc pot: $\boxed{E^\circ_{\text{cell}} = +1.10\,\text{V}}$, so zinc reacts spontaneously with copper ions.

Quick Tip to Solve: For a metal pot in a salt solution, test whether the pot metal can reduce the solution's metal ion; subtract the anode reduction potential as given.

OR

29(c). How much charge in terms of Faraday is required for the following :

(i) 1 mol of MnO_4^- to Mn^{2+}

(ii) 1 mol of H_2O to O_2 [2 marks]

Solution:

Concept:

- One faraday, F, is the charge carried by one mole of electrons. A half-reaction that transfers n moles of electrons requires charge $Q = nF$.
- Find the electron transfer by balancing the oxidation and reduction half-reactions. The amount of the stated reactant must be matched to its coefficient; charge is reported as a positive magnitude.

Step 1: (i) Reduction of permanganate to manganese(II) In $\mathrm{MnO_4^-}$, oxygen has oxidation number -2, so manganese has oxidation number $+7$. Reduction to $\mathrm{Mn^{2+}}$ decreases it by five units, requiring five electrons per manganese ion. The balanced acidic half-reaction is

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e^- \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}.$$

Thus, one mole of permanganate ions consumes five moles of electrons. The charge required is $Q = 5F$.

Step 2: (ii) Oxidation of water to oxygen The balanced oxidation half-reaction is

$$2\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4e^-.$$

Two moles of water release four moles of electrons. Therefore, the one mole of water specified in the question releases two moles of electrons and forms half a mole of oxygen. The magnitude of the charge transferred is $Q = (4/2)F = 2F$. The value $4F$ would correspond to two moles of water, rather than the amount asked here.

Quick Tip to Solve: Balance the half-reaction first, then divide its electron coefficient by the coefficient of the reactant: for water use $4/2 = 2$, not four.

Step 3: Conclusion The required charges are $\boxed{5F}$ for (i) and $\boxed{2F}$ for (ii).

Quick Tip to Solve: Balance the half-reaction first, then divide its electron coefficient by the coefficient of the reactant: for water use $4/2 = 2$, not four.

30. The nature of bonding, structure of the coordination compound can be explained to some extent by valence bond theory. The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number. The appropriate atomic orbitals (s, p and d) of the metal hybridise to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral, octahedral and so on. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. The d-orbitals involved in the hybridisation may be either inner d-orbitals i.e. $(n-1)d$ or outer d-orbitals i.e. nd. The complexes formed are called inner orbital complex (low spin complex) and outer orbital complex (high spin complex) respectively. Further, the complexes can be paramagnetic or diamagnetic in nature. The drawbacks of this theory are that this involves number of assumptions and also does not explain the colour of the complex.

Answer the following questions : [4 marks]

30(a). Predict whether $[CoF_6]^{3-}$ is diamagnetic or paramagnetic and why ? [Atomic number : Co = 27] [1 mark]

Solution:

Concept:

- Paramagnetism results from unpaired electrons; a complex with all electrons paired is diamagnetic.
- Fluoride is a weak-field ligand, so it does not cause pairing of the metal ion's $3d$ electrons in this octahedral complex.

Step 1: Determine cobalt's oxidation state and electron count Each fluoride ligand carries charge -1. If cobalt's oxidation state is x, then $x - 6 = -3$, giving $x = +3$. Neutral cobalt is $[\mathrm{Ar}]3d^7 4s^2$; removing two $4s$ electrons and one $3d$ electron gives Co^{3+} : $[\mathrm{Ar}]3d^6$.

Step 2: Count the unpaired electrons With weak-field F^-, the d^6 ion adopts the high-spin octahedral configuration $t_{2g}^4 e_g^2$. There is one pair and four singly occupied orbitals, hence four unpaired electrons. In valence bond theory it forms an outer-orbital sp^3d^2 complex, using $4s$, $4p$ and $4d$ orbitals. A diamagnetic assignment would require complete pairing, which the weak-field fluoride ligands do not produce here.

Step 3: Conclusion $[\mathrm{CoF_6}]^{3-}$ is **paramagnetic**, because high-spin Co^{3+} has **four unpaired electrons**.

Quick Tip to Solve: First use the complex charge to obtain Co(III), then combine its d^6 count with weak-field fluoride to find four unpaired electrons.

