

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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper 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)

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 of its common ions.
- A completely filled d^{10} subshell does not satisfy this definition.

Step 1: Examine the atoms The outer configurations of zinc, cadmium and mercury are respectively $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$. Their d subshells are completely filled.

Step 2: Examine their usual ions Formation of their usual +2 ions removes the two outer s electrons, leaving $3d^{10}$, $4d^{10}$ and $5d^{10}$, respectively. These ions also lack an incompletely filled d subshell.

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

Quick Tip to Solve: Check the d -electron count in both the atom and its common ion; merely belonging to the d block is insufficient.

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

[1 mark]

Solution:

Concept:

- Variable oxidation states of transition metals arise when different numbers of ns and $(n-1)d$ electrons participate in bonding.
- Scandium has the electronic configuration $[\text{Ar}]3d^14s^2$.

Step 1: Identify the transition metal Scandium is the first transition metal of the 3d series. It has three electrons outside the argon core: two in $4s$ and one in $3d$.

Step 2: Find its usual oxidation state Loss of these three electrons produces Sc^{3+} , with the stable configuration $[\text{Ar}]$. In the usual chemistry of the 3d series, scandium shows only the +3 oxidation state.

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

Quick Tip to Solve: For Sc, count the one 3d electron and two 4s electrons: their removal gives the stable argon core.

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

[1 mark]

Solution:

Concept:

- A catalyst increases the rate of a reaction by providing an alternative pathway with lower activation energy.
- Transition metals have variable oxidation states and can form intermediate compounds or adsorb reactants on their surfaces.

Step 1: Explain intermediate formation Transition metals can change oxidation state during a reaction. This enables their compounds to form intermediates with the reactants and transfer electrons; the catalyst is regenerated at the end.

Step 2: Explain surface action Metal surfaces can adsorb reactant molecules. Adsorption brings reactants together and weakens their bonds, facilitating reaction through a pathway with a lower activation energy.

Step 3: Conclusion Transition metals and their compounds show catalytic activity because of their variable oxidation states, intermediate formation and ability to adsorb reactants.

Quick Tip to Solve: Link variable oxidation states to intermediates and surface adsorption to easier bond breaking.

4. Why are melting points of transition metals high?

[1 mark]

Solution:

Concept:

- Melting a metal requires energy to overcome its metallic bonding.
- In transition metals, both the outer *s* electrons and the *d* electrons can contribute to strong metallic bonding.

Step 1: Relate electronic structure to bonding Transition metals generally possess several unpaired *d* electrons. Participation of these electrons, together with the outer *s* electrons, produces strong bonding between the metal atoms.

Step 2: Relate bonding to melting The strong metallic bonding gives these metals high enthalpies of atomisation. Considerable thermal energy is therefore needed to disrupt the metallic lattice, so their melting points are generally high.

Step 3: Conclusion Transition metals generally have high melting points because strong metallic bonding involves both *s* and *d* electrons.

Quick Tip to Solve: Explain high melting point through strong metallic bonding and the participation of unpaired *d* electrons.

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

[1 mark]

Solution:

Concept:

- In aqueous solution, ligands split the metal ion's d orbitals into groups of different energies.
- Absorption of visible light for a $d-d$ transition can produce colour when the d subshell is partially filled.

Step 1: Consider the copper(II) ion Cu^{2+} has configuration $[\text{Ar}]3d^9$. Its partially filled d subshell permits an electron to be promoted between the split d levels by absorbing visible light, so the aqueous ion appears coloured.

Step 2: Consider the zinc(II) ion Zn^{2+} has configuration $[\text{Ar}]3d^{10}$. All its d orbitals are filled, so a $d-d$ transition is not possible. Its aqueous solution is therefore colourless.

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

Quick Tip to Solve: Remove the 4s electrons first when forming these ions, then compare the resulting d^9 and d^{10} configurations.

6. Write the name of the product when benzene diazonium chloride is treated with KI.

[1 mark]

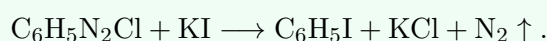
Solution:

Concept:

- An aromatic diazonium group can be replaced by iodide on treatment with potassium iodide.
- The diazonium group leaves as nitrogen gas, while the benzene ring remains intact.

Step 1: Identify the substitution Benzene diazonium chloride contains the group $-\text{N}_2^+$ attached to a phenyl group. Iodide supplied by KI replaces this diazonium group; no copper catalyst is required for this conversion.

Step 2: Write the reaction The conversion is



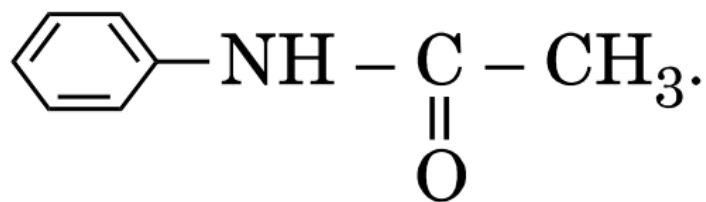
The organic product has iodine directly attached to the benzene ring.

Step 3: Conclusion The product is **iodobenzene**.

Quick Tip to Solve: For a diazonium salt with KI, replace the entire diazonium group by I and release nitrogen gas.

7. Write the IUPAC name of the following compound:

[1 mark]



Solution:

Concept:

- For an amide, the parent name comes from the carbon chain containing the carbonyl carbon.
- A substituent attached directly to the amide nitrogen is indicated by the locant *N*.

Step 1: Choose the parent amide The given structure is $\text{C}_6\text{H}_5 - \text{NH} - \text{CO} - \text{CH}_3$. The CH_3CO portion contains two carbon atoms, including the carbonyl carbon, so the parent amide is ethanamide.

Step 2: Identify the nitrogen substituent The benzene-derived C_6H_5 group is a phenyl group bonded to the amide nitrogen. It is therefore described as an *N*-phenyl substituent, rather than a substituent on the carbon chain.

Step 3: Conclusion The IUPAC name is *N*-phenylethanamide.

Quick Tip to Solve: Count the carbonyl carbon in the ethanamide parent and use N for the phenyl group attached to nitrogen.

8. Name the reducing agent used to obtain Ag from $[\text{Ag}(\text{CN})_2]^-$ complex.

[1 mark]

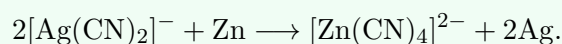
Solution:

Concept:

- An active metal can reduce a less reactive metal ion to the free metal by donating electrons.
- In cyanide extraction, silver is present as the soluble complex $[\text{Ag}(\text{CN})_2]^-$.

Step 1: Identify the displacement metal Zinc is more reactive than silver. Zinc dust is added to the solution containing the silver cyanide complex; it is oxidised while silver(I) is reduced to metallic silver.

Step 2: Write the displacement reaction The cyanide ions remain coordinated in the zinc complex:



The atoms and total charge are balanced, and zinc provides the two electrons needed to reduce two silver ions.

Step 3: Conclusion The reducing agent is zinc dust, Zn.

Quick Tip to Solve: Recall cyanide extraction: zinc dust displaces silver or gold from its soluble cyanide complex.

9. Name the vitamin whose deficiency causes convulsions.

[1 mark]

Solution:

Concept:

- Vitamins are organic nutrients required in small amounts for normal metabolism; a deficiency causes characteristic disorders.
- Vitamin B₆, also called pyridoxine, is a water-soluble member of the vitamin B group.

Step 1: Match the symptom with the vitamin The characteristic deficiency symptom asked here is convulsions. In the standard vitamin-deficiency table, this symptom is associated with vitamin B₆, which is involved in amino-acid metabolism and normal nervous-system functioning.

Step 2: Distinguish familiar deficiency diseases Vitamin B₁ deficiency causes beriberi, vitamin C deficiency causes scurvy, and vitamin D deficiency causes rickets. These do not match the stated symptom of convulsions.

Step 3: Conclusion The vitamin is vitamin B₆ (pyridoxine).

Quick Tip to Solve: Pair convulsions with B₆; use beriberi, scurvy and rickets to rule out B₁, C and D.

10. Pick out the odd one from among the following compounds on the basis of their medicinal properties:

Equanil, Luminal, Bithional, Seconal

[1 mark]

Solution:

Concept:

- Drugs are classified according to their therapeutic effects or medicinal properties.
- Tranquillisers act on the central nervous system, whereas antiseptics control microorganisms on living tissues.

Step 1: Classify the three related drugs Equanil is a tranquilliser used to relieve anxiety. Luminal and Seconal are barbiturates with sedative or hypnotic action; in the school classification, they belong to the tranquilliser group. All three act on the central nervous system.

Step 2: Classify the remaining compound Bithional is an antiseptic. It is added to soaps to impart antiseptic properties and reduce bacterial growth. Its antimicrobial action therefore differs from the central nervous system action of the other three listed drugs.

Step 3: Conclusion Bithional is the odd one: it is an antiseptic, while the other three act as tranquillisers or sedatives.

Quick Tip to Solve: Group Equanil, Luminal and Seconal by nervous-system action; Bithional belongs with antiseptics.

11. In fuel cell

[1 mark]

- (A) chemical energy is converted to electrical energy.
- (B) energy of combustion of fuel is converted to chemical energy.
- (C) energy of combustion of fuel is converted to electrical energy.
- (D) electrical energy is converted to chemical energy.

Correct Answer: Options (A) and (C) both describe the fuel-cell conversion to electrical energy; the textbook-specific wording is (C).

Solution:

Concept:

- A fuel cell is a galvanic cell in which fuel and oxidant are supplied continuously to sustain a redox reaction.
- The chemical energy released by the fuel reaction is converted directly into electrical energy.

Step 1: Identify the fuel-cell conversion In a hydrogen-oxygen fuel cell, the overall reaction is $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$. Oxidation and reduction occur at separate electrodes, so electrons pass through the external circuit and produce electric current. The energy of the fuel combustion reaction is thereby obtained as electrical energy.

Step 2: Check the printed alternatives Option (C) gives the textbook description: energy of combustion of fuel is converted to electrical energy. Option (A) is also a scientifically correct general description of this same conversion. Option (B) incorrectly describes the output as chemical energy, and option (D) describes an electrolytic conversion rather than a fuel cell.

Step 3: Conclusion Options (A) and (C) are both valid: a fuel cell converts the chemical energy of its fuel reaction into electrical energy. Option (C) is the textbook-specific description, but the printed alternatives do not give a unique correct choice.

