

CBSE Class 12 Chemistry Question Paper 2020 with Solution PDF-Set 56-3-2

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 :

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 a partially filled d subshell in its atom or in at least one common oxidation state.
- The configuration d^{10} denotes a completely filled d subshell.

Step 1: Examine the atoms Zn, Cd and Hg have valence configurations $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$, respectively. Their d subshells are completely filled.

Step 2: Examine their usual ions Loss of the two outer s electrons gives Zn^{2+} , Cd^{2+} and Hg^{2+} , each retaining a filled d^{10} subshell. Thus their usual ions also lack a partially filled d subshell.

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

Quick Tip to Solve: Check the d configuration of both the atom and its usual cation; a filled d subshell excludes transition character.

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

[1 mark]

Solution:

Concept:

- Variable oxidation states arise when both outer $4s$ and inner $3d$ electrons can participate in bonding.
- Scandium has atomic configuration $[Ar]3d^14s^2$.

Step 1: Identify the stable ion Scandium loses its two $4s$ electrons and its single $3d$ electron to form Sc^{3+} , with the stable noble-gas configuration $[Ar]$.

Step 2: Relate configuration to oxidation state In its ordinary compounds scandium exhibits only the +3 oxidation state. Unlike most other transition metals in the $3d$ series, it therefore does not show variable oxidation states. Zinc is not selected because it is not a transition element.

Step 3: Conclusion Scandium (Sc) does not show variable oxidation states; its usual oxidation state is +3.

Quick Tip to Solve: For a transition metal with a single usual oxidation state in the $3d$ series, recall scandium and its stable $Sc(III)$ ion.

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.
- Transition metals commonly possess variable oxidation states and available orbitals for interaction with reactants.

Step 1: Explain intermediate formation Transition metals and their compounds can change oxidation state during a reaction. They can therefore form intermediate compounds with reactants, enable electron transfer, and return to their original state at the end of the catalytic cycle.

Step 2: Explain surface action Metal surfaces also adsorb reactant molecules through available orbitals. Adsorption brings reactants together and weakens some of their bonds, facilitating reaction along a lower-energy pathway. These properties account for their catalytic activity.

Step 3: Conclusion Their catalytic activity is due to variable oxidation states and their ability to adsorb reactants or form intermediate compounds.

Quick Tip to Solve: Connect variable oxidation states to intermediate formation, and available orbitals to adsorption of reactants.

4. Why are melting points of transition metals high?

[1 mark]

Solution:

Concept:

- Melting a metal requires overcoming the forces holding atoms together in its crystal.
- Both $(n - 1)d$ and ns electrons contribute to metallic bonding in transition metals.

Step 1: Identify the source of strong bonding Transition metals generally have several electrons available for metallic bonding, including unpaired d electrons as well as outer s electrons. Their participation produces strong interatomic attraction in the metallic lattice.

Step 2: Relate bonding to melting A considerable supply of thermal energy is needed to overcome these strong metallic bonds and disrupt the ordered solid structure. Consequently, transition metals generally have high melting points; the trend is not absolute for every element.

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

Quick Tip to Solve: Explain melting-point trends through metallic bond strength and the number of electrons participating in bonding.

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

[1 mark]

Solution:

Concept:

- Ligands split the energies of the metal ion's d orbitals in a complex.
- Absorption of visible light for a $d-d$ transition can give an aqueous transition-metal ion its colour.

Step 1: Examine copper(II) Cu^{2+} has configuration $[\text{Ar}]3d^9$. In its hydrated ion the d orbitals have different energies, and an electron can absorb visible light to move between these levels. The remaining transmitted light gives the solution its colour.

Step 2: Examine zinc(II) Zn^{2+} has configuration $[\text{Ar}]3d^{10}$. All its d orbitals are filled, so the corresponding $d-d$ transition is unavailable. Its aqueous solution therefore does not show the colour characteristic of such transitions.

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

Quick Tip to Solve: Write the cation configurations first: a partially filled d subshell allows the usual $d-d$ colour mechanism.

6. Out of *o*-dichlorobenzene and *p*-dichlorobenzene, which has higher melting point?

[1 mark]

Solution:

Concept:

- Melting point depends on how efficiently molecules pack in their solid crystal.
- Greater molecular symmetry often promotes closer and more regular packing.

Step 1: Compare molecular symmetry In *p*-dichlorobenzene, the two chlorine substituents occupy opposite positions on the benzene ring. This makes the molecule more symmetrical than *o*-dichlorobenzene, whose substituents occupy adjacent positions.

Step 2: Compare the crystal packing The greater symmetry of the para isomer permits more efficient packing in the crystal lattice. More energy is required to disrupt that lattice during melting, so its melting point is higher. The relevant comparison is solid-state packing, rather than simply the molecular dipole moment.

Step 3: Conclusion *p*-Dichlorobenzene.

Quick Tip to Solve: For isomer melting points, compare symmetry and crystal packing; the para isomer packs more efficiently here.

7. Write the product when benzene diazonium chloride reacts with ethanol.

[1 mark]

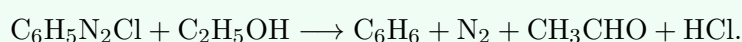
Solution:

Concept:

- An arenediazonium group can be replaced by hydrogen using ethanol as a reducing agent.
- The diazonium group leaves as nitrogen gas while ethanol is oxidised to ethanal.

Step 1: Identify replacement of the group The $-\text{N}_2^+$ group in benzene diazonium chloride is replaced by hydrogen. Thus the carbon skeleton of the benzene ring remains intact, and the principal organic product derived from the diazonium salt is benzene.

Step 2: Write the reaction The balanced reaction is



Ethanol supplies the reducing action and is converted to ethanal. Nitrogen evolution accompanies removal of the diazonium group.

Step 3: Conclusion Benzene, C_6H_6 .

Quick Tip to Solve: With ethanol, replace the diazonium group by hydrogen; do not confuse this reduction with replacement by hydroxyl.

8. Write the product obtained at cathode on electrolysis of aqueous solution of NaCl.

[1 mark]

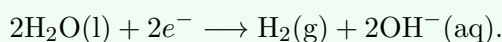
Solution:

Concept:

- At the cathode, reduction occurs: the species accepting electrons gives the cathode product.
- In aqueous sodium chloride, water is reduced more readily than sodium ions under ordinary electrolysis conditions.

Step 1: Identify the species available for reduction The aqueous solution contains Na^+ ions and water. Reduction of water is favoured over deposition of sodium metal, so sodium ions remain in solution.

Step 2: Write the cathode half-reaction The reduction is



Thus bubbles of hydrogen are evolved at the cathode; hydroxide ions are also formed in the solution.

Step 3: Conclusion The product obtained at the cathode is hydrogen gas, H_2 .

Quick Tip to Solve: For aqueous NaCl, check reduction of water before predicting deposition of sodium.

9. Name the disaccharide which on hydrolysis gives glucose and galactose.

[1 mark]

Solution:

Concept:

- Disaccharides consist of two monosaccharide units joined by a glycosidic linkage.
- Hydrolysis breaks this linkage by addition of water and reveals the constituent monosaccharides.

Step 1: Identify the constituent sugars The question specifies glucose and galactose as the hydrolysis products. This combination identifies lactose, the disaccharide commonly called milk sugar.

Step 2: Check the hydrolysis products The hydrolysis can be represented as



Maltose instead gives two glucose units, while sucrose gives glucose and fructose; neither matches the specified pair.

Step 3: Conclusion The disaccharide is lactose.

Quick Tip to Solve: Remember lactose as glucose plus galactose; sucrose contains fructose instead.

10. What type of chemical substances are used in sleeping pills?

[1 mark]

Solution:

Concept:

- Tranquilizers act on the central nervous system and are used to relieve stress, anxiety and related disturbances.
- Some tranquilizers have sedative or hypnotic action and help induce sleep.

Step 1: Identify the required action Sleeping pills contain substances that calm the central nervous system and promote sleep. In the CBSE classification of therapeutic drugs, such substances belong to the tranquilizer category.

Step 2: Connect the action to the drug class Tranquilizers with sedative or hypnotic action are used as sleeping pills. Barbiturates such as veronal provide familiar textbook examples of this class; the required answer is the category of drug, rather than a particular trade name.

Step 3: Conclusion Tranquilizers are used in sleeping pills.

Quick Tip to Solve: Link sleeping pills with tranquilizers and their sedative action on the nervous system.

11. Which of the following solutions of KCl will have the highest value of specific conductance?

[1 mark]

- (A) 0.5 M
- (B) 0.01 M
- (C) 0.1 M
- (D) 1.0 M

Correct Answer: (D) 1.0 M

Solution:

Concept:

- Specific conductance, κ , measures the conducting ability of a solution per unit geometry.
- At the same temperature, increasing the concentration of an electrolyte generally increases the number of charge-carrying ions per unit volume.

Step 1: Compare the concentrations The concentrations are 0.5 M, 0.01 M, 0.1 M and 1.0 M. Their order is $1.0 > 0.5 > 0.1 > 0.01$. For the same electrolyte KCl, the most concentrated solution has the most ions per unit volume.

Step 2: Distinguish specific and molar conductance Specific conductance increases with concentration in this comparison, so the 1.0 M solution has the highest value. The other three options have lower concentrations. Do not apply the increase of molar conductivity on dilution to specific conductance.

Step 3: Conclusion The highest specific conductance is for 1.0 M KCl, option (D).

Quick Tip to Solve: For specific conductance compare ions per unit volume; select the highest concentration.

12. The unit of the rate of reaction is the same as that of the rate constant for a

[1 mark]

- (A) first order reaction
- (B) zero order reaction
- (C) second order reaction
- (D) half-order reaction

Correct Answer: (B) zero order reaction

Solution:

Concept:

- For a reaction of overall order n , the rate law is $r = k[A]^n$, where r is the reaction rate, k is the rate constant and $[A]$ represents concentration.
- Rate has units $\text{mol L}^{-1} \text{s}^{-1}$, so the units of k are $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$.

