CBSE Class 12 Chemistry Question Paper 2017 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) **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 carry **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. What is the effect of catalyst on:

(i) Gibbs energy (ΔG) and

(ii) activation energy of a reaction? [1 mark]

Solution:

Concept:

- The reaction Gibbs energy is $\Delta G = G_{\text{products}} - G_{\text{reactants}}$ at specified conditions.
- A catalyst provides an alternative reaction pathway having a lower activation energy, E_a.

Step 1: Effect on Gibbs energy A catalyst does not change the Gibbs energies of the reactants or products. Hence it does not change ΔG, the thermodynamic driving force of the reaction, or the equilibrium constant.

Step 2: Effect on the energy barrier The alternative catalysed pathway has a lower activation energy. Consequently, a larger fraction of reacting molecules can cross the barrier at the same temperature and the reaction proceeds faster.

Step 3: Conclusion (i) ΔG remains unchanged. (ii) The activation energy decreases.

Quick Tip to Solve: A catalyst changes the pathway and rate; compare the same reactants and products when judging ΔG.

2. Write one similarity between Physisorption and Chemisorption. [1 mark]

Solution:

Concept:

- Adsorption is the accumulation of a substance at the surface of another substance.
- In both physical and chemical adsorption, attractive interactions between the adsorbate and adsorbent release energy.

Step 1: Identify the common process Both physisorption and chemisorption concentrate adsorbate particles at the adsorbent surface. Their binding mechanisms differ: physical adsorption involves weak intermolecular forces, while chemical adsorption involves chemical bonding.

Step 2: State a shared thermal property Formation of attractive interactions at the surface releases heat in either case. Therefore both adsorption processes are exothermic, even though their heats of adsorption have different magnitudes.

Step 3: Conclusion Both physisorption and chemisorption are exothermic processes: $\Delta H_{\text{ads}} < 0$.

Quick Tip to Solve: For a similarity, state the shared exothermic nature; do not confuse it with their different bond strengths.

3. Write the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number. [1 mark]

Solution:

Concept:

- Manganese belongs to group 7, so the required oxidation state is $+7$.
- The sum of oxidation states in an ion equals its net charge; oxygen normally has oxidation state -2.

Step 1: Choose the manganese oxo-anion The permanganate ion contains one manganese atom and four oxygen atoms, and has a single negative charge. Its formula is $\mathrm{MnO_4^-}$.

Step 2: Verify the oxidation state Let the oxidation state of manganese be x. For permanganate,

$$x + 4(-2) = -1 \quad \Rightarrow \quad x = +7.$$

This equals the group number of manganese, as required by the question.

Step 3: Conclusion The required oxo-anion is permanganate, $\boxed{\mathrm{MnO_4^-}}$.

Quick Tip to Solve: Check the ion charge: permanganate gives Mn(+7), whereas manganate $\mathrm{MnO_4^{2-}}$ gives Mn(+6).

4. Write the structure of 3-Bromo-2-methylprop-1-ene. [1 mark]

Solution:

Concept:

- In prop-1-ene, the three-carbon parent chain has a double bond between carbon 1 and carbon 2.
- The prefixes 2-methyl and 3-bromo place $\mathrm{CH_3}$ on carbon 2 and Br on carbon 3.

Step 1: Construct the parent chain Number the chain from the end nearest the double bond. The parent skeleton is $\mathrm{CH_2{=}CH{-}CH_3}$, with the double-bond locant 1.

Step 2: Attach the substituents Replace the hydrogen on carbon 2 by a methyl group and one hydrogen on carbon 3 by bromine. Carbon 2 then has one double bond and two single bonds, while carbon 3 becomes $\mathrm{CH_2Br}$; each carbon retains valency four.

Step 3: Conclusion The structure is $\boxed{\mathrm{CH_2{=}C(CH_3){-}CH_2Br}}$.

Quick Tip to Solve: Give the double bond the lowest locant first, then attach methyl at C-2 and bromine at C-3.

5. Write IUPAC name of the following compound:

$(CH_3)_2N\text{-}CH_2CH_3$ [1 mark]

Solution:

Concept:

- For an unsymmetrical tertiary amine, choose the longest carbon chain attached to nitrogen as the parent alkanamine.
- Other groups directly attached to nitrogen are named as N-substituents rather than carbon-chain substituents.

Step 1: Identify the parent amine The nitrogen is bonded to one ethyl group and two methyl groups. The ethyl group supplies the longest chain, so the parent is ethanamine. Nitrogen has three carbon substituents, making this a tertiary amine.

Step 2: Name the nitrogen substituents Both remaining substituents are methyl groups bonded directly to nitrogen. Each therefore receives the locant N, and their multiplicity is indicated by the prefix dimethyl.

Step 3: Conclusion The IUPAC name is $\boxed{N,N\text{-dimethylethanamine}}$.

Quick Tip to Solve: Choose the ethyl chain as the parent, then use N,N-dimethyl for the two methyl groups on nitrogen.

6. Write the reactions involved in the following reactions:

(i) Clemmensen reduction

(ii) Cannizzaro reaction [2 marks]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using amalgamated zinc and concentrated hydrochloric acid.
- Cannizzaro reaction is the disproportionation of an aldehyde without an α-hydrogen in concentrated alkali.

Step 1: (i) Clemmensen reduction Treatment with $\mathrm{Zn(Hg)}$ and concentrated HCl removes the carbonyl oxygen, reducing the carbonyl carbon. For example, acetone gives propane:

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

Here $[H]$ denotes reducing equivalents; the carbon skeleton remains unchanged.

Step 2: (ii) Cannizzaro reaction Benzaldehyde has no α-hydrogen. In concentrated aqueous sodium hydroxide, one molecule is reduced to benzyl alcohol and another is oxidised to sodium benzoate:

$$2\mathrm{C_6H_5CHO} + \mathrm{NaOH} \xrightarrow{\mathrm{conc.}} \mathrm{C_6H_5CH_2OH} + \mathrm{C_6H_5COONa}.$$

Quick Tip to Solve: For Cannizzaro, first check the absence of an α-hydrogen and write the carboxylate salt in alkali.

The immediate oxidation product in the alkaline medium is the carboxylate salt, rather than the free carboxylic acid.

Step 3: Conclusion Clemmensen reduction gives propane from acetone; the Cannizzaro reaction of benzaldehyde gives benzyl alcohol and sodium benzoate, as shown above.

Quick Tip to Solve: For Cannizzaro, first check the absence of an α-hydrogen and write the carboxylate salt in alkali.

7. Draw the structures of the following:

(i) $H_4P_2O_7$

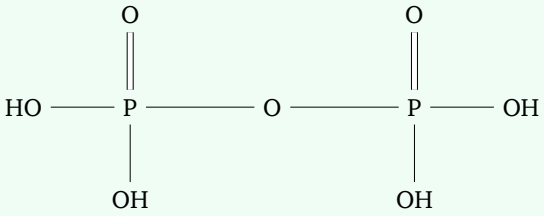
(ii) $XeOF_4$ [2 marks]

Solution:

Concept:

- In an oxyacid of phosphorus, each phosphorus atom has a tetrahedral arrangement of oxygen atoms around it; hydrogen atoms are bonded to oxygen.
- VSEPR theory places electron domains around xenon to minimise repulsion. A double bond counts as one domain, and a lone pair influences the molecular shape.

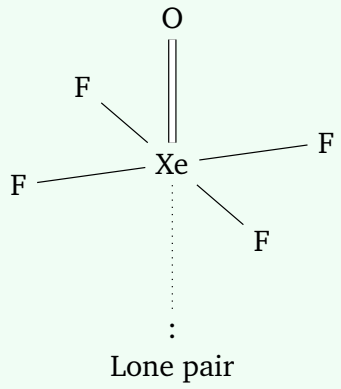
Step 1: Draw pyrophosphoric acid $H_4P_2O_7$ contains two phosphorus centres joined by a bridging oxygen, giving a $P-O-P$ linkage. Each phosphorus is also double bonded to one terminal oxygen and single bonded to two hydroxyl groups. Thus its connectivity is $(HO)_2P(=O)-O-P(=O)(OH)_2$, accounting for all four hydrogens and seven oxygens.



Structure of pyrophosphoric acid

Step 2: Draw xenon oxytetrafluoride In $XeOF_4$, xenon has four Xe–F bonds, one Xe=O bond and one lone pair: six electron domains altogether. These domains have an octahedral arrangement. The four fluorine atoms lie in one square plane, with oxygen at the apex and the lone pair opposite oxygen. The molecular shape is therefore square pyramidal; the dotted line in the sketch indicates the lone-pair direction.

Quick Tip to Solve: For the phosphorus acid, count four OH groups and one bridging O; for XeOF4, place the lone pair opposite the axial oxygen.



Square-pyramidal structure of XeOF4

Step 3: Conclusion $H_4P_2O_7$ has two tetrahedral phosphorus centres linked through oxygen; $XeOF_4$ has a square-pyramidal molecular structure.

Quick Tip to Solve: For the phosphorus acid, count four OH groups and one bridging O; for XeOF4, place the lone pair opposite the axial oxygen.

8. Define the following terms:

(i) Abnormal molar mass

(ii) van't Hoff factor (i) [2 marks]

Solution:

Concept:

- Colligative properties depend on the number of solute particles in a given amount of solvent, rather than the chemical identity of those particles.
- Association decreases the number of particles and dissociation increases it, so a molar mass inferred without accounting for these processes differs from the normal value.

