CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-1-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) This question paper 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.

You may use the following values of physical constants wherever necessary :

$c = 3 \times 10^8$ m/s

$h = 6.63 \times 10^{-34}$ Js

$e = 1.6 \times 10^{-19}$ C

$\mu_0 = 4\pi \times 10^{-7}$ T m A^{-1}

$\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 N^{-1} m^{-2}

$\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ N m^2 C^{-2}

Mass of electron $(m_e) = 9.1 \times 10^{-31}$ kg.

Mass of neutron $= 1.675 \times 10^{-27}$ kg.

Mass of proton $= 1.673 \times 10^{-27}$ kg.

Avogadro's number $= 6.023 \times 10^{23}$ per gram mole

Boltzmann's constant $= 1.38 \times 10^{-23}$ JK^{-1}

Section A (16 marks)

Questions No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

For questions number 1 to 4, two statements are given – one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below :

1. Assertion (A): All naturally occurring α-amino acids except glycine are optically active.
Reason (R): Most naturally occurring amino acids have L-configuration. [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:

- Optical activity arises from chirality: an asymmetric carbon has four different groups attached.
- L-configuration describes the relative arrangement of groups; it does not specify the direction of optical rotation.

Step 1: Judge the assertion An ordinary naturally occurring α-amino acid has $-NH_2$, $-COOH$, $-H$ and a side chain attached to its α-carbon. Except in glycine, these are four different groups, making the carbon chiral. Glycine has two hydrogen atoms on this carbon and is achiral. Thus the assertion is true.

Step 2: Judge the reason Most naturally occurring amino acids belong to the L-series. This statement about their relative configuration is true.

Step 3: Test the explanation The structural cause of optical activity is the asymmetric carbon, not membership of the L-series. L does not mean levorotatory, and a configuration label alone does not explain the glycine exception. Hence (A) is excluded; (C) and (D) are excluded because both statements are true.

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

Quick Tip to Solve: For amino-acid optical activity, count the different groups on the α-carbon; do not infer rotation from L or D.

2. Assertion (A): The boiling point of ethanol is higher than that of methoxymethane.

Reason (R): There is intramolecular hydrogen bonding in ethanol. [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: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- Intermolecular hydrogen bonds form between different molecules containing a suitable hydrogen-bond donor and acceptor.
- Stronger intermolecular attraction requires more energy for vaporisation and raises the boiling point.

Step 1: Judge the assertion Ethanol has an O – H group and forms hydrogen bonds between its molecules. Methoxymethane has no hydrogen bonded directly to oxygen, so its pure liquid cannot form such hydrogen-bond networks. Ethanol therefore has the higher boiling point; A is true.

Step 2: Judge the reason The hydrogen bonding responsible for ethanol's boiling point is intermolecular, not intramolecular. A hydrogen bond joins the hydroxyl hydrogen of one molecule to oxygen of another. Thus R is false.

Step 3: Choose the code Option (A) incorrectly treats R as a true explanation, and (B) also requires R to be true. Option (D) incorrectly rejects the true assertion. The code for a true assertion and a false reason is (C).

Step 4: Conclusion A is true and R is false. The correct option is (C).

Quick Tip to Solve: In ethanol, link the O – H group of one molecule to oxygen of another: this is intermolecular hydrogen bonding.

3. Assertion (A): The boiling points of alkyl halides decrease in the order : RI $>$ RBr $>$ RCl $>$ RF.
Reason (R): The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass. [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:

- For a fixed alkyl group, increasing halogen size and polarizability strengthens London dispersion forces.
- Boiling point depends on intermolecular attractions, rather than simply the strength of the intramolecular carbon-halogen bond.

Step 1: Judge the assertion For the same alkyl group R, iodine is the most polarizable halogen and fluorine the least. Dispersion attractions generally decrease from iodide to fluoride, giving $\mathrm{RI} > \mathrm{RBr} > \mathrm{RCl} > \mathrm{RF}$ in boiling point. Thus A is true.

Step 2: Judge the reason Alkyl chlorides, bromides and iodides have stronger intermolecular attractions, including dipole-dipole interactions, than hydrocarbons of comparable molecular mass. Their boiling points are therefore considerably higher. R is true.

Step 3: Test the explanation R compares haloalkanes with hydrocarbons; it does not explain the relative order among the four halides. That order requires the change in halogen polarizability for a fixed alkyl group. Thus (A) is unsuitable, while (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. The correct option is (B).

Quick Tip to Solve: For a halide boiling-point series, keep R fixed and compare halogen polarizability; a hydrocarbon comparison answers a different question.

4. Assertion (A): $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are examples of homoleptic complexes.
Reason (R): All the ligands attached to the metal are the same. [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:

- A homoleptic complex contains only one kind of ligand coordinated to the central metal.
- Ligands inside square brackets belong to the coordination sphere; ions outside the brackets are counter-ions.

Step 1: Judge the assertion In both $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$, six water ligands are coordinated to the metal. No second kind of ligand is present inside either coordination sphere, so both complexes are homoleptic. A is true.

Step 2: Judge the reason All ligands attached to each central metal are water molecules. Chloride ions lie outside the brackets and are counter-ions, not coordinated ligands. Thus R is true.

Step 3: Test the explanation Having the same kind of ligand at every coordination position is precisely the definition of a homoleptic complex. R therefore directly explains A. Option (B) denies this explanation, while (C) and (D) incorrectly reject one of the true statements.

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

Quick Tip to Solve: Count ligand types inside the square brackets; do not count external chloride counter-ions as ligands.

5. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because [1 mark]

(A) it gains water due to osmosis

(B) it loses water due to reverse osmosis

(C) it gains water due to reverse osmosis

(D) it loses water due to osmosis

Correct Answer: (D) it loses water due to osmosis

Solution:

Concept:

- Osmosis is spontaneous solvent flow across a semipermeable membrane from a dilute solution to a more concentrated solution.

Quick Tip to Solve: A concentrated external salt solution draws water out of cells; reserve reverse osmosis for pressure-driven flow.

- Reverse osmosis needs applied pressure greater than the osmotic pressure to force solvent against its spontaneous direction.

Step 1: Compare the solutions The concentrated salt solution outside the mango cells is hypertonic relative to the cell sap. Cell membranes allow water to pass, while the dissolved material is comparatively restricted.

Step 2: Follow the water movement Water moves out of the mango cells into the salt solution by osmosis (exosmosis). The cells lose water and turgor, so the mango shrivels.

Step 3: Check the alternatives Options (A) and (C) predict water gain and cannot explain shrinking. Option (B) calls the loss reverse osmosis, but no external pressure is applied to reverse the natural flow. Only (D) gives both the correct direction and process.

Step 4: Conclusion The mango loses water due to osmosis. The correct option is (D).

Quick Tip to Solve: A concentrated external salt solution draws water out of cells; reserve reverse osmosis for pressure-driven flow.

6. Which of the following statements is not true about glucose ? [1 mark]

(A) It is an aldohexose.

(B) On heating with HI it forms n-hexane.

(C) It exists in furanose form.

(D) It does not give Schiff's test.

Correct Answer: (C) It exists in furanose form.

Solution:

Concept:

- Glucose is an aldohexose: its open-chain structure has six carbon atoms and an aldehyde group.
- Its usual cyclic forms are six-membered pyranose hemiacetals, produced by reaction of C-1 with the hydroxyl group at C-5.

Step 1: Check the true statements Glucose has six carbon atoms and an aldehyde group in its open-chain form, so (A) is true. Prolonged heating with HI gives n-hexane, supporting an unbranched six-carbon skeleton, so (B) is true.

Step 2: Identify the incorrect ring description The predominant cyclic forms of glucose are α- and β-glucopyranose. Their ring has five carbon atoms and one oxygen atom. The CBSE structural description is therefore pyranose rather than the five-membered furanose form stated in (C).

Step 3: Check the remaining alternative Glucose does not give Schiff's test because its aldehyde group is largely masked in its cyclic hemiacetal structure. Thus (D) is true. As the question asks for the statement that is not true, the true options (A), (B) and (D) are rejected.

Step 4: Conclusion The incorrect statement is that glucose exists in furanose form. The correct option is (C).

Quick Tip to Solve: For standard glucose structure questions, recall the six-membered pyranose ring; furanose denotes a five-membered ring.

7. The best reagent for converting propanamide into propanamine is [1 mark]

(A) excess H_2

(B) Br_2 in aqueous NaOH

(C) iodine in the presence of red phosphorus

(D) $LiAlH_4$ in ether

Correct Answer: (D) $LiAlH_4$ in ether

Solution:

Concept:

- Lithium aluminium hydride reduces an amide to an amine without losing the carbonyl carbon.
- Hofmann bromamide degradation converts a primary amide to a primary amine containing one fewer carbon atom.

Step 1: Preserve the carbon chain Propanamide, $CH_3CH_2CONH_2$, and propanamine, $CH_3CH_2CH_2NH_2$, both contain three carbon atoms. Reduction must replace the amide carbonyl group with a methylene group while retaining the carbon skeleton.

Step 2: Select the reducing agent $LiAlH_4$ in dry ether, followed by hydrolytic work-up, performs this conversion:

$$CH_3CH_2CONH_2 + 4[H] \longrightarrow CH_3CH_2CH_2NH_2 + H_2O.$$

Step 3: Reject the other options $Br_2/NaOH$ causes Hofmann degradation and would form ethanamine, losing one carbon. Excess hydrogen alone is not the stated effective amide-reduction reagent, and iodine with red phosphorus is not the standard selective reagent for this conversion. Thus (A), (B) and (C) do not satisfy the required transformation.

Step 4: Conclusion The best reagent is $LiAlH_4$ in ether. The correct option is (D).

Quick Tip to Solve: Compare carbon counts first: retain three carbons with $LiAlH_4$; Hofmann degradation would give only two.

8. The acid formed when propyl magnesium bromide is treated with CO_2 followed by acid hydrolysis is : [1 mark]

(A) C_3H_7COOH

(B) C_2H_5COOH

(C) CH_3COOH

(D) C_3H_7OH

Correct Answer: (A) C_3H_7COOH

Solution:

Concept:

- A Grignard reagent $RMgBr$ attacks carbon dioxide to form a magnesium carboxylate.
- Acid hydrolysis converts $RCOOMgBr$ into $RCOOH$; the carbon dioxide carbon becomes the

Quick Tip to Solve: For Grignard reagent plus carbon dioxide, retain R and append COOH: the product gains one carbon.

carboxyl carbon.

Step 1: Identify the carbon skeleton Here $R = C_3H_7$. Reaction with carbon dioxide extends this three-carbon group by one carbon; the propyl group itself is retained.

Step 2: Apply hydrolysis and check the options

$$C_3H_7MgBr + CO_2 \longrightarrow C_3H_7COOMgBr$$

$$C_3H_7COOMgBr \xrightarrow{H_3O^+} C_3H_7COOH$$

Options (B) and (C) have too few carbon atoms. Option (D) is an alcohol and lacks the carboxyl group introduced by carbon dioxide.

Step 3: Conclusion The acid is C_3H_7COOH, butanoic acid. Hence, the correct option is (A).

Quick Tip to Solve: For Grignard reagent plus carbon dioxide, retain R and append COOH: the product gains one carbon.

9. Which is the correct order of acid strength from the following ? [1 mark]

(A) $C_6H_5OH > H_2O > ROH$

(B) $C_6H_5OH > ROH > H_2O$

(C) $ROH > C_6H_5OH > H_2O$

(D) $H_2O > C_6H_5OH > ROH$

Correct Answer: (A) $C_6H_5OH > H_2O > ROH$

Solution:

Concept:

- An acid is stronger when the conjugate base formed by losing H^+ is more stable.
- Phenoxide is resonance stabilised; an alkyl group destabilises alkoxide through its electron-releasing inductive effect.

