CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-7-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

(ii) 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. With increase in atomic number, the melting point of transition metals: [1 mark]

(A) first increases and then decreases

(B) increases continuously

(C) first decreases and then increases

(D) remains constant

Correct Answer: (A) first increases and then decreases

Solution:

Concept:

- Transition metals have strong metallic bonding because both outer s electrons and available d electrons participate in bonding.
- Across a transition series, the general melting-point trend reflects the changing strength of metallic bonding; individual elements may show irregularities.

Step 1: Follow the initial rise From the beginning towards the middle of a transition series, the number of electrons available for strong metallic bonding generally increases. Stronger bonding requires more thermal energy to disrupt the solid lattice, so the melting point generally rises.

Step 2: Follow the later fall and compare the choices Beyond the middle, increased pairing in the d subshell reduces the contribution associated with unpaired electrons, and the melting point generally falls. Thus a continuous increase, an initial decrease followed by increase, or a constant value does not describe the overall trend.

Step 3: Conclusion The melting point generally first increases and then decreases as atomic number increases across a transition series. Hence, the correct option is (A).

Quick Tip to Solve: Remember the broad peak near the middle of a transition series; the question asks for the general trend, not every exception.

2. Which of the following aqueous solutions will have the highest osmotic pressure? [1 mark]

(A) 1% KCl

(B) 1% glucose

(C) 1% urea

(D) 1% $CaCl_2$

Correct Answer: (D) 1% $CaCl_2$

Solution:

Concept:

- Osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C the molar concentration, R the gas constant and T the absolute temperature.

Quick Tip to Solve: For equal percentages, calculate ion count divided by molar mass; here KCl and calcium chloride are close, so compare numerically.

- For equal percentage concentrations at the same temperature, compare i/M, where M is molar mass; electrolytes furnish more particles by dissociation.

Step 1: Count the dissolved particles Glucose and urea do not ionise, so each has $i = 1$. Complete dissociation of KCl gives K^+ and Cl^-, hence $i = 2$. Dissociation of $CaCl_2$ gives Ca^{2+} and two Cl^-, hence $i = 3$.

Step 2: Compare particles per equal mass of solute Using molar masses in g mol^{-1}, the quantities proportional to osmotic pressure are

$$\begin{aligned} \text{KCl}: &\quad 2/74.5 = 0.02685, \\ \text{glucose}: &\quad 1/180 = 0.00556, \\ \text{urea}: &\quad 1/60 = 0.01667, \\ \text{CaCl}_2: &\quad 3/111 = 0.02703. \end{aligned}$$

Calcium chloride gives the greatest value, slightly higher than potassium chloride. Counting ions alone is insufficient because equal mass percentages do not mean equal molarity.

Step 3: Conclusion The 1% aqueous $CaCl_2$ solution has the highest osmotic pressure under the usual ideal-dissociation comparison. Hence, the correct option is (D).

Quick Tip to Solve: For equal percentages, calculate ion count divided by molar mass; here KCl and calcium chloride are close, so compare numerically.

3. A conductivity cell usually consists of two: [1 mark]

(A) Copper electrodes

(B) Platinum electrodes

(C) Zinc electrodes

(D) Iron electrodes

Correct Answer: (B) Platinum electrodes

Solution:

Concept:

- A conductivity cell measures the conductance of an electrolyte between two electrodes of known geometry.
- Platinum is a chemically resistant conductor; platinum black increases effective electrode surface area and reduces polarisation effects.

Step 1: Identify the standard electrodes A usual conductivity cell contains two platinum electrodes, often coated with platinum black. They are arranged parallel to each other with a fixed separation, so the measured conductance can be related to conductivity using the cell constant.

Step 2: Eliminate reactive metal choices Copper, zinc and iron can take part in chemical or electrode reactions in the electrolyte and may alter the solution composition. They are therefore not the standard electrode material for an ordinary conductivity cell. Platinum provides a suitable resistant

Quick Tip to Solve: Associate conductivity measurements with platinised platinum electrodes and a fixed cell constant.

conducting surface.

Step 3: Conclusion A conductivity cell usually consists of two platinum electrodes. Hence, the correct option is (B).

Quick Tip to Solve: Associate conductivity measurements with platinised platinum electrodes and a fixed cell constant.

4. Which of the following is the slope of the first order reaction in the plot of ln[R] vs. time? [1 mark]

(A) +k

(B) +k/2.303

(C) -k

(D) -k/2.303

Correct Answer: (C) -k

Solution:

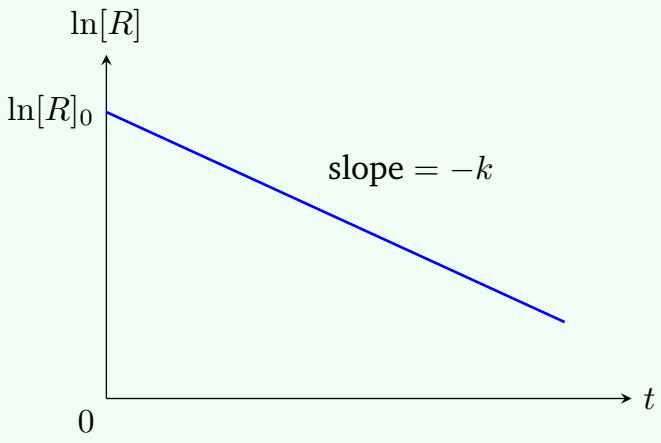
Concept:

- For a first-order reaction, $-d[R]/dt = k[R]$, where $[R]$ is reactant concentration and $k > 0$ is the rate constant.
- The integrated equation is $\ln[R] = \ln[R]_0 - kt$. For a straight line $y = c + mt$, the coefficient of time is its slope.

Step 1: Write the linear equation Integration of the first-order rate law gives

$$\ln\left(\frac{[R]}{[R]_0}\right) = -kt, \qquad \ln[R] = \ln[R]_0 - kt.$$

Thus a plot of natural logarithm of concentration against time is a descending straight line with initial intercept $\ln[R]_0$.



Schematic first-order plot of natural logarithm of reactant concentration against time

Step 2: Read the coefficient of time Comparing with $y = c + mt$, take $y = \ln[R]$ and $m = -k$. A positive slope would mean increasing reactant concentration and is incorrect here. The factor 2.303 occurs only when the equation is written with the common logarithm: $\log_{10}[R] = \log_{10}[R]_0 - kt/2.303$.

Quick Tip to Solve: Inspect the logarithm base first: natural log gives slope -k; common log gives -k/2.303.

It is absent from this natural-logarithm plot.

Step 3: Conclusion The slope of the $\ln[R]$ versus time plot is $-k$. Hence, the correct option is (C).

Quick Tip to Solve: Inspect the logarithm base first: natural log gives slope -k; common log gives -k/2.303.

5. Which of the following represents the fraction of molecules with energies equal to or greater than E_a? [1 mark]

(A) $-E_a/RT$

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

(C) $e^{+E_a/RT}$

(D) $+E_a/RT$

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

Solution:

Concept:

- In the Arrhenius treatment, the fraction of molecules with sufficient activation energy is represented by $e^{-E_a/(RT)}$.
- Here E_a is molar activation energy, R is the gas constant and T is absolute temperature; the ratio $E_a/(RT)$ is dimensionless.

Step 1: Use the activation-energy factor For positive activation energy, the energy factor is an exponential with a negative exponent:

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

It lies between zero and one, as a molecular fraction must, and increases towards one when temperature increases with activation energy fixed.

Step 2: Test the other expressions The expression $-E_a/(RT)$ is negative and cannot represent a fraction. The positive-exponent expression $e^{+E_a/(RT)}$ exceeds one for positive E_a. The bare positive ratio $E_a/(RT)$ is not the Arrhenius fraction and increases when temperature decreases, unlike the required fraction. Therefore only the negative exponential is suitable.

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

Quick Tip to Solve: A fraction must lie from zero to one: for positive activation energy, select the exponential with a negative exponent.

6. The number of moles of AgCl precipitated when excess $AgNO_3$ solution is mixed with one mole of $[Co(NH_3)_6]Cl_3$ is: [1 mark]

(A) 0

(B) 3

(C) 6

(D) 4

Correct Answer: (B) 3

Solution:

Concept:

- In a coordination compound, ions outside square brackets are counterions and dissociate in aqueous solution.
- Silver ions precipitate free chloride ions as $AgCl$ in a $1:1$ mole ratio: $Ag^+ + Cl^- \rightarrow AgCl(s)$.

Step 1: Identify ionisable chloride ions The compound dissociates as

$$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-.$$

All three chloride ions are outside the coordination sphere and are available for precipitation. The six ammonia molecules are coordinated neutral ligands and do not supply chloride ions.

Step 2: Apply the precipitation stoichiometry One mole of the compound releases three moles of chloride ions. Excess $AgNO_3$ supplies enough silver ions to precipitate all of them. Since one mole of chloride forms one mole of silver chloride, the precipitate amount is $3 \times 1 = 3$ mol. Zero would require no free chloride; six counts ammonia ligands; four is not the number of ionisable chlorides.

Step 3: Conclusion One mole of $[Co(NH_3)_6]Cl_3$ gives 3 mol of $AgCl$. Hence, the correct option is (B).

Quick Tip to Solve: Count chloride ions outside the square brackets; each gives one mole of AgCl per mole of the coordination compound.

7. Which of the following haloalkanes is most reactive towards S_N2 reaction? [1 mark]

(A) CH_3-CH_2-I

(B) CH_3-CH_2-Br

(C) CH_3-CH_2-Cl

(D) CH_3-CH_2-F

Correct Answer: (A) CH_3-CH_2-I

Solution:

Concept:

- An S_N2 reaction is a single-step nucleophilic substitution: nucleophile attack and carbon-halogen bond cleavage occur together.
- For the same alkyl group, leaving-group ability follows $I^- > Br^- > Cl^- > F^-$. A weaker carbon-halogen bond favours displacement.

Quick Tip to Solve: When the alkyl group is unchanged, rank the halogens by leaving-group ability: $I > Br > Cl > F$.

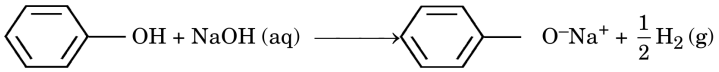
Step 1: Compare the alkyl groups All four choices are ethyl halides, CH_3CH_2X, so their carbon skeleton and steric hindrance are the same. The difference in reactivity therefore comes from the halogen rather than from primary versus secondary substitution.

Step 2: Compare the leaving groups The carbon-iodine bond is the weakest of these carbon-halogen bonds, and iodide is the best leaving group. The order is $CH_3CH_2I > CH_3CH_2Br > CH_3CH_2Cl > CH_3CH_2F$. Thus bromide and chloride are slower, while fluoride has the strongest bond and poorest leaving-group ability.

Step 3: Conclusion Ethyl iodide, CH_3CH_2I, is most reactive. Hence, the correct option is (A).

Quick Tip to Solve: When the alkyl group is unchanged, rank the halogens by leaving-group ability: $I > Br > Cl > F$.

8. The reaction suggests that phenol is: [1 mark]



(A) Basic

(B) Neutral

(C) Acidic

(D) Amphoteric

Correct Answer: (C) Acidic

Solution:

Concept:

- An acid donates a proton to a base. Phenol, C_6H_5OH, loses its phenolic proton to form the phenoxide ion, $C_6H_5O^-$.
- Phenoxide is stabilised by resonance; this makes phenol sufficiently acidic to react with aqueous $NaOH$.

Step 1: Identify the salt formation The conversion of phenol into sodium phenoxide indicates loss of the proton attached to oxygen. Hydroxide accepts that proton, so phenol acts as the acid and OH^- acts as the base.

Step 2: Apply the acid-base criterion The balanced neutralisation with aqueous sodium hydroxide is

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O.$$

The hydrogen gas displayed in the question would instead be produced with sodium metal, not aqueous sodium hydroxide. This product discrepancy does not change the classification inferred from phenoxide formation. Basic, neutral and amphoteric behaviour are not indicated by this acid-base reaction.

Step 3: Conclusion Phenol exhibits acidic behaviour by forming sodium phenoxide. Hence, the correct option is (C).

Quick Tip to Solve: Look for replacement of the phenolic proton by sodium: formation of phenoxide with aqueous alkali identifies acidic behaviour.