30(b). What is the coordination number of Co in $[Co(en)_2Cl_2]^+$? [1 mark]

Solution:

Concept:

- Coordination number is the number of donor atoms directly bonded to the central metal, rather than the number of ligand molecules.
- Ethane-1,2-diamine, abbreviated en, is bidentate: its two nitrogen atoms each donate a lone pair. A chlorido ligand is monodentate.

Step 1: Count the donors from ethane-1,2-diamine The complex contains two en molecules. Each attaches to cobalt through both nitrogen donor atoms, forming two coordinate bonds. The en ligands therefore supply $2 \times 2 = 4$ donor atoms.

Step 2: Include the chlorido donors The two chlorido ligands each contribute one donor atom, adding $2 \times 1 = 2$ more. Thus the total number of donor atoms directly attached to cobalt is $4 + 2 = 6$. Simply counting two en molecules plus two chloride ions would give four ligands, but would overlook the second donor atom on each en. The overall positive charge of the complex affects oxidation-state accounting, rather than this donor-atom count.

Step 3: Conclusion The coordination number of cobalt in $[Co(en)_2Cl_2]^+$ is $\boxed{6}$.

Quick Tip to Solve: Multiply each ligand's number by its denticity: two bidentate en ligands and two monodentate chlorido ligands give $2(2) + 2(1) = 6$.

30(c). (i) Write the IUPAC name of the given complex : $[Pt(NH_3)_2Cl_2]^{2+}$
(ii) Explain whether $[Co(NH_3)_6]^{3+}$ is an inner orbital or outer orbital complex. [2 marks]

Solution:

Concept:

- For naming a complex, name its ligands alphabetically, followed by the metal and its oxidation state in Roman numerals. NH_3 is neutral ammine and Cl^- is chlorido.
- In valence bond theory, an octahedral inner orbital complex uses two $(n-1)d$ orbitals with one ns and three np orbitals, giving d^2sp^3 hybridisation.

Step 1: (i) Determine the oxidation state and name Let the oxidation state of platinum in $[Pt(NH_3)_2Cl_2]^{2+}$ be x. The two ammonia ligands contribute zero charge, whereas the two chlorido ligands contribute -2. Hence

$$x + 2(0) + 2(-1) = +2 \quad \Rightarrow \quad x = +4.$$

List ammine before chlorido alphabetically, ignoring the multiplicative prefix di. Since this is a cationic complex, retain the name platinum. Its IUPAC name is **diamminedichloridoplatinum(IV) ion**.

Step 2: (ii) Identify the orbitals used by the cobalt complex In $[Co(NH_3)_6]^{3+}$, neutral ammonia ligands leave cobalt in the $+3$ oxidation state. Cobalt has atomic number 27; Co^{3+} has configuration $[Ar]3d^6$. In this complex, ammonia causes the six $3d$ electrons to pair in three orbitals, leaving two

Quick Tip to Solve: Use the printed $2+$ charge to obtain Pt(IV); for the cobalt complex, remember that pairing in $3d$ creates the two inner orbitals needed for d^2sp^3.

$3d$ orbitals vacant. These two inner $3d$ orbitals hybridise with one $4s$ and three $4p$ orbitals to form six d^2sp^3 orbitals. Thus, it is an **inner orbital complex** with octahedral geometry. All electrons are paired, so it is low spin and diamagnetic.

Step 3: Conclusion (i) **Diamminedichloridoplatinum(IV) ion.** (ii) $[Co(NH_3)_6]^{3+}$ is an **inner orbital**, d^2sp^3-hybridised octahedral complex.

Quick Tip to Solve: Use the printed $2+$ charge to obtain Pt(IV); for the cobalt complex, remember that pairing in $3d$ creates the two inner orbitals needed for d^2sp^3.

OR

30(c). Using valence bond theory, deduce the shape and hybridisation of $[Ni(NH_3)_6]^{2+}$. [Atomic number of Ni = 28] [2 marks]

Solution:

Concept:

- In valence bond theory, the metal ion supplies vacant orbitals which hybridise and accept lone pairs from ligands to form coordinate bonds.
- The oxidation state determines the metal-ion electronic configuration. Six donor atoms require six equivalent hybrid orbitals, directed towards the vertices of an octahedron.