Step 1: Compare phenol with water Phenol forms $C_6H_5O^-$, whose negative charge is delocalised by resonance into the aromatic ring. Hydroxide, OH^-, has no comparable resonance stabilisation. Phenol therefore loses its proton more readily than water.

Step 2: Compare water with alcohol and test the orders An alcohol forms RO^-. The electron-releasing alkyl group increases electron density on the negatively charged oxygen, making this base less stable than hydroxide. Thus water is more acidic than an ordinary alcohol. Option (B) reverses this comparison, (C) places alcohol first, and (D) incorrectly places water above phenol.

Step 3: Conclusion The order is $C_6H_5OH > H_2O > ROH$. Hence, the correct option is (A).

Quick Tip to Solve: Compare conjugate-base stability: resonance favours phenoxide, whereas an alkyl group destabilises alkoxide.

10. Alkyl halides undergoing nucleophilic bimolecular substitution reaction involve [1 mark]

(A) retention of configuration

(B) formation of racemic mixture

(C) inversion of configuration

(D) formation of carbocation

Correct Answer: (C) inversion of configuration

Solution:

Concept:

- An S_N2 reaction is a concerted bimolecular nucleophilic substitution.
- The nucleophile attacks the carbon from the side opposite the leaving group, producing Walden inversion at a stereogenic centre.

Step 1: Follow the concerted attack The nucleophile approaches from the back side of the carbon-halogen bond. Bond formation with the nucleophile and bond breaking to the halide occur together through one transition state; no free carbocation intermediate is formed.

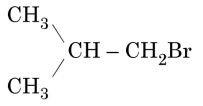
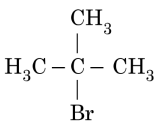
Step 2: Determine the stereochemical result As the leaving group departs, the arrangement of the other groups around the reacting carbon turns inside out, giving inversion of configuration at a chiral centre. Retention in (A) contradicts this back-side attack. Racemisation in (B) and carbocation formation in (D) are associated with the usual S_N1 mechanism, rather than this concerted process.

Step 3: Conclusion Bimolecular substitution involves inversion of configuration. Hence, the correct option is (C).

Quick Tip to Solve: Link SN2 to back-side attack and inversion; link a planar carbocation to the usual SN1 racemisation.

11. Arrange the following compounds in increasing order of their boiling points :

The correct order is [1 mark]

(i)  (ii) $CH_3CH_2CH_2CH_2Br$ (iii) 

(A) (ii) < (i) < (iii)

(B) (i) < (ii) < (iii)

(C) (iii) < (i) < (ii)

(D) (iii) < (ii) < (i)

Correct Answer: (C) (iii) < (i) < (ii)

Solution:

Concept:

- For isomeric alkyl halides of the same molecular formula, greater branching generally lowers the boiling point.
- Branching reduces molecular surface area and intermolecular contact, weakening London dispersion attractions.

Step 1: Identify the three isomers Compound (i), $(CH_3)_2CHCH_2Br$, is 1-bromo-2-methylpropane. Compound (ii), $CH_3CH_2CH_2CH_2Br$, is straight-chain 1-bromobutane. Compound (iii), $(CH_3)_3CBr$, is the most compact, most branched isomer, 2-bromo-2-methylpropane.

Step 2: Rank their intermolecular attractions All three contain the same number of carbon atoms and the same halogen, so branching provides the useful comparison. The compact compound (iii) has the weakest dispersion attractions; (i) is intermediate; the extended chain (ii) has the greatest intermolecular contact. Options (A) and (B) incorrectly put (iii) highest, and (D) reverses the relative positions of (i) and (ii).

Step 3: Conclusion The increasing boiling-point order is $(iii) < (i) < (ii)$. Hence, the correct option is (C).

Quick Tip to Solve: For alkyl-halide isomers, rank compactness first: the most branched structure normally boils lowest.

12. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]^{2+}$ is [1 mark]

(A) Diamminedichloridoplatinum(II)

(B) Diamminedichloridoplatinum(IV)

(C) Diamminedichloridoplatinum(O)

(D) Diamminedichloridoplatinate(IV)

Correct Answer: (B) Diamminedichloridoplatinum(IV)

Solution:

Concept:

- Ammine ligands are neutral; each chlorido ligand has charge -1.
- Ligands are named alphabetically, followed by the metal name and its oxidation state in Roman numerals.

Step 1: Calculate the platinum oxidation state Let the oxidation state of platinum be x. The complex ion has charge $+2$, two neutral ammine ligands and two chlorido ligands:

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

Thus platinum must be designated platinum(IV).

Step 2: Construct the name and eliminate alternatives Two ammonia ligands give diammine and two chloride ligands give dichlorido. Ammine precedes chlorido alphabetically. Because the complex is

Quick Tip to Solve: Use the displayed overall charge when finding the metal oxidation state; do not assume a neutral complex.

cationic, the metal name is platinum, without the anionic ending platinate. Options (A) and (C) use incorrect oxidation states; (D) incorrectly uses the metal name appropriate to an anionic complex.

Step 3: Conclusion The correct name is diamminedichloridoplatinum(IV). Hence, the correct option is (B).

Quick Tip to Solve: Use the displayed overall charge when finding the metal oxidation state; do not assume a neutral complex.

13. Acidified $KMnO_4$ oxidises sulphite to [1 mark]

(A) $S_2O_3^{2-}$

(B) $S_2O_8^{2-}$

(C) $SO_2(g)$

(D) SO_4^{2-}

Correct Answer: (D) SO_4^{2-}

Solution:

Concept:

- Acidified permanganate is a strong oxidising agent and is reduced from MnO_4^- to Mn^{2+}.
- Sulphite contains sulphur in oxidation state $+4$; oxidation produces sulphate with sulphur in oxidation state $+6$.

Step 1: Identify the sulphur oxidation change In SO_3^{2-}, oxygen contributes -6, so sulphur is $+4$. In SO_4^{2-}, oxygen contributes -8, so sulphur is $+6$. This rise of two units corresponds to loss of two electrons per sulphite ion.

Step 2: Confirm the product through the balanced reaction

$$2MnO_4^- + 5SO_3^{2-} + 6H^+$$

$$\longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O.$$

The sulphur product is therefore sulphate. Thiosulphate (A) and peroxodisulphate (B) are not the product of this standard oxidation. Sulphur dioxide (C) retains sulphur at $+4$, so it does not represent the required oxidation.

Step 3: Conclusion Acidified $KMnO_4$ oxidises sulphite to SO_4^{2-}. Hence, the correct option is (D).

Quick Tip to Solve: For sulphite oxidation, track sulphur from +4 to +6: the standard product is sulphate.

14. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion (Atomic no. : Cr = 24) is

[1 mark]

(A) 2.87 B.M.

(B) 3.87 B.M.

(C) 3.47 B.M.

(D) 3.57 B.M.

Correct Answer: (B) 3.87 B.M.

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\text{B.M.}$, where n is the number of unpaired electrons.
- For transition-metal cations, remove the outer $4s$ electrons before the $3d$ electrons.

Step 1: Obtain the electronic configuration Chromium, with atomic number 24, has ground-state configuration $[\text{Ar}]\,3d^5 4s^1$. Forming Cr^{3+} removes the one $4s$ electron and two $3d$ electrons, giving $[\text{Ar}]\,3d^3$. By Hund's rule these three electrons occupy separate orbitals, so $n = 3$.

Step 2: Evaluate the spin-only moment

$$\mu = \sqrt{3(3+2)}\,\text{B.M.} = \sqrt{15}\,\text{B.M.} \simeq 3.87\,\text{B.M.}$$

The orbital contribution is excluded because the question specifically requests the spin-only value. The values 2.87, 3.47 and 3.57 in (A), (C) and (D) do not equal the value calculated from three unpaired electrons.

Step 3: Conclusion The spin-only magnetic moment is $3.87\,\text{B.M.}$. Hence, the correct option is (B).

Quick Tip to Solve: Find the ion configuration before counting unpaired electrons; remove 4s electrons first.

15. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is -0.74 V. The two couples in their standard states are connected to make a cell. The cell potential will be [1 mark]

(A) +1.19 V

(B) +0.89 V

(C) +0.18 V

(D) +1.83 V

Correct Answer: (B) +0.89 V

Solution:

Concept:

- Standard reduction potentials measure the tendency to gain electrons; the couple with the higher value undergoes reduction at the cathode.
- For a galvanic cell, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$; electrode potentials are intensive quantities.

Step 1: Choose the electrodes The Sn^{4+}/Sn^{2+} potential, $+0.15\,\text{V}$, is higher than the Cr^{3+}/Cr potential, $-0.74\,\text{V}$. Hence tin(IV) is reduced and chromium metal is oxidised. Their half-reactions are $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ and $Cr \rightarrow Cr^{3+} + 3e^-$.

Step 2: Calculate and check the choices Using both tabulated values as reduction potentials,

$$E^\circ_{\text{cell}} = 0.15 - (-0.74) = +0.89\,\text{V}.$$

Balancing electrons requires factors 3 and 2 for the respective half-reactions, but these factors do not multiply the potentials. Therefore (A), (C) and (D) are inconsistent with the potential difference; adding the two signed reduction potentials would also use the wrong sign for the anode.

Step 3: Conclusion The standard cell potential is $\boxed{+0.89\,\text{V}}$. Hence, the correct option is (B).

Quick Tip to Solve: Subtract the anode reduction potential, including its negative sign; never multiply potentials when balancing electrons.

16. In case of association, abnormal molar mass of solute will [1 mark]

(A) increase

(B) decrease

(C) remain same

(D) first increase and then decrease

Correct Answer: (A) increase

Solution:

Concept:

- Colligative properties depend on the number of solute particles rather than their chemical identities.
- The van't Hoff factor i is the ratio of actual particles to particles expected without association;

Quick Tip to Solve: Association means fewer particles: a smaller colligative effect is interpreted as a larger molar mass.

$i = M_{\text{normal}}/M_{\text{apparent}}$.

Step 1: Determine the effect of association When several solute molecules combine to form an aggregate, the number of independently moving solute particles decreases. Thus association gives $i < 1$, and the measured colligative effect is smaller than the value expected for the same mass of an unassociated solute.

Step 2: Relate particle number to the calculated molar mass For example, $\Delta T_f = iK_f m$. If association is ignored when calculating molar mass from the depressed freezing point, the smaller ΔT_f gives fewer apparent moles. Therefore

$$M_{\text{apparent}} = \frac{M_{\text{normal}}}{i} > M_{\text{normal}}.$$

A decrease, option (B), would instead occur for dissociation. Option (C) requires $i = 1$; option (D) does not describe the stated association effect.

Step 3: Conclusion The abnormal (apparent) molar mass increases. Hence, the correct option is (A).

Quick Tip to Solve: Association means fewer particles: a smaller colligative effect is interpreted as a larger molar mass.

Section B (10 marks)

17. Identify A and B in each of the following reaction sequence : (1+1=2)

(a) $CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow{H_2/Ni} B$

(b) $C_6H_5NH_2 \xrightarrow[0-5°C]{NaNO_2/HCl} A \xrightarrow[H^+]{C_6H_5NH_2} B$ [2 marks]

Solution:

Concept:

- Cyanide ion substitutes a halide through its carbon atom with NaCN, producing a nitrile and adding one carbon to the chain.
- Hydrogenation reduces $-C \equiv N$ to $-CH_2NH_2$. Aniline forms a diazonium salt with nitrous acid at $0 - 5°C$.
- Aromatic diazonium salts undergo azo coupling with aniline predominantly at its para position, giving an $-N = N-$ linkage.

