CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-1-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculators is **not** allowed.

Section A (16 marks)

*Questions no. **1** to **16** are Multiple Choice type Questions, carrying **1** mark each.*

1. The equilibrium $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$: [1 mark]

(A) exists in basic medium

(B) exists in acidic medium

(C) exists in neutral medium

(D) does not exist

Correct Answer: (A) exists in basic medium

Solution:

Concept:

- Chromate, CrO_4^{2-}, and dichromate, $Cr_2O_7^{2-}$, interconvert as the pH changes.
- By Le Chatelier's principle, adding OH^- favours chromate, whereas adding H^+ favours dichromate.

Step 1: Write the medium-dependent equilibrium The conversion towards chromate in alkaline solution is represented by the balanced equation

$$Cr_2O_7^{2-} + 2\,OH^- \rightleftharpoons 2\,CrO_4^{2-} + H_2O.$$

Thus, hydroxide ions support the direction displayed in the question.

Step 2: Compare the printed choices A basic medium favours yellow chromate ions. An acidic medium instead favours orange dichromate, through $2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$. A neutral medium is not the condition specified for the conversion towards chromate, and denying the equilibrium altogether is incorrect.

Step 3: Conclusion The displayed dichromate-to-chromate conversion is associated with basic medium. Hence, the correct option is (A).

Quick Tip to Solve: Remember the direction by colour: adding base turns orange dichromate towards yellow chromate; acid reverses it.

2. Which of the following is the strongest acid? [1 mark]

(A) p-Cl–C_6H_4COOH

(B) p-OH–C_6H_4COOH

(C) C_6H_5COOH

(D) p-NO_2–C_6H_4COOH

Correct Answer: (D) p-NO_2–C_6H_4COOH

Solution:

Concept:

- An acid becomes stronger when its conjugate base is stabilised; electron-withdrawing groups stabilise a benzoate ion.
- The para-nitro group has both electron-withdrawing inductive ($-I$) and resonance ($-R$) effects.

Step 1: Compare the substituent effects The NO_2 group withdraws electron density strongly and stabilises the conjugate base of para-nitrobenzoic acid. Chlorine has a withdrawing inductive effect but also a donating resonance effect; its overall acid-strengthening effect is weaker than that of nitro.

Step 2: Eliminate the remaining options Unsubstituted benzoic acid lacks an additional withdrawing group. The para-hydroxyl group donates electron density by resonance, which outweighs its inductive withdrawal here and makes the acid weaker. Therefore the qualitative acidity order is para-nitrobenzoic acid, para-chlorobenzoic acid, benzoic acid, then para-hydroxybenzoic acid.

Step 3: Conclusion p-Nitrobenzoic acid, p-$NO_2-C_6H_4COOH$, is the strongest acid listed. Hence, the correct option is (D).

Quick Tip to Solve: For para-substituted benzoic acids, select the group that withdraws most strongly by both induction and resonance.

3. Maltose is made up of: [1 mark]

(A) glucose and fructose

(B) glucose and galactose

(C) glucose and glucose

(D) glucose and ribose

Correct Answer: (C) glucose and glucose

Solution:

Concept:

- Maltose is a disaccharide formed from two glucose units joined by an $\alpha(1 \rightarrow 4)$ glycosidic linkage.
- Hydrolysis breaks the glycosidic bond and releases the constituent monosaccharides.

Step 1: Identify the monosaccharide units In maltose, carbon 1 of one glucose unit is linked through oxygen to carbon 4 of the other glucose unit. Both units are glucose; maltose does not contain a fructose or a galactose unit.

Step 2: Check the other combinations Glucose and fructose form sucrose, whereas glucose and

Quick Tip to Solve: Keep the three common pairs distinct: maltose has two glucose units, sucrose has glucose plus fructose, and lactose has glucose plus galactose.

galactose form lactose. Glucose and ribose is also not the composition of maltose. Its hydrolysis may be written as

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2\,C_6H_{12}O_6,$$

where both product molecules are glucose.

Step 3: Conclusion Maltose consists of glucose and glucose. Hence, the correct option is (C).

Quick Tip to Solve: Keep the three common pairs distinct: maltose has two glucose units, sucrose has glucose plus fructose, and lactose has glucose plus galactose.

4. The system that forms maximum boiling azeotrope is: [1 mark]

(A) CS_2 and acetone

(B) Benzene and toluene

(C) Ethanol and acetone

(D) Chloroform and acetone

Correct Answer: (D) Chloroform and acetone

Solution:

Concept:

- A maximum-boiling azeotrope arises from a sufficiently large negative deviation from Raoult's law.
- Stronger unlike-molecule attractions lower the total vapour pressure, so a higher temperature is needed for boiling.

Step 1: Identify the strongest unlike interactions Chloroform can form hydrogen bonds with the carbonyl oxygen of acetone. These attractions make the mixture harder to vaporise than expected for an ideal solution, producing negative deviation and a maximum-boiling azeotrope.

Step 2: Compare the other systems Carbon disulphide and acetone show positive deviation because unlike attractions are weaker than the relevant like attractions. Ethanol and acetone also show positive deviation because mixing disrupts the hydrogen-bonded ethanol network. Benzene and toluene form an approximately ideal solution and do not give the stated azeotrope.

Step 3: Conclusion Chloroform and acetone form the maximum-boiling azeotrope. Hence, the correct option is (D).

Quick Tip to Solve: Link maximum boiling to minimum vapour pressure: seek stronger attractions between unlike molecules, as in chloroform and acetone.

5. A zero-order reaction is one whose rate is independent of: [1 mark]

(A) Presence of light

(B) Concentration of the reactant

(C) Temperature of the reaction

(D) Pressure of the reaction

Correct Answer: (B) Concentration of the reactant

Solution:

Concept:

- For a zero-order reaction, the rate law is $r = k[\mathrm{A}]^0 = k$, where k is the rate constant and $[\mathrm{A}]$ is reactant concentration.
- Reaction order describes the concentration dependence of rate at fixed reaction conditions, not independence from every experimental condition.

Step 1: Apply the zero exponent Because a nonzero reactant concentration raised to the zero power equals 1, changing the concentration within the zero-order regime does not change the rate. The defining feature is therefore independence from reactant concentration.

Step 2: Check the other variables The rate constant can change with temperature, so zero order does not imply temperature independence. Light can alter the rate of a photochemical process. Pressure can change reaction conditions, and independence from pressure is not the general definition of zero order. Thus the concentration statement alone expresses the defining rate law.

Step 3: Conclusion A zero-order reaction has a rate independent of the concentration of its reactant. Hence, the correct option is (B).

Quick Tip to Solve: Write the rate law before selecting an option: a zero concentration exponent removes concentration from the rate expression, while k may still depend on temperature.

6. In the Arrhenius equation, when log k is plotted against 1/T, a straight line is obtained whose: [1 mark]

(A) slope is $\frac{A}{R}$ and intercept is E_a

(B) slope is A and intercept is $\frac{-E_a}{R}$

(C) slope is $\frac{-E_a}{RT}$ and intercept is log A

(D) slope is $\frac{-E_a}{2.303\,R}$ and intercept is log A

Correct Answer: (D) slope is $\frac{-E_a}{2.303\,R}$ and intercept is log A

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a is activation energy, R is the gas constant and T is absolute temperature.

Quick Tip to Solve: Check the logarithm base first: a $\log k$ plot uses $2.303R$ in the slope denominator, while an $\ln k$ plot uses R.

- Taking common logarithms introduces the conversion factor 2.303, since $\ln x = 2.303 \log x$.

Step 1: Convert to the straight-line form Taking base-10 logarithms gives

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right).$$

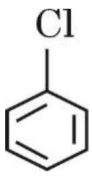
Compare this with $y = mx + c$, using $y = \log k$ and $x = 1/T$.

Step 2: Read and compare the coefficients The coefficient of $1/T$ is the slope, $-E_a/(2.303R)$, while the constant term is the intercept, $\log A$. Option (A) incorrectly gives slope A/R and intercept E_a; option (B) reverses unrelated quantities. Option (C) incorrectly includes T in the slope and omits the common-logarithm factor.

Step 3: Conclusion The slope is $-E_a/(2.303R)$ and the intercept is $\log A$. Hence, the correct option is (D).

Quick Tip to Solve: Check the logarithm base first: a $\log k$ plot uses $2.303R$ in the slope denominator, while an $\ln k$ plot uses R.

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

(A) 

(B) $CH_3-CH_2-CH_2-Cl$

(C) $CH_2=CH-Cl$

(D) $CH_2=CH-CH_2-Cl$

Correct Answer: (D) $CH_2=CH-CH_2-Cl$

Solution:

Concept:

- Allylic halides have the halogen on an sp^3 carbon adjacent to a carbon-carbon double bond.
- Resonance stabilisation of an allylic carbocation or substitution transition state increases nucleophilic substitution reactivity.

Step 1: Identify the allylic chloride In $CH_2=CH-CH_2Cl$, the chlorine-bearing carbon is next to the double bond. Ionisation can give an allylic carbocation with delocalised positive charge:

$$CH_2=CH-CH_2^+ \leftrightarrow CH_2^+-CH=CH_2.$$

Allylic stabilisation also favours the transition state of bimolecular substitution.

Step 2: Compare the other chlorides Normal propyl chloride is a primary alkyl halide but lacks allylic resonance stabilisation. In chlorobenzene and vinyl chloride, chlorine is bonded directly to an sp^2 carbon; the carbon-chlorine bond is stronger and has partial double-bond character. These compounds resist ordinary nucleophilic substitution much more than allyl chloride.

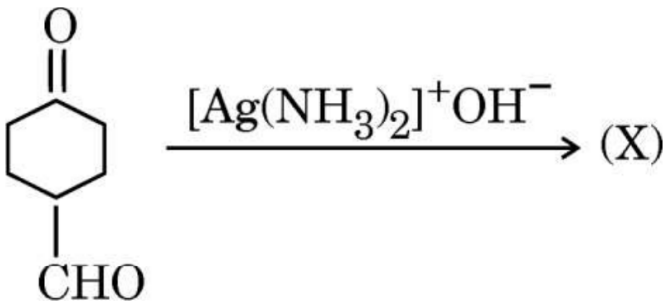
Step 3: Conclusion Allyl chloride, $CH_2=CH-CH_2Cl$, is the most reactive compound listed. Hence,

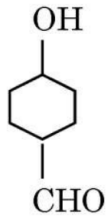
Quick Tip to Solve: Locate the carbon bonded to chlorine: chlorine on the carbon next to a double bond indicates an activated allylic halide; chlorine directly on the double bond indicates a resistant vinyl halide.

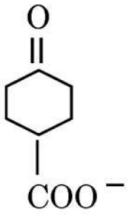
the correct option is (D).

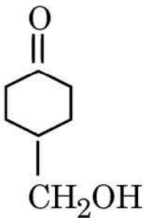
Quick Tip to Solve: Locate the carbon bonded to chlorine: chlorine on the carbon next to a double bond indicates an activated allylic halide; chlorine directly on the double bond indicates a resistant vinyl halide.

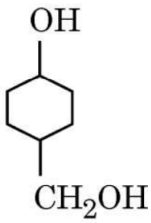
8. The product (X) obtained in the following reaction is: [1 mark]



(A) 

(B) 

(C) 

(D) 

(A) Cyclohexane ring bearing $-OH$ and $-CHO$ groups at opposite ring positions.
(B) Cyclohexanone ring bearing $-COO^-$ opposite the carbonyl group.
(C) Cyclohexanone ring bearing $-CH_2OH$ opposite the carbonyl group.
(D) Cyclohexane ring bearing $-OH$ and $-CH_2OH$ groups at opposite ring positions.

Correct Answer: (B) Cyclohexanone ring bearing $-COO^-$ opposite the carbonyl group.

Solution:

Concept:

- Tollens' reagent, $[Ag(NH_3)_2]^+$ in alkaline solution, oxidises an aldehyde group to a carboxylate group.
- An ordinary ketone group is not oxidised by this mild reagent; it remains unchanged.

Step 1: Identify the reacting groups The starting compound contains a ring ketone and an aldehyde substituent, $-CHO$, at the opposite ring carbon. Tollens reagent selectively oxidises the aldehyde.