9. Phenol reacts with conc. HNO_3 to form: [1 mark]

(A) Salicylic acid

(B) Picric acid

(C) Benzoic acid

(D) Phthalic acid

Correct Answer: (B) Picric acid

Solution:

Concept:

- The $-OH$ group activates the benzene ring towards electrophilic substitution and directs substitution to the ortho and para positions.
- Concentrated nitric acid causes extensive nitration of phenol; the nitro groups enter positions 2, 4 and 6.

Step 1: Determine the substituted positions The hydroxyl group increases electron density at the two ortho positions and the para position. With concentrated HNO_3, all three of these positions undergo nitration rather than only one position as in mild nitration.

Step 2: Identify the product name The product is 2,4,6-trinitrophenol, commonly called picric acid:

$$C_6H_5OH + 3\,HNO_3 \longrightarrow C_6H_2(NO_2)_3OH + 3\,H_2O.$$

Salicylic acid contains a carboxyl group in addition to hydroxyl; benzoic and phthalic acids are carboxylic acids. None of those products follows from nitrating phenol.

Step 3: Conclusion Phenol forms picric acid with concentrated nitric acid. Hence, the correct option is (B).

Quick Tip to Solve: For phenol, associate dilute nitric acid with mononitration and concentrated nitric acid with 2,4,6-trinitration.

10. Anilinium hydrogen sulphate on heating at 453 - 473 K produces which of the following as a major product? [1 mark]

(A) 2-aminobenzene sulphonic acid

(B) benzene sulphonic acid

(C) 2-aminobenzoic acid

(D) sulphanilic acid

Correct Answer: (D) sulphanilic acid

Solution:

Concept:

- Aniline forms the salt anilinium hydrogen sulphate with concentrated sulphuric acid. The salt is $C_6H_5NH_3^+\,HSO_4^-$.
- Heating this salt at 453–$473\,K$ gives mainly sulphanilic acid, the para sulphonic acid derivative of

Quick Tip to Solve: Remember the paired facts: heat anilinium hydrogen sulphate at 453–$473\,K$ to obtain the para product, sulphanilic acid.

aniline.

Step 1: Recognise the heating reaction The specified temperature range is the standard preparation of sulphanilic acid from anilinium hydrogen sulphate. The sulphonic acid group becomes attached to the aromatic ring, chiefly para to the amino group.

Step 2: Match the positional isomer The product has an amino group and a sulphonic acid group at positions 1 and 4: $\text{p-H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$, or 4-aminobenzenesulphonic acid. Option (A) gives the ortho isomer instead. Benzenesulphonic acid omits the amino group, and 2-aminobenzoic acid contains a carboxyl group rather than a sulphonic acid group.

Step 3: Conclusion The major product is sulphanilic acid. Hence, the correct option is (D).

Quick Tip to Solve: Remember the paired facts: heat anilinium hydrogen sulphate at 453–$473\,\text{K}$ to obtain the para product, sulphanilic acid.

11. Which of the following amines does not give foul smell of isocyanide on heating with chloroform and ethanolic KOH? [1 mark]

(A) CH_3-CH_2-NH_2

(B) CH_3-$CH(CH_3)$-CH_2-NH_2

(C) $(CH_3$-$CH_2)_3N$

(D) C_6H_5-NH_2

Correct Answer: (C) $(CH_3$-$CH_2)_3N$

Solution:

Concept:

- The carbylamine test uses chloroform and ethanolic potassium hydroxide to convert primary amines into foul-smelling isocyanides.
- Both aliphatic and aromatic primary amines react. Secondary and tertiary amines do not give this test.

Step 1: Classify the four nitrogen atoms Ethylamine in (A), 2-methylpropan-1-amine in (B), and aniline in (D) each contain $-\text{NH}_2$, so all are primary amines. Triethylamine, $(\text{CH}_3\text{CH}_2)_3\text{N}$, in (C) has three carbon groups bonded directly to nitrogen and is a tertiary amine.

Step 2: Apply the test selectively For a primary amine,

$$\text{RNH}_2 + \text{CHCl}_3 + 3\,\text{KOH} \longrightarrow \text{RNC} + 3\,\text{KCl} + 3\,\text{H}_2\text{O}.$$

The isocyanide RNC has the characteristic offensive smell. Triethylamine lacks the primary amino group and cannot undergo this conversion, whereas the other three choices respond positively.

Step 3: Conclusion Triethylamine does not give the foul smell of isocyanide. Hence, the correct option is (C).

Quick Tip to Solve: Count carbon groups attached directly to nitrogen, not branching elsewhere: only an $-\text{NH}_2$ group gives the carbylamine test.

12. Deficiency of vitamin B_1 causes the disease: [1 mark]

(A) Convulsions

(B) Beri-Beri

(C) Fissuring at corners of mouth and lips (Cheilosis)

(D) Muscular weakness

Correct Answer: (B) Beri-Beri

Solution:

Concept:

- Vitamin B_1 is thiamine, a water-soluble vitamin needed for normal carbohydrate metabolism and nerve function.
- Characteristic vitamin-deficiency diseases are identified by the specific vitamin, not just by a general symptom such as weakness.

Step 1: Recall the characteristic deficiency disease Deficiency of thiamine interferes with normal energy metabolism and can damage nerves and affect the heart. Its characteristic disease is beri-beri, which is the named disorder asked for in this question.

Step 2: Distinguish the distractors Convulsions are associated with deficiency of vitamin B_6, whereas fissuring at the mouth corners and cheilosis are associated with vitamin B_2. Muscular weakness is not the characteristic named disease that identifies vitamin B_1 deficiency in this list. These alternatives therefore do not replace the thiamine–beri-beri association.

Step 3: Conclusion Deficiency of vitamin B_1 causes beri-beri. Hence, the correct option is (B).

Quick Tip to Solve: Use the direct memory pair: B_1 = thiamine = beri-beri; B_2 deficiency points to cheilosis.

13. Assertion (A): A mixture of o-nitrophenol and p-nitrophenol can be separated by fractional distillation.

Reason (R): o-nitrophenol is steam volatile due to intramolecular hydrogen bonding. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Hydrogen bonding may be intramolecular, within one molecule, or intermolecular, between different molecules.
- Ortho-nitrophenol has intramolecular hydrogen bonding and is steam volatile; para-nitrophenol

Quick Tip to Solve: When nitrophenol isomers and steam volatility appear together, select steam distillation and link the ortho isomer to intramolecular hydrogen bonding.

has intermolecular hydrogen bonding and is much less steam volatile.

Step 1: Evaluate the assertion The standard separation of an ortho-nitrophenol and para-nitrophenol mixture uses steam distillation, because their behaviour in steam differs markedly. The assertion names fractional distillation instead of this selective steam-distillation method, so the assertion is false in the stated separation.

Step 2: Evaluate the reason In ortho-nitrophenol, the adjacent hydroxyl and nitro groups form a hydrogen bond within the same molecule. This reduces association between separate molecules, allowing ortho-nitrophenol to be carried over readily with steam. The reason is therefore true. Para-nitrophenol instead forms intermolecular hydrogen bonds and remains largely in the distillation flask.

Step 3: Check the explanatory connection The true reason explains why steam distillation separates the mixture; it does not justify the fractional-distillation method named in the false assertion. Therefore the choices requiring both statements to be true, or requiring the reason to be false, are excluded.

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

Quick Tip to Solve: When nitrophenol isomers and steam volatility appear together, select steam distillation and link the ortho isomer to intramolecular hydrogen bonding.

14. Assertion (A): Aquatic species are more comfortable in cold water than in warm water.
Reason (R): Solubility of oxygen gas in water decreases with increase in temperature. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Aquatic animals obtain the oxygen needed for respiration from oxygen dissolved in water.
- The solubility of a gas in a liquid generally decreases when the temperature increases, at the same gas pressure.

Step 1: Judge the assertion Cold water contains more dissolved O_2 than warm water under comparable conditions. The greater availability of dissolved oxygen makes respiration easier for aquatic species. Therefore, Assertion (A) is true in the context of gas solubility.

Step 2: Judge the reason On increasing temperature, oxygen molecules escape from the liquid more readily and the equilibrium solubility of O_2 decreases. Thus, Reason (R) correctly states the

Quick Tip to Solve: Link aquatic comfort to dissolved oxygen: colder water dissolves more oxygen at the same pressure.

temperature dependence of oxygen solubility and is true.

Step 3: Connect the statements The reason directly explains why cold water provides a more favourable oxygen supply for aquatic life. Option (B) wrongly denies this explanatory link, while (C) and (D) incorrectly classify one of the true statements as false.

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

Quick Tip to Solve: Link aquatic comfort to dissolved oxygen: colder water dissolves more oxygen at the same pressure.

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15. Assertion (A): First ionisation enthalpy of Cr is lower than that of Zn.

Reason (R): Zinc is a non-transition element. [1 mark]

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

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

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

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

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

Solution:

Concept:

- First ionisation enthalpy is the energy needed to remove one electron from an isolated gaseous atom to form a gaseous monovalent cation.
- A transition element has an incompletely filled d subshell in its atom or in at least one of its common oxidation states.

Step 1: Judge the assertion Chromium has configuration $[\mathrm{Ar}]\,3d^5 4s^1$, whereas zinc has $[\mathrm{Ar}]\,3d^{10}4s^2$. Removal of chromium's single 4s electron leaves the stable half-filled $3d^5$ configuration. Zinc has a larger effective nuclear attraction across the period and a filled $3d^{10}4s^2$ arrangement. Its first electron is harder to remove. Thus, the first ionisation enthalpy of Cr is lower than that of Zn, so A is true.

Step 2: Judge the reason The zinc atom and its common ion Zn^{2+} have completely filled $3d^{10}$ subshells. Zinc therefore does not meet the definition of a transition element, so R is true.

Step 3: Test the explanatory link The classification of zinc as a non-transition element follows from its filled d subshell; that classification alone does not explain the comparison of first ionisation enthalpies. The comparison requires electronic configuration and nuclear attraction. Thus, option (A) incorrectly claims an explanatory link, and (C) and (D) wrongly declare a true statement false.

Step 4: Conclusion Both A and R are true, but R is not the correct explanation of A. Hence, the correct option is (B).

Quick Tip to Solve: Distinguish the transition-element definition from ionisation energy: inspect the configuration left after removing the 4s electron.

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16. Assertion (A): Vitamin C cannot be stored in our body.

Reason (R): Vitamin C is water soluble and excreted in urine. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Vitamins are classified as water-soluble or fat-soluble according to their solubility.
- Water-soluble vitamins generally need a regular dietary supply because excess amounts are eliminated in urine rather than retained as substantial body stores.

Step 1: Judge the assertion Vitamin C, or ascorbic acid, is a water-soluble vitamin. In the usual textbook classification, it is not stored in the body to a significant extent for future use and must be supplied regularly through food. Therefore, Assertion (A) is true.

Step 2: Judge the reason Vitamin C dissolves in water, and excess vitamin C is excreted through urine. Thus, Reason (R) is also true. This differs from fat-soluble vitamins, which can be retained in body fat and the liver.

Step 3: Check the causal connection Water solubility and urinary elimination explain the lack of substantial storage of vitamin C. Thus, R correctly explains A. Option (B) wrongly rejects this connection, while (C) and (D) each wrongly classify one of the two true statements as false.

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

Quick Tip to Solve: For vitamin C, connect water solubility with urinary loss and the need for a regular dietary supply.

Section B (10 marks)

17. (a) A and B liquids on mixing show rise in temperature. Which type of deviation from Raoult's law is there and why?

(b) Why can azeotropic mixture not be separated by fractional distillation? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal solution is $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$, where x_i is the liquid mole fraction and p_i^0 the vapour pressure of pure component i at the same temperature.

Quick Tip to Solve: Heat released on mixing points to stronger unlike attractions and negative deviation; for azeotropes, remember that vapour and liquid compositions match.

- An azeotrope is a constant-boiling mixture whose vapour and liquid have the same composition at its azeotropic composition.

Step 1: Identify the deviation in part (a) A rise in temperature on mixing indicates release of heat, so the enthalpy of mixing is negative: $\Delta H_{\text{mix}} < 0$. The newly formed A–B intermolecular attractions are stronger than the A–A and B–B attractions in the pure liquids. Consequently, molecules escape into the vapour less readily. At the same temperature, their partial vapour pressures lie below the Raoult's-law values, giving a **negative deviation**.