Step 1: Compare the units of rate and rate constant The units become identical when $1 - n = 1$, giving $n = 0$. In a zero order reaction, $[A]^0 = 1$, so the rate law reduces to $r = k$. Thus both quantities have units of concentration per unit time.

Step 2: Test the other orders For first order, k has units s^{-1} ; for second order, $\text{L mol}^{-1} \text{s}^{-1}$; and for

Quick Tip to Solve: If rate and rate constant have identical units, use $r = k[A]^n$: the concentration factor must be dimensionless, so $n = 0$.

half-order, $(\text{mol L}^{-1})^{1/2}\text{s}^{-1}$. None is identical to the units of rate, so options (A), (C) and (D) are excluded.

Step 3: Conclusion The reaction is zero order. Hence, the correct option is (B).

Quick Tip to Solve: If rate and rate constant have identical units, use $r = k[A]^n$: the concentration factor must be dimensionless, so $n = 0$.

13. By which of the following reactions is blister copper obtained?

[1 mark]

- (A) $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu}$
(B) $\text{Cu}_2\text{S} + \text{FeS} \rightarrow 2\text{Cu} + \text{FeS}_2$
(C) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$
(D) $\text{Cu}_2\text{O} + \text{C} \rightarrow 2\text{Cu} + \text{CO}$

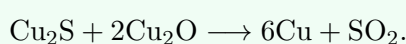
Correct Answer: (C) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$

Solution:

Concept:

- During copper extraction, copper(I) sulphide reacts with copper(I) oxide in a self-reduction reaction to produce metallic copper.
- Sulphur dioxide escaping from the molten copper produces a blistered surface as the metal solidifies, giving the name blister copper.

Step 1: Identify the self-reduction reaction Some copper(I) sulphide is first oxidised to copper(I) oxide. The remaining sulphide then reduces this oxide according to



The equation balances six copper atoms, one sulphur atom and two oxygen atoms on each side. The evolved SO_2 is responsible for the blisters.

Step 2: Exclude the alternative reactions Option (A) is displacement of copper ions from solution by zinc and does not describe blister-copper production. Option (B) involves iron sulphide and gives no sulphur dioxide. Option (D) is reduction of copper(I) oxide by carbon, producing carbon monoxide; it is not the sulphide-oxide self-reduction used to obtain blister copper. Only option (C) gives the required extraction reaction.

Step 3: Conclusion Blister copper is obtained by $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$. Hence, the correct option is (C).

Quick Tip to Solve: Associate blister copper with self-reduction of copper oxide by copper sulphide and the escape of SO_2 , then match the balanced equation.

14. EDTA is a

[1 mark]

- (A) monodentate ligand
- (B) bidentate ligand
- (C) ambidentate ligand
- (D) hexadentate ligand

Correct Answer: (D) hexadentate ligand

Solution:

Concept:

- Denticity is the number of donor atoms through which one ligand binds to a metal ion.
- EDTA has two nitrogen donor atoms and four oxygen donor atoms available for coordination.

Step 1: Count the donor sites In the usual coordinating form, EDTA^{4-} binds through the two amine nitrogen atoms and one oxygen atom from each of its four carboxylate groups. This gives $2 + 4 = 6$ donor atoms.

Step 2: Classify the ligand A ligand coordinating through six donor atoms is hexadentate. Monodentate and bidentate ligands have only one and two donor sites respectively. An ambidentate ligand can bind through alternative donor atoms, usually one at a time; this is different from EDTA binding through six sites.

Step 3: Conclusion EDTA is a hexadentate ligand, option (D).

Quick Tip to Solve: Count EDTA donor atoms as two N plus four O to obtain a denticity of six.

15. Which parts of amino acids molecules are linked through hydrogen bonds in the secondary structure of proteins?

[1 mark]

- (A) NH_2 group
- (B) COOH group
- (C) $-\text{C}(=\text{O})-$ and $-\text{NH}-$ groups
- (D) None of the above

Correct Answer: (C) $-\text{C}(=\text{O})-$ and $-\text{NH}-$ groups

Solution:

Concept:

- The secondary structure of a protein is the regular folding of its polypeptide backbone into an α -helix or a β -pleated sheet.
- The peptide linkage contains a carbonyl group, $-\text{C}(=\text{O})-$, and an $-\text{NH}-$ group.

Step 1: Identify the hydrogen-bond partners The electronegative carbonyl oxygen accepts a hydrogen bond from the hydrogen attached to the peptide nitrogen. Thus backbone $\text{C}=\text{O}$ and $\text{N}-\text{H}$ groups on suitable peptide units interact as $\text{C}=\text{O} \cdots \text{H}-\text{N}$. These attractions stabilize the secondary structure.

Step 2: Check the options Option (C) names both participating backbone groups. Options (A) and

Quick Tip to Solve: Locate the peptide linkage first: its carbonyl oxygen accepts and its N-H hydrogen donates the hydrogen bond.

(B) refer separately to amino and carboxyl groups and do not identify the peptide-backbone pair involved in the secondary structure. Option (D) is excluded because the correct pair is present.

Step 3: Conclusion The -C(=O)- and -NH- groups are linked through hydrogen bonds. The correct option is (C).

Quick Tip to Solve: Locate the peptide linkage first: its carbonyl oxygen accepts and its N-H hydrogen donates the hydrogen bond.

For questions number 16 to 20, two statements are given – one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (i), (ii), (iii) and (iv) as given below :

(i) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

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

(iii) Assertion (A) is correct, but Reason (R) is incorrect statement.

(iv) Assertion (A) is incorrect, but Reason (R) is correct statement.

16. Assertion (A): Acetic acid is stronger than formic acid.

Reason (R): In acetic acid, the electron releasing methyl group makes it difficult to break the O–H bond. [1 mark]

Solution:

Concept:

- Acid strength depends on the tendency to release H^+ and on the stability of the conjugate base.
- The methyl group has a positive inductive (+I) effect: it releases electron density toward the carboxyl group.

Step 1: Judge Assertion (A) Formic acid, HCOOH , is stronger than acetic acid, CH_3COOH . The electron-releasing methyl group in acetic acid makes proton loss less favourable and increases electron density in its negatively charged conjugate base. Thus the assertion reverses the actual order and is incorrect.

Step 2: Judge Reason (R) The methyl group releases electrons and reduces the tendency of the O-H bond to undergo ionisation with release of H^+ . In the acid-ionisation context of this question, the statement that it makes the O-H bond difficult to break is correct.

Step 3: Choose the matching code Since A is incorrect and R is correct, neither of the codes requiring both statements to be correct applies. Code (iii) also has the truth values reversed. The printed combination corresponds to code (iv).

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

Quick Tip to Solve: Compare the conjugate bases: the electron-releasing methyl group makes acetate less stable than formate.

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

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

[1 mark]

Solution:

Concept:

- Conductivity κ measures the conducting ability of a unit volume of electrolyte solution.
- Dilution reduces the number of ions per unit volume, even though molar conductivity can increase.

Step 1: Judge Assertion (A) When concentration decreases, a given volume of solution generally contains fewer charge carriers. Consequently its conductivity decreases. The assertion concerns conductivity, not molar conductivity, and is correct.

Step 2: Judge Reason (R) Dilution increases solution volume and lowers the concentration of ions. For weak electrolytes the fraction ionised may increase, but the number of ions per unit volume still decreases. Therefore the claim that the number per unit volume increases on dilution is incorrect.

Step 3: Choose the matching code The truth values are A correct and R incorrect, which is exactly code (iii). R cannot explain A because it states the opposite concentration trend; codes (i), (ii) and (iv) do not match.

Step 4: Conclusion Assertion (A) is correct and Reason (R) is incorrect. The correct code is (iii).

Quick Tip to Solve: Keep conductivity and molar conductivity separate: dilution lowers ions per unit volume and hence conductivity.

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.

[1 mark]

Solution:

Concept:

- Ethane-1,2-diamine, abbreviated en, is a bidentate ligand with two nitrogen donor atoms.
- The chelate effect increases the stability of a complex containing chelate rings compared with a comparable complex having monodentate ligands.

Step 1: Judge Assertion (A) Each en ligand binds through both nitrogen atoms to platinum, forming a chelate ring. In contrast, each NH_3 ligand binds through only one nitrogen atom. The complex $[\text{Pt}(\text{en})_2 \text{Cl}_2]^{2+}$ is more stable than the analogous ammonia complex because of chelation. The assertion says less stable and is incorrect.

Step 2: Judge Reason (R) Two bidentate en ligands form two chelate rings in $[\text{Pt}(\text{en})_2 \text{Cl}_2]^{2+}$. It therefore exhibits the chelate effect, so the reason is correct.

Step 3: Choose the matching code A is incorrect and R is correct, so code (iv) is selected. The reason supports increased stability of the en complex; it cannot support the decreased stability stated in the assertion.

Step 4: Conclusion Assertion (A) is incorrect and Reason (R) is correct. The correct code is (iv).

Quick Tip to Solve: Count donor atoms per ligand: en binds twice and forms rings, whereas ammonia binds once.

19. Assertion (A): Phenol is more acidic than *p*-methylphenol.

Reason (R): The presence of an electron releasing group in *p*-methylphenol makes it less acidic.

[1 mark]

Solution:

Concept:

- Phenol ionises to form a resonance-stabilised phenoxide ion.
- The methyl group is electron releasing; increased electron density makes a negatively charged conjugate base less stable.

Step 1: Judge Assertion (A) Phenol loses its hydroxyl proton more readily than *p*-methylphenol. The methyl substituent in *p*-methylphenol supplies electron density to the aromatic system and destabilises the corresponding phenoxide ion relative to unsubstituted phenoxide. Thus phenol is more acidic and A is correct.

Step 2: Judge Reason (R) The electron-releasing methyl group reduces the stability of the conjugate base and hence reduces the tendency to release H^+ . The statement that an electron-releasing group makes *p*-methylphenol less acidic is correct.

Step 3: Check the explanatory link R gives precisely the substituent effect responsible for the acidity order in A. Both statements are correct and R correctly explains A; code (ii) is excluded because the explanation is directly related.

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

Quick Tip to Solve: For substituted phenols, test how the substituent affects the stability of the negatively charged phenoxide ion.