Step 1: Identify the compounds in sequence (a) Ethyl chloride undergoes substitution with sodium cyanide:

$$CH_3CH_2Cl + NaCN \rightarrow CH_3CH_2CN + NaCl.$$

Thus A is propanenitrile (ethyl cyanide), CH_3CH_2CN. Catalytic hydrogenation converts its nitrile carbon into a methylene group:

$$CH_3CH_2CN + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_2NH_2.$$

B is propan-1-amine (n-propylamine). The nitrile carbon remains in the product, so this is a three-

Quick Tip to Solve: Count the cyanide carbon in (a); in (b), keep the diazonium nitrogen pair as the azo bridge and place NH2 para to it.

carbon amine.

Step 2: Identify the compounds in sequence (b) $NaNO_2$/HCl produces nitrous acid in situ, which diazotises aniline at the stated low temperature:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

A is benzenediazonium chloride. Coupling with another molecule of aniline in the stated acidic medium occurs mainly para to its amino group:

$$C_6H_5N_2^+Cl^- + C_6H_5NH_2 \rightarrow C_6H_5{-}N{=}N{-}C_6H_4{-}NH_2 + HCl.$$

The amino group in this product is para to the azo linkage; B is p-aminoazobenzene, a coloured azo compound.

Step 3: Conclusion (a) A: CH_3CH_2CN, propanenitrile; B: $CH_3CH_2CH_2NH_2$, propan-1-amine. (b) A: $C_6H_5N_2^+Cl^-$, benzenediazonium chloride; B: p-aminoazobenzene, $C_6H_5{-}N{=}N{-}C_6H_4{-}NH_2$.

Quick Tip to Solve: Count the cyanide carbon in (a); in (b), keep the diazonium nitrogen pair as the azo bridge and place NH2 para to it.

18. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured (C). An acidified solution of compound (C) oxidises iodide to (D). Identify (A), (B), (C) and (D). [2 marks]

Solution:

Concept:

- Chromite ore is oxidised during alkaline fusion in air to soluble yellow chromate, CrO_4^{2-}.
- Acidification converts chromate into dichromate: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$.
- Acidified dichromate is an oxidising agent; chromium is reduced from oxidation state +6 to +3 as iodide is oxidised to iodine.

Step 1: Identify A and B from fusion and acidification The sodium salt formed in the fusion is sodium chromate, so $A = Na_2CrO_4$. Its formation is represented by

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

Acidification converts the yellow chromate ions into dichromate ions, with sodium remaining the counter-ion. Hence $B = Na_2Cr_2O_7$, sodium dichromate.

Step 2: Identify C and the oxidation product D Adding potassium chloride produces the less soluble orange potassium dichromate:

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl.$$

Quick Tip to Solve: Follow the sequence yellow chromate, acidified dichromate, potassium dichromate, then iodine liberated from iodide.

Thus $C = K_2Cr_2O_7$. Its acidified solution oxidises iodide according to

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O.$$

Therefore D is iodine, I_2, rather than iodate; the specified reaction is the standard liberation of iodine from iodide by acidified dichromate.

Step 3: Conclusion $\boxed{A = Na_2CrO_4, \quad B = Na_2Cr_2O_7, \quad C = K_2Cr_2O_7, \quad D = I_2}$.

Quick Tip to Solve: Follow the sequence yellow chromate, acidified dichromate, potassium dichromate, then iodine liberated from iodide.

19. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal ? Justify your answer. [2 marks]

Solution:

Concept:

- A nucleophile attacks the electrophilic carbon of a polar carbonyl group, $C^{\delta+} = O^{\delta-}$. Greater positive character on this carbon favours addition.
- Resonance donation into a carbonyl group decreases its electrophilicity; bulky groups also hinder the approach of a nucleophile.

Step 1: Compare the electronic effects In benzaldehyde, C_6H_5CHO, the carbonyl group is conjugated with the benzene ring. Resonance delocalisation allows electron density from the ring to be donated towards the carbonyl carbon. Consequently, the positive charge character at that carbon decreases and it is less susceptible to nucleophilic attack. Propanal, CH_3CH_2CHO, has no such aromatic conjugation. Although its ethyl group donates electron density by the inductive effect, benzaldehyde is less reactive overall because of its resonance interaction with the phenyl ring.

Step 2: Compare the steric effects The phenyl group of benzaldehyde is bulkier than the ethyl group attached to the carbonyl carbon in propanal. It therefore offers greater steric hindrance to an incoming nucleophile. Both compounds are aldehydes and retain a hydrogen at the carbonyl carbon, but the larger adjacent phenyl group makes attack less favourable. These steric and electronic effects together support the same reactivity order.

Step 3: Conclusion Benzaldehyde is less reactive than propanal in nucleophilic addition because conjugation with the phenyl ring reduces carbonyl electrophilicity and the phenyl group causes greater steric hindrance.

Quick Tip to Solve: For an aromatic aldehyde versus an aliphatic aldehyde, compare both resonance donation to the carbonyl and crowding near its carbon.

20(A). Give reasons : (1+1=2)

(a) Cooking is faster in pressure cooker than in an open pan.

(b) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution ? What change in temperature would you observe after mixing liquids X and Y ? [2 marks]

Solution:

Concept:

- A liquid boils when its vapour pressure equals the external pressure. Increasing external pressure therefore raises its boiling temperature.
- Negative deviation from Raoult's law occurs when attractions between unlike molecules are stronger than those between like molecules; mixing is exothermic and may cause volume contraction.

Step 1: Explain faster cooking in a pressure cooker (a) Steam remains enclosed in the pressure cooker, so the pressure above the water becomes greater than atmospheric pressure. Water must attain a higher temperature before its vapour pressure can equal this increased pressure. Thus, the water boils above its normal boiling point of $100\,^{\circ}\text{C}$, and the food is cooked at a higher temperature than in an open pan. The higher cooking temperature makes cooking faster.

Step 2: Relate contraction to intermolecular attractions (b) A decrease in volume on mixing indicates that the X–Y attractions are stronger than the X–X and Y–Y attractions. The molecules come closer together and escape less readily into the vapour phase. Consequently, the vapour pressure is lower than that predicted by Raoult's law: the solution shows negative deviation. Formation of these stronger attractions releases heat, so $\Delta H_{\text{mix}} < 0$; the temperature rises just after mixing.

Step 3: Conclusion (a) Increased pressure raises the boiling point of water, giving faster cooking. (b) The mixture shows negative deviation from Raoult's law, and its temperature increases on mixing.

Quick Tip to Solve: For volume contraction on mixing, connect stronger unlike-molecule attractions with both lower vapour pressure and release of heat.

OR

20(B). Define Azeotrope. What type of Azeotrope is formed by negative deviation from Raoult's law ? Give an example. [2 marks]

Solution:

Concept:

- An azeotrope is a liquid mixture which boils at a constant temperature and has the same composition in its liquid and vapour phases at that boiling point.
- A sufficiently large negative deviation from Raoult's law lowers the total vapour pressure and can produce a maximum-boiling azeotrope.

Step 1: Define an azeotrope An azeotrope is a constant-boiling mixture whose vapour has the same composition as the liquid from which it forms. On boiling, the components therefore pass into the

Quick Tip to Solve: Lower vapour pressure requires a higher temperature to boil: associate negative deviation with a maximum-boiling azeotrope.

vapour together in the same proportion. Fractional distillation cannot separate the components beyond this azeotropic composition, because distillation requires the vapour to have a different composition from the liquid.

Step 2: Identify the type and give an example In a solution showing negative deviation, unlike-molecule attractions are stronger than the attractions in the pure liquids. Fewer molecules escape, reducing the total vapour pressure below the ideal value. When this deviation is sufficiently large, the vapour-pressure curve has a minimum and the boiling-point curve has a maximum. Thus, a maximum-boiling azeotrope forms. An example is nitric acid and water, HNO_3–H_2O, at approximately 68% nitric acid by mass.

Step 3: Conclusion An azeotrope is a constant-boiling mixture with identical liquid and vapour compositions. Negative deviation produces a maximum-boiling azeotrope, for example nitric acid and water.

Quick Tip to Solve: Lower vapour pressure requires a higher temperature to boil: associate negative deviation with a maximum-boiling azeotrope.

21. Give reasons for the following :

(a) The melting points of α-amino acids are generally higher than that of the corresponding carboxylic acids.

(b) Amino acids show amphoteric behaviour. [2 marks]

Solution:

Concept:

- An α-amino acid contains both an amino group, $-NH_2$, and a carboxyl group, $-COOH$, attached to the same carbon atom.
- Amino acids exist predominantly as zwitterions, with oppositely charged $-NH_3{}^+$ and $-COO-$ groups. They can accept as well as donate a proton.

Step 1: Explain the higher melting points (a) A proton transfers from the carboxyl group to the amino group, producing the zwitterionic form:

$$H_2N-CH(R)-COOH \rightleftharpoons H_3N^+-CH(R)-COO^-.$$

Although each zwitterion has zero net charge, its charged groups create strong electrostatic attractions in the crystal. More energy is required to overcome these attractions than the intermolecular attractions in the corresponding molecular carboxylic acids. Hence, amino acids generally have higher melting points.

Step 2: Demonstrate amphoteric behaviour (b) In an acidic medium, the carboxylate group accepts a proton, so the zwitterion acts as a base:

$$H_3N^+-CH(R)-COO^- + H^+ \longrightarrow H_3N^+-CH(R)-COOH.$$

In an alkaline medium, the ammonium group donates a proton to hydroxide, so the zwitterion acts as

Quick Tip to Solve: Start with the zwitterion: protonate $-COO-$ in acid and deprotonate $-NH_3{}^+$ in base.

an acid:

$$H_3N^+-CH(R)-COO^- + OH^- \longrightarrow H_2N-CH(R)-COO^- + H_2O.$$

Thus, amino acids react with both acids and bases and show amphoteric behaviour.

Step 3: Conclusion (a) The ionic zwitterionic structure gives strong electrostatic attractions and higher melting points. (b) Amino acids can both accept and donate protons, so they are amphoteric.

Quick Tip to Solve: Start with the zwitterion: protonate $-COO-$ in acid and deprotonate $-NH_3{}^+$ in base.

Section C (21 marks)

22. A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. [3 marks]

Solution:

Concept:

- For a dilute solution, osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature.
- Isotonic solutions have equal osmotic pressures at the same temperature. Urea, $CO(NH_2)_2$, and glucose, $C_6H_{12}O_6$, are non-electrolytes, so $i = 1$ for both.
- Molarity is $C = n/V = m/(MV)$, where m is solute mass, M is its molar mass and V is solution volume in litres.

Step 1: Calculate the molarity of urea The given solution contains $15\,\text{g}$ urea in $1\,\text{L}$ of solution. Using the molar mass $60\,\text{g mol}^{-1}$, the amount of urea is

$$n_{\text{urea}} = \frac{15\,\text{g}}{60\,\text{g mol}^{-1}} = 0.25\,\text{mol}.$$

Therefore, its molarity is

$$C_{\text{urea}} = \frac{0.25\,\text{mol}}{1\,\text{L}} = 0.25\,\text{mol L}^{-1}.$$

Step 2: Apply the isotonic condition At the same temperature, equal osmotic pressures give

$$i_{\text{urea}} C_{\text{urea}} RT = i_{\text{glucose}} C_{\text{glucose}} RT.$$

Both solutes remain as molecules in water, so their van't Hoff factors are unity. Cancelling the common factors gives

$$C_{\text{glucose}} = C_{\text{urea}} = 0.25\,\text{mol L}^{-1}.$$

Equal osmotic pressure therefore means equal molar concentration here, rather than equal mass concentration.

