CBSE Class 12 Chemistry Question Paper 2026 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.

Section A (16 marks)

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

1. Which of the following is most basic? [1 mark]

(A) Mn_2O_7

(B) MnO_2

(C) MnO

(D) Mn_2O_3

Correct Answer: (C) MnO

Solution:

Concept:

- For oxides of the same transition metal, basic character is greatest in the lower oxidation states; acidic character increases as the oxidation state rises.
- Oxygen has oxidation number -2 in these oxides. The sum of oxidation numbers in a neutral compound is zero.

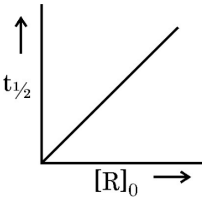
Step 1: Calculate the oxidation states For Mn_2O_7, $2x - 14 = 0$, giving $x = +7$. In MnO_2, $x - 4 = 0$, so $x = +4$. In MnO, $x - 2 = 0$, so $x = +2$. In Mn_2O_3, $2x - 6 = 0$, so $x = +3$.

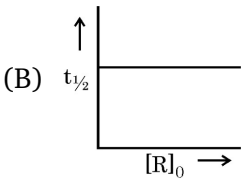
Step 2: Compare the oxide character MnO contains manganese in the lowest oxidation state among the four options and is the most ionic and most basic oxide. Mn_2O_3 is basic but less basic than MnO; MnO_2 is amphoteric, while Mn_2O_7 is acidic. Thus the highest oxygen content does not indicate the strongest basic character.

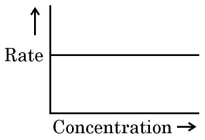
Step 3: Conclusion MnO is the most basic oxide. Hence, the correct option is (C).

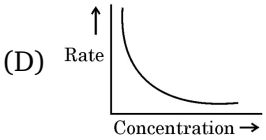
Quick Tip to Solve: For oxides of the same metal, calculate the metal oxidation state first: the lowest state usually gives the most basic oxide.

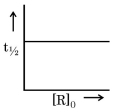
2. Which of the following curve represents the first order reaction? [1 mark]

(A) 

(B) 

(C) 

(D) 

Correct Answer: (B) 

Solution:

Concept:

- For a first-order reaction, the rate is $k[R]$, where k is the rate constant and $[R]$ is the reactant concentration.
- Its half-life is $t_{1/2} = \ln 2/k = 0.693/k$, independent of the initial reactant concentration $[R]_0$ at a fixed temperature.

Step 1: Identify the half-life graph Since k is constant at a fixed temperature, changing $[R]_0$ does not change $t_{1/2}$ for a first-order reaction. The graph of half-life against initial concentration must therefore be a horizontal straight line, as shown in (B).

Step 2: Check the other curves In (A), half-life increases linearly with $[R]_0$; this is the zero-order relation $t_{1/2} = [R]_0/(2k)$. In (C), rate is constant despite a change in concentration, again indicating zero order. Curve (D) shows rate falling as concentration increases, whereas a first-order rate must increase linearly with concentration through the origin.

Step 3: Conclusion The constant half-life graph represents a first-order reaction. Hence, the correct option is (B).

Quick Tip to Solve: Read both axes before choosing a kinetic graph: first order means constant half-life, but rate proportional to concentration.

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

(A) 0.1 M KCl

(B) 0.1 M $CaCl_2$

(C) 0.1 M Glucose

(D) 0.1 M Urea

Correct Answer: (B) 0.1 M $CaCl_2$

Solution:

Concept:

- Osmotic pressure is a colligative property: $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature.
- At the same temperature and molarity, osmotic pressure increases with the number of dissolved particles produced per formula unit of solute.

Step 1: Count the dissolved particles In dilute aqueous solution, $KCl \longrightarrow K^+ + Cl^-$ gives approximately two ions, so $i \approx 2$. $CaCl_2 \longrightarrow Ca^{2+} + 2\,Cl^-$ gives approximately three ions, so $i \approx 3$. Glucose and urea are molecular nonelectrolytes and do not dissociate, giving $i = 1$ for each.

Step 2: Compare the osmotic pressures All four solutions have $C = 0.1\,\text{mol}\,\text{L}^{-1}$. At a common temperature, the factor CRT is the same for each. Hence their osmotic pressures are in the approximate ratio $2 : 3 : 1 : 1$ in the printed order. Neither a larger molecular mass nor equal molarity alone makes their osmotic pressures equal; the particle count matters.

Step 3: Conclusion The $0.1\,\text{M}$ solution of $CaCl_2$ has the highest osmotic pressure. Hence, the correct option is (B).

Quick Tip to Solve: With equal molarity and temperature, count ions per solute formula unit; three particles from calcium chloride beat two from potassium chloride.

4. For a reaction: $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$, the rate of reaction with respect to NH_3 is [1 mark]

(A) $+\frac{1}{3}\frac{\Delta[NH_3]}{\Delta t}$

(B) $-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

(C) $+\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t}$

(D) $+\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

Correct Answer: (D) $+\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

Solution:

Concept:

- The rate of reaction is the concentration change per unit time divided by the species' stoichiometric coefficient.

Quick Tip to Solve: For a named species, use its own coefficient in the denominator and choose plus for a product or minus for a reactant.

- A positive sign is used for a product because its concentration increases; a negative sign is used for a reactant because its concentration decreases.

Step 1: Use the coefficient of ammonia In $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$, the coefficient of the product NH_3 is 2. For a time interval Δt, its concentration increases by $\Delta[NH_3]$. Dividing this formation rate by 2 gives the reaction rate:

$$r = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}.$$

Step 2: Check the sign and numerical factor Option (A) incorrectly uses the coefficient 3 of hydrogen for ammonia. Option (C) uses 4, which is not ammonia's coefficient. Option (B) has the correct factor but the wrong sign: a negative sign would make the reaction rate negative as ammonia forms. The positive factor $1/2$ in (D) satisfies both requirements.

Step 3: Conclusion The rate is $r = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$. Hence, the correct option is (D).

Quick Tip to Solve: For a named species, use its own coefficient in the denominator and choose plus for a product or minus for a reactant.

5. How many Faradays are required to reduce 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+} in acidic medium? [1 mark]

(A) 2

(B) 3

(C) 6

(D) 4

Correct Answer: (C) 6

Solution:

Concept:

- One Faraday is the charge carried by one mole of electrons. Thus the number of Faradays required equals the number of moles of electrons transferred.
- Reduction lowers oxidation number, and the total electron requirement includes every atom of the element being reduced in the given formula unit.

Step 1: Calculate the electron gain In $Cr_2O_7^{2-}$, let chromium have oxidation number x. Then $2x + 7(-2) = -2$, so $x = +6$. Reduction to Cr^{3+} requires three electrons per chromium atom. Each dichromate ion contains two chromium atoms, so its total gain is $2 \times 3 = 6$ electrons.

Step 2: Balance the half-reaction In acidic medium, the balanced reduction half-reaction is

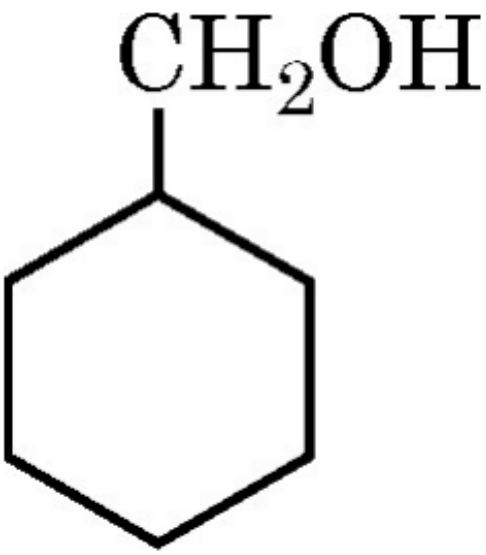
$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O.$$

Therefore, one mole of dichromate consumes six moles of electrons. Choosing 3 would count only one chromium atom; 2 counts the atoms without their oxidation-state change, and 4 does not satisfy the electron balance.

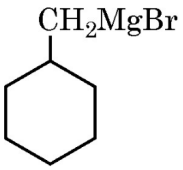
Step 3: Conclusion The charge required is $6F$, or six Faradays. Hence, the correct option is (C).

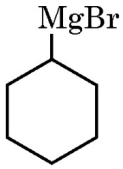
Quick Tip to Solve: Multiply the oxidation-state decrease per chromium atom by the two chromium atoms in each dichromate ion before converting to Faradays.

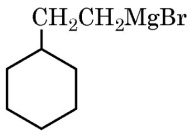
6. Which of the following Grignard Reagent will be used to prepare the compound shown when treated with methanal? [1 mark]

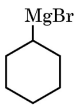


(A) CH_3MgBr

(B) 

(C) 

(D) 

Correct Answer: (C) 

Solution:

Concept:

- A Grignard reagent RMgBr reacts with methanal and then undergoes acidic hydrolysis to give the primary alcohol RCH_2OH.
- Methanal supplies the carbon of the terminal CH_2OH group; R is the organic group already present in the reagent.

Step 1: Identify the required organic group The product is cyclohexylmethanol, $C_6H_{11}CH_2OH$. Comparing it with RCH_2OH gives $R = C_6H_{11}$, a saturated cyclohexyl group. The required reagent therefore has MgBr directly attached to the ring.

Step 2: Compare the options Option (C) is $C_6H_{11}MgBr$ and gives the required product after methanal addition and hydrolysis. Option (A) gives ethanol; options (B) and (D) give products containing

Quick Tip to Solve: Replace the target's terminal CH_2OH group with MgBr to identify the reagent for a methanal reaction.

respectively one and two extra methylene groups between the ring and CH_2OH.

Step 3: Conclusion The reagent is cyclohexylmagnesium bromide, $C_6H_{11}MgBr$. Hence, the correct option is (C).

Quick Tip to Solve: Replace the target's terminal CH_2OH group with MgBr to identify the reagent for a methanal reaction.

7. The secondary valency of Pt in $[Pt(en)_2Cl_2]^{2+}$ is [1 mark]

(A) 6

(B) 5

(C) 4

(D) 2

Correct Answer: (A) 6

Solution:

Concept:

- Werner's secondary valency is the coordination number: the number of donor atoms directly bonded to the central metal ion.
- Ethane-1,2-diamine, denoted en, is bidentate and supplies two nitrogen donor atoms; a chlorido ligand, Cl^-, is monodentate.

Step 1: Count donor atoms from the ligands In $[Pt(en)_2Cl_2]^{2+}$, the two en ligands each form two coordinate bonds with platinum. They therefore supply $2 \times 2 = 4$ donor atoms. The two chlorido ligands supply another $2 \times 1 = 2$ donor atoms.

Step 2: Distinguish coordination number from oxidation state The total number of donor atoms is $4 + 2 = 6$. The oxidation state follows $x + 2(0) + 2(-1) = +2$, giving $x = +4$; this is not the secondary valency. Thus option (C) confuses oxidation state with coordination number, option (D) confuses the charge with coordination number, and option (B) undercounts donor atoms.

Step 3: Conclusion The secondary valency of platinum is 6. Hence, the correct option is (A).

Quick Tip to Solve: Count ligand donor atoms, not ligand molecules: each en contributes two to the coordination number.

8. $(CH_3)_3C - OC_2H_5$ **on reaction with HI gives** [1 mark]

(A) $(CH_3)_3C$-I and C_2H_5-I

(B) $(CH_3)_3C$-OH and C_2H_5-I

(C) $(CH_3)_3C$-I and C_2H_5-OH

(D) $(CH_3)_3C$-OH and C_2H_5-OH

Correct Answer: (C) $(CH_3)_3C$-I and C_2H_5-OH

Solution:

Concept:

- Hydrogen iodide protonates an ether oxygen, making carbon–oxygen bond cleavage possible.
- In a tertiary alkyl ether, cleavage at the tertiary carbon proceeds by the S_N1 pathway because the tertiary carbocation is stabilised.

Step 1: Identify the two alkyl groups The ether $(CH_3)_3C{-}O{-}C_2H_5$ contains a tertiary butyl group and a primary ethyl group. After protonation of oxygen, the bond to the tertiary carbon breaks readily, yielding a tertiary butyl carbocation and ethanol. Thus the usual rule of iodide attacking the less hindered group does not decide the cleavage of this tertiary ether.