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

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

[1 mark]

Solution:

Concept:

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

Step 1: Judge Assertion (A) Osmotic pressure is the pressure required to prevent osmosis through a semipermeable membrane. At a fixed temperature it depends on the concentration of dissolved particles, rather than on their chemical nature. Therefore it is a colligative property and A is correct.

Step 2: Judge Reason (R) The relation $\pi = CRT$ gives $\pi \propto C$ when temperature is fixed. Here concentration represents the number of solute particles per unit volume; for a dissociating or associating solute the particle correction is included as $\pi = iCRT$. R is correct.

Quick Tip to Solve: Hold temperature fixed in $\pi = CRT$ and identify concentration as the number of dissolved particles per unit volume.

Step 3: Check the explanatory link The proportionality to solute-particle concentration explains why osmotic pressure is colligative. Both A and R are correct and R correctly explains A, giving code (i).

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

Quick Tip to Solve: Hold temperature fixed in $\pi = CRT$ and identify concentration as the number of dissolved particles per unit volume.

Section B (14 marks)

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

NaAlF₄ in the extraction of Aluminium

[1 mark]

Solution:

Concept:

- Aluminium is obtained by electrolytic reduction of alumina in a molten fluoride-containing bath.
- A flux helps form a readily conducting melt suitable for electrolysis.

Step 1: Identify its role in the bath The sodium aluminium fluoride named in the question, NaAlF₄, serves as a flux in the extraction of aluminium. The fluoride-containing bath helps dissolve alumina and permits electrolysis at a lower temperature than would be needed to melt pure alumina.

Step 2: Explain why this assists extraction Pure alumina has a very high melting temperature. The fluoride melt lowers the effective melting temperature of the electrolyte mixture and improves its electrical conductivity, making the passage of current and electrolytic reduction practicable. Its role is to improve the molten bath; it is not the reducing agent for aluminium.

Step 3: Conclusion NaAlF₄ acts as a flux: it lowers the melting temperature of the alumina-containing bath and increases its electrical conductivity.

Quick Tip to Solve: For the fluoride additive, state the two bath improvements: lower melting temperature and higher conductivity.

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

CO in the refining of Ni

[1 mark]

Solution:

Concept:

- In the Mond process, carbon monoxide converts nickel into the volatile complex nickel tetracarbonyl, Ni(CO)₄.
- The carbonyl decomposes on stronger heating to deposit pure nickel and regenerate carbon monoxide.

Step 1: Formation of the volatile carbonyl Impure nickel is heated in a stream of CO at about

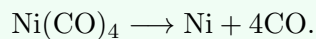
Quick Tip to Solve: Remember Mond refining as formation of a volatile carbonyl followed by its thermal decomposition.

330–350 K:



The volatile carbonyl separates nickel from nonvolatile impurities.

Step 2: Deposition of pure nickel On heating the separated vapour to about 450–470 K, it decomposes:



Nickel is deposited in a pure form, while CO can be reused.

Step 3: Conclusion CO acts as the complex-forming agent in Mond refining: it forms volatile $\text{Ni}(\text{CO})_4$, whose thermal decomposition yields pure Ni.

Quick Tip to Solve: Remember Mond refining as formation of a volatile carbonyl followed by its thermal decomposition.

OR

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

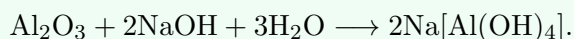
[2 marks]

Solution:

Concept:

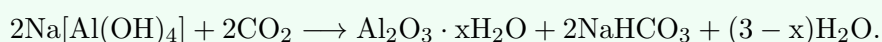
- Bauxite is leached with concentrated NaOH: amphoteric alumina dissolves as soluble sodium aluminate while insoluble impurities are separated.
- Carbonation precipitates hydrated alumina; heating the precipitate gives pure Al_2O_3 .

Step 1: Leach the ore with alkali Heat powdered bauxite with concentrated NaOH at about 473–523 K under pressure. Alumina dissolves according to



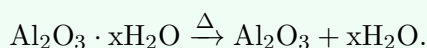
Filter to remove insoluble impurities such as iron oxide. Sodium aluminate remains in the filtrate.

Step 2: Precipitate hydrated alumina Pass CO_2 through the aluminate solution and seed it with freshly prepared hydrated alumina to aid precipitation:



Separate and wash the precipitate; soluble impurities remain in the mother liquor.

Step 3: Calcine the precipitate Heat hydrated alumina strongly, at about 1470 K, to remove water:



This produces the anhydrous alumina required for extraction.

Step 4: Conclusion Pure alumina is obtained by alkaline leaching, precipitation of hydrated alumina

Quick Tip to Solve: Write the three stages in order: dissolve alumina, precipitate its hydrate, then remove water by heating.

by carbonation, and calcination to Al_2O_3 .

Quick Tip to Solve: Write the three stages in order: dissolve alumina, precipitate its hydrate, then remove water by heating.

22. 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:

- For $\text{A} + 3\text{B} \rightarrow 2\text{C}$, the reaction rate is normalised by the stoichiometric coefficients:

$$r = -\frac{d[\text{A}]}{dt} = -\frac{1}{3} \frac{d[\text{B}]}{dt} = \frac{1}{2} \frac{d[\text{C}]}{dt}.$$

- Formation and disappearance rates are positive magnitudes; reactant concentration derivatives themselves are negative.

Step 1: (i) Calculate the rate of reaction The stated formation rate is $d[\text{C}]/dt = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Divide by the coefficient of C, which is 2:

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

The reaction rate is half the unnormalised product formation rate.

Step 2: (ii) Calculate the disappearance rate of B Three moles of B disappear for every two moles of C formed. Thus

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

Equivalently, multiply the formation rate of C by 3/2. A positive sign is appropriate because disappearance is requested as a rate magnitude.

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: First divide a species rate by its coefficient; then multiply the reaction rate by the coefficient of the requested species.

23. (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:

- Ligand charges determine the oxidation state; an anionic cobalt complex uses the metal name cobaltate.
- Fluoride is a weak-field ligand. In valence-bond theory, a high-spin octahedral cobalt(III) fluoride complex uses outer-orbital sp^3d^2 hybridisation.
- In $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$, en is neutral bidentate ethane-1,2-diamine. Cis and trans describe the relative positions of the two chloride ligands.

Step 1: (a) Name and hybridisation Let the cobalt oxidation state be x . Since each fluoro ligand has charge -1 , $x - 6 = -3$, giving $x = +3$. The IUPAC name is hexafluoridocobaltate(III) ion. Cobalt has configuration $[\text{Ar}]3d^74s^2$; hence Co^{3+} is $3d^6$. Weak-field fluoride does not produce the pairing needed for two empty inner 3d orbitals. The octahedral complex therefore uses one 4s, three 4p and two 4d orbitals: sp^3d^2 hybridisation.

Step 2: (b) Isomerism and the optically active form The complex exhibits geometrical isomerism (cis and trans) and optical isomerism. In the cis form, the chloride ligands occupy adjacent positions. Its two en chelate rings permit two nonsuperimposable mirror-image arrangements, called Δ and Λ , so the cis isomer is optically active. The trans form has opposite chloride positions and is optically inactive owing to its symmetry.

Step 3: Conclusion (a) Hexafluoridocobaltate(III) ion; sp^3d^2 . (b) Geometrical and optical isomerism; cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$ is the optically active structure.

Quick Tip to Solve: For two en ligands and two identical monodentate ligands in an octahedral complex, check the cis form for optical activity.

24(a). Write two differences between physisorption and chemisorption. [2 marks]

Solution:

Concept:

- Adsorption is accumulation of a substance at a surface. Its classification depends on the interaction binding the adsorbate to the adsorbent.
- Physisorption involves weak intermolecular forces, whereas chemisorption involves formation of chemical bonds.

Step 1: Difference 1: nature of attraction In physisorption the adsorbate is retained by weak van der Waals forces; no chemical bond forms with the surface. In chemisorption, chemical bonds form between the adsorbate and adsorbent. This distinction concerns the actual binding mechanism, rather than whether the substance is merely present on a surface.

Quick Tip to Solve: Pair each difference across the two types: first compare forces, then compare the requirement for chemical compatibility.

Step 2: Difference 2: specificity Physisorption is generally nonspecific: many gases can be adsorbed on a given surface through intermolecular attraction. Chemisorption is highly specific: it occurs only when the adsorbate and the adsorbent can form suitable chemical bonds. For example, hydrogen chemisorbs on a nickel surface, whereas ordinary physical adsorption does not require such a chemically compatible pair.

Step 3: Conclusion Two differences are: physisorption uses weak van der Waals forces and is generally nonspecific; chemisorption involves chemical bonds and is highly specific.

Quick Tip to Solve: Pair each difference across the two types: first compare forces, then compare the requirement for chemical compatibility.

OR

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

(i) Associated colloids

(ii) O/W emulsion

[2 marks]

Solution:

Concept:

- Associated colloids form aggregates called micelles above the critical micelle concentration (CMC) and above the Kraft temperature.
- 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.

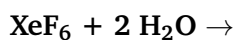
Step 1: Define associated colloids with an example Associated colloids are substances that behave as normal electrolytes at low concentration but form colloidal aggregates, called micelles, at higher concentrations. Micelles form above the critical micelle concentration and above the Kraft temperature. For example, soap such as sodium stearate forms micelles in water: its nonpolar hydrocarbon tails point inward while its ionic heads remain in contact with water.

Step 2: Define an O/W emulsion with an example An oil-in-water (O/W) emulsion has small droplets of oil dispersed throughout water, which forms the continuous phase. Milk is a suitable example: liquid fat droplets are dispersed in an aqueous medium. The order O/W therefore specifies the dispersed phase first and the dispersion medium second.

Step 3: Conclusion Associated colloids: micelle-forming substances such as soap. O/W emulsion: oil droplets dispersed in water, as in milk.

Quick Tip to Solve: For O/W, read the first letter as the dispersed liquid and the second as the continuous medium.

25. Write the products of the following reaction:



Is this reaction a redox reaction? Draw the structure of XeF_6 .

