CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) **All** questions are compulsory.
(ii) Questions number **1 to 5** are very short answer questions and carry **1** mark each.
(iii) Questions number **6 to 10** are short answer questions and carry **2** marks each.
(iv) Questions number **11 to 22** are also short answer questions and carry **3** marks each.
(v) Question number **23** is a value based question and carries **4** marks.
(vi) Questions number **24 to 26** are long answer questions and carry **5** marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Write the formula of the compound of phosphorus which is obtained when conc. HNO_3 oxidises P_4. [1 mark]

Solution:

Concept:

- Concentrated nitric acid is a strong oxidising agent. It converts elemental phosphorus, whose oxidation state is zero, into its highest common oxidation state, $+5$.
- Orthophosphoric acid contains phosphorus in the $+5$ state and has formula H_3PO_4.

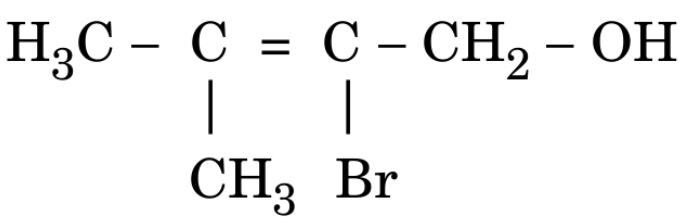
Step 1: Identify the oxidation product On oxidation of P_4 by concentrated HNO_3, phosphorus forms orthophosphoric acid. The product is an oxoacid, rather than a lower oxidation-state acid such as H_3PO_3.

Step 2: Check the formula For H_3PO_4, the oxidation-state sum is $3(+1) + x + 4(-2) = 0$, giving $x = +5$. This agrees with oxidation of phosphorus by concentrated nitric acid.

Step 3: Conclusion The required formula is $\boxed{H_3PO_4}$ (orthophosphoric acid).

Quick Tip to Solve: For oxidation of elemental phosphorus by concentrated nitric acid, recall the highest-state oxoacid, H_3PO_4.

2. Write the IUPAC name of the following compound: [1 mark]



Solution:

Concept:

- The parent chain must contain the carbon bonded to the principal functional group $-OH$ and the carbon-carbon double bond.
- Number the chain from the $-OH$ end to give the alcohol group the lowest locant; list substituent prefixes alphabetically.

Step 1: Choose and number the parent chain The printed structure can be read as

$$HOCH_2-C(Br)=C(CH_3)-CH_3.$$

The longest chain containing both the hydroxyl group and the double bond has four carbons. Numbering from CH_2OH gives the hydroxyl group locant 1 and the double bond locant 2, so the parent is but-2-en-1-ol.

Step 2: Locate the substituents The bromine substituent is on carbon 2, and the extra methyl group is on carbon 3. Write bromo before methyl in alphabetical order. No E/Z descriptor is needed because

Quick Tip to Solve: Number this chain from CH_2OH, then locate Br at 2 and the extra methyl at 3.

one double-bond carbon bears two identical methyl groups.

Step 3: Conclusion The IUPAC name is $\boxed{\text{2-bromo-3-methylbut-2-en-1-ol}}$.

Quick Tip to Solve: Number this chain from CH_2OH, then locate Br at 2 and the extra methyl at 3.

3. What is the effect of adding a catalyst on

(a) Activation energy (E_a), and

(b) Gibbs energy (ΔG) of a reaction? [1 mark]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation-energy barrier, increasing the reaction rate.
- The Gibbs energy change ΔG depends on the reactant and product states at the specified conditions, not on the reaction pathway.

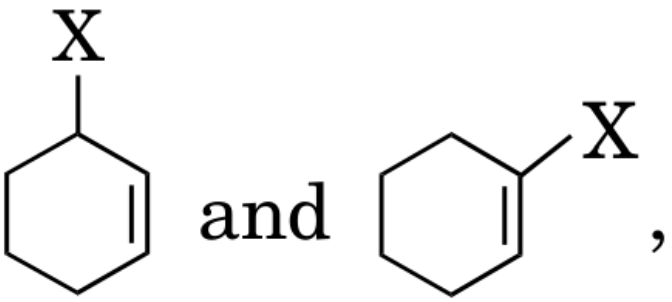
Step 1: (a) Effect on activation energy The activation energy E_a decreases on addition of a catalyst because the catalysed pathway has a lower barrier than the uncatalysed pathway. The catalyst changes the route by which the same products form.

Step 2: (b) Effect on Gibbs energy The reactants and products have the same Gibbs energies before and after the catalyst is added. Therefore $\Delta G = G_{\text{products}} - G_{\text{reactants}}$ remains unchanged. A catalyst changes the rate of attaining equilibrium, but does not change the equilibrium constant or thermodynamic favourability.

Step 3: Conclusion (a) E_a decreases. (b) ΔG remains unchanged.

Quick Tip to Solve: Separate the kinetic barrier E_a from the thermodynamic state difference ΔG.

4. Out of the two compounds shown below, which is an example of an allylic halide? [1 mark]



Solution:

Concept:

- An allylic halide has the halogen attached to an sp^3-hybridised carbon immediately adjacent to a carbon-carbon double bond.
- A halogen attached directly to an sp^2 carbon of the double bond forms a vinylic halide.

Step 1: Inspect the first structure In the left-hand compound, the carbon bonded to X is the saturated ring carbon next to the double bond. This carbon is sp^3-hybridised and occupies the allylic position.

Step 2: Compare the second structure In the right-hand compound, X is attached directly to one of the two carbons that form the double bond. That carbon is sp^2-hybridised, so the compound is a vinylic halide. Adjacency to the double bond, rather than attachment to a double-bond carbon, distinguishes the allylic compound.

Step 3: Conclusion The first (left-hand) compound is the allylic halide.

Quick Tip to Solve: Check the carbon carrying X: adjacent to $C=C$ means allylic; on $C=C$ means vinylic.

5. What type of colloid is formed when a liquid is dispersed in a solid? Give an example. [1 mark]

Solution:

Concept:

- A colloid is classified by the physical states of its dispersed phase and dispersion medium.
- When the dispersed phase is liquid and the dispersion medium is solid, the colloidal system is called a gel.

Step 1: Identify both phases The question states that liquid is dispersed in solid. Thus liquid is the dispersed phase, while the solid constitutes the continuous dispersion medium. The order of these phases is essential for the classification.

Step 2: Give a suitable example Jelly is a familiar gel: liquid is held within a solid network. It exemplifies a liquid-in-solid colloid. This differs from an emulsion, in which both the dispersed phase and the dispersion medium are liquids.

Step 3: Conclusion The colloid is a $\boxed{\text{gel}}$; an example is jelly.

Quick Tip to Solve: For this classification, write dispersed phase first: liquid in solid gives a gel, such as jelly.

6(a). Arrange the following compounds in the increasing order of their acid strength:
p-cresol, p-nitrophenol, phenol

(b) Write the mechanism (using curved arrow notation) of the following reaction:

$CH_2 = CH_2 \xrightarrow{H_3O^+} CH_3 - CH_2^+ + H_2O$ [2 marks]

Solution:

Concept:

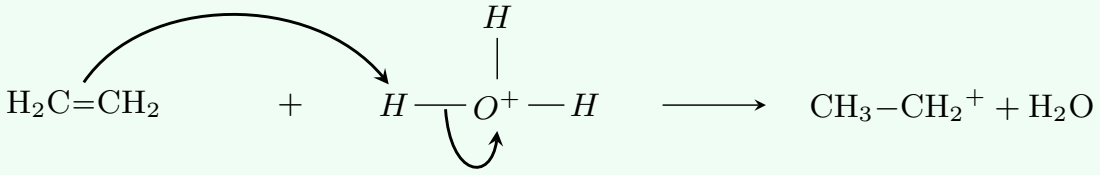
- Acidity increases when the conjugate phenoxide ion is stabilised. An electron-donating group destabilises it, whereas an electron-withdrawing group stabilises it.
- In electrophilic protonation, the alkene π electron pair forms a bond to a proton; the donor O–H bond breaks with its electron pair returning to oxygen.

Step 1: (a) Compare the substituent effects The para methyl group in p-cresol donates electron density by its $+I$ effect and hyperconjugation, making its phenoxide ion less stable than phenoxide itself. The para nitro group withdraws electron density through $-I$ and $-R$ effects and stabilises p-nitrophenoxide by delocalisation. Thus p-cresol is weaker than phenol, while p-nitrophenol is stronger.

Step 2: (b) Show formation of the ethyl carbocation Ethene acts as an electron-pair donor. Draw a curved arrow from the $C = C$ bond to a hydrogen of H_3O^+, and a second curved arrow from that O–H bond to oxygen. A new C–H bond forms at one carbon; the other becomes the positively charged carbon. The oxonium ion loses its proton and becomes water:

$$CH_2{=}CH_2 + H_3O^+ \longrightarrow CH_3{-}CH_2{}^+ + H_2O.$$

Either alkene carbon can receive the proton because ethene is symmetrical. The printed reaction ends at the carbocation, so no subsequent water attack is included.



Curved arrows for protonation of ethene

Step 3: Conclusion (a) $\boxed{\text{p-cresol} < \text{phenol} < \text{p-nitrophenol}}$.
(b) Proton transfer from H_3O^+ to ethene produces $CH_3CH_2{}^+$ and H_2O, with the two curved arrows shown.

Quick Tip to Solve: Place curved-arrow tails on electron pairs: the alkene π bond and the hydronium O–H bond.