Quick Tip to Solve: A fuel cell continuously supplies current from a fuel redox reaction: chemical energy becomes electrical energy.

12. In a Leclanche dry cell, the cathode is

[1 mark]

- (A) Zn container
- (B) MnO_2
- (C) Graphite rod
- (D) NH_4Cl

Correct Answer: (C) Graphite rod

Solution:

Concept:

- In a galvanic cell, oxidation occurs at the anode and reduction occurs at the cathode.
- The Leclanche dry cell has a zinc container as anode and a graphite rod surrounded by manganese dioxide and carbon as its cathode assembly.

Quick Tip to Solve: For a dry cell remember: zinc can is anode, central graphite rod is cathode, moist salts are electrolyte.

Step 1: Identify the cathode conductor The central graphite rod serves as the positive electrode and conducts the electrons into the surrounding cathodic mixture. In the standard description of the dry cell, this rod is named the cathode.

Step 2: Distinguish the other components The zinc container is oxidised and hence is the anode, not the cathode. Manganese dioxide is the active cathodic material/depolariser surrounding the rod. Ammonium chloride forms part of the moist electrolyte paste; it is not an electrode.

Step 3: Conclusion The cathode is the graphite rod, option (C).

Quick Tip to Solve: For a dry cell remember: zinc can is anode, central graphite rod is cathode, moist salts are electrolyte.

13. The rate constant for a first order reaction is equal to the initial rate of reaction when the initial concentration of the reactant is [1 mark]

- (A) 1×10^{-2} M
- (B) 1 M
- (C) 10 M
- (D) 0.1 M

Correct Answer: (B) 1 M

Solution:

Concept:

- For a first-order reaction, the rate law is $r = k[A]$, where k is the rate constant and $[A]$ is reactant concentration.
- The initial rate is $r_0 = k[A]_0$; rate and rate constant have different units, so the stated equality means numerical equality in the usual units.

Step 1: Apply the initial rate law With rate expressed in $\text{mol L}^{-1} \text{s}^{-1}$ and k in s^{-1} , their numerical values are equal when the numerical concentration in mol L^{-1} is unity. Thus $r_0 = k \times 1$ for an initial concentration of 1 M.

Step 2: Check the alternative concentrations At 10^{-2} M, the numerical initial rate is $0.01k$; at 10 M, it is $10k$; and at 0.1 M, it is $0.1k$. Only unity concentration gives the required numerical equality.

Step 3: Conclusion The initial concentration is 1 M, option (B).

Quick Tip to Solve: Insert the concentration into $r_0 = k[A]_0$; for a first-order reaction, unity concentration makes the numerical factor one.

14. On the basis of crystal field theory, electronic configuration of d^4 complex when $\Delta_o > P$ is [1 mark]

- (A) $t_{2g}^3 e_g^1$
- (B) $t_{2g}^2 e_g^2$
- (C) $t_{2g}^1 e_g^3$
- (D) $t_{2g}^4 e_g^0$

Correct Answer: (D) $t_{2g}^4 e_g^0$

Solution:

Concept:

- In an octahedral crystal field, the three t_{2g} orbitals are lower in energy than the two e_g orbitals.
- Δ_o is the octahedral splitting energy and P is pairing energy; when $\Delta_o > P$, pairing in the lower orbitals is favoured.

Step 1: Place the first three electrons The first three d electrons occupy the three lower-energy t_{2g} orbitals singly according to Hund's rule. This gives t_{2g}^3 before the fourth electron is placed.

Step 2: Place the fourth electron and test the options Promoting the fourth electron to e_g costs Δ_o , whereas pairing it in t_{2g} costs the smaller energy P . It therefore pairs in a t_{2g} orbital, giving a low-spin configuration. Option (A) is the high-spin arrangement when splitting is smaller; options (B) and (C) put still more electrons into the higher set and cannot be the ground-state distribution under the stated condition.

Step 3: Conclusion The configuration is $t_{2g}^4 e_g^0$, option (D).

Quick Tip to Solve: Compare splitting with pairing: if $\Delta_o > P$, pair in t_{2g} before occupying e_g .

15. Which of the following is a non-reducing sugar? [1 mark]

- (A) Sucrose
- (B) Maltose
- (C) Glucose
- (D) Lactose

Correct Answer: (A) Sucrose

Solution:

Concept:

- A reducing sugar has a free anomeric carbon that can provide an open-chain carbonyl group and reduce reagents such as Tollens' reagent.
- When both anomeric carbons participate in the glycosidic linkage, the sugar has no free reducing end.

Step 1: Examine the linkage in sucrose Sucrose contains glucose and fructose joined through the anomeric carbon of each unit: C-1 of glucose and C-2 of fructose. Both centres are therefore locked in the glycosidic linkage; neither can open to furnish a free carbonyl group.

Quick Tip to Solve: For a disaccharide, check whether both anomeric carbons are linked: sucrose has no free reducing end.

Step 2: Check the other choices Maltose and lactose each retain one free anomeric carbon and are reducing disaccharides. Glucose can form an open-chain aldehyde group and is also reducing. Thus options (B), (C) and (D) do not satisfy the question.

Step 3: Conclusion The non-reducing sugar is **sucrose**, option (A).

Quick Tip to Solve: For a disaccharide, check whether both anomeric carbons are linked: sucrose has no free reducing end.

16. Assertion (A): Non-ideal solutions form azeotropic mixture.

Reason (R): Maximum boiling azeotropes are formed by a solution showing negative deviation.

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

[1 mark]

Solution:

Concept:

- Azeotropes are constant-boiling mixtures with the same composition in the liquid and vapour phases; simple fractional distillation cannot separate their components.
- A sufficiently large positive deviation from Raoult's law produces a minimum-boiling azeotrope, while a sufficiently large negative deviation produces a maximum-boiling azeotrope.

Step 1: Judge Assertion (A) In the intended textbook context, non-ideal solutions exhibiting sufficiently large deviations form azeotropic mixtures. Their boiling-point versus composition curve has a minimum or a maximum. Assertion (A) is therefore treated as correct.

Step 2: Judge Reason (R) For negative deviation, unlike-molecule attractions are stronger and the total vapour pressure is lower than the ideal value. At the azeotropic composition, this gives a maximum boiling point. Reason (R) is correct.

Step 3: Test the explanatory link Reason (R) describes only the maximum-boiling class. It does not explain the general formation of azeotropes by non-ideal solutions, since sufficiently large positive deviations also give minimum-boiling azeotropes.

Step 4: Conclusion Both A and R are correct, but R is not the correct explanation of A. The correct code is (ii).

Quick Tip to Solve: An assertion about azeotropes generally cannot be explained by a reason covering only maximum-boiling azeotropes.

17. Assertion (A): The complex $[\text{Cr}(\text{H}_2\text{O})_3 \text{Cl}_3]$ does not give precipitate with AgNO_3 solution.

Reason (R): The complex $[\text{Cr}(\text{H}_2\text{O})_3 \text{Cl}_3]$ is non-ionizable.

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

[1 mark]

Solution:

Concept:

- Only chloride ions outside the coordination sphere are available to precipitate with silver nitrate: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl(s)}$.
- Ligands inside square brackets are coordinated to the metal and are not released as free counter-ions merely by dissolving the complex.

Step 1: Judge Assertion (A) In $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$, all three chloride ligands lie within the coordination sphere. No chloride counter-ion is present outside the brackets. Hence an aqueous silver nitrate test does not give the usual silver chloride precipitate, so A is correct.

Step 2: Judge Reason (R) The charge of chromium is +3, the three chlorido ligands contribute -3, and water is neutral. The entire complex is neutral and has no counter-ions to dissociate from it. In this coordination-compound context, it is non-ionizable, so R is correct.

Step 3: Connect the two statements Because the complex does not dissociate to furnish free chloride ions, silver ions cannot produce the characteristic AgCl precipitate. The non-ionizable nature directly explains the observation in A.

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

Quick Tip to Solve: Count chloride ions outside the square brackets to predict the silver nitrate precipitate.

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

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

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

[1 mark]

Solution:

Concept:

- Conductivity κ measures the ability of a unit volume of electrolyte solution to conduct electricity.
- Dilution decreases the number of ions per unit volume, even though the degree of ionization of a weak electrolyte may increase.

Step 1: Judge Assertion (A) When concentration decreases, the solution contains fewer charge-carrying ions per unit volume. Therefore its conductivity decreases. Assertion (A) is correct for the stated dilution trend.

Step 2: Judge Reason (R) Adding solvent increases the volume occupied by the ions. Thus the number of ions per unit volume decreases, rather than increases, on dilution. Reason (R) states the opposite trend and is incorrect.

Quick Tip to Solve: Keep conductivity and molar conductivity distinct: dilution lowers the former but increases the latter.

Step 3: Choose the appropriate code The decrease in conductivity must not be confused with the increase in molar conductivity on dilution. Molar conductivity refers to the contribution associated with a mole of electrolyte; it is not the conductivity of a unit volume. A is true while R is false.

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 distinct: dilution lowers the former but increases the latter.

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

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

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

[1 mark]

Solution:

Concept:

- Nucleophilic addition begins with attack on the electrophilic carbonyl carbon.
- Alkyl groups donate electron density by the +I effect and also hinder approach to the carbonyl carbon.

Step 1: Judge Assertion (A) Aldehydes are generally more reactive than ketones towards nucleophilic addition. An aldehyde has one alkyl group and a hydrogen attached to its carbonyl carbon, whereas a ketone has two alkyl groups. Ketones therefore have greater electron donation and greater steric hindrance. A is incorrect.

Step 2: Judge Reason (R) The two alkyl groups of a ketone donate more electron density towards the carbonyl group than the single alkyl group of an aldehyde. This lowers the partial positive charge on the carbonyl carbon of a ketone, making it less electrophilic. R is correct.

Step 3: Use the statements to select the code The lower electrophilicity stated in R actually helps explain why ketones are less reactive, contrary to A. Since A is false and R is true, neither code for two true statements is applicable.

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

Quick Tip to Solve: Compare both the alkyl electron donation and crowding: two alkyl groups make ketones less susceptible to nucleophilic attack.

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

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

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

[1 mark]

Solution:

Concept:

- The oxygen atom in an alcohol has two bond pairs and two lone pairs, giving approximately tetrahedral electron-pair geometry.

Quick Tip to Solve: Count oxygen's lone pairs first: their stronger repulsion compresses the angle between its two bonds.

- Lone pairs occupy more space and exert stronger repulsion than bond pairs, compressing the angle between the O–C and O–H bonds.

