CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-2-2

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) Section A : Questions number **1 to 5** are very short answer questions and carry **1** mark each.

(iii) Section B : Questions number **6 to 12** are short answer questions and carry **2** marks each.

(iv) Section C : Questions number **13 to 24** are also short answer questions and carry **3** marks each.

(v) Section D : Questions number **25 to 27** are long answer questions and carry **5** marks each.

(vi) There is no overall choice. However, an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.

(vii) Use of log tables, if necessary. Use of calculators is not allowed.

Section A (5 marks)

1(a). What is the basic structural difference between starch and cellulose? [1 mark]

Solution:

Concept:

- Both starch and cellulose are polysaccharides formed by joining D-glucose units through glycosidic bonds.
- The configuration of the glucose units and their glycosidic linkages distinguishes these two polymers.

Step 1: Identify the units in starch Starch is a polymer of α-D-glucose. Its amylose component contains $\alpha(1 \rightarrow 4)$ glycosidic linkages. Amylopectin contains these linkages along its chains and $\alpha(1 \rightarrow 6)$ linkages at branch points.

Step 2: Compare the units in cellulose Cellulose is a straight-chain polymer of β-D-glucose units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds. Thus the fundamental difference is the alpha versus beta configuration, rather than the identity of the monosaccharide.

Step 3: Conclusion Starch contains α-D-glucose units with alpha glycosidic bonds, whereas cellulose contains β-D-glucose units with beta glycosidic bonds.

Quick Tip to Solve: Remember alpha for starch and beta for cellulose; both contain D-glucose, so naming glucose alone does not distinguish them.

OR

1(b). Write the products obtained after hydrolysis of DNA. [1 mark]

Solution:

Concept:

- DNA is a polynucleotide. Each nucleotide contains a sugar, a phosphate group and a nitrogenous base.
- Complete hydrolysis breaks the links in the polymer and separates the components of its nucleotides.

Step 1: Identify the sugar and phosphate products The sugar in DNA is 2-deoxy-D-ribose, rather than the D-ribose present in RNA. Complete hydrolysis therefore releases 2-deoxy-D-ribose and phosphoric acid, H_3PO_4, from the sugar-phosphate backbone.

Step 2: Identify the nitrogenous bases The nitrogenous bases released are adenine, guanine, cytosine and thymine. Adenine and guanine are purines, while cytosine and thymine are pyrimidines. Uracil belongs to RNA and is not included among the usual DNA hydrolysis products.

Step 3: Conclusion Complete hydrolysis of DNA gives phosphoric acid, 2-deoxy-D-ribose, adenine, guanine, cytosine and thymine.

Quick Tip to Solve: List the three component types first: phosphate, deoxyribose and bases. For DNA, use thymine instead of uracil.

2. Arrange the following in increasing order of pK_b values:

$C_6H_5CH_2NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$ [1 mark]

Solution:

Concept:

- For a base, $pK_b = -\log_{10} K_b$, where K_b is its base dissociation constant. A stronger base has a smaller pK_b.
- A nitrogen lone pair readily available for protonation increases basicity; delocalisation of that pair into a benzene ring decreases it.

Step 1: Compare the availability of the lone pair In benzylamine, $C_6H_5CH_2NH_2$, the intervening CH_2 group prevents direct conjugation of the nitrogen lone pair with the ring. In aniline and N-methylaniline, nitrogen is directly attached to the ring, so its lone pair is delocalised. Benzylamine is therefore the strongest base of the three.

Step 2: Compare the two aromatic amines The methyl group in $C_6H_5NHCH_3$ donates electron density through its positive inductive effect, making it more basic than $C_6H_5NH_2$. Thus basic strength decreases from benzylamine to N-methylaniline to aniline. Reverse this relationship when comparing their pK_b values.

Step 3: Conclusion The increasing order of pK_b is

$$C_6H_5CH_2NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2.$$

Quick Tip to Solve: First rank basic strength using lone-pair availability, then reverse that order for pKb; the intervening methylene group makes benzylamine stand out.

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

Solution:

Concept:

- Colloids are classified using the physical states of the dispersed phase and the dispersion medium.
- A liquid dispersed in a solid dispersion medium forms a gel.

Step 1: Identify the two phases The question specifies that the dispersed phase is a liquid and that the continuous dispersion medium is a solid. The classification must follow this stated order: dispersed phase first, dispersion medium second.

Step 2: Match the classification to an example Jelly is a familiar example: liquid is held throughout a solid network, producing a gel. It differs from an emulsion, where both phases are liquids, and from a sol, where a solid is dispersed in a liquid. Therefore neither of these other names fits the given phase combination.

Step 3: Conclusion The colloid is a gel; jelly is an example.

Quick Tip to Solve: Write the phase pair as liquid-in-solid before naming the colloid. This immediately gives gel, with jelly as a standard example.

4. Out of Chlorobenzene and p-nitrochlorobenzene, which one is more reactive towards nucleophilic substitution reaction and why? [1 mark]

Solution:

Concept:

- Nucleophilic aromatic substitution is facilitated by electron-withdrawing groups at the ortho or para position relative to the leaving group.
- A nitro group withdraws electron density by inductive and resonance effects and stabilises the anionic intermediate.

Step 1: Identify the activating group In p-nitrochlorobenzene, the NO_2 group lies para to chlorine. It withdraws electron density from the aromatic ring and facilitates nucleophilic attack at the carbon bearing chlorine.