OR

6(b). Write the structures of the products when Butan-2-ol reacts with the following:

(a) CrO_3

(b) $SOCl_2$ [2 marks]

Solution:

Concept:

- Butan-2-ol, $CH_3CH(OH)CH_2CH_3$, is a secondary alcohol: its hydroxyl-bearing carbon is bonded to two carbon groups.
- Oxidation converts a secondary alcohol into a ketone. Thionyl chloride replaces the hydroxyl group by chlorine, preserving the carbon skeleton.

Step 1: (a) Oxidation with chromium trioxide CrO_3 is an oxidising agent. Removal of the hydroxyl hydrogen and the hydrogen attached to carbon 2 forms a carbonyl group at that same carbon:

$$CH_3CH(OH)CH_2CH_3 + [O] \longrightarrow CH_3C(=O)CH_2CH_3 + H_2O.$$

The organic product is butan-2-one. The starting alcohol is secondary, so oxidation gives a ketone rather than an aldehyde. The carbon chain and position of the functional group are retained.

Step 2: (b) Reaction with thionyl chloride Thionyl chloride converts the alcohol into its corresponding alkyl chloride. The hydroxyl group on carbon 2 is replaced by chlorine:

$$CH_3CH(OH)CH_2CH_3 + SOCl_2 \longrightarrow CH_3CH(Cl)CH_2CH_3 + SO_2 + HCl.$$

The organic product is 2-chlorobutane. Sulphur dioxide and hydrogen chloride are the gaseous by-products. This substitution does not move the chlorine to the terminal carbon or alter the four-carbon skeleton.

Step 3: Conclusion (a) Butan-2-one: $CH_3C(=O)CH_2CH_3$. (b) 2-Chlorobutane: $CH_3CH(Cl)CH_2CH_3$.

Quick Tip to Solve: Locate carbon 2 first: oxidation changes C–OH into C=O; SOCl2 replaces only OH by Cl.

7. Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a face-centred cubic (f.c.c.) structure. (Atomic mass of Al = 27 g mol^{-1}) [2 marks]

Solution:

Concept:

- The amount of aluminium is $n = m/M$, where m is sample mass and M is molar mass. Its atom count is nN_A, with $N_A = 6.022 \times 10^{23}$ mol^{-1}.
- An f.c.c. unit cell contains four atoms: eight corner atoms contribute one atom in total and six face-centred atoms contribute three atoms.

Step 1: Find the number of aluminium atoms The given mass is 8.1 g and the molar mass is 27 g mol^{-1}.

Quick Tip to Solve: Convert grams to atoms using Avogadro's constant, then divide by 4 for an f.c.c. lattice.

Therefore,

$$n = \frac{8.1}{27} = 0.30\,\text{mol}, \qquad N_{\text{atoms}} = 0.30(6.022 \times 10^{23}) = 1.8066 \times 10^{23}.$$

This is the total number of atoms in the sample, not the number of unit cells. The molar-mass conversion counts individual aluminium atoms.

Step 2: Divide by the f.c.c. atom count Each corner atom is shared by eight cells and each face atom by two cells. Thus the effective number of atoms per cell is

$$Z = 8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4.$$

Consequently,

$$N_{\text{cells}} = \frac{N_{\text{atoms}}}{Z} = \frac{1.8066 \times 10^{23}}{4} = 4.5165 \times 10^{22}.$$

The answer is a count, so no unit of mass or amount of substance is attached to it.

Step 3: Conclusion The sample contains approximately $\boxed{4.52 \times 10^{22}}$ f.c.c. unit cells.

Quick Tip to Solve: Convert grams to atoms using Avogadro's constant, then divide by 4 for an f.c.c. lattice.

8. Draw the structures of the following:

(a) H_2SO_3

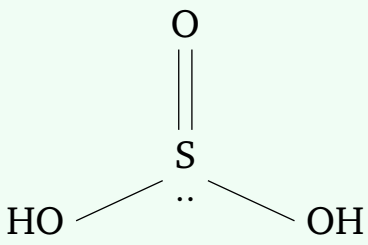
(b) $HClO_3$ [2 marks]

Solution:

Concept:

- In these oxoacids the acidic hydrogen is attached to oxygen as an $-OH$ group, not directly to the central atom.
- Sulphurous acid has one $S = O$ bond and two $S - OH$ bonds. Chloric acid has two $Cl = O$ bonds and one $Cl - OH$ bond.

Step 1: (a) Structure of sulphurous acid For H_2SO_3, place sulphur at the centre and attach three oxygen atoms. Two oxygens each carry a hydrogen, giving two hydroxyl groups; the third oxygen is doubly bonded to sulphur. The structural formula is $HO - S(= O) - OH$. Sulphur also has one lone pair, so its three S–O bond directions form a trigonal pyramidal arrangement. The drawing shows connectivity schematically.

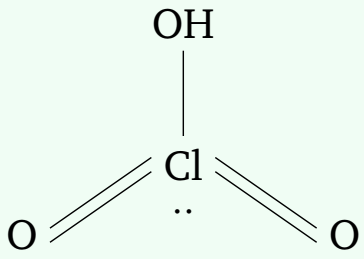


Sulphurous acid: two hydroxyl groups and one oxo group

Step 2: (b) Structure of chloric acid For $HClO_3$, place chlorine at the centre with three oxygen atoms.

Quick Tip to Solve: Attach every acidic H to oxygen; H2SO3 has two OH groups, while HClO3 has just one.

One oxygen carries the single hydrogen and forms an $-\mathrm{OH}$ group; the other two form double bonds with chlorine. Its structural formula is $\mathrm{HO-Cl(=O)_2}$. Chlorine has one lone pair. Counting the labels in the drawing gives exactly one hydrogen, one chlorine and three oxygen atoms.



Chloric acid: one hydroxyl group and two oxo groups

Step 3: Conclusion The structures are $\boxed{\mathrm{HO-S(=O)-OH}}$ and $\boxed{\mathrm{HO-Cl(=O)_2}}$, respectively.

Quick Tip to Solve: Attach every acidic H to oxygen; H2SO3 has two OH groups, while HClO3 has just one.

9. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. [2 marks]

Solution:

Concept:

- The mercury cell is a primary cell traditionally used in hearing aids. Its anode is zinc amalgam and its cathode is mercuric oxide mixed with carbon.
- In the alkaline electrolyte, zinc is oxidised at the anode and mercuric oxide is reduced at the cathode. Electrons appear on the product side for oxidation and on the reactant side for reduction.

Step 1: Identify the cell and write the anode reaction The cell is the mercury cell, containing an alkaline electrolyte such as KOH with ZnO. Zinc in the zinc-amalgam anode changes from oxidation state 0 to $+2$ and releases two electrons:

$$\mathrm{Zn(Hg)} + 2\mathrm{OH^-} \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\mathrm{e^-}.$$

Here $\mathrm{Zn(Hg)}$ denotes zinc amalgam; mercury in the amalgam is not consumed in this half-reaction. Both the atoms and the net charge of -2 are balanced.

Step 2: Write the cathode reaction and combine At the cathode, mercury in mercuric oxide changes from oxidation state $+2$ to 0 by accepting two electrons:

$$\mathrm{HgO} + \mathrm{H_2O} + 2\mathrm{e^-} \longrightarrow \mathrm{Hg} + 2\mathrm{OH^-}.$$

Adding the two half-reactions cancels electrons, hydroxide ions and water, giving

$$\mathrm{Zn} + \mathrm{HgO} \longrightarrow \mathrm{ZnO} + \mathrm{Hg}.$$

There is no net change in electrolyte-ion concentration, which helps the cell deliver a nearly constant

Quick Tip to Solve: For the mercury cell, remember Zn loses two electrons at the anode and HgO gains them at the cathode.

potential during its useful life.

Step 3: Conclusion The mercury cell is used in hearing aids.

Anode: $\mathrm{Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-}$.

Cathode: $\mathrm{HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-}$.

Quick Tip to Solve: For the mercury cell, remember Zn loses two electrons at the anode and HgO gains them at the cathode.

10. Using IUPAC norms write the formulae for the following:

(a) Sodium dicyanidoaurate(I)

(b) Tetraamminechloridonitrito-N-platinum(IV) sulphate [2 marks]

Solution:

Concept:

- The metal oxidation state and ligand charges determine the charge of the coordination entity. Cyanido, chlorido and nitrito each carry charge -1, while ammine, $\mathrm{NH_3}$, is neutral.
- Write the coordinated ligands with the metal inside square brackets and balance the resulting charge using counter-ions outside the brackets.

Step 1: (a) Sodium dicyanidoaurate(I) Gold(I) has oxidation state $+1$, while the prefix di specifies two cyanido ligands. The charge of the complex is $+1 + 2(-1) = -1$, giving $\mathrm{[Au(CN)_2]^-}$. One $\mathrm{Na^+}$ ion balances this charge, so the ratio of sodium ions to complex anions is one to one.

Step 2: (b) Tetraamminechloridonitrito-N-platinum(IV) sulphate Platinum has oxidation state $+4$. The four ammine ligands are neutral; the single chlorido and nitrito ligands each have charge -1. Hence the complex charge is $+4 - 1 - 1 = +2$. Nitrito-N specifies coordination through nitrogen, written as $\mathrm{NO_2}$ in the formula. The coordination entity is therefore $\mathrm{[Pt(NH_3)_4Cl(NO_2)]^{2+}}$. One sulphate ion, $\mathrm{SO_4^{2-}}$, balances one complex cation, making the entire salt electrically neutral.

Step 3: Conclusion (a) $\boxed{\mathrm{Na[Au(CN)_2]}}$.