Step 1: Define abnormal molar mass Abnormal molar mass is the apparent molar mass calculated from a colligative property when the solute undergoes association or dissociation in solution, and hence differs from its normal molar mass. Association gives fewer particles and a smaller colligative effect, so the apparent molar mass is higher. Dissociation gives more particles, so the apparent molar mass is lower.

Step 2: Define the van't Hoff factor The van't Hoff factor i is the ratio of the observed colligative property to the value calculated assuming no association or dissociation. Equivalently,

$$i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}.$$

It is dimensionless: $i > 1$ for dissociation, $i < 1$ for association, and $i = 1$ when neither occurs.

Step 3: Conclusion Abnormal molar mass is the apparent value affected by association or dissociation; i measures the resulting change in effective solute-particle number.

Quick Tip to Solve: Remember the ratio as normal mass divided by apparent mass: dissociation raises i but lowers the apparent molar mass.

9. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.

Given: $\lambda^\circ(H^+)$ = 349.6 S cm^2 mol^{-1} and $\lambda^\circ(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}. [2 marks]

Solution:

Concept:

- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m is its molar conductivity and Λ_m° is its value at infinite dilution.
- Kohlrausch's law gives the limiting molar conductivity as the sum of the limiting ionic contributions, each multiplied by its stoichiometric coefficient.

Step 1: Obtain the limiting molar conductivity Acetic acid dissociates as

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3COO^-}.$$

One mole of acid yields one mole of each ion at complete dissociation. Therefore,

$$\begin{aligned}\Lambda_m^\circ(\mathrm{CH_3COOH}) &= \lambda^\circ(\mathrm{H^+}) + \lambda^\circ(\mathrm{CH_3COO^-}) \\ &= 349.6 + 40.9 \\ &= 390.5\,\mathrm{S\,cm^2\,mol^{-1}}.\end{aligned}$$

Step 2: Calculate the fraction dissociated At infinite dilution the weak acid is effectively completely dissociated. The ratio of its conductivity at the stated concentration to its limiting conductivity gives the fraction dissociated:

$$\alpha = \frac{39.05}{390.5} = 0.100.$$

Both conductivities use identical units, which cancel. Multiplication by 100 converts this fraction to a percentage.

Step 3: Conclusion The degree of dissociation is $\boxed{\alpha = 0.10}$, corresponding to $\boxed{10\%}$ dissociation.

Quick Tip to Solve: Add the two limiting ionic conductivities before dividing; the degree of dissociation is a unitless fraction between zero and one.

10(a). Complete the following chemical equations:

(i) F_2 + 2Cl$^-$ $\longrightarrow$

(ii) 2XeF$_2$ + 2H$_2$O $\longrightarrow$ [2 marks]

Solution:

Concept:

- Fluorine is a stronger oxidising agent than chlorine: it accepts electrons from chloride ions and liberates elemental chlorine.
- Xenon difluoride reacts with water to form xenon, hydrogen fluoride and oxygen. Chemical equations must conserve both atoms and charge.

Quick Tip to Solve: For XeF2 hydrolysis, put all fluorine into HF first; balancing H and O then gives oxygen gas alongside xenon.

Step 1: Complete the reaction with chloride Chloride ions lose electrons while fluorine gains them:

$$2Cl^- \longrightarrow Cl_2 + 2e^-, \qquad F_2 + 2e^- \longrightarrow 2F^-.$$

Adding the half-reactions gives the balanced equation

$$\boxed{F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2}.$$

There are two fluorine atoms and two chlorine atoms on either side, and the total charge is -2 on both sides.

Step 2: Complete the hydrolysis of xenon difluoride Water hydrolyses xenon difluoride; xenon is released, fluorine forms hydrogen fluoride, and oxygen is evolved. With the reactant coefficients given in the question,

$$\boxed{2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2}.$$

The equation contains two Xe, four F, four H and two O atoms on each side, and all species are neutral. Xenon is reduced from $+2$ to zero, while oxygen is oxidised from -2 to zero.

Step 3: Conclusion The products are (i) $2F^- + Cl_2$ and (ii) $2Xe + 4HF + O_2$, with the balanced equations shown above.

Quick Tip to Solve: For XeF2 hydrolysis, put all fluorine into HF first; balancing H and O then gives oxygen gas alongside xenon.

OR

10(b). What happens when

(i) HCl is added to MnO_2?

(ii) PCl_5 is heated?

Write the equations involved. [2 marks]

Solution:

Concept:

- Manganese dioxide oxidises chloride ions of concentrated hydrochloric acid to chlorine, while manganese is reduced from $+4$ to $+2$.
- Phosphorus pentachloride undergoes reversible thermal dissociation into phosphorus trichloride and chlorine.

Step 1: (i) Add hydrochloric acid to manganese dioxide On warming manganese dioxide with concentrated hydrochloric acid, greenish-yellow chlorine gas is evolved. Manganese(II) chloride and water are also formed:

$$MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O.$$

Two chloride ions supply the two electrons required to reduce one manganese atom; the remaining chloride ions form manganese(II) chloride. The equation conserves every atom.

Quick Tip to Solve: Balance the MnO2 reaction by first making two waters, then use four HCl; for PCl5, split the five chlorine atoms as three plus two.

Step 2: (ii) Heat phosphorus pentachloride On heating, phosphorus pentachloride dissociates to phosphorus trichloride and chlorine:

$$PCl_5 \overset{\Delta}{\rightleftharpoons} PCl_3 + Cl_2.$$

This is a reversible thermal dissociation. One mole of pentachloride produces one mole each of trichloride and chlorine; heating favours the dissociation.

Step 3: Conclusion HCl with MnO_2 liberates Cl_2, forming $MnCl_2$ and water; heated PCl_5 dissociates into PCl_3 and Cl_2.

Quick Tip to Solve: Balance the MnO2 reaction by first making two waters, then use four HCl; for PCl5, split the five chlorine atoms as three plus two.

11. Give reasons:

(i) Acetylation of aniline reduces its activation effect.

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

(iii) 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 by resonance donation. Its availability also governs the basicity of an amine, that is, its tendency to accept a proton.
- Alkyl groups increase electron density by the positive inductive effect. Protonation of an amino group removes its lone pair from donation and changes its directing influence.

Step 1: (i) Explain the effect of acetylation Acetylation converts the amino group of aniline, $-NH_2$, into the acetamido group, $-NHCOCH_3$, forming acetanilide. In the latter, the nitrogen lone pair is delocalised towards the carbonyl group as well as the benzene ring. Competition from the carbonyl group makes the lone pair less available for donation into the ring. Thus the ring receives less electron density, and its activation towards electrophilic substitution decreases. The acetamido group still directs substitution mainly to ortho and para positions.

Step 2: (ii) Compare methylamine and aniline as bases In methylamine, CH_3NH_2, the methyl group supplies electron density to nitrogen through its positive inductive effect. Its lone pair is localised and readily accepts a proton. In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised over the benzene ring by resonance and is therefore less available for bonding to a proton. The phenyl group also has an electron-withdrawing inductive effect. Consequently methylamine is more basic than aniline.

Step 3: (iii) Explain the formation of meta-nitroaniline The strongly acidic nitrating mixture protonates a substantial fraction of aniline:

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

In the anilinium ion, nitrogen has no lone pair available for donation into the ring. The positively

Quick Tip to Solve: Before predicting amine basicity or ring orientation, check whether the nitrogen lone pair is localised, shared with a carbonyl, shared with a ring, or consumed by protonation.

charged $-NH_3^+$ group withdraws electron density, deactivates the ring and is meta directing. Nitration of this protonated species therefore gives a significant amount of the meta product, which yields meta-nitroaniline after work-up. Unprotonated aniline retains its ortho/para directing effect, accounting for the other isomers.

Step 4: Conclusion Acetylation reduces lone-pair donation into the ring; methylamine has a more available nitrogen lone pair than aniline; and protonation to the meta-directing anilinium ion explains significant meta-nitroaniline formation.

Quick Tip to Solve: Before predicting amine basicity or ring orientation, check whether the nitrogen lone pair is localised, shared with a carbonyl, shared with a ring, or consumed by protonation.

12. Give reasons:

(i) Thermal stability decreases from H_2O to H_2Te.

(ii) Fluoride ion has higher hydration enthalpy than chloride ion.

(iii) Nitrogen does not form pentahalide. [3 marks]

Solution:

Concept:

- Thermal stability of a covalent hydride depends on its bond strength. Greater bond dissociation enthalpy generally means greater resistance to thermal decomposition.
- Hydration enthalpy is the enthalpy change when gaseous ions become surrounded by water molecules. Smaller ions of equal charge interact more strongly with polar water molecules.
- The compact second-shell valence orbitals of nitrogen permit an octet; nitrogen cannot accommodate ten electrons around itself in an ordinary pentahalide.

Step 1: (i) Compare the group 16 hydrides Down group 16, the size of the central atom increases from oxygen to tellurium. The $E-H$ bond becomes longer, and overlap between the hydrogen $1s$ orbital and the central atom's valence orbital becomes less effective. Consequently the bond dissociation enthalpy decreases and the bond is more easily broken by heat. Hence thermal stability decreases in the order

$$H_2O > H_2S > H_2Se > H_2Te.$$

Step 2: (ii) Compare fluoride and chloride hydration Both F^- and Cl^- carry the same charge, but fluoride is smaller. It therefore has a higher charge density and exerts a stronger electrostatic attraction on the positive, hydrogen ends of water molecules. Hydration releases more energy for fluoride. Thus fluoride has a higher magnitude of hydration enthalpy; with the usual signed convention, its hydration enthalpy is more negative than that of chloride.