Step 2: Explain the separation limit in part (b) Fractional distillation separates components by producing vapour with a composition different from that of the liquid, usually richer in the more volatile component. At the azeotropic composition, however, the vapour composition equals the liquid composition. Boiling and condensing therefore reproduce the same mixture instead of enriching either component. Thus, repeated fractionation cannot separate an azeotropic mixture into its pure components.

Step 3: Conclusion (a) The liquids show negative deviation because stronger A–B attractions make mixing exothermic and reduce the vapour pressure. (b) An azeotrope cannot be separated by fractional distillation because its liquid and vapour compositions are identical.

Quick Tip to Solve: Heat released on mixing points to stronger unlike attractions and negative deviation; for azeotropes, remember that vapour and liquid compositions match.

18. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions? [2 marks]

Solution:

Concept:

- Molecularity is the number of reacting species that participate together in a single elementary reaction step. It is a positive whole number.
- The order of a reaction is the sum of the exponents of reactant concentrations in its experimentally determined rate law. For $r = k[A]^m[B]^n$, the overall order is $m + n$.

Step 1: Relate molecularity to one elementary event An elementary reaction occurs in a single step, so the participating reacting species can be counted for that event. This count defines its molecularity. A complex reaction proceeds through several elementary steps, each with its own participating species and molecularity. Its overall balanced equation does not represent a single simultaneous collision. Hence, no molecularity can be assigned to the overall complex reaction by adding its stoichiometric coefficients.

Step 2: Relate order to the observed rate law The rate law describes how the measured reaction rate depends on reactant concentrations. It can be determined experimentally for either an elementary reaction or an overall complex reaction. For a complex reaction, the mechanism and its kinetically controlling steps determine this concentration dependence; the powers need not equal the coefficients of the overall equation. Therefore, reaction order is applicable to both elementary and complex reactions, and may be zero, integral or fractional.

Quick Tip to Solve: Count reacting species only for an elementary step; find order by adding concentration exponents in the rate law, never from an overall complex equation.

Step 3: Conclusion Molecularity applies only to an elementary step because it counts species taking part in one event. Order applies to elementary and complex reactions because it is obtained from the experimentally determined rate law.

Quick Tip to Solve: Count reacting species only for an elementary step; find order by adding concentration exponents in the rate law, never from an overall complex equation.

19. Write two differences between DNA and RNA. [2 marks]

Solution:

Concept:

- DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) are polynucleotides. Each nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group.
- Both contain adenine, guanine and cytosine; the identity of the pentose sugar and the fourth base distinguishes them chemically.

Step 1: Compare the pentose sugars DNA contains 2-deoxyribose, whereas RNA contains ribose. At the $2'$ carbon of the sugar, DNA has a hydrogen atom in place of the hydroxyl group present in RNA. Thus, the sugar of DNA contains one less oxygen atom than ribose.

Step 2: Compare the nitrogenous bases DNA contains thymine as its fourth base, whereas RNA contains uracil in place of thymine. Therefore, the base sets are adenine, guanine, cytosine and thymine for DNA, and adenine, guanine, cytosine and uracil for RNA.

Step 3: Conclusion The two differences are: DNA has deoxyribose and thymine, while RNA has ribose and uracil.

Quick Tip to Solve: Compare sugar and base separately: remember DNA as deoxyribose plus thymine, and RNA as ribose plus uracil.

20(a). Write the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. Draw the structure of geometrical isomer of this complex which is optically inactive. [2 marks]

Solution:

Concept:

- Ethane-1,2-diamine (en) is a neutral bidentate ligand; each en supplies two nitrogen donor atoms. Chlorido is a monodentate ligand of charge -1.
- An octahedral complex of the type $[M(en)_2Cl_2]$ has cis and trans geometrical isomers. The trans form has opposite chlorido ligands and is optically inactive.

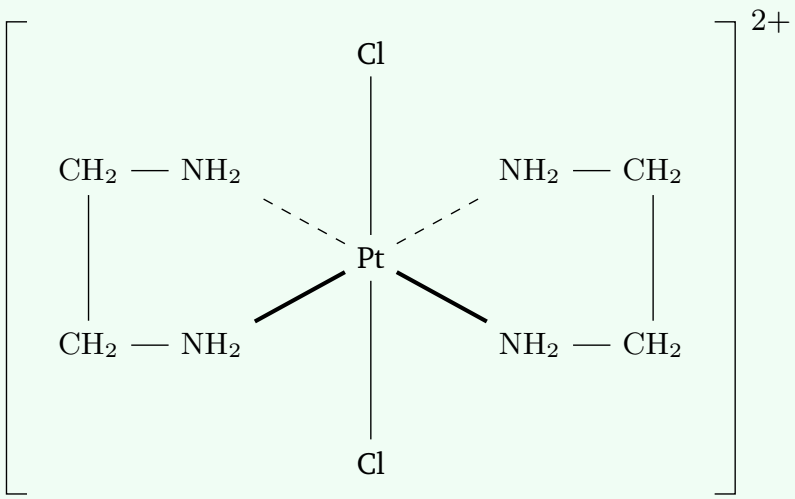
Step 1: Find the oxidation state and name the ion Let the oxidation state of platinum be x. The two en ligands are neutral and the two chlorido ligands contribute -2, so

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

Quick Tip to Solve: Count each en as two donor atoms but zero charge; place the two Cl ligands opposite each other to obtain the inactive trans isomer.

Name the ligands alphabetically: chlorido precedes ethane-1,2-diamine. Use dichlorido for two chloride ligands and bis(ethane-1,2-diamine) for two bidentate en ligands. Since the complex is a cation, the metal name is platinum, followed by (IV).

Step 2: Draw the optically inactive geometrical isomer The coordination number is six: four nitrogen donors from the two en ligands and two chlorido ligands. In the trans isomer shown below, the two chlorido ligands occupy opposite axial positions, making a 180° angle at platinum. Each pair of nitrogen donors joined by an en chain occupies adjacent equatorial positions. This arrangement has a plane of symmetry and is superimposable on its mirror image, so it is optically inactive.



Octahedral trans isomer; each en chain joins two adjacent nitrogen donors.

Step 3: Conclusion The IUPAC name is dichloridobis(ethane-1,2-diamine)platinum(IV) ion. The optically inactive geometrical isomer is $\text{trans-}[\text{Pt(en)}_2\text{Cl}_2]^{2+}$.

Quick Tip to Solve: Count each en as two donor atoms but zero charge; place the two Cl ligands opposite each other to obtain the inactive trans isomer.

OR

20(b). (i) Write the formula of the following coordination compound:
Pentaamminecarbonatocobalt(III)chloride
(ii) Write the IUPAC name of the linkage isomer of the complex $[Co(NH_3)_5(NO_2)]Cl_2$. [2 marks]

Solution:

Concept:

- Ammine (NH_3) is a neutral ligand, while carbonato (CO_3^{2-}) carries charge -2. Counterions balance the net charge of the coordination entity.
- Linkage isomers have the same composition but differ in the donor atom of an ambidentate ligand. Nitrite can bind through nitrogen (nitro) or through oxygen (nitrito-O).

Step 1: Write the formula of pentaamminecarbonatocobalt(III) chloride Cobalt(III) contributes $+3$,

Quick Tip to Solve: Balance the complex charge before adding chloride ions; for a nitro linkage isomer, change the donor from N to O without changing composition.

five ammine ligands contribute zero and one carbonato ligand contributes -2. The complex ion therefore carries charge $+1$:

$$+3 + 5(0) - 2 = +1.$$

One chloride ion is needed outside the coordination brackets to balance this charge. The formula is $[Co(NH_3)_5(CO_3)]Cl$; chloride is the counterion, not a coordinated chlorido ligand.

Step 2: Identify and name the linkage isomer In $[Co(NH_3)_5(NO_2)]Cl_2$, the nitro ligand is attached through nitrogen. Its linkage isomer attaches the same nitrite ion through oxygen, written as $[Co(NH_3)_5(ONO)]Cl_2$. The two chloride counterions require a $+2$ complex; with a -1 nitrito ligand and neutral ammines, cobalt remains in oxidation state $+3$. Its name is pentaammine(nitrito-O)cobalt(III) chloride.

Step 3: Conclusion (i) $[Co(NH_3)_5(CO_3)]Cl$.

(ii) Pentaammine(nitrito-O)cobalt(III) chloride, the oxygen-bonded linkage isomer.

Quick Tip to Solve: Balance the complex charge before adding chloride ions; for a nitro linkage isomer, change the donor from N to O without changing composition.

21. Why are haloarenes less reactive towards nucleophilic substitution reaction? How does the presence of nitro (-NO_2) group at ortho- and para-positions in haloarenes increase the reactivity towards nucleophilic substitution reaction? [2 marks]

Solution:

Concept:

- Resonance between a halogen lone pair and the aromatic ring gives the aryl carbon-halogen bond partial double-bond character. Its cleavage is consequently more difficult than cleavage of an alkyl carbon-halogen bond.
- An electron-withdrawing nitro group at an ortho or para position stabilises the anionic intermediate in nucleophilic aromatic substitution by resonance.

Step 1: Explain the low reactivity of haloarenes In a haloarene, a lone pair on the halogen is conjugated with the ring's π-electron system. The resulting resonance gives the $C-X$ bond partial double-bond character, making it shorter and stronger than in haloalkanes. Also, the bonded carbon is sp^2-hybridised; its greater s-character holds the bonding electrons more strongly. An ordinary S_N1 reaction is unfavourable because it would form an unstable phenyl carbocation, and the aryl framework makes the usual backside attack of an S_N2 reaction difficult.

Step 2: Explain activation by ortho and para nitro groups A nitro group withdraws electron density from the ring, making the carbon bearing the halogen more susceptible to nucleophilic attack. In the addition step, attack at that carbon gives a negatively charged intermediate. Its negative charge is delocalised to the ortho and para positions. A nitro group at either of these positions can accept this charge through resonance and delocalise it further onto its oxygen atoms. Stabilisation of this intermediate lowers the barrier to substitution; halide is then eliminated and aromaticity is restored. A meta nitro group cannot provide the same resonance stabilisation of the intermediate.

Quick Tip to Solve: For nitro activation, track the intermediate's negative charge to ortho and para positions; only a nitro group there can stabilise it directly by resonance.

Step 3: Conclusion Haloarenes resist nucleophilic substitution because their aryl carbon-halogen bond is strong and has partial double-bond character. An ortho or para $-NO_2$ group increases reactivity by stabilising the negatively charged substitution intermediate through resonance.

Quick Tip to Solve: For nitro activation, track the intermediate's negative charge to ortho and para positions; only a nitro group there can stabilise it directly by resonance.

Section C (21 marks)

22(a). Write the name of the cell which is generally used in inverters. Write the reactions taking place at anode and cathode of this cell, when it is in use. [3 marks]

Solution:

Concept:

- An inverter commonly uses a rechargeable lead storage battery containing a lead anode, a lead dioxide cathode and aqueous sulphuric acid as electrolyte.
- When the battery supplies current, it discharges as a galvanic cell: oxidation occurs at the anode and reduction occurs at the cathode.
- During discharge, both electrodes form $PbSO_4$; electrons released by lead travel through the external circuit to the lead dioxide electrode.

Step 1: Identify the cell and operating process The cell generally used in inverters is the lead storage cell, also called the lead-acid storage battery. Its negative electrode is lead, Pb, and its positive electrode is lead dioxide, PbO_2. The phrase "when it is in use" means that the battery supplies electrical energy, so the required reactions are its discharge reactions. The reverse reactions occur during charging.

Step 2: Write the oxidation reaction at the anode Lead is oxidised from oxidation state zero to $+2$. It releases two electrons and combines with sulphate ions from the electrolyte to form solid lead sulphate:

$$Pb\,(s) + {SO_4}^{2-}(aq) \longrightarrow PbSO_4(s) + 2\,e^-.$$

The two electrons on the product side identify this as oxidation. The sulphate ion converts the oxidised lead into sparingly soluble $PbSO_4$.

Step 3: Write the reduction reaction at the cathode Lead in PbO_2 is reduced from $+4$ to $+2$. In the acidic electrolyte it accepts the two electrons supplied by the anode:

$$PbO_2(s) + {SO_4}^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O\,(l).$$

Adding the half-reactions cancels the electrons and gives the overall discharge reaction:

$$Pb\,(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O\,(l).$$

Sulphuric acid is consumed during discharge, and its concentration decreases.