Step 2: Capture the carbocation and compare the choices Iodide combines with the tertiary carbocation. The net ether-cleavage reaction is

$$(CH_3)_3C{-}O{-}C_2H_5 + HI \longrightarrow (CH_3)_3C{-}I + C_2H_5OH.$$

Option (B) would retain oxygen on the tertiary group, contrary to this pathway. Option (D) gives two alcohols and is not cleavage by hydrogen iodide. Option (A) requires further reaction of the ethanol with additional hot excess hydrogen iodide; that condition is not specified here.

Step 3: Conclusion The products are tert-butyl iodide and ethanol. Hence, the correct option is (C).

Quick Tip to Solve: For an ether containing a tertiary alkyl group, put iodine on the tertiary carbon and retain oxygen on the other group.

9. Aniline on direct nitration yields [1 mark]

(A) 51%-ortho, 47%-para, 2%-meta derivatives

(B) 51%-meta, 47%-ortho, 2%-para derivatives

(C) 51%-para, 47%-meta, 2%-ortho derivatives

(D) 51%-ortho, 47%-meta, 2%-para derivatives

Correct Answer: (C) 51%-para, 47%-meta, 2%-ortho derivatives

Solution:

Concept:

- The amino group in free aniline directs electrophilic substitution to the ortho and para positions.
- In the strongly acidic nitrating mixture, aniline is protonated to the anilinium ion, $C_6H_5NH_3{}^+$,

Quick Tip to Solve: Remember the direct-nitration order para:meta:ortho as $51 : 47 : 2$; protonation explains why meta is unexpectedly abundant.

which is meta directing.

Step 1: Account for the substantial meta product Direct nitration exposes aniline to concentrated nitric and sulphuric acids. Protonation converts much of $C_6H_5NH_2$ into $C_6H_5NH_3^+$. The nitrogen lone pair is no longer available for donation to the ring, and the positively charged substituent directs nitration towards the meta position. Therefore the meta product cannot be just the small 2% fraction in option (A).

Step 2: Match the known nitration distribution The standard product distribution for direct nitration is 51% para-nitroaniline, 47% meta-nitroaniline and 2% ortho-nitroaniline. Free aniline accounts for ortho/para substitution, with para favoured over the sterically crowded ortho position. Options (B) and (D) assign the large fractions to the wrong isomers; in particular, neither matches the small ortho fraction.

Step 3: Conclusion Direct nitration gives 51% para, 47% meta and 2% ortho derivatives. Hence, the correct option is (C).

Quick Tip to Solve: Remember the direct-nitration order para:meta:ortho as $51 : 47 : 2$; protonation explains why meta is unexpectedly abundant.

10. Which of the following is 'not' true about enantiomers? [1 mark]

(A) They have the same chemical reactivity.

(B) They have the same specific rotation.

(C) They have the same melting or boiling point.

(D) They have the same refractive index.

Correct Answer: (B) They have the same specific rotation.

Solution:

Concept:

- Enantiomers are non-superimposable mirror-image stereoisomers.
- Under identical conditions, their specific rotations have equal magnitudes but opposite signs; their ordinary physical properties are identical in an achiral environment.

Step 1: Compare the optical rotations If one pure enantiomer has specific rotation $[\alpha] = +a$, its mirror image has $[\alpha] = -a$, at the same temperature, wavelength and solvent conditions. They rotate plane-polarised light through equal angles in opposite directions. Since the sign is part of the specific rotation, it is incorrect to call their specific rotations the same.

Step 2: Check the remaining properties Enantiomers have the same melting point, boiling point and refractive index under identical achiral conditions, so (C) and (D) are true. Their chemical reactivity towards achiral reagents is also the same, which is the usual meaning of (A) here. Chiral reagents or biological environments can distinguish them, but that does not change the defining opposite optical rotations.

Step 3: Conclusion The statement that enantiomers have the same specific rotation is not true. Hence, the correct option is (B).

Quick Tip to Solve: In enantiomer questions, distinguish equal magnitude of optical rotation from equal signed specific rotation.

11. An example of non-reducing sugar is [1 mark]

(A) Glucose

(B) Sucrose

(C) Lactose

(D) Maltose

Correct Answer: (B) Sucrose

Solution:

Concept:

- A reducing sugar has a free anomeric centre that allows formation of an open-chain carbonyl form capable of reducing the test reagent.
- A glycosidic bond involving both anomeric centres prevents this ring opening; the disaccharide is then non-reducing.

Step 1: Examine the linkage in sucrose Sucrose contains glucose and fructose units joined through the anomeric carbon C-1 of glucose and the anomeric carbon C-2 of fructose. Both centres participate in the glycosidic bond, leaving no free hemiacetal or hemiketal group. Consequently, intact sucrose cannot produce the free carbonyl form needed to reduce Tollens' or Fehling's reagent.

Step 2: Eliminate the reducing sugars Glucose has a free anomeric centre and can open to an aldehyde form, so option (A) is reducing. Lactose and maltose each retain one free anomeric centre despite being disaccharides, so options (C) and (D) are also reducing. The presence of a glycosidic bond alone is therefore insufficient: both anomeric centres must be blocked.

Step 3: Conclusion Sucrose is the non-reducing sugar among the given choices. Hence, the correct option is (B).

Quick Tip to Solve: For a disaccharide, check whether one anomeric carbon remains free; sucrose locks both and is non-reducing.

12. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives [1 mark]

(A) Azobenzene

(B) Benzene

(C) Chlorobenzene

(D) p-hydroxyazobenzene

Correct Answer: (D) p-hydroxyazobenzene

Solution:

Concept:

- Aromatic diazonium ions undergo azo coupling with activated aromatic rings such as phenol in weakly basic medium.
- The phenolic group directs substitution mainly to the para position, forming an azo linkage

Quick Tip to Solve: In phenol–diazonium coupling, retain the hydroxyl group and attach the $-N=N-C_6H_5$ group para to it.

$-N=N-$ between the two aromatic rings.

Step 1: Identify the coupling partner and site In weakly basic solution, formation of phenoxide increases electron density in the phenol ring, especially at the ortho and para positions. The benzene diazonium ion acts as the electrophile. Coupling occurs predominantly at the less hindered para position of phenol, while the hydroxyl group remains on that ring.

Step 2: Identify the azo product The resulting structure is $C_6H_5-N=N-C_6H_4-OH$, with the hydroxyl group para to the azo linkage on the phenol-derived ring. Azobenzene in (A) lacks the hydroxyl group. Benzene in (B) would require replacement of the diazonium group by hydrogen, and chlorobenzene in (C) would require a substitution reaction such as the Sandmeyer reaction. Neither is the stated coupling reaction.

Step 3: Conclusion The product is p-hydroxyazobenzene. Hence, the correct option is (D).

Quick Tip to Solve: In phenol–diazonium coupling, retain the hydroxyl group and attach the $-N=N-C_6H_5$ group para to it.

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13. Assertion (A): The presence of -OH group in phenols directs the incoming group to ortho and para positions.

Reason (R): -OH group in phenols activates the aromatic ring towards electrophilic substitution reaction.

Select the correct answer from the codes (A), (B), (C) and (D). [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:

- The oxygen lone pair in phenol is delocalised into the aromatic ring by resonance.
- This resonance donation increases electron density mainly at the ortho and para positions and activates them towards electrophilic substitution.

Step 1: Evaluate the assertion The hydroxyl group donates a lone pair into the conjugated benzene ring. Resonance structures place increased electron density at the two ortho positions and the para position. An incoming electrophile therefore attacks these positions preferentially. Thus Assertion (A) is true.

Step 2: Evaluate the reason Lone-pair donation makes the phenol ring more reactive towards electrophiles than benzene. Although oxygen also withdraws electrons by the inductive effect, its

Quick Tip to Solve: For phenol, connect both enhanced reactivity and ortho/para orientation to oxygen lone-pair donation into the ring.

resonance donation dominates the substitution behaviour. The hydroxyl group therefore activates the aromatic ring, so Reason (R) is true.

Step 3: Connect activation with orientation In phenol, this activation arises through resonance donation and is concentrated at the ortho and para positions. The same effect stabilises the intermediates for substitution at those positions. Thus the activation stated in the reason explains the ortho/para direction in the assertion. Option (B) overlooks this connection; (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: For phenol, connect both enhanced reactivity and ortho/para orientation to oxygen lone-pair donation into the ring.

14. Assertion (A): Actinoids show irregularities in their electronic configurations.
Reason (R): In actinoids 5f, 6d and 7s orbitals are of comparable energies.
Select the correct answer from the codes (A), (B), (C) and (D). [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:

- Actinoids involve progressive filling of the $5f$ subshell, with valence electrons also able to occupy $6d$ and $7s$ orbitals.
- When subshell energies are close, electron repulsions and small energy changes can alter the most stable electron distribution.

Step 1: Evaluate the assertion Actinoid ground-state configurations do not follow an entirely regular pattern in which every added electron simply enters $5f$. The distribution between $5f$ and $6d$, along with the outer $7s$ electrons, shows irregularities across the series. Therefore Assertion (A) is true.

Step 2: Evaluate the reason The $5f$, $6d$ and $7s$ orbitals in actinoids have comparable energies. Their relative energies vary with nuclear charge and electron interactions, so the energy cost of changing the distribution among them can be small. Therefore Reason (R) is true.

Step 3: Link the energy closeness to irregular filling Because these orbital energies are close, a slightly different electron arrangement may have lower total energy for a particular element. This directly explains why a single simple filling pattern has exceptions. Thus (B) wrongly denies the explanatory

Quick Tip to Solve: When actinoid configurations look irregular, check the small energy differences among $5f$, $6d$ and $7s$.

link, while (C) and (D) wrongly classify one of the true statements as false.

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

Quick Tip to Solve: When actinoid configurations look irregular, check the small energy differences among $5f$, $6d$ and $7s$.

15. Assertion (A): Components of azeotropes are easily separated by fractional distillation.
Reason (R): Components of an azeotrope have same composition in liquid and vapour phase.
Select the correct answer from the codes (A), (B), (C) and (D). [1 mark]

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

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

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

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

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

Solution:

Concept:

- An azeotrope is a constant-boiling mixture whose equilibrium liquid and vapour have the same composition at a given pressure.
- Fractional distillation separates components only when vaporisation produces a vapour of different composition from the liquid.

Step 1: Evaluate the assertion At the azeotropic composition, repeated vaporisation and condensation do not enrich either component. Therefore the components cannot be separated by fractional distillation, and Assertion (A) is false.

Step 2: Evaluate the reason For each component, its mole fraction in the vapour equals its mole fraction in the liquid at the azeotropic composition. Reason (R) correctly states this defining property and is true.

Step 3: Relate the two statements The true reason explains why separation fails; it does not support the assertion that separation is easy. Options (A) and (B) incorrectly treat the assertion as true, while (C) also incorrectly makes the reason false.

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

Quick Tip to Solve: For an azeotrope, remember liquid composition equals vapour composition; repeated distillation therefore gives no enrichment.

16. Assertion (A): The two strands of DNA are complementary to each other.

Reason (R): The hydrogen bonds are formed between specific pairs of bases.

Select the correct answer from the codes (A), (B), (C) and (D). [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:

- DNA contains two antiparallel polynucleotide strands held together by hydrogen bonds between complementary nitrogenous bases.
- Adenine pairs with thymine through two hydrogen bonds, while guanine pairs with cytosine through three hydrogen bonds.

Step 1: Evaluate the assertion Each base in one DNA strand determines which base occurs opposite it in the other strand. Thus the two strands are complementary rather than identical in base sequence. Assertion (A) is true.

Step 2: Evaluate the reason Hydrogen bonding is specific: adenine pairs with thymine and guanine with cytosine. These pairings join one purine with one pyrimidine and maintain the regular width of the double helix. Reason (R) is true.

Step 3: Check the explanatory link The specificity of hydrogen bonding fixes the complementary base opposite each base of the first strand. It therefore directly explains complementarity. Option (B) misses this link; options (C) and (D) incorrectly declare one of the true statements false.

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

Quick Tip to Solve: Write the complementary sequence by replacing adenine with thymine and guanine with cytosine, then remember that the two strands run antiparallel.

Section B (10 marks)

17. What type of deviation from Raoult's law is shown by mixture of ethanol and acetone? Give reason. What will happen to the boiling point of the solution on mixing ethanol and acetone? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary solution gives $p = x_1 p_1^\circ + x_2 p_2^\circ$, where x_i is liquid mole fraction and p_i° is the pure-component vapour pressure at the same temperature.
- Weaker effective attractions in a mixture increase the escaping tendency of molecules, causing a positive deviation from Raoult's law. Boiling occurs when vapour pressure equals external pressure.