Step 3: (iii) Explain the absence of nitrogen pentahalides In a pentahalide, five covalent bonds would place ten electrons around the central atom. Nitrogen belongs to the second period and its valence shell contains only $2s$ and $2p$ orbitals; there are no $2d$ orbitals. It cannot expand its octet to accommodate five ordinary covalent bonds. Its small size further disfavors surrounding it with five halogen atoms. Therefore nitrogen does not form pentahalides such as NCl_5.

Quick Tip to Solve: Use bond strength for hydride stability, charge density for hydration, and the second-period octet limit for nitrogen pentahalides; distinguish hydration magnitude from its negative sign.

Step 4: Conclusion Decreasing $E - H$ bond strength lowers hydride thermal stability down group 16; the small fluoride ion is hydrated more strongly; and nitrogen cannot expand its second-shell octet to form a pentahalide.

Quick Tip to Solve: Use bond strength for hydride stability, charge density for hydration, and the second-period octet limit for nitrogen pentahalides; distinguish hydration magnitude from its negative sign.

13. Define the following:

(i) Anionic detergents

(ii) Limited spectrum antibiotics

(iii) Tranquilizers [3 marks]

Solution:

Concept:

- Synthetic detergents are classified according to the charge carried by the water-attracting end of their surface-active ion.
- Antibiotics are classified by the range of microorganisms on which they act, whereas tranquilizers are classified by their calming action on the nervous system.

Step 1: Define anionic detergents Anionic detergents are synthetic cleansing agents in which the large anion is the surface-active species. They are commonly sodium salts of sulphonated long-chain hydrocarbons or sodium salts of sulphated long-chain alcohols. The long hydrocarbon chain attracts grease and the negatively charged head interacts with water. For example, sodium lauryl sulphate has the condensed formula $CH_3(CH_2)_{11}OSO_3{}^- Na^+$; its organic anion provides the cleansing action.

Step 2: Define limited spectrum antibiotics Limited spectrum antibiotics are antibiotics effective against a single organism or a very limited group of microorganisms. Their antibacterial action is therefore restricted to particular susceptible organisms, rather than extending over many different types. They should be distinguished from broad spectrum antibiotics, which act against a wide range of Gram-positive and Gram-negative bacteria.

Step 3: Define tranquilizers Tranquilizers are drugs used to treat stress and mild or severe mental diseases. They reduce anxiety and tension and produce a calming effect by acting on the central nervous system. They can also improve mood and help relieve irritability or excitement. Diazepam is an example of a tranquilizer; this class is identified by its calming action rather than an antibacterial or cleansing action.

Step 4: Conclusion Anionic detergents cleanse through their negatively charged surface-active ions; limited spectrum antibiotics act on a single organism or a restricted group; tranquilizers reduce anxiety and mental tension through their action on the nervous system.

Quick Tip to Solve: Link each definition to its distinguishing feature: negative active ion, restricted antimicrobial range, and calming nervous-system action, respectively.

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

(i) Nylon-6

(ii) Melamine - formaldehyde polymer

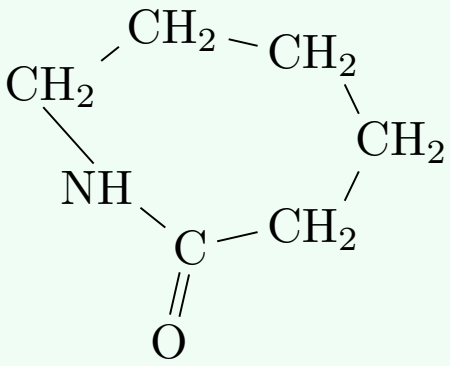
(iii) Teflon [3 marks]

Solution:

Concept:

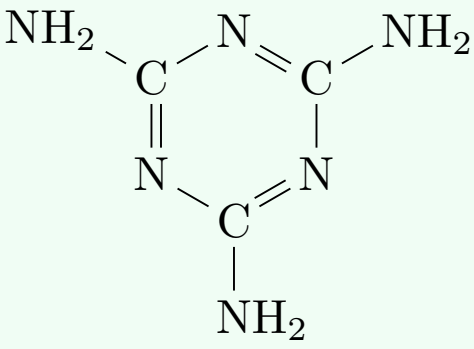
- A monomer is the small molecule from which a polymer is formed. The functional groups and bonds of the monomer determine the mode of polymerisation.
- Nylon-6 is obtained by ring-opening polymerisation of caprolactam; melamine-formaldehyde resin forms by condensation; Teflon forms by addition across a carbon-carbon double bond.

Step 1: Write the monomer of Nylon-6 The monomer is ε-caprolactam, a cyclic amide containing six carbon atoms in a seven-membered ring. Its ring consists of one $-NH-$, one $-CO-$ and five $-CH_2-$ groups, with the carbonyl carbon directly bonded to nitrogen. Its structure is shown below. On heating with water, ring opening ultimately gives the Nylon-6 repeating unit $[-NH-(CH_2)_5-CO-]_n$.



Structure of caprolactam

Step 2: Write both monomers of melamine-formaldehyde resin This resin requires two monomers: melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde (methanal), $H-C(=O)-H$. Melamine has a six-membered ring with alternating carbon and nitrogen atoms and one $-NH_2$ group attached to each ring carbon. The displayed structure below specifies the positions of all three amino groups. Formaldehyde reacts at these amino groups and further condensation produces a cross-linked thermosetting resin.



Structure of melamine

Quick Tip to Solve: For Nylon-6 count the carbonyl carbon among the six carbons; for the resin give both monomers; for Teflon restore the double bond in the repeating unit.

Step 3: Write the monomer of Teflon The monomer is tetrafluoroethene, $F_2C{=}CF_2$. Each carbon of ethene carries two fluorine atoms. During addition polymerisation the carbon-carbon double bond opens, while all four fluorine atoms remain attached to the carbon skeleton:

$$n\,CF_2{=}CF_2 \longrightarrow [-CF_2{-}CF_2-]_n.$$

Thus the alkene structure, rather than the saturated repeating unit alone, identifies the required monomer.

Step 4: Conclusion Nylon-6: ε-caprolactam, the cyclic amide shown above. Melamine-formaldehyde polymer: melamine, with three amino groups on the triazine ring, and HCHO. Teflon: tetrafluoroethene, $CF_2{=}CF_2$.

Quick Tip to Solve: For Nylon-6 count the carbonyl carbon among the six carbons; for the resin give both monomers; for Teflon restore the double bond in the repeating unit.

15(a). Write structures of compounds A, B and C in each of the following reactions:

(i) $C_6H_5Br \xrightarrow{Mg/\text{dry ether}} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_{2(g)}} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$ [3 marks]

Solution:

Concept:

- Magnesium in dry ether converts an organic bromide into a Grignard reagent, $R{-}MgBr$. Reaction with CO_2, followed by acidic hydrolysis, gives $R{-}COOH$, adding one carbon atom.
- Stephen reduction converts a nitrile to an aldehyde through an iminium salt. An aldehyde with an alpha-hydrogen undergoes aldol addition in dilute base and dehydration on heating.

Step 1: Identify A in sequence (i) Bromobenzene reacts with magnesium in dry ether to form phenylmagnesium bromide. Dry conditions are essential because water would destroy the Grignard reagent.

$$C_6H_5Br + Mg \xrightarrow{\text{dry ether}} C_6H_5MgBr.$$

Therefore, the structure of A is $C_6H_5{-}MgBr$, with magnesium bonded to the phenyl group.

Step 2: Identify B and C in sequence (i) The phenyl group attacks the carbon atom of carbon dioxide, forming the magnesium carboxylate. Acidic hydrolysis gives benzoic acid:

$$C_6H_5MgBr + CO_2 \longrightarrow C_6H_5COOMgBr,$$
$$C_6H_5COOMgBr + HCl \longrightarrow C_6H_5COOH + MgBrCl.$$

The acid represents the product of the printed acidic work-up; hence B is $C_6H_5{-}C(=O){-}OH$. Phosphorus pentachloride replaces its hydroxyl group by chlorine:

$$C_6H_5COOH + PCl_5 \longrightarrow C_6H_5COCl + POCl_3 + HCl.$$

Quick Tip to Solve: Track carbon atoms: Grignard carboxylation adds one carbon, Stephen reduction retains the nitrile carbon, and ethanal aldol addition doubles the two-carbon skeleton.

Thus C is benzoyl chloride, $C_6H_5-C(=O)-Cl$.

Step 3: Identify A in sequence (ii) Tin(II) chloride and hydrochloric acid reduce ethanenitrile to an iminium salt. Hydrolysis gives ethanal rather than an alcohol:

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

Therefore A is $CH_3-C(=O)-H$. The nitrile carbon becomes the aldehyde carbon without changing the number of carbon atoms.