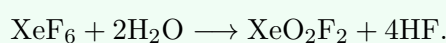
[2 marks]

Solution:

Concept:

- Partial hydrolysis replaces fluorine atoms of a xenon fluoride with oxygen, releasing hydrogen fluoride.
- A redox reaction requires a change in oxidation number. Fluorine is -1 , oxygen is -2 and hydrogen is $+1$ here.
- In XeF_6 , xenon has six bond pairs and one lone pair; its molecular shape is distorted octahedral.

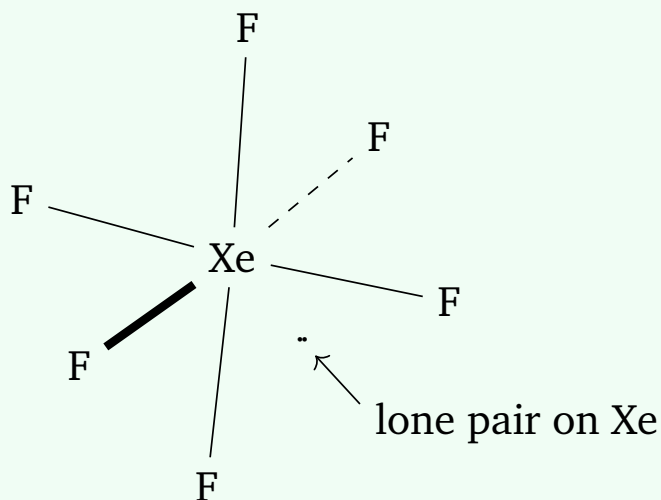
Step 1: Write the balanced partial-hydrolysis reaction Two water molecules supply two oxygen atoms, replacing four fluorine atoms. The products are xenon dioxydifluoride and hydrogen fluoride:



The equation balances one Xe, six F, four H and two O atoms on each side. Complete hydrolysis with three water molecules would give a different oxide, so the stated amount of water must be used.

Step 2: Check oxidation numbers In XeF_6 , $x + 6(-1) = 0$, so xenon is $+6$. In XeO_2F_2 , $x + 2(-2) + 2(-1) = 0$, giving xenon $+6$ again. H, O and F also retain their oxidation numbers. Thus no atom is oxidised or reduced, and this hydrolysis is not a redox reaction.

Step 3: Describe and draw the structure The six fluorine atoms surround xenon in a distorted octahedral arrangement. The additional lone pair on xenon repels the bonding pairs and prevents a regular octahedral shape. The drawing shows all six Xe–F bonds and the lone pair on the central atom.



Distorted octahedral structure of xenon hexafluoride (schematic)

Step 4: Conclusion The products are XeO_2F_2 and 4HF . The reaction is not redox; XeF_6 has a distorted octahedral structure.

Quick Tip to Solve: Count the water molecules first: two water molecules give the dioxide difluoride, not complete hydrolysis.

26. Define the following terms:

(i) Glycosidic linkage

(ii) Native protein

[2 marks]

Solution:

Concept:

- A glycosidic linkage is the oxygen linkage joining monosaccharide units in carbohydrates.
- A protein's biological activity depends on its characteristic folded three-dimensional conformation.

Step 1: Define glycosidic linkage The linkage through an oxygen atom that joins two monosaccharide units is called a glycosidic linkage. It forms by the elimination of a water molecule between hydroxyl groups of the sugar units, involving the anomeric carbon of a sugar. For example, maltose has an $\alpha(1 \rightarrow 4)$ glycosidic linkage between two glucose units; the oxygen bridge joins C-1 of one unit to C-4 of the other.

Step 2: Define native protein A native protein is a protein in its natural, correctly folded state, with its characteristic three-dimensional structure and biological activity intact. Its specific folding is maintained by interactions such as hydrogen bonds and other stabilising interactions. For example, an enzyme in its natural folded state has the active-site shape needed for its normal function. Loss of this natural conformation by denaturation generally causes loss of activity.

Step 3: Conclusion A glycosidic linkage is an oxygen bridge between sugar units. A native protein possesses its natural conformation and biological activity.

Quick Tip to Solve: For native protein, mention both the natural folded structure and the retained biological activity.

27. Give reasons:

(i) Unbranched chain detergents are preferred over branched chain detergents.

(ii) Aspartame is not used in cooking hot dishes.

[2 marks]

Solution:

Concept:

- The environmental persistence of a detergent depends on whether microorganisms can biodegrade its hydrocarbon chain.
- An artificial sweetener used in hot food must retain its chemical stability and sweetness on heating.

Step 1: Explain the preference for unbranched detergents Unbranched or straight-chain detergents are preferred because microorganisms can degrade their hydrocarbon chains more readily. They are therefore biodegradable and do not accumulate in water to the same extent. Highly branched-chain detergents resist microbial degradation and persist in water bodies, causing long-lasting foam and pollution. The preference is thus based on easier biodegradation and reduced environmental persistence.

Step 2: Explain why aspartame is unsuitable for hot dishes Aspartame is not stable at cooking temperatures. On heating, it decomposes and consequently loses its sweetness, so it cannot reliably

Quick Tip to Solve: Link detergent chain shape to biodegradation, and link aspartame to heat instability rather than low sweetening power.

sweeten hot cooked dishes. It is therefore used mainly in cold foods, soft drinks and other products that do not require high-temperature preparation. Its usefulness as a sweetener depends on preserving the molecule; sweetness at room temperature does not imply heat stability.

Step 3: Conclusion Straight-chain detergents are more readily biodegradable; aspartame decomposes on heating and loses its sweetness.

Quick Tip to Solve: Link detergent chain shape to biodegradation, and link aspartame to heat instability rather than low sweetening power.

Section C (21 marks)

28. 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, $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations.
- If a fraction x has reacted, the fraction remaining is $1 - x$. A rate constant calculated using time in minutes has unit min^{-1} .

Step 1: Convert completion into the amount remaining Let the initial amount be a . Since the reaction is 40% complete in 80 min, the remaining amount is $0.60a$, not $0.40a$. Consequently the concentration ratio in the integrated rate equation is $a/(0.60a) = 10/6$. Using the supplied value of $\log 6$,

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

This form uses the given logarithm directly; there is no need to use the listed value of $\log 5$.

Step 2: Calculate the rate constant Substitute the elapsed time and the ratio into the first-order equation:

$$k = \frac{2.303}{80} (0.2218) = 0.0063851 \text{ min}^{-1}.$$

The initial amount cancels, as expected for the integrated first-order expression. Keep this unrounded value for the subsequent time calculation.

Step 3: Calculate the total time for ninety percent completion At 90% completion, $0.10a$ remains. Thus $a/(a - x) = 10$, and $\log 10 = 1$. The required time, measured from the start of the reaction, is

$$t_{90} = \frac{2.303}{k} \log 10 = \frac{2.303}{0.0063851} = 360.685 \text{ min}.$$

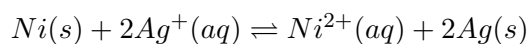
Equivalently, dividing the two integrated equations gives $t_{90}/80 = 1/0.2218$, which independently checks the arithmetic.

Quick Tip to Solve: For percentage completion, put the percentage remaining in the denominator; here use 60 initially and 10 at the target.

Step 4: Conclusion $k = 6.385 \times 10^{-3} \text{ min}^{-1}$ and $t_{90} \approx 361 \text{ min}$, measured from the start.

Quick Tip to Solve: For percentage completion, put the percentage remaining in the denominator; here use 60 initially and 10 at the target.

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



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

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

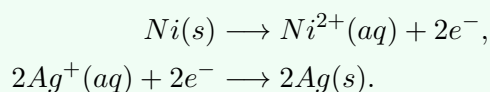
[3 marks]

Solution:

Concept:

- The standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using both tabulated potentials as reduction potentials.
- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$. The maximum electrical work delivered by the cell is its positive magnitude nFE_{cell}° .
- At 298 K, $E_{\text{cell}}^\circ = (0.0591/n) \log K_c$, where n is the number of electrons transferred in the balanced cell reaction.

Step 1: Identify the electrodes and electron transfer Nickel is oxidised and silver ions are reduced. The balanced half-reactions are



Hence $n = 2$. The silver electrode is the cathode and the nickel electrode is the anode. Using the supplied reduction potentials,

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

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

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(1.05) \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

The cell delivers 202.65 kJ per mole of reaction. Work done on the system is negative.

Step 3: Relate the potential to the equilibrium constant Combine $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$ with $\Delta_r G^\circ = -2.303RT \log K_c$. At the stated temperature,

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

The large positive logarithm indicates that products are strongly favoured at equilibrium.

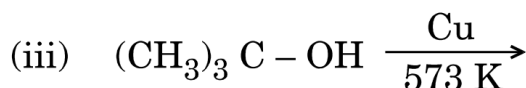
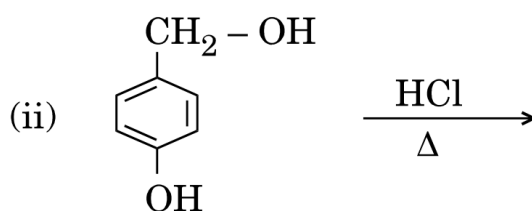
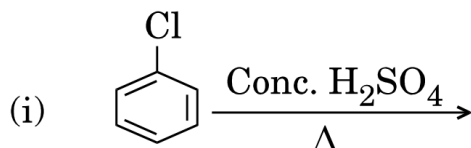
Quick Tip to Solve: Count two electrons from nickel oxidation, and subtract the negative nickel reduction potential when finding the cell voltage.

Step 4: Conclusion Maximum work delivered is $202.65 \text{ kJ mol}^{-1}$; equivalently $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$. Also $\log K_c \approx 35.53$.

Quick Tip to Solve: Count two electrons from nickel oxidation, and subtract the negative nickel reduction potential when finding the cell voltage.

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

[3 marks]

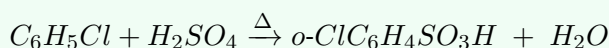


Solution:

Concept:

- Chlorine deactivates a benzene ring by its inductive effect but directs electrophilic substitution to the ortho and para positions through resonance donation.
- Hydrogen chloride replaces the hydroxyl group of a benzylic alcohol by chlorine; the phenolic hydroxyl group attached directly to the aromatic ring remains unchanged.
- Over heated copper at 573 K, tertiary alcohols undergo dehydration because the carbon carrying $-\text{OH}$ has no hydrogen for alcohol dehydrogenation.

