

CBSE Class 12 Chemistry Question Paper 2020 with Solution PDF-Set 56-3-1

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 comprises **four** Sections – **A, B, C** and **D**. There are **37** questions in the question paper. **All** questions are compulsory.
- (ii) **Section A** – Questions no. **1** to **20** are very short answer type questions, carrying **1** mark each. Answer these questions in one word or one sentence.
- (iii) **Section B** – Questions no. **21** to **27** are short answer type questions, carrying **2** marks each.
- (iv) **Section C** – Questions no. **28** to **34** are long answer type-I questions, carrying **3** marks each.
- (v) **Section D** – Questions no. **35** to **37** are long answer type-II questions, carrying **5** marks each.
- (vi) There is no overall choice in the question paper. However, an internal choice has been provided in 2 questions of two marks, 2 questions of three marks and all the 3 questions of five marks. You have to attempt only one of the choices in such questions.
- (vii) In addition to this, separate instructions are given with each section and question, wherever necessary.
- (viii) Use of calculators and log tables is not permitted.

Section A (20 marks)

Read the given passage and answer the questions number 1 to 5 that follow : $1 \times 5 = 5$

The d-block of the periodic table contains the elements of the groups 3 – 12 and are known as transition elements. In general, the electronic configuration of these elements is $(n-1)d^{1-10}ns^{1-2}$. The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e., 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation states, complex formation, formation of coloured ions and alloys, catalytic activity, etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

1. Why are Zn, Cd and Hg non-transition elements?

[1 mark]

Solution:

Concept:

- A transition element has an incompletely filled *d* subshell in its atom or in at least one of its common oxidation states.
- A completely filled *d* subshell contains ten electrons and is represented by d^{10} .

Step 1: Inspect the atomic configurations The outer electronic configurations of Zn, Cd and Hg are respectively $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$. Thus their atoms have filled *d* subshells.

Step 2: Inspect the common ions On forming their common +2 ions, these atoms lose the two outer *s* electrons. Their *d* subshells remain completely filled: Zn^{2+} is $3d^{10}$, Cd^{2+} is $4d^{10}$, and Hg^{2+} is $5d^{10}$.

Step 3: Conclusion Zn, Cd and Hg are non-transition elements because their atoms and common ions have completely filled *d* subshells.

Quick Tip to Solve: Check the *d*-electron count in both the atom and its common ions; membership of the *d* block alone is insufficient.

2. Which transition metal of 3d series does not show variable oxidation states?

[1 mark]

Solution:

Concept:

- Variable oxidation states arise when different numbers of outer *s* and *d* electrons can participate in bonding.
- Scandium has the ground-state configuration $[\text{Ar}] 3d^1 4s^2$.

Step 1: Count the available outer electrons Scandium has two *4s* electrons and one *3d* electron outside its argon core. Removal of all three gives the usual ion Sc^{3+} .

Step 2: Identify the stable oxidation state Sc^{3+} has the stable argon configuration, with an empty *3d* subshell. Further removal would involve a core electron. In the usual chemistry of the *3d* transition series, scandium shows only the +3 oxidation state.

Step 3: Conclusion The metal is scandium (Sc), which shows the +3 oxidation state.

Quick Tip to Solve: Recall Sc: $3d^1 4s^2$ gives +3. Zinc is excluded because it is not a transition element.

3. Why do transition metals and their compounds show catalytic activity?

[1 mark]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with lower activation energy and is regenerated during the reaction.
- Transition metals can show variable oxidation states and can form intermediate complexes with reactants.

Step 1: Relate oxidation states to intermediate formation A transition-metal ion can accept and release electrons by changing its oxidation state. It may form an intermediate compound with a reactant and then regenerate its original state, allowing the reaction to proceed through lower-energy steps.

Step 2: Consider catalysis on metal surfaces Finely divided transition metals can adsorb reactant molecules on their surfaces. Adsorption brings reactants close together and weakens their bonds, making their conversion into products easier.

Step 3: Conclusion Their catalytic activity is due to variable oxidation states and intermediate formation; metal surfaces also promote reactions through adsorption.

Quick Tip to Solve: For transition-metal catalysis, link variable oxidation states to intermediates and surface adsorption to weakened reactant bonds.

4. Why are melting points of transition metals high?

[1 mark]

Solution:

Concept:

- Melting requires sufficient energy to overcome the forces holding a metal lattice together.
- In transition metals, both outer ns and $(n-1)d$ electrons can participate in metallic bonding.

Step 1: Identify the source of strong bonding Transition metals generally possess several electrons available for metallic bonding, including electrons from the partially filled d subshell. Their participation produces strong attraction between the metal cores and delocalised electrons.

Step 2: Connect bonding to melting These strong metallic bonds give transition metals high enthalpies of atomisation. Considerable thermal energy is therefore required to disrupt the ordered solid lattice, so their melting points are generally high.

Step 3: Conclusion Transition metals generally have high melting points because participation of s and d electrons produces strong metallic bonding.

Quick Tip to Solve: Explain the trend through bond strength: more electrons participating in metallic bonding generally mean more energy is needed to melt the metal.

5. Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution?

[1 mark]

Solution:

Concept:

- In an aqueous transition-metal ion, water ligands split the d orbitals into groups of different energies.
- Absorption of visible light for a $d-d$ transition produces colour when suitable occupied and vacant d levels are available.

Step 1: Examine the copper ion Cu^{2+} has configuration $[\text{Ar}] 3d^9$, so its d subshell is incomplete. An electron can be excited between the split d levels by absorbing visible light, making the aqueous ion coloured.

Step 2: Examine the zinc ion Zn^{2+} has configuration $[\text{Ar}] 3d^{10}$. All its d orbitals are filled, so no $d-d$ transition is possible. Its aqueous solution does not absorb visible light by this mechanism.

Step 3: Conclusion Aqueous Cu^{2+} is coloured because its $3d^9$ configuration permits $d-d$ transitions, whereas $3d^{10} \text{Zn}^{2+}$ is colourless.

Quick Tip to Solve: Remove the $4s$ electrons before counting $3d$ electrons: Cu^{2+} is d^9 , whereas Zn^{2+} is d^{10} .

Questions number 6 to 10 are one word answers :

6. Name the cell which was used in the Apollo Space Programme.

[1 mark]

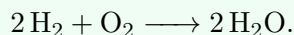
Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.
- In a hydrogen–oxygen fuel cell, hydrogen is the fuel and oxygen is the oxidant.

Step 1: Identify the electrochemical system The Apollo Space Programme used hydrogen–oxygen fuel cells to provide electrical power. The reactants were supplied to their respective electrodes, where oxidation and reduction occurred.

Step 2: State the useful overall reaction Hydrogen and oxygen combine electrochemically to form water:



Along with generating electricity, this system supplied water that could be used by the astronauts.

Step 3: Conclusion The cell used was the hydrogen–oxygen fuel cell.

Quick Tip to Solve: Associate Apollo with a hydrogen–oxygen fuel cell: the overall products are electrical energy and useful water.

7. How many coulombs are required for the oxidation of 1 mol of H_2O to O_2 ?

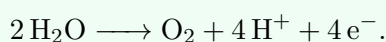
[1 mark]

Solution:

Concept:

- Faraday's law gives $Q = n_e F$, where n_e is the amount of electrons transferred in moles and $F = 96500 \text{ C mol}^{-1}$.
- In H_2O , oxygen has oxidation state -2 ; in O_2 , its oxidation state is zero.

Step 1: Balance the oxidation half-reaction The oxidation half-reaction is



Hence two moles of water release four moles of electrons. One mole of water therefore requires transfer of two moles of electrons.

Step 2: Calculate the charge For one mole of water, $n_e = 2 \text{ mol}$. Thus

$$Q = 2 \times 96500 = 193000 \text{ C}.$$

The four-electron factor belongs to one mole of oxygen formed, not to one mole of water oxidised.

Step 3: Conclusion The required charge is $1.93 \times 10^5 \text{ C}$, or $2F$.

Quick Tip to Solve: Use two electrons per water molecule; four electrons correspond to two water molecules and one oxygen molecule.

8. Write the slope value obtained in the plot of $\ln[R]$ vs. time for a first order reaction.

[1 mark]

Solution:

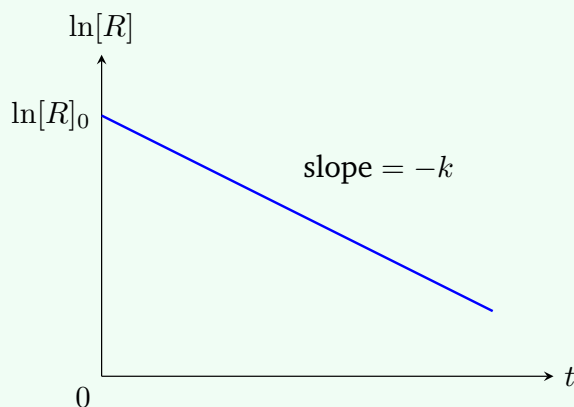
Concept:

- The integrated first-order rate law is $\ln[R] = \ln[R]_0 - kt$, where $[R]_0$ and $[R]$ are the initial and remaining reactant concentrations, t is time, and k is the rate constant.
- In a straight-line equation $y = c + mx$, the coefficient m of the horizontal-axis variable is the slope.

Step 1: Identify the plotted variables Set $y = \ln[R]$ and $x = t$. The first-order rate law becomes a straight line with intercept $\ln[R]_0$; the concentration decreases with time as the reactant is consumed.

Step 2: Compare with the straight-line equation Comparing $\ln[R] = \ln[R]_0 + (-k)t$ with $y = c + mx$, the coefficient of time is negative. Equivalently, $\Delta \ln[R] / \Delta t = -k$. Since $k > 0$, the line slopes downwards. If time is measured in seconds, the slope has unit s^{-1} .

Quick Tip to Solve: For a natural-log plot the slope is directly $-k$; the factor 2.303 belongs to a common-log plot instead.



Schematic first-order natural-log plot with slope $-k$.

Step 3: Conclusion The slope of the plot of $\ln[R]$ against time is $-k$, where k is the first-order rate constant.

Quick Tip to Solve: For a natural-log plot the slope is directly $-k$; the factor 2.303 belongs to a common-log plot instead.

9. Name the disaccharide which on hydrolysis gives two molecules of glucose.

[1 mark]

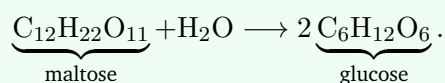
Solution:

Concept:

- A disaccharide contains two monosaccharide units joined by a glycosidic linkage. Hydrolysis breaks this linkage by adding water.
- Maltose contains two D-glucose units connected through an α -(1 $\rightarrow$ 4) glycosidic linkage.

Step 1: Identify the constituent units The required sugar must have glucose as both of its monosaccharide units. Maltose has this composition, whereas sucrose contains glucose and fructose and lactose contains glucose and galactose.

Step 2: Write the hydrolysis reaction Hydrolysis of maltose with dilute acid or the enzyme maltase cleaves its glycosidic bond, releasing two glucose molecules:



Thus, both products have the same monosaccharide identity.

Step 3: Conclusion The disaccharide is **maltose**, which yields two molecules of glucose on hydrolysis.

Quick Tip to Solve: Remember the product pairs: maltose gives glucose + glucose, sucrose gives glucose + fructose, and lactose gives glucose + galactose.