Step 1: Determine the electronic configuration of the central ion Ammonia is a neutral ligand, so the oxidation state of nickel in $[Ni(NH_3)_6]^{2+}$ is $+2$. For atomic number 28, neutral nickel has configuration $[Ar]3d^84s^2$. Removal of the two $4s$ electrons gives Ni^{2+} : $[Ar]3d^8$. The eight electrons occupy the five $3d$ orbitals with three pairs and two unpaired electrons.

Step 2: Select the hybrid orbitals for six ammonia ligands There are six monodentate ammonia ligands, each donating one nitrogen lone pair. Thus six vacant orbitals are needed. An inner-orbital d^2sp^3 arrangement would need two vacant $3d$ orbitals, but a $3d^8$ ion cannot provide two: even complete pairing leaves at most one of the five $3d$ orbitals vacant. Nickel therefore uses one $4s$, three $4p$ and two outer $4d$ orbitals to form six sp^3d^2 hybrid orbitals. These accept the six ligand lone pairs and point along the six metal-ligand directions of an octahedron. The two unpaired $3d$ electrons also account for the paramagnetism of this outer-orbital complex.

Step 3: Conclusion $[Ni(NH_3)_6]^{2+}$ has $\boxed{sp^3d^2}$ hybridisation and an $\boxed{\text{octahedral}}$ shape. It is an outer-orbital complex.

Quick Tip to Solve: For octahedral nickel(II), first count its eight d electrons: they cannot leave two inner d orbitals vacant, so use the outer d orbitals.

Section E (15 marks)

31(a). An amide 'A' with molecular formula C_7H_7ON undergoes Hoffmann Bromamide degradation reaction to give amine 'B'. 'B' on treatment with nitrous acid at 273-278 K forms 'C' and on treatment with chloroform and ethanolic potassium hydroxide forms 'D'. 'C' on treatment with ethanol gives 'E'. Identify 'A', 'B', 'C', 'D' and 'E' and write the sequence of chemical equations. [5 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ into RNH_2, with loss of the carbonyl carbon and hence one fewer carbon atom in the amine.
- A primary aromatic amine undergoes diazotisation with nitrous acid in acid medium at 273–278 K, giving an arenediazonium salt.
- The carbylamine reaction of a primary amine with chloroform and alcoholic alkali produces an isocyanide. Ethanol reduces an arenediazonium salt to the corresponding arene while itself becoming ethanal.

Step 1: Identify the amide A and its degradation product B The given molecular formula C_7H_7ON fits benzamide, $C_6H_5CONH_2$: the phenyl group contributes five hydrogen atoms and the amide group contributes two. Hofmann degradation removes the carbonyl carbon, retaining the phenyl group attached to nitrogen. Thus A is benzamide and B is aniline, $C_6H_5NH_2$. The balanced equation is

$$C_6H_5CONH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O.$$

Bromine and aqueous sodium hydroxide are the Hofmann bromamide reagents. The carbonate product contains the carbon lost from the amide.

Step 2: Form C by diazotisation of aniline Aniline is a primary aromatic amine. Nitrous acid is generated in situ from sodium nitrite and hydrochloric acid. At the stated low temperature, aniline gives benzenediazonium chloride, C, $C_6H_5N_2^+Cl^-$. Its formation is represented by

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278\,K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

The low temperature is essential because aromatic diazonium salts decompose readily on warming. Hydrochloric acid supplies the chloride counter-ion in this conventional diazotisation equation.

Step 3: Form D by the carbylamine reaction In the separate reaction of B with chloroform and ethanolic potassium hydroxide, the primary amino group of aniline forms an isocyanide. Therefore D is phenyl isocyanide, C_6H_5NC, with phenyl attached to nitrogen in the $-N\equiv C$ group. On heating,

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{ethanol, heat}} C_6H_5NC + 3KCl + 3H_2O.$$

This reaction identifies primary amines; the product is an isocyanide rather than benzonitrile, which

Quick Tip to Solve: Track the lost carbon in Hofmann degradation, and distinguish phenyl isocyanide (phenyl-N-C) from benzonitrile (phenyl-C-N).

would have the phenyl group bonded to carbon.