Quick Tip to Solve: With alkaline Tollens reagent, change only the aldehyde to carboxylate and leave an ordinary ketone unchanged.

Step 2: Apply oxidation and compare the options The substituent changes as $-\mathrm{CHO} \longrightarrow -\mathrm{COO}^-$ in the alkaline medium, while the ring $\mathrm{C}=\mathrm{O}$ group is retained. Thus the structure in (B) fits both changes. Option (A) reduces the ketone and leaves the aldehyde; (C) reduces the aldehyde to an alcohol; (D) reduces both groups. None of these reductions occurs with Tollens reagent.

Step 3: Conclusion The product is the ring ketone bearing carboxylate. Hence, the correct option is (B).

Quick Tip to Solve: With alkaline Tollens reagent, change only the aldehyde to carboxylate and leave an ordinary ketone unchanged.

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

(A) CH_3CHO

(B) CH_3COCl

(C) CH_3COCH_3

(D) CH_3COOH

Correct Answer: (D) CH_3COOH

Solution:

Concept:

- Boiling requires overcoming intermolecular attractions; stronger attractions generally raise the boiling point.
- A carboxylic acid has both an O–H hydrogen-bond donor and a carbonyl oxygen acceptor, enabling strongly hydrogen-bonded association.

Step 1: Compare the available functional groups The compounds are ethanal, ethanoyl chloride, propanone and ethanoic acid. The first three are polar and show dipole–dipole attractions, but none contains an O–H or N–H group capable of donating a conventional hydrogen bond between its own molecules.

Step 2: Identify the strongest association Ethanoic acid, CH_3COOH, forms intermolecular hydrogen bonds and associates as cyclic dimers. More energy is needed to separate these associated molecules on boiling. This gives the acid a higher boiling point than the aldehyde, acyl chloride or ketone listed, despite the other compounds also possessing polar bonds.

Step 3: Conclusion CH_3COOH has the highest boiling point. Hence, the correct option is (D).

Quick Tip to Solve: For these small carbonyl compounds, look for a carboxylic acid group: its hydrogen-bonded association dominates.

10. Phenol does not undergo nucleophilic substitution reaction easily due to: [1 mark]

(A) Partial double bond character of C–OH bond

(B) Partial double bond character of C–C bond

(C) Acidic nature of phenol

(D) Instability of phenoxide ion

Correct Answer: (A) Partial double bond character of C–OH bond

Solution:

Concept:

- In phenol, an oxygen lone pair overlaps with the aromatic ring and participates in resonance.
- This conjugation gives the bond joining the ring carbon to oxygen partial double-bond character, making it shorter and stronger.

Step 1: Locate the bond that must break Replacing the hydroxyl group by a nucleophile requires cleavage of the bond between the aromatic carbon and oxygen. Resonance strengthens this $C-OH$ bond through partial double-bond character, so its cleavage is difficult under ordinary nucleophilic substitution conditions.

Step 2: Check the proposed explanations Option (A) describes the relevant strengthened bond. Partial double-bond character of a ring C–C bond in (B) does not identify the bond being substituted. The acidity of phenol in (C) concerns loss of a proton from oxygen, not replacement of the hydroxyl group. Option (D) is false because the phenoxide ion is stabilised by resonance.

Step 3: Conclusion The partial double-bond character of the $C-OH$ bond is responsible. Hence, the correct option is (A).

Quick Tip to Solve: Distinguish cleavage of O–H during acidic ionisation from cleavage of the aryl C–O bond during substitution.

11. The suitable Grignard reagent used for the synthesis of $(CH_3)_2CH–CH_2–OH$ with methanal is: [1 mark]

(A) $(CH_3)_2CH–CH_2MgBr$ / H_2O

(B) CH_3MgBr / H_2O

(C) $(CH_3)_2CHMgBr$ / H_2O

(D) $CH_3CH_2CH_2MgBr$ / H_2O

Correct Answer: (C) $(CH_3)_2CHMgBr$ / H_2O

Solution:

Concept:

- Methanal reacts with a Grignard reagent $RMgBr$, followed by hydrolysis, to give RCH_2OH.
- The carbon of methanal becomes the terminal CH_2OH carbon, adding one carbon to the organic group R.

Step 1: Work backwards from the target alcohol The required alcohol is $(CH_3)_2CHCH_2OH$. Removing

Quick Tip to Solve: For methanal plus a Grignard reagent, remove CH2OH from the product to read off the group attached to MgBr.

the terminal CH_2OH unit leaves $R = (CH_3)_2CH-$, the isopropyl group. Therefore the required reagent is isopropylmagnesium bromide.

Step 2: Write the sequence and reject the alternatives

$$(CH_3)_2CHMgBr + HCHO \longrightarrow (CH_3)_2CHCH_2OMgBr$$
$$(CH_3)_2CHCH_2OMgBr + H_2O \longrightarrow (CH_3)_2CHCH_2OH + Mg(OH)Br.$$

Option (A) would give an alcohol with five carbons; (B) gives ethanol; (D) gives straight-chain butan-1-ol. Only (C) gives the required branched four-carbon alcohol. Water is used after addition, since it would destroy the Grignard reagent if present initially.

Step 3: Conclusion The suitable reagent is $(CH_3)_2CHMgBr$, followed by hydrolysis. Hence, the correct option is (C).

Quick Tip to Solve: For methanal plus a Grignard reagent, remove CH2OH from the product to read off the group attached to MgBr.

12. All proteins on hydrolysis give: [1 mark]

(A) Enzymes

(B) α-amino acids

(C) Glucose

(D) Polypeptides

Correct Answer: (B) α-amino acids

Solution:

Concept:

- Proteins are polymers of α-amino acids joined through peptide bonds, $-CO-NH-$.
- Complete hydrolysis cleaves peptide bonds by addition of water and releases the constituent amino acids.

Step 1: Identify the structural units In an α-amino acid, the amino group and carboxyl group are attached to the same alpha carbon. These amino acids undergo condensation to produce peptide linkages and form polypeptide chains, which constitute proteins.

Step 2: Distinguish complete and partial hydrolysis Complete hydrolysis breaks the peptide chain into its constituent α-amino acids. Shorter polypeptides can occur during partial hydrolysis, but are not the final products intended here. Enzymes are commonly proteins themselves rather than the universal products of protein hydrolysis. Glucose is a carbohydrate monomer and is not released by cleavage of protein peptide bonds.

Step 3: Conclusion All proteins on complete hydrolysis give α-amino acids. Hence, the correct option is (B).

Quick Tip to Solve: Relate the hydrolysis product to the polymer linkage: peptide bonds give amino acids, while glycosidic bonds can give sugars.

13. Assertion (A): Fluoroacetic acid is stronger acid than chloroacetic acid.

Reason (R): This is due to greater electron withdrawing nature of F than Cl. [1 mark]

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

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

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

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

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

Solution:

Concept:

- A carboxylic acid is stronger when its conjugate base is more stabilised after release of H^+.
- An electron-withdrawing substituent exerts a negative inductive effect through sigma bonds and stabilises the carboxylate ion.

Step 1: Judge the assertion Fluoroacetic acid, FCH_2COOH, is stronger than chloroacetic acid, $ClCH_2COOH$. Both halogens occur at the same position relative to the carboxyl group, allowing their electron-withdrawing strengths to be compared directly. The assertion is true.

Step 2: Judge the reason Fluorine is more electronegative than chlorine and has a stronger electron-withdrawing inductive effect. Therefore the reason stating that F withdraws electrons more strongly than Cl is true.

Step 3: Check the explanatory link The stronger negative inductive effect of fluorine stabilises FCH_2COO^- more effectively than chlorine stabilises $ClCH_2COO^-$. This favours acid dissociation and directly explains the greater acidity. Option (B) incorrectly denies this link; (C) incorrectly calls the reason false; (D) incorrectly calls the assertion false.

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

Quick Tip to Solve: When substituent positions match, compare their negative inductive effects to predict carboxylic acid strength.

14. Assertion (A): p-nitroaniline is a weaker base than p-toluidine.

Reason (R): The electron donating –NO_2 group in p-nitroaniline makes it a weaker base. [1 mark]

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

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

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

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

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

Solution:

Concept:

- An amine acts as a base by donating its nitrogen lone pair to bind H^+; greater lone-pair availability generally increases basicity.
- A nitro group withdraws electrons by inductive and resonance effects, while a methyl group donates electron density by its positive inductive effect.

Step 1: Judge the assertion In para-nitroaniline, the $-NO_2$ group withdraws electron density and reduces the availability of the amino nitrogen lone pair. In para-toluidine, the $-CH_3$ group donates electron density. Thus para-nitroaniline is the weaker base, so the assertion is true.

Step 2: Judge the reason The reason calls $-NO_2$ an electron-donating group. This is incorrect: the nitro group is strongly electron withdrawing. The printed reason is therefore false, even though its statement that para-nitroaniline is weaker is consistent with the assertion.

Step 3: Select the assertion–reason combination The correct combination is a true assertion and a false reason. Options (A) and (B) require a true reason and are excluded. Option (D) requires a false assertion and is also excluded. The electron-withdrawing nature of the nitro group, rather than electron donation, accounts for the reduced basicity.

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

Quick Tip to Solve: Read the sign of the substituent effect carefully: NO2 withdraws electrons, whereas CH3 increases electron density.

15. Assertion (A): $\Delta_{mix}H$ for an ideal solution is not equal to zero.

Reason (R): A–B interactions in an ideal solution are same as between A–A and B–B interactions.

[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 ideal solution has similar intermolecular attractions between unlike molecules (A–B) and like molecules (A–A and B–B).
- The enthalpy of mixing is $\Delta_{\text{mix}}H = H_{\text{solution}} - (H_A + H_B)$. For an ideal solution, $\Delta_{\text{mix}}H = 0$.

Step 1: Examine the assertion Mixing breaks some A–A and B–B attractions and forms A–B attractions. In an ideal solution, the energy needed to separate the original molecules equals the energy released when unlike molecules interact. Thus mixing produces no net enthalpy change. The assertion that $\Delta_{\text{mix}}H \neq 0$ is false.

Step 2: Examine the reason The stated similarity of A–B, A–A and B–B interactions is the defining microscopic condition for an ideal solution. The reason is therefore true.

Step 3: Check the assertion–reason relationship The true reason accounts for zero enthalpy of mixing; it cannot support the false assertion of a nonzero value. Options (A) and (B) incorrectly call the assertion true, while (C) also incorrectly calls 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 ideal solutions, recall both zero enthalpy of mixing and zero volume change before judging an assertion.

16. Assertion (A): Separation of Zr and Hf is difficult.

Reason (R): Zr and Hf are radioactive. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Lanthanide contraction is the gradual reduction in atomic and ionic radii across the lanthanide series, arising from poor shielding by $4f$ electrons.
- Zirconium (Zr) and hafnium (Hf) belong to the same group. Their nearly equal sizes lead to very similar chemical properties.

Step 1: Examine the assertion Zirconium is a $4d$-series element and hafnium is its $5d$-series counterpart. Lanthanide contraction largely offsets the expected increase in size for Hf. Consequently, their common $+4$ ions have nearly equal radii and similar chemical behaviour, making separation difficult. The assertion is true.

Step 2: Examine the reason Zr and Hf are not classified as radioactive elements: both possess stable naturally occurring isotopes. The existence of some radioactive isotopes does not make the statement that both elements are radioactive correct. The reason is false.

Step 3: Check whether the reason explains the assertion The difficulty of separation follows from their closely similar sizes and chemical properties, rather than radioactivity. Options (A) and (B) wrongly accept the reason; option (D) wrongly rejects the assertion.

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

Quick Tip to Solve: For Zr–Hf similarity, connect lanthanide contraction to nearly equal ionic radii and similar chemical properties.

Section B (10 marks)

17. What happens when D-glucose is treated with the following reagents?

(a) H_2N–OH

(b) $(CH_3CO)_2O$ [2 marks]

Solution:

Concept:

- The open-chain form of D-glucose, $CHO - (CHOH)_4 - CH_2OH$, contains one aldehyde group and five hydroxyl groups.

Quick Tip to Solve: Identify the functional group attacked: hydroxylamine tests the carbonyl, whereas acetylation counts all five hydroxyl groups.