Step 1: Judge Assertion (A) The ideal tetrahedral angle is approximately 109.5° . Two lone pairs on oxygen alter the arrangement of the bonding pairs, so the C–O–H bond angle in alcohols is slightly smaller than this ideal value. Assertion (A) is correct.

Step 2: Judge Reason (R) The two lone electron pairs on oxygen exert strong repulsive interactions. Together with their stronger repulsion of the bond pairs, these interactions shift the bonding pairs closer together. This is the electron-pair-repulsion explanation given for the decrease in the C–O–H angle. Reason (R) is correct.

Step 3: Check whether R explains A The effect of the oxygen lone pairs is precisely what compresses the bond angle below the tetrahedral value. Thus R supplies the cause of the geometrical observation in A.

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

Quick Tip to Solve: Count oxygen's lone pairs first: their stronger repulsion compresses the angle between its two bonds.

Section B (14 marks)

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

NaAlF_4 in the extraction of Aluminium.

[1 mark]

Solution:

Concept:

- Aluminium is obtained by electrolytic reduction of alumina dissolved in a molten fluoride bath.
- A suitable fluoride additive improves the electrolyte by lowering its melting point and increasing its electrical conductivity.

Step 1: Identify the role of the additive NaAlF_4 acts as a flux in the extraction of aluminium. It helps produce a molten electrolyte at a temperature lower than that required for pure alumina, whose melting point is very high.

Step 2: Explain its practical benefit The fluoride bath also increases the electrical conductivity of the electrolyte. Consequently, alumina can be electrolysed in a conducting molten medium at a lower operating temperature, reducing the energy required to maintain the bath. The additive assists the electrolyte; aluminium is obtained by reduction at the cathode.

Step 3: Conclusion NaAlF_4 lowers the melting point of the alumina-containing bath and increases its electrical conductivity.

Quick Tip to Solve: For a fluoride additive in aluminium extraction, recall both effects: lower melting point and higher conductivity.

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

CO in the refining of Ni

[1 mark]

Solution:

Concept:

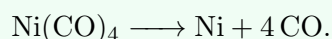
- Mond refining separates nickel through a volatile carbonyl intermediate. Carbon monoxide is the ligand that forms this intermediate.
- Nickel tetracarbonyl, Ni(CO)_4 , forms at a lower temperature and decomposes at a higher temperature to release pure nickel.

Step 1: Form the volatile carbonyl Impure nickel is heated with carbon monoxide at about 330–350 K. Nickel reacts to form volatile nickel tetracarbonyl:



The volatile compound is separated from impurities that do not form such a carbonyl.

Step 2: Recover pure nickel The separated carbonyl vapour is heated at about 450–470 K, where it decomposes:



Nickel is deposited in pure form and carbon monoxide is released. Thus CO enables purification through formation and decomposition of a volatile compound.

Step 3: Conclusion CO forms volatile Ni(CO)_4 with nickel; thermal decomposition of this carbonyl gives pure nickel in the Mond process.

Quick Tip to Solve: For Mond refining, remember the sequence: nickel + CO, volatile carbonyl, then heating to obtain pure nickel.

OR

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

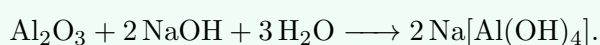
[2 marks]

Solution:

Concept:

- Leaching selectively dissolves alumina from bauxite in concentrated aqueous sodium hydroxide, leaving insoluble impurities for filtration.
- The dissolved aluminate is converted to hydrated alumina, which on heating yields pure Al_2O_3 .

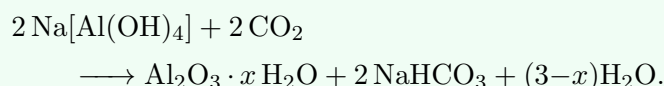
Step 1: Dissolve alumina as sodium aluminate Bauxite is treated with concentrated NaOH at about 473–523 K under pressure. The alumina component dissolves as sodium aluminate:



Insoluble impurities, including iron oxide, are removed by filtration, leaving the aluminate solution.

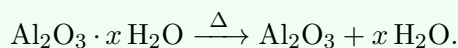
Quick Tip to Solve: Write the three chemical stages in order: dissolve alumina in NaOH, precipitate the hydrate, then remove its water by heating.

Step 2: Precipitate hydrated alumina Carbon dioxide is passed through the filtered solution. Seeding with freshly prepared hydrated alumina promotes precipitation:



This separates hydrated alumina from the soluble substances remaining in the liquid.

Step 3: Obtain anhydrous alumina The precipitated hydrated alumina is filtered, washed and heated strongly, at about 1470 K, to remove water:



The solid residue is pure alumina, suitable for the subsequent electrolytic extraction of aluminium.

Step 4: Conclusion Pure alumina is prepared by alkaline leaching to form sodium aluminate, precipitation of hydrated alumina with CO_2 , and heating the precipitate to give Al_2O_3 .

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

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

[2 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance, the adsorbate, on the surface of another substance, the adsorbent.
- Physisorption involves weak van der Waals forces; chemisorption involves formation of chemical bonds between the adsorbate and the surface.

Step 1: Compare the nature of the attractive forces In physisorption, the adsorbate is held by weak van der Waals forces, with no new chemical bond to the surface. Consequently its enthalpy of adsorption is relatively low, commonly about $20\text{--}40\text{ kJ mol}^{-1}$. In chemisorption, chemical bonds are formed, so adsorption is stronger and its enthalpy is relatively high, commonly about $80\text{--}240\text{ kJ mol}^{-1}$. This is the first difference.

Step 2: Compare specificity Physisorption is not highly specific: weak intermolecular attractions can act between many different adsorbate and adsorbent pairs. Chemisorption is highly specific because chemical bonding occurs only when the adsorbate and the surface have suitable chemical properties. Thus a surface may physically adsorb several gases, while chemically adsorbing only those with which it can form bonds. This is the second difference.

Step 3: Conclusion The two differences are: physisorption uses weak van der Waals forces and is not highly specific, whereas chemisorption forms stronger chemical bonds and is highly specific.

Quick Tip to Solve: Use paired contrasts under the same two headings: nature of forces and specificity. Chemical bonding immediately identifies chemisorption.

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

(i) Associated colloids

(ii) O/W emulsion

[2 marks]

Solution:

Concept:

- A colloid contains dispersed particles in a continuous dispersion medium. Associated colloids arise when smaller molecules or ions aggregate into colloidal particles.
- An emulsion is a colloid in which both phases are liquids. O/W denotes oil dispersed in water, with water forming the continuous phase.

Step 1: Define associated colloids and give an example Associated colloids are substances that behave as normal strong electrolytes at low concentration, but at higher concentration form aggregates of colloidal size called micelles. Micelles form above the critical micelle concentration and above the appropriate micelle formation temperature, called the Kraft temperature. A suitable example is soap, such as sodium stearate, in water. In a soap micelle the hydrophobic hydrocarbon tails point inward and the hydrophilic ionic heads face the surrounding water.

Step 2: Define an oil-in-water emulsion and give an example An O/W, or oil-in-water, emulsion is an emulsion in which small oil droplets form the dispersed phase and water is the dispersion medium. A suitable example is milk: droplets of liquid fat are dispersed in its aqueous phase. The order O/W therefore identifies the dispersed phase first and the continuous medium second; the oil droplets remain distributed throughout the water.

Step 3: Conclusion (i) Associated colloids form micellar aggregates at suitable higher concentration, for example soap in water. (ii) An O/W emulsion has oil as the dispersed phase and water as the dispersion medium, for example milk.

Quick Tip to Solve: Read O/W as oil droplets in water. For associated colloids, include the word micelles and use soap as the example.

23. 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:

- The rate of reaction is obtained by dividing a species' rate of concentration change by its stoichiometric coefficient, using a minus sign for reactants.
- For $A + 3B \rightarrow 2C$, the common reaction rate is $r = -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$, where brackets

Quick Tip to Solve: Divide C's formation rate by its coefficient 2 to obtain r; multiply r by B's coefficient 3 to get B's disappearance rate.

denote molar concentration and t is time.

Step 1: Calculate the rate of reaction The rate of formation of C is positive and equals $d[C]/dt = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Since two moles of C are formed for each stoichiometric amount of reaction, divide this formation rate by 2:

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

This coefficient-normalised quantity is the rate requested in part (i).

Step 2: Calculate the rate of disappearance of B Three moles of B disappear for every two moles of C formed. The positive rate of disappearance is therefore three times the reaction rate:

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

The derivative $d[B]/dt$ itself is negative because B is consumed; the requested disappearance rate is its positive 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: Divide C's formation rate by its coefficient 2 to obtain r ; multiply r by B's coefficient 3 to get B's disappearance rate.

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

(i) Analgesics

(ii) Cationic detergent

[2 marks]

Solution:

Concept:

- Analgesics are drugs that relieve pain without causing unconsciousness or mental confusion.
- A cationic detergent has its long hydrocarbon chain in the positively charged ion; the counter-ion is negatively charged.

Step 1: Define analgesics and give an example Analgesics reduce or abolish pain without producing unconsciousness, mental confusion, incoordination or paralysis, or another disturbance of the nervous system. Aspirin is a suitable example of a non-narcotic analgesic: it relieves mild pain such as a headache. Thus the defining property is pain relief, rather than the induction of sleep or anaesthesia.

Step 2: Define a cationic detergent and give an example Cationic detergents are generally quaternary ammonium salts of amines, with acetate, chloride or bromide as the anion. The nitrogen bears a positive charge, and the cation contains the long hydrophobic hydrocarbon chain responsible for detergent action. A suitable example is cetyltrimethylammonium bromide, with formula $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+ \text{Br}^-$. Its organic cation is the detergent-active species; bromide is the counter-ion.

Step 3: Conclusion (i) Analgesics relieve pain without causing unconsciousness; example: aspirin.

Quick Tip to Solve: For a cationic detergent, locate the long alkyl chain on the positively charged nitrogen-containing ion; pair the definition with cetyltrimethylammonium bromide.

(ii) Cationic detergents are detergents whose active organic ion is positively charged; example: cetyltrimethylammonium bromide.

Quick Tip to Solve: For a cationic detergent, locate the long alkyl chain on the positively charged nitrogen-containing ion; pair the definition with cetyltrimethylammonium bromide.

25. (a) How can you show that complexes $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionization isomers?