Step 4: Conclusion The cell is the lead storage battery. During use, Pb is oxidised to $PbSO_4$ at the

Quick Tip to Solve: For discharge of a lead storage battery, remember that both electrodes become $PbSO_4$: put electrons on the right for lead and on the left for lead dioxide.

anode, while PbO_2 is reduced to $PbSO_4$ at the cathode according to the half-reactions above.

Quick Tip to Solve: For discharge of a lead storage battery, remember that both electrodes become $PbSO_4$: put electrons on the right for lead and on the left for lead dioxide.

OR

22(b). Explain why electrolysis of an aqueous solution of NaCl gives H_2 gas at cathode and Cl_2 gas at anode? Write overall reaction.

(Given: $E^\circ_{Na^+/Na} = -2.71\,\text{V}$, $E^\circ_{H_2O/H_2} = -0.83\,\text{V}$, $E^\circ_{Cl_2/2\,Cl^-} = +1.36\,\text{V}$, $E^\circ_{H^+/O_2/H_2O} = +1.23\,\text{V}$**)** [3 marks]

Solution:

Concept:

- At the cathode, reduction occurs. A more positive reduction potential favours reduction.
- At the anode, oxidation occurs. Product selection also depends on overpotential: the extra potential needed for an electrode reaction.
- Oxygen evolution has a substantial overpotential; hence chloride oxidation can occur preferentially during electrolysis of aqueous sodium chloride.

Step 1: Compare the cathodic reduction processes The competing reductions are formation of sodium metal and reduction of water:

$$\begin{aligned} Na^+ + e^- &\longrightarrow Na, & E^\circ &= -2.71\,\text{V},\\ 2\,H_2O + 2\,e^- &\longrightarrow H_2 + 2\,OH^-, & E^\circ &= -0.83\,\text{V}. \end{aligned}$$

The reduction potential for water is more positive than that for Na^+. Therefore water is reduced more readily, and hydrogen gas is evolved at the cathode. Sodium ions remain in solution.

Step 2: Explain the anodic product using overpotential Chloride oxidation competes with water oxidation. The reduction potentials are $+1.36\,\text{V}$ for the chlorine/chloride couple and $+1.23\,\text{V}$ for the oxygen/water couple. Considering these values alone would suggest that water should oxidise more readily than chloride. Oxygen evolution requires a considerable overpotential. Consequently chloride is preferentially oxidised:

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^-.$$

Thus chlorine gas is released at the anode.

Step 3: Combine the two electrode reactions Add the cathodic water-reduction reaction and the anodic chloride-oxidation reaction. Cancelling two electrons gives

$$2\,H_2O\,(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq).$$

Including spectator sodium ions gives the overall reaction:

$$2\,NaCl\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2(g) + Cl_2(g).$$

Quick Tip to Solve: Compare the reduction potentials to choose the cathode product; at the anode of aqueous NaCl, remember the oxygen overpotential before predicting the gas.

Step 4: Conclusion Water reduction yields H_2 at the cathode; chloride oxidation yields Cl_2 at the anode owing to oxygen overpotential. The overall reaction also forms NaOH.

Quick Tip to Solve: Compare the reduction potentials to choose the cathode product; at the anode of aqueous NaCl, remember the oxygen overpotential before predicting the gas.

23. 0.3 g of acetic acid (Molar mass = 60 g mol^{-1}) dissolved in 30 g of benzene shows a depression in freezing point equal to 0.45°C. Calculate the percentage association of acid if it forms a dimer in the solution.

(Given: K_f for benzene = 5.12 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- Depression in freezing point is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f is the cryoscopic constant and m is the molality calculated before association.
- Acetic acid associates into dimers in benzene: $2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$. Association decreases the total number of solute particles and hence gives $i < 1$.
- For a fraction α associated into dimers, $i = 1 - \alpha/2$.

Step 1: Calculate the initial molality The number of moles of acetic acid added is its mass divided by its molar mass:

$$n = \frac{0.3\,\text{g}}{60\,\text{g mol}^{-1}} = 0.005\,\text{mol}.$$

The solvent mass is $30\,\text{g} = 0.030\,\text{kg}$, so

$$m = \frac{0.005\,\text{mol}}{0.030\,\text{kg}} = \frac{1}{6}\,\text{mol kg}^{-1}.$$

Molality uses the mass of the solvent, not the total mass of the solution.

Step 2: Obtain the van't Hoff factor Without association, the expected depression would be

$$K_f m = 5.12 \times \frac{1}{6} = 0.85333\,\text{K}.$$

A temperature difference of $0.45°\text{C}$ equals $0.45\,\text{K}$. Therefore

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.45}{0.85333} = 0.52734375.$$

The value below unity confirms association.

Step 3: Find the associated fraction Of one mole of acid, α moles associate, producing $\alpha/2$ moles of dimers and leaving $1 - \alpha$ moles of monomers. Thus

$$i = (1 - \alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}.$$

Quick Tip to Solve: For dimerisation, first calculate $i = \Delta T_f/(K_f m)$, then use $\alpha = 2(1 - i)$; do not confuse the associated fraction with the number of dimers formed.

Solving for the associated fraction gives

$$\begin{aligned}\alpha &= 2(1-i) = 2(1-0.52734375)\\ &= 0.9453125,\\ 100\alpha &= 94.53125\%.\end{aligned}$$

Step 4: Conclusion The percentage association of acetic acid in benzene is approximately $\boxed{94.5\%}$.

Quick Tip to Solve: For dimerisation, first calculate $i = \Delta T_f/(K_f m)$, then use $\alpha = 2(1-i)$; do not confuse the associated fraction with the number of dimers formed.

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24. A compound (A) with molecular formula C_4H_9I which is a primary alkyl halide, reacts with alcoholic KOH to give compound (B). Compound (B) reacts with HI to give (C) which is an isomer of (A). When (A) reacts with Na metal in the presence of dry ether, it gives a compound (D), C_8H_{18}, which is different from the compound formed when n-butyl iodide reacts with sodium. Write the structures of (A), (B), (C) and (D). Write the chemical equation when compound (A) is reacted with alcoholic KOH. [3 marks]

Solution:

Concept:

- A primary alkyl iodide has iodine on a carbon bonded to only one other carbon. The two primary isomers of C_4H_9I are butan-1-yl iodide and 1-iodo-2-methylpropane.
- Alcoholic KOH causes beta-elimination of HI to give an alkene. Addition of HI to an unsymmetrical alkene follows Markovnikov's rule: hydrogen adds to the carbon already bearing more hydrogen atoms.
- In the Wurtz reaction, sodium in dry ether couples two alkyl groups: $2\mathrm{RI} + 2\mathrm{Na} \longrightarrow \mathrm{R{-}R} + 2\mathrm{NaI}$.

Step 1: Identify the primary iodide A Coupling n-butyl iodide gives n-octane. Since the stated Wurtz product D is different, A cannot be n-butyl iodide. Therefore A is the other primary isomer, isobutyl iodide (1-iodo-2-methylpropane):

$$\mathrm{A} = (\mathrm{CH_3})_2\mathrm{CHCH_2I}.$$

Step 2: Obtain B by elimination and C by addition Removal of iodine from the terminal carbon and a beta-hydrogen from the adjacent carbon forms 2-methylpropene:

$$(\mathrm{CH_3})_2\mathrm{CHCH_2I} + \mathrm{KOH} \xrightarrow{\text{alcohol, heat}} \mathrm{CH_2 = C(CH_3)_2} + \mathrm{KI} + \mathrm{H_2O}.$$

Thus B is $\mathrm{CH_2 = C(CH_3)_2}$. On adding HI, hydrogen goes to the terminal $\mathrm{CH_2}$ carbon and iodine to the more substituted carbon:

$$\mathrm{CH_2 = C(CH_3)_2} + \mathrm{HI} \longrightarrow (\mathrm{CH_3})_3\mathrm{CI}.$$

C is tert-butyl iodide (2-iodo-2-methylpropane), an isomer of A.

Quick Tip to Solve: Use the Wurtz clue first: a product other than n-octane rules out n-butyl iodide and fixes the branched primary isomer.

Step 3: Couple two isobutyl groups to obtain D Sodium couples the two terminal carbon atoms that previously carried iodine:

$$2(CH_3)_2CHCH_2I + 2Na \xrightarrow{\text{dry ether}} (CH_3)_2CHCH_2CH_2CH(CH_3)_2 + 2NaI.$$

The product is 2,5-dimethylhexane. Its molecular formula is C_8H_{18}, as required, and its branched skeleton distinguishes it from n-octane.

Step 4: Conclusion The required structures are

$$A = (CH_3)_2CHCH_2I,$$
$$B = CH_2 = C(CH_3)_2,$$
$$C = (CH_3)_3CI,$$
$$D = (CH_3)_2CHCH_2CH_2CH(CH_3)_2.$$

The alcoholic-KOH equation is the beta-elimination equation shown above.

Quick Tip to Solve: Use the Wurtz clue first: a product other than n-octane rules out n-butyl iodide and fixes the branched primary isomer.

25. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at constant volume:

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

Calculate rate constant.

[Given: $\log 2 = 0.3010,\ \log 10 = 1$**]** [3 marks]

S.No.	Time/s	Total Pressure/atm
1	0	0·5
2	100	0·625

Solution:

Concept:

- For a first order reaction, $k = \frac{2.303}{t} \log \frac{p_0}{p_A}$, where p_0 and p_A are the initial and remaining partial pressures of the reactant, and t is the elapsed time.
- At constant temperature and volume, pressure is proportional to the number of moles. The printed reaction $2N_2O_5 \longrightarrow 2N_2O_4 + O_2$ increases total pressure, so total pressure must first be converted to the remaining reactant's partial pressure.

Step 1: Relate total pressure to decomposition Initially only N_2O_5 is present, so $p_0 = 0.500$ atm. Let x atm be the pressure-equivalent amount of N_2O_5 decomposed after 100 s. From the printed

Quick Tip to Solve: For the printed 2-to-3 gaseous stoichiometry, use remaining reactant pressure $p_A = 3p_0 - 2P_t$ before applying the logarithmic rate law.

stoichiometry, the partial pressures are

$$p_{N_2O_5} = p_0 - x,$$
$$p_{N_2O_4} = x,$$
$$p_{O_2} = x/2.$$

Hence the total pressure is $P_t = p_0 + x/2$. The rise in total pressure is due to the oxygen produced, not the amount of reactant remaining.

Step 2: Find the remaining reactant pressure Using $P_{100} = 0.625$ atm,

$$x = 2(P_{100} - p_0) = 2(0.625 - 0.500) = 0.250 \text{ atm}.$$

Therefore

$$p_A = p_0 - x = 0.500 - 0.250 = 0.250 \text{ atm}.$$

Thus half of the initial N_2O_5 remains after 100 s; using 0.625 atm directly in the first order formula would incorrectly treat the total mixture pressure as reactant pressure.

Step 3: Substitute in the first order integrated law

$$\begin{aligned} k &= \frac{2.303}{100} \log \frac{0.500}{0.250} \\ &= \frac{2.303}{100} \log 2 \\ &= \frac{2.303 \times 0.3010}{100} \\ &= 6.932 \times 10^{-3} \text{ s}^{-1}. \end{aligned}$$

The pressure ratio is dimensionless; the unit of k is inverse seconds because time was supplied in seconds.

Step 4: Conclusion The first order rate constant is $\boxed{k = 6.93 \times 10^{-3} \text{ s}^{-1}}$.

Quick Tip to Solve: For the printed 2-to-3 gaseous stoichiometry, use remaining reactant pressure $p_A = 3p_0 - 2P_t$ before applying the logarithmic rate law.

26. Write the reaction of D-Glucose with the following:

(a) HCN

(b) Br_2 water

(c) $(CH_3CO)_2O$ [3 marks]

Solution:

Concept:

- The open-chain form of D-glucose is $CHO{-}(CHOH)_4{-}CH_2OH$. It contains an aldehyde group and five alcoholic hydroxyl groups, so different reagents test different functional groups.
- HCN adds to a carbonyl group to form a cyanohydrin. Bromine water is a mild oxidant which

Quick Tip to Solve: Match each reagent to its target: HCN adds to the carbonyl, bromine water oxidises only CHO, and acetic anhydride acetylates all five OH groups.

converts an aldehyde group into a carboxylic acid group. Acetic anhydride acetylates alcoholic hydroxyl groups.