Step 1: Sulphonation of chlorobenzene Concentrated sulphuric acid on heating introduces a sulphonic acid group, $-\text{SO}_3\text{H}$, into the ring by electrophilic aromatic substitution. Chlorine directs this substitution to the ortho and para positions. The products are 2-chlorobenzenesulphonic acid and 4-chlorobenzenesulphonic acid, with the para isomer predominant because it has less steric crowding:

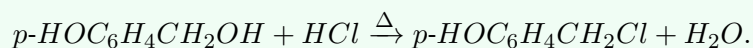


and the analogous para substitution gives $p\text{-ClC}_6\text{H}_4\text{SO}_3\text{H}$. These are alternative substitution products; the chlorine atom remains on the ring.

Step 2: Reaction of the benzylic alcohol with hydrogen chloride The substrate contains two different hydroxyl groups. The $-\text{CH}_2\text{OH}$ group is a benzylic alcohol: protonation of its hydroxyl group enables

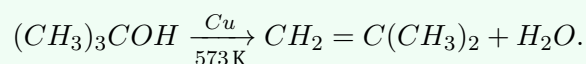
Quick Tip to Solve: Distinguish the benzylic and phenolic hydroxyl groups in (ii); for (iii), check whether the hydroxyl-bearing carbon has a hydrogen.

water to leave, followed by replacement with chloride. The phenolic $-OH$ is not replaced by HCl because its aromatic carbon-oxygen bond has partial double-bond character. Therefore,



The organic product is 4-(chloromethyl)phenol, also called *p*-hydroxybenzyl chloride.

Step 3: Pass tert-butyl alcohol over heated copper In $(CH_3)_3COH$, the hydroxyl-bearing carbon is bonded to three carbon atoms and has no hydrogen. It therefore cannot form a carbonyl compound by the dehydrogenation characteristic of primary and secondary alcohols. Instead, loss of water produces an alkene:



All three methyl groups are equivalent, so elimination gives the same organic product, 2-methylpropene, in each case.

Step 4: Conclusion (i) Ortho- and para-chlorobenzenesulphonic acids (para predominant); (ii) $p-HOC_6H_4CH_2Cl$; (iii) $CH_2 = C(CH_3)_2$, 2-methylpropene.

Quick Tip to Solve: Distinguish the benzylic and phenolic hydroxyl groups in (ii); for (iii), check whether the hydroxyl-bearing carbon has a hydrogen.

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

(i) Buna-N

(ii) Natural rubber

(iii) Nylon-6

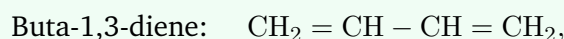
[3 marks]

Solution:

Concept:

- A monomer is a small molecule whose units join repeatedly to form a polymer. Copolymers require more than one kind of monomer.
- Identify each polymer by its characteristic starting material: Buna-N is a diene-nitrile copolymer, natural rubber is a polyisoprene, and nylon-6 is a polyamide.

Step 1: (i) Monomers of Buna-N Buna-N is prepared by copolymerisation of buta-1,3-diene and acrylonitrile (prop-2-enenitrile). Their structures are

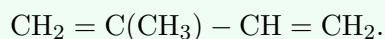


Both monomers participate in chain formation through their carbon-carbon double bonds. The nitrile group remains attached to the copolymer chain.

Step 2: (ii) Monomer of natural rubber The monomer is isoprene, whose systematic name is

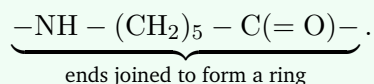
Quick Tip to Solve: Remember the N in Buna-N as the nitrile monomer; for nylon-6 count five methylene carbons plus the carbonyl carbon in caprolactam.

2-methylbuta-1,3-diene. Its structure is



Natural rubber is cis-1,4-polyisoprene: polymerisation links the terminal carbons of this conjugated diene, leaving one double bond in each repeating unit.

Step 3: (iii) Monomer of nylon-6 Nylon-6 is obtained by ring-opening polymerisation of caprolactam, a cyclic amide. Its structure may be written in condensed cyclic form as



The carbonyl carbon is bonded back to the nitrogen to close the seven-membered ring. Ring opening gives the polyamide repeating unit $[-\text{NH} - (\text{CH}_2)_5 - \text{CO}-]_n$.

Step 4: Conclusion The required monomers are: (i) buta-1,3-diene and acrylonitrile; (ii) isoprene; (iii) caprolactam, with structures as shown above.

Quick Tip to Solve: Remember the N in Buna-N as the nitrile monomer; for nylon-6 count five methylene carbons plus the carbonyl carbon in caprolactam.

32(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:

- Lyophilic means solvent-loving; lyophobic means solvent-hating. The classification depends on the affinity between the dispersed phase and the dispersion medium.
- Coagulation is the aggregation of colloidal particles into larger particles that separate from the dispersion medium. Stability can arise from electric charge and from solvation.

Step 1: Define lyophobic sol and give an example A lyophobic sol is a colloidal dispersion in which the dispersed-phase particles have little or no affinity for the dispersion medium. Such a sol cannot ordinarily be prepared merely by mixing the material with the solvent and is generally irreversible after coagulation. For example, a gold sol in water is lyophobic. Its particles are stabilised mainly by their common electric charge, which opposes aggregation.

Step 2: Define 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. It forms readily when a suitable substance is mixed with the medium and is generally reversible. A starch sol in water is a suitable example. Water molecules associate with the dispersed starch and form a hydrated protective layer around it.

Step 3: Explain the greater difficulty of coagulation Lyophilic particles are stabilised by both their charge and extensive solvation (hydration when the medium is water). The solvated layer prevents close contact and aggregation. Thus, merely neutralising the charge is not sufficient: the protective

Quick Tip to Solve: For the comparison, name both protections of a lyophilic sol: electric charge and hydration; charge neutralisation alone does not remove hydration.

solvent layer must also be removed or weakened. Lyophobic sols have little such solvation protection and therefore coagulate more readily on addition of a suitable electrolyte. Lyophilic sols generally require much larger electrolyte concentrations or a suitable solvent that removes their hydration layer.

Step 4: Conclusion A gold sol in water is lyophobic, whereas a starch sol in water is lyophilic. Coagulation of the lyophilic sol is more difficult because its particles possess both charge stability and a protective solvated layer.

Quick Tip to Solve: For the comparison, name both protections of a lyophilic sol: electric charge and hydration; charge neutralisation alone does not remove hydration.

OR

32(b). Define the following terms:

(i) Shape-selective catalysis

(ii) Kraft temperature

(iii) Peptization

[3 marks]

Solution:

Concept:

- Catalysis can depend on the geometry of pores as well as on the chemical activity of the catalyst surface.
- Micelles form only under suitable concentration and temperature conditions. Peptization converts an existing precipitate into colloidal particles by using an electrolyte.

Step 1: (i) Shape-selective catalysis Shape-selective catalysis is catalysis in which the reaction selectivity depends on the pore structure of the catalyst and the sizes and shapes of the reactant and product molecules. Only molecules of suitable dimensions can enter the pores, react at the internal active sites, or leave as products. Zeolites show this behaviour because they possess pores and cavities of definite dimensions. Thus molecular fit influences which reaction is favoured.

Step 2: (ii) Kraft temperature The Kraft (Krafft) temperature is the minimum temperature above which a surfactant forms micelles, provided that its concentration is at least the critical micelle concentration (CMC). Below this temperature, its solubility is too low for the required micelle-forming concentration to be attained. Therefore, both conditions must be satisfied: temperature above the Kraft temperature and concentration above the CMC. Temperature alone is not sufficient at an arbitrarily low surfactant concentration.

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. Ions from the electrolyte are adsorbed on the precipitate particles, giving them the same charge. Mutual repulsion then helps disperse them as colloidal particles. For example, a little ferric chloride peptizes freshly precipitated ferric hydroxide through adsorption of Fe^{3+} ions.

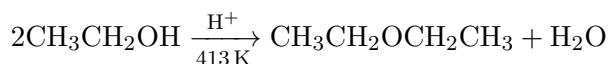
Step 4: Conclusion Shape-selective catalysis depends on molecular fit in catalyst pores; Kraft temperature is the threshold temperature for micelle formation; peptization disperses a fresh precipitate into

Quick Tip to Solve: Keep Kraft temperature distinct from CMC: the former is a temperature threshold, whereas the latter is a concentration threshold for micelle formation.

a sol using a small amount of electrolyte.

Quick Tip to Solve: Keep Kraft temperature distinct from CMC: the former is a temperature threshold, whereas the latter is a concentration threshold for micelle formation.

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



(b) Write the preparation of phenol from cumene.

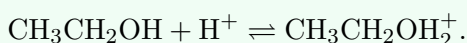
[3 marks]

Solution:

Concept:

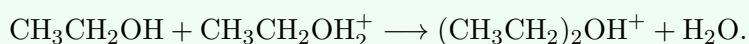
- At 413 K, acid-catalysed intermolecular dehydration of ethanol gives ethoxyethane. Protonation converts the poor leaving group $-\text{OH}$ into water.
- A second ethanol molecule acts as the nucleophile; loss of a proton regenerates the acid catalyst.
- Cumene is isopropylbenzene. Oxidation to cumene hydroperoxide followed by acidic cleavage gives phenol and acetone.

Step 1: (a) Protonate ethanol The oxygen lone pair accepts a proton, producing protonated ethanol:



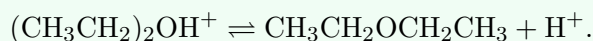
Water can now leave readily because it is neutral and stable. This activation is essential: direct displacement of hydroxide from neutral ethanol is unfavourable.

Step 2: Attack by the second ethanol molecule The oxygen of another ethanol molecule attacks the primary carbon of protonated ethanol. Water leaves in the same substitution step; a free primary carbocation is not required:



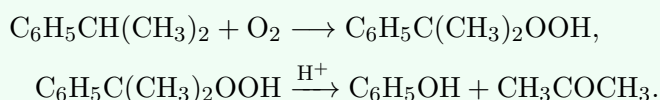
The product is the protonated ether, whose oxygen has three bonds and a positive charge.