Step 4: Identify B and C in sequence (ii) Ethanal contains alpha-hydrogens. In dilute sodium hydroxide, two ethanal molecules combine by aldol addition, forming the beta-hydroxy aldehyde 3-hydroxybutanal:

$$2\,CH_3CHO \xrightarrow{\text{dil. } NaOH} CH_3-CH(OH)-CH_2-CHO.$$

Hence B is $CH_3-CH(OH)-CH_2-CHO$. Heating removes water between its alpha and beta carbon atoms to produce the conjugated aldehyde but-2-enal (crotonaldehyde):

$$CH_3-CH(OH)-CH_2-CHO \xrightarrow{heat} CH_3-CH{=}CH-CHO + H_2O.$$

Consequently C is $CH_3-CH{=}CH-CHO$, retaining the terminal aldehyde group.

Step 5: Conclusion In (i), A = C_6H_5MgBr, B = C_6H_5COOH, and C = C_6H_5COCl. In (ii), A = CH_3CHO, B = $CH_3CH(OH)CH_2CHO$, and C = $CH_3CH{=}CHCHO$.

Quick Tip to Solve: Track carbon atoms: Grignard carboxylation adds one carbon, Stephen reduction retains the nitrile carbon, and ethanal aldol addition doubles the two-carbon skeleton.

OR

15(b). Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Propanone to Propene [3 marks]

Solution:

Concept:

- An acid chloride undergoes controlled hydrogenation in the Rosenmund reaction to give the corresponding aldehyde. A poisoned palladium catalyst prevents further reduction.
- Strong oxidation converts the side chain of an alkylbenzene containing a benzylic hydrogen into a carboxyl group. A ketone can be reduced to a secondary alcohol, which undergoes dehydration to an alkene.

Step 1: (i) Convert benzoic acid into benzaldehyde First convert benzoic acid into benzoyl chloride

Quick Tip to Solve: For an acid-to-aldehyde conversion, insert an acid chloride and use Rosenmund reduction; for ketone-to-alkene, insert the corresponding alcohol.

using thionyl chloride. Then reduce the acid chloride by the Rosenmund method:

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$$

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl.$$

The poisoned catalyst stops hydrogenation at the aldehyde stage. Direct strong reduction of the acid would instead give benzyl alcohol.

Step 2: (ii) Oxidise ethylbenzene into benzoic acid Heat ethylbenzene with alkaline potassium permanganate, then acidify the potassium benzoate formed:

$$C_6H_5CH_2CH_3 \xrightarrow[\Delta]{\text{alkaline } KMnO_4} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH.$$

The carbon attached directly to the benzene ring becomes the carboxyl carbon; the rest of the side chain is oxidised away.

Step 3: (iii) Convert propanone into propene Reduce propanone with sodium borohydride, followed by aqueous work-up, to obtain propan-2-ol. Dehydrate this alcohol by heating with concentrated sulphuric acid:

$$CH_3COCH_3 \xrightarrow{NaBH_4,\ \text{then } H_2O} CH_3CH(OH)CH_3 \xrightarrow[443\,K]{\text{conc. } H_2SO_4} CH_3CH{=}CH_2 + H_2O.$$

The first transformation reduces the carbonyl group; the second removes water from the alcohol.

Step 4: Conclusion The required routes are benzoic acid → benzoyl chloride → benzaldehyde; ethylbenzene → potassium benzoate → benzoic acid; and propanone → propan-2-ol → propene. Each uses at most two steps.

Quick Tip to Solve: For an acid-to-aldehyde conversion, insert an acid chloride and use Rosenmund reduction; for ketone-to-alkene, insert the corresponding alcohol.

16. (a) Write the principle of method used for the refining of germanium.

(b) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably?

(c) What is the significance of leaching in the extraction of aluminium? [3 marks]

Solution:

Concept:

- Zone refining uses the difference in impurity solubility in solid and molten metal to obtain a highly pure metal.
- Froth flotation separates sulphide ores through selective wetting. Leaching selectively dissolves a useful ore component while leaving insoluble impurities behind.

Step 1: (a) State the principle of germanium refining Germanium is purified by zone refining. Its impurities are more soluble in the molten metal than in the solid metal. A narrow molten zone is

Quick Tip to Solve: Match each process to its selective property: zone refining to molten-phase solubility, flotation to sulphide wetting, and bauxite leaching to alkali solubility.

made to travel along an impure germanium rod. As the zone advances, relatively pure germanium crystallises behind it, while the impurities remain preferentially in the melt and move with the zone. Repetition concentrates the impurities at one end, which is cut off, leaving highly pure germanium for semiconductor applications.

Step 2: (b) Select the ore for froth flotation PbS, galena, is preferably concentrated by froth flotation because it is a sulphide ore. Sulphide particles are preferentially wetted by oil, whereas gangue particles are wetted by water. Air bubbles carry the oil-coated sulphide particles to the froth, which is collected, while much of the gangue remains in the water. $PbCO_3$, a carbonate ore, is not the preferred ore for this process.

Step 3: (c) Explain the significance of leaching in aluminium extraction Leaching concentrates bauxite by selectively dissolving its alumina in hot concentrated sodium hydroxide solution under pressure, forming soluble sodium aluminate. For alumina the reaction can be represented as

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4].$$

Insoluble impurities such as iron oxides are removed by filtration. Aluminium hydroxide is subsequently precipitated from the filtered solution and heated to yield purified alumina:

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O.$$

Thus leaching supplies purified alumina for electrolytic reduction rather than reducing aluminium directly.

Step 4: Conclusion (a) Germanium is zone-refined because impurities prefer the molten phase. (b) PbS is concentrated by froth flotation. (c) Leaching separates alumina from bauxite impurities to prepare purified Al_2O_3.

Quick Tip to Solve: Match each process to its selective property: zone refining to molten-phase solubility, flotation to sulphide wetting, and bauxite leaching to alkali solubility.

17. Following compounds are given to you:

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

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

(ii) Write the compound which is optically active.

(iii) 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 rear. Less steric hindrance gives higher reactivity: primary $>$ secondary $>$ tertiary halides with the same leaving group.
- A tetrahedral carbon attached to four different groups is a chiral centre. In the usual comparison of alkyl halides towards β-elimination, tertiary halides react most readily because alkene formation is

Quick Tip to Solve: First classify the carbon bearing Br as primary, secondary or tertiary; then separately check for four different groups when deciding optical activity.

favoured.

Step 1: (i) Compare substitution In 1-bromopentane, $CH_3CH_2CH_2CH_2CH_2Br$, the carbon bonded to bromine is primary and is readily approached by a nucleophile. In 2-bromopentane this carbon is secondary; in 2-bromo-2-methylbutane it is tertiary and strongly hindered. Since all three have the same leaving group, the order is

$$\text{1-bromopentane} > \text{2-bromopentane} > \text{2-bromo-2-methylbutane}.$$

Thus the primary compound is the fastest towards S_N2.

Step 2: (ii) Check chirality In 2-bromopentane, $CH_3CH(Br)CH_2CH_2CH_3$, carbon 2 is bonded to four different groups: $-Br$, $-H$, $-CH_3$ and $-CH_2CH_2CH_3$. Therefore it has a chiral centre and its individual enantiomers are optically active. A racemic mixture would have no net optical rotation. In 1-bromopentane the brominated carbon has two hydrogen atoms, while in 2-bromo-2-methylbutane it has two identical methyl groups; neither has a chiral centre.

Step 3: (iii) Compare elimination 2-Bromo-2-methylbutane, $(CH_3)_2C(Br)CH_2CH_3$, is a tertiary halide with available β-hydrogens. It undergoes β-elimination most readily among the given compounds under comparable elimination conditions. Removal of bromine and a hydrogen on an adjacent carbon can give the more substituted, stable alkene 2-methylbut-2-ene as the major product with a usual small base:

$$(CH_3)_2C(Br)CH_2CH_3 \xrightarrow[\Delta]{\text{alcoholic KOH}} (CH_3)_2C{=}CHCH_3 + KBr + H_2O.$$

Step 4: Conclusion (i) 1-Bromopentane is most reactive towards S_N2. (ii) 2-Bromopentane is the optically active compound. (iii) 2-Bromo-2-methylbutane is most reactive towards β-elimination.

Quick Tip to Solve: First classify the carbon bearing Br as primary, secondary or tertiary; then separately check for four different groups when deciding optical activity.

18. Following data are obtained for the reaction:

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

t/s: 0, 300, 600

$[N_2O_5]$/mol L^{-1}: 1.6×10^{-2}, 0.8×10^{-2}, 0.4×10^{-2}

(a) Show that it follows first order reaction.

(b) Calculate the half-life.

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

Solution:

Concept:

- For a first-order reaction, the rate constant is $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are reactant concentrations initially and at time t.

Quick Tip to Solve: When the concentration halves in equal successive time intervals, use that interval as the half-life, then verify a constant first-order rate constant.

- The half-life $t_{1/2}$ is the time for the reactant concentration to become half its initial value. For first-order kinetics, $t_{1/2} = 0.693/k$, independent of the starting concentration.

Step 1: (a) Calculate the rate constant at 300 s Taking $A = N_2O_5$, initially $[A]_0 = 1.6 \times 10^{-2}$ mol L^{-1}. At $t = 300$ s, $[A]_t = 0.8 \times 10^{-2}$ mol L^{-1}. Substitution in the first-order expression gives

$$k_1 = \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303(0.3010)}{300} = 2.311 \times 10^{-3}\,s^{-1}.$$

Step 2: (a) Check the rate constant at 600 s Using the initial concentration and that at 600 s,

$$k_2 = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303(0.6021)}{600} = 2.311 \times 10^{-3}\,s^{-1}.$$

Thus $k_1 = k_2$ within the rounding of the supplied logarithms: the data satisfy the first-order integrated rate equation. Also, the concentration halves from 1.6×10^{-2} to 0.8×10^{-2} and then to 0.4×10^{-2} mol L^{-1} in successive equal intervals of 300 s, showing concentration-independent half-life.