Step 1: Reaction with HCN: cyanohydrin formation HCN adds across the carbon-oxygen double bond of the aldehyde group. The carbonyl carbon acquires a CN group and the oxygen becomes OH:

$$\begin{aligned}&\mathrm{CHO{-}(CHOH)_4{-}CH_2OH + HCN}\\&\quad\longrightarrow \mathrm{NC{-}CH(OH){-}(CHOH)_4{-}CH_2OH.}\end{aligned}$$

The product is glucose cyanohydrin. The original four CHOH groups and terminal CH_2OH group remain unchanged; the new nitrile carbon increases the carbon count by one.

Step 2: Reaction with bromine water: gluconic acid formation Bromine water oxidises the aldehyde end of glucose to a carboxylic acid while retaining its alcoholic groups:

$$\begin{aligned}&\mathrm{CHO{-}(CHOH)_4{-}CH_2OH + Br_2 + H_2O}\\&\quad\longrightarrow \mathrm{COOH{-}(CHOH)_4{-}CH_2OH + 2HBr.}\end{aligned}$$

The product is D-gluconic acid. The terminal primary alcohol is unchanged under this mild oxidation; oxidation of both ends would require a stronger oxidant such as nitric acid.

Step 3: Reaction with acetic anhydride: pentaacetate formation All five hydroxyl groups are acetylated by acetic anhydride, usually in the presence of pyridine:

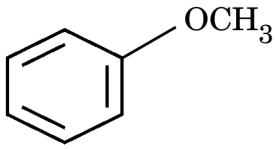
$$\begin{aligned}&\text{D-glucose} + 5(\mathrm{CH_3CO})_2\mathrm{O}\\&\quad\xrightarrow{\text{pyridine}}\ \text{glucose pentaacetate} + 5\mathrm{CH_3COOH.}\end{aligned}$$

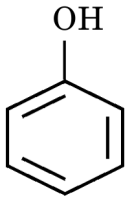
Each $-OH$ is changed into $-OCOCH_3$; the pentaacetate is the acetylated cyclic glucose derivative. Formation of a pentaacetate establishes the presence of five hydroxyl groups in glucose, rather than six.

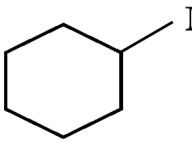
Step 4: Conclusion D-glucose gives (a) glucose cyanohydrin with HCN, (b) D-gluconic acid with bromine water, and (c) glucose pentaacetate with acetic anhydride, according to the balanced reactions above.

Quick Tip to Solve: Match each reagent to its target: HCN adds to the carbonyl, bromine water oxidises only CHO, and acetic anhydride acetylates all five OH groups.

27. Write structure of the products of the following reactions: [3 marks]

(a)  $+ HI \longrightarrow$

(b)  $+$ conc. $HNO_3 \longrightarrow$

(c)  $+ HCHO \xrightarrow{H^+/H_2O}$

Solution:

Concept:

- Hydrogen iodide cleaves an aryl alkyl ether at the alkyl–oxygen bond; the aryl–oxygen bond has partial double-bond character and is not cleaved by an ordinary nucleophilic substitution.
- The $-OH$ group activates the phenol ring and directs nitration to its ortho and para positions.
- A Grignard reagent RMgBr adds to formaldehyde, and acidic hydrolysis converts the alkoxide into the primary alcohol RCH_2OH.

Step 1: Cleave anisole with hydrogen iodide (a) Protonation of the ether oxygen makes the methyl group susceptible to attack by iodide. The iodide ion attacks this unhindered methyl carbon, rather than the aromatic carbon. The two products are phenol and methyl iodide:

$$C_6H_5-O-CH_3 + HI \longrightarrow C_6H_5-OH + CH_3-I.$$

Thus the oxygen remains bonded to the benzene ring. Iodobenzene and methanol are not the products of this cleavage.

Step 2: Nitrate all three activated positions of phenol (b) Concentrated nitric acid introduces nitro groups at both ortho positions and the para position relative to $-OH$. The product is 2,4,6-trinitrophenol, also called picric acid. Its condensed structural formula is $HO-C_6H_2(NO_2)_3$, with $-OH$ at carbon 1 and $-NO_2$ at carbons 2, 4 and 6:

$$C_6H_5OH + 3\,HNO_3 \longrightarrow HO-C_6H_2(NO_2)_3 + 3\,H_2O.$$

Concentrated acid gives the trinitro product rather than only an ortho/para mononitrophenol mixture.

Step 3: Add one carbon to the cyclohexyl group (c) The cyclohexyl group adds to the carbonyl carbon of formaldehyde. Protonation of the resulting alkoxide gives cyclohexylmethanol:

$$C_6H_{11}-MgBr + HCHO \longrightarrow C_6H_{11}-CH_2-OMgBr$$

Quick Tip to Solve: For anisole keep the ring–oxygen bond intact; for formaldehyde plus a Grignard reagent append $-CH_2OH$ to the original carbon group.

$$C_6H_{11}-CH_2-OMgBr \xrightarrow{H^+/H_2O} C_6H_{11}-CH_2-OH.$$

The C_6H_{11} group denotes the saturated six-membered cyclohexyl ring. The $-CH_2OH$ group is outside that ring, so this is not cyclohexanol.

Step 4: Conclusion The products are (a) C_6H_5-OH and CH_3-I; (b) 2,4,6-trinitrophenol, $HO-C_6H_2(NO_2)_3$; and (c) cyclohexylmethanol, $C_6H_{11}-CH_2-OH$.

Quick Tip to Solve: For anisole keep the ring–oxygen bond intact; for formaldehyde plus a Grignard reagent append $-CH_2OH$ to the original carbon group.

28. Give reasons for the following:

(a) Benzoic acid does not undergo Friedel-Crafts reaction.

(b) HCHO is more reactive than CH_3CHO towards addition of HCN.

(c) Vinyl group directly attached with carboxylic acid should decrease the acidity of corresponding carboxylic acid due to resonance, but on the contrary it increases the acidity. [3 marks]

Solution:

Concept:

- Friedel–Crafts alkylation and acylation are electrophilic aromatic substitutions requiring an adequately electron-rich aromatic ring.
- Nucleophilic addition to a carbonyl group becomes faster when its carbon is more electrophilic and less sterically hindered.
- A carboxylic acid is stronger when an electron-withdrawing substituent stabilises its carboxylate ion; inductive and resonance effects must be considered together.

Step 1: Examine the deactivation of the benzoic acid ring (a) The $-COOH$ group withdraws electron density from the benzene ring by both its negative inductive effect and its negative resonance effect. It strongly deactivates the ring towards electrophilic substitution. Therefore the ring is insufficiently reactive for Friedel–Crafts alkylation or acylation under the usual conditions. In addition, the carboxyl group can interact with the Lewis acid catalyst, $AlCl_3$, further hindering the reaction. The presence of an aromatic ring alone does not guarantee a Friedel–Crafts reaction.

Step 2: Compare the carbonyl carbons of the two aldehydes (b) In addition of HCN, the nucleophile CN^- attacks the electron-deficient carbonyl carbon. Formaldehyde, HCHO, has two small hydrogen atoms attached to this carbon and no electron-donating alkyl group. Ethanal, CH_3CHO, has a methyl group whose positive inductive effect lowers the positive character of the carbonyl carbon. That methyl group also obstructs the approaching nucleophile more than hydrogen does. Both the electronic and steric factors therefore make HCHO more reactive towards HCN than CH_3CHO.

Step 3: Compare the opposing effects of the vinyl group (c) A directly attached vinyl group gives an unsaturated acid of the form $CH_2=CH-COOH$. Its resonance donation tends to reduce acidity. However, the carbon of the vinyl group directly attached to $-COOH$ is sp^2-hybridised and is more electronegative than an sp^3-hybridised alkyl carbon because it has greater s-character. It exerts an electron-withdrawing, negative inductive effect that stabilises the carboxylate ion. This effect

Quick Tip to Solve: For carbonyl addition compare both electron donation and crowding; for vinyl-substituted acids compare the inductive effect of sp^2 carbon with its opposing resonance effect.

predominates over the opposing resonance contribution, so the unsaturated acid is more acidic than the corresponding saturated acid.

Step 4: Conclusion Benzoic acid resists Friedel–Crafts reaction because –COOH strongly deactivates its ring. HCHO adds HCN faster because it has less steric hindrance and no electron-donating methyl group. The vinyl group's dominant negative inductive effect increases carboxylic-acid acidity.

Quick Tip to Solve: For carbonyl addition compare both electron donation and crowding; for vinyl-substituted acids compare the inductive effect of sp^2 carbon with its opposing resonance effect.

Section D (8 marks)

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

29(a). The Crystal Field Theory (CFT) of coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges) on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields. In tetrahedral coordination entity formation, the d-orbital splitting is smaller as compared to the octahedral entity.

Answer the following questions:

On the basis of CFT, explain why $[Ti(H_2O)_6]Cl_3$ complex is coloured? What happens on heating the complex $[Ti(H_2O)_6]Cl_3$? Give reason.

[Atomic no.: Ti = 22] [2 marks]

Solution:

Concept:

- In an octahedral ligand field, the five d orbitals split into a lower-energy t_{2g} set and a higher-energy e_g set, separated by Δ_o.
- Absorption of visible light of energy $h\nu = \Delta_o$ can promote an electron between these sets; the observed colour is complementary to the absorbed colour.

Step 1: Find the titanium ion and its d-electron configuration The three chloride ions in $[Ti(H_2O)_6]Cl_3$ are counterions, while the six water ligands are neutral. Thus the metal ion is Ti^{3+}. Titanium has atomic number 22 and configuration $[Ar]3d^2 4s^2$; removal of the two 4s electrons and one 3d electron gives Ti^{3+} the configuration $3d^1$. In the octahedral aqua complex this one electron occupies the lower t_{2g} level.

Step 2: Explain the colour and the effect of heating The electron absorbs visible light and undergoes a d–d transition from t_{2g} to e_g. The light transmitted is therefore coloured; the hexaaquatitanium(III) complex appears violet. On heating, water ligands are lost and the original hydrated complex loses its violet colour. Removal of the coordinating water destroys the original octahedral aqua field, so its characteristic visible-light absorption no longer occurs. The colour change is due to loss of water and a changed crystal field, rather than a change in the original d^1 electron count.

Step 3: Conclusion The $3d^1$ ion Ti^{3+} gives a violet aqua complex through a $t_{2g} \rightarrow e_g$ transition. Heating removes water and the hydrated complex loses its characteristic colour because its aqua-ligand

Quick Tip to Solve: First use the counterions to find Ti^{3+}; its single d electron makes a visible d–d transition possible, while loss of water changes that ligand field.

crystal field is disrupted.

Quick Tip to Solve: First use the counterions to find Ti^{3+}; its single d electron makes a visible d–d transition possible, while loss of water changes that ligand field.

29(b). What is crystal field splitting energy? [1 mark]

Solution:

Concept:

- Free-ion d orbitals are degenerate, meaning that all five have the same energy before a ligand field acts.
- Ligand–electron repulsion separates them into groups of different energies. Their energy separation is the crystal field splitting energy, denoted Δ.

Step 1: Identify the levels produced by the ligand field When ligands surround a metal ion, different d orbitals experience different amounts of repulsion according to their orientations. The original degenerate set therefore splits into a lower-energy set and a higher-energy set.

Step 2: Express the splitting energy The difference between the energies of these two sets is the crystal field splitting energy. For an octahedral complex,

$$\Delta_o = E(e_g) - E(t_{2g}),$$

where e_g is the upper set and t_{2g} the lower set. This is an orbital-energy separation, not the energy cost of pairing two electrons in one orbital.

Step 3: Conclusion Crystal field splitting energy is the energy difference between the two sets of d orbitals formed when a ligand field removes their degeneracy.

Quick Tip to Solve: Define Δ as the gap between the split d-orbital sets; distinguish it from the electron-pairing energy P.

OR

29(b). On the basis of Δ_o and P (pairing energy), how can you differentiate between a strong field ligand and a weak field ligand? [1 mark]

Solution:

Concept:

- In an octahedral crystal field, Δ_o is the energy gap between the lower t_{2g} and higher e_g orbitals.
- Pairing energy P is the energy required to pair two electrons in the same orbital. Electrons choose the arrangement with the lower energy cost.