Step 1: Examine the intermolecular attractions Pure ethanol molecules are associated through hydrogen bonding. When acetone is added, its molecules enter between ethanol molecules and disrupt part of this hydrogen-bonded association. Although ethanol can also interact with acetone, the mixed attractions are effectively weaker than the attractions in the unmixed liquids.

Step 2: Connect the attractions with vapour pressure Molecules escape into the vapour more readily, so the observed total vapour pressure is greater than the ideal value at the same temperature and composition:

$$p_{\text{observed}} > x_1 p_1^\circ + x_2 p_2^\circ.$$

This establishes a positive deviation from Raoult's law.

Step 3: Determine the boiling-point change Since the mixture has a higher vapour pressure than the corresponding ideal solution, it reaches the external pressure at a lower temperature. Its boiling point is therefore lowered relative to the ideal value expected for that composition.

Step 4: Conclusion Ethanol and acetone show positive deviation from Raoult's law because mixing disrupts ethanol's hydrogen bonding and weakens the effective attractions. The boiling point is lowered relative to ideal-solution behaviour.

Quick Tip to Solve: Link weaker attractions to easier escape, higher vapour pressure and a lower boiling temperature; compare with the ideal mixture at the same composition.

18(a). Write IUPAC names of the following coordination compounds:

(i) $[\mathbf{Ag(NH_3)_2}][\mathbf{Ag(CN)_2}]$

(ii) $K_3[\mathbf{Fe(C_2O_4)_3}]$ [2 marks]

Solution:

Concept:

- Name the cation before the anion. Ligands are named before the metal, followed by its oxidation state in Roman numerals; an anionic complex takes the metal ending "-ate".
- NH_3 is neutral ammine, CN^- is cyanido, and $C_2O_4^{2-}$ is oxalato. For several oxalato ligands, use the multiplicative prefix tris.

Quick Tip to Solve: Find each complex ion's charge before its metal oxidation state; remember argentate for anionic silver and ferrate for anionic iron.

Step 1: Name the two silver complexes in part (i) In $[Ag(NH_3)_2][Ag(CN)_2]$, the ions are $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$. Neutral ammine ligands leave the cationic silver oxidation state at $+1$. For the anion, let silver's oxidation state be z:

$$z + 2(-1) = -1 \quad \Rightarrow \quad z = +1.$$

The cation is diamminesilver(I); the anion is dicyanidoargentate(I). The Latin-derived metal name argentate is used for anionic silver.

Step 2: Name the iron complex in part (ii) Three K^+ ions require the complex $[Fe(C_2O_4)_3]^{3-}$. Each oxalato ligand has charge -2, giving

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

The anion is tris(oxalato)ferrate(III). Place potassium first; do not use a numerical prefix for the potassium counterions.

Step 3: Conclusion (i) Diamminesilver(I) dicyanidoargentate(I).
(ii) Potassium tris(oxalato)ferrate(III).

Quick Tip to Solve: Find each complex ion's charge before its metal oxidation state; remember argentate for anionic silver and ferrate for anionic iron.

OR

18(b). (i) Give a chemical test to show that $[Co(NH_3)_5SO_4]Cl$ and $[Co(NH_3)_5Cl]SO_4$ are ionisation isomers.
(ii) What is meant by the 'Chelate effect'? Give an example. [2 marks]

Solution:

Concept:

- Ionisation isomers exchange a ligand inside the coordination sphere with a counterion outside it. They therefore give different free ions in aqueous solution.
- The chelate effect is the enhanced stability of a complex containing a multidentate ligand compared with an analogous complex containing comparable monodentate ligands.

Step 1: Identify the free ions in part (i) The square brackets identify the coordination sphere. On dissolving, the compounds ionise as follows:

$$[Co(NH_3)_5SO_4]Cl \longrightarrow [Co(NH_3)_5SO_4]^+ + Cl^-$$

$$[Co(NH_3)_5Cl]SO_4 \longrightarrow [Co(NH_3)_5Cl]^{2+} + {SO_4}^{2-}$$

Thus the first supplies free chloride, while the second supplies free sulfate.

Step 2: Apply a precipitation test Add aqueous silver nitrate to fresh aqueous samples. The first

Quick Tip to Solve: Test the ion outside the brackets for ionisation isomerism; for the chelate effect, compare ring-forming en with monodentate ammonia.

compound immediately gives a white precipitate of silver chloride:

$$Ag^{+} + Cl^{-} \longrightarrow AgCl\downarrow$$

The second does not give this immediate chloride precipitate because its chloride is coordinated. Alternatively, aqueous barium chloride gives a white sulfate precipitate immediately with the second compound but not the first:

$$Ba^{2+} + {SO_4}^{2-} \longrightarrow BaSO_4\downarrow$$

These different free-ion tests establish ionisation isomerism.

Step 3: Explain the chelate effect in part (ii) A multidentate ligand attaches through two or more donor atoms to the same metal ion and forms rings. The resulting chelate complex is generally more stable than its comparable monodentate analogue. For example, $[Ni(en)_3]^{2+}$ is more stable than $[Ni(NH_3)_6]^{2+}$; en denotes ethane-1,2-diamine, a bidentate ligand binding through both nitrogen atoms.

Step 4: Conclusion (i) The first isomer gives an immediate white $AgCl$ precipitate with silver nitrate; the second gives an immediate white $BaSO_4$ precipitate with barium chloride.

(ii) Enhanced stability due to multidentate ligand binding is the chelate effect, exemplified by $[Ni(en)_3]^{2+}$ relative to $[Ni(NH_3)_6]^{2+}$.

Quick Tip to Solve: Test the ion outside the brackets for ionisation isomerism; for the chelate effect, compare ring-forming en with monodentate ammonia.

19. Why are haloarenes less reactive towards nucleophilic substitution reaction? Give two reasons.

[2 marks]

Solution:

Concept:

- Nucleophilic substitution requires breaking the carbon–halogen bond, so a stronger $C-X$ bond makes substitution more difficult.
- In a haloarene, the halogen is bonded directly to an sp^2-hybridised aromatic carbon; its lone pair can also overlap with the ring's π system.

Step 1: Reason 1: resonance strengthens the bond A lone pair on the halogen is delocalised into the benzene ring by resonance. Consequently, the carbon–halogen bond acquires partial double-bond character. It is therefore shorter and stronger than an ordinary carbon–halogen single bond and is difficult to cleave during nucleophilic substitution.

Step 2: Reason 2: hybridisation holds the bond more strongly The carbon bonded to halogen in a haloarene is sp^2-hybridised, whereas the corresponding carbon in a haloalkane is sp^3-hybridised. The sp^2 orbital has greater s-character and holds the bonding electrons closer to the carbon nucleus. This contributes to a shorter, stronger $C-X$ bond in haloarenes and makes its cleavage harder.

Step 3: Conclusion Haloarenes are less reactive towards nucleophilic substitution because of (i) partial double-bond character of the $C-X$ bond due to resonance and (ii) the stronger bond formed

Quick Tip to Solve: For two reasons, distinguish resonance (partial double-bond character) from hybridisation (greater s-character of aromatic carbon).

by the sp^2-hybridised aromatic carbon.

Quick Tip to Solve: For two reasons, distinguish resonance (partial double-bond character) from hybridisation (greater s-character of aromatic carbon).

20. Following reaction takes place in one step:

$2A + B \rightarrow 2C$

How will the rate of above reaction change if the volume of the reaction vessel is decreased to one third of its original volume? Will there be any change in the order of reaction with the reduced volume? [2 marks]

Solution:

Concept:

- For an elementary reaction occurring in one step, the powers in its rate law equal the reactant stoichiometric coefficients.
- Concentration is amount divided by volume: $[A] = n_A/V$. At unchanged temperature the rate constant k remains unchanged; the order is the sum of the powers in the rate law.

Step 1: Write the elementary rate law The given reaction $2A + B \longrightarrow 2C$ takes place in one step. Thus its rate law is

$$r = k[A]^2[B].$$

It is second order with respect to A, first order with respect to B, and has overall order $2 + 1 = 3$. The one-step condition is essential for using these coefficients as rate-law powers.

Step 2: Apply the decrease in volume Compare the rates immediately before and after compression, with amounts of both reactants and temperature unchanged. When $V' = V/3$, both concentrations become three times their original values:

$$[A]' = 3[A], \qquad [B]' = 3[B].$$

Substitution into the same rate law gives

$$\frac{r'}{r} = \frac{k(3[A])^2(3[B])}{k[A]^2[B]} = 3^2 \times 3 = 27.$$

Compression changes concentrations, but does not change the exponents in the stipulated elementary rate law.

Step 3: Conclusion The reaction rate becomes 27 times the original rate. The overall order remains 3; there is no change in order on reducing the volume.

Quick Tip to Solve: With volume reduced by a factor of three, multiply each reactant concentration by three, then raise this factor to the total order.

21. Differentiate between the following:

(i) Acidic amino acids and basic amino acids

(ii) Nucleotide and Nucleoside [2 marks]

Solution:

Concept:

- The acidic or basic character of an amino acid depends on the relative numbers of its acidic carboxyl groups and basic amino groups.
- A nucleoside contains a nitrogenous base linked to a pentose sugar. Addition of a phosphate group to the sugar gives a nucleotide.

Step 1: (i) Compare acidic and basic amino acids Acidic amino acids contain more carboxyl groups $(-COOH)$ than amino groups $(-NH_2)$. For example, glutamic acid has two carboxyl groups and one amino group:

$$HOOC - CH(NH_2) - CH_2 - CH_2 - COOH.$$

Basic amino acids contain more amino groups than carboxyl groups. For example, lysine has two amino groups and one carboxyl group:

$$H_2N - CH_2 - CH_2 - CH_2 - CH_2 - CH(NH_2) - COOH.$$

Thus the distinguishing feature is an excess of acidic groups or an excess of basic groups, respectively.

Step 2: (ii) Compare nucleotide and nucleoside A nucleoside consists of a nitrogenous base and a pentose sugar (ribose or deoxyribose), joined by a glycosidic bond; it contains no phosphate group. Adenosine is an example. A nucleotide contains the same base–sugar unit plus a phosphate group attached to the sugar through a phosphoester linkage. Adenosine monophosphate is an example. Hence a nucleotide is a phosphorylated nucleoside.

Step 3: Conclusion (i) Acidic amino acids have excess carboxyl groups; basic amino acids have excess amino groups. (ii) A nucleotide contains base, sugar and phosphate, whereas a nucleoside contains only base and sugar.

Quick Tip to Solve: Count carboxyl and amino groups for part (i); look specifically for a phosphate group when distinguishing the two compounds in part (ii).

Section C (21 marks)

22. Compound 'X' with molecular formula C_4H_9Br reacts with aqueous KOH to give an alcohol. The rate of this reaction depends only on the concentration of the compound 'X'. When an optically active isomer 'Y' of the compound 'X' was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound 'Y' and aqueous KOH both.

(a) Write down the structural formula of both 'X' and 'Y'.

(b) Out of 'X' and 'Y', which one will undergo racemisation and why?

(c) Out of 'X' and 'Y', which one will form product with inversion of configuration and why? [3 marks]

Solution:

Concept:

- S_N1 has rate k[haloalkane] and a planar carbocation intermediate; tertiary carbocations are favoured.
- S_N2 has rate k[haloalkane][OH^-]; concerted backside attack gives inversion. Racemisation requires formation of both enantiomers from a chiral substrate.

Step 1: (a) Identify X Dependence of rate only on $[X]$ indicates S_N1. The tertiary isomer of C_4H_9Br readily forms a tertiary carbocation, so

$$X = (CH_3)_3C - Br,$$

2-bromo-2-methylpropane (tert-butyl bromide). Its hydrolysis gives $(CH_3)_3COH$, 2-methylpropan-2-ol.

Step 2: (a) Identify Y The optically active isomer is an individual enantiomer of 2-bromobutane:

$$Y = CH_3 - CH(Br) - CH_2 - CH_3.$$

Carbon 2 bears four different groups: H, Br, CH_3 and C_2H_5. The stated dependence on both $[Y]$ and $[OH^-]$ identifies its reaction here as S_N2.

Step 3: (b) Check racemisation against the structures X follows the S_N1 mechanism normally associated with racemisation: loss of Br^- forms a planar carbocation, allowing attack from either face. However, this specific X has three identical methyl groups and is achiral, as is its alcohol product. Attack from opposite faces gives the same molecule, not enantiomers. Thus neither compound actually racemises under the stated conditions: X is achiral and Y follows the specified S_N2 pathway. The usual racemisation rule for a chiral S_N1 substrate cannot apply to this X.