- Hydroxylamine converts a carbonyl group into an oxime, $C = N - OH$; acetic anhydride acetylates each hydroxyl group.

Step 1: Reaction with hydroxylamine The aldehyde group reacts with NH_2OH, replacing its carbonyl oxygen with $N - OH$ through condensation. D-glucose forms glucose oxime with elimination of water:

$$CHO - (CHOH)_4 - CH_2OH + NH_2OH \longrightarrow HON = CH - (CHOH)_4 - CH_2OH + H_2O.$$

This reaction supports the presence of a carbonyl group in glucose. The hydroxyl groups remain unchanged.

Step 2: Reaction with acetic anhydride All five hydroxyl groups undergo acetylation, each $-OH$ becoming $-OCOCH_3$. D-glucose gives glucose pentaacetate. The acetylation stoichiometry is

$$C_6H_{12}O_6 + 5(CH_3CO)_2O \longrightarrow C_{16}H_{22}O_{11} + 5CH_3COOH.$$

Formation of a pentaacetate shows that glucose contains five hydroxyl groups; each consumes one molecule of acetic anhydride.

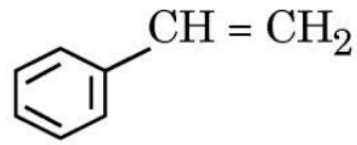
Step 3: Conclusion (a) Hydroxylamine forms glucose oxime. (b) Acetic anhydride forms glucose pentaacetate.

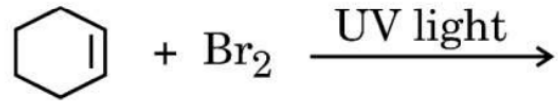
Quick Tip to Solve: Identify the functional group attacked: hydroxylamine tests the carbonyl, whereas acetylation counts all five hydroxyl groups.

18(a). Draw the structures of major monohalo products in each of the following reactions:

(i)

(ii) [2 marks]

(i) 

(ii) 

Solution:

Concept:

- Addition of HBr to an unsymmetrical alkene without peroxide follows Markovnikov orientation; the more stable carbocation controls the major product.
- Under UV light, bromination at an allylic carbon proceeds by a free-radical substitution. An allylic carbon is a saturated carbon adjacent to a $C = C$ bond.

Quick Tip to Solve: Read the conditions first: HBr without peroxide gives benzylic Markovnikov addition; UV bromination gives allylic substitution.

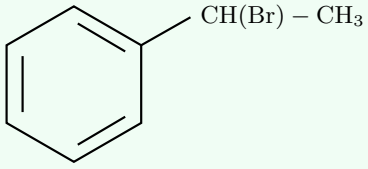
Step 1: (i) Addition of HBr to styrene In $C_6H_5 - CH = CH_2$, proton addition to the terminal carbon gives the resonance-stabilised benzylic carbocation $C_6H_5 - CH^+ - CH_3$. Bromide attacks it, giving

$$C_6H_5 - CH = CH_2 + HBr \longrightarrow C_6H_5 - CH(Br) - CH_3.$$

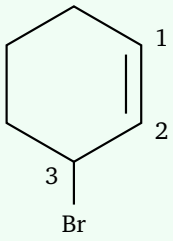
This orientation is favoured over formation of a terminal primary carbocation.

Step 2: (ii) Bromination of cyclohexene under UV light UV light initiates radical bromination. An allylic hydrogen is replaced by bromine via a resonance-stabilised cyclohexenyl radical, forming 3-bromocyclohex-1-ene and HBr. The equivalent allylic positions give the same constitutional product. The ring double bond remains: UV light and the request for a monohalo product select substitution, whereas addition would give a dibromo product.

(i)



(ii)



Major monohalo products: (i) benzylic bromide; (ii) allylic bromide.

Step 3: Conclusion (i) $C_6H_5 - CH(Br) - CH_3$, 1-bromo-1-phenylethane. (ii) 3-bromocyclohex-1-ene. The product structures are shown above.

Quick Tip to Solve: Read the conditions first: HBr without peroxide gives benzylic Markovnikov addition; UV bromination gives allylic substitution.

OR

18(b). Give reasons for the following:

(i) Grignard reagent should be prepared under anhydrous conditions.

(ii) Alkyl halides give alcohol with aqueous KOH whereas in the presence of alcoholic KOH, alkenes are formed. [2 marks]

Solution:

Concept:

- A Grignard reagent, $RMgX$, contains a strongly polar carbon-magnesium bond; its carbon acts as a strong base and reacts with substances containing an acidic hydrogen.
- Hydroxide can act as a nucleophile in substitution or as a base in elimination. The solvent changes which behaviour predominates.

Step 1: (i) Prevent decomposition by moisture Water protonates the carbon of a Grignard reagent,

Quick Tip to Solve: Associate aqueous KOH with replacement of X by OH, and hot alcoholic KOH with loss of HX across adjacent carbons.

destroying the reagent and forming the corresponding hydrocarbon:

$$\mathrm{RMgX} + \mathrm{H_2O} \longrightarrow \mathrm{RH} + \mathrm{Mg(OH)X}.$$

Thus, even traces of moisture consume the reagent before it can undergo the intended reaction. It must therefore be prepared in dry ether using dry apparatus under anhydrous conditions.

Step 2: (ii) Compare aqueous and alcoholic KOH In aqueous KOH, hydroxide ions act mainly as nucleophiles and replace the halogen atom, giving an alcohol by substitution:

$$\mathrm{R{-}X} + \mathrm{KOH(aq)} \longrightarrow \mathrm{R{-}OH} + \mathrm{KX}.$$

In alcoholic KOH, basic action is favoured. A hydrogen is removed from the carbon adjacent to the carbon bearing the halogen (the β-carbon), while the halogen leaves; a carbon-carbon double bond forms. For example,

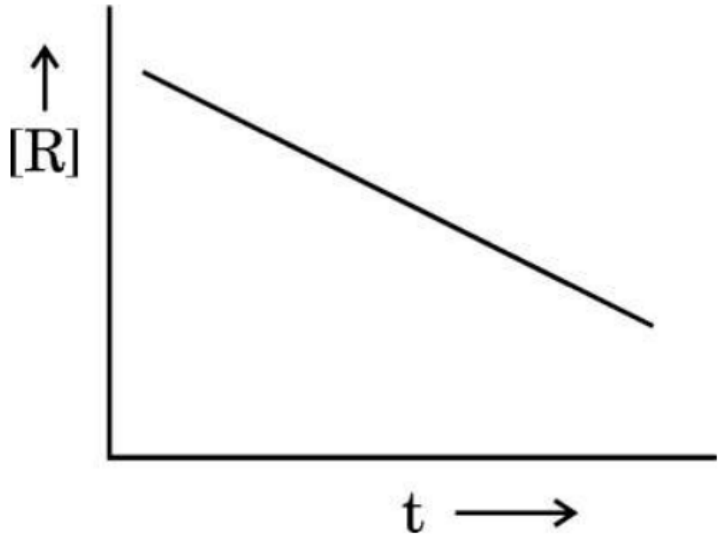
$$\mathrm{CH_3CH_2Br} + \mathrm{KOH(alc)} \xrightarrow{\Delta} \mathrm{CH_2{=}CH_2} + \mathrm{KBr} + \mathrm{H_2O}.$$

This elimination of hydrogen halide is called dehydrohalogenation; it requires an available β-hydrogen.

Step 3: Conclusion Grignard reagents require anhydrous conditions because water converts them into hydrocarbons. Aqueous KOH favours nucleophilic substitution to alcohols, whereas alcoholic KOH favours elimination to alkenes.

Quick Tip to Solve: Associate aqueous KOH with replacement of X by OH, and hot alcoholic KOH with loss of HX across adjacent carbons.

19. For a chemical reaction R → P, the variation in the concentration [R] vs time t plot is given as:
(a) Predict the order of the reaction and write the unit of rate constant (k) for this order of reaction.
(b) What is the slope of the curve? [2 marks]



Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[\mathrm{R}]/dt = k$, where k is the rate constant.
- The integrated zero-order rate equation is $[\mathrm{R}] = [\mathrm{R}]_0 - kt$, where $[\mathrm{R}]_0$ is the initial concentration and t is time.

Step 1: (a) Identify the order and the unit of k The graph of reactant concentration against time is a straight line sloping downwards. Compare its form with the equation of a straight line, $y = c + mt$:

$$[\mathrm{R}] = [\mathrm{R}]_0 - kt.$$

A constant decrease in concentration per unit time means the rate does not depend on concentration, which identifies zero-order kinetics. Since k equals the rate, its unit is concentration divided by time:

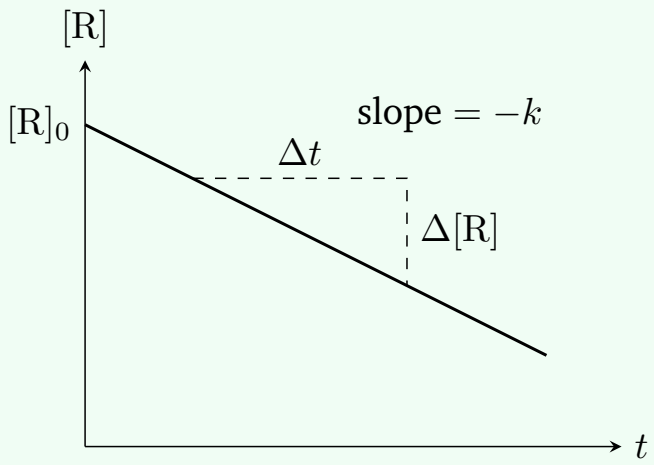
$$[k] = \mathrm{mol\,L^{-1}\,s^{-1}}.$$

Equivalently, the unit is $\mathrm{M\,s^{-1}}$. These are the standard units when concentration is in molarity and time is in seconds.

Step 2: (b) Determine the slope For two points on the straight line,

$$m = \frac{[\mathrm{R}]_2 - [\mathrm{R}]_1}{t_2 - t_1} = \frac{-k(t_2 - t_1)}{t_2 - t_1} = -k.$$

The slope is negative because the reactant is consumed as time increases. Its magnitude equals the positive rate constant; the vertical intercept represents the initial reactant concentration.



A zero-order concentration-time line with slope $-k$.

Step 3: Conclusion (a) The reaction is zero order and k has unit $\mathrm{mol\,L^{-1}\,s^{-1}}$. (b) The slope of the concentration-time line is $-k$.

Quick Tip to Solve: Match the plotted variables to the integrated law: a straight [R]-versus-t line has slope -k for zero order.

20. Write the chemical equations when:

(a) Ethanal is treated with 2,4-dinitrophenylhydrazine?

(b) Propanone is treated with Zn(Hg) and conc. HCl? [2 marks]

Solution:

Concept:

- An aldehyde or ketone reacts with 2,4-dinitrophenylhydrazine (2,4-DNP) to form a 2,4-dinitrophenylhydrazone by condensation, with elimination of water.
- Clemmensen reduction uses zinc amalgam, $\mathrm{Zn(Hg)}$, and concentrated hydrochloric acid to convert a carbonyl group $>\mathrm{C{=}O}$ into a methylene group $>\mathrm{CH_2}$.

Step 1: (a) Reaction of ethanal with 2,4-DNP The terminal $-\mathrm{NH_2}$ group of the hydrazine reagent reacts with the carbonyl group of ethanal. The oxygen of the carbonyl and two hydrogens from the terminal amino group are eliminated as water, and a $\mathrm{C{=}N}$ bond forms:

$$\mathrm{CH_3CHO + H_2N{-}NH{-}C_6H_3(NO_2)_2} \longrightarrow \mathrm{CH_3CH{=}N{-}NH{-}C_6H_3(NO_2)_2 + H_2O.}$$

In this equation the two nitro groups occupy positions 2 and 4 on the phenyl ring relative to the hydrazine substituent. The product is ethanal 2,4-dinitrophenylhydrazone, obtained as a yellow-orange precipitate.

Step 2: (b) Clemmensen reduction of propanone Zinc amalgam in concentrated hydrochloric acid reduces the ketonic carbonyl carbon to $-\mathrm{CH_2}-$, leaving the three-carbon skeleton intact:

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

Here $[H]$ denotes reducing hydrogen supplied by the reaction conditions. The organic product is propane; under these conditions the carbonyl is fully reduced to a methylene group rather than stopping at an alcohol.