Step 3: Regenerate the acid catalyst Deprotonation of the oxonium ion gives the neutral ether:



Combining these steps yields the reaction printed in the question at 413 K.

Step 4: (b) Prepare phenol from cumene Oxidise cumene with air or oxygen to form cumene hydroperoxide, then subject it to acidic hydrolysis (acid-catalysed cleavage):



The aromatic group forms phenol, while the three-carbon side chain forms acetone, an industrially

Quick Tip to Solve: For ethanol at 413 K write the intermolecular ether mechanism; track oxygen's positive charge through both oxonium intermediates.

useful coproduct.

Step 5: Conclusion Ethanol forms ethoxyethane through protonation, nucleophilic displacement of water and deprotonation. Cumene gives phenol by oxidation to its hydroperoxide and acidic cleavage, with acetone as coproduct.

Quick Tip to Solve: For ethanol at 413 K write the intermolecular ether mechanism; track oxygen's positive charge through both oxonium intermediates.

OR

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

(i) Sodium phenoxide to o-hydroxybenzoic acid

(ii) Acetone to propene

(iii) Phenol to chlorobenzene

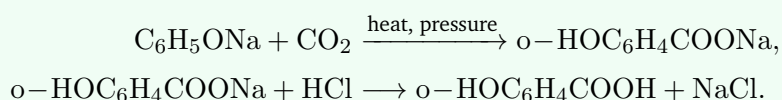
[3 marks]

Solution:

Concept:

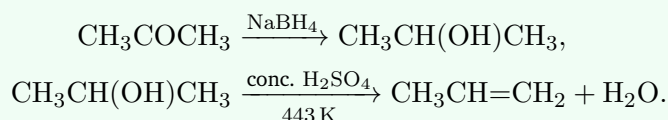
- Kolbe's reaction carboxylates sodium phenoxide with carbon dioxide; acidification gives salicylic acid, or o-hydroxybenzoic acid.
- Reduction of a ketone gives a secondary alcohol. Dehydration of that alcohol produces an alkene with the same carbon skeleton.
- Phenol can be reduced to benzene using zinc dust; electrophilic chlorination of benzene requires a Lewis acid catalyst.

Step 1: (i) Sodium phenoxide to o-hydroxybenzoic acid Heat sodium phenoxide with carbon dioxide at about 400 K under pressure of 4–7 atm. The major product is sodium salicylate. Acidify this salt using dilute hydrochloric acid:



The carboxyl group enters mainly ortho to OH. Acidification converts the sodium salt to the free acid.

Step 2: (ii) Acetone to propene First reduce acetone with sodium borohydride, followed by aqueous work-up, to give propan-2-ol. Heat the alcohol with concentrated sulphuric acid at about 443 K to dehydrate it:

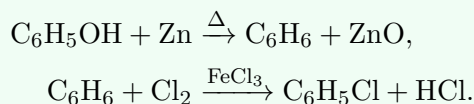


Reduction gives the alcohol; loss of water gives the alkene. Equivalent methyl groups lead to the same propene.

Step 3: (iii) Phenol to chlorobenzene Heat phenol with zinc dust to remove oxygen and form benzene.

Quick Tip to Solve: For phenol to chlorobenzene, remove the OH with zinc dust before chlorination; chlorine alone leaves the OH on the ring.

Then chlorinate benzene with chlorine in the presence of anhydrous ferric chloride:



Zinc removes the hydroxyl oxygen first. Direct chlorination of phenol retains OH and gives chlorophenols instead.

Step 4: Conclusion The required routes are: sodium phenoxide $\rightarrow$ sodium salicylate $\rightarrow$ salicylic acid; acetone $\rightarrow$ propan-2-ol $\rightarrow$ propene; phenol $\rightarrow$ benzene $\rightarrow$ chlorobenzene.

Quick Tip to Solve: For phenol to chlorobenzene, remove the OH with zinc dust before chlorination; chlorine alone leaves the OH on the ring.

34. 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

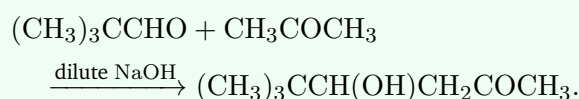
[3 marks]

Solution:

Concept:

- The aldehyde $(\text{CH}_3)_3\text{CCHO}$ has no alpha hydrogen: its carbon next to $-\text{CHO}$ is bonded to three methyl groups.
- Acetone has alpha hydrogens and forms an enolate in dilute alkali. Its enolate can add to the aldehyde carbonyl in a crossed aldol reaction.
- Hydrogen cyanide adds across a carbonyl group to give a cyanohydrin. Aldehydes without alpha hydrogens undergo Cannizzaro disproportionation in concentrated alkali.

Step 1: (i) Reaction with acetone and dilute NaOH Dilute sodium hydroxide removes an alpha hydrogen from acetone. The resulting acetone enolate attacks the carbonyl carbon of the aldehyde. Protonation of the alkoxide gives the beta-hydroxy ketone:



The aldehyde carbonyl becomes $-\text{CH}(\text{OH})-$, while the acetone carbonyl remains a ketone. No heating or dehydration condition is specified, so the crossed aldol addition product is written. On subsequent heating it can lose water to give $(\text{CH}_3)_3\text{CCH}=\text{CHCOCH}_3$.

Step 2: (ii) Reaction with HCN Cyanide attacks the electrophilic carbonyl carbon; protonation of the oxygen gives the cyanohydrin:

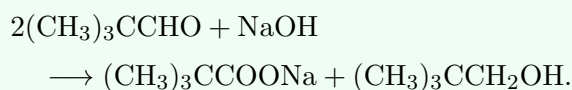


Both $-\text{OH}$ and $-\text{CN}$ are attached to the former carbonyl carbon. Its original hydrogen remains

Quick Tip to Solve: Inspect the carbon immediately beside CHO: no alpha H means Cannizzaro in concentrated alkali, while acetone supplies the enolate in part (i).

attached, and the carbon skeleton of the aldehyde is retained.

Step 3: (iii) Reaction with concentrated NaOH Since there is no alpha hydrogen, the aldehyde undergoes the Cannizzaro reaction instead of self-aldol addition. One molecule is oxidised to sodium 2,2-dimethylpropanoate and a second is reduced to 2,2-dimethylpropan-1-ol:



The product in the alkaline medium is the carboxylate salt, not the free carboxylic acid. The two aldehyde molecules supply the oxidised and reduced products in equal molar amounts.

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: Inspect the carbon immediately beside CHO: no alpha H means Cannizzaro in concentrated alkali, while acetone supplies the enolate in part (i).

Section D (15 marks)

35(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: $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- Osmotic pressure is a colligative property: $\pi = iCRT$, where i is the van't Hoff factor, C is the molarity, R is the gas constant and T is the absolute temperature.
- For $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$, each dissociated formula unit gives two ions. If the fraction dissociated is α , the relative number of solute particles is $i = (1 - \alpha) + 2\alpha = 1 + \alpha$.

Step 1: Calculate the analytical molarity and temperature The molarity counts the NaCl formula units initially dissolved, before accounting for the extra particles produced by dissociation. Since the stated volume is one litre of solution,

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

Convert the temperature to kelvin: $T = 27 + 273 = 300 \text{ K}$. The volume is already the volume of solution, so no density conversion is needed.

Step 2: Determine the particle factor and dissociation fraction If NaCl did not dissociate, its osmotic pressure would be

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

Quick Tip to Solve: For NaCl, divide the measured osmotic pressure by CRT , then subtract one; use temperature in kelvin.

The measured pressure is larger because dissociation produces additional solute particles. Therefore

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

For a 1:1 electrolyte, $i = 1 + \alpha$, hence

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

This is physically consistent: the value lies between zero and one, and i lies between one and two.

Step 3: Conclusion The degree of dissociation of NaCl is $\alpha \approx 0.931$, or approximately 93.1%.

Quick Tip to Solve: For NaCl, divide the measured osmotic pressure by CRT , then subtract one; use temperature in kelvin.

35(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 the liquid at constant temperature.
- A sudden reduction of pressure reduces dissolved-gas solubility; gas released as bubbles in blood can cause decompression sickness (the bends).

Step 1: State Henry's law 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 partial pressure, x is its mole fraction in the liquid, and K_H is Henry's law constant for the particular gas, solvent and temperature. Thus increasing pressure increases the amount of gas dissolved.

Step 2: Explain the use of helium in diving tanks At the high pressure experienced underwater, nitrogen from ordinary air dissolves more extensively in the diver's blood. During ascent, pressure falls and dissolved nitrogen can form bubbles, causing the painful and dangerous bends. Diluting air with helium lowers the nitrogen partial pressure and therefore reduces nitrogen uptake. Helium is much less soluble in blood than nitrogen, so the helium-containing breathing mixture reduces the risk of decompression sickness.

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

Quick Tip to Solve: Connect descent with higher gas solubility and ascent with bubble formation; helium dilution lowers nitrogen uptake.

35(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 obeys $\Delta T_f = iK_fm$, where m is the initial solute molality, K_f is the solvent's cryoscopic constant and i accounts for dissociation.
- The monoprotic acid dissociates as $\text{FCH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{FCH}_2\text{COO}^-$. If α is the fraction dissociated, one initial mole gives $(1 - \alpha) + 2\alpha = 1 + \alpha$ moles of particles; hence $i = 1 + \alpha$.

Step 1: Calculate the molality before dissociation The amount of fluoroacetic acid initially dissolved is

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

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

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

A freezing-point difference of 1°C has the same numerical value as a difference of 1 K.

Step 2: Obtain the van't Hoff factor and degree of dissociation Without dissociation, the predicted freezing-point depression would be

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

The observed depression is 1.00 K, so the extra solute particles give

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

Since this acid produces two particles per dissociated molecule,

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

The small positive value is consistent with partial dissociation of a weak monoprotic acid.