Step 4: Obtain E from the diazonium salt using ethanol Ethanol replaces the diazonium group of C by hydrogen, releasing nitrogen gas. The aromatic product E is benzene, C_6H_6, while ethanol is oxidised to ethanal. The balanced equation is

$$C_6H_5N_2^+Cl^- + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Thus the two reactions of aniline branch separately: diazotisation gives C and then E, whereas the carbylamine test gives D directly.

Step 5: Conclusion A is benzamide $(C_6H_5CONH_2)$; B is aniline $(C_6H_5NH_2)$; C is benzenediazonium chloride $(C_6H_5N_2^+Cl^-)$; D is phenyl isocyanide (C_6H_5NC); and E is benzene (C_6H_6). The equations above give the complete sequence and the separate carbylamine branch.

Quick Tip to Solve: Track the lost carbon in Hofmann degradation, and distinguish phenyl isocyanide (phenyl-N-C) from benzonitrile (phenyl-C-N).

OR

31(b). (i) (1) What is Hinsberg's reagent ?

(2) Arrange the following compounds in the increasing order of their basic strength in gaseous phase :

$C_2H_5NH_2$, $(C_2H_5)_3N$, $(C_2H_5)_2NH$

(ii) Give reasons for the following :

(1) Methyl amine is more basic than aniline.

(2) Aniline readily reacts with bromine water to give 2, 4, 6-tribromoaniline.

(3) Primary amines have higher boiling points than tertiary amines. [5 marks]

Solution:

Concept:

- Amines are bases because the lone pair on nitrogen accepts a proton. Electron-donating alkyl groups increase electron density on nitrogen through their positive inductive effect.
- In the gaseous phase, the basicity of these ethylamines follows the alkyl-group effect; aqueous solvation effects do not determine this order.
- The nitrogen lone pair in aniline is delocalised into the benzene ring by resonance. This reduces its availability for protonation but activates the ring towards electrophilic substitution at the ortho and para positions.
- Intermolecular hydrogen bonding requires a hydrogen attached to an electronegative atom. Primary amines contain $N-H$ bonds, whereas tertiary amines do not.

Step 1: (i)(1) Identify Hinsberg's reagent Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. It is used to distinguish primary, secondary and tertiary amines through their different reactions and solubility behaviour in alkali. A primary amine forms a sulphonamide with an $N-H$

Quick Tip to Solve: Check the phase before ordering amine basicity: use increasing alkyl donation for these gaseous ethylamines, and check for N-H bonds when comparing their hydrogen bonding.

hydrogen, which dissolves in alkali; a secondary amine forms a sulphonamide without that hydrogen, insoluble in alkali. A tertiary amine does not form a sulphonamide under the test conditions.

Step 2: (i)(2) Compare basic strength in the gaseous phase Ethylamine, diethylamine and triethylamine contain one, two and three ethyl groups, respectively. Each ethyl group exerts a positive inductive effect, increasing electron density on nitrogen and stabilising the protonated amine. In the gaseous phase there is no solvent hydration to reverse this trend. Hence the increasing basic-strength order is

$$C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N.$$

Step 3: (ii)(1) Explain why methylamine is more basic than aniline In methylamine, CH_3NH_2, the methyl group donates electron density towards nitrogen by its positive inductive effect. The nitrogen lone pair is localised and readily available to accept H^+. In aniline, $C_6H_5NH_2$, this lone pair participates in resonance with the benzene ring, so it is less available for protonation. The phenyl group's negative inductive effect also reduces electron density at nitrogen. Consequently, methylamine accepts a proton more readily and is more basic.

Step 4: (ii)(2) Explain rapid tribromination of aniline The $-NH_2$ group strongly activates the benzene ring by donating its lone pair through resonance. This increases electron density especially at the two ortho positions and the para position, making electrophilic substitution by bromine very easy. Therefore bromine water substitutes all three positions without a Lewis-acid catalyst, giving a white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr.$$

The three bromine atoms occupy positions 2, 4 and 6 relative to the amino group at position 1.