Step 4: (c) Explain inversion for Y In Y, OH^- attacks carbon 2 from the side opposite the $C - Br$ bond. Bond formation and bond cleavage occur simultaneously, reversing the arrangement of groups at that stereocentre (Walden inversion). The product is butan-2-ol, $CH_3CH(OH)CH_2CH_3$, with inverted configuration.

Step 5: Conclusion (a) $X = (CH_3)_3CBr$, $Y = CH_3CH(Br)CH_2CH_3$. (b) Neither actually racemises: the S_N1 substrate X is achiral. (c) Y gives inversion by S_N2 backside attack.

Quick Tip to Solve: Use rate laws to identify mechanisms, then check chirality before claiming racemisation: X has three identical methyl groups.

23. Write the reaction involved in the following:

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedal-Crafts acylation of anisole [3 marks]

Solution:

Concept:

- Phenol undergoes electrophilic substitution mainly at the ortho and para positions because the hydroxyl group donates electron density to the ring.
- Reimer-Tiemann formylation introduces $-\mathrm{CHO}$, whereas Kolbe's reaction introduces $-\mathrm{COOH}$ after acidification.
- In anisole, the methoxy group directs Friedel-Crafts acylation to the ortho and para positions; the less crowded para product predominates.

Step 1: (a) Write the Reimer-Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. The major product is 2-hydroxybenzaldehyde (salicylaldehyde), with the formyl group ortho to the hydroxyl group. The overall reaction, showing the neutral product after work-up, is

$$\mathrm{C_6H_5OH + CHCl_3 + 3\,NaOH \longrightarrow C_6H_4(OH)CHO + 3\,NaCl + 2\,H_2O.}$$

The product shown is the ortho isomer; a small amount of the para isomer may also form.

Step 2: (b) Write Kolbe's reaction Sodium phenoxide reacts with carbon dioxide at about $400\,\mathrm{K}$ under pressure (about 4–7 atm) to form sodium salicylate. Acidification gives 2-hydroxybenzoic acid (salicylic acid):

$$\mathrm{C_6H_5ONa + CO_2 \longrightarrow C_6H_4(OH)COONa,}$$
$$\mathrm{C_6H_4(OH)COONa + HCl \longrightarrow C_6H_4(OH)COOH + NaCl.}$$

In both products, the oxygen-containing substituents occupy adjacent ring positions. Here Kolbe's reaction means carboxylation of phenoxide.

Step 3: (c) Write Friedel-Crafts acylation of anisole Treat anisole with acetyl chloride in the presence of anhydrous aluminium chloride. Acetylation occurs at the ortho and para positions relative to $-\mathrm{OCH_3}$:

$$\mathrm{C_6H_5OCH_3 + CH_3COCl \xrightarrow{anhyd.\ AlCl_3} C_6H_4(OCH_3)(COCH_3) + HCl.}$$

The product formula represents two positional isomers: 2-methoxyacetophenone (ortho, minor) and 4-methoxyacetophenone (para, major). The para position is less sterically hindered.

Step 4: Conclusion Reimer-Tiemann reaction gives salicylaldehyde, Kolbe's reaction gives salicylic acid after acidification, and acetylation of anisole gives mainly para-methoxyacetophenone along with its ortho isomer.

Quick Tip to Solve: Match the reagents to the incoming group: chloroform/base introduces $-\mathrm{CHO}$, carbon dioxide introduces $-\mathrm{COOH}$, and acetyl chloride introduces $-\mathrm{COCH_3}$.

24. Give reasons for the following:

(a) Carboxylic acids have higher boiling point than alcohols of comparable molecular masses.

(b) Alpha (α) hydrogens of aldehydes and ketones are acidic in nature.

(c) Nucleophilic addition of ammonia and its derivatives does not occur with carbonyl group in strongly acidic medium. [3 marks]

Solution:

Concept:

- Boiling requires overcoming intermolecular attractions. Extensive hydrogen bonding increases the energy needed to separate molecules.
- Acidity increases when the conjugate base formed by proton loss is stabilised. An enolate ion delocalises its negative charge between the alpha carbon and oxygen.
- A nitrogen nucleophile needs an available lone pair to attack the electrophilic carbonyl carbon; protonation removes that availability.

Step 1: (a) Compare the intermolecular association Carboxylic acid molecules associate into cyclic dimers held together by two intermolecular hydrogen bonds. Each carboxyl group provides an $O-H$ hydrogen-bond donor and a carbonyl oxygen acceptor. This strong association requires more energy to overcome during vaporisation. Alcohols also form hydrogen bonds, but the doubly hydrogen-bonded acid dimers produce stronger association; consequently, carboxylic acids have higher boiling points than alcohols of comparable molecular masses.

Step 2: (b) Explain the acidity of alpha hydrogens An alpha hydrogen is bonded to the carbon immediately next to a carbonyl group. Removal of this hydrogen as H^+ forms an enolate ion. For example, the conjugate base of ethanal has the resonance forms

$$CH_2{}^- - CH{=}O \longleftrightarrow CH_2{=}CH{-}O^-.$$

The negative charge is delocalised rather than confined to carbon, and one contributor places it on the more electronegative oxygen atom. The electron-withdrawing inductive effect of the carbonyl group also favours proton loss. Thus alpha hydrogens are more acidic than ordinary alkane hydrogens, although aldehydes and ketones remain weak acids.

Step 3: (c) Examine the nucleophile in strongly acidic medium Ammonia and its derivatives act as nucleophiles through the nitrogen lone pair. In strongly acidic medium they become protonated, for example

$$NH_3 + H^+ \longrightarrow NH_4{}^+.$$

The nitrogen lone pair is used to form the new bond to the proton, so the protonated species cannot carry out the required nucleophilic attack on the carbonyl carbon. The concentration of free nitrogen nucleophile becomes very small and addition is suppressed. Mild acidity can activate the carbonyl group, but excessive acidity deactivates the nucleophile.

Step 4: Conclusion The three reasons are strong hydrogen-bonded dimer formation in carboxylic acids, resonance stabilisation of the enolate formed by loss of an alpha proton, and protonation of ammonia or its derivatives in strongly acidic medium.

Quick Tip to Solve: For boiling point examine intermolecular bonds; for acidity draw the conjugate base; for nucleophilic addition check whether the attacking atom still has a free lone pair.

25. Define the following terms:

(a) Anomers

(b) Invert sugar

(c) Glycosidic linkage [3 marks]

Solution:

Concept:

- Cyclisation of a monosaccharide converts its carbonyl carbon into an anomeric carbon. Different configurations at that carbon give anomers.
- A disaccharide can be hydrolysed into its constituent monosaccharides by cleavage of its glycosidic linkage.
- Optical rotation of a mixture depends on the contributions of all its optically active components; hydrolysis can therefore change its sign.

Step 1: (a) Define anomers Anomers are cyclic stereoisomers of a sugar which differ only in configuration at the anomeric carbon. This is the carbon that was the carbonyl carbon in the open-chain form. For example, α-D-glucose and β-D-glucose differ in the arrangement of the hydroxyl group at C-1; their configurations at the other stereogenic centres are unchanged. In ketoses such as fructose, the anomeric carbon is C-2.

Step 2: (b) Define invert sugar Invert sugar is the equimolar mixture of D-glucose and D-fructose obtained by hydrolysis of sucrose, using dilute acid or the enzyme invertase:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

The two monosaccharide products are glucose and fructose, respectively. Sucrose is dextrorotatory, whereas the hydrolysis mixture is laevorotatory because the negative rotation of fructose exceeds the positive rotation of glucose in magnitude. This reversal, or inversion, of the direction of optical rotation gives invert sugar its name.

Step 3: (c) Define a glycosidic linkage A glycosidic linkage is the covalent $C-O-C$ linkage joining two monosaccharide units through an oxygen atom, involving the anomeric carbon of at least one unit. It forms by condensation with elimination of a water molecule. For example, maltose has an $\alpha(1 \to 4)$ glycosidic linkage between C-1 of one glucose unit and the oxygen attached to C-4 of the other. Hydrolysis of the linkage releases the constituent monosaccharides.

Step 4: Conclusion Anomers differ only at the anomeric carbon; invert sugar is the glucose-fructose mixture formed from sucrose; and a glycosidic linkage is the oxygen bridge covalently connecting monosaccharide units.

Quick Tip to Solve: Identify the anomeric carbon before naming anomers, and remember that "invert" describes the reversal of optical rotation on sucrose hydrolysis.

26. For the first order thermal decomposition reaction, following data was obtained:

$\mathbf{C_2H_5Cl}(g) \rightarrow \mathbf{C_2H_4}(g) + \mathbf{HCl}(g)$

Calculate rate constant. [Given: log 3 = 0.48] [3 marks]

S. No.	Time(s)	Total Pressure (atm)
1	0	0.30
2	30	0.50

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$, where a is the initial reactant concentration and $a - x$ is its concentration after time t.
- At constant temperature and volume, gas partial pressure is proportional to the amount present. In $\mathrm{C_2H_5Cl(g)} \longrightarrow \mathrm{C_2H_4(g)} + \mathrm{HCl(g)}$, one mole of reactant forms two moles of gaseous products, so the total pressure rises as decomposition proceeds.

Step 1: Relate total pressure to decomposition Initially only $\mathrm{C_2H_5Cl}$ is present, with pressure $P_0 = 0.30\,\text{atm}$. Let x be the pressure corresponding to the amount decomposed after $30\,\text{s}$. The partial pressures of reactant, ethene and hydrogen chloride then become $P_0 - x$, x and x, respectively. Thus

$$P_t = (P_0 - x) + x + x = P_0 + x.$$

Using the measured total pressure, $x = 0.50 - 0.30 = 0.20\,\text{atm}$.

Step 2: Find the remaining reactant pressure The reactant partial pressure at $30\,\text{s}$ is

$$P_{\mathrm{C_2H_5Cl}} = P_0 - x = 2P_0 - P_t = 2(0.30) - 0.50 = 0.10\,\text{atm}.$$

The total pressure $0.50\,\text{atm}$ includes both products and cannot be substituted for the remaining reactant concentration in the first-order equation.

Step 3: Substitute in the integrated rate equation Replacing the concentration ratio by the reactant partial-pressure ratio and using the supplied logarithm gives

$$\begin{aligned} k &= \frac{2.303}{30} \log \frac{0.30}{0.10} \\ &= \frac{2.303 \times 0.48}{30}\,\text{s}^{-1}. \end{aligned}$$

The pressure units cancel inside the logarithm; because time is in seconds, the rate constant has unit s^{-1}.

Step 4: Conclusion The first-order rate constant is $\boxed{k = 3.6848 \times 10^{-2}\,\text{s}^{-1} \approx 3.68 \times 10^{-2}\,\text{s}^{-1}}$.

Quick Tip to Solve: For a gaseous decomposition of the form one molecule to two molecules, first calculate the remaining reactant pressure as $2P_0 - P_t$, then apply the first-order formula.

27(a). Answer the following:

(i) Why is the Equilibrium Constant (K_c) related to E°_{cell} and not to E_{cell}?

(ii) Two metals 'A' and 'B' have standard electrode potential values of -0.24 V and $+0.80$ V respectively. Which of these will liberate hydrogen gas from dil. H_2SO_4?

(iii) Write the cell reaction which occurs in lead storage battery when it is in charging. [3 marks]

Solution:

Concept:

- Standard cell potential is related to standard Gibbs energy by $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, while $\Delta G^\circ = -RT\ln K_c$. Here n is the number of transferred electrons, F the Faraday constant and T the absolute temperature.
- A metal releases hydrogen from dilute acid when its oxidation coupled with $2\,H^+ + 2\,e^- \longrightarrow H_2$ gives a positive cell potential. The standard hydrogen electrode has reduction potential zero.
- Charging a secondary battery reverses its spontaneous discharge reaction by supplying electrical energy from an external source.

Step 1: (i) Connect equilibrium with standard potential Combining the two expressions for standard Gibbs energy gives

$$-nFE^\circ_{\text{cell}} = -RT\ln K_c, \qquad E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K_c.$$

At a fixed temperature, both K_c and E°_{cell} are characteristic of the cell reaction. In contrast, E_{cell} depends on the actual concentrations through the reaction quotient Q. At equilibrium, $Q = K_c$ and $E_{\text{cell}} = 0$; this zero value alone does not distinguish different equilibrium constants. Substituting these equilibrium conditions into the Nernst equation produces the relation to E°_{cell}.