Step 3: (b) Calculate the half-life Using the calculated rate constant,

$$t_{1/2} = \frac{0.693}{2.311 \times 10^{-3}}\,s \simeq 300\,s.$$

This agrees directly with each halving interval in the table. The small rounding difference in the two calculated values of k has no physical significance.

Step 4: Conclusion The reaction follows first-order kinetics, with $k \simeq 2.31 \times 10^{-3}\,s^{-1}$ and half-life $\boxed{t_{1/2} = 300\,s}$.

Quick Tip to Solve: When the concentration halves in equal successive time intervals, use that interval as the half-life, then verify a constant first-order rate constant.

19. Write one difference between each of the following:

(i) Multimolecular colloid and Macromolecular colloid

(ii) Sol and Gel

(iii) O/W emulsion and W/O emulsion [3 marks]

Solution:

Concept:

- A colloid contains a dispersed phase distributed through a continuous dispersion medium. Colloids may be classified by the nature of the dispersed particles or by the physical states of the two phases.
- In an emulsion both phases are liquids. O/W denotes oil dispersed in water, whereas W/O denotes water dispersed in oil; the phase after the slash is the continuous medium.

Step 1: (i) Multimolecular and macromolecular colloids The difference is the nature of each colloidal particle. In a multimolecular colloid, many small atoms or molecules aggregate to form one particle of colloidal dimensions, as in gold sol or sulphur sol. The constituent atoms or molecules themselves

Quick Tip to Solve: For each pair, state one common basis of comparison: particle constitution, physical states of phases, or which liquid is the continuous medium.

are smaller than colloidal size. In a macromolecular colloid, each individual large molecule already has colloidal dimensions and behaves as a colloidal particle, as in starch or a protein solution. Thus the comparison is an aggregate of many small units versus a single macromolecule.

Step 2: (ii) Sol and gel The difference is the physical state of the dispersed phase and dispersion medium. In a sol, a solid is the dispersed phase and a liquid is the dispersion medium, for example gold sol. In a gel, a liquid is dispersed in a solid medium or solid network, for example jelly. Hence their phase arrangements are solid-in-liquid and liquid-in-solid, respectively.

Step 3: (iii) O/W and W/O emulsions The difference is which liquid forms the dispersed droplets. In an oil-in-water (O/W) emulsion, oil droplets are dispersed throughout a continuous aqueous medium; milk is a familiar example. In a water-in-oil (W/O) emulsion, water droplets are dispersed throughout a continuous oil medium; butter is a familiar example. Thus water is the medium in O/W, while oil is the medium in W/O.

Step 4: Conclusion (i) Multimolecular: aggregates of small units; macromolecular: individual large molecules. (ii) Sol: solid in liquid; gel: liquid in solid. (iii) O/W: oil in water; W/O: water in oil.

Quick Tip to Solve: For each pair, state one common basis of comparison: particle constitution, physical states of phases, or which liquid is the continuous medium.

20. (i) What type of isomerism is shown by the complex $[Co(en)_3]Cl_3$?
(ii) Write the hybridisation and magnetic character of $[Co(C_2O_4)_3]^{3-}$. (At. no. of Co = 27)
(iii) Write the IUPAC name of the following complex: $[Cr(NH_3)_3Cl_3]$. [3 marks]

Solution:

Concept:

- Optical isomers are non-superimposable mirror images. Three bidentate ethane-1,2-diamine ligands, abbreviated en, can form a chiral octahedral arrangement around a metal ion.
- The oxidation state determines the metal's d-electron count. In valence bond theory, an inner-orbital octahedral complex uses d^2sp^3 hybridisation; magnetic character depends on whether unpaired electrons remain.
- In naming a coordination entity, name ligands alphabetically before the metal, use prefixes to indicate their numbers, and give the metal oxidation state in Roman numerals. Neutral complexes retain the ordinary metal name.

Step 1: (i) Identify the isomerism of the en complex In $[Co(en)_3]Cl_3$, each neutral en ligand binds through two nitrogen atoms, giving coordination number six and an octahedral coordination sphere. The three chelate rings have two non-superimposable mirror-image arrangements, conventionally denoted Δ and Λ. Therefore the complex shows optical isomerism. Because all three bidentate ligands are identical, there is no distinct cis-trans pair for this tris-chelate complex. The three chloride ions lie outside the coordination sphere.

Step 2: (ii) Determine hybridisation and magnetic character Each oxalato ligand has charge -2. Let

Quick Tip to Solve: First calculate the metal oxidation state from the complex charge; then use it both for the electron count and the Roman numeral in the name.

the oxidation state of cobalt be x; then

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

Cobalt has atomic number 27: the atom is $[\mathrm{Ar}]3d^7 4s^2$, so Co^{3+} is $[\mathrm{Ar}]3d^6$. In this cobalt(III) complex the six d electrons pair in the lower-energy orbitals, giving the low-spin octahedral arrangement $t_{2g}^6 e_g^0$. Two vacant inner $3d$ orbitals, one $4s$ and three $4p$ orbitals form six d^2sp^3 hybrid orbitals for the six donor oxygen atoms. There are no unpaired electrons, so the complex is diamagnetic.

Step 3: (iii) Name the chromium complex In $[\mathrm{Cr(NH_3)_3Cl_3}]$, the three ammine ligands are neutral and each chlorido ligand carries charge -1. The complex is neutral, so chromium is in oxidation state $+3$. Alphabetically, ammine precedes chlorido; the prefix tri indicates three of each ligand. Since the coordination entity is neutral, the metal is named chromium, with oxidation state (III).

Step 4: Conclusion (i) Optical isomerism. (ii) d^2sp^3 hybridisation; diamagnetic. (iii) Triamminetrichloridochromium(III).

Quick Tip to Solve: First calculate the metal oxidation state from the complex charge; then use it both for the electron count and the Roman numeral in the name.

21. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes.

(Given: Molar mass of Ag = 108 g mol^{-1}, 1F = 96500 C mol^{-1})

(b) Define fuel cell. [3 marks]

Solution:

Concept:

- Faraday's law relates the mass deposited to the charge passed: $m = MIt/(nF)$, where M is the molar mass, I the current, t the time in seconds, and n the number of electrons needed per metal ion.
- One mole of electrons carries a charge of one faraday, $F = 96500\,\mathrm{C\ mol^{-1}}$. For silver deposition, $\mathrm{Ag^+ + e^- \rightarrow Ag}$, so $n = 1$.
- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy through redox reactions.

Step 1: (a) Calculate the charge passed Convert the given duration into seconds before using the current, since an ampere is a coulomb per second:

$$t = 15 \times 60 = 900\,\mathrm{s}, \qquad Q = It = 2 \times 900 = 1800\,\mathrm{C}.$$

This charge reaches the cathode, where silver ions gain electrons and are deposited as metallic silver.

Step 2: (a) Apply the cathode reaction and Faraday's law The cathode reaction is $\mathrm{Ag^+ + e^- \rightarrow Ag(s)}$. Thus one mole of electrons deposits one mole, or $108\,\mathrm{g}$, of silver. The amount of electrons transferred

Quick Tip to Solve: Convert minutes to seconds, then use one electron per silver ion: $m = 108It/96500$ in grams for silver deposition.

is $Q/F = 1800/96500$ mol, and hence

$$m = \frac{MQ}{F} = \frac{108 \times 1800}{96500}\,\text{g} = 2.0145\,\text{g}.$$

The electron stoichiometry is unity; no extra factor of two is introduced despite the current being 2 A.

Step 3: (b) Define a fuel cell A fuel cell is a galvanic cell that converts the chemical energy of a fuel and an oxidising agent, supplied continuously to its electrodes, directly into electrical energy. For example, a hydrogen–oxygen fuel cell uses hydrogen as fuel and oxygen as oxidant, with water as the reaction product. It can continue supplying electrical energy while the reactants are supplied.

Step 4: Conclusion (a) The mass of silver deposited is $\boxed{2.01\,\text{g}}$. (b) A fuel cell is a galvanic cell converting the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.

Quick Tip to Solve: Convert minutes to seconds, then use one electron per silver ion: $m = 108It/96500$ in grams for silver deposition.

22. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if 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}) [3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_f m$, where K_f is the molal depression constant of the solvent, m is solute molality, and i is the van't Hoff factor.
- Sucrose and glucose are non-electrolytes in water, so $i = 1$. With the same solvent, their freezing-point depressions are proportional to their molalities.
- A 10% solution by mass contains 10 g solute in 100 g solution: the solvent mass is therefore 90 g, or 0.090 kg.

Step 1: Find the depression for the sucrose solution The freezing point of pure water is 273.15 K, while that of the given sucrose solution is 269.15 K. Therefore,

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

The depression is positive because a dissolved nonvolatile solute lowers the freezing point relative to the pure solvent.