Step 3: Convert the glucose amount to mass In one litre of the glucose solution, the amount of

Quick Tip to Solve: For isotonic non-electrolytes at the same temperature and volume, use $m_1/M_1 = m_2/M_2$: here $15 \times 180/60 = 45\,\text{g}$.

glucose is 0.25 mol. Multiplying by its molar mass gives

$$m_{\text{glucose}} = (0.25\,\text{mol})(180\,\text{g mol}^{-1}) = 45\,\text{g}.$$

As a check, glucose has three times the molar mass of urea, so equal numbers of molecules in equal solution volumes require three times the solute mass.

Step 4: Conclusion The mass of glucose present in one litre of its isotonic solution is $\boxed{45\,\text{g}}$.

Quick Tip to Solve: For isotonic non-electrolytes at the same temperature and volume, use $m_1/M_1 = m_2/M_2$: here $15 \times 180/60 = 45$ g.

23. Calculate $\Delta_r G^\circ$ and log K_C of the reaction :

$Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Given : $E^\circ_{Ag^+/Ag} = 0.80$ V, $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V

[R = 8.314 J K^{-1} mol^{-1}, F = 96500 C mol^{-1}] [3 marks]

Solution:

Concept:

- For the reaction as written, the standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- The equilibrium relation is $\Delta_r G^\circ = -RT\ln K_C = -2.303RT\log K_C$, with R the gas constant and T the absolute temperature. Standard electrode potentials here are used at 298 K.

Step 1: Identify the oxidation and reduction Iron(II) loses an electron, whereas silver(I) gains that electron. The half-reactions are

$$\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-,$$
$$\text{Ag}^{+}(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}\,(\text{s}).$$

Adding them gives the printed reaction without multiplying either half-reaction; therefore $n = 1$. Silver is the cathode and the iron couple is the anode. The given iron value is a reduction potential, so subtract it without changing its sign first:

$$E^\circ_{\text{cell}} = 0.80 - 0.77 = 0.03\,\text{V}.$$

Step 2: Calculate the standard Gibbs energy Substitute the electron count, Faraday constant and cell potential:

$$\Delta_r G^\circ = -(1)(96500)(0.03) = -2895\,\text{J mol}^{-1}.$$

The unit follows from C $\times$ V = J. The negative sign shows that the forward reaction is thermodynamically favoured under standard conditions.

Quick Tip to Solve: Count electrons from the balanced half-reactions first: here n is 1. Subtract 0.77 from 0.80, and use the factor 2.303 when converting ln K to log K.

Step 3: Obtain the logarithm of the equilibrium constant Combine the Gibbs-energy and equilibrium expressions, using the common logarithm requested in the question:

$$\log K_C = \frac{nFE^\circ_{\text{cell}}}{2.303RT} = \frac{2895}{2.303 \times 8.314 \times 298} \simeq 0.507.$$

Thus $K_C = 10^{0.507} \simeq 3.21$, consistent with a positive cell potential. Pure solid silver has unit activity and does not appear in the equilibrium expression.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -2.895\,\text{kJ mol}^{-1}}$ and $\boxed{\log K_C \simeq 0.507}$ at 298 K.

Quick Tip to Solve: Count electrons from the balanced half-reactions first: here n is 1. Subtract 0.77 from 0.80, and use the factor 2.303 when converting ln K to log K.

24(a). Arrange the following in decreasing order of pK_b :

Aniline, p-nitroaniline, p-methylaniline [1 mark]

Solution:

Concept:

- $pK_b = -\log K_b$: a smaller base-dissociation constant means a larger pK_b, so decreasing pK_b means increasing basic strength.
- Electron-withdrawing groups reduce the availability of the nitrogen lone pair; electron-donating groups increase its availability for accepting a proton.

Step 1: Compare the substituent effects In p-nitroaniline, the para NO_2 group withdraws electron density by both inductive and resonance effects, making nitrogen's lone pair least available. In p-methylaniline, the CH_3 group donates electron density through its positive inductive effect and hyperconjugation, making it more basic than aniline.

Step 2: Reverse the basic-strength order The basic-strength order is p-nitroaniline < aniline < p-methylaniline. Because pK_b increases as basic strength decreases, the weakest base must be placed first in the requested decreasing pK_b order.

Step 3: Conclusion Decreasing pK_b: $\boxed{\text{p-nitroaniline} > \text{aniline} > \text{p-methylaniline}}$.

Quick Tip to Solve: Write the basic-strength order from NO2 withdrawing and CH3 donating, then reverse it to obtain the pKb order.

24(b). Account for the following :

(i) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(ii) Methylamine in water reacts with $FeCl_3$ to precipitate hydrated ferric oxide. [2 marks]

Solution:

Concept:

- An aromatic diazonium group is conjugated with the benzene ring; resonance delocalisation stabilises the aromatic diazonium ion.
- Amines are weak bases in water: the nitrogen lone pair accepts a proton from water, generating hydroxide ions.
- Iron(III) ions form insoluble ferric hydroxide with hydroxide ions; the precipitate is commonly described as hydrated ferric oxide.

Step 1: Explain the relative stability of diazonium salts In an aromatic diazonium ion, such as $C_6H_5N_2^+$, the diazonium group participates in resonance with the aromatic ring. Delocalisation stabilises the ion, so aromatic diazonium salts can be maintained in cold solution, typically at 273–278 K. Aliphatic diazonium ions have no corresponding conjugation with an aromatic ring and readily decompose with evolution of the very stable N_2 molecule. Thus aromatic diazonium salts are more stable than their aliphatic counterparts.

Step 2: Show how methylamine produces the precipitate The lone pair on methylamine's nitrogen accepts a proton from water:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-.$$

The hydroxide ions produced combine with iron(III) ions supplied by $FeCl_3$:

$$Fe^{3+} + 3\,OH^- \longrightarrow Fe(OH)_3(s).$$

The reddish-brown insoluble $Fe(OH)_3$ precipitate is hydrated ferric oxide. Removal of hydroxide ions by precipitation drives further ionisation of methylamine. The overall reaction may be represented as

$$FeCl_3 + 3\,CH_3NH_2 + 3\,H_2O \longrightarrow Fe(OH)_3(s) + 3\,CH_3NH_3Cl.$$

Step 3: Conclusion (i) Resonance stabilisation makes aromatic diazonium salts more stable. (ii) Methylamine generates OH^- in water, which precipitates Fe^{3+} as hydrated ferric oxide, $Fe(OH)_3$.

Quick Tip to Solve: For diazonium stability, identify conjugation with the benzene ring. For the ferric precipitate, write the amine-water equilibrium before the Fe3+ precipitation equation.

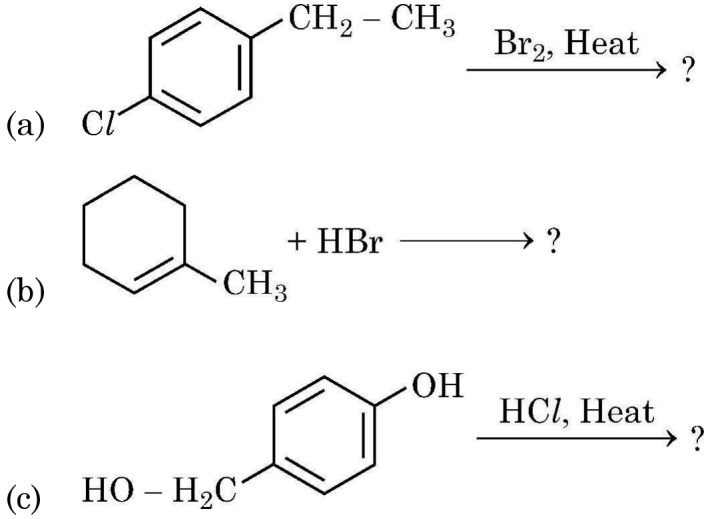
25(A). **Draw the structure of the major monohalo product for each of the following reactions : (1+1+1=3)**

(a)

(b)

(c)

[3 marks]



Solution:

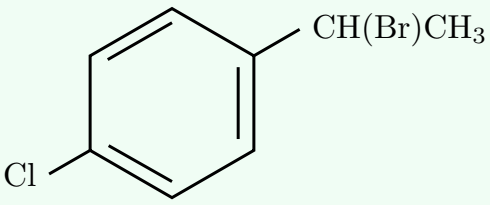
Concept:

- Bromination with heat proceeds by free radicals; a resonance-stabilised benzylic radical favours side-chain substitution.
- Ordinary HBr addition follows Markovnikov addition: bromine bonds to the more substituted carbon of the double bond.
- HCl replaces the hydroxyl group of a benzylic alcohol by chlorine; a phenolic hydroxyl group does not undergo this substitution.

Step 1: (a) Brominate the benzylic carbon The substrate is para-chloroethylbenzene. With Br_2 and heat, bromination occurs at the side-chain carbon directly attached to the benzene ring, because the intermediate benzylic radical is resonance stabilised. One benzylic hydrogen is replaced by bromine:

$$p\text{-}ClC_6H_4CH_2CH_3 \xrightarrow{Br_2,\ heat} p\text{-}ClC_6H_4CH(Br)CH_3.$$

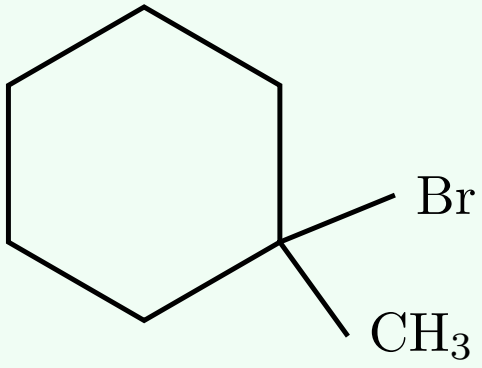
The chlorine already on the ring remains attached; the terminal methyl carbon is not the preferred site.



(a) Benzylic bromination product

Quick Tip to Solve: Identify the reaction site before drawing: benzylic H for hot bromine, the substituted alkene carbon for HBr, and CH2OH for HCl.

Step 2: (b) Add HBr across the double bond The alkene is 1-methylcyclohex-1-ene. No peroxide is stated, so ionic Markovnikov addition applies. Hydrogen attaches to the alkene carbon carrying more hydrogen, producing a tertiary carbocation at the carbon carrying the methyl group. Bromide then attacks this carbon. Thus Br and CH_3 occupy the same ring carbon, giving 1-bromo-1-methylcyclohexane; the double bond becomes a single bond.

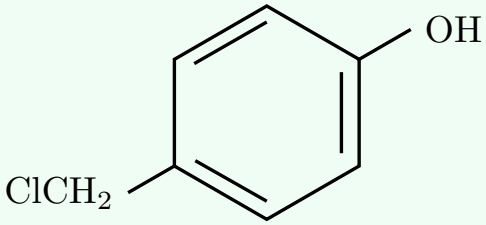


(b) 1-bromo-1-methylcyclohexane

Step 3: (c) Replace the benzylic alcohol hydroxyl group The substrate contains both a phenolic $-OH$ and a benzylic $-CH_2OH$ group in para positions. Heating with HCl replaces the benzylic hydroxyl group with chlorine:

$$p\text{-}HOC_6H_4CH_2OH + HCl \longrightarrow p\text{-}HOC_6H_4CH_2Cl + H_2O.$$

The phenolic carbon-oxygen bond has partial double-bond character and does not undergo the ordinary alcohol substitution. Therefore the phenolic OH is retained.