10. Name the class of the synthetic detergent which is used in toothpaste.

[1 mark]

Solution:

Concept:

- Synthetic detergents are classified as anionic, cationic or non-ionic according to the charge on the surface-active part of the molecule in water.
- Anionic detergents have a negatively charged hydrophilic head attached to a long hydrophobic hydrocarbon chain.

Step 1: Identify the detergent used in toothpaste Toothpaste commonly contains an alkyl sulphate such as sodium lauryl sulphate, $C_{12}H_{25}OSO_3Na$. It acts as a cleansing and foaming agent, helping the paste spread during brushing.

Step 2: Classify its surface-active ion In water the sodium salt gives Na^+ and the long-chain ion $C_{12}H_{25}OSO_3^-$. The latter is the surface-active component and carries a negative charge. Therefore its class is determined by the anion, rather than the sodium counter-ion.

Step 3: Conclusion Anionic detergents are used in toothpaste; sodium lauryl sulphate is a common example.

Quick Tip to Solve: Classify a detergent by the charge on its long-chain surface-active ion: a sulphate head with negative charge means anionic.

Questions number 11 to 15 are multiple choice questions :

11. Which of the following is refined by the zone refining process?

[1 mark]

- (A) Cu
- (B) Zn
- (C) Ge
- (D) Sn

Correct Answer: (C) Ge

Solution:

Concept:

- Zone refining exploits the greater solubility of impurities in molten metal than in the corresponding solid.
- Very pure semiconductors are required because even small concentrations of impurities affect their electrical properties.

Step 1: Identify the application of the method A narrow molten zone is moved along a rod of the impure material. As the zone advances, purified solid crystallises behind it and impurities concentrate in the molten region. Repeated passes collect the impurities at one end, which is removed.

Step 2: Compare the listed elements Germanium is a semiconductor commonly purified by zone refining. Copper is commonly refined electrolytically, while volatile zinc is purified by distillation. Tin is associated with liquation in the standard refining methods. Thus germanium is the intended

Quick Tip to Solve: Associate zone refining with ultrapure semiconductors such as germanium and silicon; impurities travel with the molten zone.

application among these choices.

Step 3: Conclusion Germanium (Ge) is refined by zone refining. Hence, the correct option is (C).

Quick Tip to Solve: Associate zone refining with ultrapure semiconductors such as germanium and silicon; impurities travel with the molten zone.

12. Racemisation occurs in

[1 mark]

- (A) S_N2 reaction
- (B) S_N1 reaction
- (C) Neither S_N2 nor S_N1 reactions
- (D) S_N2 reaction as well as S_N1 reaction

Correct Answer: (B) S_N1 reaction

Solution:

Concept:

- Racemisation is the formation of both enantiomeric configurations from an optically active reactant, reducing or eliminating its optical activity.
- An S_N1 substitution proceeds through a planar carbocation, whereas S_N2 substitution occurs by concerted backside attack.

Step 1: Examine the unimolecular substitution In an S_N1 reaction at a chiral carbon, departure of the leaving group produces a planar, sp^2 -hybridised carbocation. The nucleophile can approach from either face, giving products with both configurations. This explains the racemisation associated with this mechanism.

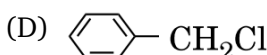
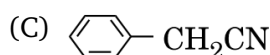
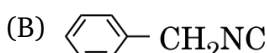
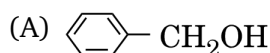
Step 2: Test the other options In an S_N2 reaction, the nucleophile attacks from the side opposite the leaving group and produces inversion of configuration, rather than racemisation. Therefore the choices stating S_N2 alone or both mechanisms are incorrect; the choice stating neither is also incorrect.

Step 3: Conclusion Racemisation occurs in an S_N1 reaction. Hence, the correct option is (B).

Quick Tip to Solve: Link a planar carbocation to attack from either face and racemisation; link backside attack to inversion in an S_N2 reaction.

13. $\text{C}_6\text{H}_5-\text{CH}_2-\text{NH}_2$ on heating with CHCl_3 and alcoholic KOH gives foul smell of

[1 mark]



Correct Answer: (B)  CH_2NC

Solution:

Concept:

- Primary amines give the carbylamine test: heating with chloroform and alcoholic potassium hydroxide produces a foul-smelling isocyanide.
- An isocyanide has the connectivity $\text{R}-\text{N}\equiv\text{C}$, whereas a nitrile has $\text{R}-\text{C}\equiv\text{N}$.

Step 1: Identify the amine and apply the reaction Benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, is a primary amine because its nitrogen bears one organic group and two hydrogen atoms. It therefore gives the carbylamine reaction:



The reaction is carried out on heating in alcoholic medium, and the benzyl group remains attached to nitrogen.

Step 2: Compare the structures in the options Option (B) shows benzyl isocyanide, $\text{C}_6\text{H}_5\text{CH}_2\text{NC}$. Option (A) is benzyl alcohol, option (C) is benzyl cyanide with the opposite linkage of the terminal carbon and nitrogen, and option (D) is benzyl chloride. These three structures are not the carbylamine product.

Step 3: Conclusion The foul-smelling product is benzyl isocyanide, $\text{C}_6\text{H}_5\text{CH}_2\text{NC}$. Hence, the correct option is (B).

Quick Tip to Solve: In the carbylamine test, replace the primary amine's $-\text{NH}_2$ group by $-\text{NC}$; do not reverse the linkage to $-\text{CN}$.

14. One mole of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ compound reacts with excess AgNO_3 solution to yield two moles of AgCl (s). The structural formula of the compound is

(A) $[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$ (B) $[\text{Cr}(\text{H}_2\text{O})_3 \text{Cl}_3] \cdot 3\text{H}_2\text{O}$ (C) $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$ (D) $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$

[1 mark]

Solution:

Concept:

- Chloride ions outside the coordination sphere are ionisable and give a precipitate with silver nitrate.
- Coordinated chloride remains attached to the metal in this test; one mole of free Cl^- gives one mole of AgCl .

Step 1: Count the ionisable chloride ions The precipitation reaction is $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}(\text{s})$.

Quick Tip to Solve: Count only chloride ions outside the square brackets when predicting immediate silver chloride precipitation.

Since one mole of the compound yields two moles of AgCl, its formula must contain two chloride counterions outside the square brackets. The remaining one of the three chlorides is coordinated to chromium.

Step 2: Compare the four structures Option (A), $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, contains two external chloride ions and therefore gives two moles of precipitate. Its five coordinated waters and one lattice water also account for all six waters. Options (B), (C) and (D) contain zero, one and three external chloride ions, respectively, so they give zero, one and three moles of AgCl per mole of compound.

Step 3: Conclusion The structural formula is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$. Hence, the correct option is (A).

Quick Tip to Solve: Count only chloride ions outside the square brackets when predicting immediate silver chloride precipitation.

15. Peptide linkage is present in

(A) Carbohydrates (B) Vitamins (C) Proteins (D) Rubber

[1 mark]

Solution:

Concept:

- A peptide bond is the amide linkage $-\text{CO}-\text{NH}-$ joining amino acid residues.
- Proteins are polypeptides formed by condensation of amino acids, with elimination of water at each new peptide linkage.

Step 1: Identify how a peptide bond forms The carboxyl group of one amino acid reacts with the amino group of another. Loss of the carboxyl hydroxyl group and a hydrogen from the amino group as water produces the $-\text{CO}-\text{NH}-$ linkage. Repetition joins many amino acid residues into the polypeptide chain of a protein.

Step 2: Eliminate the other classes Carbohydrate units are joined by glycosidic linkages, not peptide bonds. Vitamins are a chemically diverse group and are not characterised by peptide-linked amino acid chains. Rubber is a polymer of isoprene with a carbon-chain backbone. Thus, among the given classes, the characteristic peptide linkage belongs to proteins.

Step 3: Conclusion Peptide linkage is present in proteins. Hence, the correct option is (C).

Quick Tip to Solve: Associate peptide bonds with amino acid chains, and glycosidic bonds with linked sugar units.

16. Assertion (A): Conductivity of an electrolyte decreases with decrease in concentration.

Reason (R): Number of ions per unit volume increases on dilution.

Select the correct answer from codes (i), (ii), (iii), (iv): (i) Both A and R correct and R is correct explanation of A. (ii) Both A and R correct but R is not correct explanation of A. (iii) A correct, R incorrect. (iv) A incorrect, R correct. [1 mark]

Solution:

Concept:

- Conductivity measures the ability of a solution of specified dimensions to carry current and depends on the number of charge carriers per unit volume.
- Dilution decreases ion concentration, although molar conductivity increases because ionic mobility and, for weak electrolytes, dissociation increase.

Step 1: Evaluate the assertion On dilution, fewer ions are present per unit volume of the solution. Its conductivity therefore decreases with decreasing electrolyte concentration. The assertion is correct; it refers to conductivity, not molar conductivity.

Step 2: Evaluate the reason The reason claims that the number of ions per unit volume increases on dilution. This is incorrect: adding solvent increases the volume and lowers the ion concentration. Even when a weak electrolyte ionises to a greater extent, its number of ions per unit volume decreases on dilution.

Step 3: Test the explanatory link The stated reason cannot explain the correct assertion because it reverses the actual concentration change. The codes requiring both statements to be correct are therefore excluded, as is the code declaring the assertion incorrect.

Step 4: Conclusion Assertion (A) is correct, but Reason (R) is incorrect. Hence, the correct option is (iii).

Quick Tip to Solve: For dilution questions, distinguish conductivity, which decreases, from molar conductivity, which increases.

17. Assertion (A): The C–O–H bond angle in alcohols is slightly less than the tetrahedral angle.

Reason (R): This is due to the repulsive interaction between the two lone electron pairs on oxygen.

Select the correct answer from codes (i), (ii), (iii), (iv). [1 mark]

Solution:

Concept:

- Oxygen in an alcohol has two bond pairs and two lone pairs, giving an approximately tetrahedral electron-pair arrangement.
- Lone pairs occupy more space than bond pairs; their repulsions compress the angle between the two bonds.

Step 1: Evaluate the assertion The ideal tetrahedral angle is approximately 109.5° . The two lone pairs on oxygen distort this ideal arrangement, so the C–O–H bond angle in the standard description of alcohols is slightly smaller. The assertion is correct.

Quick Tip to Solve: Count the two lone pairs on alcohol oxygen before comparing its bond angle with the ideal tetrahedral angle.

Step 2: Evaluate the reason Oxygen carries two nonbonding electron pairs in addition to its carbon and hydrogen bonds. Repulsive interaction involving these lone pairs is stronger than bond-pair repulsion. The lone pairs spread apart and push the bonding pairs closer together. The reason is correct.

Step 3: Relate the reason to the assertion The enhanced repulsion of the lone pairs is precisely the electron-pair effect responsible for compression of the bond angle. Thus, the reason explains the assertion, rather than merely stating an unrelated correct fact. Codes (ii), (iii) and (iv) do not describe this relationship.

Step 4: Conclusion Both Assertion (A) and Reason (R) are correct, and R correctly explains A. Hence, the correct option is (i).

Quick Tip to Solve: Count the two lone pairs on alcohol oxygen before comparing its bond angle with the ideal tetrahedral angle.

18. Assertion (A): $[\text{Pt}(\text{en})_2 \text{Cl}_2]^{2+}$ complex is less stable than $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2]^{2+}$ complex.

Reason (R): $[\text{Pt}(\text{en})_2 \text{Cl}_2]^{2+}$ complex shows chelate effect.

Select the correct answer from codes (i), (ii), (iii), (iv).

