CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-S-2 - Compartment

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

(ii) This question paper is divided into **five** sections – **Section A, B, C, D and E**.

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

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

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

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

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

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

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

(x) Use of calculator is not allowed.

Section A (16 marks)

Questions no. ***1*** *to* ***16*** *are Multiple Choice type Questions, carrying* ***1*** *mark each.* $16 \times 1 = 16$

1. When phenyl methyl ether is heated with HI, it produces : [1 mark]

(A) Methyl chloride and Iodobenzene

(B) Benzene and Methanol

(C) Iodobenzene and Methanol

(D) Phenol and Methyl iodide

Correct Answer: (D) Phenol and Methyl iodide

Solution:

Concept:

- Ether cleavage by HI begins with protonation of oxygen, making the ether susceptible to nucleophilic attack.
- An aryl carbon bonded to oxygen is sp^2-hybridised; the methyl carbon is accessible to an S_N2 attack.

Step 1: Protonate the ether Phenyl methyl ether is anisole, $C_6H_5OCH_3$. Its oxygen accepts a proton from HI. The resulting oxonium ion has a good leaving group, so iodide attacks the methyl group and breaks the methyl–oxygen bond.

Step 2: Identify both products

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I.$$

The aryl–oxygen bond is retained because ordinary substitution at the phenyl carbon is unfavourable. Thus iodobenzene is not formed. Methanol is also not the cleavage product, and methyl chloride cannot form when the reagent supplies iodide, not chloride.

Step 3: Conclusion The products are phenol and methyl iodide. Hence, the correct option is (D).

Quick Tip to Solve: In an aryl methyl ether, break the methyl–oxygen bond with HI; retain the aryl–oxygen bond.

2. Out of the following organic compounds, the one which will react with Lucas reagent at room temperature is : [1 mark]

(A) CH_2=CH-CH_2OH

(B) $CH_3CH_2CH_2OH$

(C) $C_6H_5CH_2OH$

(D) $(CH_3)_3COH$

Correct Answer: Intended (D); (A) and (C) also react at room temperature, so the printed question has multiple defensible choices.

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous $ZnCl_2$; formation of an insoluble alkyl chloride produces turbidity.
- Tertiary carbocations are stabilised by alkyl groups; allylic and benzylic carbocations are stabilised by resonance.

Step 1: Apply the usual Lucas classification $(CH_3)_3COH$ is a tertiary alcohol. It forms the stable tert-butyl carbocation readily and hence gives tert-butyl chloride and immediate turbidity at room temperature. Ordinary primary propan-1-ol, option (B), does not give the usual room-temperature Lucas test.

Step 2: Check the resonance exceptions Option (A), allyl alcohol, and option (C), benzyl alcohol, are primary alcohols but are exceptions to the simple primary/secondary/tertiary rule. Their allylic and benzylic intermediates are resonance stabilised, so they too can react with Lucas reagent at room temperature. Therefore the wording does not specify a unique chemically valid choice. The expected choice from the usual tertiary-alcohol classification is (D), but excluding both resonance-stabilised alcohols would be incorrect.

Step 3: Conclusion Option (D), tert-butanol, is the intended immediate Lucas-test answer; (A) and (C) can also react at room temperature, so the printed single-choice question is not unique.

Quick Tip to Solve: Before applying the Lucas rule, check whether a primary alcohol is allylic or benzylic.

3. Which of the following amines has the highest boiling point ? [1 mark]

(A) 2,2-Dimethyl propanamine

(B) 3-Methylbutanamine

(C) 2-Methylbutanamine

(D) Pentanamine

Correct Answer: (D) Pentanamine

Solution:

Concept:

- Primary amines can form intermolecular hydrogen bonds through their $N-H$ bonds.

- For isomeric amines with the same functional group, branching reduces surface contact and weakens dispersion attractions.

Step 1: Compare the functional groups All four choices are primary amines with five carbon atoms. They have the same molecular formula and comparable ability to form intermolecular hydrogen bonds. Thus neither molecular mass nor the number of N–H bonds distinguishes the candidates.

Step 2: Compare chain shapes Pentanamine has an unbranched carbon chain and the greatest effective surface contact between neighbouring molecules. Its dispersion attractions are therefore strongest, requiring more energy for vaporisation. Options (A), (B) and (C) are branched isomers, so their compact shapes reduce contact and lower their boiling points relative to the straight-chain amine.

Step 3: Conclusion Pentanamine has the highest boiling point. Hence, the correct option is (D).

Quick Tip to Solve: For isomeric primary amines, first hold hydrogen bonding constant, then compare carbon-chain branching.

4. A compound $CaCl_2.6H_2O$ undergoes complete dissociation in water. The Van't Hoff factor (i) is : [1 mark]

(A) 9

(B) 6

(C) 4

(D) 3

Correct Answer: (D) 3

Solution:

Concept:

- The van't Hoff factor i counts the solute particles produced per formula unit dissolved, for complete dissociation.
- Water of crystallisation joins the solvent on dissolution and is not counted as an additional solute particle.

Step 1: Write complete dissociation

$$CaCl_2 \cdot 6H_2O \longrightarrow Ca^{2+}(aq) + 2Cl^{-}(aq) + 6H_2O(l).$$

One formula unit yields one calcium ion and two chloride ions. The six water molecules become part of the aqueous solvent.

Step 2: Count solute particles For complete dissociation, each dissolved formula unit produces $1 + 2 = 3$ solute particles, so $i = 3$. Counting the six solvent-water molecules would incorrectly give 9. The values 6 and 4 also fail to represent the actual number of dissolved ions per formula unit.

Step 3: Conclusion The van't Hoff factor is $i = 3$. Hence, the correct option is (D).

Quick Tip to Solve: Ignore water of crystallisation when counting solute ions: calcium chloride gives one cation and two anions.

5. Which one of the following halides contains $C_{sp^2} - X$ bond ? [1 mark]

(A) Alkyl halide

(B) Allyl halide

(C) Benzyl halide

(D) Vinyl halide

Correct Answer: (D) Vinyl halide

Solution:

Concept:

- The hybridisation in a carbon–halogen bond refers to the carbon directly attached to the halogen X.
- A carbon in a carbon–carbon double bond is sp^2-hybridised, whereas a saturated tetrahedral carbon is sp^3-hybridised.

Step 1: Locate the halogen-bearing carbon A vinyl halide has the form $CH_2 = CH - X$. Here the halogen is bonded directly to a double-bonded carbon. That carbon uses sp^2 hybrid orbitals for its sigma bonds, so the C–X bond is a $C_{sp^2} - X$ bond.

Step 2: Eliminate the other classes An alkyl halide has X on a saturated sp^3 carbon. In an allyl halide, $CH_2 = CH - CH_2X$, X is attached to the saturated carbon next to the double bond. In a benzyl halide, $C_6H_5CH_2X$, X is likewise attached to the saturated side-chain carbon, not to the aromatic ring. Both therefore have $C_{sp^3} - X$ bonds.

Step 3: Conclusion Vinyl halide contains the required $C_{sp^2} - X$ bond. Hence, the correct option is (D).

Quick Tip to Solve: Inspect the carbon bonded directly to X; a nearby double bond or benzene ring does not make that carbon sp2.

6. Identify the Freon from the following compounds : [1 mark]

(A) CCl_2F_2

(B) CCl_2Br_2

(C) $CH_2Cl\text{-}CHCl_2$

(D) $CHCl_2\text{-}CHCl_2$

Correct Answer: (A) CCl_2F_2

Solution:

Concept:

- Freons are chlorofluorocarbon compounds historically used as refrigerants.
- The common refrigerant Freon-12 is dichlorodifluoromethane, with formula CCl_2F_2.

Step 1: Recognise the refrigerant formula Option (A), CCl_2F_2, contains one carbon bearing two chlorine atoms and two fluorine atoms. This is dichlorodifluoromethane, commonly called Freon-12, and it is the familiar Freon listed among the options.

Step 2: Check each alternative Option (B), CCl_2Br_2, contains bromine instead of fluorine and is not Freon-12. Option (C), $CH_2Cl - CHCl_2$, is a chlorinated two-carbon compound without fluorine. Option (D), $CHCl_2 - CHCl_2$, is also a chlorinated two-carbon compound without fluorine. None has the chlorofluorocarbon composition required for the listed Freon.

Step 3: Conclusion The Freon is CCl_2F_2. Hence, the correct option is (A).

Quick Tip to Solve: Recall Freon-12 as dichlorodifluoromethane: one carbon, two chlorine atoms and two fluorine atoms.

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7. The transition element which shows both +1 and +2 oxidation states is : [1 mark]

(A) Sc

(B) Mn

(C) Cu

(D) Zn

Correct Answer: (C) Cu

Solution:

Concept:

- Copper has electronic configuration $[Ar]3d^{10}4s^1$. Electrons are removed from the outer $4s$ orbital before the $3d$ orbitals.
- A transition element has an incompletely filled d subshell in its atom or in at least one of its common ions.

Step 1: Form the two copper ions Removal of the $4s$ electron gives $Cu^+ : [Ar]3d^{10}$. Removing one further electron gives $Cu^{2+} : [Ar]3d^9$. Copper thus commonly exhibits both +1 and +2 oxidation states, and the partly filled d subshell of Cu^{2+} establishes its transition-element character.

Step 2: Compare the remaining elements Scandium chiefly exhibits +3, so it does not fit the stated pair of common oxidation states. Manganese commonly exhibits +2 and several higher oxidation states; +1 is not its characteristic pair with +2 in this context. Zinc chiefly exhibits +2 and has a filled $3d^{10}$ subshell both as an atom and as Zn^{2+}, so it is not classified as a transition element.

Step 3: Conclusion The element is copper, Cu. Hence, the correct option is (C).

Quick Tip to Solve: Use copper's 3d10 4s1 configuration: losing one and then two electrons gives Cu+ and Cu2+.

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8. If the half-life period of a first order reaction is 1386 s, then the rate constant of this reaction is : [1 mark]

(A) 0.5×10^{-2} s^{-1}

(B) 0.5×10^{-3} s^{-1}

(C) 5×10^{-2} s^{-1}

(D) 5×10^{-3} s^{-1}

Correct Answer: (B) 0.5×10^{-3} s^{-1}

Solution:

Concept:

- For a first order reaction, the half-life is $t_{1/2} = \ln 2/k$, where k is the rate constant.
- The rate constant has units of reciprocal time and does not depend on the initial concentration.