(c) 4-(chloromethyl)phenol

Step 4: Conclusion Products: (a) p-$ClC_6H_4CH(Br)CH_3$, (b) 1-bromo-1-methylcyclohexane, and (c) p-$HOC_6H_4CH_2Cl$, as drawn.

Quick Tip to Solve: Identify the reaction site before drawing: benzylic H for hot bromine, the substituted alkene carbon for HBr, and CH2OH for HCl.

OR

25(B)(a). How do you convert :

Chlorobenzene to biphenyl [1 mark]

Solution:

Concept:

- The Fittig reaction couples two aryl halide molecules with sodium metal in dry ether.
- An aryl carbon bonded to halogen forms a new carbon-carbon bond with the corresponding carbon of another aryl group.

Step 1: Choose the coupling reaction Chlorobenzene is an aryl halide. Treat it with sodium metal in dry ether to join two phenyl groups. The dry solvent prevents sodium from reacting with moisture.

Step 2: Write the balanced conversion

$$2\,C_6H_5Cl + 2\,Na \xrightarrow{\text{dry ether}} C_6H_5{-}C_6H_5 + 2\,NaCl.$$

Both chlorine atoms leave as sodium chloride; the two benzene rings retain their aromatic structures.

Step 3: Conclusion Chlorobenzene gives biphenyl by the Fittig reaction using sodium in dry ether.

Quick Tip to Solve: For coupling two aryl halides, remember Fittig: sodium metal and dry ether join the two aryl groups.

25(B)(b). How do you convert :

Propene to 1-Iodopropane [1 mark]

Solution:

Concept:

- HBr in the presence of peroxide adds to an alkene by the anti-Markovnikov radical mechanism.
- The Finkelstein reaction replaces bromide by iodide using sodium iodide in dry acetone.

Step 1: First obtain the primary bromide Add HBr to propene in the presence of peroxide. Bromine attaches to the terminal carbon, yielding 1-bromopropane:

$$CH_3CH{=}CH_2 \xrightarrow{\text{HBr, peroxide}} CH_3CH_2CH_2Br.$$

Step 2: Replace bromine by iodine Treat the primary bromide with NaI in dry acetone:

$$CH_3CH_2CH_2Br + NaI \xrightarrow{\text{dry acetone}} CH_3CH_2CH_2I + NaBr\downarrow .$$

Precipitation of NaBr drives the substitution. Direct addition of HI cannot give this terminal iodide: the peroxide effect operates with HBr only.

Step 3: Conclusion Propene is converted into 1-iodopropane through 1-bromopropane: HBr/peroxide, followed by NaI in dry acetone.

Quick Tip to Solve: Use HBr with peroxide to place halogen on the terminal carbon, then exchange Br for I with NaI in acetone.

25(B)(c). How do you convert :

2-bromobutane to but-2-ene. [1 mark]

Solution:

Concept:

- Alcoholic KOH on heating removes a beta hydrogen and a halogen from adjacent carbons: beta elimination.
- According to the Saytzeff rule, the more substituted alkene is the major elimination product.

Step 1: Choose elimination conditions Heat 2-bromobutane with alcoholic KOH. The base removes a hydrogen from a carbon adjacent to the carbon bearing bromine, while bromide leaves. These conditions favour dehydrohalogenation.

Step 2: Form the major alkene Removing a hydrogen from carbon 3 gives the internal double bond:

$$CH_3CHBrCH_2CH_3 + KOH \xrightarrow{\text{alcohol, heat}} CH_3CH{=}CHCH_3 + KBr + H_2O.$$

But-2-ene is more substituted than but-1-ene and is the major product. Aqueous KOH would instead favour substitution.

Step 3: Conclusion Heat 2-bromobutane with alcoholic KOH to obtain but-2-ene as the major product.

Quick Tip to Solve: Alcoholic KOH plus heat means elimination; select the more substituted double bond for the major alkene.

26. The elements of 3d transition series are given as : (1+1+1=3)

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following :

(a) Copper has exceptionally positive $E^{\circ}_{M^{2+}/M}$ value, why ?

(b) Which element is a strong reducing agent in +2 oxidation state and why ?

(c) Zn^{2+} salts are colourless. Why ? [3 marks]

Solution:

Concept:

- The standard electrode potential reflects the energy balance between atomisation, ionisation and hydration of the metal ion.
- A reducing agent loses electrons and is oxidised; stability of the resulting electronic configuration can favour oxidation.
- Colour in many transition-metal ions arises from transitions between split, partially filled d orbitals.

Step 1: (a) Positive potential of copper To form aqueous Cu^{2+} from copper metal, atomisation and two ionisations require energy. Copper has high atomisation enthalpy; its second ionisation is especially costly because Cu^{+} has a stable $3d^{10}$ configuration. The hydration enthalpy of Cu^{2+} does not compensate for these requirements. Thus oxidation of copper is unfavourable relative

Quick Tip to Solve: For reducing ions, inspect the configuration after electron loss; for colourlessness, check whether the d subshell is completely filled.

to hydrogen, and the reverse reduction $\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu}$ has an exceptionally positive standard electrode potential.

Step 2: (b) Strong reducing agent Chromium is strongly reducing in the $+2$ state. The Cr^{2+} ion has configuration $3d^4$ and readily loses an electron:

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

The resulting Cr^{3+} has the stable $3d^3$ configuration. In an octahedral environment these electrons occupy the three lower-energy t_{2g} orbitals singly. This stabilisation favours oxidation of Cr^{2+}, enabling it to reduce other species.

Step 3: (c) Colourless zinc salts Zinc has configuration $[\mathrm{Ar}]3d^{10}4s^2$. Losing its two outer electrons gives $\mathrm{Zn}^{2+} = [\mathrm{Ar}]3d^{10}$. All five d orbitals are fully occupied, so the usual d–d transitions cannot occur. There is consequently no visible absorption due to d–d excitation; salts containing this ion and colourless anions are colourless.

Step 4: Conclusion (a) Copper has high atomisation and ionisation energies not compensated by hydration. (b) Cr^{2+} readily forms stable Cr^{3+}. (c) Zn^{2+} has a filled $3d^{10}$ subshell.

Quick Tip to Solve: For reducing ions, inspect the configuration after electron loss; for colourlessness, check whether the d subshell is completely filled.

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27. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.
[R = 8.314 J K^{-1} mol^{-1}; log 4 = 0.602] [3 marks]

Solution:

Concept:

- For a first-order reaction, the time for 50 percent completion is the half-life: $t_{1/2} = 0.693/k$, where k is the rate constant.
- The two-temperature Arrhenius equation is $\log(k_2/k_1) = E_a(1/T_1 - 1/T_2)/(2.303R)$, where E_a is activation energy and R the gas constant.

Step 1: Identify the half-lives At $T_1 = 300\,\mathrm{K}$, 50 percent completion takes $t_1 = 20\,\mathrm{min}$; at $T_2 = 350\,\mathrm{K}$, it takes $t_2 = 5\,\mathrm{min}$. These times are the respective half-lives, not the times for completion of the entire reaction. The first-order half-life is independent of initial concentration, so the given times directly determine the rate constants.

Step 2: Calculate the rate-constant ratio Using the same time unit at both temperatures,

$$k_1 = \frac{0.693}{20} = 0.03465\,\mathrm{min}^{-1}, \qquad k_2 = \frac{0.693}{5} = 0.1386\,\mathrm{min}^{-1}.$$

Hence $k_2/k_1 = 20/5 = 4$. Converting both half-lives to seconds would give the same dimensionless ratio.

Quick Tip to Solve: Use the inverse ratio of half-lives to obtain the rate-constant ratio; this eliminates the 0.693 factor and avoids unnecessary time-unit conversions.

Step 3: Apply the Arrhenius equation With $R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1}$ and $\log 4 = 0.602$,

$$\begin{aligned} E_a &= \frac{2.303R\log 4}{1/300 - 1/350} \\ &= \frac{2.303(8.314)(0.602)}{50/(300\times 350)} \\ &= 2.4205\times 10^4\,\text{J mol}^{-1}. \end{aligned}$$

Both the logarithm and the reciprocal-temperature difference are positive, giving a positive activation energy, consistent with faster reaction at higher temperature.

Step 4: Conclusion The activation energy is $\boxed{E_a \approx 24.2\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Use the inverse ratio of half-lives to obtain the rate-constant ratio; this eliminates the 0.693 factor and avoids unnecessary time-unit conversions.

28. (a) Write the reaction when D-glucose reacts with the following :

(i) NH_2OH

(ii) Acetic anhydride

(b) Why vitamin C cannot be stored in our body ? [3 marks]

Solution:

Concept:

- The aldehyde group in the open-chain form of glucose reacts with hydroxylamine to form an oxime, with elimination of water.
- Acetic anhydride acetylates hydroxyl groups. Formation of glucose pentaacetate demonstrates five hydroxyl groups.
- Vitamin C is water-soluble; excess quantities are excreted through urine rather than accumulated as a long-term reserve.

Step 1: (a)(i) Reaction with hydroxylamine Write the open-chain aldehyde form of D-glucose as $\text{CHO(CHOH)}_4\text{CH}_2\text{OH}$. Its carbonyl group reacts with NH_2OH by condensation to form glucose oxime:

$$\begin{aligned} &\text{CHO(CHOH)}_4\text{CH}_2\text{OH} + \text{NH}_2\text{OH} \\ &\longrightarrow \text{HON=CH(CHOH)}_4\text{CH}_2\text{OH} + \text{H}_2\text{O}. \end{aligned}$$

The carbonyl oxygen is replaced by the oxime group $=\text{N}-\text{OH}$. The reaction provides evidence for a carbonyl group in glucose; its five original hydroxyl groups remain unchanged.

Step 2: (a)(ii) Reaction with acetic anhydride Acetic anhydride, commonly used in the presence of pyridine, converts each of the five hydroxyl groups into an acetate ester. The product is glucose pentaacetate:

$$\begin{aligned} &\text{Glucose(OH)}_5 + 5(\text{CH}_3\text{CO})_2\text{O} \\ &\xrightarrow{\text{pyridine}} \text{Glucose(OCOCH}_3)_5 + 5\text{CH}_3\text{COOH}. \end{aligned}$$

Quick Tip to Solve: Associate hydroxylamine with the carbonyl group and acetic anhydride with hydroxyl groups; pentaacetate means five OH groups were acetylated.

Here the notation $\text{Glucose}(OH)_5$ denotes the glucose framework bearing its five hydroxyl groups; it is not an additional molecular formula. Every hydroxyl hydrogen is replaced by an acetyl group. The pentaacetate product confirms that all five hydroxyl groups can undergo acetylation.

Step 3: (b) Storage of vitamin C Vitamin C is a water-soluble vitamin. Excess vitamin C is eliminated in urine, so the body does not build up a lasting store of it. It therefore needs to be supplied regularly through the diet, unlike fat-soluble vitamins that can accumulate in body tissues.

Step 4: Conclusion D-glucose forms glucose oxime with NH_2OH and glucose pentaacetate with acetic anhydride. Vitamin C cannot be stored as a lasting reserve because it is water-soluble and excess is excreted in urine.

Quick Tip to Solve: Associate hydroxylamine with the carbonyl group and acetic anhydride with hydroxyl groups; pentaacetate means five OH groups were acetylated.