Step 2: (ii) Compare each metal with hydrogen Taking the supplied values as standard reduction potentials, the cell potential for metal oxidation and hydrogen-ion reduction is

$$E^\circ_{\text{cell}} = 0 - E^\circ_{\text{metal ion/metal}}.$$

For metal A it is $0 - (-0.24) = +0.24\,\text{V}$; for metal B it is $0 - (+0.80) = -0.80\,\text{V}$. Thus A can reduce hydrogen ions of dilute H_2SO_4 to H_2, whereas B cannot under the usual conditions of this comparison.

Step 3: (iii) Reverse the lead-battery discharge reaction During charging, the $PbSO_4$ formed on both plates is converted back to lead at the negative plate and lead dioxide at the positive plate. Sulfuric acid is regenerated, so its concentration increases. The overall charging reaction is

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

This reaction requires an external electrical supply; it runs in the opposite direction during discharge.

Step 4: Conclusion (i) $\ln K_c = nFE^\circ_{\text{cell}}/(RT)$. (ii) Metal A liberates hydrogen. (iii) Charging regenerates Pb, PbO_2 and H_2SO_4 from $PbSO_4$ and water, as in the equation above.

Quick Tip to Solve: Use standard potential for the equilibrium constant, compare a metal's reduction potential with zero for hydrogen liberation, and reverse the discharge equation for battery charging.

OR

27(b). What type of battery is Mercury cell? Why it is more advantageous than dry cell? Write overall reaction taking place in Mercury cell. [3 marks]

Solution:

Concept:

- A primary cell supplies electricity through a chemical reaction and is not designed to be recharged. A mercury cell uses a zinc-mercury amalgam anode, a mercuric oxide cathode and an alkaline electrolyte.
- Cell voltage depends on the reaction quotient through the Nernst equation. When the overall reaction does not change the electrolyte composition and involves condensed phases, the voltage remains nearly constant during useful operation.

Step 1: Identify the battery type A mercury cell is a **primary battery**, usually made as a small button cell. Zinc in the zinc-mercury amalgam undergoes oxidation, while HgO undergoes reduction. The electrolyte is an alkaline paste containing KOH and ZnO. It is suited to devices drawing small currents for a long period, such as watches and hearing aids.

Step 2: Explain its advantage over a dry cell A mercury cell supplies a nearly constant potential of about $1.35\,\mathrm{V}$ throughout most of its useful life. Its overall reaction does not consume electrolyte ions or produce a net change in their concentration. Therefore, the reaction quotient and cell potential remain nearly unchanged while the reacting phases are present. A conventional dry cell has a voltage that falls appreciably during use, so the stable voltage of the mercury cell is advantageous for small electronic devices requiring a steady supply.

Step 3: Combine the electrode reactions In the alkaline medium the electrode reactions are

$$\begin{aligned} \text{Anode:} \quad & \mathrm{Zn(Hg) + 2\,OH^- \longrightarrow ZnO\,(s) + H_2O\,(l) + 2\,e^-} \\ \text{Cathode:} \quad & \mathrm{HgO\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow Hg\,(l) + 2\,OH^-}. \end{aligned}$$

Here $\mathrm{Zn(Hg)}$ denotes zinc present in amalgam. Adding the equations cancels the two electrons, water and hydroxide ions, giving

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

Zinc is oxidised from oxidation state zero to $+2$, and mercury is reduced from $+2$ to zero; hence electron transfer is balanced.

Step 4: Conclusion The mercury cell is a primary battery, advantageous for its nearly constant $1.35\,\mathrm{V}$ output. Its overall reaction is $\mathrm{Zn(Hg) + HgO\,(s) \longrightarrow ZnO\,(s) + Hg\,(l)}$.

Quick Tip to Solve: Add the alkaline electrode reactions and cancel $\mathrm{OH^-}$ and water; their cancellation directly explains why electrolyte concentration, and therefore mercury-cell voltage, stays nearly constant.

28. Calculate the boiling point of a solution containing 0.61 g of benzoic acid (Molar mass = 122 g mol^{-1}) in 5 g of CS_2 in which it dimerises to the extent of 88%. The boiling point and K_b of CS_2 are 46.2 °C and 2.3 K kg mol^{-1} respectively. [3 marks]

Solution:

Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality calculated using the solute's normal molar mass.
- Association reduces the number of dissolved particles. When a fraction α of solute molecules forms dimers, $i = 1 - \alpha/2$; two associated molecules count as one solute particle.

Step 1: Calculate the molality before association The amount of benzoic acid and the mass of the solvent CS_2 in kilograms are

$$n = \frac{0.61}{122} = 0.005\,\text{mol}, \qquad w_{\text{solvent}} = 5 \times 10^{-3}\,\text{kg}.$$

Hence the analytical molality is

$$m = \frac{0.005}{0.005} = 1.00\,\text{mol kg}^{-1}.$$

Use the mass of solvent, rather than the total mass of solution, in this denominator.

Step 2: Account for dimerisation The degree of association is $\alpha = 88/100 = 0.88$. Starting with one mole of benzoic acid molecules, $1 - \alpha$ mole remains unassociated and $\alpha/2$ mole of dimers is formed. Thus the ratio of actual particles to the original number is

$$i = (1 - \alpha) + \frac{\alpha}{2} = 1 - \frac{0.88}{2} = 0.56.$$

This factor is below unity because dimerisation lowers the particle concentration without changing the mass of solute added.

Step 3: Find the elevation in boiling point Substitute the van't Hoff factor, the given constant and the molality:

$$\Delta T_b = 0.56 \times 2.3 \times 1.00 = 1.288\,\text{K}.$$

A temperature difference of $1.288\,\text{K}$ equals a difference of $1.288\,^\circ\text{C}$. Since the nonvolatile solute elevates the boiling point, this difference must be added to the pure solvent's boiling point.

Step 4: Conclusion The boiling point of the solution is

$$T_b = 46.2 + 1.288 = 47.488\,^\circ\text{C} \approx \boxed{47.49\,^\circ\text{C}}.$$

Quick Tip to Solve: For dimerisation use $i = 1 - \alpha/2$, not $1 - \alpha$: the associated molecules still contribute particles as dimers.

Section D (8 marks)

*The following questions are case-based questions. Each question has an internal choice and carries **4(2 + 1 + 1)** marks each. Read the passage carefully and answer the questions that follow.*

29. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometry of coordination compounds. The Crystal Field Theory (CFT) of coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields. Answer the following questions: [4 marks]

29(a). In octahedral crystal field, energies of which d-orbitals will be raised when ligands approach the central metal atom/ion? Give reason in support of your answer. [2 marks]

Solution:

Concept:

- In an octahedral complex, six ligands approach along the positive and negative directions of the three Cartesian axes.
- Crystal-field splitting arises from unequal electrostatic repulsions between ligand electron pairs and electrons in differently oriented metal d-orbitals.

Step 1: Identify the orbitals facing the ligands The lobes of $d_{x^2-y^2}$ point along the x- and y-axes, while the principal lobes of d_{z^2} point along the z-axis. These two orbitals form the doubly degenerate e_g set and face the incoming ligands directly.

Step 2: Compare their repulsion and energy Direct approach causes greater electrostatic repulsion for the e_g orbitals than for d_{xy}, d_{yz}, d_{xz}, whose lobes lie between the axes. Relative to the average energy of the five orbitals in the spherical field, the e_g set rises by $3\Delta_o/5$, whereas the t_{2g} set falls by $2\Delta_o/5$. Here Δ_o is the octahedral splitting energy; the weighted average remains unchanged.

Step 3: Conclusion The energies of $d_{x^2-y^2}$ and d_{z^2} are raised because their lobes point towards the approaching ligands and experience the greatest repulsion.

Quick Tip to Solve: For an octahedral field, first place ligands on the axes: orbitals pointing along those axes belong to the higher-energy set.

29(b) Using crystal field theory, write the electronic configuration of central metal atom/ion of the following : (1 mark total)

29(b)(i). $[CoF_6]^{3-}$

Solution:

Concept:

- In an octahedral field, the five d-orbitals split into the lower-energy t_{2g} set and the higher-energy e_g set.
- A weak-field ligand gives a small splitting Δ_o. When $\Delta_o < P$, where P is the pairing energy,

Quick Tip to Solve: For $[CoF_6]^{3-}$, find the $+3$ oxidation state first, then fill six d-electrons in the high-spin order because fluoride is weak field.

electrons occupy the higher set before pairing in the lower set.

Step 1: Find the cobalt d-electron count Each fluoride ligand has charge -1. If cobalt has oxidation state x, then $x - 6 = -3$, giving $x = +3$. Cobalt has atomic number 27 and configuration $[\mathrm{Ar}]\, 3d^7 4s^2$; removal of two 4s electrons and one 3d electron gives Co^{3+} with $3d^6$.

Step 2: Fill the split orbitals for fluoride Fluoride is a weak-field ligand, so this octahedral complex is high spin. Place one electron in each of the three t_{2g} orbitals, then one in each of the two e_g orbitals. The sixth electron pairs in a t_{2g} orbital. Thus four electrons occupy the lower set and two occupy the upper set; four electrons remain unpaired.

Step 3: Conclusion The CFT electronic configuration of Co^{3+} in $[CoF_6]^{3-}$ is $\boxed{t_{2g}^4 e_g^2}$ (high-spin d^6).

Quick Tip to Solve: For $[CoF_6]^{3-}$, find the $+3$ oxidation state first, then fill six d-electrons in the high-spin order because fluoride is weak field.

29(b)(ii). **$[Co(NH_3)_6]^{3+}$** **[At. No. : Co = 27]**

Solution:

Concept:

- In an octahedral crystal field, t_{2g} comprises three lower-energy d-orbitals, while e_g comprises two higher-energy d-orbitals.
- When the octahedral splitting Δ_o exceeds pairing energy P, electrons pair in t_{2g} before occupying e_g, producing a low-spin configuration.

Step 1: Determine the cobalt oxidation state Ammonia is a neutral ligand. Therefore the $+3$ charge of $[Co(NH_3)_6]^{3+}$ is the oxidation state of cobalt. With atomic number 27, cobalt is $[\mathrm{Ar}]\, 3d^7 4s^2$. Removing both 4s electrons and one 3d electron gives Co^{3+} with six d-electrons.

Step 2: Apply the low-spin filling order Ammonia produces a sufficiently strong field around Co^{3+} that $\Delta_o > P$. After the three lower t_{2g} orbitals are singly occupied, the next three electrons pair within that set. All six d-electrons therefore fit into t_{2g}, leaving both e_g orbitals empty. There are no unpaired electrons.

Step 3: Conclusion The CFT electronic configuration of Co^{3+} in $[Co(NH_3)_6]^{3+}$ is $\boxed{t_{2g}^6 e_g^0}$ (low-spin d^6).

Quick Tip to Solve: Both cobalt complexes in this question are d^6; the ligand field changes their distribution, not the total d-electron count.

29(c). **$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why? [Atomic No.: Ni = 28]** [1 mark]

Solution:

Concept:

- Paramagnetism requires one or more unpaired electrons; a species with all electrons paired is diamagnetic.
- The oxidation state of nickel, and hence its d-electron count, depends on the charges of the ligands and of the whole complex.

Step 1: Count electrons in the chloride complex In $[NiCl_4]^{2-}$, four Cl^- ligands give nickel the oxidation state $+2$. Thus Ni^{2+} is $3d^8$. In a tetrahedral field the arrangement is $e^4t_2^4$, with two unpaired electrons in the upper set; the complex is therefore paramagnetic.

Step 2: Count electrons in the carbonyl complex In $Ni(CO)_4$, carbon monoxide is neutral, so nickel has oxidation state zero. In the complex the metal has a filled $3d^{10}$ configuration, with all d-electrons paired. It is therefore diamagnetic, although its geometry is also tetrahedral.

Step 3: Conclusion $[NiCl_4]^{2-}$ has two unpaired electrons and is paramagnetic; $Ni(CO)_4$ has no unpaired electrons and is diamagnetic. Equal geometry does not imply equal d-electron counts.

Quick Tip to Solve: Always determine the metal oxidation state before comparing magnetism: chloride gives nickel(II), whereas neutral CO leaves nickel in oxidation state zero.

OR

29(c). **Write hybridization and magnetic behaviour of the complex $[Fe(CN)_6]^{3-}$. [Atomic No.: Fe = 26]** [1 mark]

Solution:

Concept:

- The oxidation state gives the metal d-electron count; cyanide, CN^-, is a strong-field ligand.
- For an octahedral complex, strong-field pairing may provide two vacant inner d-orbitals for d^2sp^3 hybridisation.