[1 mark]

Solution:

Concept:

- Ethane-1,2-diamine, abbreviated en, is a bidentate ligand that coordinates through two nitrogen donor atoms.
- The chelate effect enhances the stability of a complex containing multidentate ligands compared with a corresponding complex containing similar monodentate ligands.

Step 1: Evaluate the assertion In $[\text{Pt}(\text{en})_2 \text{Cl}_2]^{2+}$, each en ligand attaches at two sites and forms a chelate ring. In $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2]^{2+}$, ammonia is monodentate and forms no chelate ring. The chelated en complex is more stable in the stated comparison, so the assertion that it is less stable is incorrect.

Step 2: Evaluate the reason Each en ligand produces a five-membered ring containing platinum, two nitrogen atoms and two carbon atoms. Hence the complex with two en ligands does show the chelate effect. The reason is correct.

Step 3: Check the relationship Chelation supports increased stability, which is opposite to the claim in the assertion. Therefore, the reason cannot explain that false assertion. Codes (i) and (ii) incorrectly treat both statements as true, while code (iii) incorrectly reverses their truth values.

Step 4: Conclusion Assertion (A) is incorrect, but Reason (R) is correct. Hence, the correct option is (iv).

Quick Tip to Solve: Identify en as bidentate: chelate-ring formation indicates greater stability than comparable ammonia complexes.

19. Assertion (A): Osmotic pressure is a colligative property.

Reason (R): Osmotic pressure is directly proportional to molarity.

Select the correct answer from codes (i), (ii), (iii), (iv).

[1 mark]

Solution:

Concept:

- A colligative property depends on the number of solute particles rather than their chemical identity.
- For a dilute ideal solution, osmotic pressure is $\pi = CRT$, where $C = n/V$ is the molar concentration of solute particles, R is the gas constant and T is absolute temperature.

Step 1: Evaluate the assertion At a given temperature, osmotic pressure depends on how many solute particles occupy a given volume of solution. It does not depend on the chemical nature of those particles. Thus osmotic pressure is a colligative property, and the assertion is correct.

Step 2: Evaluate the reason From $\pi = CRT$, keeping temperature fixed gives $\pi \propto C$. Osmotic pressure is therefore directly proportional to molarity in the dilute-solution law. For electrolytes, particle multiplication is included through the van't Hoff factor in $\pi = iCRT$. The reason is correct.

Step 3: Test the explanation Molar concentration measures the number of particles per unit volume. The pressure law therefore explains why particle concentration, rather than chemical identity, determines osmotic pressure. The reason explains the assertion, excluding code (ii); codes (iii) and (iv) each wrongly declare one statement false.

Step 4: Conclusion Both Assertion (A) and Reason (R) are correct, and R correctly explains A. Hence, the correct option is (i).

Quick Tip to Solve: Write $\pi = (n/V)RT$ to see directly that osmotic pressure depends on the number of dissolved particles.

20. Assertion (A): Reactivity of ketones is more than aldehydes.

Reason (R): The carbonyl carbon of ketones is less electrophilic as compared to aldehydes.

Select the correct answer from codes (i), (ii), (iii), (iv).

[1 mark]

Solution:

Concept:

- Nucleophilic addition occurs at the electrophilic carbon atom of a carbonyl group.
- Alkyl groups donate electron density by the inductive effect and also hinder the approach of a nucleophile; both effects reduce carbonyl reactivity.

Step 1: Evaluate the assertion In nucleophilic addition, aldehydes are generally more reactive than ketones. An aldehyde has one alkyl group and one hydrogen attached to the carbonyl carbon, whereas a ketone has two alkyl groups. Ketones therefore offer greater steric hindrance to attack. The assertion gives the reversed order and is incorrect.

Step 2: Evaluate the reason The two alkyl groups of a ketone donate more electron density towards its carbonyl carbon than the single alkyl group of a comparable aldehyde. This reduces the partial

Quick Tip to Solve: Compare both effects of the extra alkyl group in a ketone: electron donation and steric crowding each slow nucleophilic addition.

positive charge on the ketone carbonyl carbon, making it less electrophilic. The reason is correct.

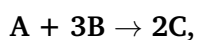
Step 3: Check the causal relationship A less electrophilic carbonyl carbon is attacked less readily by a nucleophile. The reason therefore supports the lower reactivity of ketones and contradicts the assertion. Codes requiring a true assertion, or a false reason, do not fit these evaluations.

Step 4: Conclusion Assertion (A) is incorrect, but Reason (R) is correct. Hence, the correct option is (iv).

Quick Tip to Solve: Compare both effects of the extra alkyl group in a ketone: electron donation and steric crowding each slow nucleophilic addition.

Section B (14 marks)

21. In the given reaction



the rate of formation of C is $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Calculate the

(i) rate of reaction, and

(ii) rate of disappearance of B.

[2 marks]

Solution:

Concept:

- A reaction rate is normalised by the stoichiometric coefficients, so the same positive rate is obtained from every reactant and product.
- For $A + 3B \rightarrow 2C$, $r = -d[A]/dt = -(1/3)d[B]/dt = (1/2)d[C]/dt$, where brackets denote molar concentration and t is time.

Step 1: Use the coefficient of the product The given rate of formation is $d[C]/dt = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Since two moles of C are formed per unit stoichiometric progress, divide this rate by 2:

$$r = \frac{1}{2} \frac{d[C]}{dt} = \frac{2.5 \times 10^{-4}}{2} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

Step 2: Use the coefficient of the reactant Three moles of B disappear for every two moles of C formed. Its disappearance rate is therefore three times the reaction rate:

$$-\frac{d[B]}{dt} = 3r = 3(1.25 \times 10^{-4}) = 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

The derivative $d[B]/dt$ is negative because the reactant concentration falls, whereas its rate of disappearance is reported as a positive quantity.

Step 3: Conclusion (i) Rate of reaction: $1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. (ii) Rate of disappearance of B: $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$.

Quick Tip to Solve: Divide the formation rate of C by 2 to get the reaction rate, then multiply by 3 for B's disappearance rate.

22(i). Write the role of the following:

NaAlF₄ in the extraction of Aluminium

[1 mark]

Solution:

Concept:

- Aluminium is extracted by electrolysis of alumina dissolved in a molten fluoride electrolyte.
- The fluoride bath acts as a solvent for alumina and provides a fluid, electrically conducting medium for electrolysis.

Step 1: Identify the role in the bath The sodium aluminium fluoride NaAlF₄ specified in the question is a fluoride component of the electrolytic bath. It helps lower the fusion temperature of the mixture containing alumina, allowing electrolysis at a temperature well below the melting point of pure alumina.

Step 2: State its electrical function The molten fluoride medium improves the electrical conductivity of the electrolyte. This enables current to pass through the bath efficiently while aluminium ions are reduced at the cathode. The fluoride is an electrolyte additive; it is not the reducing agent for alumina.

Step 3: Conclusion It lowers the fusion temperature of the alumina-containing bath and increases its electrical conductivity.

Quick Tip to Solve: For a fluoride additive in aluminium extraction, state both a lower operating temperature and improved electrical conductivity.

22(ii). Write the role of the following:

CO in the refining of Ni

[1 mark]

Solution:

Concept:

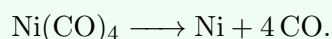
- Mond refining separates nickel by forming a volatile compound and then thermally decomposing the purified vapour.
- Carbon monoxide is a ligand that combines with nickel to form volatile nickel tetracarbonyl, Ni(CO)₄.

Step 1: Form the volatile carbonyl Impure nickel reacts with carbon monoxide at about 330–350 K:



The volatile nickel carbonyl is separated from the non-volatile impurities, transferring nickel into a purified vapour stream.

Step 2: Recover pure nickel On heating the carbonyl to about 450–470 K, it decomposes:



Pure nickel is deposited and carbon monoxide is liberated for reuse. Thus the separation depends on

Quick Tip to Solve: Remember Mond refining as carbonyl formation at lower temperature followed by decomposition at higher temperature.

reversible carbonyl formation and volatility.

Step 3: Conclusion CO converts nickel into volatile $\text{Ni}(\text{CO})_4$, which decomposes on heating to yield pure nickel in Mond's process.

Quick Tip to Solve: Remember Mond refining as carbonyl formation at lower temperature followed by decomposition at higher temperature.

OR

22(b). Write the chemical equations involved in the leaching of bauxite ore to prepare pure alumina.

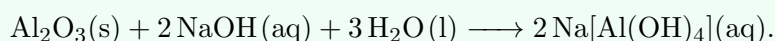
[2 marks]

Solution:

Concept:

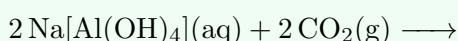
- Alumina is amphoteric and dissolves in hot concentrated sodium hydroxide to form soluble sodium aluminate, while insoluble impurities can be filtered off.
- Carbon dioxide precipitates hydrated alumina from the aluminate solution; heating the precipitate gives pure anhydrous alumina.

Step 1: Leach the alumina with alkali Digest powdered bauxite with concentrated NaOH at about 473–523 K under pressure. The alumina component forms soluble sodium aluminate:



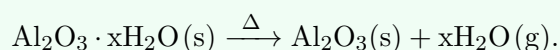
Filter the mixture to remove insoluble impurities such as iron oxide. This selectively brings the aluminium compound into solution.

Step 2: Precipitate hydrated alumina Pass CO_2 through the filtered solution and seed with freshly prepared hydrated alumina to assist precipitation:



Here x denotes the hydration number. Separate and wash the hydrated alumina precipitate to remove soluble salts.

Step 3: Calcine the precipitate Heat the washed precipitate to about 1470 K. It loses its water of hydration, leaving pure alumina:



Step 4: Conclusion The sequence is alkaline leaching to soluble aluminate, precipitation of hydrated alumina, and calcination to pure Al_2O_3 .

Quick Tip to Solve: Write the three stages in order: dissolve in NaOH, precipitate with CO_2 , and heat to remove water of hydration.

23(a). Write two differences between physisorption and chemisorption.

[2 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance, the adsorbate, on the surface of another substance, the adsorbent.
- Physisorption and chemisorption differ in the forces binding the adsorbate to the surface; this also changes the amount of heat released during adsorption.

Step 1: Compare the binding forces First difference: nature of interaction. In physisorption, the adsorbate is held on the surface by weak van der Waals forces, without formation of new chemical bonds. In chemisorption, the adsorbate forms chemical bonds with surface atoms. Thus chemisorption involves a much stronger and more specific interaction between the surface and the adsorbed species.

Step 2: Compare the enthalpies of adsorption Second difference: heat of adsorption. Physisorption has a relatively low magnitude of enthalpy of adsorption, usually about $20\text{--}40\text{ kJ mol}^{-1}$. Chemisorption has a high magnitude, usually about $80\text{--}240\text{ kJ mol}^{-1}$, because chemical bond formation releases more energy. These are magnitudes of heat evolved; adsorption is generally exothermic and its enthalpy change is negative.

Step 3: Conclusion Physisorption involves weak van der Waals forces and low heat of adsorption; chemisorption involves chemical bond formation and high heat of adsorption.

Quick Tip to Solve: Pair the two comparisons: weaker intermolecular attraction gives lower heat release, while chemical bond formation gives higher heat release.

OR

23(b). Define the following terms with a suitable example of each:

(i) Associated colloids

(ii) O/W emulsion

[2 marks]

Solution:

Concept:

- Associated colloids arise by aggregation of small dissolved species into colloidal-sized particles called micelles.
- An emulsion is a colloidal dispersion of one liquid in another immiscible liquid; O/W identifies oil as the dispersed phase and water as the dispersion medium.