Step 3: Conclusion Ethanal forms its 2,4-dinitrophenylhydrazone with loss of water, while propanone undergoes Clemmensen reduction to propane.

Quick Tip to Solve: For 2,4-DNP replace carbonyl O by N-NH-Ar; for Zn(Hg)/HCl replace carbonyl O by two H atoms.

21. Calculate the potential of Iron electrode in which the concentration of Fe^{2+} ion is 0.01 M.
($E^{\circ}_{Fe^{2+}/Fe}$ = − 0.45 V at 298 K)
[Given: log 10 = 1] [2 marks]

Solution:

Concept:

- Electrode potentials are written as reduction potentials. The iron half-reaction involves $n = 2$ electrons:
$$\mathrm{Fe}^{2+} + 2\mathrm{e}^- \longrightarrow \mathrm{Fe(s)}.$$
- At 298 K, the Nernst equation is $E = E^\circ - (0.0591/n)\log Q$. A pure solid has unit activity, and the dilute ion activity is represented by its molar concentration relative to 1 M.

Step 1: Write the reaction quotient and Nernst equation For reduction of iron(II) ions to solid iron, the reaction quotient is
$$Q = \frac{a_{\mathrm{Fe(s)}}}{a_{\mathrm{Fe}^{2+}}} = \frac{1}{[\mathrm{Fe}^{2+}]}.$$
Here the concentration is used numerically in molarity. Therefore,
$$E = E^\circ - \frac{0.0591}{2}\log\frac{1}{[\mathrm{Fe}^{2+}]} = E^\circ + \frac{0.0591}{2}\log[\mathrm{Fe}^{2+}].$$
The sign follows directly from the reduction half-reaction; iron metal itself contributes no concentration term.

Step 2: Substitute the ion concentration Given $[\mathrm{Fe}^{2+}] = 0.01 = 10^{-2}$ M, the supplied $\log 10 = 1$ gives $\log(0.01) = -2$. Substituting the standard reduction potential,
$$\begin{aligned} E &= -0.45 + \frac{0.0591}{2}(-2) \\ &= -0.45 - 0.0591 \\ &= -0.5091\ \mathrm{V}. \end{aligned}$$
The concentration is below the standard value, so the reduction potential becomes more negative than E°, consistent with the calculation.

Step 3: Conclusion The iron electrode potential at 298 K is $\boxed{E = -0.5091\ \mathrm{V} \approx -0.51\ \mathrm{V}}$.

Quick Tip to Solve: For a metal-ion/metal reduction electrode use E = E standard + (0.0591/n) log ion concentration; dilution lowers E.

Section C (21 marks)

22. The following initial rate data were obtained for the reaction:

2NO (g) + Br_2 (g) $\rightarrow$ 2NOBr (g)

(a) What is the order with respect to NO and Br_2 in the reaction?

(b) Calculate the rate constant (k).

(c) Determine the rate of reaction when concentration of NO and Br_2 are 0.4 M and 0.2 M, respectively.

[3 marks]

Expt. No.	[NO]/mol L^{-1}	[Br_2]/mol L^{-1}	Initial Rate (mol L^{-1} s^{-1})
1	0·05	0·05	$1{\cdot}0 \times 10^{-3}$
2	0·05	0·15	$3{\cdot}0 \times 10^{-3}$
3	0·15	0·05	$9{\cdot}0 \times 10^{-3}$

Solution:

Concept:

- The experimental rate law is $r = k[\mathrm{NO}]^m[\mathrm{Br_2}]^n$, where m, n are individual orders and k is the rate constant. The balanced equation alone does not establish the orders.
- Compare experiments keeping one concentration constant; the rate ratio then isolates the order in the other reactant. Overall order is $m + n$.

Step 1: (a) Find each individual order Experiments 1 and 2 have the same NO concentration. Bromine concentration triples from 0.05 to $0.15\,\mathrm{mol\,L^{-1}}$, and the rate triples:

$$\frac{3.0 \times 10^{-3}}{1.0 \times 10^{-3}} = \left(\frac{0.15}{0.05}\right)^n, \quad 3 = 3^n, \quad n = 1.$$

Experiments 1 and 3 have the same bromine concentration. NO concentration triples and the rate increases ninefold:

$$\frac{9.0 \times 10^{-3}}{1.0 \times 10^{-3}} = \left(\frac{0.15}{0.05}\right)^m, \quad 9 = 3^m, \quad m = 2.$$

The reaction is therefore second order in NO, first order in bromine, and third order overall.

Step 2: (b) Calculate the rate constant Use experiment 1 in $r = k[\mathrm{NO}]^2[\mathrm{Br_2}]$:

$$k = \frac{1.0 \times 10^{-3}}{(0.05)^2(0.05)} = \frac{1.0 \times 10^{-3}}{1.25 \times 10^{-4}} = 8.0\,\mathrm{L^2 mol^{-2} s^{-1}}.$$

Rate has units $\mathrm{mol\,L^{-1}s^{-1}}$. Dividing by concentration cubed gives the displayed units of k.

Step 3: (c) Calculate the requested rate At the same temperature, insert the new concentrations $[\mathrm{NO}] = 0.4\,\mathrm{mol\,L^{-1}}$ and $[\mathrm{Br_2}] = 0.2\,\mathrm{mol\,L^{-1}}$:

$$r = 8.0(0.4)^2(0.2) = 8.0(0.16)(0.2) = 0.256\,\mathrm{mol\,L^{-1}s^{-1}}.$$

Quick Tip to Solve: Compare experiments 1 and 2 for bromine, then 1 and 3 for NO: tripling causes rate factors 3 and 9, giving orders 1 and 2.

Step 4: Conclusion (a) NO: order 2; Br_2: order 1. (b) $k = 8.0\,L^2mol^{-2}s^{-1}$. (c) $r = 0.256\,mol\,L^{-1}s^{-1}$.

Quick Tip to Solve: Compare experiments 1 and 2 for bromine, then 1 and 3 for NO: tripling causes rate factors 3 and 9, giving orders 1 and 2.

23. When a certain conductivity cell was filled with 0.05 M KCl solution, it has a resistance of 100 ohm at 25°C. When the same cell was filled with 0.02 M $AgNO_3$ solution, the resistance was 90 ohm. Calculate the conductivity and molar conductivity of $AgNO_3$ solution.

(Given: Conductivity of 0.05 M KCl solution = 1.35×10^{-2} ohm^{-1} cm^{-1}) [3 marks]

Solution:

Concept:

- Conductance is $G = 1/R$, where R is resistance. Conductivity is $\kappa = G(l/A)$, with cell constant $l/A = \kappa R$, where l is electrode separation and A is electrode area.
- For conductivity in S cm^{-1} and concentration C in mol L^{-1}, molar conductivity is $\Lambda_m = 1000\kappa/C$. The factor 1000 converts litres into cubic centimetres.

Step 1: Calibrate the cell using KCl The KCl solution has known conductivity $\kappa_{KCl} = 1.35 \times 10^{-2}$ S cm^{-1} and measured resistance $R_{KCl} = 100\,\Omega$. Hence

$$\frac{l}{A} = \kappa_{KCl} R_{KCl} = (1.35 \times 10^{-2})(100) = 1.35\,cm^{-1}.$$

The cell constant depends on the geometry of this cell. Since the same cell is used for the second solution, its value remains unchanged; the KCl concentration is not used as the $AgNO_3$ concentration.

Step 2: Find the conductivity of silver nitrate For $AgNO_3$, $R = 90\,\Omega$, so $G = 1/90$ S. Therefore

$$\kappa_{AgNO_3} = \frac{l/A}{R} = \frac{1.35}{90} = 0.015\,S\,cm^{-1} = 1.50 \times 10^{-2}\,\Omega^{-1}cm^{-1}.$$

This conductivity exceeds that of the calibration solution, consistent with the smaller resistance measured in the same cell.

Step 3: Convert conductivity into molar conductivity The silver nitrate concentration is $C = 0.02$ mol L^{-1}. Using the concentration of this solution gives

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000(0.015)}{0.02} = 750\,S\,cm^2mol^{-1}.$$

Equivalently, 0.02 mol L^{-1} $= 2.0 \times 10^{-5}$ mol cm^{-3}, and dividing conductivity by this concentration gives the same result and units.

Step 4: Conclusion The $AgNO_3$ solution has conductivity $1.50 \times 10^{-2}\,\Omega^{-1}cm^{-1}$ and molar conductivity $750\,\Omega^{-1}cm^2mol^{-1}$.

Quick Tip to Solve: First calculate the fixed cell constant from KCl; then divide by the AgNO3 resistance and use only its 0.02 M concentration for molar conductivity.

24. (a) Which of the following is an allylic halide?

(i) CH_3–CH=CH–Br

(ii) CH_2=CH–CH(Br)–CH_3

(b) Out of chlorobenzene and 2,4,6-trinitrochlorobenzene, which is more reactive towards nucleophilic substitution and why?

(c) Which isomer of C_4H_9Cl has the lowest boiling point? [3 marks]

Solution:

Concept:

- In an allylic halide, the halogen is bonded to an sp^3-hybridised carbon adjacent to a carbon-carbon double bond. A halogen directly bonded to a double-bond carbon gives a vinylic halide.
- Electron-withdrawing nitro groups at positions ortho or para to the halogen facilitate nucleophilic aromatic substitution by stabilising its anionic intermediate through resonance.
- Among comparable constitutional isomers, increased branching usually lowers boiling point by reducing effective surface contact and London dispersion attractions.

Step 1: (a) Identify the allylic halide In (i), $CH_3 - CH = CH - Br$, bromine is attached directly to one of the sp^2 carbons of the double bond. This is a vinylic halide.

In (ii), $CH_2 = CH - CH(Br) - CH_3$, bromine is attached to a saturated sp^3 carbon immediately next to the double bond. It is therefore the allylic halide. The defining feature is the position of the carbon carrying bromine, rather than merely the presence of a double bond somewhere in the molecule.

Step 2: (b) Explain the difference in aromatic substitution reactivity 2,4,6-Trinitrochlorobenzene is more reactive towards nucleophilic substitution than chlorobenzene. Its three $-NO_2$ groups lie at the two ortho positions and the para position relative to chlorine. Their electron-withdrawing effect makes the carbon bearing chlorine more susceptible to nucleophilic attack.

In the addition step, the resulting negatively charged intermediate is stabilised by delocalisation of charge into these nitro groups. Subsequent elimination of chloride restores aromaticity. Chlorobenzene lacks this stabilisation; moreover, resonance between chlorine and the ring gives its C–Cl bond partial double-bond character, making substitution difficult under ordinary conditions.

Step 3: (c) Identify the isomer with the lowest boiling point The most highly branched isomer is tert-butyl chloride, $(CH_3)_3CCl$, whose IUPAC name is 2-chloro-2-methylpropane. Its compact shape provides less effective surface contact between molecules than the less branched butyl chlorides. Consequently its London dispersion attractions are weaker, so less energy is needed to separate its molecules into the vapour phase and its boiling point is the lowest among the isomers.

Step 4: Conclusion (a) Compound (ii), $CH_2 = CH - CH(Br) - CH_3$. (b) 2,4,6-Trinitrochlorobenzene, because its ortho/para nitro groups stabilise the anionic substitution intermediate. (c) tert-Butyl chloride, or 2-chloro-2-methylpropane.

Quick Tip to Solve: Locate the carbon bonded to Br: adjacent to C=C means allylic, directly on C=C means vinylic. For the butyl chlorides, choose the most branched isomer.

25. (a) Write the formula for the following coordination compound:

Potassium tetrahydroxidozincate (II)

(b) Arrange the following complexes in the increasing order of conductivity of their solution:

$[Cr(NH_3)_5Cl]Cl_2$, $[Cr(NH_3)_3Cl_3]$, $[Cr(NH_3)_6]Cl_3$

(c) Identify the type of isomerism exhibited by the following complexes:

(i) $[Co(NH_3)_5NO_2]^{2+}$

(ii) $[Co(en)_3]Cl_3$ [3 marks]

Solution:

Concept:

- A complex formula follows from the metal oxidation state, ligand charges and the counter-ions needed for electrical neutrality.
- At comparable concentration, conductivity generally increases with the number of mobile ions produced; ligands inside square brackets do not dissociate as counter-ions.
- An ambidentate ligand can show linkage isomerism. An octahedral complex with three bidentate ligands can show optical isomerism.