Step 1: Find the iron configuration If the oxidation state of iron is x, then $x + 6(-1) = -3$, giving $x = +3$. Iron has atomic number 26, so Fe^{3+} has configuration $[Ar]3d^5$.

Step 2: Apply strong-field pairing The six cyanide ligands produce a strong octahedral field. The five d-electrons occupy the lower set as $t_{2g}^5e_g^0$: two orbitals contain pairs and the third contains one electron. Two inner 3d-orbitals are available for bonding, giving d^2sp^3 hybridisation. The remaining unpaired electron causes paramagnetism.

Step 3: Conclusion $[Fe(CN)_6]^{3-}$ is an inner-orbital, d^2sp^3-hybridised octahedral complex and is paramagnetic with one unpaired electron.

Quick Tip to Solve: Strong-field does not automatically mean diamagnetic: a low-spin d5 ion still retains one unpaired electron.

30. The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Aliphatic amines are stronger bases than ammonia whereas aromatic amines are weaker bases than ammonia. Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their high reactivity. Substitution tends to occur at ortho-and para-positions. Hinsberg reagent is used for the identification and distinction between primary, secondary and tertiary amines. Aryldiazonium salts, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes.

Answer the following questions : [4 marks]

30(a)(i). Why CH_3-NH_2 is a stronger base than $(CH_3)_3N$ in aqueous solution ? [1 mark]

Solution:

Concept:

- Aqueous basicity depends on both electron donation to nitrogen and the hydration stability of the conjugate ammonium ion.
- A more strongly solvated conjugate acid favours proton acceptance by the amine in water.

Step 1: Compare the protonated ions Methylamine gives $CH_3NH_3^+$, while trimethylamine gives $(CH_3)_3NH^+$. The methylammonium ion has three nitrogen-bound hydrogens and is hydrated more effectively by hydrogen bonding; the bulky trimethylammonium ion has only one nitrogen-bound hydrogen and poorer access for surrounding water molecules.

Step 2: Balance induction against hydration Three methyl groups increase electron density on nitrogen more than one methyl group through the positive inductive effect. However, in aqueous solution the greater hydration and stabilisation of $CH_3NH_3^+$ outweigh this advantage of trimethylamine. Consequently the equilibrium for proton acceptance is more favourable for methylamine.

Step 3: Conclusion CH_3NH_2 is the stronger base in water because its conjugate acid is more effectively hydrated and stabilised than $(CH_3)_3NH^+$.

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

30(a)(ii). Write structural formulae of the compound A and B :

$$CH_3CONH_2 \xrightarrow{NaOBr} A \xrightarrow[Base]{C_6H_5COCl} B$$

[1 mark]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ into RNH_2, removing the carbonyl carbon.
- A primary amine reacts with benzoyl chloride in base to give an N-substituted benzamide; base

Quick Tip to Solve: Track the carbonyl carbon: Hofmann degradation removes the original amide carbonyl, while benzoylation introduces a new carbonyl from benzoyl chloride.

neutralises the acid formed.

Step 1: Identify the degradation product Acetamide, CH_3CONH_2, loses its carbonyl carbon on reaction with sodium hypobromite. The methyl group remains attached to nitrogen, so A is methylamine with structural formula CH_3-NH_2.

Step 2: Benzoylate the amine Methylamine attacks the carbonyl carbon of benzoyl chloride. Replacement of chloride gives the amide in which nitrogen retains its methyl group and one hydrogen:

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

The base removes the liberated acid, allowing acylation to proceed.

Step 3: Conclusion $A = CH_3-NH_2$ (methylamine) and $B = C_6H_5-C(=O)-NH-CH_3$ (N-methylbenzamide).

Quick Tip to Solve: Track the carbonyl carbon: Hofmann degradation removes the original amide carbonyl, while benzoylation introduces a new carbonyl from benzoyl chloride.

30(b). A compound 'X' with molecular formula C_3H_9N reacts with Hinsberg reagent to give a product insoluble in alkali. Identify 'X'. [1 mark]

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. Its reaction distinguishes primary, secondary and tertiary amines.
- A secondary amine forms an alkali-insoluble sulphonamide because its product has no acidic $N-H$ hydrogen.

Step 1: Determine the class of amine The compound reacts with Hinsberg reagent, so it is not a tertiary amine, which does not form a sulphonamide. A primary amine gives a sulphonamide containing an acidic $N-H$ bond and hence soluble in alkali. The stated insoluble reaction product therefore identifies a secondary amine.

Step 2: Distribute the three carbon atoms A secondary amine contains two alkyl groups on nitrogen. With three carbon atoms in total, these must be a methyl group and an ethyl group. The structure is $CH_3-NH-CH_2CH_3$; its sulphonamide, $C_6H_5SO_2N(CH_3)CH_2CH_3$, has no nitrogen-bound hydrogen and cannot form a salt with alkali.

Step 3: Conclusion X is **N-methylethanamine** (ethylmethylamine), $CH_3-NH-CH_2CH_3$.

Quick Tip to Solve: In the Hinsberg test, distinguish an insoluble reaction product from no reaction: the former identifies a secondary amine.

OR

30(b). How can you convert aniline to benzonitrile? [1 mark]

Solution:

Concept:

- A primary aromatic amine undergoes diazotisation with nitrous acid generated in situ from $NaNO_2$ and HCl at 273–278 K.
- In the Sandmeyer reaction, cuprous cyanide replaces the diazonium group by $-CN$, with release of nitrogen gas.

Step 1: Diazotise aniline Treat aniline with sodium nitrite and dilute hydrochloric acid, keeping the mixture at 273–278 K to preserve the diazonium salt:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2{}^+Cl^- + NaCl + 2\,H_2O.$$

Step 2: Replace the diazonium group Treat benzenediazonium chloride with cuprous cyanide. The diazonium group is replaced by a cyanide group bonded to the ring through carbon:

$$C_6H_5N_2{}^+Cl^- + CuCN \longrightarrow C_6H_5CN + N_2 + CuCl.$$

Step 3: Conclusion Convert aniline first to benzenediazonium chloride using $NaNO_2/HCl$ at 273–278 K, then use $CuCN$ to obtain benzonitrile, C_6H_5CN.

Quick Tip to Solve: For replacing an aromatic amino group by cyanide, form the cold diazonium salt first and then apply the Sandmeyer reaction with cuprous cyanide.

30(c). Why is -NH_2 group of aniline acetylated before carrying out nitration? [1 mark]

Solution:

Concept:

- The $-NH_2$ group strongly activates the benzene ring towards electrophilic substitution; direct nitration can also cause oxidation and unwanted products.
- Acetylation converts $-NH_2$ into $-NHCOCH_3$. The nitrogen lone pair is partly delocalised towards the carbonyl group, reducing activation of the ring while retaining ortho/para direction.

Step 1: Identify the difficulty with direct nitration In the strongly acidic nitrating mixture, much of aniline is protonated to the anilinium ion, $C_6H_5NH_3{}^+$, which is meta-directing. Direct nitration therefore gives an unwanted mixture including a substantial meta product, and oxidation may also occur.

Step 2: Protect the amino group Acetylation produces acetanilide, $C_6H_5NHCOCH_3$, whose amino group is less basic and whose ring is less strongly activated. Nitration is consequently controlled and gives mainly the para-nitro derivative. Subsequent hydrolysis removes the acetyl protecting group to regenerate $-NH_2$.

Quick Tip to Solve: Use the sequence acetylation, nitration, then hydrolysis when a controlled para substitution is required on aniline.

Step 3: Conclusion Aniline is acetylated to protect and moderate the activating effect of $-NH_2$, preventing unwanted direct-nitration reactions and enabling predominantly para nitration.

Quick Tip to Solve: Use the sequence acetylation, nitration, then hydrolysis when a controlled para substitution is required on aniline.

Section E (15 marks)

31(a). Calculate emf and ΔG for the following cell at 298 K:

Mg$(s)|$**Mg**$^{2+}(0.01\ M)\ ||$ **Ag**$^{+}(0.001\ M)|$**Ag**(s)

Given: $E^{\circ}_{Mg^{2+}/Mg} = -2.37$ **V,** $E^{\circ}_{Ag^{+}/Ag} = +0.80$ **V**

[1 F = 96500 C mol^{-1}, log 10 = 1] [5 marks]

Solution:

Concept:

- The cell emf is the cathode reduction potential minus the anode reduction potential: $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$. Electrode potentials are not multiplied by stoichiometric coefficients.
- 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.
- The Gibbs energy change under the specified conditions is $\Delta G = -nFE_{\text{cell}}$, with $F = 96500\,\text{C mol}^{-1}$. A positive emf gives a negative Gibbs energy change for the forward cell reaction.

Step 1: Write the balanced cell reaction Magnesium is oxidised at the left-hand anode, while silver ions are reduced at the right-hand cathode. Write the half-reactions and balance the electrons:

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

Adding gives $\text{Mg(s)} + 2\,\text{Ag}^{+}\text{(aq)} \longrightarrow \text{Mg}^{2+}\text{(aq)} + 2\,\text{Ag(s)}$. Thus $n = 2$; this same value must be used in both the Nernst equation and the Gibbs energy calculation.

Step 2: Find the standard cell emf Both supplied values are reduction potentials. Subtract the magnesium reduction potential from the silver reduction potential:

$$E^{\circ}_{\text{cell}} = 0.80 - (-2.37) = 3.17\,\text{V}.$$

The positive standard emf is consistent with oxidation of magnesium and reduction of silver ions in the written cell.

Step 3: Apply the Nernst equation to the given concentrations Omit the two pure metals from the reaction quotient. The coefficient of silver ions becomes the power of their concentration:

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^{+}]^2} = \frac{0.01}{(0.001)^2} = 10^4.$$

Concentrations here are understood relative to the standard concentration, so Q is dimensionless.

Quick Tip to Solve: Balance the electrons first: two silver ions give both $n = 2$ and the square on $[\text{Ag}^{+}]$ in Q. Use the nonstandard emf when calculating the requested ΔG.

Since $\log Q = 4$,

$$E_{\text{cell}} = 3.17 - \frac{0.0591}{2} \times 4$$
$$= 3.17 - 0.1182 = 3.0518\,\text{V}.$$

Since $Q > 1$, the concentration correction lowers the emf below its standard value.

Step 4: Calculate the Gibbs energy change The question asks for ΔG at the given concentrations, so use the calculated emf rather than the standard emf:

$$\Delta G = -2 \times 96500 \times 3.0518$$
$$= -588997.4\,\text{J mol}^{-1}$$
$$\simeq -589.0\,\text{kJ mol}^{-1}.$$

The molar value refers to one mole of the balanced cell reaction, which consumes one mole of magnesium and two moles of silver ions.

Step 5: Conclusion At 298 K, the cell emf is $E_{\text{cell}} \simeq 3.052\,\text{V}$ and $\Delta G \simeq -589.0\,\text{kJ mol}^{-1}$. The negative Gibbs energy change shows that the written cell reaction is spontaneous under the specified conditions.

Quick Tip to Solve: Balance the electrons first: two silver ions give both $n = 2$ and the square on $[\text{Ag}^+]$ in Q. Use the nonstandard emf when calculating the requested ΔG.

OR

31(b). For the reaction:

$2\textbf{AgCl}(s) + \textbf{H}_2(g)\,(0.4\,\textbf{atm}) \rightarrow 2\textbf{Ag}(s) + 2\textbf{H}^+(0.1\,M) + 2\textbf{Cl}^-(0.2\,M)$

Calculate emf of the cell at 25 °C.

Given: ΔG° = -43500 J mol^{-1}

[log 10 = 1, 1 F = 96500 C mol^{-1}] [5 marks]

Solution:

Concept:

- Standard Gibbs energy and standard cell emf are related by $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per balanced reaction and F is the Faraday constant.
- At 25 °C or approximately 298 K, $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$. The reaction quotient Q contains the activities of products divided by those of reactants, each raised to its stoichiometric coefficient.
- Pure solids have unit activity. For the dilute solutions use concentrations relative to 1 M; for the gas use its pressure relative to the standard pressure of 1 atm in the stated convention.

Step 1: Determine the electron transfer Hydrogen is oxidised and silver chloride is reduced. The half-reactions for the printed overall reaction are

$$\text{H}_2(\text{g}) \longrightarrow 2\,\text{H}^+(\text{aq}) + 2\,\text{e}^-,$$
$$2\,\text{AgCl}\,(\text{s}) + 2\,\text{e}^- \longrightarrow 2\,\text{Ag}\,(\text{s}) + 2\,\text{Cl}^-(\text{aq}).$$

Quick Tip to Solve: Square both ionic concentrations, keep hydrogen pressure in the denominator, and omit the solids. Here $Q = 10^{-3}$, so the Nernst correction must add to the standard emf.