Step 1: Use the half-life relation Rearranging the first order expression gives $k = 0.693/t_{1/2}$. The stated half-life is $1386\,\text{s}$, so the time unit in the answer must be s^{-1}.

Step 2: Substitute and compare

$$k = \frac{0.693}{1386} = 0.0005\,\text{s}^{-1} = 0.5 \times 10^{-3}\,\text{s}^{-1}.$$

Options (A) and (D) both give $0.005\,\text{s}^{-1}$, ten times this value. Option (C) gives $0.05\,\text{s}^{-1}$, one hundred times this value.

Step 3: Conclusion The rate constant is $0.5 \times 10^{-3}\,\text{s}^{-1}$. Hence, the correct option is (B).

Quick Tip to Solve: First divide 0.693 by the half-life, then match the power of ten without changing the numerical value.

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9. The standard electrode potential of 'A', 'B' and 'C' are +0.68 V, -2.54 V and -0.50 V respectively. The order of their reducing power is : [1 mark]

(A) A > B > C

(B) A > C > B

(C) B > C > A

(D) C > B > A

Correct Answer: (C) B > C > A

Solution:

Concept:

- A reducing agent donates electrons and is itself oxidised.
- A more negative standard reduction potential E° indicates a greater tendency of the reduced species to undergo oxidation.

Step 1: Compare the potentials The given standard reduction potentials are $E^\circ_A = +0.68\,\text{V}$, $E^\circ_B = -2.54\,\text{V}$ and $E^\circ_C = -0.50\,\text{V}$. Thus their increasing order is $B < C < A$.

Step 2: Translate into reducing strength The species B most readily gives up electrons because its reduction potential is the most negative. C is next and A is the weakest reducing agent. Therefore reducing power follows the reverse of the numerical order of reduction potentials. Options (A) and (B) wrongly place A first; option (D) wrongly places C ahead of B.

Step 3: Conclusion The reducing power is $B > C > A$. Hence, the correct option is (C).

Quick Tip to Solve: For reducing power, place the species with the most negative standard reduction potential first.

10. Silver nitrate is not stored in Zn vessel because : [1 mark]

(A) Silver nitrate gets decomposed

(B) Ag^+ gets reduced

(C) Ag gets oxidised

(D) Zn gets reduced

Correct Answer: (B) Ag^+ gets reduced

Solution:

Concept:

- Zinc is more readily oxidised than silver and can displace silver from its salt solution.
- In a redox displacement, oxidation of the vessel metal supplies electrons for reduction of the dissolved metal ions.

Step 1: Identify the electron transfer Zinc atoms in the vessel lose electrons:

$$Zn \longrightarrow Zn^{2+} + 2e^-.$$

Silver ions in the solution accept these electrons:

$$2Ag^+ + 2e^- \longrightarrow 2Ag.$$

Step 2: Explain the storage problem The net reaction is $Zn + 2AgNO_3 \longrightarrow Zn(NO_3)_2 + 2Ag$. The zinc vessel is attacked and silver deposits. The decisive change to silver nitrate is reduction of Ag^+, rather than simple decomposition. Silver is not oxidised, and zinc is oxidised rather than reduced, so (A), (C) and (D) do not describe the reaction correctly.

Step 3: Conclusion Ag^+ gets reduced to silver metal. Hence, the correct option is (B).

Quick Tip to Solve: Write the two half-reactions: the vessel metal loses electrons and the silver ions gain them.

11. Glucose on reaction with nitric acid gives : [1 mark]

(A) Gluconic acid

(B) Hexanoic acid

(C) Saccharic acid

(D) Glycolic acid

Correct Answer: (C) Saccharic acid

Solution:

Concept:

- Open-chain glucose contains an aldehyde group at one end and a primary alcohol group at the other.
- Nitric acid is a strong oxidising agent that converts both terminal groups into carboxylic acid groups.

Step 1: Identify both oxidisable ends Glucose has the open-chain structure $\mathrm{CHO}-(\mathrm{CHOH})_4-\mathrm{CH_2OH}$. Oxidation with nitric acid acts on both the aldehyde end and the terminal primary alcohol end while retaining the six-carbon chain.

Step 2: Identify the resulting acid The product is $\mathrm{HOOC}-(\mathrm{CHOH})_4-\mathrm{COOH}$, called saccharic acid (glucaric acid). Gluconic acid would result from oxidation of only the aldehyde group by a mild oxidant such as bromine water. Hexanoic acid lacks the hydroxyl groups of glucose, and glycolic acid has only two carbon atoms; neither describes this oxidation product.

Step 3: Conclusion Glucose gives saccharic acid with nitric acid. Hence, the correct option is (C).

Quick Tip to Solve: Distinguish the oxidants: bromine water oxidises one end of glucose, whereas nitric acid oxidises both ends.

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12. The value of K_H for Ar(g), CO_2(g), HCHO(g) and CH_4(g), are 40.38, 1.69, 1.84×10^{-5} and 0.418 kbar respectively at 298 K. When these gases are arranged in decreasing order of solubility, the correct order is : [1 mark]

(A) HCHO $>$ CH_4 $>$ CO_2 $>$ Ar

(B) HCHO $>$ CO_2 $>$ CH_4 $>$ Ar

(C) Ar $>$ CO_2 $>$ CH_4 $>$ HCHO

(D) CH_4 $>$ CO_2 $>$ Ar $>$ HCHO

Correct Answer: (A) HCHO $>$ CH_4 $>$ CO_2 $>$ Ar

Solution:

Concept:

- Henryś law is $p = K_H x$, where p is the gas partial pressure and x its mole fraction in solution.
- At the same temperature and gas partial pressure, solubility is inversely proportional to K_H.

Step 1: Arrange the Henry constants The printed constants, in kbar, give

$$1.84 \times 10^{-5} < 0.418 < 1.69 < 40.38.$$

These correspond respectively to HCHO, CH_4, CO_2 and Ar.

Step 2: Reverse the order for solubility Since $x = p/K_H$, the gas with the smallest constant has the greatest dissolved mole fraction. HCHO is therefore most soluble, followed by methane, carbon dioxide and argon. Option (B) interchanges methane and carbon dioxide, (C) follows increasing rather than decreasing solubility, and (D) incorrectly puts HCHO last.

Step 3: Conclusion The decreasing solubility order is $HCHO > CH_4 > CO_2 > Ar$. Hence, the correct option is (A).

Quick Tip to Solve: Arrange the supplied Henry constants in increasing order to obtain decreasing solubility at equal pressure.

13. Assertion (A): The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.
Reason (R): Two molecules of the reactants are involved in the given elementary reaction. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Molecularity counts the reacting species participating in a single elementary step.
- An overall balanced equation for a complex reaction does not establish its molecularity or mechanism.

Step 1: Judge the assertion The displayed equation $H_2 + Br_2 \longrightarrow 2HBr$ contains one hydrogen molecule and one bromine molecule on the reactant side. Its apparent molecularity, from this written equation, is therefore two. The carefully worded assertion that it appears to be two is true.

Step 2: Judge the reason The hydrogen-bromine reaction is a complex chain reaction involving elementary radical steps. The overall equation is not itself a single elementary bimolecular event. Thus the reason is false because it calls the given overall reaction elementary.

Step 3: Check the explanation and code Counting two molecules in the overall equation explains only the apparent count, not an actual elementary mechanism. Hence the reason as a whole cannot explain the assertion. Codes (A) and (B) require a true reason; code (D) reverses the truth values.

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

Quick Tip to Solve: Treat the word appears separately from a claim of actual molecularity; a balanced overall equation need not be elementary.

14. Assertion (A): p-methoxyphenol is a stronger acid than p-nitrophenol.

Reason (R): Methoxy group shows -I effect whereas nitro group shows +I effect. [1 mark]

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

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

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

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

Correct Answer: Both Assertion (A) and Reason (R) are false; none of the printed options is defensible.

Solution:

Concept:

- Acid strength of a phenol increases when its conjugate phenoxide ion is stabilised.
- A para nitro group withdraws electrons by induction and resonance; a para methoxy group donates electrons by resonance despite its inductive withdrawal.

Step 1: Judge the assertion The para nitro group stabilises the negative charge of the phenoxide ion through its electron-withdrawing effects. The para methoxy group donates by resonance and makes the phenoxide ion less stable by comparison. Thus p-nitrophenol is more acidic than p-methoxyphenol, so Assertion (A) is false.

Step 2: Judge the reason The methoxy group does show a $-I$ effect because of its oxygen atom. However, the nitro group also shows a strong $-I$ effect, not the $+I$ effect stated. Since the reason joins these two claims, the incorrect nitro-group claim makes Reason (R) false.

Step 3: Compare with the printed codes Both statements are false. Codes (A) and (B) require both to be true, code (C) requires a true assertion, and code (D) requires a true reason. None of the four printed codes represents the actual truth values, so no printed option is defensible.

Step 4: Conclusion Both Assertion (A) and Reason (R) are false. None of the printed options is correct.

Quick Tip to Solve: Judge each clause of the reason independently: a correct methoxy claim cannot rescue an incorrect nitro claim.

15. Assertion (A): Actinoids show wide range of oxidation states.
Reason (R): Due to comparable energies of 5f, 6d and 7s orbitals. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Actinoids have valence electrons in the $5f$, $6d$ and $7s$ subshells; an oxidation state describes their formal electron loss in a compound.
- When subshell energies are comparable, different numbers of electrons can participate in bonding.

Step 1: Judge the assertion Actinoids exhibit several oxidation states, especially among the earlier members. For example, uranium exhibits $+3$, $+4$, $+5$ and $+6$. Thus Assertion (A) is true.

Step 2: Judge the reason The $5f$, $6d$ and $7s$ orbitals are sufficiently close in energy for their electrons to participate in bonding. Reason (R) is therefore true.

Step 3: Connect the two statements Comparable orbital energies allow varying numbers of valence electrons to be used in compound formation. This directly accounts for the wide range of oxidation states, so the reason explains the assertion. Option (B) incorrectly denies this connection; options (C) and (D) incorrectly label a true statement false.