Step 1: (a) Balance the complex-ion charge Zinc(II) has charge $+2$ and each hydroxido ligand, OH^-, has charge -1. Thus the charge of the tetrahydroxidozincate ion is $+2 + 4(-1) = -2$. Two potassium ions are needed to neutralise it:

$$K_2[Zn(OH)_4].$$

Step 2: (b) Count the ions released into solution The neutral complex $[Cr(NH_3)_3Cl_3]$ has no counter-ions and contributes essentially no ions by dissociation. The other two complexes dissociate as

$$[Cr(NH_3)_5Cl]Cl_2 \longrightarrow [Cr(NH_3)_5Cl]^{2+} + 2\,Cl^-,$$

$$[Cr(NH_3)_6]Cl_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 3\,Cl^-.$$

They give three and four ions per formula unit, respectively. Therefore, for comparable solutions, the increasing conductivity order is

$$[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3.$$

Step 3: (c) Identify the available isomerism (i) In $[Co(NH_3)_5NO_2]^{2+}$, the nitrite ligand can coordinate through nitrogen (nitro) or through oxygen (nitrito). These different donor atoms give linkage isomerism; the oxygen-bound form is written $[Co(NH_3)_5(ONO)]^{2+}$. (ii) In $[Co(en)_3]Cl_3$, each ethane-1,2-diamine ligand (en) occupies two adjacent coordination positions. Three such chelate rings surround cobalt in an octahedral arrangement and form two non-superimposable mirror images, conventionally denoted Δ and Λ. Hence this complex exhibits optical isomerism.

Step 4: Conclusion (a) $K_2[Zn(OH)_4]$; (b) $[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3$; (c)(i) linkage isomerism, (ii) optical isomerism.

Quick Tip to Solve: For conductivity, count only the ions outside the coordination sphere plus the intact complex ion; for isomerism, look for an ambidentate ligand or three chelate rings.

26. Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (B) and (C). The compound (B) on oxidation with PCC gives compound (D) which upon treatment with dilute NaOH and subsequent heating gives compound (E). Compound (E) on catalytic hydrogenation gives compound (C). The compound (D) is oxidized further to give compound (F) which is found to be a monobasic acid (Molecular weight = 60). Identify the compounds (A), (B), (C), (D), (E) and (F). [3 marks]

Solution:

Concept:

- $LiAlH_4$ reduces an ester R_1COOR_2 to two alcohols, R_1CH_2OH and R_2OH. PCC oxidises a primary alcohol to an aldehyde.
- An aldehyde with alpha-hydrogen undergoes aldol addition in dilute alkali; heating the aldol eliminates water to form an alpha,beta-unsaturated aldehyde.
- Further oxidation preserves the aldehyde carbon skeleton and gives the corresponding carboxylic acid. Complete catalytic hydrogenation can reduce both the carbon-carbon double bond and the carbonyl group.

Step 1: Identify F, then work back to D and B The monobasic acid with molecular weight 60 is ethanoic acid, CH_3COOH: its formula mass is $2(12) + 4(1) + 2(16) = 60$. Therefore F is ethanoic acid. The aldehyde that oxidises to it is ethanal, so D is CH_3CHO. The primary alcohol that gives ethanal with PCC is ethanol, hence B is CH_3CH_2OH:

$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow{\text{oxidation}} CH_3COOH.$$

Step 2: Follow the aldol condensation and hydrogenation Ethanal contains alpha-hydrogens. Two molecules undergo aldol addition, followed by dehydration on heating:

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

$$CH_3CH(OH)CH_2CHO \xrightarrow{\text{heat}} CH_3CH{=}CHCHO + H_2O.$$

Thus E is but-2-enal (crotonaldehyde), $CH_3CH{=}CHCHO$. The stated conversion of E to the alcohol C requires complete hydrogenation of both unsaturated bonds:

$$CH_3CH{=}CHCHO + 2\,H_2 \xrightarrow{\text{catalyst}} CH_3CH_2CH_2CH_2OH.$$

Consequently, C is butan-1-ol. Reducing only the carbon-carbon double bond would give butanal, which would not be one of the alcohols produced by ester reduction.

Step 3: Reconstruct A and check its molecular formula A must be an ester yielding ethanol from its acyl portion and butan-1-ol from its alkoxy portion. Ethanol identifies the acyl group as ethanoate, and butan-1-ol identifies the alkyl group as n-butyl. Hence A is butyl ethanoate:

$$CH_3COOCH_2CH_2CH_2CH_3 \xrightarrow[\text{then water}]{LiAlH_4} CH_3CH_2OH + CH_3CH_2CH_2CH_2OH.$$

The ester contains six carbon atoms, twelve hydrogen atoms and two oxygen atoms, agreeing with $C_6H_{12}O_2$. Both reduction products and every subsequent conversion therefore fit the data.

Quick Tip to Solve: Begin with the acid of molecular weight 60, then trace backwards to ethanal and ethanol; use the aldol product to determine the ester's four-carbon alkoxy group.

Step 4: Conclusion A: butyl ethanoate, $CH_3COOCH_2CH_2CH_2CH_3$; B: ethanol, CH_3CH_2OH; C: butan-1-ol, $CH_3CH_2CH_2CH_2OH$; D: ethanal, CH_3CHO; E: but-2-enal, $CH_3CH{=}CHCHO$; F: ethanoic acid, CH_3COOH.

Quick Tip to Solve: Begin with the acid of molecular weight 60, then trace backwards to ethanal and ethanol; use the aldol product to determine the ester's four-carbon alkoxy group.

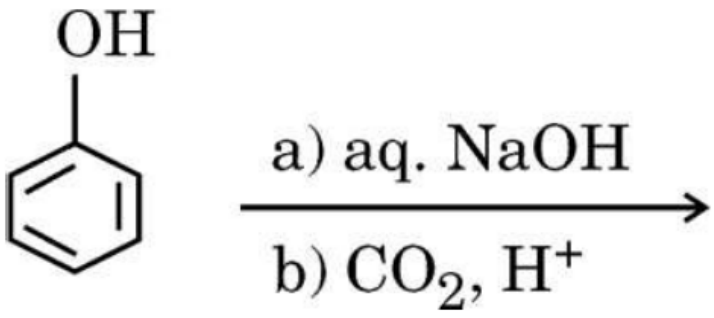
27. (a) Write the mechanism of the following reaction:

$CH_3CH_2OH \xrightarrow{H^+,\,443\,K} CH_2{=}CH_2$

(b) Write the main product in each of the following reactions:

(i) $CH_3{-}CH_2{-}CH{=}CH_2 \xrightarrow[b)\ 3H_2O_2/OH^-]{a)\ B_2H_6}$?

(ii) [3 marks]



Solution:

Concept:

- Acid-catalysed dehydration converts an alcohol to an alkene by eliminating water. Protonation changes the poor leaving group OH^- into the good leaving group H_2O.
- Hydroboration-oxidation hydrates an alkene in the anti-Markovnikov direction: the hydroxyl group appears on the less substituted carbon.
- In the Kolbe reaction, sodium phenoxide reacts with carbon dioxide and, after acidification, gives chiefly 2-hydroxybenzoic acid (salicylic acid).

Step 1: (a) Protonate the alcohol oxygen A lone pair on ethanol's oxygen accepts a proton from the acid, giving protonated ethanol (an oxonium ion):

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2{}^+.$$

Protonation is necessary because unprotonated hydroxide is a poor leaving group, whereas the protonated group can depart as neutral water.

Step 2: (a) Remove water to form the carbocation In the standard acid-catalysed dehydration mechanism, the carbon-oxygen bond in protonated ethanol breaks and water leaves, forming the ethyl carbocation. This is the slow, rate-determining step:

$$CH_3CH_2OH_2{}^+ \longrightarrow CH_3CH_2{}^+ + H_2O.$$

Quick Tip to Solve: Protonate the alcohol before eliminating water; place OH at the terminal carbon for hydroboration and COOH ortho to OH for the Kolbe reaction.

The initial protonation makes this departure possible: water leaves as a neutral molecule rather than as the strongly basic hydroxide ion.

Step 3: (a) Remove a beta-proton and regenerate the acid The carbocation loses a proton from the adjacent methyl group, the beta-carbon. The electrons of this carbon-hydrogen bond form the carbon-carbon double bond, giving ethene and regenerating the acid catalyst:

$$CH_3CH_2^+ \longrightarrow CH_2{=}CH_2 + H^+.$$

Combining protonation, loss of water and loss of a beta-proton gives the overall dehydration at the stated temperature:

$$CH_3CH_2OH \xrightarrow[443\,K]{H^+} CH_2{=}CH_2 + H_2O.$$

Step 4: (b)(i) Apply anti-Markovnikov hydration In but-1-ene, $CH_3CH_2CH{=}CH_2$, boron adds to the terminal, less substituted carbon during hydroboration with B_2H_6. Alkaline hydrogen peroxide then replaces the carbon-boron bond by a carbon-oxygen bond. Thus the hydroxyl group is placed on the terminal carbon and the main product is butan-1-ol:

$$CH_3CH_2CH{=}CH_2 \xrightarrow[2.\,H_2O_2/OH^-]{1.\,B_2H_6} CH_3CH_2CH_2CH_2OH.$$

Step 5: (b)(ii) Apply the Kolbe reaction to phenol Aqueous sodium hydroxide first converts phenol to sodium phenoxide:

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

The phenoxide ring is activated towards carboxylation with CO_2, predominantly at the ortho position. Subsequent treatment with acid gives salicylic acid, in which the hydroxyl and carboxyl groups occupy adjacent ring positions:

$$C_6H_5ONa \xrightarrow{CO_2} o\text{-}HOC_6H_4COONa \xrightarrow{H^+} o\text{-}HOC_6H_4COOH.$$

Step 6: Conclusion (a) Ethanol forms ethene through protonation and elimination, regenerating the acid catalyst. (b)(i) The product is butan-1-ol, $CH_3CH_2CH_2CH_2OH$; (ii) it is salicylic acid (2-hydroxybenzoic acid), $o\text{-}HOC_6H_4COOH$.

Quick Tip to Solve: Protonate the alcohol before eliminating water; place OH at the terminal carbon for hydroboration and COOH ortho to OH for the Kolbe reaction.

28. Answer the following: (any three)

(a) What is peptide linkage?

(b) What type of bonds hold a DNA double helix together?

(c) Which one of the following is a polysaccharide?

Sucrose, Glucose, Starch, Fructose

(d) Give one example each for water-soluble vitamins and fat-soluble vitamins. [3 marks]

Solution:

Concept:

- A peptide linkage is an amide bond formed by condensation of the carboxyl group of one amino acid with the amino group of another.
- Complementary DNA bases form hydrogen bonds, whereas a polysaccharide contains many monosaccharide units joined through glycosidic bonds.
- Vitamins are grouped by solubility: vitamins B and C are water-soluble, while vitamins A, D, E and K are fat-soluble.

Step 1: (a) Identify the peptide linkage The linkage $-CO-NH-$ joining two amino acid residues is called a peptide linkage. The $-COOH$ group of one amino acid reacts with the $-NH_2$ group of another, eliminating one molecule of water and forming this amide linkage. Repeated peptide linkages connect amino acids in a protein chain.

Step 2: (b) State the bonds between the DNA strands Hydrogen bonds between complementary nitrogenous bases hold the two strands of the DNA double helix together. Adenine pairs with thymine through two hydrogen bonds, and guanine pairs with cytosine through three. The covalent phosphodiester bonds instead form the sugar-phosphate backbone of each individual strand.

Step 3: (c) Classify the listed carbohydrates Starch is a polysaccharide made up of many glucose units. Sucrose is a disaccharide, while glucose and fructose are monosaccharides. Thus only starch belongs to the requested category.

Step 4: (d) Give examples from both vitamin groups Vitamin C is a water-soluble vitamin, and vitamin A is a fat-soluble vitamin. These provide one example for each of the two solubility classes asked for in the question.