(b) $\boxed{\mathrm{[Pt(NH_3)_4Cl(NO_2)]SO_4}}$, with the nitrito ligand bonded through N.

Quick Tip to Solve: First calculate the complex charge from the oxidation state and ligand charges; then balance it with the counter-ion.

11. (a) Based on the nature of intermolecular forces, classify the following solids:
Silicon carbide, Argon
(b) ZnO turns yellow on heating. Why?
(c) What is meant by groups 12-16 compounds? Give an example. [3 marks]

Solution:

Concept:

- Classification of solids depends on the particles in the lattice and the forces binding them: a covalent network is held by covalent bonds, whereas non-polar molecular solids are held by London dispersion forces.
- A non-stoichiometric oxide can develop a metal-excess defect when oxygen is lost and electrons compensate the charge. Group 12–16 compounds combine elements of these two periodic-table groups.

Step 1: (a) Classify silicon carbide and argon Silicon carbide, SiC, is a covalent or network solid: silicon and carbon atoms are joined by strong covalent bonds throughout the lattice. Solid argon is a non-polar molecular solid in the standard classification of solids. Its constituent particles are individual Ar atoms, held together by weak London dispersion forces; these arise from instantaneous and induced dipoles. Thus the strength and nature of the binding are very different in the two solids.

Step 2: (b) Explain the yellow colour of heated ZnO On heating, zinc oxide loses some oxygen, represented schematically by

$$\mathrm{ZnO} \xrightarrow{\text{heat}} \mathrm{Zn^{2+}} + \tfrac{1}{2}\mathrm{O_2} + 2e^{-}.$$

Its composition becomes oxygen-deficient, with excess zinc ions accommodated at interstitial sites and electrons at neighbouring interstitial sites maintaining electrical neutrality. This is a metal-excess defect. The trapped electrons absorb visible light, so the initially white oxide appears yellow on heating.

Step 3: (c) Define group 12–16 compounds and give an example These are compounds formed by combining an element of group 12 with an element of group 16. They are compound semiconductors. For example, zinc sulphide, ZnS, contains zinc from group 12 and sulphur from group 16; cadmium sulphide, CdS, is another example.

Step 4: Conclusion (a) SiC: covalent network solid; Ar: non-polar molecular solid. (b) Heated ZnO becomes yellow due to a metal-excess defect and trapped electrons. (c) Group 12–16 compounds combine elements of groups 12 and 16, for example ZnS.

Quick Tip to Solve: For ZnO, connect oxygen loss to metal excess and trapped electrons; do not describe the colour change as an impurity defect.

12. (a) A cell in which the following reaction occurs:

$2\,Fe^{3+}(aq) + 2\,I^{-}(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)$

has $E^{\circ}_{cell} = 0.236$ V at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given: 1 F = 96,500 C mol^{-1})

(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: 1 F = 96,500 C mol^{-1}) [3 marks]

Solution:

Concept:

- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of moles of electrons exchanged per mole of the reaction as written, F is the Faraday constant and E°_{cell} is the standard cell potential.
- Current transfers charge $Q = It$. The moles of electrons are Q/F, and their number is $N = (Q/F)N_A$, where $N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$.

Step 1: (a) Determine the electron transfer number The reduction and oxidation half-reactions are

$$2\text{Fe}^{3+} + 2e^- \longrightarrow 2\text{Fe}^{2+},$$
$$2\text{I}^- \longrightarrow \text{I}_2 + 2e^-.$$

Thus two electrons are transferred for the balanced reaction as written, so $n = 2$. The electron number is determined from the half-reactions, not from the total number of ions in the equation.

Step 2: (a) Calculate the standard Gibbs energy change Substituting the given values,

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(0.236)\\ &= -45548\,\text{J mol}^{-1}\\ &= -45.548\,\text{kJ mol}^{-1}.\end{aligned}$$

Since $1\,\text{C} \times 1\,\text{V} = 1\,\text{J}$, the units are energy per mole of the reaction. The negative sign is consistent with the positive standard cell potential and indicates thermodynamic feasibility under standard conditions.

Step 3: (b) Convert current and time into the number of electrons Convert the duration to seconds before using amperes:

$$t = 2 \times 3600 = 7200\,\text{s}, \qquad Q = 0.5 \times 7200 = 3600\,\text{C}.$$

Hence the amount of electrons and their number are

$$\begin{aligned}n(e^-) &= \frac{3600}{96500} = 0.03731\,\text{mol},\\ N &= \frac{3600}{96500}(6.022 \times 10^{23})\\ &= 2.247 \times 10^{22}.\end{aligned}$$

Faraday's constant gives charge per mole of electrons, so multiplying by Avogadro's constant is necessary to obtain the count of individual electrons.

Quick Tip to Solve: Count electrons using the balanced half-reactions, and always convert hours to seconds before applying Q = It.

Step 4: Conclusion (a) $\boxed{\Delta_r G^\circ = -45.548\,\text{kJ mol}^{-1}}$ (approximately $-45.5\,\text{kJ mol}^{-1}$).

(b) Approximately $\boxed{2.25 \times 10^{22}\ \text{electrons}}$ flow through the wire.

Quick Tip to Solve: Count electrons using the balanced half-reactions, and always convert hours to seconds before applying Q = It.

13. (a) What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$?

(b) Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic? (Atomic number of Ni = 28)

(c) Why are low spin tetrahedral complexes rarely observed? [3 marks]

Solution:

Concept:

- Ambidentate ligands coordinate through either of two donor atoms; changing the donor atom gives linkage isomerism.
- Magnetism depends on unpaired electrons. Low spin requires crystal-field splitting to exceed electron-pairing energy.

Step 1: (a) Identify linkage isomerism Thiocyanate, SCN^-, can attach through sulphur or nitrogen. Thus $[Co(NH_3)_5(SCN)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ have the same composition but different donor atoms attached to cobalt. This is linkage isomerism. The five ammonia ligands remain unchanged.

Step 2: (b) Compare ligand strength and electron pairing Each complex contains four singly negative ligands and has charge -2; therefore nickel is Ni^{2+}. From $Z = 28$, nickel is $[Ar]3d^8 4s^2$ and Ni^{2+} is $[Ar]3d^8$. Chloride is a weak-field ligand and does not pair the two unpaired $3d$ electrons. $[NiCl_4]^{2-}$ has sp^3 hybridisation, tetrahedral geometry and two unpaired electrons, hence it is paramagnetic. Cyanide is a strong-field ligand and causes pairing of the $3d$ electrons, leaving one $3d$ orbital vacant. $[Ni(CN)_4]^{2-}$ has dsp^2 hybridisation and square-planar geometry. All electrons are paired, so it is diamagnetic.

Step 3: (c) Explain why low spin is rare Tetrahedral crystal-field splitting Δ_t is small, approximately $\frac{4}{9}\Delta_o$ for the same metal and ligands. Usually $\Delta_t < P$, where P is the electron-pairing energy. Electrons occupy the higher-energy orbitals singly rather than pair in the lower-energy orbitals because this costs less energy. Tetrahedral complexes are therefore generally high spin and low-spin tetrahedral complexes are rarely observed.

Step 4: Conclusion (a) Linkage isomerism. (b) The chloride complex has two unpaired electrons; the cyanide complex has none. (c) Tetrahedral splitting generally cannot overcome pairing energy.

Quick Tip to Solve: Both nickel complexes contain the same d8 metal ion: identify ligand strength and geometry before deciding their magnetic behaviour.

14(a). Write one difference in each of the following:

(a) Multimolecular colloid and Associated colloid

(b) Coagulation and Peptization

(c) Homogeneous catalysis and Heterogeneous catalysis [3 marks]

Solution:

Concept:

- Colloids are classified by how the particles of the dispersed phase are formed.
- Coagulation and peptization describe opposite changes between a colloidal sol and a precipitate.
- Catalysis is homogeneous or heterogeneous according to whether the catalyst and reactants occupy the same phase or different phases.

Step 1: (a) Compare particle formation In a multimolecular colloid, many small molecules or atoms aggregate to form a particle of colloidal size, as in a gold sol or sulphur sol. In an associated colloid, substances such as soaps behave as ordinary electrolytes at low concentration, but associate to form colloidal aggregates called micelles above the critical micelle concentration and the Kraft temperature. Thus the difference is aggregation into colloidal particles versus concentration-dependent micelle formation.

Step 2: (b) Compare the direction of change Coagulation is the conversion of a colloidal sol into a precipitate by aggregation of its particles, commonly after an electrolyte neutralises their charge. Peptization is the conversion of a freshly formed precipitate into a colloidal sol by shaking it with a suitable electrolyte, called the peptizing agent. Thus coagulation removes colloidal dispersion, whereas peptization produces it.

Step 3: (c) Compare the phases In homogeneous catalysis, the catalyst and reactants are in the same phase, for example an acid catalyst in the aqueous hydrolysis of an ester. In heterogeneous catalysis, the catalyst and reactants are in different phases, for example solid iron catalysing the reaction of gaseous nitrogen and hydrogen in the Haber process. The distinction concerns phase, rather than whether the catalyst is consumed; a catalyst is regenerated in both cases.

Step 4: Conclusion (a) Multimolecular colloids contain aggregates of small particles; associated colloids form micelles under suitable conditions. (b) Coagulation converts sol to precipitate, while peptization converts precipitate to sol. (c) Homogeneous catalysis uses the same phase, whereas heterogeneous catalysis uses different phases.