Step 1: Compare the energies for a strong field ligand A strong field ligand produces a large splitting, so $\Delta_o > P$. Pairing in the lower t_{2g} set is energetically preferred to occupying the higher e_g set, giving a low spin arrangement when the electron count permits it.

Quick Tip to Solve: Compare the cost of promotion with pairing: a large splitting favours pairing.

Step 2: Compare the energies for a weak field ligand A weak field ligand produces a small splitting, so $\Delta_o < P$. Promoting an electron to the higher set costs less energy than pairing it in the lower set; hence the electrons favour a high spin arrangement.

Step 3: Conclusion Strong field ligand: $\boxed{\Delta_o > P}$; weak field ligand: $\boxed{\Delta_o < P}$.

Quick Tip to Solve: Compare the cost of promotion with pairing: a large splitting favours pairing.

29(c). Why are low spin tetrahedral complexes rarely observed? [1 mark]

Solution:

Concept:

- The tetrahedral splitting energy Δ_t is smaller than the octahedral splitting energy; for the same metal ion and ligands, approximately $\Delta_t = \frac{4}{9}\Delta_o$.
- Electrons pair only when pairing costs less energy than occupation of a higher energy orbital. The pairing energy is denoted by P.

Step 1: Assess the small tetrahedral splitting In a tetrahedral field there are only four ligands, and none approaches directly along the axes of the d-orbitals. The resulting splitting of these orbitals is relatively small.

Step 2: Compare splitting with pairing energy Usually $\Delta_t < P$, even with ligands which give appreciable splitting in octahedral complexes. It is therefore energetically cheaper for an electron to occupy a higher orbital than to pair in a lower one. The electrons remain unpaired as far as possible.

Step 3: Conclusion Low spin tetrahedral complexes are rarely observed because Δ_t is usually smaller than the pairing energy P; tetrahedral complexes therefore generally have high spin configurations.

Quick Tip to Solve: Use tetrahedral splitting, not octahedral splitting, when deciding whether pairing occurs.

30(a). Amines are usually formed from amides, imides, halides, nitro compounds, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. Amines being basic in nature, react with acids to form salts. Aryldiazonium salts, undergo replacement of the diazonium group with a variety of nucleophiles to produce aryl halides, cyanides, phenols and arenes.

Answer the following questions:

How can you convert the following?

(i) Ethanoic acid to methanamine

(ii) Propanenitrile to 1-aminopropane [2 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide to a primary amine containing one carbon atom fewer, using $Br_2/NaOH$.
- Reduction of a nitrile converts its $-C \equiv N$ group into $-CH_2NH_2$, retaining the nitrile carbon in the product.

Step 1: (i) Convert ethanoic acid into ethanamide Treat ethanoic acid with ammonia to form ammonium ethanoate. Heating the salt removes water and forms ethanamide:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

The amide is the required intermediate because its carbonyl carbon can be removed by Hofmann degradation.

Step 2: (i) Carry out Hofmann bromamide degradation Treat ethanamide with bromine and aqueous sodium hydroxide:

$$CH_3CONH_2 + Br_2 + 4NaOH$$

$$\longrightarrow CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

The two-carbon amide gives one-carbon methanamine, CH_3NH_2. Direct reduction of the acid or amide would not give this required decrease in carbon chain length.

Step 3: (ii) Reduce propanenitrile Reduce propanenitrile using lithium aluminium hydride in dry ether, followed by hydrolysis:

$$CH_3CH_2C \equiv N \xrightarrow[\text{then } H_2O]{LiAlH_4,\ \text{dry ether}} CH_3CH_2CH_2NH_2$$

The nitrile carbon becomes the terminal CH_2 carbon bonded to NH_2; all three carbons are retained and the amino group is at carbon 1.

Step 4: Conclusion (i) $CH_3COOH \rightarrow CH_3COONH_4 \rightarrow CH_3CONH_2 \rightarrow CH_3NH_2$. (ii) Reduction of CH_3CH_2CN with $LiAlH_4$ followed by hydrolysis gives $CH_3CH_2CH_2NH_2$, 1-aminopropane.

Quick Tip to Solve: Count carbon atoms first: Hofmann degradation removes one, whereas nitrile reduction retains all of them.

30(b). Why is pK_b value of aniline more than that of methylamine? [1 mark]

Solution:

Concept:

- The base dissociation constant K_b measures the tendency of an amine to accept a proton in water; $pK_b = -\log_{10} K_b$.
- A nitrogen lone pair that is more available for protonation gives a stronger base and a larger K_b.

Step 1: Compare the availability of the nitrogen lone pairs In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance, making it less available to accept a proton. In methylamine, the lone pair remains localised on nitrogen, and the methyl group increases electron density through its electron releasing inductive effect.

Step 2: Relate basic strength to the logarithmic constant Aniline is therefore a weaker base than methylamine and has a smaller K_b. Since $pK_b = -\log_{10} K_b$, a smaller base dissociation constant corresponds to a larger pK_b value.

Step 3: Conclusion Aniline has a greater pK_b than methylamine because resonance makes its nitrogen lone pair less available for protonation, whereas the methyl group increases the basicity of methylamine.

Quick Tip to Solve: Remember the inverse relation: a weaker base has a smaller Kb but a larger pKb.

30(c). Arrange the following in increasing order of their basic strength in aqueous solution: CH_3-NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ [1 mark]

Solution:

Concept:

- Basicity in aqueous solution depends on both the electron releasing inductive effect of alkyl groups and hydration of the conjugate ammonium ion.
- Hydrogen bonding with water stabilises the protonated amine; steric crowding around nitrogen reduces effective solvation.

Step 1: Compare methylamine with trimethylamine The three methyl groups in trimethylamine increase electron density at nitrogen, but the protonated ion is crowded and is hydrated less effectively. In water, this reduction in hydration outweighs the additional inductive effect when trimethylamine is compared with methylamine.

Step 2: Locate dimethylamine in the order Dimethylamine has a stronger electron releasing effect than methylamine while its conjugate acid still undergoes effective hydration. This favourable balance makes dimethylamine the strongest base of the three in aqueous solution.

Step 3: Conclusion The increasing order of basic strength in aqueous solution is

$$\boxed{(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH}.$$

Quick Tip to Solve: For methylamines in water use tertiary < primary < secondary; solvation changes the gas phase order.

OR

30(c). Give the structures of A and B in the following reaction:

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{HNO_2} B$$

[1 mark]

Solution:

Concept:

- Iron and hydrochloric acid reduce the nitro group $-NO_2$ of nitrobenzene to the amino group $-NH_2$.
- Aniline undergoes diazotisation with nitrous acid in hydrochloric acid at low temperature to give benzenediazonium chloride.

Step 1: Identify A after reduction Reduction changes the substituent on the benzene ring without changing the ring itself:

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2.$$

Thus A is aniline, with the structural group $C_6H_5-NH_2$.

Step 2: Identify B after diazotisation At 273 K, aniline reacts with nitrous acid in the acidic medium to form the diazonium salt:

$$C_6H_5NH_2 + HNO_2 + HCl$$

$$\longrightarrow [C_6H_5-N \equiv N]^+Cl^- + 2H_2O.$$

The low temperature helps retain the diazonium salt, which would otherwise readily decompose. Its diazonium group is attached to the benzene ring through nitrogen.

Step 3: Conclusion $\boxed{A = C_6H_5-NH_2}$ (aniline) and $\boxed{B = [C_6H_5-N \equiv N]^+Cl^-}$ (benzenediazonium chloride).

Quick Tip to Solve: Follow the functional group: nitro reduction gives aniline, then cold diazotisation gives the diazonium salt.

Section E (15 marks)

31(a). (i) An organic compound (X) having molecular formula $C_5H_{10}O$ can show various properties depending on its structures. Draw each of the structures if it:

(I) shows Cannizzaro reaction.

(II) reduces Tollens' reagent and has a chiral carbon.

(III) gives positive iodoform test.

(ii) Write the reaction involved in the following:

(I) Clemmensen reduction

(II) Etard reaction [5 marks]

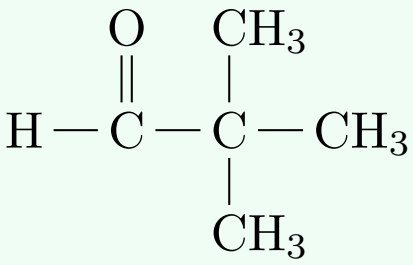
Solution:

Concept:

- Cannizzaro reaction is disproportionation of an aldehyde without an alpha-hydrogen in concentrated alkali; the alpha-carbon is the carbon next to the aldehyde group.
- Aldehydes reduce Tollens' reagent to metallic silver. A chiral carbon is bonded to four different groups.
- A methyl ketone, CH_3CO-R, gives yellow iodoform, CHI_3, with iodine and alkali.
- Clemmensen reduction converts a carbonyl group to a methylene group using zinc amalgam and concentrated hydrochloric acid. Etard oxidation converts the benzylic methyl group of toluene into an aldehyde using chromyl chloride followed by hydrolysis.

Step 1: (i)(I) Choose an aldehyde without an alpha-hydrogen The aldehyde must have formula $C_5H_{10}O$, and its adjacent carbon must carry no hydrogen. Choose **2,2-dimethylpropanal**, $(CH_3)_3CCHO$. The alpha-carbon is bonded to three methyl groups and to the aldehyde carbon, so it has no hydrogen. Its three methyl groups supply nine hydrogens and the aldehyde group supplies one, verifying the formula. In concentrated alkali one molecule is oxidised to a carboxylate and another is reduced to an alcohol:

$$2\,(CH_3)_3CCHO + NaOH \longrightarrow (CH_3)_3CCOONa + (CH_3)_3CCH_2OH.$$

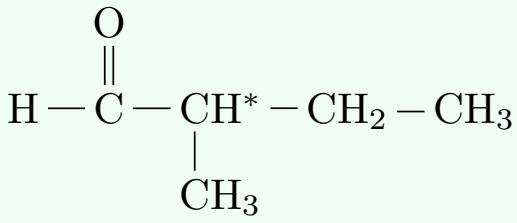


2,2-Dimethylpropanal: the alpha-carbon has no hydrogen.

Step 2: (i)(II) Choose an aldehyde with a chiral carbon **2-Methylbutanal**, $CH_3CH_2CH(CH_3)CHO$, meets both conditions. It is an aldehyde and therefore reduces Tollens' reagent. Its carbon at position 2, indicated by an asterisk in the structure, is attached to four distinct groups: $-H$, $-CHO$, $-CH_3$

Quick Tip to Solve: For the three tests, inspect the alpha-carbon for no hydrogen, list the four groups on a possible chiral carbon, and look specifically for CH_3CO^-; then count all five carbons and ten hydrogens.

and $-CH_2CH_3$. Thus this carbon is chiral. Counting the atoms gives five carbons, ten hydrogens and one oxygen. In the silver-mirror test the aldehyde is oxidised to the corresponding carboxylate while silver(I) is reduced to silver metal.

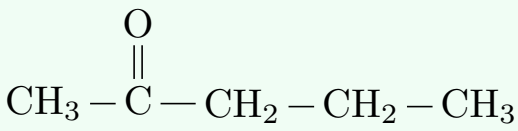


2-Methylbutanal: the asterisk identifies the chiral carbon.

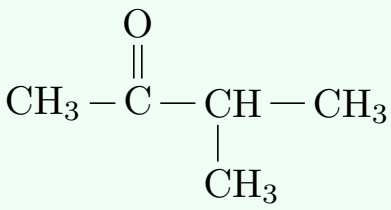
Step 3: (i)(III) Choose a methyl ketone **Pentan-2-one**, $CH_3COCH_2CH_2CH_3$, has the required CH_3CO^- group and formula $C_5H_{10}O$, so it gives the iodoform test. **3-Methylbutan-2-one**, $CH_3COCH(CH_3)_2$, is another valid structure of the same molecular formula that gives this test. Their structures are drawn below. For pentan-2-one the reaction is:

$$CH_3COCH_2CH_2CH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3\downarrow + CH_3CH_2CH_2COONa + 3\,NaI + 3\,H_2O.$$

The precipitate is yellow iodoform. Pentan-3-one lacks a methyl group directly attached to the carbonyl carbon and does not satisfy this condition.