Section D (8 marks)

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

29(a). Phenols undergo electrophilic substitution reactions readily due to the strong activating effect of OH group attached to the benzene ring. Since, the OH group increases the electron density more to o- and p- positions therefore OH group is ortho, para-directing. Reimer-Tiemann reaction is one of the examples of aldehyde group being introduced on the aromatic ring of phenol, ortho to the hydroxyl group. This is a general method used for the ortho-formylation of phenols.

Answer the following questions :

What happens when phenol reacts with

(i) Br_2/CS_2

(ii) Conc. HNO_3 [2 marks]

Solution:

Concept:

- The hydroxyl group donates an oxygen lone pair into the benzene ring by resonance, activating the ortho and para positions towards electrophilic substitution.
- Bromination in a nonpolar solvent gives monobrominated phenols, whereas concentrated nitric acid introduces three nitro groups at the activated positions.

Step 1: React with bromine in carbon disulphide With Br_2/CS_2, phenol gives a mixture of 2-bromophenol (ortho-bromophenol) and 4-bromophenol (para-bromophenol), with the para isomer as the major product because it has less steric hindrance. The substitution replaces one ring hydrogen by bromine:

$$C_6H_5OH + Br_2 \xrightarrow{CS_2} BrC_6H_4OH + HBr.$$

The formula on the right represents either monobromo isomer. This condition differs from bromine water, which gives 2,4,6-tribromophenol.

Quick Tip to Solve: Check the bromination solvent first: CS_2 means monobromination, whereas bromine water gives tribromination.

Step 2: React with concentrated nitric acid Concentrated HNO_3 gives 2,4,6-trinitrophenol, commonly called picric acid. Nitro groups occupy both ortho positions and the para position relative to the hydroxyl group:

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

Thus all three strongly activated positions undergo nitration under these conditions.

Step 3: Conclusion Br_2/CS_2 gives ortho- and para-bromophenol (para major); concentrated HNO_3 gives 2,4,6-trinitrophenol (picric acid).

Quick Tip to Solve: Check the bromination solvent first: CS_2 means monobromination, whereas bromine water gives tribromination.

29(b). Why phenol does not undergo protonation readily ? [1 mark]

Solution:

Concept:

- Protonation requires an available oxygen lone pair to accept H^+.
- In phenol, an oxygen lone pair is delocalised into the aromatic ring through resonance.

Step 1: Locate the electron pair The oxygen atom of phenol is directly attached to the benzene ring. Its lone pair overlaps with the ring π-electron system and contributes to resonance structures having increased electron density at the ortho and para positions.

Step 2: Relate resonance to proton acceptance Because the oxygen lone pair participates in delocalisation, it is less available for bonding to an incoming proton. The basic character of oxygen is consequently reduced, so formation of the protonated species $C_6H_5OH_2^+$ is not favoured readily.

Step 3: Conclusion Phenol does not undergo protonation readily because its oxygen lone pair is delocalised into the benzene ring by resonance and is less available to accept H^+.

Quick Tip to Solve: For protonation, ask whether the oxygen lone pair is localised or already participating in resonance.

29(c). Which is a stronger acid - phenol or cresol ? Give reason. [1 mark]

Solution:

Concept:

- Acid strength increases when the conjugate base produced by loss of H^+ is more stable.
- The methyl group in cresol has an electron-releasing $+I$ effect.

Step 1: Compare the conjugate bases Phenol loses a proton to form phenoxide ion, $C_6H_5O^-$, whose negative charge is delocalised by resonance. Cresol similarly forms a methyl-substituted phenoxide ion, so the difference comes from the methyl substituent.

Step 2: Apply the methyl-group effect The $-CH_3$ group releases electron density through its $+I$

Quick Tip to Solve: An electron-releasing methyl group weakens phenol acidity by making the negatively charged conjugate base less stable.

effect. This increases electron density in the cresolate conjugate base and destabilises its negative charge relative to phenoxide. Loss of a proton is therefore less favourable for cresol.

Step 3: Conclusion Phenol is the stronger acid because the electron-releasing methyl group of cresol destabilises its conjugate base and decreases its acidity.

Quick Tip to Solve: An electron-releasing methyl group weakens phenol acidity by making the negatively charged conjugate base less stable.

OR

29(c). Write the IUPAC name of the product formed in the Reimer-Tiemann reaction. [1 mark]

Solution:

Concept:

- The Reimer–Tiemann reaction introduces a formyl group, $-CHO$, mainly ortho to the phenolic hydroxyl group.
- For naming an aromatic aldehyde, benzaldehyde is the parent and the hydroxyl group is a substituent.

Step 1: Identify the reaction product Phenol reacts with chloroform and aqueous alkali, followed by acidification, to give the principal product commonly known as salicylaldehyde. In this product the $-OH$ and $-CHO$ groups occupy adjacent positions on the benzene ring.

Step 2: Assign the IUPAC name Take benzaldehyde as the parent because the aldehyde group has naming priority over the hydroxyl group. The ring carbon carrying $-CHO$ is position 1, so the adjacent hydroxyl group has locant 2. This gives the name 2-hydroxybenzaldehyde.

Step 3: Conclusion The IUPAC name of the principal product is $\boxed{\text{2-hydroxybenzaldehyde}}$.

Quick Tip to Solve: Use benzaldehyde as the parent, then place the hydroxyl substituent at carbon 2 for the ortho product.

30(a). The rate of a chemical reaction is expressed either in terms of decrease in the concentration of reactants or increase in the concentration of a product per unit time. Rate of the reaction depends upon the nature of reactants, concentration of reactants, temperature, presence of catalyst, surface area of the reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the Rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

Answer the following questions :

(i) What is a rate determining step ?

(ii) Define complex reaction. [2 marks]

Solution:

Concept:

- A reaction mechanism describes the elementary steps through which reactants are converted into products.
- The slowest elementary step acts as a bottleneck for the overall reaction.

Step 1: Define the rate-determining step The rate-determining step is the slowest step in a multistep reaction mechanism, which controls the overall rate of the reaction. Faster steps cannot make the overall process proceed faster than this bottleneck. Thus the observed kinetics depend on the controlling step and, where applicable, the preceding equilibria in the mechanism.

Step 2: Define a complex reaction A complex reaction is a reaction that takes place through two or more elementary steps rather than a single elementary event. The individual steps together form its mechanism and may involve intermediate species that are formed in one step and consumed in another. For example, a sequence $\mathrm{A} \rightarrow \mathrm{I} \rightarrow \mathrm{P}$ is complex: I is an intermediate and adding the steps gives the overall change $\mathrm{A} \rightarrow \mathrm{P}$. The overall equation alone does not describe all molecular events.

Step 3: Conclusion (i) The slowest step controlling the overall reaction rate is the rate-determining step. (ii) A reaction proceeding through two or more elementary steps is a complex reaction.

Quick Tip to Solve: To distinguish the terms, rate-determining identifies the slowest step; complex describes a mechanism with multiple steps.

30(b). What is the effect of temperature on the rate constant of a reaction ? [1 mark]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For ordinary reactions with positive activation energy, heating increases the fraction of molecules able to cross the activation barrier.

Quick Tip to Solve: Use the Arrhenius exponent: raising T makes the negative exponent less negative, so k rises.

Step 1: Read the temperature dependence At a higher absolute temperature, the magnitude of $E_a/(RT)$ decreases. Therefore the exponential factor $e^{-E_a/(RT)}$ becomes larger, and the rate constant k increases, taking A as approximately constant over a small temperature interval.

Step 2: State the usual effect For many reactions near ordinary temperatures, the rate constant becomes approximately two to three times its original value for a $10\,\text{K}$ increase in temperature. This is a useful empirical rule rather than an exact universal factor; the precise increase depends on activation energy.

Step 3: Conclusion The rate constant increases with increasing temperature; for many reactions it approximately doubles or triples for a $10\,\text{K}$ rise.

Quick Tip to Solve: Use the Arrhenius exponent: raising T makes the negative exponent less negative, so k rises.

OR

30(b). Why is molecularity applicable only for elementary reactions whereas order is applicable for elementary as well as complex reactions ? [1 mark]

Solution:

Concept:

- Molecularity counts the reacting species participating together in a single elementary step.
- Order is the sum of the concentration exponents in the experimentally determined rate law.

Step 1: Explain the restriction on molecularity An elementary reaction occurs in one step, so its molecularity has a definite meaning: the number of reacting species involved in that event. A complex reaction proceeds through several elementary steps; all species in its overall equation do not collide simultaneously. Hence an overall molecularity cannot be assigned to a complex reaction.

Step 2: Explain why order has wider applicability A rate law can be measured experimentally for either an elementary reaction or a complex reaction. For example, if $r = k[A]^m[B]^n$, its order is $m + n$, irrespective of how many elementary steps comprise the mechanism. The coefficients in the overall equation alone do not determine this order.

Step 3: Conclusion Molecularity applies only to an elementary step because it counts species in a single event; order applies to both elementary and complex reactions because it is obtained from their experimental rate laws.

Quick Tip to Solve: For a complex reaction, distinguish the overall experimental rate law from the molecularity of each individual elementary step.

30(c). The conversion of molecule X to Y follows second order kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y ? [1 mark]

Solution:

Concept:

- For second order conversion of a single reactant X, the rate law is $r = k[X]^2$.
- At constant temperature, k is unchanged; the rate ratio is the square of the concentration ratio.

Step 1: Write the initial and changed rates Let the initial concentration of X be c. The initial rate of formation of Y is $r_1 = kc^2$. When the concentration is tripled to $3c$, the new rate is $r_2 = k(3c)^2 = 9kc^2$. The comparison assumes the same temperature and reaction conditions.

Step 2: Compare the rates Therefore,

$$\frac{r_2}{r_1} = \frac{k(3c)^2}{kc^2} = 3^2 = 9.$$

The exponent is two because the conversion follows second order kinetics. A threefold rate increase would correspond to first order dependence, which is not the stated rate law.

Step 3: Conclusion The rate of formation of Y becomes nine times its initial value.

Quick Tip to Solve: Raise the concentration multiplier to the reaction order: here the multiplier is $3^2 = 9$.

Section E (15 marks)

31(A). (a) Carry out the following conversions : (2+3=5)

(i) Ethanal to But-2-enal

(ii) Propanoic acid to ethane

(b) An alkene A with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds B and C. Compound B gives positive Fehling test and also reacts with iodine and NaOH solution. Compound C does not give Fehling solution test but forms iodoform. Identify the compounds A, B and C. [5 marks]

Solution:

Concept:

- Ethanal contains alpha hydrogen and undergoes aldol addition with dilute alkali; heating the aldol removes water to give an alpha,beta-unsaturated aldehyde.
- Soda lime decarboxylates a sodium carboxylate to an alkane with one fewer carbon atom.
- Reductive ozonolysis cleaves an alkene double bond into carbonyl groups. Fehling solution detects aliphatic aldehydes; ethanal and methyl ketones give the iodoform test.

Step 1: (a)(i) Convert ethanal to but-2-enal Treat ethanal with dilute NaOH to form 3-hydroxybutanal

Quick Tip to Solve: For ozonolysis identification, use the tests first, count the carbon atoms, then reconnect the two carbonyl carbons with a double bond.

by aldol addition. Heat this product to eliminate water:

$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$$
$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH{=}CHCHO + H_2O.$$

The four-carbon product is but-2-enal; numbering starts at the aldehyde carbon, so the double bond is between carbons 2 and 3.