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

Quick Tip to Solve: For actinoid oxidation states, link variable electron participation to the closeness of 5f, 6d and 7s energies.

16. Assertion (A): Presence of -NO_2 group at meta position increases the reactivity of haloarenes towards nucleophilic substitution reactions.

Reason (R): -NO_2 group decreases the electron density over the benzene ring and thus facilitates the attack of nucleophile on haloarenes. [1 mark]

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

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

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

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

Correct Answer: (D) A is false, but R is true.

Solution:

Concept:

- In nucleophilic aromatic substitution, an electron-withdrawing $-NO_2$ group at an ortho or para position stabilises the anionic intermediate by resonance.
- Activation depends on the position of the nitro group relative to the carbon bonded to halogen.

Step 1: Judge the assertion Assertion (A) is false in the standard haloarene substitution comparison. A meta nitro group does not provide the resonance stabilisation of the anionic intermediate that an ortho or para nitro group provides, so it does not produce the stated activating effect.

Step 2: Judge the reason The nitro group is electron withdrawing and decreases electron density in the aromatic ring. This facilitates nucleophilic attack in appropriately activated haloarenes. Thus Reason (R) is true as the general electronic explanation of nitro activation.

Step 3: Check the explanatory link and codes The general electron-withdrawing effect does not make the positional assertion true: at meta, the negative charge of the substitution intermediate cannot be delocalised onto the nitro group. Options (A), (B) and (C) all require a true assertion and are excluded.

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

Quick Tip to Solve: For nitro-substituted haloarenes, check ortho or para placement before using resonance activation.

Section B (10 marks)

17(a). Define Fuel cell. Write two advantages of fuel cell over ordinary cell. [2 marks]

Solution:

Concept:

- A fuel cell is a galvanic cell: a spontaneous redox reaction converts chemical energy directly into electrical energy.
- Its fuel and oxidant are supplied continuously from outside the cell, allowing operation while the reactants continue to flow.

Step 1: Define a fuel cell A fuel cell is an electrochemical cell in which the chemical energy released

by the reaction of a continuously supplied fuel with a continuously supplied oxidant is converted directly into electrical energy. For example, hydrogen and oxygen can be supplied to electrodes to generate current, with the overall reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l).$$

Step 2: State two advantages First, a fuel cell can operate continuously as long as fuel and oxidant are supplied; unlike an ordinary primary cell, operation need not stop when a fixed stock of reactants inside the cell is exhausted. Second, a hydrogen-oxygen fuel cell is environmentally cleaner in use: its reaction product is water, so it does not generate the harmful combustion gases associated with burning conventional fuels. These advantages concern continuous electrical supply and the clean product of the hydrogen-oxygen cell.

Step 3: Conclusion A fuel cell directly converts the energy of continuously fed reactants into electricity. Continuous operation and clean water production in the hydrogen-oxygen cell are two advantages.

Quick Tip to Solve: Include continuous external supply in the definition; use the hydrogen-oxygen cell to explain clean operation.

OR

17(b). Predict the products of electrolysis in each of the following :

(i) A dilute solution of H_2SO_4 with platinum electrodes

(ii) An aqueous solution of $CuCl_2$ with platinum electrodes [2 marks]

Solution:

Concept:

- At the cathode reduction occurs, whereas oxidation occurs at the anode. Platinum acts as an inert conducting electrode.
- In aqueous electrolytes, water can compete with dissolved ions for discharge; the selected half-reactions determine the products.

Step 1: Electrolyse dilute sulphuric acid At the cathode, hydrogen ions are reduced to hydrogen gas. At the anode, water is oxidised to oxygen gas; sulphate ions remain in solution. The half-reactions are

$$\text{Cathode: } 2H^+ + 2e^- \longrightarrow H_2(g),$$
$$\text{Anode: } 2H_2O(l) \longrightarrow O_2(g) + 4H^+ + 4e^-.$$

Thus electrolysis decomposes water into hydrogen and oxygen.

Step 2: Electrolyse aqueous copper(II) chloride Copper(II) ions are preferentially reduced to copper metal at the cathode. Chloride ions are oxidised to chlorine gas at the platinum anode under the

usual aqueous copper chloride electrolysis conditions:

$$\text{Cathode: } \mathrm{Cu^{2+}(aq) + 2}e^- \longrightarrow \mathrm{Cu(s)},$$
$$\text{Anode: } \mathrm{2Cl^-(aq) \longrightarrow Cl_2(g) + 2}e^-.$$

Platinum is not consumed in either electrode reaction.

Step 3: Conclusion (i) Cathode: $\mathrm{H_2}$; anode: $\mathrm{O_2}$. (ii) Cathode: Cu; anode: $\mathrm{Cl_2}$.

Quick Tip to Solve: Write reduction at the cathode first, then select oxidation at the inert anode from the available anions or water.

18. (a) Name the reaction which can be used to distinguish chemically between aniline and N,N-dimethylaniline.

(b) Why can aniline not be prepared by the ammonolysis of chlorobenzene under normal conditions ?

[2 marks]

Solution:

Concept:

- The carbylamine reaction is given by primary amines on heating with chloroform and alcoholic potassium hydroxide; tertiary amines do not give this reaction.
- In chlorobenzene, resonance gives the carbon-chlorine bond partial double-bond character, resisting cleavage during ordinary ammonolysis.

Step 1: Distinguish the two amines Use the carbylamine reaction. Aniline, a primary aromatic amine, reacts with chloroform and alcoholic potassium hydroxide on heating to form phenyl isocyanide with an offensive smell:

$$\mathrm{C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{heat} C_6H_5NC + 3KCl + 3H_2O}.$$

N,N-dimethylaniline is a tertiary amine and does not give this reaction, so no corresponding isocyanide is formed.

Step 2: Explain the failure of ordinary ammonolysis In chlorobenzene, a lone pair on chlorine is delocalised into the benzene ring. The carbon-chlorine bond consequently acquires partial double-bond character and becomes shorter and stronger than the corresponding bond in a haloalkane. The carbon bonded to chlorine is also sp^2-hybridised. These features make cleavage and nucleophilic substitution by ammonia difficult under normal conditions, so ordinary ammonolysis does not prepare aniline from chlorobenzene.

Step 3: Conclusion (a) Carbylamine reaction. (b) Resonance strengthens the aryl carbon-chlorine bond, preventing normal ammonolysis of chlorobenzene.

Quick Tip to Solve: Identify aniline as primary and N,N-dimethylaniline as tertiary before choosing the carbylamine reaction.

19. Visha diluted the solutions of two electrolytes 'A' and 'B'. She observed that Λ_m of 'A' increased 1.6 times whereas Λ_m of 'B' increased 22 times. Which of the two is a weak electrolyte and why? [2 marks]

Solution:

Concept:

- Molar conductivity, Λ_m, is the conductivity contribution of the ions produced by one mole of electrolyte; it increases on dilution.
- A weak electrolyte is only partly ionised. Dilution increases its degree of ionisation substantially, whereas a strong electrolyte is already almost completely dissociated.

Step 1: Compare the observed increases For electrolyte A the molar conductivity becomes only 1.6 times its initial value. For electrolyte B it becomes 22 times its initial value. The much larger increase for B indicates a large increase in the number of ions supplied by each mole of electrolyte, rather than merely a small improvement in ionic mobility.

Step 2: Relate dilution to ionisation For a weak electrolyte, dilution shifts the ionisation equilibrium towards the ions. Its degree of ionisation therefore rises markedly and so does Λ_m. For a strong electrolyte, the ions are already present almost completely; dilution mainly reduces interionic attractions and increases ionic mobility, producing a relatively modest rise such as that observed for A.

Step 3: Conclusion Electrolyte B is the weak electrolyte because its molar conductivity increases 22 times on dilution, indicating a large increase in its degree of ionisation.

Quick Tip to Solve: Compare the factors of increase in molar conductivity: the very large increase signals increased ionisation of a weak electrolyte.

20. By giving reasons, explain that how the rate of reaction for a given reaction will be affected when :
(a) the temperature is increased.
(b) catalyst is added. [2 marks]

Solution:

Concept:

- The rate constant obeys the Arrhenius equation $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- A reaction occurs through effective collisions: reacting particles must have sufficient energy to cross the activation-energy barrier.

Step 1: (a) Increase the temperature On increasing temperature, a larger fraction of the reacting molecules has energy equal to or greater than the activation energy. The number of effective collisions per unit time consequently increases. In the Arrhenius expression, increasing T makes $-E_a/(RT)$ less negative, so k increases. At the same reactant concentrations, the rate of the reaction therefore increases.

Step 2: (b) Add a catalyst A positive catalyst provides an alternative reaction pathway with a lower activation energy. At the same temperature, more reactant molecules can cross this lower barrier, increasing the rate constant and hence the reaction rate. The catalyst is regenerated during the

reaction. It accelerates approach to equilibrium without changing the equilibrium constant or the equilibrium composition.

Step 3: Conclusion (a) Increasing temperature increases the reaction rate by increasing the fraction of molecules able to overcome the activation barrier. (b) Adding a catalyst increases the rate by providing a pathway of lower activation energy.

Quick Tip to Solve: Distinguish the two reasons: temperature changes the energy distribution; a catalyst lowers the activation barrier.

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21. Give one point of difference between the following :

(a) α-helix and β-pleated sheet structure of proteins

(b) Amylose and Amylopectin [2 marks]

Solution:

Concept:

- The α-helix and β-pleated sheet are secondary structures of proteins, stabilised by hydrogen bonds involving peptide backbone groups.
- Amylose and amylopectin are the two polysaccharide components of starch; they differ in the branching of their glucose chains.

Step 1: (a) Compare the protein structures In an α-helix, a polypeptide chain coils into a right-handed helix, stabilised by hydrogen bonds within the same helical chain. In a β-pleated sheet, extended polypeptide chain segments lie alongside one another to form a sheet, stabilised by hydrogen bonds between adjacent segments. Thus the distinguishing structural feature is a coiled helix versus an extended pleated sheet.