Pentan-2-one



3-Methylbutan-2-one

Both methyl ketones give a positive iodoform test.

Step 4: (ii)(I) Write Clemmensen reduction An aldehyde or ketone is reduced using **zinc amalgam,** $Zn(Hg)$**, and concentrated** HCl. The carbonyl oxygen is removed as water, and the carbonyl carbon gains hydrogen. For example, propanone becomes propane:

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

Quick Tip to Solve: For the three tests, inspect the alpha-carbon for no hydrogen, list the four groups on a possible chiral carbon, and look specifically for CH_3CO^-; then count all five carbons and ten hydrogens.

In general, $RCHO$ becomes RCH_3, whereas the carbonyl group in a ketone becomes a $-CH_2-$ group. This reaction uses an acidic medium.

Step 5: (ii)(II) Write the Etard reaction Toluene is oxidised with **chromyl chloride**, CrO_2Cl_2, in a nonaqueous solvent such as CS_2. The Etard complex formed is then hydrolysed to yield benzaldehyde:

$$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2\ /\ CS_2} C_6H_5CH(OCrOHCl_2)_2 \xrightarrow{H_2O} C_6H_5CHO.$$

Thus the side-chain $-CH_3$ group becomes $-CHO$, while the benzene ring is retained. Controlled oxidation through the complex distinguishes this preparation of benzaldehyde from vigorous oxidation of the side chain to benzoic acid.

Step 6: Conclusion The required structures are 2,2-dimethylpropanal for Cannizzaro reaction, 2-methylbutanal for Tollens' reduction with chirality, and pentan-2-one (also 3-methylbutan-2-one) for iodoform formation. Clemmensen reduction gives a hydrocarbon from a carbonyl compound; the Etard reaction gives benzaldehyde from toluene.

Quick Tip to Solve: For the three tests, inspect the alpha-carbon for no hydrogen, list the four groups on a possible chiral carbon, and look specifically for CH_3CO^-; then count all five carbons and ten hydrogens.

OR

31(b). Answer the following questions:

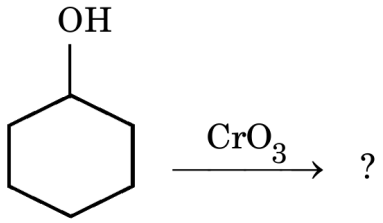
(i) Draw structure of the methyl hemiacetal of methanal.

(ii) There are two $-NH_2$ groups in semicarbazide. However only one is involved in the formation of semicarbazones. Give reason.

(iii) How will you convert ethanol to 3-hydroxybutanal?

[5 marks]

(iv) Complete the following equation :



(v) Write the final product formed when phthalic acid is treated with NH_3 followed by strong heating.

Solution:

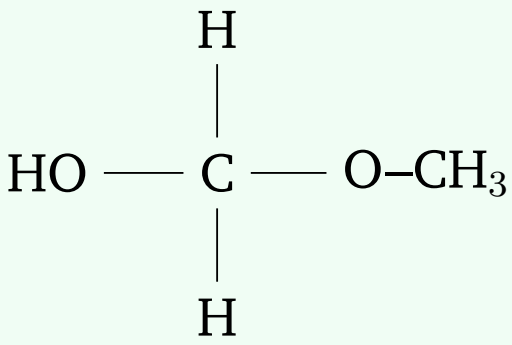
Concept:

- A hemiacetal contains an $-OH$ group and an $-OR$ group attached to the same carbon. Addition of methanol to methanal gives the methyl hemiacetal.
- A nitrogen lone pair delocalised into a neighbouring carbonyl group is less available for nucleophilic attack. The terminal hydrazino amino group of semicarbazide remains available to attack aldehydes and ketones.
- Aldehydes with an alpha hydrogen undergo aldol addition with dilute alkali. Secondary alcohols oxidise to ketones, whereas an ortho dicarboxylic acid forms a cyclic imide on treatment with ammonia and heating.

Step 1: (i) Draw the methyl hemiacetal Methanal, $HCHO$, reacts with methanol, CH_3OH, by addition across its carbonyl group:

$$HCHO + CH_3OH \rightleftharpoons HOCH_2OCH_3.$$

The former carbonyl carbon retains its two hydrogen atoms and now bears both hydroxyl and methoxy groups. Its bonds are shown below.



Methyl hemiacetal of methanal: hydroxyl and methoxy on the same carbon.

Step 2: (ii) Identify the reactive amino group in semicarbazide Semicarbazide has the structure $H_2N-NH-C(=O)-NH_2$. The lone pair on the amino nitrogen directly attached to $C=O$ is delocalised by resonance with the carbonyl group, giving its C–N bond partial double-bond character. That amino group is consequently much less nucleophilic. The terminal H_2N-NH- nitrogen has an available lone pair and attacks the carbonyl carbon of an aldehyde or ketone. Condensation followed by loss of water produces

$$R_2C=O + H_2N-NH-CONH_2 \longrightarrow R_2C=N-NH-CONH_2 + H_2O.$$

Thus only the terminal hydrazino amino group participates in semicarbazone formation.

Step 3: (iii) Convert ethanol into 3-hydroxybutanal First convert ethanol into ethanal by passing its vapour over heated copper at $573\,K$:

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

Quick Tip to Solve: For the aldol conversion, stop at cold dilute alkali: heating removes water and would destroy the requested 3-hydroxybutanal product.

Then carry out aldol addition using cold dilute sodium hydroxide:

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

Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Ethanal has alpha hydrogens, permitting this addition. Avoid heating the aldol product, since dehydration would instead give but-2-enal.

Step 4: (iv) Complete the cyclohexanol oxidation Cyclohexanol is a secondary alcohol. Chromium trioxide oxidises the carbon carrying the hydroxyl group to a carbonyl group while retaining the six-membered ring:

$$C_6H_{11}OH + [O] \xrightarrow{CrO_3} C_6H_{10}O + H_2O.$$

The product $C_6H_{10}O$ is cyclohexanone, a cyclic ketone.

Step 5: (v) Form the cyclic imide of phthalic acid The two carboxyl groups in phthalic acid occupy adjacent positions on the benzene ring. Reaction with ammonia followed by strong heating eliminates water and gives the five-membered cyclic imide, phthalimide:

$$C_6H_4(COOH)_2 + NH_3 \xrightarrow{\Delta} C_6H_4(CO)_2NH + 2H_2O.$$

The imide nitrogen bears one hydrogen and joins the two acyl groups; the formula distinguishes the cyclic imide from an ammonium carboxylate salt.

Step 6: Conclusion (i) The methyl hemiacetal is $HOCH_2OCH_3$. (ii) Only the terminal hydrazino $-NH_2$ reacts because the carbonyl-bound amino lone pair is delocalised. (iii) Ethanol is converted to ethanal, then to $CH_3CH(OH)CH_2CHO$ by aldol addition. (iv) Cyclohexanone is formed. (v) The final product is phthalimide, $C_6H_4(CO)_2NH$.

Quick Tip to Solve: For the aldol conversion, stop at cold dilute alkali: heating removes water and would destroy the requested 3-hydroxybutanal product.

32(a)(i). Calculate the emf of the following cell at $25^\circ C$:

$Zn(s) \mid Zn^{2+}(0.1\,M) \parallel H^+(0.01\,M) \mid H_2(g)(1\,bar), Pt(s)$

[Given: $E^\circ_{Zn^{2+}/Zn} = -0.76\,V$, $E^\circ_{2H^+/H_2} = 0.00\,V$, $\log 10 = 1$**]** [3 marks]

Solution:

Concept:

- The cell emf is the cathode reduction potential minus the anode reduction potential: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$.
- At 298 K, the Nernst equation is $E_{cell} = E^\circ_{cell} - (0.0591/n)\log Q$, where n is the number of electrons exchanged and Q is the reaction quotient. Pure solids have unit activity, and the gas pressure is measured relative to 1 bar.

Step 1: Identify the cell reaction and standard emf Zinc at the left electrode undergoes oxidation,

Quick Tip to Solve: Balance the zinc–hydrogen reaction first: its two hydrogen ions make the denominator $[H^+]^2$ and its two electrons set $n = 2$.

while hydrogen ions at the right electrode undergo reduction:

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

Adding the half-reactions gives $\mathrm{Zn(s)} + 2\mathrm{H^+(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{H_2(g)}$, with $n = 2$. The platinum electrode is inert and provides a conducting surface. Using the supplied reduction potentials,

$$E^\circ_{\text{cell}} = 0.00 - (-0.76) = 0.76\,\text{V}.$$

Step 2: Calculate the reaction quotient The square on the hydrogen-ion concentration follows from its coefficient 2 in the balanced cell reaction. The solid zinc does not appear in the quotient. With the stated concentrations and hydrogen pressure,

$$Q = \frac{[\mathrm{Zn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.1 \times 1}{(0.01)^2} = 1000.$$

Thus $\log Q = \log(10^3) = 3$. Concentrations here are the numerical concentrations relative to the standard concentration, as used in the CBSE Nernst calculation.

Step 3: Apply the Nernst equation at the stated temperature Substitute the reaction quotient and electron-transfer number:

$$\begin{aligned} E_{\text{cell}} &= 0.76 - \frac{0.0591}{2}\log 1000 \\ &= 0.76 - \frac{0.0591}{2} \times 3 \\ &= 0.76 - 0.08865 = 0.67135\,\text{V}. \end{aligned}$$

Since $Q > 1$, the Nernst correction lowers the emf relative to its standard value. This provides a check on the subtraction sign.

Step 4: Conclusion The emf of the cell at 25°C is $E_{\text{cell}} \approx 0.671\,\text{V}$.

Quick Tip to Solve: Balance the zinc–hydrogen reaction first: its two hydrogen ions make the denominator $[\mathrm{H^+}]^2$ and its two electrons set $n = 2$.

32(a)(ii). State Faraday's second law of electrolysis. How much electricity is required in terms of Faraday for the reduction of 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+}? [2 marks]

Solution:

Concept:

- Faraday's second law states that when the same quantity of electricity passes through different electrolytes, the masses of substances deposited or liberated are proportional to their chemical equivalent masses.
- One Faraday, F, is the charge carried by one mole of electrons. The charge required is determined by the electron balance of the reduction half-reaction.

Quick Tip to Solve: Multiply the oxidation-state decrease per chromium atom by the two chromium atoms in one dichromate ion.

Step 1: State the quantitative form of the law For the same charge passing through two electrolytes, $m_1/m_2 = E_1/E_2$, where m denotes the deposited mass and $E = M/z$ is the equivalent mass; M is molar mass and z is the number of electrons transferred per formula unit.

Step 2: Count the electrons required by dichromate In $Cr_2O_7^{2-}$, chromium has oxidation state $+6$. Each chromium atom gains three electrons to form Cr^{3+}, and one dichromate ion contains two chromium atoms. The balanced reduction is

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

Thus one mole of dichromate consumes six moles of electrons, so the required charge is $Q = 6F$.

Step 3: Conclusion For equal charge, deposited masses are proportional to equivalent masses. Reduction of 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+} requires $\boxed{6F}$ of electricity.

Quick Tip to Solve: Multiply the oxidation-state decrease per chromium atom by the two chromium atoms in one dichromate ion.

OR

32(b)(i). The conductivity of 0.20 M solution of KCl is 2.48 $\times$ 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
[Given: $\lambda^\circ_{(K^+)}$ = 73.5 S cm^2 mol^{-1}, $\lambda^\circ_{(Cl^-)}$ = 76.5 S cm^2 mol^{-1}] [2 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/C$ when conductivity κ is in S cm^{-1} and concentration C is in mol L^{-1}.
- Kohlrausch's law gives the limiting molar conductivity as the sum of the limiting ionic conductivities. The conductivity ratio used to calculate α is $\Lambda_m/\Lambda_m^\circ$.

Step 1: Calculate the molar conductivity Substitute the given conductivity and concentration in their stated units:

$$\Lambda_m = \frac{1000(2.48 \times 10^{-2})}{0.20} = 124\,\text{S cm}^2\,\text{mol}^{-1}.$$

The factor 1000 converts the concentration from moles per litre to moles per cubic centimetre, making the units consistent with conductivity.

Step 2: Calculate the limiting value and the requested ratio Each formula unit of KCl gives one potassium ion and one chloride ion, so

$$\begin{aligned}\Lambda_m^\circ &= \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-} \\ &= 73.5 + 76.5 = 150\,\text{S cm}^2\,\text{mol}^{-1}, \\ \alpha &= \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{124}{150} = 0.8267.\end{aligned}$$

Quick Tip to Solve: First add the two limiting ionic conductivities, then divide the calculated molar conductivity by their sum.