Their sum is the given reaction. Therefore $n = 2$, since two electrons pass through the external circuit for one occurrence of the balanced reaction. The solid silver chloride is a reactant of unit activity and is not replaced by a dissolved concentration in Q.

Step 2: Obtain the standard cell emf Use the given standard Gibbs energy change for the reaction as written:

$$\begin{aligned} E^\circ_{\text{cell}} &= -\frac{\Delta G^\circ}{nF} \\ &= -\frac{-43500}{2 \times 96500} \\ &= 0.22539\,\text{V}. \end{aligned}$$

The negative standard Gibbs energy gives a positive standard cell emf. This is the standard value; the specified concentrations and gas pressure still require a Nernst correction.

Step 3: Form and evaluate the reaction quotient Both ionic products have coefficient 2, and hydrogen is a reactant with coefficient 1. Omitting the pure solids AgCl and Ag therefore gives

$$Q = \frac{[\text{H}^+]^2[\text{Cl}^-]^2}{p_{\text{H}_2}} = \frac{(0.1)^2(0.2)^2}{0.4} = \frac{0.0004}{0.4} = 0.001.$$

The concentrations and pressure in this expression represent their numerical ratios to standard values, making Q dimensionless. Thus $\log Q = \log(10^{-3}) = -3$.

Step 4: Apply the concentration and pressure correction Substitute the standard emf, $n = 2$ and $\log Q = -3$ into the Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= 0.22539 - \frac{0.0591}{2}(-3) \\ &= 0.22539 + 0.08865 \\ &= 0.31404\,\text{V}. \end{aligned}$$

Because $Q < 1$, its logarithm is negative and the correction increases the emf above E°_{cell}. This sign check is consistent with the small ionic product activities favouring the forward reaction.

Step 5: Conclusion The emf of the cell at $25\,^\circ\text{C}$ under the specified conditions is $E_{\text{cell}} \simeq 0.314\,\text{V}$. The positive value corresponds to a spontaneous forward reaction as written.

Quick Tip to Solve: Square both ionic concentrations, keep hydrogen pressure in the denominator, and omit the solids. Here $Q = 10^{-3}$, so the Nernst correction must add to the standard emf.

32(a). (i) An organic compound (X) has the molecular formula $C_5H_{10}O$. Draw structures for (X) if it:

(I) does not give Tollen's test but gives a positive iodoform test.

(II) does not give Tollen's test and iodoform test but undergoes Aldol condensation.

(III) undergoes Cannizzaro's reaction.

(ii) Show how each of the following compounds can be converted to benzoic acid:

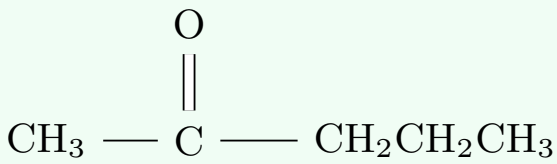
(I) Acetophenone (II) Ethyl benzene [5 marks]

Solution:

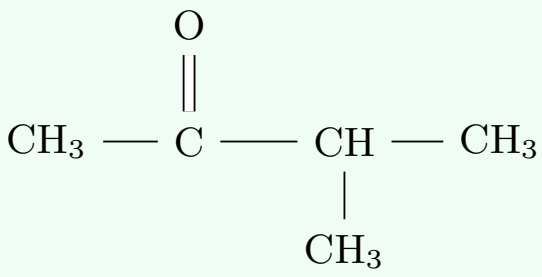
Concept:

- Tollens' reagent oxidises an aldehyde to a carboxylate and produces a silver mirror; ordinary ketones do not respond. Thus a negative Tollens' test directs us to a ketone here.
- A methyl ketone, $RCOCH_3$, gives yellow iodoform with $I_2/NaOH$. An aldehyde or ketone with at least one α-hydrogen can undergo aldol condensation.
- An aldehyde lacking α-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali. Oxidation or haloform cleavage followed by acidification can give benzoic acid from suitable aromatic side chains.

Step 1: (i)(I) Identify a methyl ketone A negative Tollens' test excludes an aldehyde, while a positive iodoform test requires the $-COCH_3$ group. A suitable structure is pentan-2-one, $CH_3COCH_2CH_2CH_3$. It has five carbon atoms and molecular formula $C_5H_{10}O$, and its carbonyl is bonded to two carbon groups. Its terminal methyl group directly attached to the carbonyl gives the haloform reaction. The branched isomer 3-methylbutan-2-one, $CH_3COCH(CH_3)_2$, is another valid answer; both structures are shown below.



Pentan-2-one



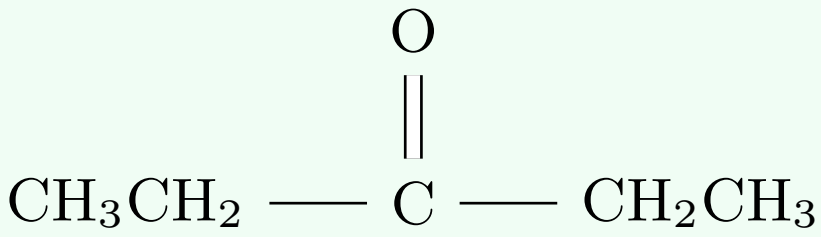
3-Methylbutan-2-one

Two methyl ketones satisfying condition (I).

Step 2: (i)(II) Identify a ketone without a methyl-carbonyl group Pentan-3-one, $CH_3CH_2COCH_2CH_3$, is a ketone and therefore does not give Tollens' test. The carbonyl carbon is bonded to an ethyl group on each side, so there is no CH_3CO- group and the iodoform test is negative. However, each

Quick Tip to Solve: Check for $-COCH_3$ before applying the iodoform test, and count hydrogens on the carbon next to $-CHO$, not the aldehydic hydrogen, for Cannizzaro reaction.

adjacent CH_2 group contains α-hydrogens. Dilute alkali can remove an α-hydrogen to form an enolate, permitting aldol addition and subsequent dehydration on heating. This satisfies all three conditions, unlike pentan-2-one, which gives iodoform.

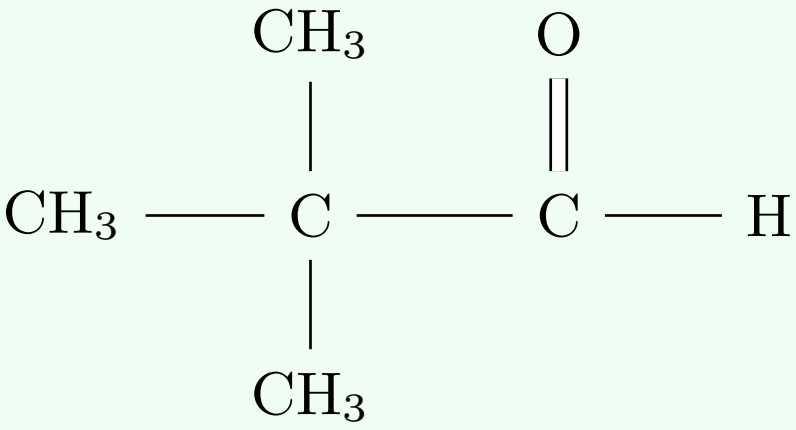


Pentan-3-one: alpha-hydrogens are present, but no methyl-carbonyl group.

Step 3: (i)(III) Identify an aldehyde without alpha-hydrogen Choose 2,2-dimethylpropanal, $(CH_3)_3CCHO$. Its carbon atom immediately adjacent to $-CHO$ is bonded to three methyl groups and the aldehyde carbon, so it has no hydrogen. The aldehydic hydrogen itself is not an α-hydrogen. Consequently the compound undergoes Cannizzaro reaction instead of aldol condensation. With $R = (CH_3)_3C$, its disproportionation is

$$2RCHO + NaOH \longrightarrow RCOONa + RCH_2OH.$$

One aldehyde molecule is oxidised to the carboxylate and the other is reduced to the primary alcohol.



2,2-Dimethylpropanal has no hydrogen on its alpha-carbon.

Step 4: (ii)(I) Convert acetophenone by the haloform reaction Acetophenone is a methyl ketone. Treat it with iodine and aqueous sodium hydroxide, warming as required; cleavage gives sodium benzoate and yellow iodoform. Acidify the benzoate with dilute hydrochloric acid:

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

Quick Tip to Solve: Check for $-COCH_3$ before applying the iodoform test, and count hydrogens on the carbon next to $-CHO$, not the aldehydic hydrogen, for Cannizzaro reaction.

Acidification is essential because the initial alkaline reaction produces a salt, not the free acid.

Step 5: (ii)(II) Oxidise the side chain of ethylbenzene Ethylbenzene has benzylic hydrogens, so vigorous oxidation with hot alkaline potassium permanganate converts its side chain into a benzoate group. Subsequent acidification gives benzoic acid:

$$C_6H_5CH_2CH_3 \xrightarrow[\Delta]{KMnO_4/OH^-} C_6H_5COO^- \xrightarrow{H^+} C_6H_5COOH.$$

The carbon attached directly to the ring becomes the carboxyl carbon; the terminal side-chain carbon is removed by oxidation. The aromatic ring remains intact under this standard side-chain oxidation.

Step 6: Conclusion (i) Suitable structures are (I) pentan-2-one (also 3-methylbutan-2-one), (II) pentan-3-one and (III) 2,2-dimethylpropanal. (ii) Acetophenone gives benzoic acid by $I_2/NaOH$, then acidification; ethylbenzene gives it by hot alkaline $KMnO_4$, then acidification.

Quick Tip to Solve: Check for $-COCH_3$ before applying the iodoform test, and count hydrogens on the carbon next to $-CHO$, not the aldehydic hydrogen, for Cannizzaro reaction.

OR

32(b). Answer the following questions:

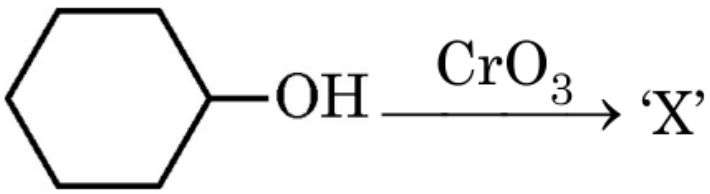
(i) Draw structure of the 2, 4-dinitrophenyl hydrazone derivative of benzaldehyde.

(ii) Arrange the following in increasing order of their reactivity towards HCN: Di-tert. butyl ketone, Acetaldehyde, Acetone.

(iii) Give a simple chemical test to distinguish between benzoic acid and ethyl benzoate.

(iv) Write the name of the reagent to convert Ethanenitrile to Ethanal.

(v) Draw the structure of 'X' in the following reaction: [5 marks]



Solution:

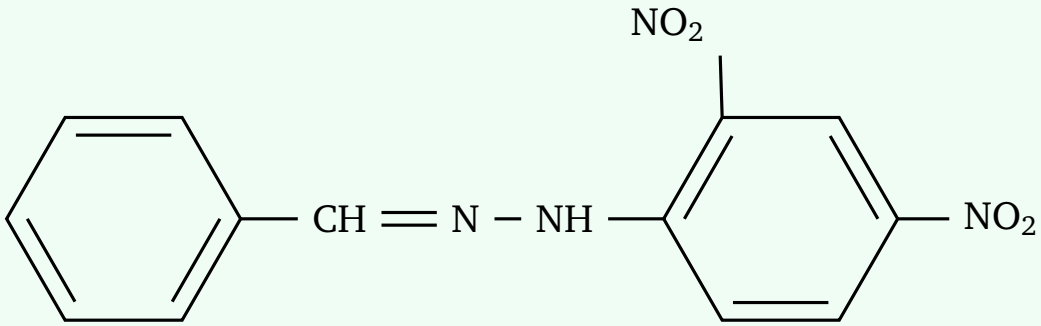
Concept:

- Aldehydes react with 2,4-dinitrophenylhydrazine by condensation: the carbonyl oxygen is replaced by the $=N-NH-Ar$ group, with elimination of water.
- Nucleophilic addition to a carbonyl group becomes slower as steric crowding and the electron-donating effect of alkyl groups increase.
- Carboxylic acids release CO_2 from aqueous sodium hydrogencarbonate. Esters do not give this immediate acid-base reaction.
- Controlled reduction of a nitrile followed by hydrolysis gives an aldehyde. Oxidation of a secondary

Quick Tip to Solve: In the hydrazone, keep the aldehydic H and replace only carbonyl O by the hydrazone group. For HCN addition, compare carbonyl crowding before comparing alkyl electron donation.

alcohol gives a ketone.