Step 2: (b) Compare the starch components Amylose is an essentially unbranched polymer of α-D-glucose units joined by $\alpha(1 \rightarrow 4)$ glycosidic linkages. Amylopectin is branched: its main chains also contain $\alpha(1 \rightarrow 4)$ linkages, while $\alpha(1 \rightarrow 6)$ linkages produce the branch points. Thus the requested difference is unbranched amylose versus branched amylopectin.

Step 3: Conclusion (a) The α-helix is coiled, whereas the β-pleated sheet consists of extended chains arranged side by side. (b) Amylose is unbranched, whereas amylopectin is branched.

Quick Tip to Solve: Associate amylopectin with branch points: its extra $\alpha(1 \rightarrow 6)$ linkages distinguish it from amylose.

Section C (21 marks)

22. The following data were obtained during the kinetic studies of the reaction :

A + 2B → C + 2D

Experiment	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial rate of formation of C (M min^{-1})
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

Determine the order of reaction with respect to each reactant and the overall order of the reaction. Write the rate law expression for the reaction. [3 marks]

Solution:

Concept:

- For the reaction $\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C} + 2\,\mathrm{D}$, assume the experimental rate law $r = k[A]^m[B]^n$, where m and n are the orders with respect to A and B.
- Compare experiments in which one concentration is constant to isolate the effect of the other. The overall order is $m + n$, not the sum of stoichiometric coefficients.

Step 1: Find the order with respect to B Compare experiments 1 and 3: $[A]$ stays at $0.10\,\mathrm{mol\,L^{-1}}$, while $[B]$ increases from 0.10 to $0.30\,\mathrm{mol\,L^{-1}}$. The rate remains $3.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}min^{-1}}$. Therefore

$$\frac{r_3}{r_1} = \left(\frac{0.30}{0.10}\right)^n, \qquad 1 = 3^n, \qquad n = 0.$$

The rate is independent of the concentration of B for the given data.

Step 2: Find the order with respect to A Compare experiments 3 and 2: $[B]$ is fixed at $0.30\,\mathrm{mol\,L^{-1}}$, and $[A]$ increases from 0.10 to $0.30\,\mathrm{mol\,L^{-1}}$. The rate increases from 3.0×10^{-4} to $9.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}min^{-1}}$. Thus

$$\frac{9.0 \times 10^{-4}}{3.0 \times 10^{-4}} = \left(\frac{0.30}{0.10}\right)^m, \qquad 3 = 3^m, \qquad m = 1.$$

Step 3: Write and check the rate law The sum of the partial orders is $m + n = 1 + 0 = 1$. Hence $r = k[A][B]^0 = k[A]$. Experiment 1 gives

$$k = \frac{3.0 \times 10^{-4}}{0.10} = 3.0 \times 10^{-3}\,\mathrm{min^{-1}}.$$

For experiment 4 this predicts $r = (3.0 \times 10^{-3})(0.20) = 6.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}min^{-1}}$, agreeing with the table.

Step 4: Conclusion Order with respect to A: 1; order with respect to B: 0; overall order: 1. The rate law is $r = k[A]$, with $k = 3.0 \times 10^{-3}\,\mathrm{min^{-1}}$.

Quick Tip to Solve: Use experiments 1 and 3 to eliminate A, then experiments 3 and 2 to eliminate B; never infer reaction orders from coefficients.

23. Calculate emf of the following cell at 298 K :

Mg(s) | Mg^{2+} (0.001 M) || Cu^{2+} (0.0001 M) | Cu(s)

Given: E°_{cell} = 2.71 V, log 10 = 1 [3 marks]

Solution:

Concept:

- The Nernst equation at 298 K is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Activities of pure solid electrodes are unity. In the dilute-solution approximation, ionic concentrations determine Q.

Step 1: Write the electrode and overall reactions The left electrode is the anode:

$$\mathrm{Mg(s)} \rightarrow \mathrm{Mg^{2+}(aq)} + 2\mathrm{e^-}.$$

The right electrode is the cathode:

$$\mathrm{Cu^{2+}(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{Cu(s)}.$$

Adding gives

$$\mathrm{Mg(s)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Mg^{2+}(aq)} + \mathrm{Cu(s)}.$$

Thus $n = 2$; the copper-ion concentration belongs in the denominator of the reaction quotient.

Step 2: Evaluate the reaction quotient Only the aqueous ions appear in the concentration quotient:

$$Q = \frac{[\mathrm{Mg^{2+}}]}{[\mathrm{Cu^{2+}}]} = \frac{0.001}{0.0001} = 10.$$

The solids do not appear. Hence $\log Q = \log 10 = 1$.

Step 3: Substitute in the Nernst equation Using the given standard emf,

$$\begin{aligned} E_{\text{cell}} &= 2.71 - \frac{0.0591}{2}\log 10 \\ &= 2.71 - 0.02955 \\ &= 2.68045\,\mathrm{V}. \end{aligned}$$

Since $Q > 1$, the concentration correction decreases the emf relative to its standard value, as expected.

Step 4: Conclusion The emf of the cell at 298 K is $\boxed{E_{\text{cell}} \approx 2.68\,\mathrm{V}}$.

Quick Tip to Solve: Write the balanced cell reaction first: its products and reactants fix the order of concentrations in Q.

24. Give plausible explanation for each of the following :

(a) Sodium hydrogen sulphite is used for separation and purification of aldehydes.

(b) 2,2,6-trimethylcyclohexanone does not form cyanohydrin.

(c) Only one -NH_2 group of semicarbazide is involved in the formation of semicarbazone. [3 marks]

Solution:

Concept:

- The carbonyl carbon is electrophilic, so nucleophiles can add to the $C = O$ group; accessibility of that carbon affects the reaction.
- Resonance delocalisation of a nitrogen lone pair into a carbonyl group reduces its availability for nucleophilic attack.

Step 1: (a) Separation using sodium hydrogen sulphite Aldehydes react with sodium hydrogen sulphite to form crystalline addition compounds:

$$RCHO + NaHSO_3 \rightleftharpoons RCH(OH)SO_3Na.$$

These solids can be filtered off and washed to separate them from impurities that do not form such compounds. Treatment of the purified addition compound with dilute acid or alkali regenerates the aldehyde. Formation of an isolable solid followed by reversible regeneration makes the method useful for separation and purification.

Step 2: (b) Steric hindrance to cyanohydrin formation In 2,2,6-trimethylcyclohexanone, three methyl groups occupy positions adjacent to the carbonyl group. Their crowding strongly obstructs approach of CN^- to the carbonyl carbon. Formation of the tetrahedral addition product increases crowding further. Consequently, nucleophilic addition is strongly hindered and cyanohydrin formation does not occur readily.

Step 3: (c) Selective reaction of semicarbazide Semicarbazide has the structure

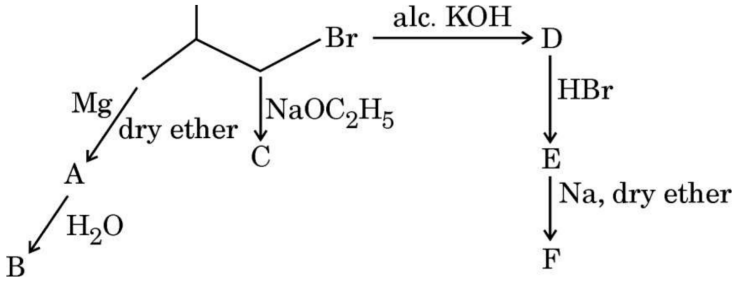
$$H_2N - NH - C(= O) - NH_2.$$

The lone pair on the $-NH_2$ group directly attached to $C = O$ is delocalised by resonance, making that group amide-like and a poor nucleophile. The terminal hydrazino H_2N- group has an available lone pair and attacks the aldehyde or ketone. Condensation eliminates water and forms $R_2C = N - NH - C(= O) - NH_2$; the amide $-NH_2$ group remains unchanged.

Step 4: Conclusion Bisulphite purification relies on reversible crystalline-adduct formation; methyl-group crowding suppresses cyanohydrin formation; only the terminal hydrazino $-NH_2$ group of semicarbazide is sufficiently nucleophilic.

Quick Tip to Solve: In semicarbazide, first locate the nitrogen bonded directly to C=O: its lone pair is tied up by resonance.

25(a). **Identify 'A' to 'F' in the following reaction sequence :** [3 marks]



Solution:

Concept:

- Magnesium in dry ether converts RBr into the Grignard reagent RMgBr; water then gives RH.
- A primary haloalkane undergoes substitution with ethoxide, elimination with alcoholic KOH, and Wurtz coupling with sodium in dry ether. HBr adds to an unsymmetrical alkene by Markovnikov addition when no peroxide is specified.

Step 1: Identify A and B from the Grignard branch The starting compound is $(CH_3)_2CHCH_2Br$. Magnesium inserts into its carbon-bromine bond:

$$(CH_3)_2CHCH_2Br \xrightarrow[\text{dry ether}]{Mg} (CH_3)_2CHCH_2MgBr.$$

Thus A is 2-methylpropylmagnesium bromide. Hydrolysis replaces the $-MgBr$ group by hydrogen:

$$(CH_3)_2CHCH_2MgBr + H_2O \rightarrow (CH_3)_2CHCH_3 + Mg(OH)Br.$$

Therefore B is 2-methylpropane.

Step 2: Identify C by nucleophilic substitution Ethoxide replaces bromide at the primary carbon to form an ether:

$$(CH_3)_2CHCH_2Br + NaOC_2H_5 \rightarrow (CH_3)_2CHCH_2OC_2H_5 + NaBr.$$

Hence C is 1-ethoxy-2-methylpropane (ethyl isobutyl ether).

Step 3: Identify D and E through elimination and addition Alcoholic KOH removes a beta hydrogen and bromide, giving $D = CH_2 = C(CH_3)_2$, 2-methylpropene. Addition of HBr places hydrogen on the terminal carbon and bromine on the more substituted carbon. Thus $E = (CH_3)_3CBr$, 2-bromo-2-methylpropane.

Step 4: Identify F by Wurtz coupling The formal Wurtz coupling joins the two carbon centres bearing bromine:

$$2(CH_3)_3CBr + 2Na \xrightarrow{\text{dry ether}} (CH_3)_3C - C(CH_3)_3 + 2NaBr.$$

Accordingly F is 2,2,3,3-tetramethylbutane, the coupling product required by the stated sequence.