Step 5: (ii)(3) Explain the boiling-point difference Primary amines, RNH_2, contain two $N-H$ bonds and form intermolecular $N-H\cdots N$ hydrogen bonds. Additional energy is needed to overcome these attractions during boiling. Tertiary amines, R_3N, have no $N-H$ bond and cannot form hydrogen bonds with one another, although they can accept hydrogen bonds from water. Thus, for amines of comparable molar mass, primary amines have stronger intermolecular association and higher boiling points than tertiary amines.

Step 6: Conclusion Hinsberg's reagent is $C_6H_5SO_2Cl$. In the gaseous phase, ethylamine $<$ diethylamine $<$ triethylamine in basic strength. Methylamine is more basic than aniline because its nitrogen lone pair is more available; aniline undergoes rapid 2,4,6-tribromination because $-NH_2$ activates the ring; and primary amines boil higher than comparable tertiary amines because they form intermolecular hydrogen bonds.

Quick Tip to Solve: Check the phase before ordering amine basicity: use increasing alkyl donation for these gaseous ethylamines, and check for N-H bonds when comparing their hydrogen bonding.

32. Attempt any five of the following :

(a) Why Zinc is not regarded as a transition element ?

(b) What is Lanthanoid contraction ?

(c) Why is first ionization enthalpy of chromium lower than that of Zn ?

(d) Why are transition elements good catalysts ?

(e) Compounds of transition metals are generally coloured. Give reason.

(f) Out of $KMnO_4$ and K_2MnO_4, which one is paramagnetic and why ?

(g) Complete the following ionic equation : $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow$ _____ [5 marks]

Solution:

Concept:

- A transition element has a partially filled d subshell in its atom or in at least one of its common oxidation states. A filled d^{10} subshell does not satisfy this definition.
- Electronic configuration and effective nuclear attraction determine ionization enthalpy, magnetic behaviour and many characteristic properties of transition metals.
- Unpaired electrons cause paramagnetism. In a ligand field, excitation between split d energy levels can absorb visible light and give a transition-metal compound its colour.
- A redox half-equation must conserve both atoms and charge; in acidic solution, oxygen and hydrogen are balanced using H_2O and H^+, respectively.

Step 1: (a) Why zinc is not a transition element Zinc has the electronic configuration $[\mathrm{Ar}]\,3d^{10}4s^2$. Its common ion, Zn^{2+}, has configuration $[\mathrm{Ar}]\,3d^{10}$. Thus, both the atom and its common ion have completely filled d subshells. Zinc lacks a partially filled d subshell and therefore is not regarded as a transition element, although it belongs to the d block.

Step 2: (b) Lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic and ionic radii, particularly the radii of Ln^{3+} ions, across the lanthanoid series as atomic number increases. The added 4f electrons shield the increasing nuclear charge poorly. Consequently, effective nuclear attraction increases and the electron cloud contracts.

Step 3: (c) First ionization enthalpies of chromium and zinc Chromium has configuration $[\mathrm{Ar}]\,3d^5 4s^1$, whereas zinc has $[\mathrm{Ar}]\,3d^{10}4s^2$. The first electron removed from chromium is its sole 4s electron, leaving the stable half-filled $3d^5$ configuration. Zinc has a greater effective nuclear attraction across the period and a stable filled $3d^{10}4s^2$ configuration; its 4s electron is held more strongly. Hence, removing the first electron requires less energy for chromium than for zinc.

Step 4: (d) Catalytic activity of transition elements Transition metals can exhibit variable oxidation states, allowing them to form intermediate compounds with reactants and participate in electron-transfer steps. Their surfaces can also adsorb reactants, bringing them together and weakening bonds. These processes provide an alternative reaction pathway with lower activation energy; the catalyst is regenerated at the end of the catalytic cycle.

Step 5: (e) Colour of transition-metal compounds In many transition-metal ions, the d subshell is partially filled. Surrounding ligands split the d orbitals into groups of different energies. Absorption of an appropriate wavelength of visible light promotes an electron from a lower to a higher d level, a d–d transition. The remaining transmitted or reflected light gives the compound its observed colour. This

Quick Tip to Solve: For manganate and permanganate, calculate Mn's oxidation state first; Mn(VI) is d1 and Mn(VII) is d0, immediately distinguishing their magnetic behaviour.

explains the general trend; ions with d^0 or d^{10} configurations cannot undergo such d–d transitions.