Step 1: Define associated colloids and give an example Associated colloids are substances that behave as normal strong electrolytes at low concentration but form colloidal aggregates, or micelles, at higher concentration. Micelle formation occurs above the critical micelle concentration and above the Krafft temperature. For example, soap such as sodium stearate, $\text{C}_{17}\text{H}_{35}\text{COONa}$, forms micelles in water. Its hydrocarbon tails point inward, away from water, while its ionic heads face the surrounding water.

Step 2: Identify the phases in an O/W emulsion An oil-in-water (O/W) emulsion consists of tiny

Quick Tip to Solve: Read O/W as oil droplets in water; for associated colloids, include micelles and the concentration condition in your definition.

droplets of oil dispersed throughout a continuous aqueous medium. Milk is a suitable example: liquid fat droplets form the dispersed phase and water forms the dispersion medium. The notation gives the dispersed liquid first, so an O/W emulsion is distinguished from a W/O emulsion by which liquid is continuous.

Step 3: Conclusion (i) Associated colloids form micelles by aggregation, as in an aqueous soap solution above its critical micelle concentration. (ii) An O/W emulsion has oil droplets dispersed in water, as in milk.

Quick Tip to Solve: Read O/W as oil droplets in water; for associated colloids, include micelles and the concentration condition in your definition.

24. (a) Write the IUPAC name and hybridisation of the complex $[\text{CoF}_6]^{3-}$. (Given: Atomic number of Co = 27)

(b) What type of isomerism is shown by the complex $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$? Name the structure of an isomer of this complex which is optically active. [2 marks]

Solution:

Concept:

- The oxidation state of the central metal is found by adding the ligand charges to the metal oxidation state and equating the sum to the complex charge. An anionic cobalt complex uses the name cobaltate.
- Fluorido is a weak-field ligand. In valence-bond theory, a high-spin octahedral complex can use the outer-orbital hybridisation sp^3d^2 .
- Geometrical isomers differ in ligand positions; optical isomers are non-superimposable mirror images. The ligand en is neutral, bidentate ethane-1,2-diamine.

Step 1: Determine the name and hybridisation in part (a) Let the oxidation state of cobalt in $[\text{CoF}_6]^{3-}$ be x . Then

$$x + 6(-1) = -3, \quad x = +3.$$

The IUPAC name is hexafluoridocobaltate(III) ion. Cobalt has configuration $[\text{Ar}]3d^74s^2$, so Co^{3+} is $3d^6$. The weak-field fluorido ligands do not force pairing of the initially unpaired $3d$ electrons. Two vacant inner $3d$ orbitals are therefore unavailable, and the complex uses one $4s$, three $4p$ and two $4d$ orbitals: sp^3d^2 hybridisation with octahedral geometry.

Step 2: Identify the isomers in part (b) In $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$, two bidentate en ligands occupy four coordination positions and the two chlorido ligands occupy the remaining two. The chlorido ligands can be adjacent, giving the cis isomer, or opposite, giving the trans isomer. Thus the complex shows geometrical isomerism. The cis structure also exists as a pair of non-superimposable mirror images and is optically active; the trans structure is optically inactive.

Step 3: Conclusion (a) Hexafluoridocobaltate(III) ion; sp^3d^2 hybridisation. (b) Geometrical (cis-trans) and optical isomerism are shown; the cis isomer is the optically active structure.

Quick Tip to Solve: For an octahedral complex with two en ligands and two identical monodentate ligands, identify cis and trans first; the cis form gives the optical pair.

25. Give reasons:

(i) Shaving soaps contain glycerol.

(ii) Antacids should not be used for longer time.

[2 marks]

Solution:

Concept:

- A humectant attracts and retains water, helping a preparation stay moist. Glycerol contains three hydroxyl groups and forms hydrogen bonds with water.
- Antacids are mild bases that neutralise excess stomach acid. Gastric acid is also needed for normal digestion, so excessive neutralisation is undesirable.

Step 1: Explain the role of glycerol in shaving soap Glycerol is added as a humectant to prevent rapid drying. Its hydroxyl groups interact strongly with water through hydrogen bonding, enabling it to retain moisture in the lather. The moist lather softens facial hair and helps keep the skin from becoming dry during shaving. Thus glycerol is included principally for moisture retention, rather than as the soap's cleansing component.

Step 2: Explain the limitation of prolonged antacid use Antacids neutralise excess hydrochloric acid and temporarily relieve acidity. However, prolonged or excessive use can make the stomach contents too alkaline and disturb the normal acidic conditions required for digestion. It can also stimulate further acid secretion, so repeated neutralisation does not provide lasting control of excessive acid production. This is why antacids should not be used continuously for a long time.

Step 3: Conclusion (i) Glycerol retains water and prevents shaving lather and skin from drying. (ii) Prolonged antacid use can make the stomach too alkaline and stimulate additional acid production, disturbing normal digestion.

Quick Tip to Solve: Link glycerol to moisture retention, and distinguish temporary acid neutralisation by antacids from control of acid secretion.

26. Define the following terms:

(i) Oligosaccharides

(ii) Invert sugar

[2 marks]

Solution:

Concept:

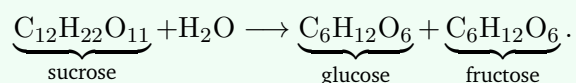
- Carbohydrates can be classified by the number of monosaccharide units produced on complete hydrolysis; hydrolysis breaks glycosidic linkages using water.
- Optical rotation of a mixture depends on the rotations of its components. Inversion of sugar refers to a reversal in the sign of optical rotation after hydrolysis.

Step 1: Define oligosaccharides by their hydrolysis products Oligosaccharides are carbohydrates that yield two to ten monosaccharide units on complete hydrolysis. They include disaccharides, trisaccharides and the other small members of this range. For example, sucrose is a disaccharide because each molecule yields one glucose molecule and one fructose molecule on hydrolysis. The

Quick Tip to Solve: Remember the two-to-ten range for oligosaccharides; for invert sugar, name both products and the reversal from positive to negative rotation.

classification counts the total number of monosaccharide units, not merely the number of different kinds formed.

Step 2: Define invert sugar and explain the inversion Invert sugar is the equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose, using dilute acid or the enzyme invertase:

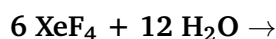


Sucrose is dextrorotatory, whereas the resulting mixture is laevorotatory because fructose's negative rotation exceeds glucose's positive rotation in magnitude. This change from positive to negative rotation explains the name invert sugar.

Step 3: Conclusion (i) Oligosaccharides yield two to ten monosaccharide units on complete hydrolysis. (ii) Invert sugar is the laevorotatory, equimolar glucose–fructose mixture formed by hydrolysing sucrose.

Quick Tip to Solve: Remember the two-to-ten range for oligosaccharides; for invert sugar, name both products and the reversal from positive to negative rotation.

27. Write the products of the following reaction:



Is this reaction a disproportionation reaction? Give reasons in support of your answer.

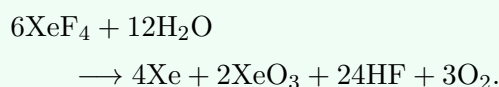
[2 marks]

Solution:

Concept:

- Hydrolysis is reaction with water. Complete hydrolysis of xenon tetrafluoride produces xenon, xenon trioxide, hydrogen fluoride and oxygen.
- In disproportionation, the same element in one initial oxidation state undergoes both oxidation and reduction. Fluorine has oxidation state -1 , while oxygen in XeO_3 has oxidation state -2 .

Step 1: Write and balance the hydrolysis reaction The products corresponding to the given amounts of xenon tetrafluoride and water are



There are six xenon atoms, twenty-four fluorine atoms, twenty-four hydrogen atoms and twelve oxygen atoms on each side, so the equation is balanced.

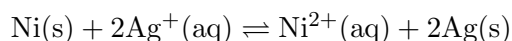
Step 2: Compare the oxidation states of xenon In XeF_4 , let the oxidation state of xenon be x . Then $x + 4(-1) = 0$, giving $x = +4$. The product Xe has oxidation state zero, whereas in XeO_3 , $x + 3(-2) = 0$, giving $x = +6$. Thus some xenon is reduced, $+4 \rightarrow 0$, and some is oxidised, $+4 \rightarrow +6$, in the same reaction.

Step 3: Conclusion The products are $4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$. Yes, this is a disproportionation reaction because xenon in the $+4$ state is simultaneously reduced to 0 and oxidised to $+6$.

Quick Tip to Solve: For disproportionation, track the same element: Xe goes from $+4$ to both 0 and $+6$; merely listing hydrolysis products is not enough.

Section C (21 marks)

28. Calculate the maximum work and $\log K_c$ for the given reaction at 298 K:



Given:

$$E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}, \quad E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$$

$$1 \text{ F} = 96500 \text{ C mol}^{-1}$$

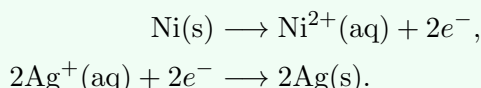
[3 marks]

Solution:

Concept:

- For a galvanic cell, $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, with both tabulated values expressed as reduction potentials.
- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred and F is the Faraday constant. The maximum electrical work delivered by the cell is $-\Delta_r G^\circ$.
- At 298 K, $E_{\text{cell}}^\circ = (0.0591/n) \log K_c$, with potential in volts and a base-ten logarithm.

Step 1: Identify the half-reactions and cell potential Nickel is oxidised at the anode and silver ions are reduced at the cathode:



Therefore $n = 2$. Using the given reduction potentials,

$$E_{\text{cell}}^\circ = 0.80 - (-0.25) = 1.05 \text{ V}.$$

Do not double the silver reduction potential when doubling its half-reaction.

Step 2: Calculate the maximum electrical work For one mole of reaction as written,

$$\Delta_r G^\circ = -2(96500)(1.05) = -202650 \text{ J mol}^{-1}.$$

Hence maximum work delivered is $202.65 \text{ kJ mol}^{-1}$; work done on the system has the opposite sign.

Step 3: Obtain the equilibrium constant logarithm Combining $\Delta_r G^\circ = -RT \ln K_c$ with the cell-potential relation gives

$$\log K_c = \frac{nE_{\text{cell}}^\circ}{0.0591} = \frac{2(1.05)}{0.0591} \approx 35.53.$$

The large positive logarithm shows that equilibrium strongly favours the products.

Step 4: Conclusion Maximum electrical work delivered is $202.65 \text{ kJ mol}^{-1}$, with $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$, and $\log K_c \approx 35.53$ at 298 K.

Quick Tip to Solve: Count two electrons from the nickel half-reaction, subtract the negative nickel reduction potential, and never double the silver electrode potential.

29. A first order reaction is 40% complete in 80 minutes. Calculate the value of rate constant (k). In what time will the reaction be 90% completed?

[Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$, $\log 5 = 0.6771$, $\log 6 = 0.7782$] [3 marks]

Solution:

Concept:

- For a first-order reaction, the integrated rate law is $k = \frac{2.303}{t} \log \frac{a}{a-x}$, where a is the initial concentration and $a-x$ is the concentration remaining after time t .
- Percentage completion measures reactant consumed. Thus 40% completion leaves 60% unreacted, whereas 90% completion leaves 10%. For a first-order reaction, k has units of inverse time.