Step 1: (i) Form the benzaldehyde hydrazone The terminal $-NH_2$ group of 2,4-dinitrophenylhydrazine condenses with the $-CHO$ group of benzaldehyde. The aldehydic hydrogen is retained, while water is eliminated. The product has the connectivity $C_6H_5-CH=N-NH-C_6H_3(NO_2)_2$, with the two nitro groups at positions 2 and 4 relative to the hydrazino attachment on the second benzene ring. Its structure is shown below; the $C=N$ bond links the benzaldehyde carbon to the hydrazine nitrogen.



Benzaldehyde 2,4-dinitrophenylhydrazone

Step 2: (ii) Compare addition of HCN Cyanide attacks the electrophilic carbonyl carbon. In di-tert-butyl ketone, both bulky tert-butyl groups obstruct this attack, and their electron-donating effect reduces the carbonyl carbon's positive character. Acetone is less crowded, but has two electron-donating methyl groups. Acetaldehyde has only one methyl group and one small hydrogen atom, so addition is easiest. Thus, the increasing reactivity is

$$\text{Di-tert-butyl ketone} < \text{Acetone} < \text{Acetaldehyde}.$$

Step 3: (iii) Add aqueous sodium hydrogencarbonate Add aqueous $NaHCO_3$ separately to the samples. Benzoic acid produces brisk effervescence of carbon dioxide:

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2\uparrow.$$

The gas turns limewater milky. Ethyl benzoate gives no such effervescence under these conditions because it is an ester and lacks the acidic carboxyl hydrogen.

Step 4: (iv) Use Stephen reduction The reagent is stannous chloride (tin(II) chloride), $SnCl_2$, with hydrochloric acid, followed by hydrolysis with water. The nitrile is first partially reduced to the iminium salt; hydrolysis then replaces the imino group by oxygen to give ethanal:

$$CH_3CN \xrightarrow{SnCl_2/HCl} CH_3CH{=}NH\cdot HCl \xrightarrow{H_2O} CH_3CHO.$$

The hydrolysis step is essential. A strong reducing agent such as $LiAlH_4$ would instead reduce the nitrile to an amine.

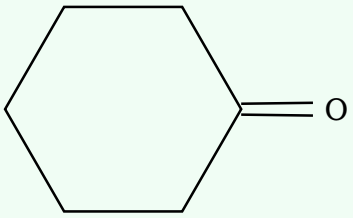
Step 5: (v) Oxidise the secondary alcohol The printed reactant is cyclohexanol. Its hydroxyl-bearing carbon is attached to two other carbons, making it a secondary alcohol. Oxidation with CrO_3 removes hydrogen from this carbon and from the hydroxyl group, creating a carbonyl group while retaining

Quick Tip to Solve: In the hydrazone, keep the aldehydic H and replace only carbonyl O by the hydrazone group. For HCN addition, compare carbonyl crowding before comparing alkyl electron donation.

the six-membered ring:

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

Therefore, X is cyclohexanone, whose structure is drawn below.



Cyclohexanone, X

Step 6: Conclusion (i) The derivative is benzaldehyde 2,4-dinitrophenylhydrazone, as drawn. (ii) Di-tert-butyl ketone $<$ acetone $<$ acetaldehyde. (iii) Aqueous $NaHCO_3$ gives effervescence with benzoic acid only. (iv) Use $SnCl_2/HCl$, followed by hydrolysis. (v) X is cyclohexanone.

Quick Tip to Solve: In the hydrazone, keep the aldehydic H and replace only carbonyl O by the hydrazone group. For HCN addition, compare carbonyl crowding before comparing alkyl electron donation.

33(a). (i) From the given data of E° values, answer the following questions:

(I) Why $E^{\circ}_{M^{2+}/M}$ show irregular trend in the above values?

(II) Why is $E^{\circ}_{Cu^{2+}/Cu}$ value exceptionally positive?

(III) Why $E^{\circ}_{Mn^{2+}/Mn}$ value is highly negative?

(ii) Write the ionic equations for the oxidising action of potassium permanganate for its reaction with I^- in both acidic and alkaline solutions. [5 marks]

$E^{\circ}_{M^{2+}/M}$	V	Cr	Mn	Fe	Co	Ni	Cu
	–1.18	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34

Solution:

Concept:

- The standard reduction potential $E^{\circ}_{M^{2+}/M}$ measures the tendency of the aqueous divalent ion to gain electrons. Its value depends on the overall free-energy change, with $\Delta G^{\circ} = -nFE^{\circ}$, where $n = 2$ and F is Faraday's constant.
- Atomisation of the metal, its first two ionisation steps and hydration of the gaseous divalent ion together control the stability of the aqueous ion relative to the metal.
- The reduction product of MnO_4^- depends on the medium: Mn^{2+} in acidic solution and MnO_2 in the usual alkaline oxidation of iodide to iodate.

Step 1: (i)(I) Explain the irregular trend The conversion of M(s) to M^{2+}(aq) involves atomisation, removal of two electrons and hydration. Atomisation and ionisation require energy, whereas hydration releases energy. These contributions do not vary uniformly across the series because the electronic configurations and strengths of metallic bonding differ. Their combined effect therefore produces an

Quick Tip to Solve: Identify both oxidation-state changes before balancing: acidic iodide oxidation transfers one electron per iodine atom, while alkaline oxidation to iodate transfers six.

irregular series of standard reduction potentials rather than a simple monotonic trend. The extra stability of particular electronic configurations also influences the ease of forming the divalent ions.

Step 2: (i)(II) Account for copper's positive potential Copper has high atomisation and ionisation energy requirements. In particular, the second ionisation removes an electron from the filled $3d^{10}$ configuration of Cu^{+}. The hydration enthalpy of Cu^{2+} does not compensate sufficiently for the energy needed to form the gaseous ion from the metal. Consequently, oxidation of copper to its aqueous divalent ion is relatively unfavourable, while the reverse reduction is favoured relative to the standard hydrogen electrode. This accounts for the positive value $E^{\circ}_{Cu^{2+}/Cu} = +0.34\,V$.

Step 3: (i)(III) Account for manganese's negative potential The manganese atom has configuration $[Ar]3d^5 4s^2$. Loss of its two $4s$ electrons gives Mn^{2+} with the especially stable half-filled $3d^5$ configuration. This stability favours formation of the aqueous divalent ion and makes its reduction to the metal comparatively difficult. The corresponding standard reduction potential is therefore highly negative, $-1.18\,V$, as given in the table.

Step 4: (ii) Balance the oxidation in acidic solution Permanganate gains five electrons per manganese atom, while two iodide ions lose two electrons to form iodine:

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O,$$

$$2\,I^- \longrightarrow I_2 + 2\,e^-.$$

Multiply the first half-reaction by two and the second by five to cancel ten electrons. The required ionic equation is

$$\boxed{2\,MnO_4^- + 16\,H^+ + 10\,I^- \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,I_2}.$$

Step 5: (ii) Balance the oxidation in alkaline solution Iodide is oxidised to iodate, with iodine changing from -1 to $+5$. Each permanganate ion is reduced from manganese $+7$ to $+4$:

$$I^- + 6\,OH^- \longrightarrow IO_3^- + 3\,H_2O + 6\,e^-,$$

$$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-.$$

Add the iodide half-reaction to twice the permanganate half-reaction and cancel water and hydroxide ions. This gives

$$\boxed{2\,MnO_4^- + I^- + H_2O \longrightarrow 2\,MnO_2 + IO_3^- + 2\,OH^-}.$$

Both equations conserve atoms and charge; the alkaline equation has total charge -3 on each side.

Step 6: Conclusion The irregular potentials reflect the competing atomisation, ionisation and hydration contributions. Copper's energy cost of ion formation gives its positive potential; the stable $3d^5$ configuration of Mn^{2+} accounts for manganese's highly negative value. Permanganate converts I^- to I_2 in acid and to IO_3^- in alkaline solution, according to the balanced equations above.

Quick Tip to Solve: Identify both oxidation-state changes before balancing: acidic iodide oxidation transfers one electron per iodine atom, while alkaline oxidation to iodate transfers six.

OR

33(b). Answer the following questions:

(i) Name a member of the lanthanoid series

(I) which exhibits +4 oxidation state

(II) which exhibits +2 oxidation state.

(ii) Why transition metals act as good catalyst?

(iii) Why Cr has higher melting point than Mn?

(iv) What happens when acidic solution of potassium permanganate is allowed to stand for sometime? Give the equation involved. What is this type of reaction called? [5 marks]

Solution:

Concept:

- Lanthanoid ions can attain unusually stable empty, half-filled or filled $4f$ subshells; these configurations explain selected oxidation states besides the common $+3$ state.
- Transition-metal catalysis commonly involves variable oxidation states and the formation of intermediate complexes or adsorption of reactants, providing a pathway of lower activation energy.
- Stronger metallic bonding generally raises the melting point. A disproportionation reaction requires the same element in one initial oxidation state to undergo both oxidation and reduction.

Step 1: (i) Identify suitable lanthanoids (I) Cerium exhibits the $+4$ oxidation state, for example in CeO_2. The Ce^{4+} ion has the stable configuration $[Xe]4f^0$.

(II) Europium exhibits the $+2$ oxidation state, for example in $EuCl_2$. The Eu^{2+} ion has configuration $[Xe]4f^7$, with a stable half-filled $4f$ subshell. Thus cerium and europium are valid examples for the two requested states, respectively.

Step 2: (ii) Explain catalytic activity Transition metals can change oxidation state readily and form intermediate compounds or complexes with reactants. They can accept electrons in one step and donate them in a later step, regenerating the catalyst. Finely divided metals also adsorb reactant molecules on their surfaces, bringing them together and weakening bonds that must break. These processes provide an alternative reaction pathway with lower activation energy. For example, iron catalyses the synthesis of ammonia, while V_2O_5 catalyses the oxidation of SO_2 in the Contact process.

Step 3: (iii) Compare metallic bonding in chromium and manganese Chromium has atomic configuration $[Ar]3d^5 4s^1$, whereas manganese has $[Ar]3d^5 4s^2$. Chromium has six unpaired valence electrons in this atomic description, compared with five for manganese. Greater participation of unpaired electrons in interatomic bonding gives chromium stronger metallic bonding. Manganese's stable half-filled $3d^5$ arrangement contributes to its comparatively weak metallic bonding and anomalously low melting point in the middle of the series. Consequently, more energy is needed to melt chromium than manganese.

Step 4: (iv) Describe the change in acidic permanganate on standing An acidic solution of potassium permanganate undergoes slow decomposition on standing. Oxygen is liberated and brown manganese dioxide can separate, with fading of the purple permanganate colour. The balanced ionic equation for this decomposition is

$$\boxed{4\,MnO_4^- + 4\,H^+ \longrightarrow 4\,MnO_2 + 3\,O_2 + 2\,H_2O}.$$

Quick Tip to Solve: Check the ion's charge before naming disproportionation: MnO_4^- contains manganese(VII), whereas MnO_4^{2-} contains manganese(VI) and can form both higher and lower oxidation states.

Manganese changes from $+7$ to $+4$, gaining a total of twelve electrons for four manganese atoms. Six oxygen atoms change from -2 to zero in $3\,O_2$, losing twelve electrons. Thus this is a redox decomposition reaction.

It is not disproportionation of manganese: manganese in permanganate already has its highest usual oxidation state, $+7$, and is only reduced here. The familiar disproportionation on acidification belongs to manganate, MnO_4^{2-}, whose manganese is initially $+6$:

$$3\,MnO_4^{2-} + 4\,H^+ \longrightarrow 2\,MnO_4^- + MnO_2 + 2\,H_2O.$$

In that different reaction, manganese is both oxidised to $+7$ and reduced to $+4$. The printed question specifies permanganate, so the redox decomposition equation is the applicable answer.

Step 5: Conclusion (i) Cerium shows $+4$, and europium shows $+2$. (ii) Variable oxidation states and intermediate formation or adsorption account for transition-metal catalysis. (iii) Stronger metallic bonding gives chromium a higher melting point than manganese. (iv) Acidic permanganate slowly undergoes redox decomposition, liberating O_2 and forming MnO_2; this must be distinguished from the disproportionation of manganate.

Quick Tip to Solve: Check the ion's charge before naming disproportionation: MnO_4^- contains manganese(VII), whereas MnO_4^{2-} contains manganese(VI) and can form both higher and lower oxidation states.