Step 6: (f) Paramagnetism of manganate and permanganate In $KMnO_4$, charge balance gives $1 + x - 8 = 0$, so manganese is in the $+7$ oxidation state and has a $3d^0$ configuration. There are no unpaired d electrons, so permanganate is diamagnetic. In K_2MnO_4, $2 + x - 8 = 0$, giving manganese in the $+6$ oxidation state with a $3d^1$ configuration. Its one unpaired electron makes K_2MnO_4 paramagnetic.

Step 7: (g) Complete and check the dichromate half-equation Each chromium atom is reduced from $+6$ to $+3$, so the two chromium atoms accept six electrons in total. The seven oxygen atoms form seven water molecules using the fourteen hydrogen ions:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O.$$

Both sides contain two chromium atoms, seven oxygen atoms and fourteen hydrogen atoms. The net charge on the left is $-2 + 14 - 6 = +6$, equal to the charge of $2Cr^{3+}$ on the right.

Step 8: Conclusion (a) Zn and Zn^{2+} have filled d^{10} subshells. (b) Lanthanoid contraction is the gradual decrease in radii across the lanthanoid series. (c) Cr loses its 4s electron more readily than Zn. (d) Variable oxidation states and adsorption account for catalytic activity. (e) Visible-light absorption in d–d transitions generally produces colour. (f) K_2MnO_4 is paramagnetic because Mn(VI) is d^1. (g) The products are $2Cr^{3+} + 7H_2O$. Any five of these parts may be attempted.

Quick Tip to Solve: For manganate and permanganate, calculate Mn's oxidation state first; Mn(VI) is d1 and Mn(VII) is d0, immediately distinguishing their magnetic behaviour.

33(a). (i) Define reverse osmosis.

(ii) Why are aquatic species more comfortable in cold water in comparison to warm water ?

(iii) A solution containing 2 g of glucose (M = 180 g mol^{-1}) in 100 g of water is prepared at 303 K. If the vapour pressure of pure water at 303 K is 32.8 mm Hg, what would be the vapour pressure of the solution ? [5 marks]

Solution:

Concept:

- Osmosis is the passage of solvent through a semipermeable membrane towards the solution. An external pressure exceeding the osmotic pressure reverses this flow.
- Gas dissolution in water is generally exothermic; increasing temperature reduces the solubility of dissolved oxygen at the same external pressure.
- For a solution of a non-volatile solute, Raoult's law gives $p = x_{\text{water}} p^\circ$, where p° is pure water's vapour pressure and x_{water} is its mole fraction.

Step 1: (i) Define reverse osmosis Reverse osmosis is the process in which solvent is forced to flow from the solution through a semipermeable membrane to the pure-solvent side by applying a pressure greater than the osmotic pressure on the solution side. The membrane permits solvent molecules to pass but retains the solute. This reverses ordinary osmosis and is used for desalination.

Quick Tip to Solve: For the glucose calculation, convert both masses into moles and multiply 32.8 by the water mole fraction, 500/501; the resulting pressure must be slightly below that of pure water.

Step 2: (ii) Explain the advantage of cold water The solubility of gases in water decreases as temperature rises. Therefore, at a given oxygen pressure, cold water contains more dissolved oxygen than warm water. Aquatic species obtain the oxygen needed for respiration from this dissolved oxygen, so its greater availability makes cold water more comfortable for them.

Step 3: (iii) Calculate the mole fraction of water Glucose is a non-volatile, non-electrolyte solute. Using the molar mass of water as $18\,\text{g mol}^{-1}$, the mole amounts are

$$n_{\text{glucose}} = \frac{2}{180} = \frac{1}{90}\,\text{mol},$$
$$n_{\text{water}} = \frac{100}{18} = \frac{50}{9}\,\text{mol}.$$

Hence the solvent mole fraction is

$$x_{\text{water}} = \frac{n_{\text{water}}}{n_{\text{water}} + n_{\text{glucose}}} = \frac{50/9}{50/9 + 1/90} = \frac{500}{501}.$$

Step 4: Apply Raoult's law at 303 K Only water contributes appreciably to the vapour above the solution because glucose is non-volatile. Thus,

$$p = x_{\text{water}} p^{\circ} = \frac{500}{501} \times 32.8 = 32.7345\,\text{mm Hg}.$$

The pressure is slightly below that of pure water, as expected for a non-volatile solute.