Step 2: (a)(ii) Convert propanoic acid to ethane First neutralise propanoic acid with NaOH to obtain sodium propanoate. Heat the dry salt with soda lime, a mixture of NaOH and CaO:

$$CH_3CH_2COOH + NaOH \longrightarrow CH_3CH_2COONa + H_2O$$
$$CH_3CH_2COONa + NaOH \xrightarrow{CaO,\,\Delta} CH_3CH_3 + Na_2CO_3.$$

Decarboxylation removes the carboxyl carbon from the three-carbon acid, leaving the required two-carbon alkane.

Step 3: (b) Identify carbonyl compound B B gives a positive Fehling test, so it is an aliphatic aldehyde. It also reacts with iodine and NaOH to give iodoform. The aldehyde satisfying both tests is ethanal, CH_3CHO. Its CH_3CO arrangement accounts for the iodoform reaction, whereas most other aldehydes do not give this test.

Step 4: Identify carbonyl compound C C does not give the Fehling test but forms iodoform, indicating a methyl ketone. A contains five carbon atoms and B accounts for two, so C must contain three carbon atoms. Therefore C is propanone, CH_3COCH_3, a three-carbon methyl ketone.

Step 5: Reconstruct alkene A and verify ozonolysis Join the two carbonyl carbon atoms of ethanal and propanone by a double bond, retaining their substituents. This gives $CH_3CH{=}C(CH_3)_2$, named 2-methylbut-2-ene. Its molecular formula is C_5H_{10}, as required. Reductive ozonolysis verifies the assignment:

$$CH_3CH{=}C(CH_3)_2 \xrightarrow[Zn/H_2O]{O_3} CH_3CHO + CH_3COCH_3.$$

The carbon bearing H produces the aldehyde, while the carbon bearing two methyl groups produces the ketone.

Step 6: Conclusion (a) Use aldol addition followed by dehydration for ethanal to but-2-enal, and sodium salt formation followed by soda lime decarboxylation for propanoic acid to ethane. (b) A is 2-methylbut-2-ene, B is ethanal and C is propanone.

Quick Tip to Solve: For ozonolysis identification, use the tests first, count the carbon atoms, then reconnect the two carbonyl carbons with a double bond.

OR

31(B). An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to get a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives But-1-ene. Identify (A), (B) and (C) and write chemical equations for the reactions involved. [5 marks]

Solution:

Concept:

- Acid-catalysed hydrolysis of an ester gives a carboxylic acid and an alcohol. The ester linkage splits in the presence of water.
- A primary alcohol is oxidised by chromic acid to the corresponding carboxylic acid without changing its carbon skeleton.
- Dehydration removes water from an alcohol to produce an alkene. Its position identifies the carbon bearing the original hydroxyl group.

Step 1: Identify alcohol (C) from dehydration But-1-ene has the structure $CH_2{=}CHCH_2CH_3$. The primary alcohol that loses water to give this alkene is butan-1-ol, $CH_3CH_2CH_2CH_2OH$. A primary alcohol is also required because oxidation of (C) gives a carboxylic acid rather than a ketone. Thus (C) is butan-1-ol, containing four carbon atoms.

Step 2: Identify acid (B) by oxidation Chromic acid oxidises the terminal $-CH_2OH$ group of butan-1-ol into $-COOH$. The four-carbon chain remains unchanged, so (B) is butanoic acid, $CH_3CH_2CH_2COOH$. The balanced equation, with $[O]$ denoting an oxygen equivalent supplied by the oxidant, is

$$CH_3CH_2CH_2CH_2OH + 2[O] \xrightarrow{H_2CrO_4} CH_3CH_2CH_2COOH + H_2O.$$

Secondary butanols would produce ketones on oxidation and therefore do not satisfy this clue.

Step 3: Construct ester (A) and check its molecular formula Since hydrolysis yields butanoic acid and butan-1-ol, (A) is their ester, butyl butanoate (butan-1-yl butanoate):

$$CH_3CH_2CH_2C(=O)OCH_2CH_2CH_2CH_3.$$

Combining $C_4H_8O_2$ for the acid with $C_4H_{10}O$ for the alcohol and subtracting H_2O gives $C_8H_{16}O_2$, exactly the given formula. Acid hydrolysis is represented by

$$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \overset{\text{dil. } H_2SO_4}{\rightleftharpoons} CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH.$$

The acid catalyses the reaction and is not consumed.

Step 4: Write the dehydration equation Heating butan-1-ol with concentrated sulphuric acid at about $443\,K$ eliminates water from adjacent carbon atoms to give the stated alkene:

$$CH_3CH_2CH_2CH_2OH \xrightarrow[443\,K]{\text{conc. } H_2SO_4} CH_2{=}CHCH_2CH_3 + H_2O.$$

Quick Tip to Solve: Start with the alkene clue: identify the primary four-carbon alcohol, oxidise it to its acid, then join that acid and alcohol through the ester linkage.

This confirms both the four-carbon skeleton and the terminal hydroxyl group used in identifying (C).

Step 5: Conclusion (A) is butyl butanoate, $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$; (B) is butanoic acid, $CH_3CH_2CH_2COOH$; and (C) is butan-1-ol, $CH_3CH_2CH_2CH_2OH$. The hydrolysis, oxidation and dehydration equations above satisfy all three observations.

Quick Tip to Solve: Start with the alkene clue: identify the primary four-carbon alcohol, oxidise it to its acid, then join that acid and alcohol through the ester linkage.

32(A). For the complex $[Fe(en)_2Cl_2]Cl$, identify :

(a) the oxidation number of iron.

(b) the hybridization and the shape of the complex.

(c) the magnetic behaviour of the complex.

(d) whether there is an optical isomer of the complex ? If so draw its structure.

(e) IUPAC name of the complex.

(At. no. of Fe = 26) [5 marks]

Solution:

Concept:

- Ethane-1,2-diamine, $en = H_2NCH_2CH_2NH_2$, is a neutral bidentate ligand: each molecule supplies two nitrogen donor atoms. Chlorido ligands have charge -1.
- Six donor atoms give an octahedral coordination sphere. In the usual valence-bond treatment, the strong-field ligand en promotes pairing and an inner-orbital d^2sp^3 complex.
- Optical isomers are non-superimposable mirror images. The cis form of $[M(en)_2Cl_2]$ has two such forms, whereas its trans form is optically inactive.

Step 1: (a) Determine the oxidation number The chloride outside the square brackets is the counter-ion. Hence the complex ion has charge $+1$. If iron has oxidation number x, the two neutral en ligands contribute zero and the two coordinated chlorido ligands contribute -2:

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

Thus the metal is iron(III); the outer chloride must not be counted as a seventh donor atom.

Step 2: (b) Find the hybridization and shape Iron has atomic number 26 and configuration $[Ar]3d^64s^2$. Removal of two $4s$ electrons and one $3d$ electron gives Fe^{3+} : $[Ar]3d^5$. Each en supplies two donor atoms, so the coordination number is $2 \times 2 + 2 = 6$. With the strong-field en ligands, the five $3d$ electrons pair into three orbitals, leaving two vacant $3d$ orbitals. These combine with one $4s$ and three $4p$ orbitals to form six d^2sp^3 hybrid orbitals. The coordination geometry is octahedral.

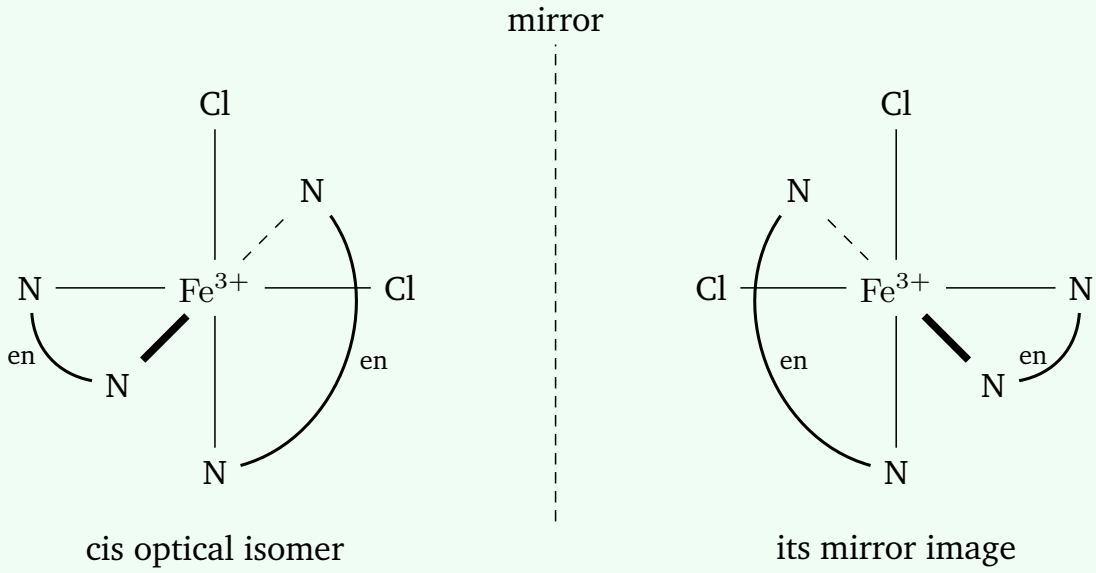
Step 3: (c) Explain the magnetic behaviour The low-spin octahedral d^5 arrangement is $t_{2g}^5e_g^0$. In the three lower-energy orbitals the occupancies are $(2, 2, 1)$, so one electron remains unpaired. The complex is therefore paramagnetic. Its spin-only magnetic moment is

$$\mu = \sqrt{n(n+2)}\,\mu_B = \sqrt{1(1+2)}\,\mu_B = \sqrt{3}\,\mu_B \approx 1.73\,\mu_B.$$

Quick Tip to Solve: Count en twice when finding coordination number, but assign it zero charge when finding the oxidation number.

Pairing cannot make an odd-electron d^5 ion completely diamagnetic.

Step 4: (d) Identify and draw the optical isomers Yes. In the cis arrangement the two coordinated chlorido ligands occupy adjacent positions. The two en chelate rings produce a pair of non-superimposable mirror images, shown below. Every N is an en donor atom; each curved N–N connection represents the $-CH_2CH_2-$ bridge of one en ligand. The solid and dashed bonds distinguish positions towards and away from the viewer. Reflection reverses the handedness of the chelate arrangement. The trans arrangement, with opposite chlorido ligands, is optically inactive.



Mirror-image cis complex ions; curved bridges join the two N donors of each en ligand.

Step 5: (e) Write the IUPAC name Ligands are listed alphabetically: chlorido precedes ethane-1,2-diamine. There are two chlorido ligands and two bidentate en ligands; use dichlorido and bis(ethane-1,2-diamine). Since the complex ion is cationic, the metal retains the name iron, followed by oxidation state (III). Finally name the chloride counter-ion.

Step 6: Conclusion (a) $+3$; (b) d^2sp^3, octahedral; (c) paramagnetic with one unpaired electron; (d) the cis form has a pair of optical isomers; (e) dichloridobis(ethane-1,2-diamine)iron(III) chloride.

Quick Tip to Solve: Count en twice when finding coordination number, but assign it zero charge when finding the oxidation number.

OR

32(B). (a) Using IUPAC norms write the names of the following:

(i) $[Co(NH_3)_4Cl(NO_2)]Cl$

(ii) $K_3[Fe(CN)_6]$

(iii) $[Cr(C_2O_4)_3]^{3-}$

(b) What is crystal field splitting energy? Why are low spin tetrahedral complexes not formed?