Step 5: Conclusion $A = (CH_3)_2CHCH_2MgBr$; $B = (CH_3)_3CH$; $C = (CH_3)_2CHCH_2OC_2H_5$; $D = CH_2 = C(CH_3)_2$; $E = (CH_3)_3CBr$; $F = (CH_3)_3C - C(CH_3)_3$.

Quick Tip to Solve: Track the carbon bonded to Br in each branch: substitution preserves the skeleton, whereas Wurtz coupling joins two copies at that carbon.

OR

25(b). What happens when :

(i) methyl chloride is treated with KCN ?

(ii) methyl bromide is treated with NaI in dry acetone ?

(iii) methyl bromide is treated with silver fluoride ? [3 marks]

Solution:

Concept:

- Nucleophilic substitution replaces the halogen in a methyl halide by an incoming nucleophile. The methyl carbon is readily accessible for an S_N2 attack.
- Alkali-metal cyanides give nitriles; halogen exchange with NaI in dry acetone is the Finkelstein reaction, while replacement by fluorine using a metallic fluoride is the Swarts reaction.

Step 1: Part (i): Reaction with potassium cyanide KCN is predominantly ionic and supplies the ambident cyanide ion, CN^-. With an alkyl halide, attack occurs mainly through its carbon end, forming a carbon–carbon bond:

$$CH_3Cl + KCN \longrightarrow CH_3C \equiv N + KCl.$$

The organic product is ethanenitrile (acetonitrile). Its carbon chain contains one carbon more than the starting methyl halide; it is a nitrile, rather than an isocyanide.

Step 2: Part (ii): Reaction with sodium iodide Iodide displaces bromide from methyl bromide in dry acetone:

$$CH_3Br + NaI \xrightarrow{\text{dry acetone}} CH_3I + NaBr \downarrow.$$

This Finkelstein reaction produces iodomethane. NaI is soluble in acetone whereas NaBr precipitates, removing a product from the reaction mixture and driving the exchange forward.

Step 3: Part (iii): Reaction with silver fluoride Silver fluoride replaces bromine by fluorine in a Swarts reaction:

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr \downarrow.$$

The organic product is fluoromethane (methyl fluoride); insoluble silver bromide is also formed.

Step 4: Conclusion The products are (i) ethanenitrile, CH_3CN; (ii) iodomethane, CH_3I; and (iii) fluoromethane, CH_3F.

Quick Tip to Solve: For KCN, attach the carbon end of CN to the methyl group; for NaI or AgF, replace only the halogen.

26. (a) Write IUPAC name of the complex $[Co(H_2O)(CN)(en)_2]^{2+}$.

(b) Write the hybridization of $[Ni(CO)_4]$ and predict its magnetic behaviour. [Atomic number: Ni = 28]

(c) What type of isomerism is shown by $[Co(en)_3]^{3+}$? [3 marks]

Solution:

Concept:

- The oxidation state of the metal follows from the total charge and ligand charges. Ligand names are written alphabetically, ignoring multiplicative prefixes.
- In valence-bond theory, the available hybrid orbitals determine geometry; a complex with no unpaired electrons is diamagnetic. Optical isomers are non-superimposable mirror images.

Step 1: Part (a): Determine the oxidation state and name In $[Co(H_2O)(CN)(en)_2]^{2+}$, water and ethane-1,2-diamine (en) are neutral, while cyanido has charge -1. If cobalt has oxidation state x, then

$$x + 0 - 1 + 2(0) = +2 \quad \Rightarrow \quad x = +3.$$

The ligand names in alphabetical order are aqua, cyanido and ethane-1,2-diamine. The two en ligands require the prefix bis, with parentheses around the complex ligand name. Since the complex is cationic, the metal retains the name cobalt. Its IUPAC name is aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion.

Step 2: Part (b): Hybridization and magnetic behaviour All four CO ligands are neutral, so nickel is in oxidation state zero. Its atomic configuration is initially $[Ar]3d^8 4s^2$. In the presence of the strong-field CO ligands, the electrons pair to give a filled $3d^{10}$ set. One vacant $4s$ and three vacant $4p$ orbitals hybridize to form four sp^3 orbitals which accept ligand electron pairs. Thus $[Ni(CO)_4]$ is tetrahedral and sp^3-hybridized. All its electrons are paired, so it is diamagnetic.

Step 3: Part (c): Identify the isomerism In $[Co(en)_3]^{3+}$, three bidentate en ligands occupy six coordination positions in an octahedral arrangement. Their chelate arrangement gives two mirror-image forms, conventionally denoted Δ and Λ, which cannot be superimposed. Consequently the complex shows optical isomerism.

Step 4: Conclusion (a) Aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion. (b) sp^3, tetrahedral and diamagnetic. (c) Optical isomerism.

Quick Tip to Solve: Count ligand charges before naming cobalt; remember that neutral Ni(CO)4 has a fully paired d10 metal configuration.

27. Give reasons for the following :

(a) Phenol is more acidic than alcohol.

(b) t-butyl bromide on reaction with sodium ethoxide gives alkene as main product and not ether.

(c) p-nitrophenol is not steam volatile while o-nitrophenol is steam volatile. [3 marks]

Solution:

Concept:

- Acidity increases when the conjugate base is stabilized. Resonance stabilization of phenoxide is compared with the localized charge of an alkoxide.
- Steric hindrance favours elimination over substitution at a tertiary carbon. Intermolecular hydrogen bonding causes molecular association and reduces volatility.

Step 1: Part (a): Compare the conjugate bases Phenol loses a proton to form phenoxide, whereas an alcohol forms an alkoxide:

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+, \qquad ROH \rightleftharpoons RO^- + H^+.$$

In phenoxide, the negative charge is delocalized by resonance from oxygen into the aromatic ring, giving greater stabilization. In an alkoxide, the negative charge remains localized mainly on oxygen; the electron-releasing inductive effect of an alkyl group further destabilizes it. Proton loss from phenol is therefore more favourable, making phenol more acidic than an alcohol.

Step 2: Part (b): Explain the formation of an alkene The carbon bearing bromine in tert-butyl bromide is tertiary and heavily hindered, so backside attack by ethoxide in the S_N2 pathway required for Williamson ether synthesis is difficult. Ethoxide is a strong base and readily abstracts a hydrogen from a neighbouring (beta) carbon. Simultaneous loss of bromide gives beta-elimination, forming 2-methylpropene as the major product:

$$(CH_3)_3CBr + NaOC_2H_5 \longrightarrow CH_2 = C(CH_3)_2 + C_2H_5OH + NaBr.$$

Thus the tertiary substrate favours elimination rather than formation of an ether.

Step 3: Part (c): Compare hydrogen bonding and volatility In o-nitrophenol, the adjacent hydroxyl and nitro groups form an intramolecular hydrogen bond. This reduces hydrogen bonding between different molecules and hence reduces molecular association; the compound is sufficiently volatile to distil with steam. In p-nitrophenol the groups are too far apart for such an intramolecular bond, so molecules form intermolecular hydrogen bonds and associate. More energy is needed to separate these molecules, giving lower volatility; p-nitrophenol is therefore not steam volatile.

Step 4: Conclusion (a) Phenoxide is resonance-stabilized. (b) A hindered tertiary halide with a strong base favours beta-elimination. (c) o-Nitrophenol has intramolecular hydrogen bonding, while p-nitrophenol has intermolecular hydrogen bonding.

Quick Tip to Solve: For acidity compare conjugate-base stability; for steam volatility distinguish hydrogen bonds within one molecule from those between molecules.

28. Methanamine reacts with benzoyl chloride to form a product 'P'. Give the structure and IUPAC name of 'P'. Can 'P' undergo Hoffmann bromamide degradation reaction ? If yes, then give the structure of the product. If no, then give reason. [3 marks]

Solution:

Concept:

- Primary amines undergo benzoylation: the nitrogen attacks the carbonyl carbon of benzoyl chloride and an amide forms.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into RNH_2 using bromine and alkali; the product has one fewer carbon atom.

Step 1: Identify the benzoylation product Methanamine is CH_3NH_2, and benzoyl chloride is C_6H_5COCl. One hydrogen attached to nitrogen is replaced by the benzoyl group. Hence the reaction is

$$C_6H_5COCl + CH_3NH_2 \longrightarrow C_6H_5C(=O)NHCH_3 + HCl.$$

The acid formed is neutralised by alkali or excess amine during benzoylation. The product contains the carbonyl group bonded directly to nitrogen; it is an amide, not a salt or a simple mixture.

Step 2: Name the product and test its suitability for degradation The parent amide is benzamide, $C_6H_5CONH_2$. Replacement of one nitrogen-bound hydrogen by methyl gives the IUPAC name N-methylbenzamide. Thus P is a secondary amide, $C_6H_5CONHCH_3$, whereas the usual Hofmann bromamide degradation requires a primary amide containing the $-CONH_2$ group. Having only one N–H bond is insufficient for the standard degradation sequence. Therefore this reaction cannot be used to convert P to an amine with one fewer carbon atom.

Step 3: Conclusion $P = C_6H_5C(=O)NHCH_3$, N-methylbenzamide. It does not undergo Hofmann bromamide degradation because it lacks the primary amide group $-CONH_2$.

Quick Tip to Solve: Before applying Hofmann degradation, check that the amide nitrogen carries two hydrogens.

Section D (8 marks)

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

29(a). Reduce carbohydrates, increase protein to check diabetes, older people may need greater carbohydrates reduction. An average Indian derives 61-64% of energy from consumption of food rich in carbohydrates. A study published in the Journal of Diabetes Care has recommended reducing this to 49-56% for remission or prevention of Type 2 diabetes, one of the leading cause of death worldwide. Along with reducing carbohydrate intake, the study suggests that one should also increase protein intake up to 14-20% of the total energy consumption. Fat should contribute not more than 21-27% of the total energy consumption. In simple words, 50% of the plate should consist of fruits and green vegetables, 25% carbohydrates, 25% food rich in protein. Type 1 diabetes is due to deficiency of insulin.