Step 5: Conclusion (a) Peptide linkage: $-CO-NH-$. (b) Hydrogen bonds. (c) Starch. (d) Water-soluble: vitamin C; fat-soluble: vitamin A. Any three of these four parts may be attempted.

Quick Tip to Solve: Remember DNA strand-to-strand bonds as hydrogen bonds; reserve phosphodiester bonds for the backbone of each strand.

Section D (8 marks)

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

29. Batteries and fuel cells are very useful forms of galvanic cell. Any battery or cell that we use as a source of electrical energy is basically a galvanic cell. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries – primary batteries and secondary batteries.

In the primary batteries, the reaction occurs only once and after use over a period of time the battery becomes dead and cannot be reused again, whereas the secondary batteries are rechargeable.

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. To solve this problem, galvanic cells are designed in such a way that energy of combustion of fuels is directly converted into electrical energy, and these are known as fuel cells. One such fuel cell was used in the Apollo space programme.

Answer the following questions: [4 marks]

29(a). How do primary batteries differ from secondary batteries? [1 mark]

Solution:

Concept:

- A galvanic cell converts chemical energy of a spontaneous redox reaction into electrical energy.
- Recharging requires reversal of the discharge reaction by passing an external current through the cell.

Step 1: Describe a primary battery In a primary battery, the discharge reaction is not practically reversible. Once the active reactants have been consumed, the battery cannot be restored by recharging and is discarded. A dry cell is a familiar example.

Step 2: Describe a secondary battery In a secondary battery, the discharge reaction is reversible. An external electrical supply drives the reverse reaction and regenerates the reactants, allowing repeated charging and use. A lead storage battery is an example. The distinction is rechargeability, rather than a requirement that one type must have a higher voltage.

Step 3: Conclusion Primary batteries cannot be recharged after discharge, whereas secondary batteries can be recharged by reversing their cell reaction with an external current.

Quick Tip to Solve: Compare the reversibility of the discharge reaction: irreversible means primary; reversible and rechargeable means secondary.

29(b). The cell potential of Mercury cell is 1.35 V, and remains constant during its life. Give reason. [1 mark]

Solution:

Concept:

- A cell potential depends on the activities of the species appearing in its net cell reaction.

Quick Tip to Solve: Add the mercury-cell half-reactions first: hydroxide ions cancel, revealing why electrolyte concentration does not change the voltage.

- Pure solids and pure liquids have constant unit activity; they do not introduce a changing concentration into the reaction quotient.

Step 1: Write the net mercury-cell reaction In a mercury cell, zinc amalgam is oxidised and mercury(II) oxide is reduced. The overall discharge reaction is

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

Hydroxide ions involved in the half-reactions cancel when those reactions are added.

Step 2: Relate the reaction to constant voltage No dissolved ion with a concentration that changes during discharge appears in the overall reaction. Thus the electrolyte concentration does not introduce a changing reaction quotient, and the cell potential remains nearly constant at $1.35\,\mathrm{V}$ during its useful life, until the active material is exhausted.

Step 3: Conclusion The mercury cell maintains a potential of $1.35\,\mathrm{V}$ because its net reaction contains no ions whose concentration changes during discharge.

Quick Tip to Solve: Add the mercury-cell half-reactions first: hydroxide ions cancel, revealing why electrolyte concentration does not change the voltage.

29(c). Write the reactions involved in the recharging of the lead storage battery. [2 marks]

Solution:

Concept:

- A lead storage battery is a secondary cell: external electrical energy reverses the discharge reaction during recharging.
- Lead sulphate on the two electrodes is converted back into lead and lead dioxide, respectively, while sulphuric acid is regenerated.

Step 1: Write the reduction during charging At the negative electrode, lead sulphate accepts electrons and is converted back into metallic lead. This electrode is the cathode during charging because reduction occurs here:

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

Sulphate ions return to the electrolyte as the discharged negative plate is restored.

Step 2: Write the oxidation during charging At the positive electrode, lead sulphate is oxidised to lead dioxide. This electrode is the anode during charging:

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

Lead is oxidised from oxidation state $+2$ in lead sulphate to $+4$ in lead dioxide. An external source removes the released electrons from this electrode and supplies them to the negative electrode.

Step 3: Combine the charging half-reactions Adding the two half-reactions cancels two electrons. The regenerated hydrogen and sulphate ions restore sulphuric acid in the electrolyte. The net reaction

Quick Tip to Solve: Reverse the discharge equation to obtain charging: both lead sulphate plates disappear and sulphuric acid is regenerated.

is the reverse of the discharge reaction:

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

Consequently, the concentration of sulphuric acid increases during charging.

Step 4: Conclusion Recharging reduces $PbSO_4$ to Pb at the negative electrode and oxidises $PbSO_4$ to PbO_2 at the positive electrode. Overall, $2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$.

Quick Tip to Solve: Reverse the discharge equation to obtain charging: both lead sulphate plates disappear and sulphuric acid is regenerated.

OR

29(c). Write two advantages of fuel cells over other galvanic cells. [2 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy through an electrochemical reaction.
- In an ordinary battery, a finite amount of reactant is stored inside the cell; its operation is limited by consumption of these reactants.

Step 1: Compare the duration of operation Fuel cells can operate continuously as long as fuel and oxidant are supplied and products are removed. For example, supplying hydrogen and oxygen keeps a hydrogen–oxygen fuel cell working. Unlike a conventional cell whose stored active materials become exhausted, the fuel cell does not need periodic replacement or recharging merely because its initial supply of reactants has been consumed.

Step 2: Compare efficiency and cleanliness Fuel cells convert chemical energy directly into electrical energy with high efficiency. In the hydrogen–oxygen fuel cell, the overall reaction is

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

Its reaction product is water, so operation does not produce polluting combustion gases. Thus this fuel cell provides a clean source of electricity. This cleanliness refers to the cell reaction itself.

Step 3: Conclusion Two advantages are: (i) continuous operation while fuel and oxidant are supplied, and (ii) efficient, clean electrical-energy generation, with water as the product in the hydrogen–oxygen fuel cell.

Quick Tip to Solve: Compare reactant supply first: a fuel cell is fed continuously, while an ordinary battery stores a finite quantity of reactants.

30. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds whereas 'The Crystal Field Theory' for coordination compounds is based on the effect of different crystal fields (provided by 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. The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron. Coordination compounds find extensive applications in metallurgical processes, analytical and medicinal chemistry.

Answer the following questions: [4 marks]

30(a). What is crystal field splitting energy? [1 mark]

Solution:

Concept:

- The five d-orbitals of a free metal ion have the same energy and are called degenerate orbitals.
- Ligands produce an electrostatic field that splits these orbitals into groups of different energies.

Step 1: Identify the splitting caused by ligands When ligands approach the central metal ion, their repulsion with electrons in different d-orbitals is unequal because the orbitals point in different directions. Consequently, the original degeneracy is removed.

Step 2: Define the energy separation Crystal field splitting energy, denoted by Δ, is the energy difference between the groups of d-orbitals formed in the ligand field. For an octahedral complex, it is $\Delta_o = E(e_g) - E(t_{2g})$, where t_{2g} is the lower-energy group and e_g is the higher-energy group.

Step 3: Conclusion Crystal field splitting energy is the energy gap between the sets of d-orbitals produced by the ligand field; in an octahedral complex this gap is Δ_o.

Quick Tip to Solve: Define the gap between the split orbital groups, rather than the energy of either group alone.

30(b). Give reason for the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory. [1 mark]

Solution:

Concept:

- In an octahedral field, the metal d-orbitals split into lower-energy t_{2g} and higher-energy e_g groups.
- Absorption of visible light can promote a d-electron across the gap Δ_o; the observed colour is complementary to the absorbed light.

Step 1: Find the metal-ion electron configuration Water is neutral, so the metal in $[Ti(H_2O)_6]^{3+}$ is Ti^{3+}. Titanium has configuration $[Ar]3d^2 4s^2$; removal of three electrons gives Ti^{3+} : $[Ar]3d^1$. Its single d-electron occupies a lower-energy t_{2g} orbital.

Step 2: Explain the absorption and observed colour The electron absorbs visible light of energy $h\nu = \Delta_o$ and undergoes a d-d transition from t_{2g} to e_g. Absorption mainly in the green region leaves the transmitted light with the complementary violet colour.

Quick Tip to Solve: For titanium(III), identify the single d electron, then link its excitation across the octahedral gap to the complementary colour.

Step 3: Conclusion The complex is violet because its $3d^1$ electron undergoes a $t_{2g} \rightarrow e_g$ transition by absorbing visible light, and the remaining transmitted light appears violet.

Quick Tip to Solve: For titanium(III), identify the single d electron, then link its excitation across the octahedral gap to the complementary colour.

30(c). $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why. [Atomic No.: Cr = 24, Ni = 28] [2 marks]

Solution:

Concept:

- A complex with one or more unpaired electrons is paramagnetic; a complex in which all electrons are paired is diamagnetic.
- Find the metal oxidation state before counting d-electrons. Ligand strength and geometry determine their arrangement in the complex.

Step 1: Count unpaired electrons in the chromium complex Since NH_3 is neutral, the chromium oxidation state in $[Cr(NH_3)_6]^{3+}$ is $+3$. Chromium has configuration $[Ar]3d^5 4s^1$, so Cr^{3+} is $3d^3$. In the octahedral field its configuration is $t_{2g}^3 e_g^0$: the three electrons occupy the three lower-energy orbitals singly according to Hund's rule. Thus three unpaired electrons remain. No pairing is necessary to make two $3d$-orbitals available for d^2sp^3 hybridisation.

Step 2: Explain pairing in the nickel complex In $[Ni(CN)_4]^{2-}$, four cyanide ligands contribute charge -4, so $x - 4 = -2$ gives nickel oxidation state $x = +2$. Nickel is $[Ar]3d^8 4s^2$, hence Ni^{2+} is $3d^8$. The strong-field ligand CN^- causes pairing of the $3d$-electrons, leaving one $3d$-orbital vacant for dsp^2 hybridisation. The resulting square-planar complex has all eight d-electrons paired and therefore no unpaired electrons.

Step 3: Conclusion $[Cr(NH_3)_6]^{3+}$ is paramagnetic because it has three unpaired electrons, whereas square-planar $[Ni(CN)_4]^{2-}$ is diamagnetic because all its electrons are paired.

Quick Tip to Solve: Use Cr(III) as d3 and Ni(II) as d8; cyanide makes the nickel complex square planar with paired electrons.

OR

30(c). Explain why $[Fe(CN)_6]^{3-}$ is an inner orbital complex, whereas $[Fe(H_2O)_6]^{3+}$ is an outer orbital complex. [Atomic No.: Fe = 26] [2 marks]

Solution:

Concept:

- The oxidation state of iron is $+3$ in both complexes, so Fe^{3+} has the electronic configuration $[Ar]\,3d^5$.
- In valence bond theory, an octahedral inner orbital complex uses two $3d$ orbitals in d^2sp^3 hybridisa-

Quick Tip to Solve: First find the metal's oxidation state; for this d^5 ion, strong-field cyanide leaves two inner orbitals vacant, while weak-field water leaves all five occupied.

tion; an outer orbital complex uses two $4d$ orbitals in sp^3d^2 hybridisation.

Step 1: Cyanide produces an inner orbital complex In $[Fe(CN)_6]^{3-}$, six cyanide ions contribute -6, so iron must contribute $+3$. Cyanide is a strong-field ligand: it causes the five $3d$ electrons to pair as far as possible, occupying three $3d$ orbitals with occupancies $2, 2, 1$. Thus two $3d$ orbitals become vacant. These two inner $3d$ orbitals, one $4s$ and three $4p$ orbitals form six d^2sp^3 hybrid orbitals to accept ligand lone pairs. The complex is octahedral and has one unpaired electron.

Step 2: Water produces an outer orbital complex In $[Fe(H_2O)_6]^{3+}$, water is neutral, so iron is again Fe^{3+}. Water is a weak-field ligand and does not cause pairing of the five $3d$ electrons. Each of the five $3d$ orbitals remains singly occupied, leaving no vacant pair of inner $3d$ orbitals for bonding. One $4s$, three $4p$ and two outer $4d$ orbitals therefore hybridise as sp^3d^2. This octahedral complex has five unpaired electrons.