Quick Tip to Solve: For each pair, compare one common feature: particle formation, direction of conversion, and the phases of catalyst and reactants.

OR

14(b). (a) Write the dispersed phase and dispersion medium of milk.

(b) Write one similarity between physisorption and chemisorption.

(c) Write the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$. [3 marks]

Solution:

Concept:

- An emulsion is a colloidal dispersion of one liquid in another liquid; the droplets form the dispersed phase and the surrounding continuous liquid is the dispersion medium.
- Adsorption is accumulation at a surface. Both physical and chemical adsorption release heat as the adsorbate interacts with the adsorbent.
- Hydrolysis of a suitable salt can produce finely divided insoluble material as a colloidal sol.

Step 1: (a) Identify the two phases in milk Milk is an oil-in-water emulsion. Its dispersed phase consists of liquid fat or oil droplets, and its dispersion medium is water. The fat droplets are distributed throughout the continuous aqueous phase; therefore the order of the phases is oil in water. Although milk also contains proteins and dissolved substances, the requested emulsion phases are fat and water.

Step 2: (b) State a similarity of the adsorption processes Both physisorption and chemisorption are exothermic processes: their enthalpy of adsorption is negative, $\Delta H_{\text{ads}} < 0$. Attraction between an adsorbate and the surface releases energy, whether it arises from weak physical forces or chemical bond formation. The magnitude of the released heat differs, but its negative sign is a shared property and supplies the required similarity.

Step 3: (c) Prepare ferric hydroxide sol by hydrolysis The chemical method is hydrolysis of ferric chloride. Add a small quantity of ferric chloride solution to boiling water. Hydrolysis produces colloidal ferric hydroxide, giving a reddish-brown sol:

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3\,(\text{sol}) + 3HCl.$$

The product remains finely dispersed under the preparation conditions. The hydrochloric acid and other dissolved electrolytes can subsequently be removed by dialysis to improve the stability of the sol. The reaction involves hydrolysis, not merely dissolving ferric hydroxide in water.

Step 4: Conclusion (a) Dispersed phase: liquid fat (oil); dispersion medium: water. (b) Both adsorption processes are exothermic. (c) Ferric hydroxide sol is prepared by hydrolysis of ferric chloride in boiling water.

Quick Tip to Solve: Name the dispersed droplets before the continuous medium, and identify hydrolysis by the salt reacting with water to form the hydroxide sol.

15. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.

(Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021) [3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$, where k is the rate constant, t is elapsed time, and $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations.
- The fraction remaining is one minus the fraction decomposed. Thus 25% decomposition leaves 75% reactant, whereas 75% completion leaves 25% reactant.

Step 1: Calculate the rate constant from 25% decomposition Take the initial amount as 100 units. After 20 min, 25 units have decomposed and 75 units remain. Substitution in the integrated first-order law gives

$$\begin{aligned} k &= \frac{2.303}{20}\log\frac{100}{75} = \frac{2.303}{20}\log\frac{4}{3} \\ &= \frac{2.303}{20}(0.6021 - 0.4771) \\ &= 0.01439375\,\text{min}^{-1}. \end{aligned}$$

The concentration ratio is dimensionless, so the unit of the rate constant is reciprocal minutes.

Step 2: Find the total time for 75% completion At 75% completion, the amount remaining is 25 units. The required time is measured from the start of the reaction, and the same rate constant applies:

$$\begin{aligned} t_{75\%} &= \frac{2.303}{k}\log\frac{100}{25} \\ &= 20\frac{\log 4}{\log 4 - \log 3} \\ &= 20\frac{0.6021}{0.1250} \\ &= 96.336\,\text{min}. \end{aligned}$$

This exceeds 20 minutes because the reaction slows as the reactant concentration falls; equal percentage-point changes need not take equal times.

Step 3: Conclusion The time required for 75% completion is $\boxed{96.34\,\text{min}}$ from the start of the reaction.

Quick Tip to Solve: Use the percentage remaining in the logarithm; divide the two first-order equations to cancel both the initial concentration and 2.303.

16. The following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(a) Write the compound which is most reactive towards S_N2 reaction.

(b) Write the compound which is optically active.

(c) Write the compound which is most reactive towards β-elimination reaction. [3 marks]

Solution:

Concept:

- In an S_N2 reaction, the nucleophile attacks the carbon bearing the leaving group from the back side. Less steric hindrance favours the reaction: primary alkyl halide $>$ secondary $>$ tertiary.
- A tetrahedral carbon bonded to four different groups is a chiral centre. An individual enantiomer of such a compound can rotate plane-polarised light.
- In β-elimination, hydrogen is removed from a carbon adjacent to the carbon bearing the halogen, producing an alkene. The usual reactivity order of comparable alkyl halides is tertiary $>$ secondary $>$ primary.

Step 1: (a) Compare reactivity towards S_N2 In 1-bromopentane the carbon bearing Br is primary, in 2-bromopentane it is secondary, and in 2-bromo-2-methylbutane it is tertiary. Since the leaving group is Br in all three, compare steric hindrance around the reaction centre. The primary carbon of 1-bromopentane is most accessible to back-side attack. Therefore 1-bromopentane is the most reactive towards S_N2; the tertiary compound is the least suitable for this mechanism.

Step 2: (b) Identify the optically active compound Carbon 2 of 2-bromopentane is attached to Br, H, CH_3, and $CH_2CH_2CH_3$. These are four different groups, so this carbon is chiral and 2-bromopentane is the optically active compound. In 2-bromo-2-methylbutane the corresponding carbon has two identical methyl groups, while the terminal carbon of 1-bromopentane has two hydrogen atoms; neither has a chiral centre. A racemic mixture of the enantiomers of 2-bromopentane would show no net rotation, but the compound has the required optical isomerism.

Step 3: (c) Compare reactivity towards β-elimination 2-Bromo-2-methylbutane is a tertiary alkyl halide and has available β-hydrogens on adjacent carbons. It undergoes elimination most readily among the given compounds, following the order tertiary $>$ secondary $>$ primary. Removal of HBr can form a substituted alkene, with 2-methylbut-2-ene favoured under ordinary Saytzeff conditions. Hence the most reactive compound towards β-elimination is 2-bromo-2-methylbutane.

Step 4: Conclusion (a) $\boxed{\text{1-Bromopentane}}$; (b) $\boxed{\text{2-Bromopentane}}$; (c) $\boxed{\text{2-Bromo-2-methylbutane}}$.

Quick Tip to Solve: Classify the Br-bearing carbon first; then test chirality by listing all four groups attached to that carbon.

17. Write the principle of the following:

(a) Zone refining

(b) Froth floatation process

(c) Chromatography [3 marks]

Solution:

Concept:

- Separation and purification depend on differences in physical behaviour of the components: solubility in two phases, wetting by different liquids, or adsorption on a solid surface.
- A suitable process selectively carries the impurity or one component into a different phase, allowing separation without requiring all components to react chemically.

Step 1: (a) Principle of zone refining Zone refining is based on the fact that impurities are more soluble in the molten metal than in the solid metal. A narrow molten zone is created in an impure metal rod and moved slowly along it. As the rear edge of the zone cools, relatively pure metal crystallises, while the impurities preferentially remain dissolved in the liquid zone. Repeated movement of the molten zone concentrates impurities at one end of the rod; that impure end is then removed. This method is used to obtain very pure semiconductor materials such as silicon and germanium.

Step 2: (b) Principle of froth floatation Froth floatation is based on the difference in the wetting properties of ore particles and gangue. Sulphide ore particles are preferentially wetted by oil, whereas gangue particles are wetted by water. Air is blown through the agitated aqueous suspension containing a suitable collector and frothing agent. The oil-wetted ore particles attach to air bubbles and rise with the froth, while the water-wetted gangue remains in the water and settles. The ore-rich froth is skimmed off to obtain the concentrated ore. Thus selective wetting makes the separation possible.

Step 3: (c) Principle of chromatography In adsorption chromatography, separation is based on the different extents to which the components of a mixture are adsorbed on a stationary adsorbent. A solvent or other mobile phase carries the mixture over the adsorbent. A component that is more strongly adsorbed is retained longer and moves more slowly, whereas a weakly adsorbed component moves faster with the mobile phase. These differences produce separate bands that can be collected. Therefore differential adsorption, rather than equal movement of all components, is the principle used in this metallurgical separation method.

Step 4: Conclusion (a) Zone refining: greater solubility of impurities in molten metal than in solid metal. (b) Froth floatation: preferential wetting of sulphide ore by oil and gangue by water. (c) Chromatography: differential adsorption of mixture components on an adsorbent.

Quick Tip to Solve: Associate zone refining with solubility, froth floatation with wetting, and chromatography with differential adsorption.

18. Write the structures of compounds A, B and C in the following reactions:

(a) $CH_3 - COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH(aq)} B \xrightarrow{CHCl_3+alc.\,KOH} C$

(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$ [3 marks]

Solution:

Concept:

- Heating a carboxylic acid with ammonia gives an amide through dehydration of the ammonium carboxylate.
- Hofmann bromamide degradation converts $\mathrm{RCONH_2}$ into $\mathrm{RNH_2}$, removing the carbonyl carbon. The carbylamine reaction converts a primary amine into an isocyanide.
- A diazonium group can be replaced by a nitro group using nitrite and copper on heating. Reduction gives an amine, which can then undergo acetylation.

Step 1: Identify the amide in sequence (a) Acetic acid first forms ammonium acetate with ammonia. Heating dehydrates this salt to acetamide:

$$\mathrm{CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.}$$

Thus A has the condensed structural formula $\mathrm{CH_3{-}C(=O){-}NH_2}$. The two-carbon skeleton is retained at this stage.