(b) Write the formula of the following complex using IUPAC norms:

Potassium trioxalatochromate (III)

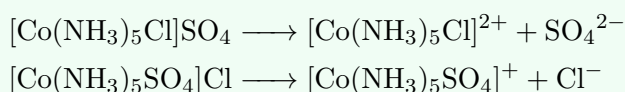
[2 marks]

Solution:

Concept:

- Ionisation isomers have the same overall composition but exchange a coordinated ligand with a counter-ion, so they release different ions in aqueous solution.
- In a complex salt, the sum of the oxidation state of the metal and the charges of its ligands determines the charge of the coordination entity. Oxalato is the bidentate ligand $\text{C}_2\text{O}_4^{2-}$.

Step 1: Identify the ions released by the two complexes In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, chloride is inside the coordination sphere and sulfate is the free counter-ion. In $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$, sulfate is coordinated and chloride is the free counter-ion. Their dissociation is:



Test fresh aqueous solutions for these free counter-ions. The first gives an immediate white precipitate of BaSO_4 with BaCl_2 ; the second gives an immediate white precipitate of AgCl with AgNO_3 . These different ionisation products demonstrate ionisation isomerism.

Step 2: Construct the formula of potassium trioxalatochromate(III) Chromium has oxidation state +3. Three oxalato ligands contribute $3(-2) = -6$, giving the complex ion a charge of $+3 - 6 = -3$. Hence the coordination entity is $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$. Three K^+ counter-ions are required to form the electrically neutral potassium salt.

Step 3: Conclusion (a) The complexes are ionisation isomers because they release SO_4^{2-} and Cl^- , respectively, as confirmed by the precipitate tests. (b) The required formula is $\boxed{\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]}$.

Quick Tip to Solve: Test the ion outside the square brackets; for the formula, combine Cr(III) with three oxalato ions first, then balance the resulting negative charge with potassium ions.

26. (a) How can you explain the absence of an aldehyde group in the pentaacetate of D-glucose?

(b) Name the bases present in RNA. Which one of these is not present in DNA?

[2 marks]

Solution:

Concept:

- D-glucose mainly exists as a cyclic hemiacetal, formed by reaction of its aldehyde group with the hydroxyl group on carbon 5. The hydroxyl group on carbon 1 is the anomeric hydroxyl group.
- RNA and DNA contain nitrogenous bases. Both have adenine, guanine and cytosine; RNA has uracil where DNA has thymine.

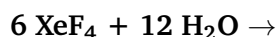
Step 1: Explain why glucose pentaacetate has no free aldehyde group In cyclic D-glucose, the aldehyde carbon becomes the hemiacetal carbon, carbon 1. Acetylation converts all five hydroxyl groups, including the anomeric hydroxyl group at carbon 1, into acetate ester groups. This locks the cyclic structure: the pentaacetate cannot undergo the usual ring opening to produce the free -CHO group. Consequently glucose pentaacetate does not react with hydroxylamine to form an oxime, confirming the absence of a free aldehyde group. Acetylation has blocked the anomeric hydroxyl rather than leaving an open-chain aldehyde available.

Step 2: List the RNA bases and compare them with DNA The four nitrogenous bases present in RNA are adenine, guanine, cytosine and uracil. Adenine and guanine are purine bases; cytosine and uracil are pyrimidine bases. DNA also contains adenine, guanine and cytosine, but its fourth base is thymine. Therefore uracil is the RNA base that is absent from DNA.

Step 3: Conclusion (a) Acetylation of the anomeric hydroxyl locks the cyclic glucose structure, preventing formation of a free aldehyde group. (b) RNA contains adenine, guanine, cytosine and uracil; uracil is absent from DNA.

Quick Tip to Solve: For glucose pentaacetate, focus on the acetylated anomeric hydroxyl at carbon 1; for RNA versus DNA, remember uracil replaces thymine.

27. Write the products of the following reaction:



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

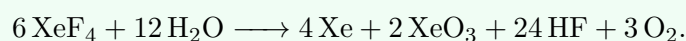
[2 marks]

Solution:

Concept:

- Hydrolysis of xenon tetrafluoride produces xenon, xenon trioxide, hydrogen fluoride and oxygen. A balanced equation must conserve every element.
- Disproportionation occurs when the same element in one oxidation state is simultaneously oxidised to a higher state and reduced to a lower state.

Step 1: Complete and balance the hydrolysis reaction The products are Xe, XeO_3 , HF and O_2 . For the coefficients given in the question, the complete equation is



Quick Tip to Solve: Check xenon in the sequence $+4 \rightarrow 0$ and $+4 \rightarrow +6$; opposite changes from the same starting oxidation state identify disproportionation.

The products contain six xenon atoms in total, twenty-four fluorine atoms and twenty-four hydrogen atoms. Of the twelve oxygen atoms supplied by water, six enter 2XeO_3 and six enter 3O_2 . Thus all four elements are balanced.

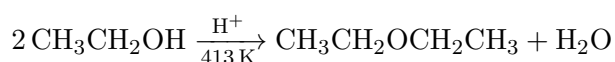
Step 2: Compare the oxidation states of xenon Fluorine has oxidation state -1 , so xenon has oxidation state $+4$ in XeF_4 . Elemental Xe has oxidation state zero, while oxygen has oxidation state -2 in XeO_3 , making xenon $+6$ there. Therefore one portion of Xe(IV) is reduced to Xe(0), and another portion is oxidised to Xe(VI). Both changes involve xenon from the same starting compound, which satisfies the definition of disproportionation. Oxygen is also evolved during this hydrolysis.

Step 3: Conclusion The products are $4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$. Yes, this is a disproportionation reaction: Xe(IV) is simultaneously reduced to Xe(0) and oxidised to Xe(VI).

Quick Tip to Solve: Check xenon in the sequence $+4 \rightarrow 0$ and $+4 \rightarrow +6$; opposite changes from the same starting oxidation state identify disproportionation.

Section C (21 marks)

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



(b) Write the preparation of phenol from cumene.

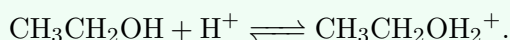
[3 marks]

Solution:

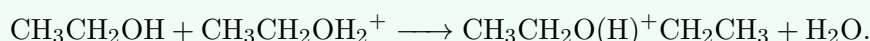
Concept:

- Acid-catalysed intermolecular dehydration of ethanol at 413 K produces ethoxyethane. Protonation converts the poor leaving group $-\text{OH}$ into the good leaving group water.
- An unprotonated ethanol molecule acts as the nucleophile; the final deprotonation regenerates the acid catalyst.
- Cumene is isopropylbenzene, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$. Oxidation followed by acid cleavage of its hydroperoxide gives phenol and acetone.

Step 1: Protonate ethanol in part (a) The oxygen atom of ethanol donates a lone pair to a proton. The resulting ethyloxonium ion contains a water leaving group:



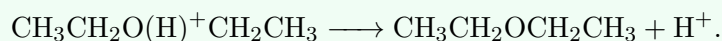
Step 2: Form the carbon–oxygen bond A second, unprotonated ethanol molecule attacks the primary carbon of the ethyloxonium ion through its oxygen lone pair. Water leaves in this nucleophilic substitution step:



The product is protonated diethyl ether.

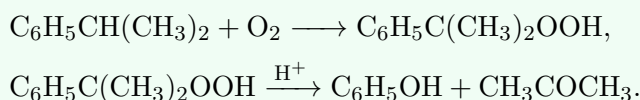
Quick Tip to Solve: For ethanol-to-ether, show water leaving only after protonation and recover H^+ at the end. For cumene-to-phenol, remember both the hydroperoxide intermediate and acetone coproduct.

Step 3: Regenerate the acid catalyst The protonated ether loses a proton to give neutral ethoxyethane:



The intermediates cancel, and the acid catalyst is recovered. Ether formation is favoured at 413 K.

Step 4: Prepare phenol from cumene in part (b) First oxidise cumene with air or oxygen to cumene hydroperoxide. Then cleave the hydroperoxide with dilute acid:



Acid cleavage gives phenol and acetone as coproducts.

Step 5: Conclusion (a) Protonation, nucleophilic attack by a second ethanol molecule and deprotonation produce ethoxyethane and water. (b) Cumene is oxidised to its hydroperoxide, which on acid cleavage gives phenol and acetone.

Quick Tip to Solve: For ethanol-to-ether, show water leaving only after protonation and recover H^+ at the end. For cumene-to-phenol, remember both the hydroperoxide intermediate and acetone coproduct.

OR

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

(i) Sodium phenoxide to o-hydroxybenzoic acid

(ii) Acetone to propene

(iii) Phenol to chlorobenzene

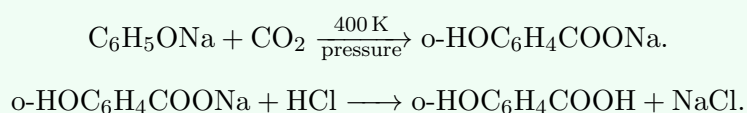
[3 marks]

Solution:

Concept:

- Kolbe's reaction introduces a carboxyl group ortho to the oxygen substituent of sodium phenoxide; acidification gives salicylic acid.
- Reduction converts a ketone into a secondary alcohol, and dehydration of that alcohol gives an alkene.
- Heating phenol with zinc dust removes its oxygen substituent to form benzene. Electrophilic chlorination then gives chlorobenzene.

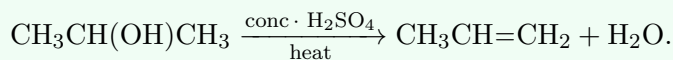
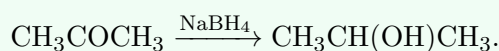
Step 1: Convert sodium phenoxide into salicylic acid Heat sodium phenoxide with carbon dioxide under pressure, at about 400 K, to obtain sodium salicylate. Acidify the salt to obtain o-hydroxybenzoic acid:



The carboxyl group enters mainly at the ortho position; acidification gives salicylic acid.

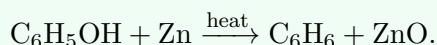
Quick Tip to Solve: Work backwards from each target group: $-\text{COOH}$ needs Kolbe carboxylation, an alkene needs alcohol dehydration, and chlorobenzene needs removal of phenol's oxygen before chlorination.

Step 2: Convert acetone into propene Reduce acetone using NaBH_4 to propan-2-ol. Then heat the alcohol with concentrated sulphuric acid to eliminate water:



The carbon skeleton is unchanged. Loss of water from adjacent carbon atoms forms the double bond.