Step 3: Conclusion The degree of dissociation of FCH_2COOH is 0.0753 , or approximately 7.53% .

Quick Tip to Solve: Use kilograms of water to calculate molality; for this monoprotic acid, $\alpha = \Delta T_f / (K_fm) - 1$.

35(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, depending on the number of solute particles: $\Delta T_b = iK_b m$. Dissociation increases the effective particle concentration.
- Osmosis transfers water through a selectively permeable membrane from a less concentrated solution to a more concentrated solution. A concentrated salt solution is hypertonic to microbial cells.

Step 1: Compare KCl and glucose solutions KCl is an electrolyte and dissociates in water into K^+ and Cl^- , whereas glucose is a non-electrolyte and remains as intact molecules. Thus, for the stated equal dilute concentrations, KCl produces more solute particles than glucose. Its van't Hoff factor is approximately two, compared with one for glucose. Consequently its boiling-point elevation is greater, and 0.1 M KCl has the higher boiling point.

Step 2: Explain preservation of meat by salting Adding salt produces a concentrated, hypertonic medium around microorganisms present on the meat. Water leaves their cells by osmosis into the more concentrated external medium. This loss of water causes dehydration or plasmolysis and inhibits their growth and activity. Since microbial activity responsible for spoilage is suppressed, salted meat can be preserved for a longer time.

Step 3: Conclusion (i) KCl gives more dissolved particles through ionic dissociation, so its boiling point is higher. (ii) Salt draws water out of microbial cells by osmosis and inhibits spoilage.

Quick Tip to Solve: For colligative properties count particles; for salting identify the hypertonic medium and the direction of water flow.

36(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:

- Noble-gas reactivity depends on the energy needed to disturb the closed-shell configuration and on atomic size.
- An oxoacid is stronger when its conjugate base is stabilised by electron withdrawal and resonance.
- Effective sideways overlap favours multiple bonds; weaker multiple bonding favours catenation and single-bonded rings.

Step 1: Explain the difference between helium and xenon Helium has the compact, completely filled $1s^2$ configuration and an extremely high ionisation enthalpy. Its electrons are very strongly bound,

Quick Tip to Solve: For each reason connect the observed behaviour to its cause: ionisation enthalpy, conjugate-base stability, or multiple-bond overlap.

so ordinary chemical reagents cannot cause it to form compounds. Xenon has a much larger atom and lower ionisation enthalpy; strongly electronegative elements such as fluorine and oxygen can therefore form compounds with xenon.

Step 2: Compare the two chlorine oxoacids In HClO_4 , three additional oxygen atoms withdraw electron density from the O – H group, facilitating proton release. The conjugate base ClO_4^- has its negative charge delocalised over four oxygen atoms and is much more stabilised than ClO^- , the conjugate base of HOCl . Thus perchloric acid loses a proton more readily.

Step 3: Explain molecular form and physical state The small oxygen atoms have effective $2p$ - $2p$ sideways overlap and form a strong O = O bond. Oxygen therefore exists as small O_2 molecules with weak intermolecular attractions and is a gas. The larger sulphur atoms show poor $3p$ - $3p$ sideways overlap, so sulphur prefers S – S single bonds and forms puckered S_8 rings. These larger, more polarisable molecules have stronger intermolecular attractions and form a solid at room temperature.

Step 4: Conclusion Helium is too small and difficult to ionise to react like xenon; HClO_4 has a more stabilised conjugate base than HOCl ; oxygen forms gaseous O_2 , whereas sulphur forms solid S_8 .

Quick Tip to Solve: For each reason connect the observed behaviour to its cause: ionisation enthalpy, conjugate-base stability, or multiple-bond overlap.

36(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.

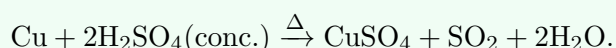
[2 marks]

Solution:

Concept:

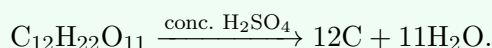
- An oxidising agent accepts electrons and is itself reduced during the reaction.
- A dehydrating agent removes the elements of water from a substance; concentrated sulphuric acid has a strong affinity for water.

Step 1: Show oxidising action with copper On heating copper with concentrated sulphuric acid,



Copper changes from oxidation state 0 to +2, while sulphur in the acid changes from +6 to +4 in SO_2 . Thus the acid oxidises copper and is itself reduced.

Step 2: Show dehydrating action with sucrose Concentrated sulphuric acid removes hydrogen and oxygen in the proportion of water from sugar:



The sugar becomes a black mass of carbon. Here the acid is written above the arrow because its role is to extract water; this demonstrates dehydration rather than a change in carbon caused by oxidation with the acid.

Quick Tip to Solve: To identify oxidising action, show the reduction of sulphur from +6 to +4; for dehydration, show removal of water from sugar.

Step 3: Conclusion The copper reaction demonstrates oxidising action, and the conversion of sucrose to carbon demonstrates dehydrating action of concentrated H_2SO_4 .

Quick Tip to Solve: To identify oxidising action, show the reduction of sulphur from +6 to +4; for dehydration, show removal of water from sugar.

OR

36(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 a gaseous ion becomes surrounded by water molecules.
- For ions of equal charge, smaller ionic radius gives stronger ion-dipole attraction and a greater magnitude of hydration enthalpy.

Step 1: Compare the ionic sizes Both F^- and Cl^- have charge -1 , but F^- is smaller because it has fewer occupied electron shells. Its charge is concentrated over a smaller volume, giving it a higher charge density.

Step 2: Relate size to hydration The smaller fluoride ion attracts the positive ends of polar water molecules more strongly. More energy is released when its hydration shell forms, so its hydration enthalpy is more negative than that of chloride. The phrase "more" here refers to the magnitude of the energy released, rather than a larger signed numerical value.

Step 3: Conclusion F^- has a greater magnitude of hydration enthalpy than Cl^- because its smaller size produces stronger attraction to water molecules.

Quick Tip to Solve: For equally charged ions, compare radius first: the smaller ion has the more exothermic hydration enthalpy.

36(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:

- In SO_2 and TeO_2 , the group-16 element is in oxidation state $+4$.
- Down group 16, the stability of the highest oxidation state $+6$ decreases, while that of lower oxidation states increases.

Step 1: Explain reducing action of sulphur dioxide Sulphur can readily pass from $+4$ in SO_2 to its stable $+6$ state, as in sulphate. In undergoing oxidation it supplies electrons to another reactant, so

Quick Tip to Solve: Always describe the change undergone by the agent itself: a reducing agent is oxidised and an oxidising agent is reduced.

SO₂ acts as a reducing agent.

Step 2: Explain oxidising action of tellurium dioxide For the heavier element tellurium, the +6 state is less stable and lower oxidation states are increasingly favoured. Tellurium in TeO₂ can accept electrons and be reduced from +4, for example to elemental tellurium. In this process it oxidises the other reactant, so TeO₂ shows oxidising action.

Step 3: Conclusion SO₂ is readily oxidised from +4 to +6, whereas TeO₂ tends to be reduced to a lower oxidation state; hence their reducing and oxidising actions, respectively.

Quick Tip to Solve: Always describe the change undergone by the agent itself: a reducing agent is oxidised and an oxidising agent is reduced.

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

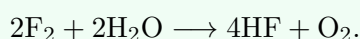
[2 marks]

Solution:

Concept:

- Halogens act as oxidising agents by gaining electrons to form halide ions.
- Fluorine is sufficiently strong to oxidise water to oxygen; iodine has much weaker oxidising power.

Step 1: Write the reaction of fluorine with water Fluorine reacts vigorously with water according to



Fluorine changes from oxidation state 0 to -1 in hydrogen fluoride. Oxygen in water changes from -2 to 0 in oxygen gas. Thus fluorine is reduced while water is oxidised. The equation contains four fluorine atoms, four hydrogen atoms and two oxygen atoms on each side.

Step 2: Explain the behaviour of iodine Iodine is a much weaker oxidising agent than fluorine. It cannot oxidise water to oxygen under ordinary conditions, so the corresponding reaction producing HI and O₂ does not occur. This is the reason iodine is described as not reacting with water in this comparison; its low oxidising power cannot drive the oxidation that fluorine readily causes.

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

Quick Tip to Solve: Balance fluorine and hydrogen first, then use the remaining two oxygen atoms as one oxygen molecule.

36(c). Draw the structure of XeF₂.

[1 mark]

Solution:

Concept:

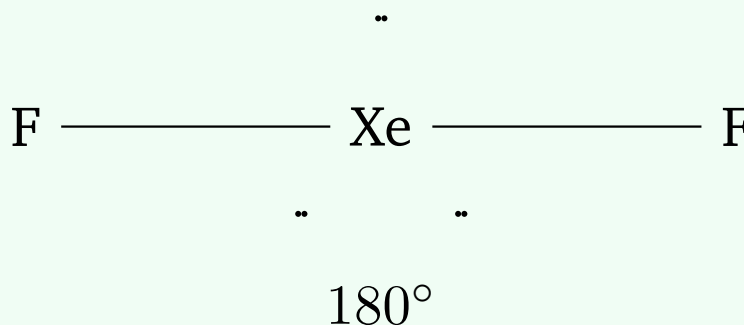
- VSEPR theory: electron pairs around Xe repel each other and adopt positions that minimise repulsion.
- In XeF₂, Xe has two bonding pairs and three lone pairs: the electron-pair arrangement is trigonal

Quick Tip to Solve: Count lone pairs on Xe first: three equatorial lone pairs leave two opposite axial bonds.

bipyramidal.

Step 1: Count the electron pairs Xe has eight valence electrons. Formation of two Xe–F single bonds leaves six non-bonding electrons on Xe, or three lone pairs. Thus its VSEPR notation is AX_2E_3 .

Step 2: Place bonds and lone pairs The three lone pairs occupy the equatorial positions, where they experience fewer 90° interactions. The two Xe–F bonds occupy opposite axial positions, giving an F–Xe–F angle of 180° . Lone pairs determine the electron-pair arrangement but are excluded when naming the molecular shape.



Linear structure of xenon difluoride; the three lone pairs on Xe are equatorial.

Step 3: Conclusion XeF_2 is linear: F–Xe–F, with a bond angle of 180° .