Step 3: Conclusion $[Fe(CN)_6]^{3-}$ uses inner $3d$ orbitals and has d^2sp^3 hybridisation, whereas $[Fe(H_2O)_6]^{3+}$ uses outer $4d$ orbitals and has sp^3d^2 hybridisation.

Quick Tip to Solve: First find the metal's oxidation state; for this d^5 ion, strong-field cyanide leaves two inner orbitals vacant, while weak-field water leaves all five occupied.

Section E (15 marks)

31. Answer any five questions of the following:

(a) N,N-diethyl-benzenesulphonamide is insoluble in alkali. Give reason.

(b) Aniline does not undergo Friedel-Crafts reaction. Why?

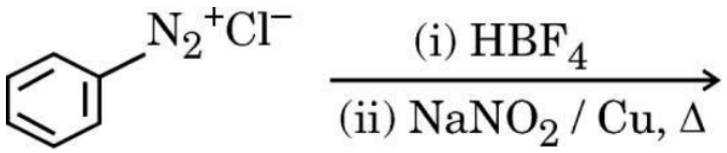
(c) Write a simple chemical test to distinguish between methylamine and aniline.

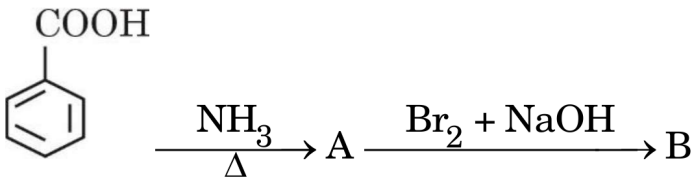
(d) Write the chemical reaction involved in Gabriel phthalimide synthesis.

(e) How will you convert aniline to p-bromoaniline?

(f) Complete the following reaction:

(g) Write the structures of A and B in the following reaction: [5 marks]





Solution:

Concept:

- Sulphonamides dissolve in alkali only when an acidic $N-H$ hydrogen can be removed to form a salt. A Lewis acid can bind aniline's nitrogen lone pair.
- Primary aliphatic amines react with nitrous acid to liberate nitrogen, whereas aniline forms a diazonium salt at 273–278 K. Protecting aniline's amino group controls bromination.
- Gabriel synthesis gives primary amines by alkylating phthalimide and hydrolysing the product. Hofmann bromamide degradation converts an amide into a primary amine with one fewer carbon atom.

Step 1: (a) Insolubility of N,N-diethyl-benzenesulphonamide Its structure is $C_6H_5SO_2N(C_2H_5)_2$. Both hydrogens originally attached to nitrogen have been replaced by ethyl groups, so there is no acidic $N-H$ hydrogen. Alkali cannot deprotonate this sulphonamide to form a water-soluble ionic salt; hence it remains insoluble in alkali.

Step 2: (b) Why aniline does not undergo Friedel-Crafts reaction Aniline's nitrogen lone pair coordinates with the Lewis acid catalyst $AlCl_3$, forming a salt-like Lewis acid-base complex. This withdraws electron density from the amino group and strongly deactivates the benzene ring towards electrophilic substitution. Hence the usual Friedel-Crafts alkylation or acylation fails.

Step 3: (c) Distinguish methylamine from aniline Treat separate samples with freshly prepared nitrous acid, using $NaNO_2$ and dilute HCl at 273–278 K. Methylamine gives brisk evolution of colourless

Quick Tip to Solve: For (f), read both reagent lines: nitrite with copper gives nitrobenzene. For (e), protect the amino group before bromination to avoid the tribromo product.

nitrogen:

$$CH_3NH_2 + HNO_2 \longrightarrow CH_3OH + N_2 \uparrow + H_2O.$$

Aniline instead gives benzenediazonium chloride, without brisk nitrogen evolution at this low temperature:

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

As confirmation, couple this cold diazonium solution with phenol in alkaline medium: an orange azo dye forms.

Step 4: (d) Gabriel phthalimide synthesis First form potassium phthalimide, then react it with a primary alkyl halide $R - X$. Hydrolysis liberates the primary amine RNH_2:

$$C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O,$$
$$C_6H_4(CO)_2NK + R - X \longrightarrow C_6H_4(CO)_2NR + KX,$$
$$C_6H_4(CO)_2NR + 2NaOH \xrightarrow{\Delta} C_6H_4(COONa)_2 + RNH_2.$$

Here $C_6H_4(CO)_2NH$ denotes cyclic phthalimide. The method prepares primary aliphatic amines; aryl halides do not undergo the required nucleophilic substitution.

Step 5: (e) Convert aniline into p-bromoaniline Protect $-NH_2$ by acetylation to form acetanilide, brominate in glacial acetic acid, and hydrolyse the resulting p-bromoacetanilide:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH,$$
$$C_6H_5NHCOCH_3 + Br_2 \xrightarrow{CH_3COOH} p\text{-}BrC_6H_4NHCOCH_3 + HBr,$$
$$p\text{-}BrC_6H_4NHCOCH_3 + H_2O \xrightarrow{H^+,\Delta} p\text{-}BrC_6H_4NH_2 + CH_3COOH.$$

The para product predominates because the acetamido group is ortho/para directing and the para position is less sterically hindered. Acid hydrolysis initially gives the ammonium salt; neutralisation liberates p-bromoaniline. Direct bromination of aniline with bromine water would give 2,4,6-tribromoaniline.

Step 6: (f) Complete the diazonium reaction HBF_4 first forms benzenediazonium tetrafluoroborate. The printed second treatment, $NaNO_2/Cu$ with heat, replaces the diazonium group by $-NO_2$:

$$C_6H_5N_2^+Cl^- + HBF_4 \longrightarrow C_6H_5N_2^+BF_4^- + HCl,$$
$$C_6H_5N_2^+BF_4^- + NaNO_2 \xrightarrow{Cu,\Delta} C_6H_5NO_2 + N_2 + NaBF_4.$$

Therefore the required product is nitrobenzene. Heating the tetrafluoroborate alone would give fluorobenzene, but the stated nitrite/copper treatment gives nitrobenzene.

Step 7: (g) Identify A and B Benzoic acid reacts with ammonia to form ammonium benzoate, which loses water on heating to give benzamide, A. Bromine and sodium hydroxide then cause Hofmann bromamide degradation, yielding aniline, B:

$$C_6H_5COOH + NH_3 \xrightarrow{\Delta} C_6H_5C(=O)NH_2 + H_2O,$$
$$C_6H_5CONH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O.$$

Quick Tip to Solve: For (f), read both reagent lines: nitrite with copper gives nitrobenzene. For (e), protect the amino group before bromination to avoid the tribromo product.

Thus A has the structure $C_6H_5 - C(=O) - NH_2$, and B has the structure $C_6H_5 - NH_2$. The carbonyl carbon is removed in the degradation.

Step 8: Conclusion Answers to all seven alternatives are given above; any five may be selected. The reaction products are a primary alkylamine in (d), p-bromoaniline in (e), nitrobenzene in (f), and A = benzamide, B = aniline in (g).

Quick Tip to Solve: For (f), read both reagent lines: nitrite with copper gives nitrobenzene. For (e), protect the amino group before bromination to avoid the tribromo product.

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

(1) The melting and boiling points of Zn, Cd and Hg are low.

(2) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

(3) E° value of Cu^{2+}/Cu is + 0.34 V.

(ii) Complete and balance the following chemical equations:

(1) $KMnO_4 \xrightarrow{heat}$?

(2) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow$? [5 marks]

Solution:

Concept:

- Metallic bonding depends on the electrons available for delocalisation. A completely filled d^{10} subshell contributes little to the strong metallic bonding characteristic of many transition metals.
- Redox behaviour is related to the stability of the product electronic configuration: Cr^{3+} is $3d^3$, whereas Mn^{2+} is half-filled $3d^5$.
- The standard reduction potential reflects the overall energy balance of atomisation, ionisation and hydration. Redox equations must conserve both atoms and total charge.

Step 1: (i)(1) Explain the low melting and boiling points Zn, Cd and Hg have completely filled $(n-1)d^{10}$ subshells and outer ns^2 configurations. Their filled d orbitals do not provide unpaired d electrons for the strong metallic bonding seen in many other members of the d-block. Consequently their metallic bonds are relatively weak. Less energy is required to separate the atoms, so their melting and boiling points are low compared with most transition metals. Mercury has especially weak metallic bonding and is liquid at room temperature.

Step 2: (i)(2) Compare the two d-four ions Although both ions initially have d^4 configurations, they attain stable configurations by opposite changes. Chromium(II) readily loses an electron:

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

The product Cr^{3+} has a stable $3d^3$ configuration (t_{2g}^3 in an octahedral field). By donating an electron, Cr^{2+} reduces another species and therefore acts as a strong reducing agent. Manganese(III) readily gains an electron:

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

This produces the especially stable half-filled $3d^5$ configuration. By accepting an electron, Mn^{3+}

Quick Tip to Solve: For the two d^4 ions, write their stable products first: Cr^{3+} means electron loss (reducing), whereas Mn^{2+} means electron gain (oxidising). Check the dichromate equation's charge as well as its atoms.

oxidises another species and therefore acts as a strong oxidising agent.

Step 3: (i)(3) Account for the positive copper reduction potential Converting solid copper into aqueous Cu^{2+} requires atomisation of copper and removal of two electrons. Copper has high atomisation and ionisation enthalpies; removal of the second electron disrupts the stable $3d^{10}$ configuration of Cu^{+}. The energy released by hydration of Cu^{2+} is insufficient to compensate for these energy requirements. Thus oxidation of copper to aqueous Cu^{2+} is energetically unfavourable relative to the standard hydrogen electrode, while the reverse reduction has a positive standard potential:

$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s), \qquad E^{\circ} = +0.34\,V.$$

Step 4: (ii)(1) Complete thermal decomposition of permanganate On heating, potassium permanganate gives potassium manganate, manganese dioxide and oxygen. The balanced equation is

$$2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2.$$

Potassium and manganese each have two atoms on either side, and the eight oxygen atoms on the left equal $4 + 2 + 2$ on the right. Manganese is reduced from $+7$ to $+6$ and $+4$, while part of the oxygen is oxidised from -2 to zero.

Step 5: (ii)(2) Complete oxidation of iodide by dichromate In acidic solution dichromate is reduced to chromium(III), while iodide is oxidised to iodine. The half-reactions are

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

Adding them and cancelling electrons gives

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

Both sides contain two chromium atoms, seven oxygen atoms, fourteen hydrogen atoms and six iodine atoms. The left-hand charge is $-2 - 6 + 14 = +6$, equal to the charge of the two Cr^{3+} ions on the right.

Step 6: Conclusion Zn, Cd and Hg have weak metallic bonding; Cr^{2+} is reducing because it forms stable Cr^{3+}, while Mn^{3+} is oxidising because it forms half-filled Mn^{2+}. Copper's hydration enthalpy cannot compensate for its atomisation and ionisation requirements, giving $E^{\circ}_{Cu^{2+}/Cu} = +0.34\,V$. The completed reactions produce $K_2MnO_4 + MnO_2 + O_2$ on heating permanganate, and $2Cr^{3+} + 3I_2 + 7H_2O$ from the given acidic dichromate reaction.

Quick Tip to Solve: For the two d^4 ions, write their stable products first: Cr^{3+} means electron loss (reducing), whereas Mn^{2+} means electron gain (oxidising). Check the dichromate equation's charge as well as its atoms.

OR

32(b). (i) Out of Cu_2Cl_2 and $CuCl_2$, which is more stable in aqueous solution and why?
(ii) Write the general electronic configuration of f-block elements.
(iii) Predict which of the following will be coloured in aqueous solution and why?
Sc^{3+}, Fe^{3+}, Zn^{2+}
[Atomic number: Sc = 21, Fe = 26, Zn = 30]
(iv) How can you obtain potassium dichromate from sodium chromate?
(v) Why do transition metals and their compounds show catalytic activities? [5 marks]

Solution:

Concept:

- The stability of an oxidation state in water depends on the energy required to form the ion and its hydration enthalpy. Stronger hydration can stabilise a more highly charged ion.
- Inner transition elements fill the $(n-2)f$ subshell. Ions with partially filled d subshells can absorb visible light, whereas d^0 and d^{10} ions have no ordinary d-d transitions.
- Acidification converts yellow chromate ions into orange dichromate ions. The lower solubility of potassium dichromate allows its crystallisation from a mixture containing sodium dichromate and potassium chloride.
- Transition metals can adopt several oxidation states and form intermediate complexes. Their surfaces can adsorb reactants and provide a reaction pathway with lower activation energy.