[5 marks]

Solution:

Concept:

- Determine the metal oxidation state from the charge on the coordination entity. Ammine is neutral; chlorido, nitrito and cyanido each have charge -1, while oxalato has charge -2.
- In IUPAC names, ligand names precede the metal in alphabetical order, ignoring numerical prefixes. The oxidation state follows the metal in Roman numerals; an anionic coordination entity uses a metal name ending in -ate.
- Crystal field splitting energy, Δ, is the energy difference between the two sets of metal d orbitals formed in a ligand field. Electron pairing depends on its size relative to pairing energy P.

Step 1: (a)(i) Name the cobalt complex The chloride outside the bracket is a counter-ion, so the complex ion has charge $+1$. If cobalt has oxidation state x, then

$$x + 4(0) - 1 - 1 = +1 \quad \Rightarrow \quad x = +3.$$

The ligands are four ammine ligands, one chlorido ligand and one N-bonded nitrito ligand, written NO_2. Their alphabetical order is ammine, chlorido, nitrito. Therefore the name is **tetraamminechloridonitrito-N-cobalt(III) chloride**. The outer chloride is named after the complete coordination cation.

Step 2: (a)(ii) Name the iron complex Three potassium ions contribute charge $+3$, so $[Fe(CN)_6]$ has charge -3. Therefore

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

There are six cyanido ligands. Since the coordination ion is anionic, iron is named ferrate. The compound is **potassium hexacyanidoferrate(III)**. The potassium subscript is essential: three potassium ions imply iron(III), whereas four would imply iron(II).

Step 3: (a)(iii) Name the chromium complex ion Each oxalato ligand carries charge -2. For three such ligands,

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

Oxalato is a bidentate ligand; the multiplicative prefix tris is used. Because the coordination ion is negative, the metal is named chromate. Its name is **tris(oxalato)chromate(III) ion**.

Step 4: (b) Define splitting energy and explain tetrahedral spin In a free metal ion the five d orbitals are degenerate. When ligands approach, unequal repulsions separate them into two groups. The energy gap between these groups is the crystal field splitting energy. In an octahedral field the gap is Δ_o, between the lower t_{2g} and upper e_g sets; in a tetrahedral field it is Δ_t, between the lower e and

Quick Tip to Solve: First balance the charge inside the brackets, then alphabetize ligands; the three potassium ions here require iron(III).

upper t_2 sets. For comparable ligands and metal ions,

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

The tetrahedral splitting is small and is generally less than the electron pairing energy: $\Delta_t < P$. It is energetically preferable for electrons to occupy higher orbitals singly rather than pair in the lower orbitals. Thus tetrahedral complexes are normally high spin, and low spin tetrahedral complexes are not formed in the usual CBSE treatment.

Step 5: Conclusion (a) (i) Tetraamminechloridonitrito-N-cobalt(III) chloride; (ii) potassium hexacyanidoferrate(III); (iii) tris(oxalato)chromate(III) ion. (b) Crystal field splitting energy is the separation of the two sets of d orbitals; tetrahedral complexes remain high spin because $\Delta_t < P$.

Quick Tip to Solve: First balance the charge inside the brackets, then alphabetize ligands; the three potassium ions here require iron(III).

33(A)(a). Write the cell reaction and calculate the e.m.f. of the following cell at 298 K :
Sn(s) | Sn^{2+} (0.004 M) || H^+ (0.02 M) | H_2(g) (1 Bar) | Pt(s)
(Given : $E^\circ_{Sn^{2+}/Sn}$ = -0.14 V, $E^\circ_{H^+|H_2(g),\,Pt}$ = 0.00 V) [3 marks]

Solution:

Concept:

- In the written cell, oxidation occurs at the left-hand electrode (anode) and reduction at the right-hand electrode (cathode). Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Write the half reactions and cell reaction Tin at the left electrode is oxidised, while hydrogen ions at the right electrode are reduced on the inert platinum surface:

$$\text{Anode: } \mathrm{Sn(s)} \longrightarrow \mathrm{Sn^{2+}(aq)} + 2\mathrm{e^-},$$
$$\text{Cathode: } \mathrm{2H^+(aq)} + 2\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}.$$

Adding these cancels the electrons and gives

$$\mathrm{Sn(s)} + \mathrm{2H^+(aq)} \longrightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}.$$

Thus $n = 2$; the stoichiometric coefficient of hydrogen ions is also 2, so their concentration enters Q as a square.

Step 2: Find the standard potential and reaction quotient The given potentials are both reduction potentials. Hence

$$E^\circ_{\text{cell}} = 0.00 - (-0.14) = 0.14\,\text{V}.$$

Quick Tip to Solve: Square the hydrogen-ion concentration in the reaction quotient because the balanced reaction consumes two hydrogen ions.

The gas pressure is 1 bar, equal to its standard pressure. Therefore

$$Q = \frac{[\mathrm{Sn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.004 \times 1}{(0.02)^2} = 10.$$

Here concentrations are used numerically relative to the standard concentration, as in the board-level Nernst calculation. Tin solid and the inert platinum electrode do not appear in the quotient.

Step 3: Apply the Nernst equation Using $\log 10 = 1$,

$$\begin{aligned} E_{\mathrm{cell}} &= 0.14 - \frac{0.0591}{2}\log 10 \\ &= 0.14 - 0.02955 \\ &= 0.11045\,\mathrm{V}. \end{aligned}$$

Since $Q > 1$, the Nernst correction lowers the potential below its standard value. The remaining positive potential confirms that the cell reaction is spontaneous in the direction written at the supplied concentrations.

Step 4: Conclusion The cell reaction is $\mathrm{Sn(s) + 2H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)}$, and the e.m.f. at 298 K is $\boxed{E_{\mathrm{cell}} \approx 0.110\,\mathrm{V}}$.

Quick Tip to Solve: Square the hydrogen-ion concentration in the reaction quotient because the balanced reaction consumes two hydrogen ions.

33(A)(b). Account for the following :

(i) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH_3COOH decreases on dilution. [2 marks]

Solution:

Concept:

- Standard electrode potentials predict thermodynamic feasibility; actual electrode products also depend on the extra potential, called overpotential, needed for a reaction to proceed at an appreciable rate.
- Conductivity κ depends on the number of mobile ions per unit volume, whereas molar conductivity Λ_m refers to one mole of electrolyte.

Step 1: Explain liberation of chlorine at the anode Oxidation of water to oxygen is thermodynamically favoured by the standard potential values, but oxygen evolution has a high overpotential. Consequently, oxidation of chloride ions occurs more readily under the conditions of electrolysis of aqueous sodium chloride:

$$2\mathrm{Cl^-}(aq) \longrightarrow \mathrm{Cl_2}(g) + 2e^-.$$

Thus, the actual anode reaction cannot be selected using standard potential values alone; the kinetic requirement for oxygen evolution must also be considered.

Quick Tip to Solve: For dilution questions, distinguish conductivity per unit volume from molar conductivity; increased ionisation does not make their trends identical.

Step 2: Explain the decrease in conductivity on dilution Acetic acid is a weak electrolyte and ionises according to

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+.$$

Dilution increases its degree of ionisation, but increases the solution volume sufficiently that the number of ions per unit volume decreases. Hence the conductivity decreases. This is consistent with $\kappa = \Lambda_m c/1000$, where c is in $\mathrm{mol\,L^{-1}}$: molar conductivity increases on dilution even though conductivity decreases.

Step 3: Conclusion (i) Chlorine is liberated because oxygen evolution requires a high overpotential. (ii) The conductivity of acetic acid decreases because dilution reduces the number of conducting ions per unit volume.

Quick Tip to Solve: For dilution questions, distinguish conductivity per unit volume from molar conductivity; increased ionisation does not make their trends identical.

OR

33(B)(a). Write the anode and cathode reactions and the overall cell reaction occurring in a lead storage battery during its use. [2 marks]

Solution:

Concept:

- During discharge a lead storage battery acts as a galvanic cell: oxidation occurs at the lead anode and reduction occurs at the lead dioxide cathode.
- Sulphuric acid supplies H^+ and SO_4^{2-}; both electrodes form lead sulphate during use.

Step 1: Write the anode oxidation reaction Lead metal loses two electrons and combines with sulphate ions to form solid lead sulphate:

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

The oxidation state of lead increases from zero to $+2$, so this electrode is the anode during discharge.

Step 2: Write the cathode reduction reaction Lead dioxide accepts the electrons released at the anode. In the acidic electrolyte, lead(IV) is reduced to lead(II), forming lead sulphate and water:

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

Step 3: Combine the electrode reactions Add the two half-reactions and cancel the two electrons. The ionic reactants $4H^+ + 2SO_4^{2-}$ correspond to two formula units of sulphuric acid. Sulphuric acid is

Quick Tip to Solve: In a discharging lead battery both electrodes become $PbSO_4$; put electrons on the product side for Pb and the reactant side for PbO_2.

consumed as the battery discharges, so its concentration falls during use.

Step 4: Conclusion The anode and cathode reactions are as written above. The overall discharge reaction is

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

Quick Tip to Solve: In a discharging lead battery both electrodes become $\mathrm{PbSO_4}$; put electrons on the product side for Pb and the reactant side for $\mathrm{PbO_2}$.

33(B)(b). Calculate the potential for half-cell containing 0.01 M $K_2Cr_2O_7$(aq), 0.01 M Cr^{3+}(aq) and 1.0×10^{-4} M H^+(aq).

The half cell reaction is

$Cr_2O_7^{2-}$(aq) + 14H^+(aq) + 6e^- → 2Cr^{3+}(aq) + 7H_2O(l)

and the standard electrode potential is given as E° = 1.33 V.

[Given : log 10 = 1] [3 marks]

Solution:

Concept:

- At 298 K, the reduction potential is given by the Nernst equation $E = E^\circ - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Powers in the reaction quotient equal the stoichiometric coefficients. Pure liquid water has unit activity and is omitted; dilute-solution ion activities are represented by their molar concentrations.

Step 1: Identify the electron transfer and reaction quotient The given reduction half-reaction is

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

Thus $n = 6$, not two: each chromium atom is reduced from $+6$ to $+3$, and there are two chromium atoms. Electrons are excluded from Q, so

$$Q = \frac{[\mathrm{Cr^{3+}}]^2}{[\mathrm{Cr_2O_7^{2-}}][\mathrm{H^+}]^{14}}.$$

Step 2: Substitute the concentrations Potassium dichromate supplies one dichromate ion per formula unit, giving $[\mathrm{Cr_2O_7^{2-}}] = 0.01$ M. With $[\mathrm{Cr^{3+}}] = 0.01$ M and $[\mathrm{H^+}] = 10^{-4}$ M,

$$Q = \frac{(10^{-2})^2}{10^{-2}(10^{-4})^{14}} = \frac{10^{-4}}{10^{-58}} = 10^{54}.$$

Therefore $\log Q = 54$, using the given $\log 10 = 1$. The large value reflects the strong dependence on hydrogen-ion concentration through its fourteenth power.

Quick Tip to Solve: In the dichromate Nernst equation use six electrons and raise the hydrogen-ion concentration to the fourteenth power before taking the logarithm.

Step 3: Calculate the reduction potential Apply the Nernst equation with $E^\circ = 1.33\,\text{V}$:

$$\begin{aligned} E &= 1.33 - \frac{0.0591}{6} \times 54 \\ &= 1.33 - 0.5319 \\ &= 0.7981\,\text{V}. \end{aligned}$$

The potential is below its standard value because the large reaction quotient reduces the driving force for the reduction half-reaction.

Step 4: Conclusion The half-cell reduction potential at $298\,\text{K}$ is approximately $\boxed{0.80\,\text{V}}$.

Quick Tip to Solve: In the dichromate Nernst equation use six electrons and raise the hydrogen-ion concentration to the fourteenth power before taking the logarithm.