Step 3: Convert phenol into chlorobenzene First distil phenol with zinc dust. Zinc removes the oxygen of phenol as zinc oxide, producing benzene:



Chlorinate benzene using chlorine in the presence of anhydrous ferric chloride:



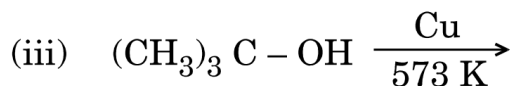
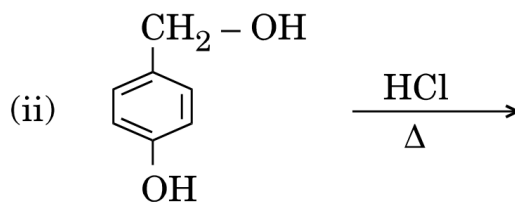
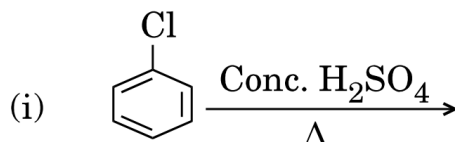
Direct chlorination of phenol retains its hydroxyl group, so remove the oxygen first.

Step 4: Conclusion (i) Use CO_2 under pressure followed by acidification. (ii) Reduce acetone to propan-2-ol and dehydrate it. (iii) Heat phenol with zinc dust to form benzene, then chlorinate with $\text{Cl}_2/\text{FeCl}_3$.

Quick Tip to Solve: Work backwards from each target group: $-\text{COOH}$ needs Kolbe carboxylation, an alkene needs alcohol dehydration, and chlorobenzene needs removal of phenol's oxygen before chlorination.

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

[3 marks]

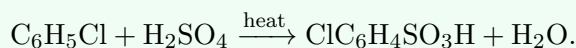


Solution:

Concept:

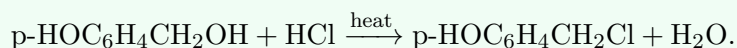
- Chlorine is deactivating but ortho/para-directing in electrophilic aromatic substitution.
- Hydrogen chloride replaces a benzylic alcohol group, but retains a phenolic hydroxyl group.
- Tertiary alcohols over copper at 573 K undergo dehydration rather than dehydrogenation.

Step 1: Sulphonate chlorobenzene in reaction (i) Hot concentrated sulphuric acid introduces $-\text{SO}_3\text{H}$ ortho or para to chlorine:



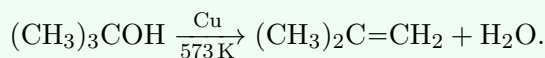
The products are *o*- and *p*-chlorobenzenesulphonic acid, with the less hindered para isomer predominating. Chlorine stays attached to the ring.

Step 2: Replace the benzylic hydroxyl group in reaction (ii) Hydrogen chloride converts the side-chain group $-\text{CH}_2\text{OH}$ into $-\text{CH}_2\text{Cl}$:



The product is 4-(chloromethyl)phenol. The phenolic carbon–oxygen bond has partial double-bond character, so the ring-bound hydroxyl group remains unchanged.

Step 3: Dehydrate the tertiary alcohol in reaction (iii) The hydroxyl-bearing carbon of this tertiary alcohol has no hydrogen, preventing dehydrogenation to a carbonyl compound. It eliminates water instead:

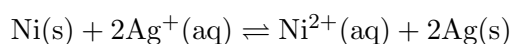


All three methyl groups are equivalent, so only one alkene is formed.

Step 4: Conclusion (i) *o*- and *p*-chlorobenzenesulphonic acids, with the para isomer as the major product; (ii) *p*-HOC₆H₄CH₂Cl, 4-(chloromethyl)phenol; (iii) (CH₃)₂C=CH₂, 2-methylpropene.

Quick Tip to Solve: Identify which site reacts: chlorobenzene undergoes ring sulphonation, the benzylic hydroxyl group is replaced by chloride, and a tertiary alcohol over hot copper gives an alkene.

30. Calculate the maximum work and log K_c for the given reaction at 298 K:



Given:

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

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

[3 marks]

Solution:

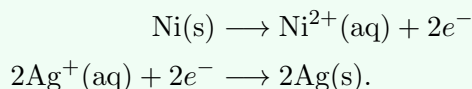
Concept:

- The standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using reduction potentials for both electrodes. The electrode with the higher reduction potential is the cathode.

Quick Tip to Solve: Count two electrons from nickel oxidation, subtract the negative nickel reduction potential, and use the same n in both work and equilibrium calculations.

- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred per reaction and F is the Faraday constant. Maximum electrical work delivered has magnitude $-\Delta_r G^\circ$.
- At equilibrium, $\Delta_r G^\circ = -RT \ln K_c$; hence $\log K_c = nFE_{\text{cell}}^\circ / (2.303RT)$. At 298 K, this is $nE_{\text{cell}}^\circ / 0.0591$.

Step 1: Identify the electrodes and electron transfer Nickel is oxidised, while silver ions are reduced:



Thus $n = 2$. Silver is the cathode and nickel is the anode, so

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

Electrode potentials are not multiplied by the coefficients of the half-reactions.

Step 2: Calculate the maximum work Substitute $n = 2$, $F = 96500 \text{ C mol}^{-1}$ and $E^\circ = 1.05 \text{ V}$:

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

Since $\text{C} \times \text{V} = \text{J}$, the units are those of energy per mole of reaction. The negative Gibbs energy change indicates that the forward reaction is spontaneous under standard conditions. The maximum electrical work obtainable is the positive magnitude $202650 \text{ J mol}^{-1}$.

Step 3: Calculate the equilibrium constant logarithm Combining the Gibbs energy and equilibrium relations gives

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

The large positive logarithm is consistent with strong favouring of products under standard conditions.

Step 4: Conclusion The maximum electrical work delivered is $202.65 \text{ kJ mol}^{-1}$ (equivalently, the thermodynamic work on the cell is $-202.65 \text{ kJ mol}^{-1}$); $\log K_c \approx 35.53$.

Quick Tip to Solve: Count two electrons from nickel oxidation, subtract the negative nickel reduction potential, and use the same n in both work and equilibrium calculations.

31. 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, $k = (2.303/t) \log([A]_0/[A]_t)$, where $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations and t is elapsed time.
- Completion percentage is the amount consumed; the integrated rate law uses the amount remaining.

Quick Tip to Solve: Convert 40 percent completion to 60 percent remaining, then use $\log(10/6) = 1 - \log 6$ to find k directly from the supplied logarithms.

If 40% is consumed, 60% remains; if 90% is consumed, 10% remains.

Step 1: Express the concentration ratio after 80 minutes Take the initial amount as 100 units. After 80 min, 40 units have reacted and 60 units remain. Since the volume is unchanged, the concentration ratio equals the amount ratio:

$$\frac{[A]_0}{[A]_{80}} = \frac{100}{60} = \frac{10}{6}.$$

The fraction 40/100 represents material consumed and must not be substituted for the remaining fraction in the first order equation.

Step 2: Evaluate the rate constant Using the supplied $\log 6 = 0.7782$,

$$\begin{aligned}\log\left(\frac{10}{6}\right) &= \log 10 - \log 6 = 1 - 0.7782 = 0.2218, \\ k &= \frac{2.303}{80}(0.2218) \\ &= 0.006385 \text{ min}^{-1}.\end{aligned}$$

The inverse-minute unit follows from using time in minutes. The logarithm is dimensionless because it is a ratio of like concentrations.

Step 3: Find the time for 90 percent completion When 90% is complete, the remaining amount is 10 units out of the original 100, so the concentration ratio is $100/10 = 10$. Applying the same rate constant,

$$t_{90} = \frac{2.303}{k} \log 10 = \frac{2.303}{0.006385} \approx 360.7 \text{ min}.$$

This is the total time from the beginning of the reaction. It exceeds 80 minutes because progressively smaller concentrations make a first order reaction slower as it proceeds.

Step 4: Conclusion The rate constant is $k = 6.385 \times 10^{-3} \text{ min}^{-1}$. The total time for 90% completion is approximately 360.7 min, or 361 min.

Quick Tip to Solve: Convert 40 percent completion to 60 percent remaining, then use $\log(10/6) = 1 - \log 6$ to find k directly from the supplied logarithms.

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

(i) Neoprene

(ii) Melamine-formaldehyde polymer

(iii) Teflon

[3 marks]

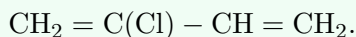
Solution:

Concept:

- A monomer is the small molecule from which a polymer forms. Addition polymerisation opens multiple bonds without eliminating a small molecule.
- Condensation polymers form by reactions of functional groups. Melamine-formaldehyde requires two different monomers, so both names and structures must be given.

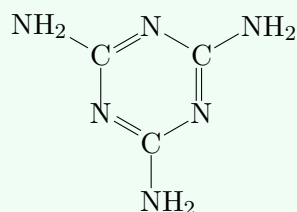
Quick Tip to Solve: Pair neoprene with chloroprene and Teflon with $\text{CF}_2=\text{CF}_2$; give both monomers and melamine's ring for the condensation resin.

Step 1: Monomer of neoprene Neoprene is formed from chloroprene, or 2-chlorobuta-1,3-diene. Its structure is

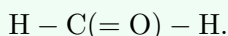


This four-carbon chain has double bonds at positions 1 and 3, with chlorine on carbon 2. Chloroprene undergoes predominantly 1,4-addition to form neoprene; its chlorine substituent distinguishes it from buta-1,3-diene.

Step 2: Monomers of melamine-formaldehyde polymer The two monomers are melamine and formaldehyde. Melamine is 2,4,6-triamino-1,3,5-triazine. Its six-membered ring has alternating carbon and nitrogen atoms, with an amino group on each carbon:

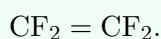


Formaldehyde (methanal) has the structure



Melamine's three amino groups react with formaldehyde to form a cross-linked condensation polymer.

Step 3: Monomer of Teflon Teflon is formed from tetrafluoroethene (tetrafluoroethylene). Its structure is



Each carbon carries two fluorine atoms. Opening the carbon-carbon double bond gives the repeating unit $-\text{CF}_2 - \text{CF}_2-$, with no small molecule eliminated.

Step 4: Conclusion (i) Neoprene: chloroprene, $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$. (ii) Melamine-formaldehyde: melamine (ring shown above) and formaldehyde, $\text{H} - \text{C}(=\text{O}) - \text{H}$. (iii) Teflon: tetrafluoroethene, $\text{CF}_2 = \text{CF}_2$.