Step 2: Compare the molalities at equal mass percentage Take 100 g of each solution. Each has 10 g of solute and 0.090 kg of water. Using the supplied molar masses,

$$m_{\text{sucrose}} = \frac{10/342}{0.090}, \qquad m_{\text{glucose}} = \frac{10/180}{0.090}.$$

Quick Tip to Solve: At equal mass percentages in the same solvent, divide depressions in the inverse ratio of solute molar masses; use the given sucrose data to cancel K_f.

Thus $m_{\text{glucose}}/m_{\text{sucrose}} = 342/180 = 1.90$. The glucose solution contains more dissolved molecules per kilogram of water because glucose has the smaller molar mass.

Step 3: Calculate the glucose solution's freezing point Since both solutions use water and both solutes have $i = 1$, the common K_f cancels from the ratio:

$$\frac{\Delta T_{f,\text{glucose}}}{4.00} = \frac{342}{180}, \qquad \Delta T_{f,\text{glucose}} = 7.60\,\text{K}.$$

Subtract this depression from the pure-water freezing point:

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

This is lower than the sucrose solution's freezing point, as expected from its greater molality.

Step 4: Conclusion The freezing point of the 10% glucose solution is $\boxed{265.55\,\text{K}}$.

Quick Tip to Solve: At equal mass percentages in the same solvent, divide depressions in the inverse ratio of solute molar masses; use the given sucrose data to cancel K_f.

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, Ritu a class XII student decided to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. Principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins rich food like fruits, salads, sprouts etc. The decision was welcomed by the parents and students.

After reading the above passage, answer the following questions:

(i) What are the values (at least two) displayed by Ritu?

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

(iii) Write the two types of secondary structure of proteins.

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

Solution:

Concept:

- Food awareness involves concern for health and social responsibility: knowledge is useful when it leads to informed action for the welfare of others.
- Starch is the principal storage polysaccharide of plants. Proteins show regular secondary structures stabilised by hydrogen bonding between peptide groups.
- Vitamins are classified by solubility. The B-group vitamins and vitamin C belong to the water-soluble group.

Step 1: (i) Identify the values shown by Ritu Ritu displays health awareness and concern for the welfare of others: she recognises a possible food-related danger and wants fellow students to be protected. She also shows social responsibility and initiative by approaching the principal with a

Quick Tip to Solve: Remember bread as a source of starch, protein folding as helix or sheet, and water-soluble vitamins as the B group plus C.

practical suggestion. Her action demonstrates that she is prepared to apply scientific information to improve the school environment. Any two of these clearly expressed values answer this part.

Step 2: (ii) Name the polysaccharide in bread Bread is commonly made from cereal flour, which contains starch as its major carbohydrate polysaccharide. Starch consists of glucose units and has two components, amylose and amylopectin. Thus, the polysaccharide asked for here is starch; glucose itself is a monosaccharide and is not the required answer.

Step 3: (iii) State the secondary structures of proteins The two types are the α-helix and the β-pleated sheet. In the α-helix, a polypeptide chain coils into a helix with intrachain hydrogen bonding. In the β-pleated sheet, extended polypeptide segments lie alongside one another and are held together by hydrogen bonds. These are local arrangements of the polypeptide backbone, distinct from its amino-acid sequence.

Step 4: (iv) Give water-soluble vitamin examples Vitamin B_1 (thiamine) and vitamin C (ascorbic acid) are two examples of water-soluble vitamins. Other members of the B group are also acceptable examples. Vitamins A, D, E and K are fat-soluble, so they should not be selected for this part.

Step 5: Conclusion (i) Health awareness and social responsibility (also initiative and concern for others); (ii) starch; (iii) α-helix and β-pleated sheet; (iv) vitamin B_1 and vitamin C.

Quick Tip to Solve: Remember bread as a source of starch, protein folding as helix or sheet, and water-soluble vitamins as the B group plus C.

24(a). An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

(b) Write any two differences between amorphous solids and crystalline solids. [5 marks]

Solution:

Concept:

- For a cubic unit cell, $\rho = \dfrac{ZM}{a^3 N_A}$, where ρ is density, Z is the number of atoms per unit cell, M is molar mass, a is edge length and N_A is Avogadro's constant.
- The atom counts for simple cubic, body-centred cubic and face-centred cubic unit cells are respectively 1, 2 and 4. These counts identify the cubic structure from its density.
- Crystalline solids have a regular arrangement extending over long distances, whereas amorphous solids possess only short-range order. Their melting behaviour also differs.

Step 1: (a) Convert the edge length and obtain the unit-cell volume The given quantities are $M = 93\,\text{g mol}^{-1}$, $\rho = 11.5\,\text{g cm}^{-3}$ and $a = 300\,\text{pm}$. Since the density is expressed per cubic centimetre, convert the edge length into centimetres before using the density relation:

$$1\,\text{pm} = 10^{-10}\,\text{cm},$$
$$a = 300 \times 10^{-10} = 3.00 \times 10^{-8}\,\text{cm},$$
$$a^3 = (3.00 \times 10^{-8})^3 = 2.70 \times 10^{-23}\,\text{cm}^3.$$

Quick Tip to Solve: Convert pm to cm before cubing: $300\,\text{pm} = 3.00 \times 10^{-8}\,\text{cm}$. Compare the calculated Z with $1, 2, 4$ to identify the cubic cell.

Thus the mass of one unit cell is ρa^3. The mass of one atom is M/N_A, so their ratio gives the number of atoms contained in a unit cell.

Step 2: (a) Calculate the number of atoms in a unit cell Rearranging the density relation and substituting $N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$,

$$\begin{aligned} Z &= \frac{\rho a^3 N_A}{M} \\ &= \frac{11.5 \times 2.70 \times 10^{-23} \times 6.022 \times 10^{23}}{93} \\ &= 2.01 \simeq 2. \end{aligned}$$

The small departure from an integer is due to rounding of the supplied density and edge length. A body-centred cubic cell contains eight corner atoms, each shared among eight cells, and one atom entirely inside the cell. Its effective atom count is therefore $8 \times \frac{1}{8} + 1 = 2$.

Step 3: (b) State two differences **Arrangement of particles:** Crystalline solids possess long-range order: a regular, repeating arrangement extends throughout the crystal. Amorphous solids have only short-range order, with no regular repeating pattern over long distances.

Melting behaviour: A crystalline solid has a sharp, definite melting point. An amorphous solid gradually softens over a range of temperatures instead of melting sharply at one temperature.

Step 4: Conclusion (a) $Z \simeq 2$, so the element has a body-centred cubic (bcc) unit cell. (b) Crystalline solids have long-range order and a sharp melting point; amorphous solids have only short-range order and soften over a temperature range.

Quick Tip to Solve: Convert pm to cm before cubing: $300\,\text{pm} = 3.00 \times 10^{-8}\,\text{cm}$. Compare the calculated Z with $1, 2, 4$ to identify the cubic cell.

OR

24(b). (a) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a f.c.c. structure. (Atomic mass of Al = 27 g mol^{-1})

(b) Give reasons:

(i) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.

(ii) Silicon on doping with Phosphorus forms n-type semiconductor.

(iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances. [5 marks]

Solution:

Concept:

- In a face-centred cubic (f.c.c.) unit cell, eight corner atoms contribute $8 \times \frac{1}{8} = 1$ atom and six face-centred atoms contribute $6 \times \frac{1}{2} = 3$ atoms. Thus each unit cell contains $Z = 4$ atoms.
- The number of atoms in a sample is $N = (m/M)N_A$, where m is its mass, M its molar mass and $N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$. The number of unit cells is N/Z.
- Schottky defects involve vacancies of equal numbers of cations and anions; Frenkel defects involve

Quick Tip to Solve: For aluminium in an f.c.c. lattice, first convert grams to atoms, then divide by four; for magnetic order, compare whether the opposite moments cancel completely.

displacement of a small ion from its normal site to an interstitial site.

- Donor impurities provide mobile electrons in n-type semiconductors. Antiparallel magnetic moments give zero resultant when equal, but a nonzero resultant when unequal.

Step 1: (a) Calculate the number of aluminium atoms The amount of aluminium in the sample is

$$n = \frac{m}{M} = \frac{8.1\,\text{g}}{27\,\text{g mol}^{-1}} = 0.30\,\text{mol}.$$

Therefore, the total number of atoms is

$$N = nN_{\text{A}} = 0.30 \times 6.022 \times 10^{23} = 1.8066 \times 10^{23}.$$

Step 2: (a) Use the effective number of atoms per cell An f.c.c. unit cell contains four effective atoms, after allowing for the sharing of corner and face atoms with neighbouring cells. Hence,

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

Dividing by four is essential: the atom count itself is not the unit-cell count.

Step 3: (b)(i) Explain the defect in sodium chloride In NaCl, the sizes of the cation and anion are sufficiently comparable and the coordination number is high, so it favours Schottky defects. Equal numbers of Na^+ and Cl^- ions are missing from their lattice sites, preserving electrical neutrality and the stoichiometric ratio. A Frenkel defect requires an ion, generally a much smaller cation, to occupy an interstitial site. The Na^+ ion is too large to fit readily into the available interstitial sites, so NaCl does not normally exhibit Frenkel defects.

Step 4: (b)(ii) Explain phosphorus doping of silicon Silicon has four valence electrons, whereas phosphorus has five. When a phosphorus atom replaces a silicon atom in the lattice, four of its electrons form covalent bonds with neighbouring silicon atoms. The fifth electron is only weakly bound and can become available for conduction. Thus phosphorus acts as a donor, and electrons become the majority charge carriers, producing an n-type semiconductor. The crystal as a whole remains electrically neutral.