Thus the degree obtained by the conductivity-ratio calculation is about 82.7%. For a strong electrolyte such as KCl, this ratio is an apparent degree: interionic interactions reduce ionic mobility at finite concentration, even though the electrolyte is essentially fully dissociated.

Step 3: Conclusion The molar conductivity is $\boxed{124\,\text{S cm}^2\ \text{mol}^{-1}}$, and the requested conductivity-ratio value is $\boxed{\alpha \approx 0.827\ (82.7\%)}$.

Quick Tip to Solve: First add the two limiting ionic conductivities, then divide the calculated molar conductivity by their sum.

32(b)(ii). Calculate $\Delta_r G^\circ$ of the following cell:

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

[Given: $E^\circ_{Mg^{2+}/Mg}$ = -2.37 V, $E^\circ_{Cu^{2+}/Cu}$ = +0.34 V, 1 F = 96500 C mol^{-1}] [2 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred in the balanced reaction and F is the charge per mole of electrons.

Step 1: Identify the electron transfer and calculate the potential Magnesium is oxidised at the anode and copper ions are reduced at the cathode:

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

Hence $n = 2$, not one, for the reaction as written. Using the supplied reduction potentials,

$$E^\circ_{\text{cell}} = 0.34 - (-2.37) = 2.71\,\text{V}.$$

Step 2: Find the standard Gibbs energy change Substitution gives

$$\begin{aligned}\Delta_r G^\circ &= -(2)(96500)(2.71)\\ &= -523030\,\text{J mol}^{-1}\\ &= -523.03\,\text{kJ mol}^{-1}.\end{aligned}$$

Here C $\times$ V = J. The negative sign agrees with the positive standard cell potential and indicates a spontaneous forward reaction under standard conditions.

Step 3: Conclusion For the balanced cell reaction, $\boxed{\Delta_r G^\circ = -523.03\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Subtract the magnesium reduction potential as a negative number, and use two electrons for the Mg/Cu reaction.

32(b)(iii). What type of cell is mercury cell? Why is it more advantageous than dry cell? [1 mark]

Solution:

Concept:

- A primary cell supplies electricity through a reaction that cannot be conveniently reversed by recharging. A mercury cell belongs to this category.
- A cell maintains a nearly constant potential when the overall discharge reaction produces no significant change in the concentration of electrolyte ions.

Step 1: Classify the cell A mercury cell is a primary electrochemical cell. It uses a zinc amalgam anode and a mercury(II) oxide cathode in an alkaline electrolyte.

Step 2: Explain its advantage over a dry cell Its overall discharge reaction is

$$\mathrm{Zn(Hg) + HgO\,(s) \longrightarrow ZnO\,(s) + Hg\,(l).}$$

Electrolyte ions do not appear in the net reaction, so their concentration remains essentially unchanged during use. The mercury cell therefore maintains a nearly constant voltage of about $1.35\,\mathrm{V}$ throughout its useful life, whereas the voltage of a dry cell falls during discharge.

Step 3: Conclusion A mercury cell is a $\boxed{\text{primary cell}}$. Its advantage is a nearly constant output voltage during its useful life.

Quick Tip to Solve: Connect constant mercury-cell voltage with the absence of electrolyte ions from its overall discharge reaction.

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

(I) The $E^{\circ}_{Mn^{2+}/Mn}$ value for manganese is highly negative, whereas $E^{\circ}_{Mn^{3+}/Mn^{2+}}$ is highly positive.

(II) Actinoids show wide range of oxidation states.

(III) Transition metals have high melting points.

(ii) Complete the following ionic equations:

(I) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow$

(II) $2MnO_4^- + H_2O + I^- \rightarrow$ [5 marks]

Solution:

Concept:

- The standard reduction potential measures the tendency of a species to gain electrons. The half-filled $3d^5$ configuration of Mn^{2+} has extra stability.
- Actinoid oxidation states depend on the participation of $5f$, $6d$ and $7s$ electrons in bonding. Strong metallic bonding in transition metals involves both ns and $(n-1)d$ electrons.
- Balance a redox equation by conserving atoms and total charge. In acidic medium permanganate forms Mn^{2+}; with iodide in neutral or weakly alkaline medium it forms MnO_2 while iodide is oxidised to iodate.

Step 1: (i)(I) Explain the two manganese reduction potentials Manganese has configuration

Quick Tip to Solve: First identify the medium: acidic permanganate gives Mn^{2+}, whereas the printed iodide reaction gives MnO_2. Then equalise electron transfer and check the total charge.

$[\mathrm{Ar}]3d^5 4s^2$, and Mn^{2+} has the particularly stable half-filled configuration $[\mathrm{Ar}]3d^5$. Formation of Mn^{2+} from the metal is favoured, whereas the reverse reduction, $\mathrm{Mn}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Mn}$, is relatively unfavourable. Hence $E^\circ_{\mathrm{Mn}^{2+}/\mathrm{Mn}}$ is highly negative. By contrast, Mn^{3+} is $3d^4$. It readily accepts one electron to attain the stable $3d^5$ configuration of Mn^{2+}:

$$\mathrm{Mn}^{3+} + \mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}.$$

This favourable reduction accounts for the highly positive $E^\circ_{\mathrm{Mn}^{3+}/\mathrm{Mn}^{2+}}$.

Step 2: (i)(II) Explain the oxidation states of actinoids The energies of the $5f$, $6d$ and $7s$ subshells in actinoids are relatively close. Therefore differing numbers of electrons from these subshells can participate in bonding, giving a wide range of oxidation states. In particular, early actinoids can use more of their $5f$ electrons in addition to their outer electrons.

Step 3: (i)(III) Explain the high melting points Transition metals generally have strong metallic bonds because both their ns and available $(n-1)d$ electrons participate in metallic bonding. Many unpaired d electrons contribute to strong interatomic interactions and high enthalpies of atomisation. Considerable energy is consequently needed to overcome these bonds on melting, so the melting points are generally high.

Step 4: (ii)(I) Complete the acidic sulphite reaction Sulphur changes from $+4$ in sulphite to $+6$ in sulphate, losing two electrons per sulphite ion. Manganese changes from $+7$ in permanganate to $+2$, gaining five electrons per manganese atom. Five sulphite ions supply the ten electrons needed by two permanganate ions. Balancing oxygen and hydrogen with water and hydrogen ions gives

$$\begin{aligned} &5\mathrm{SO}_3^{2-} + 2\mathrm{MnO}_4^- + 6\mathrm{H}^+ \\ &\quad\longrightarrow 5\mathrm{SO}_4^{2-} + 2\mathrm{Mn}^{2+} + 3\mathrm{H_2O}. \end{aligned}$$

Both sides have total charge -6, with all atoms conserved.

Step 5: (ii)(II) Complete the iodide reaction Here permanganate is reduced to manganese dioxide: manganese falls from $+7$ to $+4$, gaining three electrons per atom. Iodide is oxidised from -1 to $+5$ in iodate, losing six electrons. Thus one iodide ion reacts with two permanganate ions. The balanced equation is

$$\begin{aligned} &2\mathrm{MnO}_4^- + \mathrm{H_2O} + \mathrm{I}^- \\ &\quad\longrightarrow 2\mathrm{MnO_2} + \mathrm{IO}_3^- + 2\mathrm{OH}^-. \end{aligned}$$

The eight oxygen atoms from permanganate and one from water give four in manganese dioxide, three in iodate and two in hydroxide. Both sides have charge -3.

Step 6: Conclusion (i) The stability of half-filled $3d^5$ Mn^{2+} explains both manganese potentials; nearby $5f, 6d, 7s$ energies explain actinoid oxidation states; strong metallic bonding explains high transition-metal melting points. (ii)(I) The products are $5\mathrm{SO}_4^{2-} + 2\mathrm{Mn}^{2+} + 3\mathrm{H_2O}$. (ii)(II) The products are $2\mathrm{MnO_2} + \mathrm{IO}_3^- + 2\mathrm{OH}^-$.

Quick Tip to Solve: First identify the medium: acidic permanganate gives Mn^{2+}, whereas the printed iodide reaction gives $\mathrm{MnO_2}$. Then equalise electron transfer and check the total charge.

OR

33(b). Answer the following questions:

(i) Name two elements of 3d series for which the third ionisation enthalpies are quite high.

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

(iii) Write any one consequence of lanthanoid contraction.

(iv) How do you prepare potassium manganate from pyrolusite ore?

(v) Why is the ability of oxygen more than fluorine to stabilise higher oxidation states of transition metals? [5 marks]

Solution:

Concept:

- The third ionisation enthalpy is the energy required for $M^{2+}(g) \rightarrow M^{3+}(g) + e^-$. Removing an electron from a particularly stable half-filled or fully filled subshell requires high energy.
- A species with an unpaired electron is paramagnetic; a species whose electrons are all paired is diamagnetic. The manganese oxidation state follows from the overall charge and the usual oxidation state -2 of oxygen.
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series because $4f$ electrons shield the increasing nuclear charge poorly.
- Oxidation of MnO_2 in strongly alkaline conditions gives manganate(VI). Oxygen can stabilise high metal oxidation states through strong metal–oxygen multiple bonding.

Step 1: (i) Identify the elements with high third ionisation enthalpies The two elements are manganese (Mn) and zinc (Zn). Their divalent ions have the configurations

$$Mn^{2+} : [Ar]3d^5, \qquad Zn^{2+} : [Ar]3d^{10}.$$

The half-filled $3d^5$ subshell of Mn^{2+} and the fully filled $3d^{10}$ subshell of Zn^{2+} are particularly stable. The third ionisation removes a $3d$ electron and disrupts these stable configurations, so it requires quite high energy in both cases.

Step 2: (ii) Compare the magnetic behaviour of the two salts In $KMnO_4$, charge balance gives $1 + x - 8 = 0$, so manganese is in the $+7$ oxidation state and has the $3d^0$ configuration. It has no unpaired electrons and is diamagnetic.

In K_2MnO_4, charge balance gives $2 + x - 8 = 0$, so manganese is in the $+6$ oxidation state and has the $3d^1$ configuration. This leaves one unpaired electron; hence K_2MnO_4 is paramagnetic.

Step 3: (iii) State a consequence of lanthanoid contraction Zirconium (Zr) and hafnium (Hf) have nearly equal atomic radii and consequently very similar chemical properties. Although Hf is in the period below Zr, the contraction caused by filling the intervening $4f$ subshell largely offsets the expected increase in size. Their chemical similarity also makes their separation difficult.

Step 4: (iv) Prepare potassium manganate from pyrolusite Pyrolusite, MnO_2, is fused with potassium hydroxide in the presence of air or oxygen. Manganese is oxidised from $+4$ to $+6$, forming green potassium manganate:

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

Quick Tip to Solve: First calculate the manganese oxidation state: $+7$ gives d-zero permanganate, while $+6$ gives d-one manganate with one unpaired electron.

The alkaline fusion supplies the potassium ions and the strongly basic medium required to obtain the manganate salt. The equation conserves two manganese atoms, four potassium atoms, four hydrogen atoms and ten oxygen atoms on each side.

Step 5: (v) Explain oxygen's greater ability to stabilise high oxidation states Oxygen can form strong multiple bonds with transition metals, involving both σ and π bonding. This additional bonding stabilises metals in high oxidation states. Fluorine generally forms only single bonds with the metal, so its high electronegativity alone does not provide the same stabilisation. For example, manganese reaches $+7$ in $\mathrm{Mn_2O_7}$, whereas its highest fluoride is $\mathrm{MnF_4}$, with manganese in $+4$.

Step 6: Conclusion (i) Mn and Zn; (ii) $\mathrm{K_2MnO_4}$, because its $\mathrm{Mn(VI)}$ centre is $3d^1$; (iii) nearly equal sizes and similar chemistry of Zr and Hf; (iv) alkaline oxidative fusion of pyrolusite gives $\mathrm{K_2MnO_4}$; (v) oxygen stabilises high oxidation states by strong metal–oxygen multiple bonding.

Quick Tip to Solve: First calculate the manganese oxidation state: $+7$ gives d-zero permanganate, while $+6$ gives d-one manganate with one unpaired electron.