Quick Tip to Solve: Pair neoprene with chloroprene and Teflon with $\text{CF}_2=\text{CF}_2$; give both monomers and melamine's ring for the condensation resin.

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

Solution:

Concept:

- A sol is a colloidal dispersion of a solid dispersed phase in a liquid dispersion medium. The terms lyophilic and lyophobic describe the affinity of the dispersed phase for that medium.
- Colloidal stability can arise from electrical charge on particles and from solvation: surrounding solvent molecules form a protective layer around the particles.

Quick Tip to Solve: Compare the two stabilising factors: lyophobic sols rely mainly on charge, while lyophilic sols have charge plus a protective solvent layer.

Step 1: Define a lyophobic sol and give an example A lyophobic sol is a colloidal sol in which the dispersed phase has little or no affinity for the dispersion medium. Such sols do not form simply by mixing the solid with the solvent and require special preparation methods. An example is a gold sol in water; arsenic sulphide sol in water is another example. Their stability is mainly due to the electrical charge on the dispersed particles.

Step 2: Define a lyophilic sol and give an example A lyophilic sol is a colloidal sol in which the dispersed phase has a strong affinity for the dispersion medium. It can generally be prepared by directly bringing the substance into contact with a suitable solvent. Examples are starch sol in water and gelatin sol in water. The dispersed particles are extensively solvated, that is, surrounded by molecules of the dispersion medium.

Step 3: Explain the difference in coagulation Lyophilic particles are stabilised by both their charge and their protective solvation layer. Coagulation therefore requires removal of the solvation layer as well as neutralisation of the charge. A comparatively large amount of electrolyte, often together with a suitable solvent that removes the solvation layer, is needed. Lyophobic particles have little solvation and depend mainly on charge for stability; a relatively small amount of a suitable electrolyte can neutralise their charge and coagulate them.

Step 4: Conclusion Gold sol in water is lyophobic, whereas starch sol in water is lyophilic. Coagulation of a lyophilic sol is more difficult because both its charge and its solvation layer must be overcome.

Quick Tip to Solve: Compare the two stabilising factors: lyophobic sols rely mainly on charge, while lyophilic sols have charge plus a protective solvent layer.

OR

33(b). Define the following terms:

(i) Shape-selective catalysis

(ii) Kraft temperature

(iii) Peptization

[3 marks]

Solution:

Concept:

- Catalytic selectivity can depend on the size and shape of the reactant and product molecules relative to the pores of a solid catalyst.
- Micelles form from associated surfactant molecules only under suitable concentration and temperature conditions; peptization instead converts an existing precipitate into a colloidal sol.

Step 1: (i) Shape-selective catalysis Shape-selective catalysis is catalysis in which the reaction depends on the pore structure of the catalyst and on the size and shape of the reactant and product molecules. Only molecules of suitable dimensions can enter the pores, react at the catalytic sites, or leave the pores as products. Zeolites, which have a porous aluminosilicate framework, are typical shape-selective catalysts. Thus their pore dimensions help select which reaction can occur.

Step 2: (ii) Kraft temperature The Kraft temperature, also called the Krafft temperature and denoted

Quick Tip to Solve: For Kraft temperature, state the temperature threshold and remember that the surfactant concentration must also exceed its CMC.

by T_K , is the minimum temperature above which a surfactant can form micelles in solution when its concentration exceeds the critical micelle concentration (CMC). Below this temperature the surfactant's solubility is insufficient to reach the concentration required for micelle formation. Both the temperature condition and the concentration condition must therefore be satisfied for an associated colloid to form.

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 of the electrolyte are adsorbed on the precipitate particles and impart the same charge to them. Mutual repulsion then separates the particles and disperses them as a sol. For example, freshly precipitated $\text{Fe}(\text{OH})_3$ can be peptized using a small amount of FeCl_3 solution.

Step 4: Conclusion Shape-selective catalysis depends on pore and molecular dimensions; Kraft temperature is the threshold temperature for micelle formation at a suitable concentration; peptization converts a fresh precipitate into a sol using a small amount of electrolyte.

Quick Tip to Solve: For Kraft temperature, state the temperature threshold and remember that the surfactant concentration must also exceed its CMC.

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

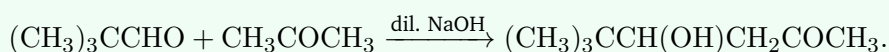
[3 marks]

Solution:

Concept:

- In $(\text{CH}_3)_3\text{CCHO}$, the carbon next to the aldehyde group has no hydrogen. This aldehyde therefore cannot supply an enolate for an aldol reaction, but its carbonyl group can accept attack by the acetone enolate.
- HCN adds across a carbonyl group to form a cyanohydrin. An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali, forming an alcohol and a carboxylate salt.

Step 1: (i) Reaction with acetone and dilute NaOH Acetone has alpha hydrogens, so dilute alkali produces its enolate. This nucleophile attacks the carbonyl carbon of $(\text{CH}_3)_3\text{CCHO}$. Protonation of the resulting alkoxide gives the crossed aldol addition product, a beta-hydroxy ketone:



The original aldehyde carbonyl carbon becomes the carbon bearing the hydroxyl group, while the acetone carbonyl group remains intact. No heating is specified, so the aldol addition product is written.

Step 2: (ii) Reaction with HCN Cyanide attacks the aldehyde carbonyl carbon, followed by protonation

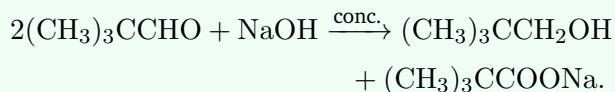
Quick Tip to Solve: Count alpha hydrogens first: acetone supplies the enolate in (i), while the aldehyde's lack of alpha hydrogens explains Cannizzaro reaction in (iii).

of oxygen. The product is the cyanohydrin:



Thus the former carbonyl carbon now carries both OH and CN, with its original hydrogen retained.

Step 3: (iii) Reaction with concentrated NaOH The absence of an alpha hydrogen enables Cannizzaro disproportionation. One aldehyde molecule is reduced to the primary alcohol and another is oxidised to the sodium carboxylate:



The products are neopentyl alcohol and sodium 2,2-dimethylpropanoate. In the alkaline reaction medium the oxidised product is the salt, rather than the free carboxylic acid.

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

Quick Tip to Solve: Count alpha hydrogens first: acetone supplies the enolate in (i), while the aldehyde's lack of alpha hydrogens explains Cannizzaro reaction in (iii).

Section D (15 marks)

35(a). Give reasons:

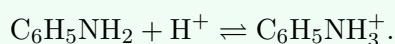
- (i) Although $-\text{NH}_2$ group is o/p directing in electrophilic substitution reactions, yet aniline, on nitration gives good yield of m-nitroaniline.
- (ii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.
- (iii) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. [3 marks]

Solution:

Concept:

- The directing effect of an amino group depends on whether it is free or protonated. The free $-\text{NH}_2$ group donates its lone pair to the benzene ring, whereas $-\text{NH}_3^+$ is electron withdrawing and meta directing.
- Basicity in water depends jointly on the electron-donating inductive effect of alkyl groups and the hydration and stability of the conjugate acid.
- Alkyl halides undergo nucleophilic substitution with ammonia and with the amines subsequently formed, allowing repeated alkylation.

Step 1: (i) Explain nitration in strongly acidic medium Nitration uses concentrated nitric acid and sulphuric acid. In this strongly acidic mixture, aniline is protonated:



The anilinium ion has no free nitrogen lone pair available for donation to the ring. Its positively

Quick Tip to Solve: For aqueous amine basicity, compare hydration as well as the inductive effect; for nitration, first identify whether nitrogen is protonated.

charged group withdraws electron density and directs incoming electrophiles mainly to the meta position. Therefore a substantial amount of meta-nitroaniline is obtained, even though unprotonated aniline is ortho/para directing.

Step 2: (ii) Compare basicity in water Dimethylamine accepts a proton to form $(\text{CH}_3)_2\text{NH}_2^+$, whereas trimethylamine forms $(\text{CH}_3)_3\text{NH}^+$. Although the third methyl group strengthens the electron-donating inductive effect, the bulky groups in the tertiary ammonium ion hinder hydration. The secondary ammonium ion is better hydrated and has two N–H bonds available for hydrogen bonding with water, compared with one in the tertiary ion. The combined inductive and solvation effects favour dimethylamine, so it is more basic in aqueous solution.

Step 3: (iii) Explain the product mixture from ammonolysis The primary amine first produced is itself a nucleophile and reacts further with unreacted alkyl halide. Successive alkylation gives secondary amines, tertiary amines and finally quaternary ammonium salts:



Thus ammonolysis usually gives a mixture that is difficult to separate, rather than a pure primary amine. A large excess of ammonia increases the proportion of the primary amine but does not make the method generally suitable for obtaining it pure.

Step 4: Conclusion (i) Protonation makes aniline meta directing in the nitrating mixture. (ii) Better hydration of its conjugate acid makes dimethylamine more basic in water. (iii) Repeated alkylation makes ammonolysis yield a mixture of amines.

Quick Tip to Solve: For aqueous amine basicity, compare hydration as well as the inductive effect; for nitration, first identify whether nitrogen is protonated.

35(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

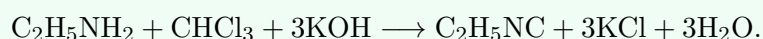
[2 marks]

Solution:

Concept:

- The carbylamine test is given by primary amines only: heating with chloroform and alcoholic potassium hydroxide forms a foul-smelling isocyanide.
- Primary aliphatic amines give unstable diazonium species with nitrous acid, whereas aniline gives a diazonium salt stable at 273–278 K.

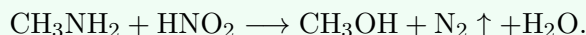
Step 1: (i) Distinguish ethylamine from diethylamine Heat separate samples with chloroform and alcoholic KOH. Ethylamine, a primary amine, gives the characteristic offensive odour of ethyl isocyanide:



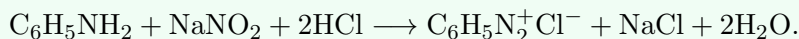
Diethylamine is secondary and gives no carbylamine reaction, hence no isocyanide odour under this test.

Quick Tip to Solve: Use the carbylamine test to separate primary from secondary amines; use cold nitrous acid to distinguish primary aliphatic from aromatic amines.