Step 1: Translate the given completion into remaining reactant Take the initial amount as 100 units. After 80 min, 40 units have reacted and 60 units remain. The concentration ratio in the integrated rate law is therefore

$$\frac{a}{a-x} = \frac{100}{60} = \frac{10}{6}.$$

Using the supplied value $\log 6 = 0.7782$,

$$\log \frac{10}{6} = \log 10 - \log 6 = 1 - 0.7782 = 0.2218.$$

The denominator must represent the unreacted amount, so $100/40$ would be the wrong ratio.

Step 2: Evaluate the rate constant Substitute the elapsed time and concentration ratio:

$$\begin{aligned} k &= \frac{2.303}{80} \times 0.2218 \\ &= 0.006385 \text{ min}^{-1} \\ &\approx 6.39 \times 10^{-3} \text{ min}^{-1}. \end{aligned}$$

The time was used in minutes, so the rate constant is expressed in min^{-1} . This constant applies throughout the reaction at the same temperature.

Step 3: Find the time for ninety percent completion When 90% is complete, $a-x = 0.10a$, so the ratio becomes $a/(a-x) = 10$. Hence

$$\begin{aligned} t_{90} &= \frac{2.303}{k} \log 10 \\ &= \frac{80}{0.2218} \\ &\approx 360.7 \text{ min}. \end{aligned}$$

This is the total time measured from the start of the reaction. The time is not proportional to percentage completion, because the instantaneous rate falls as the reactant concentration decreases.

Step 4: Conclusion The rate constant is $k \approx 6.39 \times 10^{-3} \text{ min}^{-1}$, and the reaction is 90% complete after approximately 360.7 min from its start.

Quick Tip to Solve: Use the fraction left: 40% complete means 60% remains. Computing $\log(10/6)$ from the supplied $\log 6$ avoids unnecessary logarithm values.

30. Write the names and structures of the monomers in the following polymers:

(i) Buna-S

(ii) Nylon-6,6

(iii) Bakelite

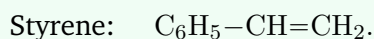
[3 marks]

Solution:

Concept:

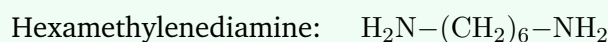
- A monomer is a small molecule whose units join repeatedly to form a polymer. Addition polymers retain the atoms of their unsaturated monomers.
- Condensation polymers form from monomers with reactive functional groups, usually with elimination of small molecules such as water. Identify both the carbon skeleton and the functional groups.

Step 1: Identify the two monomers of Buna-S Buna-S is a copolymer of 1,3-butadiene and styrene (phenylethene). Their condensed structural formulae are:



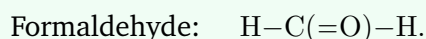
Both contain carbon-carbon double bonds that take part in addition polymerisation. The styrene molecule contains a phenyl group attached to an ethene unit.

Step 2: Identify the two monomers of Nylon-6,6 Nylon-6,6 is formed from hexamethylenediamine (hexane-1,6-diamine) and adipic acid (hexanedioic acid):



The amino and carboxyl groups react to form amide linkages with elimination of water. Each monomer contains six carbon atoms; the two carboxyl carbons must be counted in adipic acid.

Step 3: Identify the two monomers of Bakelite Bakelite is a condensation polymer of phenol and formaldehyde (methanal):



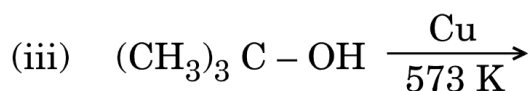
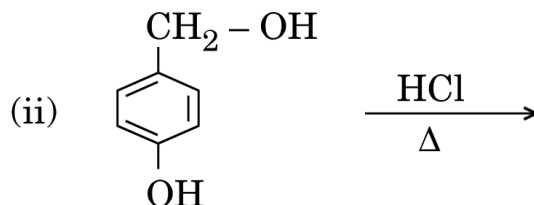
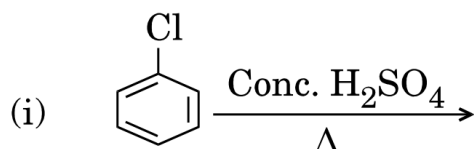
Formaldehyde enables methylene bridges to form between phenol rings at their ortho and para positions, ultimately producing a cross-linked polymer.

Step 4: Conclusion Buna-S: 1,3-butadiene and styrene; Nylon-6,6: hexamethylenediamine and adipic acid; Bakelite: phenol and formaldehyde, with the structures shown above.

Quick Tip to Solve: For Nylon-6,6, count all carbon atoms: the diamine has six methylene groups, while adipic acid has four methylene groups plus two carboxyl carbons.

31. Write the major product(s) of the following reactions:

[3 marks]



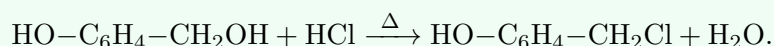
Solution:

Concept:

- Chlorine deactivates benzene towards electrophilic substitution but directs substitution to the ortho and para positions by resonance donation.
- HCl replaces a benzylic alcoholic hydroxyl group by chlorine; a phenolic hydroxyl group remains unchanged.
- Tertiary alcohols undergo dehydration over copper at 573 K, since the hydroxyl-bearing carbon has no hydrogen for dehydrogenation.

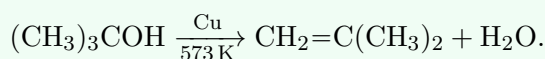
Step 1: Sulphonate chlorobenzene in part (i) Concentrated sulphuric acid introduces $-\text{SO}_3\text{H}$ at the ortho and para positions relative to chlorine. Para-chlorobenzenesulphonic acid is the major product because it is less sterically hindered; ortho-chlorobenzenesulphonic acid also forms.

Step 2: Replace the benzylic hydroxyl group in part (ii) Only the $-\text{CH}_2\text{OH}$ group becomes $-\text{CH}_2\text{Cl}$. The phenolic $-\text{OH}$ group is unchanged:



The substituents remain para to each other. The product is 4-(chloromethyl)phenol, or para-hydroxybenzyl chloride.

Step 3: Dehydrate the tertiary alcohol in part (iii) 2-Methylpropan-2-ol is tertiary and therefore undergoes dehydration:

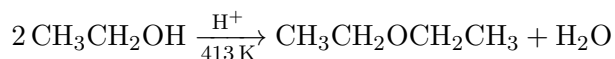


The product is 2-methylpropene.

Step 4: Conclusion (i) Para-chlorobenzenesulphonic acid (major), with the ortho isomer. (ii) $p\text{-HO}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$. (iii) 2-Methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)_2$.

Quick Tip to Solve: In part (ii), identify which hydroxyl group is attached to the benzylic carbon: HCl replaces this group, leaving the ring-bonded hydroxyl group intact.

32(a). Write the mechanism of the following reaction:



(b) Write the preparation of phenol from cumene.

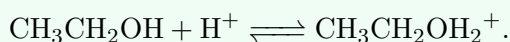
[3 marks]

Solution:

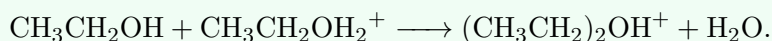
Concept:

- At 413 K, acid-catalysed intermolecular dehydration of ethanol forms ethoxyethane.
- Another ethanol molecule attacks the primary carbon by an $\text{S}_{\text{N}}2$ process. Deprotonation then regenerates the acid catalyst.
- Cumene is oxidised by air to cumene hydroperoxide, which cleaves in aqueous acid to yield phenol and acetone.

Step 1: Protonate ethanol in part (a) The oxygen lone pair of ethanol accepts a proton, making departure of water possible:



Step 2: Form the ether bond by nucleophilic substitution A second ethanol molecule attacks the ethyl carbon through its oxygen lone pair. Formation of the new carbon-oxygen bond and departure of water occur together:



This concerted substitution gives protonated ether, without forming a free primary carbocation.

Step 3: Regenerate the acid catalyst Loss of a proton from oxygen gives neutral ethoxyethane:

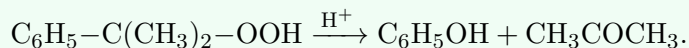


The acid catalyst is regenerated.

Step 4: Prepare phenol from cumene in part (b) Oxidise cumene (isopropylbenzene) with oxygen from air to form cumene hydroperoxide:



Treat the hydroperoxide with dilute aqueous acid. Acidic cleavage yields phenol and acetone:



Step 5: Conclusion (a) The acid-catalysed substitution forms ethoxyethane. (b) Cumene hydroperoxide undergoes acidic cleavage to give phenol and acetone.

Quick Tip to Solve: Keep the positive charge on oxygen throughout the ether mechanism, regenerate the acid in the last step, and include the hydroperoxide intermediate in the cumene route.

32(b). How can you convert the following:

(i) Sodium phenoxide to o-hydroxybenzoic acid

(ii) Acetone to propene

(iii) Phenol to chlorobenzene

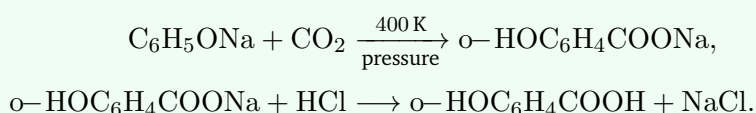
[3 marks]

Solution:

Concept:

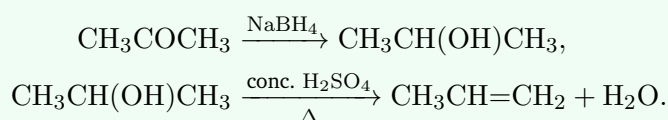
- In the Kolbe reaction, sodium phenoxide reacts with carbon dioxide under pressure to introduce a carboxyl group mainly at the ortho position; acidification gives salicylic acid.
- Reduction converts a ketone into a secondary alcohol, which loses water on heating with concentrated sulphuric acid to give an alkene.
- Heating phenol with zinc dust removes its oxygen as zinc oxide. Benzene then undergoes electrophilic chlorination with chlorine and anhydrous ferric chloride.

Step 1: (i) Sodium phenoxide to o-hydroxybenzoic acid Heat sodium phenoxide with carbon dioxide at about 400 K under 4–7 atm pressure, then acidify the sodium salicylate formed:



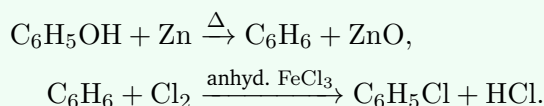
Acidification changes the carboxylate salt into the free carboxylic acid.

Step 2: (ii) Acetone to propene First reduce acetone to propan-2-ol using sodium borohydride. Then dehydrate the alcohol with concentrated sulphuric acid on heating:



The carbon skeleton remains unchanged throughout this sequence.

Step 3: (iii) Phenol to chlorobenzene Distil phenol with zinc dust to form benzene, then chlorinate benzene in the presence of anhydrous ferric chloride:



Direct chlorination of phenol substitutes chlorine on the activated ring and does not replace its hydroxyl group, so benzene is the required intermediate.

Step 4: Conclusion The three conversions proceed through sodium salicylate, propan-2-ol and benzene, respectively, giving o-hydroxybenzoic acid, propene and chlorobenzene.

Quick Tip to Solve: For phenol to chlorobenzene, remove the OH group with zinc dust first; direct chlorination retains OH on the ring.