Step 2: Apply degradation and the carbylamine reaction in (a) Bromine and aqueous potassium hydroxide convert acetamide into methylamine by Hofmann degradation:

$$\mathrm{CH_3CONH_2 + Br_2 + 4\,KOH \longrightarrow CH_3NH_2 + 2\,KBr + K_2CO_3 + 2\,H_2O.}$$

Hence B is $\mathrm{CH_3{-}NH_2}$, with one carbon fewer than the amide. Methylamine is a primary amine and therefore reacts with chloroform and alcoholic potassium hydroxide:

$$\mathrm{CH_3NH_2 + CHCl_3 + 3\,KOH \longrightarrow CH_3NC + 3\,KCl + 3\,H_2O.}$$

C is methyl isocyanide, structurally $\mathrm{CH_3{-}N{\equiv}C}$. The methyl group is attached to nitrogen, distinguishing this product from methyl cyanide.

Step 3: Identify all three products in sequence (b) Nitrite and copper on heating replace the diazonium group with $-\mathrm{NO_2}$, releasing nitrogen. Thus A is nitrobenzene, $\mathrm{C_6H_5{-}NO_2}$. Iron and hydrochloric acid reduce the nitro group to an amino group, giving B as aniline, $\mathrm{C_6H_5{-}NH_2}$, after work-up. Acetyl chloride in pyridine acylates the amino nitrogen:

$$\mathrm{C_6H_5NH_2 + CH_3COCl \longrightarrow C_6H_5NHCOCH_3 + HCl.}$$

Pyridine removes the hydrogen chloride produced. Thus C is acetanilide, with structure $\mathrm{C_6H_5{-}NH{-}C(=O){-}CH_3}$; acetylation occurs on nitrogen rather than on the benzene ring.

Step 4: Conclusion (a) A: $\mathrm{CH_3CONH_2}$, B: $\mathrm{CH_3NH_2}$, C: $\mathrm{CH_3{-}N{\equiv}C}$. (b) A: $\mathrm{C_6H_5NO_2}$, B: $\mathrm{C_6H_5NH_2}$, C: $\mathrm{C_6H_5NHCOCH_3}$.

Quick Tip to Solve: Count carbons through Hofmann degradation, then attach the isocyanide carbon to nitrogen; in the aromatic route, track replacement, reduction and nitrogen acetylation.

19. Write the structures of the monomers used for getting the following polymers:

(a) Nylon-6,6

(b) Melamine-formaldehyde polymer

(c) Buna-S [3 marks]

Solution:

Concept:

- A monomer is a small molecule that joins repeatedly with other monomer molecules to form a polymer. Functional groups identify the monomers of condensation polymers.
- Nylon-6,6 is a polyamide; melamine-formaldehyde is a cross-linked condensation resin. Buna-S is an addition copolymer made from a diene and a substituted ethene.

Step 1: Write the two monomers of nylon-6,6 Nylon-6,6 is obtained from hexamethylenediamine (hexane-1,6-diamine) and adipic acid (hexanedioic acid). Their condensed structural formulae are

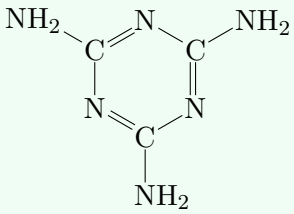
$$H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$$

and

$$HOOC-CH_2-CH_2-CH_2-CH_2-COOH.$$

The first has six carbons and two terminal amino groups; the second has six carbons, including its two carboxyl carbons. The amino and carboxyl groups form amide links with elimination of water, explaining both the polyamide classification and the two sixes in the name.

Step 2: Specify the structures for melamine-formaldehyde resin The monomers are melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde (methanal), $H-C(=O)-H$. The structure of melamine is the closed six-membered ring



Thus ring nitrogen and ring carbon alternate, with one $-NH_2$ group on each ring carbon. Melamine contains three amino groups, so reaction with formaldehyde can form a cross-linked network rather than a simple linear chain.

Step 3: Write both unsaturated monomers of Buna-S Buna-S is the copolymer of buta-1,3-diene and styrene (phenylethene). Their structures are

$$CH_2=CH-CH=CH_2 \quad \text{and} \quad C_6H_5-CH=CH_2.$$

Butadiene supplies the conjugated diene units, while styrene supplies units bearing a phenyl group. Both have carbon-carbon double bonds that participate in addition polymerisation; no water molecule is eliminated in this process. The letter S identifies styrene, so acrylonitrile is not the second monomer of Buna-S.

Quick Tip to Solve: For nylon-6,6 count all six carbons in each monomer; for Buna-S remember S means styrene, then write its phenyl group attached to ethene.

Step 4: Conclusion Nylon-6,6: $H_2N(CH_2)_6NH_2$ and $HOOC(CH_2)_4COOH$. Melamine-formaldehyde: the alternating N/C triazine ring with three $-NH_2$ groups, and HCHO. Buna-S: $CH_2{=}CH{-}CH{=}CH_2$ and $C_6H_5CH{=}CH_2$.

Quick Tip to Solve: For nylon-6,6 count all six carbons in each monomer; for Buna-S remember S means styrene, then write its phenyl group attached to ethene.

20. Define the following:

(a) Anionic detergents

(b) Limited spectrum antibiotics

(c) Antiseptics [3 marks]

Solution:

Concept:

- Detergents are surface-active cleansing agents with a hydrophobic hydrocarbon portion and a hydrophilic ionic portion. The charge on the cleansing-active ion determines the detergent class.
- Antibiotics act against microorganisms; their spectrum describes the range of organisms against which they act. Antiseptics are antimicrobial substances suitable for use on living tissues.

Step 1: Define anionic detergents Anionic detergents are detergents in which the anionic part of the molecule is responsible for the cleansing action. Common examples are sodium salts of sulphated long-chain alcohols and of alkylbenzenesulphonic acids. Sodium lauryl sulphate has the structure $CH_3(CH_2)_{11}OSO_3^-\,Na^+$. Its long hydrocarbon chain interacts with oily dirt, while the negatively charged sulphate head interacts with water. The cleansing-active species is therefore the anion; the sodium ion is its counterion. These agents help disperse grease in water for removal.

Step 2: Define limited spectrum antibiotics Limited spectrum antibiotics are antibiotics effective against a single organism or a particular disease. Their activity is highly specific rather than extending over a wide range of microorganisms. The word spectrum refers to the range of susceptible organisms, not to the amount of medicine taken or the duration of treatment. They are distinguished from broad spectrum antibiotics, which act against a wide range of Gram-positive and Gram-negative bacteria, and from narrow spectrum agents acting against a restricted bacterial group.

Step 3: Define antiseptics Antiseptics are chemical substances that kill microorganisms or inhibit their growth and can be applied to living tissues such as skin, wounds and cuts. Their use helps prevent microbial infection at the site of application. For example, tincture of iodine is used as an antiseptic. Suitability for living tissue is the key distinction from disinfectants used on inanimate surfaces such as floors and drains. The effect of a substance depends on its concentration; a chemical suitable as an antiseptic in a dilute solution may be unsuitable for living tissues at a higher concentration.

Step 4: Conclusion (a) Anionic detergents have a negatively charged cleansing-active ion. (b) Limited spectrum antibiotics act against a single organism or a particular disease. (c) Antiseptics kill or inhibit microbes and are suitable for application to living tissues.

Quick Tip to Solve: Identify each definition by its distinguishing feature: anionic charge, specificity to an organism or disease, and safe application to living tissues.

21. Give reasons for the following:

(a) Red phosphorus is less reactive than white phosphorus.

(b) Electron gain enthalpies of halogens are largely negative.

(c) N_2O_5 is more acidic than N_2O_3. [3 marks]

Solution:

Concept:

- Allotrope reactivity depends on structural stability: strained bonds are more readily attacked than bonds in a stable network.
- Electron gain enthalpy is the enthalpy change when an isolated gaseous atom accepts an electron; a negative value denotes release of energy.
- For oxides of the same non-metal, acidic character generally increases with the oxidation state of the central atom.

Step 1: (a) Compare the structures of phosphorus allotropes White phosphorus consists of discrete tetrahedral P_4 molecules. Their $P-P-P$ bond angles are only 60°, so the bonds are strained and the molecules are relatively unstable. Red phosphorus has a polymeric structure in which phosphorus units are linked to form a more stable network with much less angle strain. Consequently its bonds are less readily attacked, making red phosphorus less reactive than white phosphorus.

Step 2: (b) Explain the energy released on electron addition Halogen atoms have the valence-shell configuration ns^2np^5, so each needs only one electron to complete its octet. Their high effective nuclear charge and relatively small size produce a strong attraction for the incoming electron. Addition of this electron gives the stable noble-gas configuration ns^2np^6 and releases considerable energy. Thus their electron gain enthalpies are largely negative; the sign refers to an exothermic electron-addition process.

Step 3: (c) Compare the nitrogen oxides Nitrogen has oxidation state $+5$ in N_2O_5 but $+3$ in N_2O_3. The higher oxidation-state oxide is more acidic. Their corresponding acids further show this difference:

$$N_2O_5 + H_2O \longrightarrow 2HNO_3,$$
$$N_2O_3 + H_2O \longrightarrow 2HNO_2.$$

Nitric acid is a strong acid, whereas nitrous acid is a weak acid. Hence the nitric-acid anhydride N_2O_5 has greater acidic character.