Step 2: (ii) Distinguish aniline from methylamine Treat both samples with sodium nitrite and dilute hydrochloric acid at 273–278 K, generating nitrous acid in situ. Methylamine liberates nitrogen with brisk effervescence and forms methanol:



Aniline forms benzenediazonium chloride without immediate nitrogen evolution at this temperature:



The cold diazonium solution can additionally be coupled with phenol in alkaline medium to give a coloured azo dye.

Step 3: Conclusion Ethylamine gives a positive carbylamine test; diethylamine does not. With cold nitrous acid, methylamine evolves nitrogen, whereas aniline forms a stable diazonium salt.

Quick Tip to Solve: Use the carbylamine test to separate primary from secondary amines; use cold nitrous acid to distinguish primary aliphatic from aromatic amines.

OR

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



[1 mark]

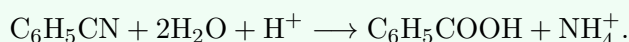
Solution:

Concept:

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

Step 1: Identify A by cyanation CuCN replaces $-\text{N}_2^+$ by $-\text{C} \equiv \text{N}$. Therefore A is benzonitrile, with structure $\text{C}_6\text{H}_5 - \text{C} \equiv \text{N}$. The benzene ring is preserved and the carbon of cyanide becomes attached to it.

Step 2: Identify B by acidic hydrolysis Hydrolysis of the nitrile gives benzoic acid:

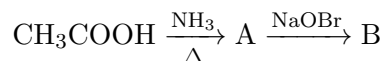


The nitrile carbon is retained as the carboxyl carbon, so B has the structure $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{OH}$.

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

Quick Tip to Solve: Track the cyanide carbon: Sandmeyer cyanation adds it, and hydrolysis retains it as the carboxyl carbon.

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



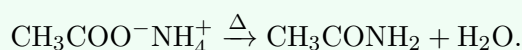
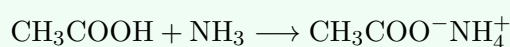
[1 mark]

Solution:

Concept:

- Acetic acid and ammonia first form ammonium acetate; heating this salt eliminates water to form an amide.
- Hofmann bromamide degradation with sodium hypobromite converts RCONH_2 into RNH_2 , losing the carbonyl carbon.

Step 1: Identify A after heating with ammonia Acetic acid forms ammonium acetate with ammonia, and heating gives acetamide:



Thus A has the structure $\text{CH}_3 - \text{C}(=\text{O}) - \text{NH}_2$.

Step 2: Identify B after Hofmann degradation Sodium hypobromite converts acetamide into methylamine, containing one fewer carbon atom. The carbonyl carbon is removed, while the methyl group remains bonded to nitrogen; therefore B is $\text{CH}_3 - \text{NH}_2$.

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

Quick Tip to Solve: In Hofmann degradation remove the carbonyl carbon from the amide; acetamide with two carbons gives methylamine with one.

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

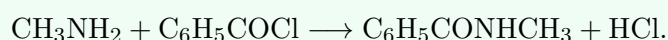
[2 marks]

Solution:

Concept:

- Primary amines undergo benzoylation with benzoyl chloride: the acyl group $\text{C}_6\text{H}_5\text{CO}-$ replaces a hydrogen on nitrogen.
- An amide derived from benzoic acid is named as a benzamide; an alkyl group bonded to nitrogen is indicated by the prefix *N*-.

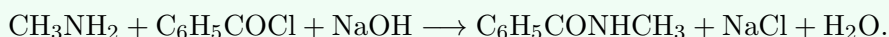
Step 1: Write the benzoylation reaction Methylamine attacks the carbonyl carbon of benzoyl chloride. Chloride is displaced and one nitrogen hydrogen is removed, giving the amide:



The product has the structure $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH} - \text{CH}_3$, with the benzoyl group attached to

Quick Tip to Solve: Write the benzoyl fragment as $\text{C}_6\text{H}_5\text{CO}$ and attach it to the amine nitrogen; use *N*-methyl in the name because CH_3 is bonded to nitrogen.

nitrogen. In the usual alkaline conditions, NaOH neutralises the liberated acid; the net equation is



Step 2: Name the product The parent amide is benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$. In the product, one hydrogen attached to its nitrogen is replaced by a methyl group. The locant *N* shows that this methyl group is on the amide nitrogen, rather than on the benzene ring. Hence the IUPAC name is *N*-methylbenzamide.

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

Quick Tip to Solve: Write the benzoyl fragment as $\text{C}_6\text{H}_5\text{CO}$ and attach it to the amine nitrogen; use *N*-methyl in the name because CH_3 is bonded to nitrogen.

35(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:

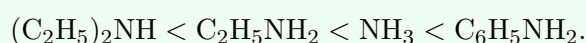
Concept:

- The base dissociation constant K_b measures the strength of a base in water; $pK_b = -\log_{10} K_b$, so stronger bases have smaller pK_b .
- Ethyl groups increase electron density on nitrogen by the positive inductive effect. In aniline, the nitrogen lone pair is delocalised into the benzene ring.

Step 1: Compare the basic strengths In aqueous solution diethylamine is more basic than ethylamine because its two ethyl groups increase electron density on nitrogen, while its conjugate acid remains effectively hydrated. Ethylamine is more basic than ammonia due to its electron-releasing ethyl group. Aniline is weaker than ammonia because resonance reduces the availability of its nitrogen lone pair for accepting a proton.

Step 2: Reverse the order for pK_b The basic-strength order is $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$. As pK_b decreases when basic strength increases, the requested increasing order starts with diethylamine.

Step 3: Conclusion Increasing pK_b :



Quick Tip to Solve: First rank basic strengths, then reverse the inequality to rank their pK_b values.

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

Solution:

Concept:

- Osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is molar concentration, R the gas constant and T absolute temperature.
- For $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$, one formula unit produces two ions. If the fraction dissociated is α , then $i = 1 + \alpha$.

Step 1: Calculate the concentration and temperature The amount of sodium chloride in one litre is

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

Therefore $C = 0.100 \text{ mol L}^{-1}$, and the absolute temperature is $T = 27 + 273 = 300 \text{ K}$. The concentration used here refers to the dissolved NaCl formula units before counting the extra particles formed by dissociation.

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

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

The measured pressure is larger because dissociation increases the number of solute particles. Thus

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

The litres, moles and kelvins cancel in the denominator, leaving atm, so this ratio is dimensionless.

Step 3: Relate the particle count to dissociation Start with one mole of NaCl formula units. At equilibrium, $(1 - \alpha)$ mole remains undissociated, while α mole each of sodium and chloride ions is formed. The total particle amount is $(1 - \alpha) + \alpha + \alpha = 1 + \alpha$ mole. Hence

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

This is between zero and one, as required for a physically meaningful fraction.

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

Quick Tip to Solve: For a solute forming two ions, calculate i from the observed property and use $\alpha = i - 1$.

36(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 gas solubility and pressure at constant temperature: $p = K_H x$, where p is gas partial pressure, x its mole fraction in solution and K_H the Henry constant.
- A decrease in external pressure reduces the equilibrium solubility of a gas in a liquid.

Step 1: State Henry's law At a fixed temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas above the liquid. In mole-fraction form this is $p = K_H x$. Thus, increasing the gas pressure increases the amount of gas that can dissolve in the liquid.

Step 2: Explain helium dilution for scuba divers At the high pressure underwater, more nitrogen from compressed air dissolves in a diver's blood and tissues. During ascent, the pressure falls and dissolved nitrogen can emerge as bubbles. These bubbles cause the painful and dangerous condition called the bends. Diluting air with helium reduces the nitrogen partial pressure and hence the amount of nitrogen dissolved. Helium is also much less soluble in blood than nitrogen, so its use reduces the risk of decompression sickness.

Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature. Helium dilution lowers nitrogen uptake and thereby reduces the formation of nitrogen bubbles during ascent.

Quick Tip to Solve: Connect the diver's depth to pressure, then pressure to nitrogen solubility and bubble formation on ascent.

OR

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

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

[3 marks]

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = i K_f m$, where K_f is the cryoscopic constant, m is solute molality and i the van't Hoff factor.
- Fluoroacetic acid dissociates into two ions: $\text{FCH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{FCH}_2\text{COO}^-$. Therefore $i = 1 + \alpha$, with α the fraction dissociated.

Step 1: Find the molality The number of moles of fluoroacetic acid is

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

Quick Tip to Solve: Convert solvent mass to kilograms before calculating molality; for this acid, α equals $i - 1$.

The mass of water is $500\text{ g} = 0.500\text{ kg}$. Therefore

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

Molality uses the mass of the solvent, not the mass or volume of the whole solution.

Step 2: Calculate the van't Hoff factor A freezing-point change of 1°C is a temperature interval of 1 K. For an undissociated solute, the depression would be

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

Hence the observed particle factor is

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

Its value slightly above one shows that the acid dissociates only partially.

Step 3: Convert the particle factor to dissociation For each initial mole of acid, dissociation leaves $(1 - \alpha)$ mole of acid molecules and produces α mole of hydrogen ions and α mole of fluoroacetate ions. Thus the total is $1 + \alpha$ mole of particles, giving

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

Multiplying this fraction by 100 gives the percentage dissociation.

Step 4: Conclusion The degree of dissociation of fluoroacetic acid is $\alpha \approx 0.0753$, or approximately 7.53%.

Quick Tip to Solve: Convert solvent mass to kilograms before calculating molality; for this acid, alpha equals $i - 1$.

36(b). Give reasons:

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

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

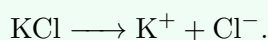
[2 marks]

Solution:

Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent's ebullioscopic constant and m the molality.
- Osmosis transfers water through a selectively permeable membrane from a dilute solution to a more concentrated solution. A concentrated salt solution causes microbial cells to lose water.

Step 1: Compare the particles produced by the solutes (i) In water, KCl dissociates into two ions:



Quick Tip to Solve: For equal dilute concentrations, compare the van't Hoff factors; for salting, identify the hypertonic surroundings and the outward flow of cellular water.

Glucose is a non-electrolyte and remains as molecules. Thus, in the dilute-solution comparison at equal stated concentration, KCl produces more dissolved particles: its van't Hoff factor is approximately 2, whereas that of glucose is 1. Its greater particle concentration causes a larger decrease in the vapour pressure of water. A higher temperature is therefore required for its vapour pressure to equal atmospheric pressure, giving a greater boiling-point elevation.