Answer the following questions :

Write any two functions of carbohydrates. [2 marks]

Solution:

Concept:

- Carbohydrates act as sources of energy and as stored food reserves in living organisms.
- Glucose is an immediately usable carbohydrate; starch and glycogen store glucose units for later use.

Step 1: Energy supply Carbohydrates provide energy for biological activities. Glucose is oxidised during cellular respiration, releasing energy that cells capture in ATP for processes such as muscle contraction and biosynthesis. Thus carbohydrates form a major energy source in the diet; this explains why the passage discusses their contribution to total energy intake.

Step 2: Storage of food energy Carbohydrates also serve as reserve food materials. Plants store carbohydrate as starch, while animals store it as glycogen, especially in liver and muscles. These polysaccharides can be broken down to supply glucose when energy is needed. This storage function is distinct from the immediate oxidation of glucose for energy.

Step 3: Conclusion Two functions are: (1) supplying energy, for example through glucose, and (2) storing food energy as starch in plants and glycogen in animals.

Quick Tip to Solve: Pair a function with an example: glucose supplies energy; starch and glycogen store it.

29(b). What are monosaccharides ? [1 mark]

Solution:

Concept:

- Carbohydrates are classified by whether hydrolysis can split them into simpler carbohydrate units.
- A monosaccharide consists of a single sugar unit and cannot be hydrolysed into simpler carbohydrates.

Step 1: State the hydrolysis criterion Monosaccharides are the simplest carbohydrates: they cannot

be hydrolysed to give simpler carbohydrate molecules. The definition concerns hydrolysis into simpler sugars, not every possible chemical reaction that a sugar can undergo.

Step 2: Illustrate the definition Glucose and fructose are examples of monosaccharides. Each represents one sugar unit, unlike sucrose, which yields simpler sugars on hydrolysis, or starch, which contains many glucose units.

Step 3: Conclusion Monosaccharides are carbohydrates that cannot be hydrolysed into simpler carbohydrates; examples are glucose and fructose.

Quick Tip to Solve: Use inability to undergo hydrolysis into simpler carbohydrates as the defining test.

29(c). Write the name of the deficiency diseases caused due to the lack of Vitamin D. [1 mark]

Solution:

Concept:

- Vitamin D supports absorption and utilisation of calcium and phosphorus needed for normal mineralisation of bones.
- Deficiency affects growing bones in children and mineralisation of existing bone in adults.

Step 1: Identify the disease in children Lack of vitamin D causes rickets in children. Inadequate mineralisation makes growing bones soft and can cause deformities such as bowed legs.

Step 2: Identify the disease in adults In adults, vitamin D deficiency causes osteomalacia, characterised by softening of bones due to defective mineralisation. This is distinguished from the childhood disease rickets.

Step 3: Conclusion Vitamin D deficiency causes rickets in children and osteomalacia in adults.

Quick Tip to Solve: Remember the age distinction: rickets affects children; osteomalacia affects adults.

OR

29(c). Name the hormone which maintains the glucose level within narrow limit in the blood. [1 mark]

Solution:

Concept:

- Hormones are chemical messengers that regulate physiological processes, including the concentration of glucose in blood.
- Insulin is a peptide hormone secreted by the beta cells of the pancreatic islets.

Step 1: Identify the hormone The hormone asked for is insulin. It is released from the pancreas and plays a central role in maintaining blood glucose within a narrow range.

Step 2: Relate the hormone to the passage Insulin promotes glucose uptake by tissues and its storage as glycogen, thereby lowering an elevated blood glucose concentration. The passage supports this identification by stating that Type 1 diabetes results from insulin deficiency.

Step 3: Conclusion The hormone is insulin.

Quick Tip to Solve: Link insulin deficiency in Type 1 diabetes with insulinś role in blood glucose regulation.

30(a). One of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over. If green light is absorbed by the complex, it appears red. Table given below, gives the relationship between different wavelengths of the light absorbed and the colour observed.

Answer the following questions :

What is spectrochemical series ? Write the relationship between Δ_t and Δ_o. [2 marks]

Coordination Entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue-green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow-orange
$[Co(CN)_6]^{3-}$	310	Ultra-Violet (U.V.)	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue-green	Violet

Solution:

Concept:

- The spectrochemical series orders ligands by increasing crystal field splitting energy, or increasing ligand field strength.
- Δ_o is the separation of the two sets of d orbitals in an octahedral field; Δ_t is the corresponding separation in a tetrahedral field.

Step 1: Define the spectrochemical series The arrangement of ligands in increasing order of their ability to split the d-orbital energies of a central metal ion is called the spectrochemical series. For example, a representative increasing order is $Cl^- < H_2O < NH_3 < CN^-$. Ligands towards the beginning are weak-field ligands, while those towards the end are strong-field ligands. This is an order of splitting ability, rather than an order of the observed colours of complexes.

Step 2: Relate tetrahedral and octahedral splitting For the same metal ion and the same ligands, the tetrahedral splitting is smaller than the octahedral splitting. The standard crystal field relation is

$$\Delta_t = \frac{4}{9}\Delta_o.$$

The factor compares magnitudes of the energy gaps; it does not imply that the ordering of the two sets of d orbitals is the same in the two geometries.

Step 3: Conclusion The spectrochemical series is the increasing order of ligand field strength, and $\boxed{\Delta_t = \frac{4}{9}\Delta_o}$ for the same metal ion and ligands.

Quick Tip to Solve: State the same-metal and same-ligand condition when using the factor 4/9.

30(b). Arrange $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ and $[Cu(H_2O)_4]^{2+}$ in increasing order of wavelength of light absorbed. [1 mark]

Solution:

Concept:

- The required order is read from the absorption wavelengths given in the table, not from the colours observed.

Step 1: Identify the tabulated wavelengths The table gives 310 nm for $[Co(CN)_6]^{3-}$, 475 nm for $[Co(NH_3)_6]^{3+}$, and 600 nm for $[Cu(H_2O)_4]^{2+}$.

Step 2: Compare the numerical values Increasing wavelength means smallest to largest. Since $310 < 475 < 600$, the cyanide complex comes first, the ammine complex second, and the aqua copper complex last. The complementary colour of a complex must not be substituted for its absorbed wavelength.

Step 3: Conclusion

$$\boxed{[Co(CN)_6]^{3-} < [Co(NH_3)_6]^{3+} < [Cu(H_2O)_4]^{2+}}$$

in increasing wavelength of absorbed light.

Quick Tip to Solve: Attach each tabulated wavelength to its complex before sorting the three values.

OR

30(b). On the basis of crystal field theory, write the electronic configuration of d^5 ion if $\Delta_o < P$. [1 mark]

Solution:

Concept:

- For an octahedral field, t_{2g} contains three lower-energy orbitals and e_g contains two higher-energy orbitals.
- When $\Delta_o < P$, promotion to e_g costs less energy than pairing in t_{2g}, where P is the pairing energy.

Step 1: Fill the lower set singly A d^5 ion has five d electrons. By Hundś rule the first three electrons occupy the three different t_{2g} orbitals with parallel spins.

Step 2: Place the remaining electrons Because $\Delta_o < P$, the fourth and fifth electrons occupy the two separate e_g orbitals instead of pairing in t_{2g}. Thus all five d orbitals are singly occupied. This is the high-spin arrangement with five unpaired electrons; the low-spin arrangement would require the opposite energy preference.

Step 3: Conclusion The electronic configuration is $\boxed{t_{2g}^3 e_g^2}$ (high spin, five unpaired electrons).

Quick Tip to Solve: Compare splitting with pairing energy before placing the fourth electron of a d5 ion.

30(c). Define crystal field splitting energy. [1 mark]

Solution:

Concept:

- The five d orbitals of a free metal ion are degenerate, meaning that they have the same energy.

Step 1: Describe the effect of ligands When ligands approach a central metal ion, their electric field interacts unequally with d orbitals of different spatial orientations. The initially degenerate orbitals therefore separate into groups of different energies.

Step 2: Identify the energy gap The difference in energy between the two sets of d orbitals produced by the ligand field is called the crystal field splitting energy. It is represented by Δ, with Δ_o for an octahedral arrangement and Δ_t for a tetrahedral arrangement. It is an orbital energy separation, rather than a difference between the colours observed.

Step 3: Conclusion Crystal field splitting energy is the energy difference between the two sets of d orbitals split by the ligand field.

Quick Tip to Solve: Define the energy difference between orbital sets, and use the geometry subscript if specified.

Section E (15 marks)

31(a)(i). An organic compound 'P' ($C_8H_{10}O$) on oxidation gave compound 'Q'. The compound 'Q' can also be obtained from a reaction of benzene with acetyl chloride in the presence of anhydrous $AlCl_3$. 'Q' on treatment with I_2 in aq. NaOH gave 'R' and a yellow compound 'S'. Identify 'P', 'Q', 'R' and 'S'. [4 marks]

Solution:

Concept:

- Friedel–Crafts acylation introduces an acetyl group, $-COCH_3$, into benzene using acetyl chloride and anhydrous $AlCl_3$.
- Oxidation of a secondary alcohol gives a ketone without changing the carbon skeleton.
- Methyl ketones give a carboxylate salt and yellow iodoform with $I_2/NaOH$.

Step 1: Identify Q from its independent preparation Benzene reacts with acetyl chloride by electrophilic substitution:

$$C_6H_6 + CH_3COCl \xrightarrow{\text{anhyd. } AlCl_3} C_6H_5COCH_3 + HCl.$$

Thus Q is acetophenone (1-phenylethanone), $C_6H_5COCH_3$. The acetyl group attaches to the aromatic ring through its carbonyl carbon. This preparation identifies the ketone unambiguously.

Step 2: Identify P by reversing the oxidation The secondary alcohol corresponding to acetophenone has an OH group at the carbon that becomes the carbonyl carbon:

$$C_6H_5CH(OH)CH_3 + [O] \longrightarrow C_6H_5COCH_3 + H_2O.$$

Therefore P is 1-phenylethanol, $C_6H_5CH(OH)CH_3$. It has eight carbon atoms, ten hydrogen atoms and one oxygen atom, agreeing with $C_8H_{10}O$. Oxidation removes two hydrogen atoms while preserving the carbon skeleton.