Step 5: (b)(iii) Compare the antiparallel magnetic arrangements In antiferromagnetic substances, equal magnetic moments align antiparallel and cancel, giving zero net magnetic moment in the ideal ordered arrangement. In ferrimagnetic substances, the oppositely directed moments are unequal, so cancellation is incomplete and a resultant magnetic moment remains. This nonzero resultant accounts for their stronger magnetic behaviour compared with antiferromagnetic substances.

Step 6: Conclusion (a) The sample contains approximately 4.52×10^{22} f.c.c. unit cells. (b) NaCl favours paired vacancies because its ions cannot readily form a Frenkel pair; phosphorus supplies extra mobile electrons to silicon; and unequal antiparallel moments leave ferrimagnetic substances with a net magnetic moment.

Quick Tip to Solve: For aluminium in an f.c.c. lattice, first convert grams to atoms, then divide by four; for magnetic order, compare whether the opposite moments cancel completely.

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

(i) Salicylic acid (2-hydroxybenzoic acid), as shown, reacts with acetic anhydride, $(CH_3CO)_2O$, in the presence of H^+.

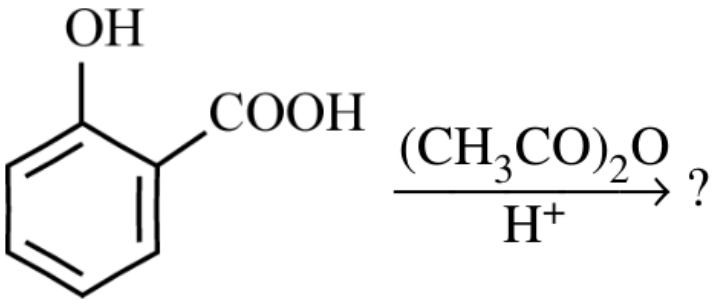
(ii) $CH_3CH(CH_3)OCH_2CH_3 \xrightarrow{HI} ? + ?$

(iii) $CH_3CH{=}CHCH_2OH \xrightarrow{PCC} ?$

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

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol [5 marks]



Solution:

Concept:

- Acetic anhydride acetylates the phenolic $-OH$ group: its hydrogen is replaced by $-COCH_3$, while the carboxyl group remains intact.
- HI first protonates an ether oxygen. Iodide then cleaves the protonated unsymmetrical ether by attacking the less hindered primary alkyl group through an S_N2 process.
- PCC (pyridinium chlorochromate) oxidises a primary alcohol to an aldehyde without oxidising an isolated carbon-carbon double bond under the usual conditions.
- Neutral ferric chloride detects phenols through coloured complex formation. Lucas reagent, concentrated HCl with anhydrous $ZnCl_2$, distinguishes alcohol classes by the time taken to form an insoluble alkyl chloride.

Step 1: (a)(i) Acetylation of salicylic acid The printed aromatic reactant has adjacent phenolic hydroxyl and carboxyl groups, so it is salicylic acid. Its phenolic oxygen undergoes acetylation with acetic anhydride in acid medium:

$$o\text{-}HOC_6H_4COOH + (CH_3CO)_2O \xrightarrow{H^+} o\text{-}CH_3COOC_6H_4COOH + CH_3COOH.$$

The organic product is acetylsalicylic acid (aspirin), also called 2-acetoxybenzoic acid. The $-COOH$ group remains attached to the ring; the phenolic $-OH$ becomes $-OCOCH_3$.

Step 2: (a)(ii) Cleavage of ethyl isopropyl ether Protonation makes the ether oxygen a suitable leaving group. Iodide attacks the primary ethyl carbon, which is less sterically hindered than the secondary isopropyl carbon. Thus the ethyl-oxygen bond is cleaved:

$$CH_3CH(CH_3)OCH_2CH_3 + HI \longrightarrow CH_3CH(OH)CH_3 + CH_3CH_2I.$$

Quick Tip to Solve: In the HI cleavage, identify the less hindered carbon bonded to oxygen: iodide attacks the primary ethyl end, leaving the isopropyl end as the alcohol.

The two products asked for are propan-2-ol and iodoethane. This is the initial ether-cleavage reaction; no excess HI or prolonged heating is specified to convert the alcohol further.

Step 3: (a)(iii) Controlled oxidation with PCC The terminal $-CH_2OH$ group is a primary alcohol group. PCC removes two hydrogen atoms to form $-CHO$, retaining the alkene linkage:

$$CH_3CH{=}CHCH_2OH \xrightarrow{PCC} CH_3CH{=}CHCHO.$$

The product is but-2-enal. Numbering begins at the aldehyde carbon, so the double bond is between carbon atoms 2 and 3. PCC stops at the aldehyde under these conditions; a carboxylic acid is not the expected product.

Step 4: (b)(i) Distinguish ethanol and phenol Add a few drops of freshly prepared neutral aqueous ferric chloride solution separately to the samples. Phenol gives a violet colour because it forms a coloured iron(III)-phenolate complex. Ethanol gives no violet colour under the same conditions. Therefore the sample giving the violet colour is phenol and the sample showing no such colour is ethanol. Neutral reagent is used because this is the standard ferric chloride test for the phenolic group.

Step 5: (b)(ii) Distinguish propanol and 2-methylpropan-2-ol Add Lucas reagent to each sample at room temperature. 2-Methylpropan-2-ol is tertiary and gives immediate turbidity, owing to rapid formation of insoluble 2-chloro-2-methylpropane:

$$(CH_3)_3COH + HCl \xrightarrow{ZnCl_2} (CH_3)_3CCl + H_2O.$$

Propanol (propan-1-ol) is primary and gives no turbidity at room temperature during the test. The tertiary alcohol reacts rapidly because ionisation produces a relatively stable tertiary carbocation; the primary alcohol does not readily ionise in this way. Compare the samples without heating so that the difference in their room-temperature behaviour is clear.

Step 6: Conclusion (a) (i) Aspirin, o-$CH_3COOC_6H_4COOH$, with acetic acid; (ii) $CH_3CH(OH)CH_3$ and CH_3CH_2I; (iii) $CH_3CH{=}CHCHO$. (b) Phenol gives a violet colour with neutral $FeCl_3$, whereas ethanol does not. 2-Methylpropan-2-ol gives immediate turbidity with Lucas reagent, whereas propanol gives no turbidity at room temperature.

Quick Tip to Solve: In the HI cleavage, identify the less hindered carbon bonded to oxygen: iodide attacks the primary ethyl end, leaving the isopropyl end as the alcohol.

OR

25(b). (a) Write the formula of reagents used in the following reactions:

(i) Bromination of phenol to 2,4,6-tribromophenol

(ii) Hydroboration of propene and then oxidation to propanol.

(b) Arrange the following compound groups in the increasing order of their property indicated:

(i) p-nitrophenol, ethanol, phenol (acidic character)

(ii) Propanol, Propane, Propanal (boiling point)

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

$$CH_3CH_2OH_2^+ \xrightarrow{CH_3CH_2OH} CH_3CH_2O^+(H)CH_2CH_3 + H_2O$$

[5 marks]

Solution:

Concept:

- The hydroxyl group activates phenol towards electrophilic substitution at the ortho and para positions. Bromine water therefore gives substitution at all three positions.
- Hydroboration followed by alkaline peroxide oxidation gives an anti-Markovnikov alcohol: the hydroxyl group appears on the less substituted carbon of the original double bond.
- Acidity increases with stabilisation of the conjugate base. Boiling point increases with the strength of intermolecular attractions for these comparably sized molecules.
- A curved arrow starts at an electron pair and ends where that pair forms a bond or becomes a lone pair. Protonated ethanol has water as a good leaving group and undergoes nucleophilic substitution with ethanol.

Step 1: (a)(i) Reagent for exhaustive bromination of phenol Use bromine water, $Br_2(aq)$. Phenol is sufficiently activated to react without a Lewis acid catalyst, producing a white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr.$$

The two ortho positions and the para position relative to $-OH$ are occupied by bromine atoms.

Step 2: (a)(ii) Reagents for hydroboration and oxidation First use diborane, B_2H_6, equivalently BH_3 in tetrahydrofuran. Then oxidise with $H_2O_2/NaOH$, that is, alkaline hydrogen peroxide:

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/NaOH]{1.\ BH_3/THF} CH_3CH_2CH_2OH.$$

Boron bonds preferentially to the terminal carbon during addition. Oxidation replaces the carbon-boron bond by a carbon-oxygen bond, giving propan-1-ol.