Step 2: Explain preservation by salting (ii) Adding salt creates a concentrated, hypertonic environment around microorganisms on the meat. Water passes out of their cells by osmosis (exosmosis), dehydrating them and causing plasmolysis. The resulting lack of available water inhibits microbial growth and activity, so decomposition is slowed and the meat remains preserved for longer.

Step 3: Conclusion (i) The 0.1 M KCl solution has a higher boiling point because dissociation produces more solute particles than glucose. (ii) Salting preserves meat by drawing water out of microorganisms and inhibiting their growth.

Quick Tip to Solve: For equal dilute concentrations, compare the van't Hoff factors; for salting, identify the hypertonic surroundings and the outward flow of cellular water.

37(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 required to remove or involve valence electrons; very high ionisation enthalpy strongly opposes chemical bonding.
- An oxoacid is stronger when electron withdrawal and stabilisation of its conjugate base make release of a proton easier.
- Oxygen readily forms a strong multiple bond, while sulphur favours single bonds and catenation; molecular size and intermolecular forces affect the physical state.

Step 1: Compare helium with xenon (i) Helium has the compact, completely filled $1s^2$ shell and exceptionally high ionisation enthalpy. Its electrons are held so strongly that even highly electronegative elements do not readily involve them in bonding. Xenon has a larger atomic size and much lower ionisation enthalpy, making its valence electrons more accessible. Consequently, xenon forms compounds with strong oxidising elements such as fluorine and oxygen, whereas helium does not form analogous ordinary compounds.

Step 2: Compare the two chlorine oxoacids (ii) In HClO_4 , three additional oxygen atoms withdraw electron density from the O–H group, making proton release easier than in HOCl . The conjugate base ClO_4^- is strongly stabilised by delocalisation of its negative charge over the oxygen atoms. ClO^- , the conjugate base of HOCl , lacks this comparable delocalisation. Both effects favour much greater acid strength for perchloric acid.

Step 3: Explain molecular form and physical state (iii) Small oxygen atoms have effective $2p-2p$

Quick Tip to Solve: Link noble-gas reactivity to ionisation enthalpy, oxoacid strength to extra oxygen atoms, and sulphur's solid state to its larger S_8 molecules.

sideways overlap and form the strong O=O double bond, so oxygen exists as diatomic O₂. Sulphur's larger 3p orbitals overlap less effectively sideways, so sulphur favours S–S single bonds and catenation, forming polyatomic S₈ rings. The larger, more polarisable S₈ molecules have stronger intermolecular dispersion forces and form a solid at room temperature; small O₂ molecules have weaker attractions and are gaseous.

Step 4: Conclusion Helium's tightly held electrons prevent xenon-like compound formation; electron withdrawal and conjugate-base stabilisation make HClO₄ stronger than HOCl; strong oxygen multiple bonding gives gaseous O₂, while sulphur catenation gives solid S₈.

Quick Tip to Solve: Link noble-gas reactivity to ionisation enthalpy, oxoacid strength to extra oxygen atoms, and sulphur's solid state to its larger S₈ molecules.

37(b). Write one reaction as an example of each, to show that conc. H₂SO₄ acts as

(i) an oxidising agent, and

(ii) a dehydrating agent.

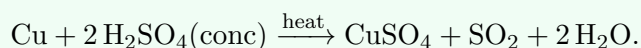
[2 marks]

Solution:

Concept:

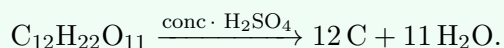
- An oxidising agent accepts electrons and is itself reduced. In concentrated H₂SO₄, sulphur in oxidation state +6 can be reduced to +4 in SO₂.
- A dehydrating agent removes the elements of water from a substance. Concentrated sulphuric acid can remove water from carbohydrates.

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



Copper changes from oxidation state 0 to +2 and is oxidised. Sulphur in the acid changes from +6 to +4 in SO₂, accepting the electrons lost by copper. Thus the concentrated acid acts as an oxidising agent. One sulphur atom remains in sulphate, while the other is reduced; the equation balances both atoms and electron transfer.

Step 2: Show the dehydrating action with sucrose (ii) Concentrated sulphuric acid removes the elements of water from sucrose, leaving a black mass of carbon:



The 22 hydrogen atoms and 11 oxygen atoms are removed in the ratio required for 11 water molecules. The carbon residue demonstrates dehydration; the acid is written over the arrow to indicate its role as the dehydrating agent.

Step 3: Conclusion Oxidising action: hot concentrated H₂SO₄ oxidises copper to CuSO₄ and is reduced to SO₂. Dehydrating action: it removes water from sucrose to leave carbon.

Quick Tip to Solve: For oxidising action, show sulphur changing from +6 to +4; for dehydration, check that hydrogen and oxygen leave in the 2 : 1 ratio of water.

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

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

[1 mark]

Solution:

Concept:

- Hydration enthalpy is the enthalpy change when gaseous ions become surrounded by water molecules. Ion-dipole attractions release energy during hydration.
- For ions of the same charge, smaller ionic radius gives greater charge density and stronger attraction to the polar water molecules.

Step 1: Compare charge and ionic size Both F^- and Cl^- carry a single negative charge, but F^- has a smaller ionic radius. The same charge is concentrated over a smaller ion, giving fluoride greater charge density.

Step 2: Relate stronger attraction to hydration energy Water molecules orient their partially positive hydrogen ends towards an anion. Their ion-dipole attraction to the smaller F^- ion is stronger, so hydration releases more energy than for Cl^- . The printed comparison refers to the magnitude of the released hydration enthalpy; with the usual signed convention, fluoride's hydration enthalpy is more negative.

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

Quick Tip to Solve: For equal ionic charges, compare radii: the smaller ion has stronger hydration and a more negative hydration enthalpy.

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

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

[1 mark]

Solution:

Concept:

- A reducing agent is oxidised by donating electrons, whereas an oxidising agent is reduced by accepting electrons.
- In group 16, the stability of oxidation state +6 decreases and that of +4 increases on descending the group, owing to the inert-pair effect.

Step 1: Explain the reducing behaviour of sulphur dioxide Sulphur is in oxidation state +4 in SO_2 . For sulphur, the higher +6 state is relatively stable, so SO_2 can readily undergo oxidation to sulphate or sulphuric acid. By giving electrons to another species during this change, it acts as a reducing agent.

Step 2: Explain the oxidising behaviour of tellurium dioxide Tellurium is also in oxidation state +4 in TeO_2 . Down the group, the inert-pair effect makes the +6 state less accessible and the +4 state more stable. Consequently, TeO_2 does not readily undergo the oxidation characteristic of SO_2 ; it

Quick Tip to Solve: Start with +4 in both dioxides, then apply the down-group decrease in stability of +6 to decide which oxide can donate electrons readily.

can instead accept electrons and be reduced to a lower oxidation state, thereby oxidising the other reactant.

Step 3: Conclusion SO_2 is reducing because sulphur(IV) is readily oxidised to sulphur(VI); TeO_2 is oxidising because tellurium(IV) resists oxidation to +6 and can undergo reduction instead.

Quick Tip to Solve: Start with +4 in both dioxides, then apply the down-group decrease in stability of +6 to decide which oxide can donate electrons readily.

37(b). Write the reaction of F_2 with water. Why does I_2 not react with water?

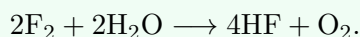
[2 marks]

Solution:

Concept:

- Fluorine is the strongest oxidising halogen: it can oxidise water to oxygen while being reduced to fluoride in hydrogen fluoride.
- A halogen reacts spontaneously with water only when its oxidising strength makes oxidation of water thermodynamically favourable.

Step 1: Write the reaction of fluorine with water Fluorine reacts vigorously with water, forming hydrogen fluoride and liberating oxygen. The balanced equation is



The equation conserves four fluorine atoms, four hydrogen atoms and two oxygen atoms. Fluorine changes from oxidation state 0 to -1 , whereas oxygen in water changes from -2 to 0.

Step 2: Explain the behaviour of iodine Iodine has much weaker oxidising power than fluorine. It cannot oxidise water to oxygen under ordinary conditions: the corresponding oxidation of water by I_2 is thermodynamically unfavourable. Thus iodine does not undergo the water-oxidation reaction shown above; the driving force available for fluorine is absent for iodine.

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

Quick Tip to Solve: Balance fluorine's reaction by writing four HF molecules, then use two water molecules to supply their hydrogen atoms.

37(c). Draw the structure of XeF_2 .

[1 mark]

Solution:

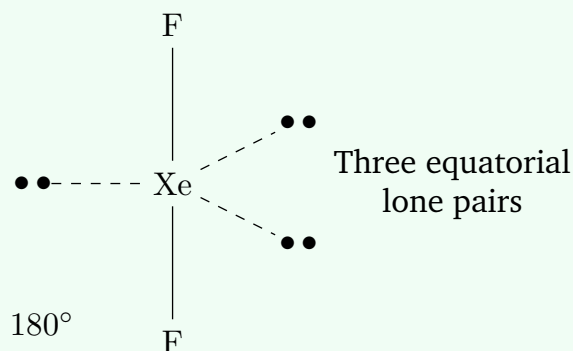
Concept:

- In VSEPR theory, XeF_2 has two bonding pairs and three lone pairs on xenon, so it is an AX_2E_3 species.
- Five electron pairs have a trigonal bipyramidal arrangement; the three lone pairs occupy equatorial positions to minimise repulsion.

Quick Tip to Solve: For XeF_2 , count two bond pairs plus three lone pairs, then place all three lone pairs equatorially to obtain a linear molecule.

Step 1: Count the electron pairs around xenon Xenon has eight valence electrons. Formation of two Xe–F bonds leaves three lone pairs on the central xenon atom. Thus the central atom has five electron-pair regions, traditionally described by sp^3d hybridisation at this level.

Step 2: Place the fluorine atoms in the axial positions The three lone pairs occupy all three equatorial positions. The two Xe–F bonds occupy the opposite axial positions, giving the following structure. Only the atom positions determine the molecular shape; the lone pairs explain why the bonds remain opposite each other.



Linear XeF₂: two axial bonds and three equatorial lone pairs on xenon.

Step 3: Conclusion XeF₂ is linear, with $\angle \text{F} - \text{Xe} - \text{F} = 180^\circ$; xenon has three equatorial lone pairs.

Quick Tip to Solve: For XeF₂, count two bond pairs plus three lone pairs, then place all three lone pairs equatorially to obtain a linear molecule.