Step 3: Use the iodoform reaction to identify R and S Acetophenone contains the methyl-ketone unit $-COCH_3$, which undergoes iodination followed by cleavage in aqueous sodium hydroxide:

$$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3 \downarrow + 3NaI + 3H_2O.$$

The yellow precipitate S is iodoform, CHI_3. The other organic product R is sodium benzoate, C_6H_5COONa. Since the medium is alkaline, R is the carboxylate salt; benzoic acid would be obtained only after a separate acidification step.

Step 4: Conclusion P: $C_6H_5CH(OH)CH_3$, 1-phenylethanol; Q: $C_6H_5COCH_3$, acetophenone; R: C_6H_5COONa, sodium benzoate; S: CHI_3, iodoform.

Quick Tip to Solve: Start with the Friedel–Crafts clue, then remember that alkaline iodoform cleavage produces the carboxylate salt.

31(a)(ii). Give the structure(s) of the product(s) when benzaldehyde is heated in the presence of conc. KOH. [1 mark]

Solution:

Concept:

- An aldehyde without an α-hydrogen undergoes the Cannizzaro reaction with concentrated alkali.
- Two aldehyde molecules disproportionate: one is reduced to an alcohol and the other is oxidised to a carboxylate salt.

Step 1: Check the reaction condition Benzaldehyde, C_6H_5CHO, has no α-hydrogen because its aldehyde group is directly attached to the benzene ring. Heating with concentrated KOH therefore causes the Cannizzaro reaction.

Step 2: Write the products and balanced equation

$$2C_6H_5CHO + KOH \xrightarrow{\Delta} C_6H_5CH_2OH + C_6H_5COOK.$$

The reduced product has the condensed structure $C_6H_5 - CH_2 - OH$, and the oxidised product is the potassium salt $C_6H_5 - C(=O)O^-K^+$. The alkaline medium gives the salt rather than free benzoic acid.

Step 3: Conclusion The products are benzyl alcohol, $C_6H_5CH_2OH$, and potassium benzoate, C_6H_5COOK.

Quick Tip to Solve: For benzaldehyde in concentrated KOH, pair one alcohol molecule with one potassium carboxylate molecule.

OR

31(b)(i). Carry out the following conversions :

(I) Propanone to Propane

(II) Acetophenone to Benzoic acid

(III) Benzyl chloride to Phenylethanoic acid [3 marks]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using $\mathrm{Zn(Hg)/conc.\ HCl}$.
- The haloform reaction cleaves methyl ketones to carboxylate salts; acidification gives the carboxylic acid.
- An alkyl halide reacts with alcoholic KCN to give a nitrile, adding one carbon atom; hydrolysis converts the nitrile group into a carboxyl group.

Step 1: I. Propanone to propane Reduce propanone using zinc amalgam and concentrated hydrochloric acid (Clemmensen reduction):

$$\mathrm{CH_3COCH_3 + 4[H] \xrightarrow{Zn(Hg)/conc.\ HCl} CH_3CH_2CH_3 + H_2O.}$$

The ketonic $> \mathrm{C = O}$ group becomes $> \mathrm{CH_2}$, while all three carbon atoms remain in the chain. A reagent that merely gives propan-2-ol would not complete this conversion.

Step 2: II. Acetophenone to benzoic acid Treat acetophenone with iodine and aqueous NaOH, then acidify the sodium benzoate formed:

$$\begin{aligned}&\mathrm{C_6H_5COCH_3 + 3I_2 + 4NaOH}\\&\quad\longrightarrow \mathrm{C_6H_5COONa + CHI_3 + 3NaI + 3H_2O,}\\&\mathrm{C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl.}\end{aligned}$$

Haloform cleavage removes the terminal methyl carbon as iodoform. Acidification is essential to obtain benzoic acid rather than its sodium salt.

Step 3: III. Benzyl chloride to phenylethanoic acid First replace chlorine with cyanide using alcoholic KCN, obtaining phenylacetonitrile (benzyl cyanide). Then hydrolyse the nitrile with dilute aqueous acid on heating:

$$\begin{aligned}&\mathrm{C_6H_5CH_2Cl + KCN \xrightarrow{alcohol} C_6H_5CH_2CN + KCl,}\\&\mathrm{C_6H_5CH_2CN + 2H_2O + HCl \xrightarrow{\Delta}}\\&\quad\mathrm{C_6H_5CH_2COOH + NH_4Cl.}\end{aligned}$$

The cyanide carbon becomes the carboxyl carbon, giving the required one-carbon chain extension. Use KCN for nitrile formation; AgCN favours an isocyanide and does not give this sequence.

Step 4: Conclusion The required sequences use (I) $\mathrm{Zn(Hg)/conc.\ HCl}$; (II) $\mathrm{I_2/NaOH}$, followed by acidification; (III) alcoholic KCN, followed by hot aqueous acidic hydrolysis.

Quick Tip to Solve: Check carbon counts: haloform cleavage removes one carbon, whereas cyanide substitution followed by hydrolysis adds one.

31(b)(ii). Give a simple chemical test to distinguish between the following pairs of compounds :

(I) Benzaldehyde and Phenol

(II) Butanal and Butan-2-one [2 marks]

Solution:

Concept:

- Neutral ferric chloride detects a phenolic hydroxyl group through formation of a coloured iron(III) complex.
- Tollens' reagent oxidises aldehydes to carboxylates while silver(I) is reduced to silver metal; ordinary ketones do not react.

Step 1: (I) Test benzaldehyde and phenol with neutral ferric chloride Add a few drops of neutral $FeCl_3$ solution to each sample separately. Phenol gives a violet colour due to formation of a coloured complex with iron(III). Benzaldehyde gives no violet colour because it has no phenolic hydroxyl group. This difference identifies phenol directly.

Step 2: (II) Test butanal and butan-2-one with Tollens' reagent Warm each sample gently with freshly prepared Tollens' reagent in separate clean test tubes. Butanal gives a silver mirror on the inner wall, whereas butan-2-one gives no silver mirror. The aldehyde is oxidised as follows:

$$CH_3CH_2CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Butan-2-one is a ketone and does not reduce this mild oxidising reagent under the test conditions.

Step 3: Conclusion Phenol gives a violet colour with neutral $FeCl_3$, while benzaldehyde does not. Butanal gives a silver mirror with Tollens' reagent, while butan-2-one does not.

Quick Tip to Solve: Use neutral ferric chloride for the phenolic group and Tollens' reagent for the aldehyde group.

32(a). (i) Write the chemical equations involved in the preparation of potassium permanganate from pyrolusite ore (MnO_2).

(ii) Give reasons for the following :

(I) Sc (Atomic No. 21) salts are white.

(II) $E^\circ_{Cu2+/Cu}$ is positive whereas $E^\circ_{Mn2+/Mn}$ is negative.

(III) Transition metals have high enthalpies of atomisation. [5 marks]

Solution:

Concept:

- Preparation of permanganate proceeds through green manganate, MnO_4^{2-}: manganese is oxidised from $+4$ to $+6$, then to $+7$.
- The colour of many transition-metal ions arises from d-d transitions, which require a partly filled d subshell.

- The standard electrode potential depends on the overall energy balance involving atomisation, ionisation and hydration, rather than on any single energy term.

Step 1: (i) Oxidise pyrolusite to potassium manganate Finely powdered pyrolusite is fused with potassium hydroxide in the presence of air or oxygen. The manganese(IV) oxide is oxidised to green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{fusion}} 2K_2MnO_4 + 2H_2O.$$

The oxidation state of manganese increases from $+4$ in the ore to $+6$ in manganate.

Step 2: (i) Convert manganate into permanganate Electrolytic oxidation of an alkaline manganate solution gives permanganate at the anode:

$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-.$$

With hydrogen evolution at the cathode, the overall equation is

$$2K_2MnO_4 + 2H_2O \xrightarrow{\text{electrolysis}} 2KMnO_4 + 2KOH + H_2.$$

Thus manganese reaches $+7$ in potassium permanganate. Alternatively, chemical oxidation with chlorine is represented by

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl.$$

Step 3: (ii)(I) Explain the white colour of scandium salts Scandium has configuration $[Ar]3d^14s^2$. Its usual ion, Sc^{3+}, has configuration $[Ar]3d^0$. Since no d electron is present, d-d absorption in the visible region cannot occur. Hence its usual salts are white and their aqueous solutions are colourless, provided the anion itself is colourless.

Step 4: (ii)(II) Compare the electrode potentials of copper and manganese For copper, the energy needed for atomisation and ionisation, especially the second ionisation from stable $Cu^+(3d^{10})$, is not compensated by hydration of Cu^{2+}. Oxidation of copper to aqueous Cu^{2+} is therefore unfavourable under standard conditions; the reverse reduction has a positive standard potential. For manganese, hydration together with the stability of half-filled $Mn^{2+}(3d^5)$ favours formation of the aqueous divalent ion from the metal. Thus its oxidation is favourable, and the reverse Mn^{2+}/Mn reduction potential is negative.

Step 5: (ii)(III) Explain high enthalpies of atomisation Transition metals have strong metallic bonding because both $(n-1)d$ and ns electrons participate in bonding. The availability of several unpaired d electrons generally strengthens interatomic bonding. Considerable energy is therefore required to separate the solid into individual gaseous atoms, giving high enthalpies of atomisation.

Step 6: Conclusion Pyrolusite is converted through K_2MnO_4 into $KMnO_4$. The d^0 configuration explains white scandium(III) salts; the overall formation-energy balance explains the opposite signs of the copper and manganese reduction potentials; strong metallic bonding explains high atomisation enthalpies.

Quick Tip to Solve: Track manganese as $+4 \rightarrow +6 \rightarrow +7$, and compare electrode potentials using the full atomisation-ionisation-hydration balance.

OR

32(b). (i) Complete and balance the following chemical equations :

(I) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+ \rightarrow$

(II) $Cu^{2+}(aq) + I^-(aq) \rightarrow$

(ii) Give reasons :

(I) Separation of mixture of lanthanoids is difficult.

(II) Chromium has higher melting point than manganese.