33. Write the products formed when $(\text{CH}_3)_3\text{C}-\text{CHO}$ reacts with the following reagents:

(i) CH_3COCH_3 in the presence of dilute NaOH

(ii) HCN

(iii) Conc. NaOH

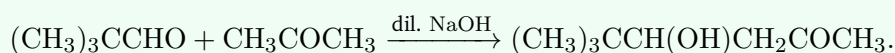
[3 marks]

Solution:

Concept:

- The carbon adjacent to the aldehyde group in $(\text{CH}_3)_3\text{CCHO}$ has no hydrogen. This aldehyde therefore cannot form its own enolate, but its carbonyl carbon can accept an attacking nucleophile.
- Acetone has alpha hydrogens and gives a crossed aldol addition with this aldehyde in dilute alkali. Cyanide adds to a carbonyl group to form a cyanohydrin.
- An aldehyde without alpha hydrogen undergoes Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised to carboxylate and another is reduced to alcohol.

Step 1: (i) Reaction with acetone and dilute NaOH Dilute alkali forms a small amount of the acetone enolate, which attacks the aldehyde carbonyl carbon. Protonation of the resulting alkoxide gives the beta-hydroxy ketone:



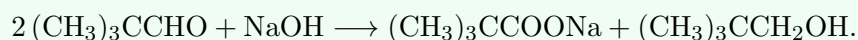
The original aldehyde carbon becomes the carbon bearing OH , while the acetone carbonyl group remains intact. This is the crossed aldol addition product under the stated conditions.

Step 2: (ii) Reaction with HCN Cyanide ion adds to the electrophilic carbonyl carbon, and the oxygen then gains a proton. The cyanohydrin formed is



Thus, OH and CN become attached to the carbon that originally belonged to the aldehyde carbonyl group. The hydrogen already bonded to that carbon is retained.

Step 3: (iii) Reaction with concentrated NaOH Since no alpha hydrogen is available, the aldehyde undergoes the Cannizzaro reaction rather than self-aldol addition:



The products are sodium 2,2-dimethylpropanoate and 2,2-dimethylpropan-1-ol. The oxidised product remains a sodium carboxylate in the alkaline reaction mixture; acidification would be needed to obtain the free acid.

Step 4: Conclusion The products are (i) $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_2\text{COCH}_3$, (ii) $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CN}$, and (iii) $(\text{CH}_3)_3\text{CCOONa}$ together with $(\text{CH}_3)_3\text{CCH}_2\text{OH}$.

Quick Tip to Solve: Count hydrogens on the carbon directly next to CHO , not on the three methyl groups: zero alpha hydrogens means Cannizzaro in concentrated alkali.

34(a). Define Lyophobic and Lyophilic sol with a suitable example of each. Why is coagulation of Lyophilic sol difficult as compared to Lyophobic sol? [3 marks]

Solution:

Concept:

- A sol is a colloidal system in which a solid dispersed phase is distributed through a liquid dispersion medium. Lyophilic and lyophobic describe the affinity between these two phases.
- Colloidal particles may be stabilised by like electrical charges, which oppose aggregation, and by solvation, in which molecules of the medium surround the dispersed particles.
- Coagulation is the aggregation of colloidal particles into larger particles that separate from the dispersion medium when the stabilising effects are sufficiently reduced.

Step 1: Define a lyophobic sol and give an example A lyophobic sol is a colloidal dispersion in which the dispersed phase has little affinity for the dispersion medium. A gold sol in water is an example. Such sols generally require special preparation methods and are relatively unstable. Their particles are stabilised mainly by electrical charge; addition of a suitable electrolyte can neutralise this charge and bring about coagulation readily.

Step 2: Define a lyophilic sol and give an example A lyophilic sol is a colloidal dispersion in which the dispersed phase has a strong affinity for the dispersion medium. A starch sol in water is an example. Starch particles interact strongly with water molecules and acquire a hydrated layer. Lyophilic sols are comparatively stable and are generally reversible: the separated dispersed phase can form a sol again on contact with a suitable amount of the medium.

Step 3: Explain the difference in ease of coagulation Lyophilic particles are protected both by their solvation layer and, when present, by their electrical charge. Neutralising the charge alone does not readily remove the protective solvent layer or make the particles aggregate. Coagulation therefore requires substantial desolvation as well as removal of electrical stabilisation. A large amount of electrolyte, or a suitable dehydrating agent in an aqueous sol, can produce these changes. Lyophobic particles have little solvation, so destruction of their charge barrier by a comparatively small amount of electrolyte allows them to aggregate much more easily.

Step 4: Conclusion Gold sol in water is lyophobic, while starch sol in water is lyophilic. Strong solvation of lyophilic particles provides additional protection against aggregation and makes their coagulation more difficult.

Quick Tip to Solve: Compare the two stabilising effects separately: charge mainly protects a lyophobic sol, while strong solvation gives a lyophilic sol additional protection.

34(b). Define the following terms:

(i) Shape-selective catalysis

(ii) Kraft temperature

(iii) Peptization

[3 marks]

Solution:

Concept:

- Catalysis may depend on the fit of molecules within the pores of a solid catalyst.
- Micelle formation requires both a sufficiently high temperature and a surfactant concentration above the critical micelle concentration (CMC).
- Adsorption of ions on particles can give them like charges and stabilise a colloidal dispersion.

Step 1: (i) Shape-selective catalysis Shape-selective catalysis is catalysis in which the reaction depends on the pore structure of the catalyst and the sizes and shapes of the reactant and product molecules. Only molecules with suitable dimensions can enter the pores, react at the active sites and leave. Zeolites are common shape-selective catalysts because they have a regular network of pores of definite size.

Step 2: (ii) Kraft temperature Kraft temperature, T_k , is the minimum temperature above which a surfactant can form micelles in its solution, provided its concentration also exceeds the CMC. Below this temperature, the solubility of the surfactant is too low for its dissolved concentration to reach the value needed for micelle formation. Thus temperature and concentration are separate necessary conditions.

Step 3: (iii) Peptization Peptization is the conversion of a freshly prepared precipitate into a colloidal sol by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte, called the peptizing agent. The precipitate adsorbs one kind of ion from the electrolyte; its particles acquire like charges, repel one another and disperse. For example, a small quantity of FeCl_3 peptizes freshly precipitated $\text{Fe}(\text{OH})_3$ into a positively charged sol.

Step 4: Conclusion Shape-selective catalysis involves molecular fit in catalyst pores; Kraft temperature is the threshold temperature for micelle formation; peptization converts a fresh precipitate into a sol using a small amount of electrolyte.

Quick Tip to Solve: For Kraft temperature, state the temperature threshold and remember that micelles also require concentration above the CMC.

Section D (15 marks)

35(a). Give reasons:

(i) Helium does not form compounds like Xenon.

(ii) HClO_4 is a stronger acid than HOCl .

(iii) Sulphur is a polyatomic solid whereas Oxygen is a diatomic gas.

[3 marks]

Solution:

Concept:

- The reactivity of noble gases depends strongly on their ionisation enthalpy and the attraction of the nucleus for the valence electrons.
- An oxoacid is stronger when electron withdrawal facilitates loss of H^+ and the conjugate base is better stabilised.
- Molecular size, bonding and intermolecular forces together determine the molecular form and physical state of an element.

Step 1: (i) Compare helium and xenon Helium has a complete $1s^2$ shell and a very small atomic size. Its electrons are held extremely strongly, giving it a very high ionisation enthalpy. It therefore does not form ordinary compounds like xenon. Xenon is larger and has a much lower ionisation enthalpy, so its valence electrons can participate in bonding with strongly electronegative elements such as fluorine and oxygen.

Step 2: (ii) Compare the two oxoacids In HClO_4 , the three additional oxygen atoms withdraw electron density from the O–H group. This increases the polarity of that bond and favours release of H^+ . Also, the negative charge in the conjugate base ClO_4^- is delocalised over four oxygen atoms, making it especially stable. In OCl^- , formed from HOCl , there is no comparable delocalisation over several oxygen atoms. Hence perchloric acid ionises much more readily.

Step 3: (iii) Compare molecular forms and physical states The small oxygen atoms form a strong $\text{O}=\text{O}$ double bond through effective $p\pi-p\pi$ overlap, so oxygen occurs as diatomic O_2 . Its small molecules experience weak intermolecular forces and are gaseous at room temperature. The larger sulphur atoms have poorer sideways orbital overlap, making multiple bonding less favourable; sulphur instead forms stable S–S single bonds and commonly exists as puckered S_8 rings. These larger, more polarisable molecules have stronger dispersion forces and form a polyatomic solid.

Step 4: Conclusion Helium is inert because its electrons are exceptionally tightly bound; HClO_4 is stronger because of electron withdrawal and conjugate-base stabilisation; sulphur forms solid S_8 , whereas oxygen forms gaseous O_2 .

Quick Tip to Solve: In part (iii), explain both the molecular form using bond formation and the physical state using intermolecular forces.

35(b). Write one reaction as an example of each, to show that conc. H_2SO_4 acts as

(i) an oxidising agent, and

(ii) a dehydrating agent.

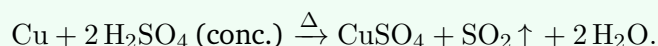
[2 marks]

Solution:

Concept:

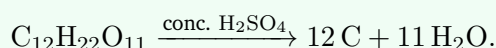
- An oxidising agent accepts electrons and is itself reduced; oxidation states reveal this change.
- A dehydrating agent removes the elements of water from a substance. Concentrated sulphuric acid has a strong affinity for water.

Step 1: (i) Oxidising action with copper Copper reacts with hot concentrated sulphuric acid as follows:



Copper is oxidised from oxidation state 0 to +2, while sulphur in the acid is reduced from +6 to +4 in sulphur dioxide. Thus concentrated H_2SO_4 oxidises copper and acts as an oxidising agent. The evolved gas is SO_2 .

Step 2: (ii) Dehydrating action with sucrose Concentrated sulphuric acid removes water from sugar, leaving a black mass of carbon:



The hydrogen and oxygen in sucrose are removed in the ratio in which they occur in water. This charring of sugar demonstrates the dehydrating action of the acid; the acid is written over the arrow to show its role in removing water.

Step 3: Conclusion Hot concentrated sulphuric acid oxidises copper to copper sulphate, forming SO_2 , and dehydrates sucrose to carbon by removing water.

Quick Tip to Solve: Show the reduction of sulphur to prove oxidising action, and use sugar charring as a direct example of dehydration.

OR

35(a)(i). Account for the following:

Hydration enthalpy of F^- ion is more than Cl^- ion.

[1 mark]

Solution:

Concept:

- Hydration enthalpy is the enthalpy change when gaseous ions become hydrated in water; this process is exothermic.
- For ions of equal charge, a smaller ionic radius gives stronger ion-dipole attraction to water molecules.

Step 1: Compare the size and charge density Both F^- and Cl^- carry one negative charge, but F^- is

Quick Tip to Solve: For equally charged ions, compare their radii: the smaller ion generally has a more negative hydration enthalpy.

smaller. Its charge is therefore concentrated in a smaller volume, so it attracts the positive hydrogen ends of nearby water molecules more strongly.

Step 2: Relate attraction to hydration enthalpy Stronger ion-water attraction releases more energy on hydration. Therefore the hydration enthalpy of F^- is more negative than that of Cl^- ; its magnitude is greater. The word “more” in the question refers to the energy released, not to a larger algebraic value of the negative enthalpy.

Step 3: Conclusion Owing to its smaller radius and higher charge density, F^- has a greater magnitude of hydration enthalpy than Cl^- :

$$|\Delta H_{\text{hyd}}(F^-)| > |\Delta H_{\text{hyd}}(Cl^-)|.$$

Quick Tip to Solve: For equally charged ions, compare their radii: the smaller ion generally has a more negative hydration enthalpy.

35(a)(ii). Account for the following:

SO_2 is a reducing agent, whereas TeO_2 is an oxidising agent in group-16 oxides.