Step 3: (b)(i) Compare acidic character Ethoxide has no resonance stabilisation; the electron-releasing ethyl group also disfavors the negative charge on oxygen. Phenoxide is stabilised by delocalisation into the aromatic ring. In p-nitrophenoxide, the para nitro group withdraws electrons by both inductive

Quick Tip to Solve: In the mechanism, start each curved arrow at an electron pair: the ethanol oxygen lone pair attacks carbon, while the C–O bond pair moves onto the departing water oxygen.

and resonance effects, stabilising the conjugate base still further. Thus the increasing order is

$$\boxed{\text{ethanol} < \text{phenol} < \text{p-nitrophenol}}.$$

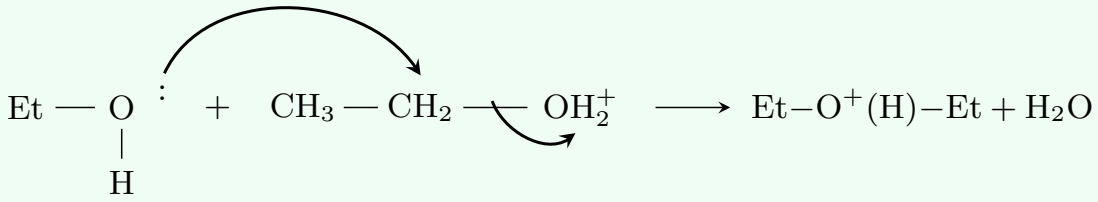
Step 4: (b)(ii) Compare boiling points Propane is nonpolar and has only weak London dispersion attractions. Propanal is polar and has additional dipole-dipole attractions, but cannot form hydrogen bonds with other propanal molecules. Propanol molecules form intermolecular hydrogen bonds through their hydroxyl groups. Consequently,

$$\boxed{\text{propane} < \text{propanal} < \text{propanol}}.$$

Step 5: (c) Show the electron-pair movement in substitution The nucleophile is the oxygen atom of an unprotonated ethanol molecule. Its lone pair attacks the primary carbon bonded to OH_2^+. At the same time, the carbon-oxygen bond to the leaving group breaks, with its electron pair moving onto the leaving oxygen. The following two curved arrows show this concerted S_N2 step; no free primary carbocation is formed. In the drawing, $Et = CH_3CH_2$.

$$CH_3CH_2OH_2^+ + CH_3CH_2OH \longrightarrow CH_3CH_2O^+(H)CH_2CH_3 + H_2O.$$

The attacking oxygen now has three bonds and carries the positive charge. This gives the protonated ether printed in the question. Subsequent loss of a proton would give neutral diethyl ether and regenerate the acid catalyst, but the printed transformation stops at the oxonium ion.



Curved arrows for attack by ethanol and departure of water; Et denotes an ethyl group.

Step 6: Conclusion (a) $Br_2(aq)$; then, for hydroboration-oxidation, B_2H_6 followed by $H_2O_2/NaOH$. (b) Ethanol $<$ phenol $<$ p-nitrophenol in acidity; propane $<$ propanal $<$ propanol in boiling point. (c) Ethanol attacks protonated ethanol by concerted substitution, giving protonated diethyl ether and water.

Quick Tip to Solve: In the mechanism, start each curved arrow at an electron pair: the ethanol oxygen lone pair attacks carbon, while the C–O bond pair moves onto the departing water oxygen.

26(a). Account for the following:

(i) Transition metals form large number of complex compounds.

(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(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 ions have high charge density and suitable vacant orbitals that can accept lone pairs from ligands, forming coordinate bonds.
- Increasing the oxidation state generally increases the covalent character and acidity of a metal oxide. A low oxidation state favours ionic, basic oxides.
- A positive standard reduction potential, E°, indicates a favourable reduction relative to the standard hydrogen electrode. Particularly stable electronic configurations influence the relative stability of oxidation states.
- Lanthanoids involve the filling of $4f$ orbitals and actinoids involve $5f$ orbitals; the availability of other valence orbitals affects their oxidation states.

Step 1: (a)(i) Explain complex formation Transition-metal ions are relatively small and often carry a high positive charge. Their high charge density produces a strong attraction for electron-pair donors called ligands. They also have suitable vacant orbitals available to accept the donated lone pairs. Consequently, they readily form coordinate bonds with several ligands and give a large number of complex compounds, for example $[Fe(CN)_6]^{4-}$.

Step 2: (a)(ii) Compare the lowest and highest oxides In a low oxidation state, the metal has a relatively low polarising power and the metal–oxygen bond has greater ionic character. Such oxides behave as bases and react with acids. As the oxidation state increases, the metal ion polarises the oxide ion more strongly, increasing covalent character. The resulting high-oxidation-state oxides are amphoteric or acidic and can react with bases. For example, MnO, containing manganese in the $+2$ state, is basic, whereas Mn_2O_7, containing manganese in the $+7$ state, is acidic. Thus, oxide acidity increases with the oxidation state of the metal.

Step 3: (a)(iii) Compare the two reduction couples The relevant electronic configurations are

$$Mn^{3+} : [Ar]\,3d^4, \quad Mn^{2+} : [Ar]\,3d^5,$$
$$Cr^{3+} : [Ar]\,3d^3, \quad Cr^{2+} : [Ar]\,3d^4.$$

Reduction of Mn^{3+} gives Mn^{2+}, which has the especially stable half-filled $3d^5$ configuration. Hence, the reduction $Mn^{3+} + e^- \rightarrow Mn^{2+}$ is strongly favoured, giving the highly positive value $E^\circ = +1.57\,V$. By comparison, Cr^{3+} has a stable $3d^3$ configuration; its reduction to Cr^{2+} produces $3d^4$, so this reduction is much less favourable. This explains the much higher reduction potential of the manganese couple.

Step 4: (b) State one similarity and one difference **Similarity:** Both lanthanoids and actinoids commonly exhibit the $+3$ oxidation state, forming trivalent ions.

Difference: Lanthanoids show predominantly the $+3$ oxidation state, with relatively few exceptions

Quick Tip to Solve: For the potential comparison, write the d-electron counts first: manganese reduction gives stable d5, whereas chromium reduction consumes stable d3.

such as $+2$ and $+4$. Actinoids show a much wider range of oxidation states because their $5f$, $6d$ and $7s$ orbitals have comparable energies and can participate in bonding.

Step 5: Conclusion Transition metals form complexes because of high ionic charge density and suitable vacant orbitals; their oxides become more acidic as oxidation state rises. The stable half-filled $3d^5$ configuration of Mn^{2+} favours reduction of Mn^{3+}, whereas stable Cr^{3+} resists reduction. Both f-block series commonly show $+3$, but actinoids exhibit a wider range of oxidation states.

Quick Tip to Solve: For the potential comparison, write the d-electron counts first: manganese reduction gives stable d5, whereas chromium reduction consumes stable d3.

OR

26(b). (a) (i) How is the variability in oxidation states of transition metals different from that of the p-block elements?

(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons. [5 marks]

Solution:

Concept:

- Variable oxidation states arise when electrons of similar energies can participate in bonding. In transition metals these include the $(n-1)d$ and ns electrons.
- The stability of an ion in water depends on the overall energy change, including hydration, rather than its electronic configuration alone.
- Chromate and dichromate ions interconvert in a pH-dependent equilibrium. Actinoid chemistry reflects both closely spaced orbital energies and radioactive instability.

Step 1: (a)(i) Compare the pattern of oxidation states Transition metals commonly exhibit oxidation states differing by one unit, because both ns and $(n-1)d$ electrons can take part in bonding and their successive involvement is possible. For example, manganese exhibits $+2, +3, +4, +5, +6$ and $+7$ oxidation states. In contrast, the common variable oxidation states of p-block elements generally differ by two units. For example, tin shows $+2$ and $+4$, and lead shows $+2$ and $+4$. This two-unit difference is associated with whether the outer ns^2 electron pair participates in bonding; its tendency to remain uninvolved is the inert-pair effect.

Step 2: (a)(ii) Identify the unstable copper ion in water Cu^+ is unstable in aqueous solution and undergoes disproportionation:

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

Although Cu^+ has a filled $3d^{10}$ configuration, Cu^{2+} has a much more negative hydration enthalpy because of its greater charge density. The energy released on hydration of Cu^{2+} more than compensates for the energy required to oxidise part of the Cu^+ to Cu^{2+}. Thus the overall disproportionation is favourable in water.

Quick Tip to Solve: For copper, compare hydration as well as electronic configuration; for dichromate, write the equilibrium before predicting the effect of adding alkali.

Step 3: (a)(iii) Explain the orange-to-yellow change Orange dichromate and yellow chromate are related by

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

An alkali supplies $\mathrm{OH^-}$, which removes $\mathrm{H^+}$ as water. By Le Chatelier's principle the equilibrium shifts towards chromate. The net conversion is

$$\mathrm{Cr_2O_7^{2-}} + 2\mathrm{OH^-} \longrightarrow 2\mathrm{CrO_4^{2-}} + \mathrm{H_2O}.$$

The solution therefore becomes yellow. Chromium remains in oxidation state $+6$, so this colour change is an acid-base equilibrium change, not a redox reaction.

Step 4: (b) Give two reasons for the complexity of actinoid chemistry First, the $5f$, $6d$ and $7s$ orbitals of actinoids have comparable energies. Different numbers of their electrons can therefore participate in bonding, producing a wider range of oxidation states than in lanthanoids, which are predominantly $+3$. This leads to more varied chemical behaviour.

Second, all actinoids are radioactive. Many have short half-lives and are available only in very small quantities; their radioactive decay and the associated handling difficulties complicate the study of their chemistry. Lanthanoids, apart from promethium, have stable naturally occurring isotopes.

Step 5: Conclusion Transition-metal oxidation states commonly differ by one unit, whereas common p-block oxidation states differ by two. $\mathrm{Cu^+}$ disproportionates in water; alkali converts orange dichromate into yellow chromate. The wide range of oxidation states and radioactivity make actinoid chemistry more complicated than lanthanoid chemistry.

Quick Tip to Solve: For copper, compare hydration as well as electronic configuration; for dichromate, write the equilibrium before predicting the effect of adding alkali.