(III) It is difficult to obtain oxidation state greater than two for Zn. [5 marks]

Solution:

Concept:

- Redox equations conserve both atoms and total charge. In acid, dichromate is reduced from chromium(VI) to chromium(III), while hydrogen sulphide is oxidised to sulphur.
- Similar ionic radii and the common $+3$ oxidation state make the chemical properties of lanthanoids very similar.
- Metallic bond strength depends on electron participation in bonding, while removal of an electron from a completely filled $3d^{10}$ subshell requires high energy.

Step 1: (i)(I) Balance dichromate with hydrogen sulphide The reduction and oxidation half-equations in acidic medium are

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O},$$
$$\mathrm{H_2S \longrightarrow S + 2H^+ + 2e^-}.$$

Multiply the second equation by three, add and cancel electrons and six hydrogen ions:

$$\boxed{\mathrm{Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)}}.$$

Both sides contain two chromium, seven oxygen, fourteen hydrogen and three sulphur atoms; their total charge is $+6$.

Step 2: (i)(II) Balance copper(II) with iodide Copper(II) oxidises iodide to iodine and is itself reduced to copper(I). Insoluble copper(I) iodide precipitates:

$$\mathrm{2Cu^{2+} + 2e^- \longrightarrow 2Cu^+},$$
$$\mathrm{2I^- \longrightarrow I_2 + 2e^-},$$
$$\mathrm{2Cu^+ + 2I^- \longrightarrow 2CuI(s)}.$$

Therefore the complete net equation is

$$\boxed{\mathrm{2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2}}.$$

Two iodide ions supply the electrons and two more form the precipitate. The net charge on each side is zero.

Step 3: (ii)(I) Explain difficult lanthanoid separation Lanthanoids predominantly form Ln^{3+} ions. Their ionic radii differ only slightly because the gradual lanthanoid contraction makes neighbouring

ions very similar in size. Their chemical properties, including complex formation and solubility behaviour, consequently differ only slightly. Ordinary chemical separation of their mixture is therefore difficult.

Step 4: (ii)(II) Compare chromium and manganese Chromium has configuration $[\mathrm{Ar}]3d^5 4s^1$, with six unpaired valence electrons available for participation in metallic bonding. Manganese is $[\mathrm{Ar}]3d^5 4s^2$; its stable half-filled $3d^5$ arrangement and paired $4s$ electrons result in weaker metallic bonding than in chromium. The stronger interatomic bonding in chromium requires more energy to disrupt on melting, so its melting point is higher.

Step 5: (ii)(III) Explain zinc's oxidation-state limit Zinc has configuration $[\mathrm{Ar}]3d^{10}4s^2$. Loss of the two outer $4s$ electrons produces Zn^{2+}, which has the stable, completely filled $3d^{10}$ subshell. Oxidation beyond $+2$ would require removing a $3d$ electron and breaking this stable configuration. The very high third ionisation enthalpy makes such oxidation difficult.

Step 6: Conclusion Dichromate forms Cr^{3+}, sulphur and water; copper(II) with iodide forms CuI and iodine, in the balanced equations above. Similar trivalent lanthanoid ions resist separation, stronger metallic bonding raises chromium's melting point, and stable $3d^{10}$ zinc(II) resists further oxidation.

Quick Tip to Solve: In the copper-iodide equation, reserve two iodide ions for oxidation and two for precipitation; omitting the latter gives an incorrect equation.

33(a). (i) Define osmotic pressure. Why is it considered as a colligative property ?

(ii) The vapour pressure of two pure liquids A and B at 400 K are 450 and 700 mmHg respectively. Find out the composition of liquid mixture if the total vapour pressure of mixture is 600 mmHg. [5 marks]

Solution:

Concept:

- Osmosis is the passage of solvent through a semipermeable membrane from pure solvent (or a dilute solution) towards a more concentrated solution. The membrane allows solvent molecules to pass but retains solute particles.
- For a dilute solution, osmotic pressure obeys $\pi V = nRT$, or $\pi = CRT$, where n is the amount of solute particles, V is solution volume, $C = n/V$, R is the gas constant and T is absolute temperature.
- For an ideal binary liquid mixture, Raoult's law gives $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$. The total pressure is $P = p_A + p_B$, with liquid-phase mole fractions satisfying $x_A + x_B = 1$.

Step 1: (i) Define osmotic pressure Osmotic pressure, π, is the minimum excess pressure that must be applied to the solution to prevent the flow of solvent into it through a semipermeable membrane separating it from pure solvent. At this pressure the net passage of solvent due to osmosis stops. It is the pressure applied on the solution side relative to the pure solvent side.

Step 2: (i) Explain its colligative nature The relation $\pi = (n/V)RT$ shows that, at a given temperature and solution volume, osmotic pressure depends on the number of dissolved solute particles and not on their chemical identity. Therefore it is a colligative property. Equimolar dilute solutions of non-electrolytes have the same osmotic pressure at the same temperature. If a solute dissociates or

associates, the actual number of particles must be used, equivalently $\pi = iCRT$ with van't Hoff factor i.

Step 3: (ii) Set up the total vapour pressure equation Applying Raoult's law to the mixture at $400\,\text{K}$, use $p_A^\circ = 450\,\text{mmHg}$, $p_B^\circ = 700\,\text{mmHg}$ and $P = 600\,\text{mmHg}$. Substituting $x_B = 1 - x_A$,

$$\begin{aligned} P &= x_A p_A^\circ + (1 - x_A) p_B^\circ, \\ 600 &= 450 x_A + 700(1 - x_A), \\ 600 &= 700 - 250 x_A. \end{aligned}$$

All pressures are expressed in the same unit, so the mole fractions obtained are dimensionless.

Step 4: (ii) Calculate and verify the liquid composition Rearranging gives

$$x_A = \frac{700 - 600}{700 - 450} = \frac{100}{250} = 0.40, \qquad x_B = 1 - 0.40 = 0.60.$$

As a check, the partial pressures are $p_A = 0.40 \times 450 = 180\,\text{mmHg}$ and $p_B = 0.60 \times 700 = 420\,\text{mmHg}$. Their sum is $600\,\text{mmHg}$, as required. These are the mole fractions in the liquid mixture; the component with the higher pure vapour pressure is B.

Step 5: Conclusion (i) Osmotic pressure is the excess pressure required on a solution to stop osmosis; it is colligative because it depends on the number of solute particles at fixed temperature and volume. (ii) The liquid mixture contains $x_A = 0.40$ and $x_B = 0.60$, i.e. 40% A and 60% B by mole, with mole ratio $A : B = 2 : 3$.

Quick Tip to Solve: Write total pressure as $P = p_B^\circ + x_A(p_A^\circ - p_B^\circ)$; it gives one unknown directly. Do not confuse liquid mole fractions with vapour composition.

OR

33(b). (i) What type of deviation from Raoult's law is expected when phenol and aniline are mixed with each other ? What change in the net volume of the mixture and enthalpy is expected ?
(ii) Boiling point of water at 750 mmHg is 99.48°C. How much sucrose (M = 342 g mol^{-1}) is to be added to 500 g of water such that it boils at 100°C ? [K_b for water = 0.52 K kg mol^{-1}] [5 marks]

Solution:

Concept:

- In an ideal solution, each component obeys Raoult's law, $p_i = x_i p_i^\circ$. Stronger attractions between unlike molecules than between like molecules reduce their escaping tendency and cause a negative deviation.
- For a dilute solution of a non-volatile, non-electrolyte solute, the elevation of boiling point is $\Delta T_b = K_b m$, where m is the moles of solute per kilogram of solvent. Sucrose does not dissociate, so its van't Hoff factor is $i = 1$.

Step 1: (i) Identify the intermolecular interaction and deviation When phenol and aniline are mixed, the hydrogen of the phenolic $-\text{OH}$ group forms a strong hydrogen bond with the lone pair on the

nitrogen atom of aniline. The resulting phenol-aniline attractions are stronger than the average attractions in the separate pure liquids. Molecules therefore escape into the vapour less readily, and the partial vapour pressures, and hence the total vapour pressure, lie below the values predicted by Raoult's law. Thus, the mixture exhibits negative deviation.

Step 2: (i) State the volume and enthalpy changes The stronger unlike-molecule attractions bring the molecules closer together. Consequently, the volume of the mixture is smaller than the sum of the volumes of the separate liquids:

$$\Delta V_{\text{mix}} = V_{\text{mixture}} - (V_{\text{phenol}} + V_{\text{aniline}}) < 0.$$

Formation of these stronger interactions releases heat. Mixing is therefore exothermic, with $\Delta H_{\text{mix}} < 0$.

Step 3: (ii) Calculate the required boiling-point elevation Both the solvent and solution boiling points must be compared at the same external pressure, namely $750\,\text{mmHg}$. At this pressure pure water boils at 99.48°C, while the desired solution must boil at 100°C. Therefore,

$$\Delta T_b = 100.00 - 99.48 = 0.52\,\text{K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius. The normal boiling point at a different pressure is not the solvent reference for this calculation.

Step 4: (ii) Obtain the amount and mass of sucrose Applying the elevation-of-boiling-point equation gives

$$m = \frac{\Delta T_b}{K_b} = \frac{0.52\,\text{K}}{0.52\,\text{K kg mol}^{-1}} = 1.00\,\text{mol kg}^{-1}.$$

The mass of solvent is $500\,\text{g} = 0.500\,\text{kg}$. Hence,

$$n_{\text{sucrose}} = m \times 0.500\,\text{kg} = 0.500\,\text{mol},$$
$$w_{\text{sucrose}} = nM = 0.500 \times 342 = 171\,\text{g}.$$

The denominator in molality is the mass of water alone, not the total mass after adding sucrose. As a check, $171/342 = 0.500$ mol in 0.500 kg water gives $m = 1$, and thus raises the boiling point by exactly $0.52\,\text{K}$.

Step 5: Conclusion (i) Phenol-aniline shows negative deviation from Raoult's law, with contraction in volume ($\Delta V_{\text{mix}} < 0$) and an exothermic enthalpy change ($\Delta H_{\text{mix}} < 0$). (ii) The required mass of sucrose is $\boxed{171\,\text{g}}$.

Quick Tip to Solve: At 750 mmHg, subtract 99.48 from 100 before using the boiling-point formula, and express the 500 g of water as 0.500 kg.