[1 mark]

Solution:

Concept:

- A reducing agent loses electrons and is oxidised; an oxidising agent gains electrons and is reduced.
- Down group 16, the stability of the +6 oxidation state decreases, while that of +4 increases because of the inert-pair effect.

Step 1: Explain the behaviour of sulphur dioxide Sulphur has oxidation state +4 in SO_2 . It can readily be oxidised to the relatively stable +6 state, for example in sulphate. Thus SO_2 supplies electrons to another substance and acts as a reducing agent.

Step 2: Apply the group trend to tellurium dioxide Tellurium also has oxidation state +4 in TeO_2 . For this heavier group-16 element, the inert-pair effect makes oxidation to +6 less favourable. Instead, TeO_2 can accept electrons and be reduced to a lower oxidation state, so it acts as an oxidising agent.

Step 3: Conclusion SO_2 is reducing because S(IV) is readily oxidised to S(VI); TeO_2 is oxidising because Te(IV) resists oxidation to Te(VI) and can undergo reduction.

Quick Tip to Solve: First assign the central atom +4 in each dioxide, then compare how easily it can reach +6 down group 16.

35(b). Write the reaction of F₂ with water. Why does I₂ not react with water?

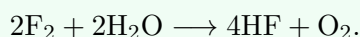
[2 marks]

Solution:

Concept:

- A halogen oxidises water only if its oxidising power is sufficient to remove electrons from water and liberate oxygen.
- Oxidising power decreases down group 17: fluorine is the strongest halogen oxidant, whereas iodine is much weaker.

Step 1: Write the reaction of fluorine with water Fluorine reacts vigorously with water, forming hydrogen fluoride and oxygen:



Fluorine is reduced from oxidation state 0 to -1, while oxygen in water is oxidised from -2 to 0. Four fluorine atoms each gain one electron, matching the four electrons lost by the two oxygen atoms.

Step 2: Explain the behaviour of iodine Iodine is a weak oxidising agent compared with fluorine. Its oxidising power is insufficient to oxidise water to oxygen, so the corresponding reaction giving hydrogen iodide and oxygen does not occur. Consequently, iodine does not react appreciably with water under ordinary conditions; simply dissolving a small amount is not this redox reaction.

Step 3: Conclusion $2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{O}_2$. Iodine does not react with water because it cannot oxidise water to oxygen.

Quick Tip to Solve: Balance the fluorine equation using four HF molecules, and explain iodine using oxidising strength rather than solubility.

35(c). Draw the structure of XeF₂.

[1 mark]

Solution:

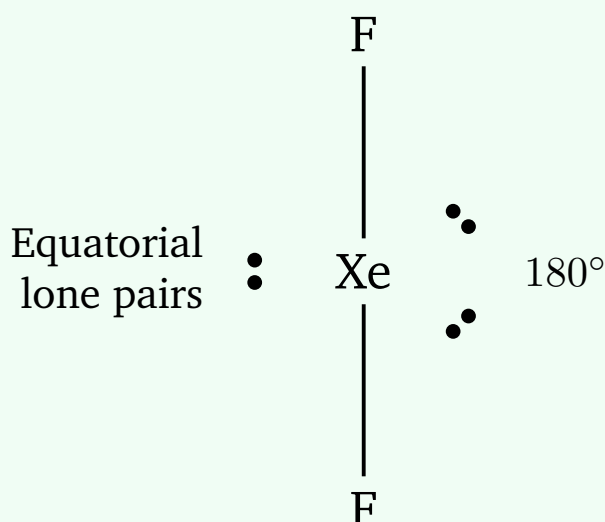
Concept:

- In VSEPR theory, both bond pairs and lone pairs around the central atom determine the electron-pair arrangement.
- XeF₂ has the AX₂E₃ arrangement: two bonded atoms and three lone pairs on xenon.

Step 1: Count the electron pairs on xenon Xenon has eight valence electrons. It forms two single Xe-F bonds and retains six non-bonding electrons as three lone pairs. There are therefore five electron-pair domains, corresponding to a trigonal-bipyramidal electron-pair arrangement and *sp*³*d* hybridisation in the usual school-level description.

Step 2: Place the lone pairs and draw the molecular structure The three lone pairs occupy equatorial positions to minimise repulsions. The two fluorine atoms occupy the opposite axial positions. Molecular shape refers to the positions of the atoms, so the F-Xe-F arrangement is linear with bond angle 180°. The central-atom lone pairs are indicated in the schematic below.

Quick Tip to Solve: Count five electron-pair domains on Xe, then place all three lone pairs equatorially to leave two opposite axial bonds.



Linear XeF₂; the three lone pairs on Xe occupy equatorial positions.

Step 3: Conclusion XeF₂ is linear: F–Xe–F, with $\angle \text{FXeF} = 180^\circ$ and three equatorial lone pairs on Xe.

Quick Tip to Solve: Count five electron-pair domains on Xe, then place all three lone pairs equatorially to leave two opposite axial bonds.

36(a). Give reasons:

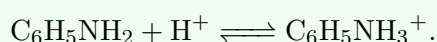
- (i) Although –NH₂ group is o/p directing in electrophilic substitution reactions, yet aniline, on nitration gives good yield of m-nitroaniline.
- (ii) (CH₃)₂NH is more basic than (CH₃)₃N in an aqueous solution.
- (iii) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. [3 marks]

Solution:

Concept:

- The directing effect of an amino group changes when its lone pair is used in protonation: –NH₂ is ortho/para directing, whereas –NH₃⁺ is meta directing.
- Basicity in water depends on the electron-donating effect of alkyl groups and the hydration of the conjugate acid.
- Alkyl halides can alkylate ammonia as well as the amines formed, leading to successive substitution on nitrogen.

Step 1: (i) Explain the formation of meta-nitroaniline Nitration uses a strongly acidic mixture of concentrated nitric and sulphuric acids. In this medium, aniline is protonated:



Unlike the amino group in free aniline, the anilinium group cannot donate a nitrogen lone pair into

Quick Tip to Solve: Link the three reasons to acid-induced protonation, conjugate-acid hydration, and repeated alkylation, respectively.

the ring; the lone pair has formed the bond to the proton. The positively charged group withdraws electron density and directs electrophilic substitution mainly to the meta position. Thus nitration of the protonated species gives an appreciable amount of meta-nitroaniline after work-up, alongside products arising from unprotonated aniline.

Step 2: (ii) Compare dimethylamine and trimethylamine in water Protonation produces $(\text{CH}_3)_2\text{NH}_2^+$ and $(\text{CH}_3)_3\text{NH}^+$, respectively. Although the third methyl group increases electron donation, it also hinders hydration around nitrogen. The dimethylammonium ion has two N–H bonds and is better hydrated than the more crowded trimethylammonium ion, which has one N–H bond. This greater stabilisation of the conjugate acid outweighs the extra electron-donating effect in trimethylamine. Hence dimethylamine is more basic in aqueous solution.

Step 3: (iii) Explain why ammonolysis does not give a pure primary amine Ammonia first reacts with an alkyl halide to form a primary amine. The primary amine still has a nitrogen lone pair and can react with more alkyl halide. Further alkylation gives a secondary amine, a tertiary amine and finally a quaternary ammonium salt. Thus the reaction generally yields a mixture that is difficult to separate. Excess ammonia favours the primary amine but does not make ordinary ammonolysis a selective method for preparing it pure.

Step 4: Conclusion (i) Protonated aniline is meta directing. (ii) Better hydration of dimethylammonium makes $(\text{CH}_3)_2\text{NH}$ more basic in water. (iii) Successive alkylation produces a mixture of amines and a quaternary ammonium salt.

Quick Tip to Solve: Link the three reasons to acid-induced protonation, conjugate-acid hydration, and repeated alkylation, respectively.

36(b). Distinguish between the following:

(i) $\text{CH}_3\text{CH}_2\text{NH}_2$ and $(\text{CH}_3\text{CH}_2)_2\text{NH}$

(ii) Aniline and CH_3NH_2

[2 marks]

Solution:

Concept:

- The carbylamine test distinguishes primary amines from secondary amines: only primary amines form foul-smelling isocyanides on heating with chloroform and alcoholic potassium hydroxide.
- Aniline readily undergoes electrophilic substitution with bromine water to give a white precipitate of 2,4,6-tribromoaniline; methylamine does not give this precipitate.

Step 1: Apply the carbylamine test to pair (i) Heat separate samples with CHCl_3 and alcoholic KOH. Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, is a primary amine and produces ethyl isocyanide with a highly offensive smell:

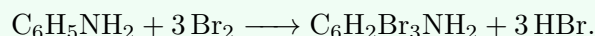


Diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, is secondary, so it gives no carbylamine reaction and no isocyanide smell. Thus the positive observation identifies ethylamine.

Step 2: Add bromine water to pair (ii) Treat separate samples of aniline and methylamine with

Quick Tip to Solve: Do not use carbylamine to distinguish aniline from methylamine: both are primary amines and respond positively.

bromine water. In aniline the amino group strongly activates the benzene ring, causing substitution at both ortho positions and the para position:



Aniline gives a white precipitate of 2,4,6-tribromoaniline. Methylamine has no benzene ring and does not give this characteristic white precipitate. The precipitate, rather than merely a colour change, is the distinguishing observation.

Step 3: Conclusion (i) Ethylamine gives a positive carbylamine test; diethylamine does not. (ii) Aniline gives a white precipitate with bromine water; methylamine does not give that precipitate.

Quick Tip to Solve: Do not use carbylamine to distinguish aniline from methylamine: both are primary amines and respond positively.

OR

36(a)(i). Write the structures of A and B in the following reactions:



[1 mark]

Solution:

Concept:

- In Sandmeyer cyanation, a diazonium group is replaced by a cyano group using copper(I) cyanide, with nitrogen gas liberated.
- Acidic hydrolysis converts a nitrile group, $-\text{C}\equiv\text{N}$, into a carboxyl group, $-\text{COOH}$, without changing the carbon skeleton.

Step 1: Replace the diazonium group Benzenediazonium chloride reacts with CuCN ; loss of N_2 permits formation of a bond between the benzene ring and the carbon of the cyano group. Therefore A is benzonitrile, with condensed structure $\text{C}_6\text{H}_5-\text{C}\equiv\text{N}$. The product is a nitrile, not phenyl isocyanide, because the ring is bonded to carbon rather than nitrogen.

Step 2: Hydrolyse the nitrile group Water in acidic medium hydrolyses the nitrile, passing through an amide intermediate and ultimately forming the carboxylic acid:

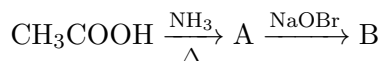


The carbon originally introduced by cyanide remains as the carboxyl carbon in B.

Step 3: Conclusion A : $\text{C}_6\text{H}_5-\text{C}\equiv\text{N}$ (benzonitrile) and B : $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{OH}$ (benzoic acid).

Quick Tip to Solve: Follow the cyano carbon: replacement introduces it, and hydrolysis retains it as the carboxyl carbon.

36(a)(ii). Write the structures of A and B in the following reactions:



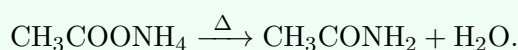
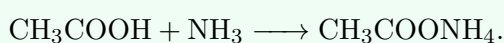
[1 mark]

Solution:

Concept:

- A carboxylic acid reacts with ammonia to form an ammonium carboxylate, which loses water on heating to give a primary amide.
- Hofmann bromamide degradation converts a primary amide into a primary amine containing one carbon atom fewer; the carbonyl carbon is removed.