Step 4: Conclusion (a) Red phosphorus has a more stable, less strained polymeric structure. (b) Halogens release energy on attaining a complete octet by electron gain. (c) Nitrogen in N_2O_5 is in the higher oxidation state, and this oxide forms the stronger acid HNO_3.

Quick Tip to Solve: Link each reason to its controlling factor: phosphorus structure, halogen octet completion, and nitrogen oxidation state.

22. Give reasons for the following:

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(c) Although -NH_2 is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline. [3 marks]

Solution:

Concept:

- A nitrogen lone pair activates a benzene ring when it can donate electron density into the ring by resonance.
- Amine basicity depends on the availability of the nitrogen lone pair for accepting a proton; electron donation increases its availability, while delocalisation decreases it.
- Protonation of an amino group removes its free lone pair and changes the substituent from activating and ortho/para directing to deactivating and meta directing.

Step 1: (a) Explain the effect of acetylation Acetylation converts the amino group of aniline, $C_6H_5NH_2$, into the acetamido group of acetanilide, $C_6H_5NHCOCH_3$. The nitrogen lone pair can now be delocalised towards the carbonyl group:

$$C_6H_5 - NH - C(=O) - CH_3 \longleftrightarrow C_6H_5 - N^+H = C(-O^-) - CH_3.$$

It is therefore less available for donation into the benzene ring than in aniline. Electron density in the ring increases less strongly, so the activation effect is reduced. The acetamido group nevertheless remains ortho/para directing.

Step 2: (b) Compare methylamine and aniline as bases In methylamine, CH_3NH_2, the methyl group exerts a positive inductive effect and increases electron density on nitrogen. Its lone pair is localised and readily accepts H^+. In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance, making it less available to bind a proton. The phenyl group's negative inductive effect also reduces electron density on nitrogen. Thus methylamine is more basic than aniline.

Step 3: (c) Explain the meta product during direct nitration Direct nitration uses a strongly acidic mixture of concentrated nitric and sulphuric acids. In this medium, aniline is protonated to the anilinium ion:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3^+.$$

The $-NH_3^+$ group has no free nitrogen lone pair to donate to the ring and strongly withdraws electron density. It is deactivating and meta directing. Nitration of the protonated species therefore produces a significant amount of meta-nitroaniline, obtained after work-up. The ortho/para-directing behaviour of neutral $-NH_2$ does not describe this protonated species.

Step 4: Conclusion (a) Acetylation diverts the nitrogen lone pair towards the carbonyl group, reducing ring activation. (b) Methylamine has a more available nitrogen lone pair and is the stronger base. (c) The acidic nitrating medium forms meta-directing anilinium ions, explaining the significant meta product.

Quick Tip to Solve: Before predicting aniline's behaviour, identify whether nitrogen is free, acetylated or protonated; these states change lone-pair availability.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Rupali a Class XII student decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to replace the bakery products with some protein and vitamin rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and the students.

After reading the above passage, answer the following questions:

(a) What are the values (at least two) displayed by Rupali?

(b) Which polysaccharide component of carbohydrates is commonly present in bread?

(c) Write the two types of secondary structures of proteins.

(d) Give two examples of water soluble vitamins. [4 marks]

Solution:

Concept:

- Food safety awareness involves concern for others, responsible action and the use of scientific information to protect community health.
- Starch is a plant storage polysaccharide composed of glucose units. Protein secondary structure is the regular arrangement of the polypeptide backbone, stabilised by hydrogen bonding.
- Vitamins are essential micronutrients. The B-group vitamins and vitamin C belong to the water-soluble class.

Step 1: (a) Identify Rupali's values from her actions Rupali displays social responsibility and concern for the health of others: she wants fellow students to be aware of harmful substances in food. She also displays scientific awareness and initiative, because she uses information from the programme and approaches the principal to obtain a practical change in the canteen. These actions show that she is prepared to act for the welfare of the school community.

Step 2: (b) Name the polysaccharide in bread Bread is made mainly from cereal flour, which contains starch. Starch is therefore the polysaccharide commonly present in bread. It consists of glucose units and has two components, amylose and amylopectin; the answer to the question is the overall polysaccharide starch.

Step 3: (c) State the two secondary structures of proteins The two types are the α-helix and the β-pleated sheet. In the α-helix, the polypeptide chain coils into a helix; in the β-pleated sheet, extended segments lie alongside one another. Both arrangements are stabilised by hydrogen bonds involving peptide $\mathrm{C}=\mathrm{O}$ and $\mathrm{N}-\mathrm{H}$ groups.

Step 4: (d) Give two water-soluble vitamins Two examples are vitamin B_1 (thiamine) and vitamin C (ascorbic acid). Both belong to the water-soluble vitamin class. Specifying a member such as B_1 makes the B-group example precise.

Step 5: Conclusion (a) Social responsibility and concern for others' health (also scientific awareness and initiative). (b) Starch. (c) α-helix and β-pleated sheet. (d) Vitamin B_1 and vitamin C.

Quick Tip to Solve: Link each value to an action in the passage; remember starch for cereal foods, helix/sheet for proteins, and B/C for water-soluble vitamins.

24(a). Account for the following:

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals.

(iii) E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

[5 marks]

Solution:

Concept:

- Transition-metal oxidation states depend on the participation of both the outer ns and inner $(n-1)d$ electrons, whose energies are relatively close.
- Metallic-bond strength depends on the electrons available for bonding; a completely filled d subshell contributes comparatively little to strong metallic bonding.
- A positive standard reduction potential E° indicates a favourable tendency for reduction under standard conditions. The relative stability of the product and reactant electronic configurations helps explain the trend.
- Lanthanoids and actinoids involve progressive filling of the $4f$ and $5f$ subshells, respectively, and both commonly form ions in the $+3$ oxidation state.

Step 1: (a)(i) Explain variable oxidation states The energies of the ns and $(n-1)d$ orbitals of transition metals are close enough that different numbers of electrons from these orbitals can participate in bonding or be removed. Consequently, more than one oxidation state is accessible. For example, iron has the configuration $[Ar]3d^6 4s^2$: loss of the two $4s$ electrons gives Fe^{2+}, while loss of one additional $3d$ electron gives Fe^{3+}. Thus, the availability of both sets of valence electrons explains the variable oxidation states.

Step 2: (a)(ii) Explain the softness of Zn, Cd and Hg Zn, Cd and Hg have the general outer electronic configuration $(n-1)d^{10}ns^2$. Their d subshells are completely filled, with no unpaired d electrons available to strengthen metallic bonding. They therefore have relatively weak metallic bonds compared with many other d-block metals, in which more valence electrons contribute to bonding. This weaker cohesion accounts for their softness; mercury is liquid at room temperature.

Step 3: (a)(iii) Compare the two standard reduction potentials For manganese, the reduction is

$$Mn^{3+}(3d^4) + e^- \longrightarrow Mn^{2+}(3d^5).$$

The product has an especially stable half-filled $3d^5$ subshell. Thus, Mn^{3+} readily accepts an electron to form Mn^{2+}, giving a highly positive standard reduction potential, $E^\circ = +1.57\,V$. In contrast, chromium undergoes

$$Cr^{3+}(3d^3) + e^- \longrightarrow Cr^{2+}(3d^4).$$

The Cr^{3+} ion is particularly stable in aqueous solution because its d^3 configuration has a stable t_{2g}^3 arrangement in the octahedral hydrated ion. Reduction to Cr^{2+} does not produce the half-filled-shell stability obtained in the manganese reaction. Hence the Cr^{3+}/Cr^{2+} reduction potential is much less positive.

Step 4: (b) State one similarity and one difference **Similarity:** Both lanthanoids and actinoids

Quick Tip to Solve: Write the ion configurations first: manganese changes from d^4 to stable d^5, whereas chromium changes from stable aqueous d^3 to d^4.

commonly show the $+3$ oxidation state in their compounds, forming M^{3+} ions.

Difference: Lanthanoids predominantly show the $+3$ oxidation state, with a limited number also showing $+2$ or $+4$. Actinoids show a much wider range of oxidation states, especially in the early members, because the $5f$, $6d$ and $7s$ orbitals have comparable energies and their electrons can participate in bonding. Thus their oxidation-state chemistry is more varied than that of the lanthanoids.

Step 5: Conclusion Transition metals exhibit variable oxidation states through participation of ns and $(n-1)d$ electrons. Filled d^{10} subshells lead to weak metallic bonding in Zn, Cd and Hg. The stable d^5 product favours reduction of Mn^{3+}. Both f-block series commonly show $+3$, but actinoids display a wider range of oxidation states.

Quick Tip to Solve: Write the ion configurations first: manganese changes from d^4 to stable d^5, whereas chromium changes from stable aqueous d^3 to d^4.

OR

24(b). (a) Following are the transition metal ions of 3d series:

Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}

(Atomic numbers: Ti = 22, V = 23, Mn = 25, Cr = 24)

Answer the following:

(i) Which ion is most stable in an aqueous solution and why?

(ii) Which ion is a strong oxidising agent and why?

(iii) Which ion is colourless and why?

(b) Complete the following equations:

(i) $2\,MnO_4^- + 16\,H^+ + 5\,S^{2-} \rightarrow$

(ii) $KMnO_4 \xrightarrow{heat}$ [5 marks]

Solution:

Concept:

- Remove the $4s$ electrons before the $3d$ electrons when forming ions. The resulting d-electron configuration helps explain stability, colour and redox behaviour.
- In an octahedral aqueous complex, a d^3 configuration has the particularly stable t_{2g}^3 arrangement. A half-filled d^5 configuration also has enhanced stability.
- An oxidising agent accepts electrons and is itself reduced. In balancing redox equations, both the number of atoms and the total electric charge must be conserved.