Quick Tip to Solve: Count lone pairs on Xe first: three equatorial lone pairs leave two opposite axial bonds.

37(a). Give reasons:

(i) Although $-\text{NH}_2$ group is o/p directing in electrophilic substitution reactions, yet aniline, on nitration gives good yield of m-nitroaniline.

(ii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

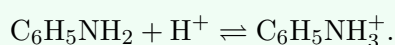
(iii) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. [3 marks]

Solution:

Concept:

- The directing effect in electrophilic substitution depends on the group actually present under the reaction conditions.
- Basicity in water depends on both electron donation to nitrogen and hydration of the conjugate acid.
- Ammonolysis is nucleophilic substitution; the amine formed can itself react further with an alkyl halide.

Step 1: (i) Explain meta nitration of aniline The strongly acidic nitrating mixture protonates aniline:

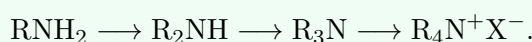


Quick Tip to Solve: For aqueous amine basicity, compare solvation of the protonated ions as well as the inductive effect.

The free $-\text{NH}_2$ group normally donates its lone pair to the ring and directs substitution to ortho and para positions. In the anilinium ion, that lone pair is tied up in the N-H bond. The positively charged $-\text{NH}_3^+$ group withdraws electrons and is meta directing. Nitration of this protonated fraction therefore gives a substantial yield of meta-nitroaniline.

Step 2: (ii) Compare the bases in aqueous solution Methyl groups increase electron density on nitrogen through the $+I$ effect, but the stability of the protonated ion in water must also be considered. The dimethylammonium ion, $(\text{CH}_3)_2\text{NH}_2^+$, is better hydrated than the bulkier trimethylammonium ion, $(\text{CH}_3)_3\text{NH}^+$. It has more N-H bonds available for hydrogen bonding and less steric obstruction to solvation. The balance of inductive effect and hydration favours dimethylamine, making it the stronger base in water.

Step 3: (iii) Explain the mixture from ammonolysis The primary amine formed is nucleophilic and undergoes further alkylation with the remaining alkyl halide. Successive substitutions produce a secondary amine, a tertiary amine and finally a quaternary ammonium salt:



Hence the reaction generally gives a mixture that is difficult to separate. Excess ammonia favours the primary amine but does not make the general method suitable for obtaining a pure primary amine directly.

Step 4: Conclusion Meta nitration results from anilinium-ion formation; dimethylamine is more basic because its conjugate acid is better hydrated; ammonolysis gives further alkylation products.

Quick Tip to Solve: For aqueous amine basicity, compare solvation of the protonated ions as well as the inductive effect.

37(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

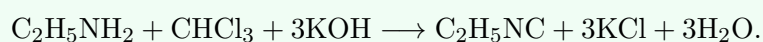
[2 marks]

Solution:

Concept:

- The carbylamine test is given only by primary amines; secondary and tertiary amines do not respond.
- Aromatic primary amines form stable diazonium salts at 273–278 K, whereas aliphatic diazonium salts decompose.

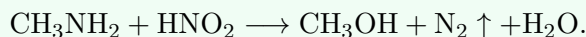
Step 1: (i) Ethylamine and diethylamine: carbylamine test Heat each sample with chloroform and alcoholic KOH in a fume hood. Ethylamine, a primary amine, forms foul-smelling ethyl isocyanide:



Diethylamine is secondary and does not form an isocyanide. Thus a positive carbylamine reaction identifies ethylamine; diethylamine gives a negative test.

Quick Tip to Solve: Carbylamine distinguishes primary from secondary amines; cold diazotisation distinguishes aromatic from aliphatic primary amines.

Step 2: (ii) Aniline and methylamine: nitrous acid test Treat each sample with NaNO_2 and dilute HCl at 273–278 K. Aniline forms benzenediazonium chloride, which couples with phenol in alkaline medium to give an orange-red azo dye. Methylamine instead gives brisk evolution of nitrogen gas and methanol:



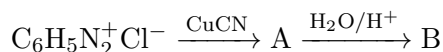
Its unstable aliphatic diazonium intermediate decomposes, so it does not give the azo-dye coupling test. The dye observation for aniline and nitrogen evolution for methylamine distinguish them clearly.

Step 3: Conclusion Ethylamine gives a positive carbylamine test and diethylamine does not. Aniline forms a diazonium salt and an azo dye; methylamine evolves N_2 with nitrous acid.

Quick Tip to Solve: Carbylamine distinguishes primary from secondary amines; cold diazotisation distinguishes aromatic from aliphatic primary amines.

OR

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



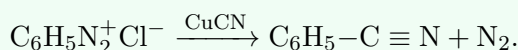
[1 mark]

Solution:

Concept:

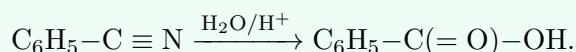
- In the Sandmeyer reaction, CuCN replaces the diazonium group of an aromatic diazonium salt by $-\text{CN}$.
- Acidic hydrolysis converts a nitrile group, $-\text{C} \equiv \text{N}$, into a carboxyl group, $-\text{COOH}$.

Step 1: Identify A by cyanation The diazonium group leaves as nitrogen gas and cyanide bonds to the benzene ring through carbon. Therefore



A is benzonitrile; the nitrile carbon is additional to the six ring carbons.

Step 2: Identify B by acidic hydrolysis Water in acidic medium hydrolyses the nitrile, through an amide intermediate, to the corresponding carboxylic acid:

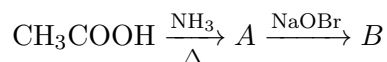


The nitrile carbon becomes the carboxyl carbon, while the benzene ring remains unchanged.

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

Quick Tip to Solve: CuCN adds a nitrile carbon to the ring; hydrolysis retains this carbon as the carboxyl carbon.

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



[1 mark]

Solution:

Concept:

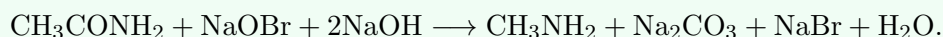
- A carboxylic acid reacts with ammonia to form an ammonium carboxylate; heating this salt eliminates water to give the corresponding amide.
- In the Hofmann bromamide reaction, an amide reacts with sodium hypobromite to form a primary amine containing one carbon atom fewer than the amide.

Step 1: Identify the amide A Acetic acid first forms ammonium acetate with ammonia. On heating, this salt loses water:



Therefore A is ethanamide (acetamide), whose carbonyl carbon is bonded to a methyl group and an amino group.

Step 2: Identify the amine B Sodium hypobromite converts ethanamide into methylamine by Hofmann degradation. The carbonyl carbon is removed, while the methyl group becomes bonded to nitrogen:



The two-carbon amide therefore gives a one-carbon primary amine; ethylamine would incorrectly retain the carbonyl carbon.

Step 3: Conclusion $A = \text{CH}_3\text{C}(=\text{O})\text{NH}_2$, $B = \text{CH}_3\text{NH}_2$.

Quick Tip to Solve: Count the carbons before and after Hofmann degradation: the amine must have exactly one carbon fewer than the starting amide.

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

[2 marks]

Solution:

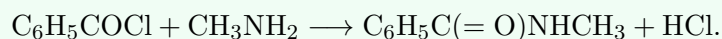
Concept:

- A primary amine undergoes benzoylation with benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, to form an amide. The nitrogen replaces the chlorine attached to the carbonyl group.
- An aqueous alkali absorbs the hydrogen chloride produced in the Schotten–Baumann reaction and helps the benzoylation proceed.

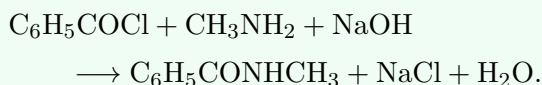
Step 1: Write the benzoylation reaction The lone pair on the nitrogen of methylamine attacks the carbonyl carbon of benzoyl chloride. Replacement of chloride and removal of one nitrogen-bound

Quick Tip to Solve: Attach the benzoyl group to the amine nitrogen and retain the methyl group on that nitrogen; use the locant N in the product name.

hydrogen give the amide:



In the presence of sodium hydroxide, the overall equation is



The product retains one N–H bond because only one hydrogen of the original primary amine is replaced by the benzoyl group.

Step 2: Name the product The parent amide is benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$. Its nitrogen carries a methyl substituent, so the substituent is denoted by the locant *N*. The product is thus *N*-methylbenzamide. It is an amide rather than an amine because nitrogen is directly bonded to the carbonyl carbon.

Step 3: Conclusion The product is $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{NHCH}_3$. Its IUPAC name is

N-methylbenzamide.

Quick Tip to Solve: Attach the benzoyl group to the amine nitrogen and retain the methyl group on that nitrogen; use the locant *N* in the product name.

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

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

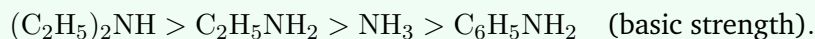
[1 mark]

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 therefore a smaller pK_b .
- Alkyl groups increase electron density on nitrogen through their electron-releasing inductive effect. In aniline, delocalisation of the nitrogen lone pair into the benzene ring reduces its availability for protonation.

Step 1: Compare the basic strengths In aqueous solution, diethylamine is more basic than ethylamine, and ethylamine is more basic than ammonia. The ethyl groups donate electron density to nitrogen, and the protonated primary and secondary amines are effectively solvated. Aniline is weakest because its lone pair participates in resonance with the aromatic ring:

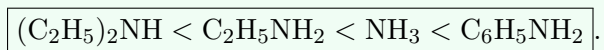


Step 2: Convert to the required pK_b order A greater basic strength means a greater K_b . Since the negative logarithm reverses this order, the strongest base must appear first when arranging increasing pK_b , and the weakest base must appear last. The inequality signs between the compound names now

Quick Tip to Solve: Rank the basic strengths first, then remember that a stronger base has a lower pK_b when writing the requested increasing order.

represent their respective pK_b values.

Step 3: Conclusion Increasing pK_b :



Quick Tip to Solve: Rank the basic strengths first, then remember that a stronger base has a lower pK_b when writing the requested increasing order.