Step 1: Form the amide on heating Ethanoic acid first forms ammonium ethanoate with ammonia. The printed heating condition then causes dehydration:



Thus A is ethanamide (acetamide), whose structure is $\text{CH}_3-\text{C}(=\text{O})-\text{NH}_2$; the heated product is not the ammonium salt.

Step 2: Apply Hofmann degradation Sodium hypobromite brings about Hofmann bromamide degradation. The methyl group of ethanamide becomes attached to nitrogen, while the carbonyl carbon is lost. The organic product B is therefore CH_3NH_2 , methylamine, with one carbon atom rather than the two in ethanamide.

Step 3: Conclusion A : $\text{CH}_3-\text{C}(=\text{O})-\text{NH}_2$ (ethanamide) and B : CH_3-NH_2 (methanamine).

Quick Tip to Solve: Count carbons before and after Hofmann degradation: a two-carbon amide gives a one-carbon amine.

36(b). Write the chemical reaction of methyl amine with benzoyl chloride and write the IUPAC name of the product obtained.

[2 marks]

Solution:

Concept:

- Primary amines undergo acylation with acid chlorides: an acyl group replaces one hydrogen attached to nitrogen, forming an amide.
- Benzoyl chloride supplies the benzoyl group. A base removes the hydrogen chloride formed and prevents protonation of the reacting amine.

Step 1: Write the benzoylation reaction Methylamine attacks the carbonyl carbon of benzoyl chloride. Replacement of chlorine by the methylamino group gives a secondary amide. In the presence of

Quick Tip to Solve: Retain the entire benzoyl group and attach the amine through nitrogen; use the locant *N* for the methyl substituent.

aqueous alkali, the overall balanced reaction is



This is benzoylation (the Schotten–Baumann reaction). The alkali neutralises the acid formed, maintaining the availability of the amine's lone pair for reaction.

Step 2: Name the amide product The structure is $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}-\text{CH}_3$. Its parent amide is benzamide, and the methyl substituent is bonded directly to the amide nitrogen. The prefix *N*-methyl specifies this attachment and distinguishes it from a methyl group on the benzene ring. Thus the IUPAC name is *N*-methylbenzamide.

Step 3: Conclusion Methylamine reacts with benzoyl chloride to give $\text{C}_6\text{H}_5\text{CONHCH}_3$, named *N*-methylbenzamide.

Quick Tip to Solve: Retain the entire benzoyl group and attach the amine through nitrogen; use the locant *N* for the methyl substituent.

36(c). Arrange the following in the increasing order of their pK_b values:

$\text{C}_6\text{H}_5\text{NH}_2$, NH_3 , $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$

[1 mark]

Solution:

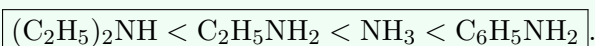
Concept:

- $pK_b = -\log_{10} K_b$, where K_b is the base dissociation constant. A stronger base has a larger K_b and hence a smaller pK_b .
- Alkyl groups increase electron density at nitrogen by their positive inductive effect; delocalisation of the lone pair into a benzene ring decreases its availability for protonation.

Step 1: Compare the basic strengths In aqueous solution, diethylamine is more basic than ethylamine: its two ethyl groups provide greater electron donation, with favourable solvation of its conjugate acid. Ethylamine is more basic than ammonia because its ethyl group donates electron density to nitrogen. Aniline is the weakest of these bases because the nitrogen lone pair is delocalised into the aromatic ring and is less available to accept a proton.

Step 2: Convert basic strength to the required order Increasing basic strength is aniline, ammonia, ethylamine, then diethylamine. Since taking the negative logarithm reverses the order of K_b , write the strongest base first when arranging increasing pK_b . Do not copy the increasing basicity order unchanged.

Step 3: Conclusion The increasing order of pK_b values is



Quick Tip to Solve: For an increasing pK_b order, start with the strongest base; the negative logarithm reverses the basicity order.

37(a). A solution contains 5.85 g NaCl (Molar mass = 58.5 g mol⁻¹) per litre of solution. It has an osmotic pressure of 4.75 atm at 27°C. Calculate the degree of dissociation of NaCl in this solution. (Given: R = 0.082 L atm K⁻¹ mol⁻¹) [3 marks]

Solution:

Concept:

- For a dilute solution, osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is the initial molar concentration of solute, R is the gas constant and T is absolute temperature.
- If one formula unit produces two ions, dissociation of a fraction α gives $i = 1 + \alpha$. Dissociation increases the number of dissolved particles and hence the osmotic pressure.

Step 1: Calculate the molarity and absolute temperature The stated mass is present in one litre of solution, so the initial concentration is

$$C = \frac{5.85/58.5}{1} = 0.100 \text{ mol L}^{-1}.$$

Convert the given temperature to kelvin before using the gas-law expression:

$$T = 27 + 273 = 300 \text{ K}.$$

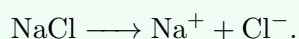
Step 2: Obtain the van't Hoff factor from osmotic pressure Without dissociation, the osmotic pressure would be

$$\pi_0 = CRT = 0.100 \times 0.082 \times 300 = 2.46 \text{ atm}.$$

The observed pressure is greater because ions provide additional solute particles. Thus

$$i = \frac{\pi}{\pi_0} = \frac{4.75}{2.46} = 1.9309.$$

Step 3: Relate the particle count to dissociation Sodium chloride dissociates according to



Starting with one mole, $1 - \alpha$ mole remains undissociated and α mole of each ion forms. The total is therefore $1 - \alpha + 2\alpha = 1 + \alpha$ mole of particles. Hence

$$\alpha = i - 1 = 1.9309 - 1 = 0.9309.$$

Step 4: Conclusion The degree of dissociation of NaCl is $\alpha \approx 0.931$, or approximately 93.1%.

Quick Tip to Solve: First calculate CRT with temperature in kelvin; for NaCl, the degree of dissociation is directly $\pi/(CRT) - 1$.

37(b). State Henry's law. Why is air diluted with helium in the tanks used by scuba divers? [2 marks]

Solution:

Concept:

- Henry's law relates the equilibrium solubility of a gas in a liquid to its partial pressure above that liquid at constant temperature.
- A fall in pressure lowers gas solubility; dissolved gas can then leave the liquid as bubbles. Helium has a low solubility in blood compared with nitrogen.

Step 1: State Henry's law mathematically At a constant temperature, the partial pressure of a gas above a solution is directly proportional to its mole fraction in the solution:

$$p = K_H x.$$

Here p is the gas's partial pressure, x is its mole fraction in the liquid and K_H is Henry's law constant for that gas-solvent pair at the stated temperature.

Step 2: Explain the use of helium in diving tanks Under the high pressure experienced at depth, more nitrogen from air dissolves in a diver's blood. As the diver ascends, the pressure decreases and dissolved nitrogen can form bubbles, causing the painful condition called the bends. Diluting air with helium reduces the nitrogen fraction and thus its partial pressure at a given total pressure. Helium is much less soluble in blood, so this substitution reduces the amount of dissolved nitrogen and the risk of bubble formation on ascent.

Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature. Helium dilution reduces nitrogen dissolution and helps reduce the risk of the bends during ascent.

Quick Tip to Solve: Connect the diving explanation in order: high pressure increases nitrogen solubility, ascent releases bubbles, and helium dilution reduces dissolved nitrogen.

OR

37(a). When 19.5 g of $\text{F}-\text{CH}_2-\text{COOH}$ (Molar mass = 78 g mol^{-1}) is dissolved in 500 g of water, the depression in freezing point is observed to be 1°C . Calculate the degree of dissociation of $\text{F}-\text{CH}_2-\text{COOH}$.

[Given: K_f for water = $1.86 \text{ K kg mol}^{-1}$]

[3 marks]

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = i K_f m$, where K_f is the solvent's molal depression constant, m is the initial solute molality and i is the van't Hoff factor.
- A monoprotic acid dissociates into two ions. If α is its degree of dissociation, the number of particles per initial molecule becomes $1 + \alpha$, so $i = 1 + \alpha$.

Quick Tip to Solve: Convert 500 g of water into 0.500 kg; for this two-ion acid use $\alpha = \Delta T_f / (K_f m) - 1$.

Step 1: Calculate the initial molality Moles of fluoroacetic acid are

$$n = \frac{19.5 \text{ g}}{78 \text{ g mol}^{-1}} = 0.250 \text{ mol.}$$

Molality uses the mass of solvent, not solution volume. The water mass is $500 \text{ g} = 0.500 \text{ kg}$, so

$$m = \frac{0.250}{0.500} = 0.500 \text{ mol kg}^{-1}.$$

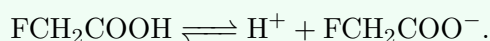
Step 2: Determine the van't Hoff factor A temperature difference of 1°C equals 1 K . For an undissociated solute the expected depression is

$$K_f m = 1.86 \times 0.500 = 0.930 \text{ K.}$$

The measured depression is larger because the acid partly dissociates. Therefore

$$i = \frac{\Delta T_f}{K_f m} = \frac{1.00}{0.930} = 1.07527.$$

Step 3: Calculate the dissociated fraction The aqueous dissociation is



For one initial mole, the equilibrium solute particles comprise $1 - \alpha$ mole of acid and α mole of each ion. Thus $i = (1 - \alpha) + 2\alpha = 1 + \alpha$, which gives

$$\alpha = 1.07527 - 1 = 0.07527.$$

Step 4: Conclusion The degree of dissociation of FCH_2COOH is $\alpha \approx 0.0753$, corresponding to 7.53% dissociation.

Quick Tip to Solve: Convert 500 g of water into 0.500 kg ; for this two-ion acid use $\alpha = \Delta T_f / (K_f m) - 1$.

37(b). Give reasons:

(i) **0.1 M KCl has higher boiling point than 0.1 M Glucose.**

(ii) **Meat is preserved for a longer time by salting.**

[2 marks]

Solution:

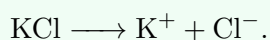
Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = i K_b m$, where i accounts for dissociation, K_b is the solvent's ebullioscopic constant and m is molality.
- Osmosis transfers water through a semipermeable membrane from a dilute solution to a more concentrated solution. A concentrated salt environment draws water out of microbial cells.

Step 1: Compare the number of particles in the two solutions (i) Potassium chloride is an electrolyte

Quick Tip to Solve: For boiling-point comparisons count dissolved particles; for salt preservation identify the outward movement of water from microbes into the concentrated salt medium.

and dissociates in water:



It therefore gives approximately two solute particles per formula unit, with i close to 2. Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, remains molecular and has $i = 1$. For these equally concentrated dilute aqueous solutions, the molalities are approximately comparable; the greater particle concentration of KCl produces a larger boiling-point elevation. Hence its solution boils at a higher temperature.

Step 2: Explain how salt inhibits microbial growth (ii) Salting creates a concentrated, hypertonic environment around microorganisms on the meat. Water moves out of their cells by osmosis through the cell membrane. This dehydration causes plasmolysis and inhibits their growth and activity. Salt also reduces the water available to support microbial growth, slowing spoilage and allowing the meat to be kept longer.

Step 3: Conclusion (i) KCl dissociation gives more solute particles and a higher boiling point than glucose at the stated dilute concentrations. (ii) Salt preserves meat by drawing water out of microbial cells and suppressing microbial growth.

Quick Tip to Solve: For boiling-point comparisons count dissolved particles; for salt preservation identify the outward movement of water from microbes into the concentrated salt medium.