Step 5: Conclusion (i) Reverse osmosis forces solvent from the solution to the pure-solvent side under pressure greater than the osmotic pressure. (ii) Cold water has more dissolved oxygen for aquatic respiration. (iii) The solution's vapour pressure at 303 K is $\boxed{32.73\,\text{mm Hg}}$ (approximately).

Quick Tip to Solve: For the glucose calculation, convert both masses into moles and multiply 32.8 by the water mole fraction, 500/501; the resulting pressure must be slightly below that of pure water.

OR

33(b). (i) Predict whether Van't Hoff factor will be less or greater than one, when Ethanoic acid is dissolved in benzene.

(ii) Define ideal solution.

(iii) Calculate the mass of $CaCl_2$ (molar mass = 111 g mol^{-1}) to be dissolved in 500 g of water to lower its freezing point by 2 K, assuming that $CaCl_2$ undergoes complete dissociation. (K_f for water = 1.86 K kg mol^{-1}) [5 marks]

Solution:

Concept:

- The van't Hoff factor i is the ratio of the observed colligative property to its calculated value without association or dissociation. Association decreases the number of solute particles, so $i < 1$; dissociation increases it, so $i > 1$.
- An ideal solution obeys Raoult's law over the entire range of composition: $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$, where x is mole fraction and p^0 is the vapour pressure of a pure component.
- For a solute that dissociates, freezing-point depression is $\Delta T_f = iK_f m$, where K_f is the solvent's molal depression constant and m is moles of solute per kilogram of solvent.

Step 1: (i) Account for ethanoic acid association in benzene Ethanoic acid molecules associate in the non-polar solvent benzene by intermolecular hydrogen bonding to form dimers:

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2.$$

Two acid molecules thus behave as one dissolved particle. The number of solute particles and the colligative effect are smaller than those calculated for unassociated acid. Therefore, the van't Hoff factor is less than unity. Complete dimerisation would give $i = 1/2$; partial dimerisation gives a value between $1/2$ and 1.

Step 2: (ii) Define an ideal solution An ideal solution is a solution that obeys Raoult's law throughout the entire range of composition at a given temperature. For its two volatile components,

$$p_A = x_A p_A^0, \qquad p_B = x_B p_B^0.$$

Its total vapour pressure is the sum of these partial pressures. Such a solution has $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$, since interactions between unlike molecules are comparable to those between like molecules.

Step 3: (iii) Determine the dissociation factor and molality Complete dissociation of calcium chloride gives one calcium ion and two chloride ions per formula unit:

$$CaCl_2 \longrightarrow Ca^{2+} + 2\,Cl^-.$$

Thus $i = 3$. The given depression is $\Delta T_f = 2\,K$, so

$$m = \frac{\Delta T_f}{iK_f} = \frac{2}{3 \times 1.86} = 0.3584\,\text{mol kg}^{-1}.$$

Quick Tip to Solve: Count the three ions from each CaCl2 formula unit before applying freezing-point depression, and convert the 500 g of solvent to 0.500 kg.

The solvent mass is $500\,\text{g} = 0.500\,\text{kg}$. Molality uses the mass of water, not the combined mass of water and salt.

Step 4: (iii) Convert required moles to salt mass Let w be the required mass of CaCl_2. Using its molar mass $M = 111\,\text{g mol}^{-1}$,

$$n = m \times 0.500 = 0.1792\,\text{mol},$$

$$w = nM = \frac{2 \times 0.500 \times 111}{3 \times 1.86}\,\text{g}$$

$$= 19.89\,\text{g}.$$

Substitution of this mass back into $3K_f m$ yields a depression of $2\,\text{K}$, consistent with the required change.

Step 5: Conclusion (i) Ethanoic acid associates into dimers in benzene, hence $\boxed{i < 1}$. (ii) An ideal solution obeys Raoult's law over the entire composition range. (iii) The required mass of calcium chloride is $\boxed{19.9\,\text{g}}$, assuming complete dissociation.

Quick Tip to Solve: Count the three ions from each CaCl2 formula unit before applying freezing-point depression, and convert the 500 g of solvent to 0.500 kg.