Step 1: (a)(i) Identify the most stable aqueous ion The configurations of the given ions are

$$Ti^{4+} : [Ar]\,3d^0, \quad V^{2+} : [Ar]\,3d^3,$$
$$Mn^{3+} : [Ar]\,3d^4, \quad Cr^{3+} : [Ar]\,3d^3.$$

Of these, Cr^{3+} is the most stable in aqueous solution. Its $3d^3$ configuration gives a stable t_{2g}^3 arrangement in its octahedral aqua complex, with substantial crystal-field stabilisation. Although V^{2+}

Quick Tip to Solve: Write each ionic d configuration first; then balance acidic permanganate with H+ and water, checking the total charge as well as every atom.

also has a d^3 configuration, it readily undergoes oxidation to the more stable higher oxidation states of vanadium in aqueous solution; electron configuration alone is therefore not sufficient to select it as the most stable ion.

Step 2: (a)(ii) Identify the strong oxidising agent $\mathrm{Mn^{3+}}$, with configuration $3d^4$, readily accepts an electron:

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

The product $\mathrm{Mn^{2+}}$ has the especially stable half-filled $3d^5$ configuration. This favourable reduction makes $\mathrm{Mn^{3+}}$ a strong oxidising agent: it oxidises another species while itself changing to $\mathrm{Mn^{2+}}$.

Step 3: (a)(iii) Identify the colourless ion $\mathrm{Ti^{4+}}$ is colourless because it has a $3d^0$ configuration. There is no d electron available to undergo a transition between the crystal-field-split d orbitals, so it cannot absorb visible light through a d-d transition. The other listed ions have partially filled d orbitals and their aqueous complexes are coloured.

Step 4: (b)(i) Complete the acidic permanganate reaction Permanganate is reduced to $\mathrm{Mn^{2+}}$, while sulfide is oxidised to elemental sulfur. The half-reactions are

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

Multiply the first by 2 and the second by 5, then add and cancel 10 electrons:

$$\boxed{\mathrm{2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S}}.$$

There are two manganese atoms, eight oxygen atoms, sixteen hydrogen atoms and five sulfur atoms on each side. The net charge is $+4$ on both sides, confirming the balance.

Step 5: (b)(ii) Complete the thermal decomposition On heating, potassium permanganate forms potassium manganate, manganese dioxide and oxygen:

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

The two potassium atoms and two manganese atoms are conserved. The eight oxygen atoms on the left appear as four in manganate, two in manganese dioxide and two in oxygen gas. Manganese is reduced from $+7$ to $+6$ and $+4$, while some oxygen is oxidised from -2 to zero.

Step 6: Conclusion (a) (i) $\mathrm{Cr^{3+}}$ is most stable in aqueous solution; (ii) $\mathrm{Mn^{3+}}$ is a strong oxidising agent; (iii) $\mathrm{Ti^{4+}}$ is colourless. (b) The products are (i) $\mathrm{2Mn^{2+} + 8H_2O + 5S}$, and (ii) $\mathrm{K_2MnO_4 + MnO_2 + O_2}$ when $\mathrm{2KMnO_4}$ is heated.

Quick Tip to Solve: Write each ionic d configuration first; then balance acidic permanganate with H+ and water, checking the total charge as well as every atom.

25(a). A 10% solution (by mass) of sucrose in water has a freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15 K.

Given:

(Molar mass of sucrose = 342 g mol^{-1})

(Molar mass of glucose = 180 g mol^{-1})

(b) Define the following terms:

(i) Molality (m)

(ii) Abnormal molar mass [5 marks]

Solution:

Concept:

- Freezing point depression is a colligative property: $\Delta T_f = T_f^0 - T_f = K_f m$ for a non-electrolyte, where K_f is the solvent's molal depression constant and m is the solute molality.
- A 10% solution by mass contains $10\,\text{g}$ solute in $100\,\text{g}$ solution, hence $90\,\text{g}$ solvent. Sucrose and glucose do not dissociate in water, so their van't Hoff factor is $i = 1$.
- Association or dissociation changes the number of solute particles. The relation $\Delta T_f = iK_f m$ connects this change to the apparent molar mass inferred from a colligative property.

Step 1: (a) Obtain the depression for sucrose The freezing point depression of the given sucrose solution is

$$\Delta T_{f,s} = 273.15 - 269.15 = 4.00\,\text{K}.$$

Take $100\,\text{g}$ of each solution. The mass of water in each is $100 - 10 = 90\,\text{g} = 0.090\,\text{kg}$. Therefore, for sucrose,

$$m_s = \frac{10/342}{0.090}\ \text{mol kg}^{-1}.$$

Use the experimentally supplied sucrose depression to compare the two solutions; a separately tabulated value of K_f is unnecessary.

Step 2: (a) Compare glucose with sucrose The glucose solution has the same solute mass and solvent mass, but more solute molecules because its molar mass is lower. Its molality is

$$m_g = \frac{10/180}{0.090}\ \text{mol kg}^{-1}.$$

Since both solutions have water as solvent and both solutes are non-electrolytes,

$$\frac{\Delta T_{f,g}}{\Delta T_{f,s}} = \frac{m_g}{m_s} = \frac{342}{180} = 1.90.$$

Hence $\Delta T_{f,g} = 4.00 \times 1.90 = 7.60\,\text{K}$. Subtracting this depression from the freezing point of pure water gives

$$T_{f,g} = 273.15 - 7.60 = 265.55\,\text{K}.$$

Step 3: (b)(i) Define molality Molality, denoted by m, is the number of moles of solute dissolved per kilogram of solvent:

$$m = \frac{n_{\text{solute}}}{w_{\text{solvent}}\ \text{in kg}}.$$

Quick Tip to Solve: For equal mass percentages in the same solvent, compare depressions using the inverse ratio of solute molar masses; the solvent mass cancels.

Its unit is mol kg^{-1}. The denominator is the mass of the solvent, not the mass of the entire solution. Because it uses masses rather than volume, molality does not change with temperature for a fixed composition.

Step 4: (b)(ii) Define abnormal molar mass Abnormal molar mass is an experimentally determined molar mass, obtained from a colligative property, that differs from the normal molar mass because the solute associates or dissociates in solution. The colligative measurement counts particles rather than individual formula units. Association reduces their number and gives a molar mass higher than the normal value; dissociation increases their number and gives a lower apparent molar mass. Quantitatively,

$$i = \frac{M_{\text{normal}}}{M_{\text{observed}}}.$$

Step 5: Conclusion (a) The freezing point of the 10% glucose solution is $\boxed{265.55\,\text{K}}$. (b) Molality is moles of solute per kilogram of solvent; abnormal molar mass is a colligatively measured molar mass differing from the normal value owing to association or dissociation.

Quick Tip to Solve: For equal mass percentages in the same solvent, compare depressions using the inverse ratio of solute molar masses; the solvent mass cancels.

OR

25(b). (a) 30 g of urea (M = 60 g mol^{-1}) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg.

(b) Write two differences between ideal solutions and non-ideal solutions. [5 marks]

Solution:

Concept:

- For a solution containing a non-volatile solute, Raoult's law gives $p_{\text{w}} = x_{\text{w}} p_{\text{w}}^0$, where x_{w} is the mole fraction of water and p_{w}^0 is its pure vapour pressure at the same temperature.
- The mole fraction of water is $x_{\text{w}} = n_{\text{w}}/(n_{\text{w}} + n_{\text{s}})$, where n_{w} and n_{s} are the amounts of solvent and solute in moles. Urea is non-volatile and does not dissociate in water.
- Ideal solutions obey Raoult's law throughout the composition range and have $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$. Non-ideal solutions show deviations due to changed intermolecular interactions on mixing.

Step 1: (a) Calculate the amounts of urea and water The molar mass of urea is $60\,\text{g mol}^{-1}$, and that of water is $18\,\text{g mol}^{-1}$. Thus,

$$n_{\text{urea}} = \frac{30}{60} = 0.500\,\text{mol},$$
$$n_{\text{w}} = \frac{846}{18} = 47.0\,\text{mol}.$$

The total amount of both components is $47.0 + 0.500 = 47.5\,\text{mol}$.

Step 2: (a) Apply Raoult's law to water Since urea is non-volatile, only water contributes appreciably

Quick Tip to Solve: Convert both masses to moles before forming the water mole fraction; use the total moles in its denominator.

to the vapour pressure. Its mole fraction in the solution is

$$x_{\mathrm{w}} = \frac{47.0}{47.5} = 0.989474.$$

With the given pure-water vapour pressure at $298\,\mathrm{K}$,

$$p_{\mathrm{w}} = \frac{47.0}{47.5} \times 23.8 = 23.5495\,\text{mm Hg}.$$

The pressure lowering is $0.2505\,\text{mm Hg}$; the solution pressure is below the pure-water value, as expected.

Step 3: (b) State two differences between ideal and non-ideal solutions First, ideal solutions obey Raoult's law at all compositions: each volatile component satisfies $p_i = x_i p_i^0$. Non-ideal solutions deviate positively or negatively from this law because unlike-molecule attractions differ from those between like molecules.

Second, mixing ideal components involves no enthalpy or volume change: $\Delta H_{\mathrm{mix}} = 0$ and $\Delta V_{\mathrm{mix}} = 0$. For non-ideal solutions these changes are generally non-zero.