Step 1: (i) Compare the copper chlorides in water Cu_2Cl_2 contains copper in the $+1$ oxidation state, whereas $CuCl_2$ contains copper in the $+2$ oxidation state. In aqueous solution, Cu^{2+} has a much more negative hydration enthalpy than Cu^+. This greater energy release on hydration compensates for the energy needed to remove the second electron from copper. Consequently, $CuCl_2$ is more stable in aqueous solution.
The instability of aqueous Cu^+ is also shown by its disproportionation:

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s).$$

Thus, the filled $3d^{10}$ configuration of isolated Cu^+ does not by itself determine its stability in water.

Step 2: (ii) State the general configuration of f-block elements The general outer electronic configuration is

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2,$$

where n is the principal quantum number of the outermost shell. The differentiating electron enters the $(n-2)f$ subshell. The $4f$ series consists of the lanthanoids and the $5f$ series consists of the actinoids; a neighbouring d subshell may contain one electron.

Step 3: (iii) Determine which aqueous ion is coloured Remove the $4s$ electrons before the $3d$ electrons

Quick Tip to Solve: For the colour test, remove 4s electrons first and count the remaining d electrons: Sc(III) is d-zero, Fe(III) is d-five and Zn(II) is d-ten. For dichromate preparation, remember acidification first and potassium chloride second.

when forming these ions:

$$\mathrm{Sc}^{3+} : [\mathrm{Ar}]\, 3d^0,$$
$$\mathrm{Fe}^{3+} : [\mathrm{Ar}]\, 3d^5,$$
$$\mathrm{Zn}^{2+} : [\mathrm{Ar}]\, 3d^{10}.$$

Fe^{3+} is coloured in aqueous solution because it has a partially filled $3d$ subshell. In the ligand field of the surrounding water molecules, the d orbitals have different energies, so electronic excitation can lead to absorption of light and the appearance of colour. Sc^{3+} and Zn^{2+} are colourless: the former has no d electrons and the latter has a completely filled d subshell, so ordinary d-d excitation is unavailable.

Step 4: (iv) Prepare potassium dichromate from sodium chromate First acidify a solution of sodium chromate with dilute sulphuric acid. Yellow chromate changes to orange dichromate:

$$2\mathrm{Na_2CrO_4} + \mathrm{H_2SO_4} \longrightarrow \mathrm{Na_2Cr_2O_7} + \mathrm{Na_2SO_4} + \mathrm{H_2O}.$$

The underlying ionic equilibrium is

$$2\mathrm{CrO_4^{2-}} + 2\mathrm{H^+} \rightleftharpoons \mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O}.$$

Add potassium chloride to the sodium dichromate solution and concentrate and cool it:

$$\mathrm{Na_2Cr_2O_7} + 2\mathrm{KCl} \longrightarrow \mathrm{K_2Cr_2O_7} + 2\mathrm{NaCl}.$$

Potassium dichromate, being less soluble than sodium dichromate, crystallises out and can be separated.

Step 5: (v) Explain catalytic activity Transition metals and their compounds show catalytic activity because their variable oxidation states enable them to take part in successive electron-transfer steps and then return to their original state. Their ability to form intermediate complexes also brings reactants together and offers an alternative reaction pathway with lower activation energy.

Solid transition metals additionally adsorb reactant molecules on their surfaces. Adsorption brings the molecules close together and can weaken their bonds, facilitating the reaction. For example, finely divided nickel catalyses hydrogenation, while $\mathrm{V_2O_5}$ catalyses the oxidation of $\mathrm{SO_2}$ to $\mathrm{SO_3}$.

Step 6: Conclusion (i) $\mathrm{CuCl_2}$ is more stable in water due to stronger hydration of Cu^{2+}. (ii) The general configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. (iii) Fe^{3+} is coloured; Sc^{3+} and Zn^{2+} are colourless. (iv) Acidify sodium chromate, add KCl, and crystallise $\mathrm{K_2Cr_2O_7}$. (v) Variable oxidation states, intermediate complex formation and surface adsorption explain catalytic activity.

Quick Tip to Solve: For the colour test, remove 4s electrons first and count the remaining d electrons: Sc(III) is d-zero, Fe(III) is d-five and Zn(II) is d-ten. For dichromate preparation, remember acidification first and potassium chloride second.

33(a). (i) At the same temperature, CO_2 gas is more soluble in water than O_2 gas. Which one of them will have higher value of K_H and why?

(ii) How does the size of blood cells change when placed in an aqueous solution containing more than 0.9% (mass/volume) sodium chloride?

(iii) 1 molal aqueous solution of an electrolyte A_2B_3 is 60% ionized. Calculate the boiling point of the solution.

(Given: K_b for H_2O = 0.52 K kg mol^{-1}) [5 marks]

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the gas partial pressure and x its mole fraction in solution. At fixed temperature and pressure, a larger K_H corresponds to lower solubility.
- Osmosis is the movement of solvent across a semipermeable membrane towards the solution of higher osmotic pressure. A hypertonic medium draws water out of blood cells.
- Elevation of boiling point is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the molal elevation constant and m the molality. For dissociation into ν ions with degree of ionization α, $i = 1+(\nu-1)\alpha$.

Step 1: (i) Compare the Henry's law constants At the same gas partial pressure, Henry's law gives $x = p/K_H$. Thus, greater solubility means a larger dissolved mole fraction and a smaller Henry's law constant. Since CO_2 is more soluble in water than O_2 at the given temperature, $K_H(CO_2) < K_H(O_2)$. The less soluble oxygen therefore has the higher value of K_H.

Step 2: (ii) Determine the direction of water movement A 0.9% (mass/volume) sodium chloride solution is isotonic with blood cells. A solution containing more than this concentration is hypertonic: its osmotic pressure is greater than that of the cell contents. The cell membrane acts as a semipermeable membrane, so water passes out of the cells into the surrounding solution by exosmosis. As the cells lose water, their volume decreases and they shrink (crenation).

Step 3: (iii) Calculate the van't Hoff factor One formula unit of A_2B_3 produces $2 + 3 = 5$ ions on complete ionization. For one mole initially, 0.40 mole remains undissociated and the ionized 0.60 mole produces $5(0.60) = 3.00$ moles of ions. The total is therefore $0.40 + 3.00 = 3.40$ moles of solute particles. Equivalently,

$$i = 1 + (5 - 1)\alpha = 1 + 4(0.60) = 3.40.$$

The given molality refers to the electrolyte before ionization; the factor i accounts for the increased particle number.

Step 4: (iii) Calculate the elevation and the boiling point Substitute $m = 1\,\text{mol kg}^{-1}$ and $K_b = 0.52\,\text{K kg mol}^{-1}$:

$$\Delta T_b = iK_b m = 3.40 \times 0.52 \times 1 = 1.768\,\text{K}.$$

At normal atmospheric pressure, pure water boils at $100\,^\circ\text{C}$, or $373.15\,\text{K}$. A temperature increment of $1.768\,\text{K}$ is also an increment of $1.768\,^\circ\text{C}$, so

$$T_b = 100 + 1.768 = 101.768\,^\circ\text{C} = 374.918\,\text{K}.$$

Step 5: Conclusion (i) O_2 has the higher K_H because it is less soluble. (ii) Blood cells shrink through

Quick Tip to Solve: Count all five ions from one formula unit of A2B3, then use i = 1 + 4 alpha before calculating the boiling point elevation.

exosmosis in the hypertonic sodium chloride solution. (iii) $i = 3.40$, giving $\Delta T_b = 1.768\,\text{K}$ and a boiling point of approximately $101.77\,^\circ\text{C}$ at normal atmospheric pressure.

Quick Tip to Solve: Count all five ions from one formula unit of A2B3, then use i = 1 + 4 alpha before calculating the boiling point elevation.

OR

33(b). (i) The vapour pressures of A and B at 25°C are 75 mm Hg and 25 mm Hg, respectively. If A and B are mixed such that the mole fraction of A in the mixture is 0.4, then calculate the mole fraction of B in vapour phase.

(ii) Define colligative property. Which colligative property is preferred for the molar mass determination of macromolecules?

(iii) Why are equimolar solutions of sodium chloride and glucose not isotonic? [5 marks]

Solution:

Concept:

- For an ideal binary liquid solution, Raoult's law gives $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$, where x denotes a liquid-phase mole fraction and p^0 the pure-component vapour pressure.
- Dalton's law gives the vapour-phase mole fraction $y_B = p_B/(p_A + p_B)$. Liquid and vapour compositions need not be equal because the components have different volatilities.
- Colligative properties depend on the number of solute particles relative to the solvent, rather than the chemical identity of those particles, for dilute solutions.
- Osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is molar concentration, R is the gas constant and T is absolute temperature. Isotonic solutions have equal osmotic pressures at the same temperature.

Step 1: (i) Calculate the partial vapour pressures The liquid-phase mole fractions add to unity. Hence $x_B = 1 - x_A = 1 - 0.4 = 0.6$. Applying Raoult's law at the given temperature,

$$p_A = 0.4 \times 75 = 30\,\text{mm Hg},$$
$$p_B = 0.6 \times 25 = 15\,\text{mm Hg},$$
$$p_{\text{total}} = p_A + p_B = 45\,\text{mm Hg}.$$

Both components are volatile, so both partial pressures must enter the total pressure.

Step 2: (i) Convert partial pressure to vapour composition For the vapour mixture, Dalton's law gives

$$y_B = \frac{p_B}{p_{\text{total}}} = \frac{15}{45} = \frac{1}{3}.$$

This is dimensionless. As a check, $y_A = 30/45 = 2/3$, so the two vapour mole fractions add to one. B has a lower pure vapour pressure and is therefore less volatile; its fraction in the vapour is lower than its liquid fraction of 0.6.

Step 3: (ii) Define the property and choose a method for macromolecules A colligative property

Quick Tip to Solve: First find both partial vapour pressures before dividing by their sum; for isotonicity compare particle concentrations iC, not just molar concentrations C.

is a property of a dilute solution that depends on the number of solute particles present relative to the number of solvent particles, and not on the nature of the solute. The four examples are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure.

Osmotic pressure is preferred for determining the molar masses of macromolecules such as proteins and polymers. Their very large molar masses make the other colligative changes extremely small at accessible concentrations. Osmotic pressure remains measurable in very dilute solutions and can be measured at room temperature, avoiding thermal decomposition or denaturation. For a non-associating, non-dissociating macromolecule of mass w in solution volume V,

$$\pi = \frac{wRT}{MV}, \qquad M = \frac{wRT}{\pi V},$$

with mutually consistent units for R, π and V.

Step 4: (iii) Compare the osmotic pressures of equimolar solutions Sodium chloride is an electrolyte and dissociates in water:

$$\mathrm{NaCl(aq)} \longrightarrow \mathrm{Na^{+}(aq) + Cl^{-}(aq)}.$$

Glucose is a non-electrolyte and remains as molecules. At the same molar concentration and temperature, dilute NaCl therefore has more dissolved particles: its ideal van't Hoff factor is approximately 2, while glucose has $i = 1$. Thus $\pi_{\mathrm{NaCl}} \approx 2CRT$ and $\pi_{\mathrm{glucose}} = CRT$. Their unequal osmotic pressures mean that they are not isotonic. Real electrolyte interactions may lower the factor from its ideal value, without changing the particle-number explanation.

Step 5: Conclusion (i) The mole fraction of B in the vapour is $\boxed{y_B = \frac{1}{3} \approx 0.333}$. (ii) Colligative properties depend on solute particle number; $\boxed{\text{osmotic pressure}}$ is preferred for macromolecular molar masses. (iii) Equimolar NaCl and glucose solutions are not isotonic because NaCl dissociates and has a higher osmotic pressure at the same temperature.

Quick Tip to Solve: First find both partial vapour pressures before dividing by their sum; for isotonicity compare particle concentrations iC, not just molar concentrations C.