Step 4: Conclusion (a) The vapour pressure of water in the solution at $298\,\mathrm{K}$ is $\boxed{23.55\,\text{mm Hg}}$. (b) Ideal solutions obey Raoult's law throughout the composition range and mix with zero enthalpy and volume changes; non-ideal solutions deviate from Raoult's law and generally have non-zero mixing changes.

Quick Tip to Solve: Convert both masses to moles before forming the water mole fraction; use the total moles in its denominator.

26(a). Write the product(s) in the following reactions:

(i) Cyclohexanone + HCN $\rightarrow$?

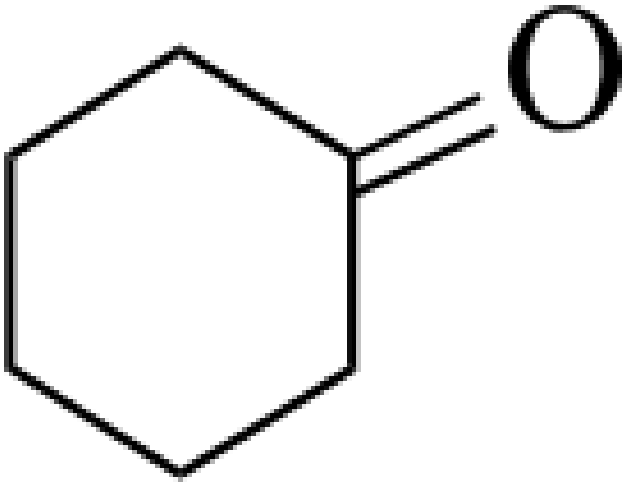
(ii) Sodium benzoate + NaOH $\xrightarrow[\Delta]{CaO}$?

(iii) CH_3-CH=CH-CN $\xrightarrow[(b)\ H_2O]{(a)\ DIBAL-H}$?

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Butanal and Butan-2-one

(ii) Benzoic acid and Phenol [5 marks]



Solution:

Concept:

- Cyanide adds to the electrophilic carbonyl carbon, and protonation of the oxygen gives a cyanohydrin: the original carbonyl carbon bears both $-\mathrm{OH}$ and $-\mathrm{CN}$.
- Heating a sodium carboxylate with soda lime ($\mathrm{NaOH/CaO}$) removes the carboxyl carbon as carbonate, giving a hydrocarbon with one fewer carbon atom.
- DIBAL-H followed by hydrolysis converts a nitrile group $-\mathrm{CN}$ into an aldehyde group $-\mathrm{CHO}$. Tollens' reagent distinguishes an aldehyde from an ordinary ketone; aqueous sodium hydrogen carbonate distinguishes a carboxylic acid from phenol.

Step 1: (a)(i) Addition of HCN to cyclohexanone The cyanide ion attacks the carbonyl carbon of cyclohexanone. The resulting alkoxide takes a proton from HCN, producing 1-hydroxycyclohexane-1-carbonitrile, the cyanohydrin of cyclohexanone:

$$\text{Cyclohexanone} + \mathrm{HCN} \longrightarrow \text{cyclohexanone cyanohydrin.}$$

The six-membered ring remains intact. At its former carbonyl carbon, the $\mathrm{C=O}$ group is replaced by a carbon bearing an OH group and a CN group; both groups are attached to that same ring carbon.

Step 2: (a)(ii) Decarboxylation of sodium benzoate Sodium benzoate loses its carboxylate carbon on heating with soda lime. The organic product is benzene, and sodium carbonate is the inorganic

Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, whereas DIBAL-H retains the nitrile carbon as CHO. For acid versus phenol, use bicarbonate rather than NaOH.

product:

$$C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3.$$

Thus the phenyl group acquires hydrogen in place of $-COONa$. Calcium oxide is the soda-lime component shown over the arrow and is not incorporated into benzene.

Step 3: (a)(iii) Controlled reduction of the nitrile DIBAL-H reduces the nitrile to an intermediate that gives an aldehyde on hydrolysis. The carbon of the nitrile is retained as the aldehyde carbon, while the carbon-carbon double bond remains:

$$CH_3CH = CHCN \xrightarrow[\text{(b) } H_2O]{\text{(a) DIBAL-H}} CH_3CH = CHCHO.$$

The product is but-2-enal (crotonaldehyde), an unsaturated aldehyde. This reagent sequence gives the aldehyde rather than reducing the nitrile completely to a primary amine.

Step 4: (b)(i) Distinguish butanal and butan-2-one Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Butanal gives a silver mirror because its aldehyde group reduces silver(I) to metallic silver while being oxidised to butanoate. Butan-2-one gives no silver mirror under these conditions:

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

The visible deposition of silver therefore identifies butanal. Merely testing for a carbonyl group would not distinguish the pair, since both compounds contain one.

Step 5: (b)(ii) Distinguish benzoic acid and phenol Add aqueous sodium hydrogen carbonate to separate samples. Benzoic acid produces brisk effervescence of carbon dioxide, whereas phenol does not:

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

Benzoic acid is strong enough to displace carbonic acid from hydrogen carbonate; carbonic acid decomposes into water and carbon dioxide. Phenol is too weakly acidic to do so. Sodium hydroxide would be unsuitable for this distinction because both substances react with it.

Step 6: Conclusion (a) The products are (i) cyclohexanone cyanohydrin, with OH and CN on the same ring carbon; (ii) benzene and sodium carbonate; and (iii) $CH_3CH = CHCHO$, but-2-enal. (b) Butanal gives a Tollens' silver mirror, but butan-2-one does not; benzoic acid gives CO_2 effervescence with $NaHCO_3$, but phenol does not.

Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, whereas DIBAL-H retains the nitrile carbon as CHO. For acid versus phenol, use bicarbonate rather than NaOH.

OR

26(b). (a) Write the reactions involved in the following:

(i) Etard reaction

(ii) Stephen reduction

(b) How will you convert the following in not more than two steps:

(i) Benzoic acid to Benzaldehyde

(ii) Acetophenone to Benzoic acid

(iii) Ethanoic acid to 2-Hydroxyethanoic acid [5 marks]

Solution:

Concept:

- Etard oxidation converts the benzylic methyl group of toluene into an aldehyde using chromyl chloride, followed by hydrolysis. Stephen reduction converts a nitrile into an iminium salt, whose hydrolysis gives an aldehyde.
- Rosenmund reduction of an acid chloride stops at the aldehyde. A methyl ketone undergoes the haloform reaction, while the Hell–Volhard–Zelinsky reaction introduces a halogen at the carbon adjacent to a carboxyl group.

Step 1: (a)(i) Etard reaction Toluene is treated with chromyl chloride in an inert solvent such as carbon disulphide. The resulting chromium complex is hydrolysed to benzaldehyde:

$$C_6H_5CH_3 \xrightarrow[CS_2]{CrO_2Cl_2} \text{Etard complex} \xrightarrow{H_2O} C_6H_5CHO.$$

The controlled oxidation changes the side-chain methyl group into $-CHO$, without converting it into a carboxyl group.

Step 2: (a)(ii) Stephen reduction A nitrile is reduced with stannous chloride and hydrochloric acid to an iminium chloride, then hydrolysed:

$$RCN \xrightarrow{SnCl_2/HCl} RCH{=}NH \cdot HCl,$$
$$RCH{=}NH \cdot HCl + H_2O \longrightarrow RCHO + NH_4Cl.$$

Here R is an alkyl or aryl group. The carbon of the nitrile becomes the aldehyde carbon; hydrolysis is essential to release the aldehyde.

Step 3: (b)(i) Benzoic acid to benzaldehyde First prepare benzoyl chloride with thionyl chloride, then carry out Rosenmund reduction using hydrogen over poisoned palladium on barium sulphate:

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl,$$
$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl.$$

The poisoned catalyst limits further hydrogenation of benzaldehyde. Direct reduction with lithium aluminium hydride would instead give benzyl alcohol.

Step 4: (b)(ii) Acetophenone to benzoic acid Acetophenone contains the methyl ketone group

Quick Tip to Solve: For the two-step conversions, identify the functional handle: acid chloride for an aldehyde, the methyl ketone for haloform cleavage, and an alpha hydrogen for HVZ halogenation.

$-COCH_3$. Treat it with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate formed:

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

$$C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl.$$

The methyl carbon is removed as yellow iodoform, while the carbonyl carbon remains in the benzoate ion. Acidification gives the required free acid.

Step 5: (b)(iii) Ethanoic acid to 2-hydroxyethanoic acid Use the Hell–Volhard–Zelinsky reaction to obtain 2-bromoethanoic acid, then replace bromine by hydroxyl using aqueous alkali followed by acidification in the work-up:

$$CH_3COOH + Br_2 \xrightarrow{\text{red P}} BrCH_2COOH + HBr,$$

$$BrCH_2COOH \xrightarrow[\text{then } H^+]{\text{aq. NaOH}} HOCH_2COOH.$$

Halogenation occurs at the alpha carbon because ethanoic acid has alpha hydrogen atoms. Aqueous hydroxide substitutes the bromine; acidification converts the hydroxyethanoate salt to 2-hydroxyethanoic acid.

Step 6: Conclusion Etard oxidation gives benzaldehyde from toluene, and Stephen reduction gives an aldehyde from a nitrile. The three conversions use, respectively, acid-chloride formation followed by Rosenmund reduction; the haloform reaction followed by acidification; and alpha bromination followed by hydrolysis with acid work-up.

Quick Tip to Solve: For the two-step conversions, identify the functional handle: acid chloride for an aldehyde, the methyl ketone for haloform cleavage, and an alpha hydrogen for HVZ halogenation.