Step 2: Explain intermediate stabilisation Attack by the nucleophile produces an anionic intermediate whose negative charge can be delocalised towards the para nitro group and onto its oxygen atoms. This resonance stabilisation facilitates substitution. Chlorobenzene lacks such an electron-withdrawing group and does not provide the same additional stabilisation.

Step 3: Conclusion p-Nitrochlorobenzene is more reactive because its para nitro group withdraws electron density and stabilises the anionic intermediate by resonance.

Quick Tip to Solve: For aromatic nucleophilic substitution, look for a nitro group ortho or para to chlorine; these positions permit resonance stabilisation of the intermediate.

5(a). Out of KCl and AgCl, which one shows Schottky defect and why? [1 mark]

Solution:

Concept:

- A Schottky defect consists of equal numbers of cation and anion vacancies in an ionic crystal, preserving electrical neutrality.
- This vacancy defect is favoured in ionic solids with comparably sized cations and anions and high coordination numbers.

Step 1: Compare the ions in potassium chloride KCl has K^+ and Cl^- ions of comparable size and a high coordination number. Such a lattice favours paired vacancies, rather than displacement of a small cation into an interstitial site.

Step 2: Relate the comparison to the defect When equal numbers of K^+ and Cl^- ions are missing from their lattice sites, the crystal retains electrical neutrality but its density decreases. By comparison, the relatively small Ag^+ ion in $AgCl$ can occupy interstitial sites, so silver chloride is also associated with Frenkel defects.

Step 3: Conclusion KCl shows Schottky defect because its cation and anion are of comparable size and it has a high coordination number.

Quick Tip to Solve: Comparable ion sizes favour Schottky vacancies; a much smaller cation can move into an interstitial site and give a Frenkel defect.

OR

5(b). Why does ZnO appear yellow on heating? [1 mark]

Solution:

Concept:

- Heating ZnO causes loss of oxygen and produces a non-stoichiometric solid with excess zinc.
- The extra zinc ions occupy interstitial sites, while electrons maintain electrical neutrality. This is a metal-excess defect.

Step 1: Explain the change on heating On heating, some oxygen leaves the lattice, creating a metal-excess defect. The process is commonly represented as

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

The Zn^{2+} ions remain in the solid at interstitial positions; this expression describes the defect formation rather than free zinc ions in solution.

Step 2: Connect the defect to the colour Electrons associated with these defects occupy interstitial sites and compensate the positive charge of the excess zinc ions. They absorb energy from visible light and can be excited to higher energy levels, changing the appearance of the solid from white to yellow.

Step 3: Conclusion ZnO appears yellow on heating because oxygen loss creates a metal-excess defect with trapped electrons that absorb visible light.

Quick Tip to Solve: Connect the colour change in heated ZnO with oxygen loss, excess zinc ions and trapped electrons; the defect electrons account for the yellow colour.

Section B (14 marks)

6. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured compound (C). An acidified solution of compound (C) oxidises Na_2SO_3 to (D). Identify (A), (B), (C) and (D). [2 marks]

Solution:

Concept:

- Chromium in chromite ore is oxidised to the yellow chromate ion, CrO_4^{2-}, during alkaline fusion in air.
- Acidification converts chromate into orange dichromate, $Cr_2O_7^{2-}$. Acidified dichromate is an oxidising agent.

Step 1: Identify A and B Fusion gives sodium chromate, so $A = Na_2CrO_4$. The balanced fusion equation is

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

Quick Tip to Solve: Use yellow chromate, orange dichromate, then sulfite-to-sulfate oxidation to identify the sequence.

On acidification, the equilibrium $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ shifts towards dichromate. Thus $B = Na_2Cr_2O_7$, sodium dichromate.

Step 2: Identify C and D Potassium chloride converts sodium dichromate into less soluble potassium dichromate:

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

Thus $C = K_2Cr_2O_7$. In acid, dichromate oxidises sulfite to sulfate:

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O.$$

Sulfur changes from $+4$ to $+6$; hence sodium sulfite gives sodium sulfate, $D = Na_2SO_4$.

Step 3: Conclusion $A = Na_2CrO_4$, $B = Na_2Cr_2O_7$, $C = K_2Cr_2O_7$, and $D = Na_2SO_4$.

Quick Tip to Solve: Use yellow chromate, orange dichromate, then sulfite-to-sulfate oxidation to identify the sequence.

7. Give reasons:

(a) A decrease in temperature is observed on mixing ethanol and acetone.

(b) Potassium chloride solution freezes at a lower temperature than water. [2 marks]

Solution:

Concept:

- Mixing absorbs heat when the energy needed to disrupt the original intermolecular attractions exceeds that released in forming new attractions: $\Delta H_{mix} > 0$.
- Freezing-point depression is a colligative property: $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the cryoscopic constant and m the molality.

Step 1: Explain cooling on mixing ethanol and acetone Ethanol molecules are associated through hydrogen bonds. Adding acetone disrupts these associations. Although acetone can interact with ethanol, the new ethanol–acetone attractions are weaker overall than the attractions disrupted during mixing. More energy is absorbed in breaking the original attractions than is released by forming the new ones. Mixing is therefore endothermic, $\Delta H_{mix} > 0$; the mixture absorbs heat from its surroundings and its temperature falls. This mixture shows positive deviation from Raoult's law.

Step 2: Explain the lower freezing point of potassium chloride solution Potassium chloride is a non-volatile solute and dissociates in water:

$$KCl(aq) \longrightarrow K^+(aq) + Cl^-(aq).$$

The dissolved ions lower the chemical potential, and hence the vapour pressure, of liquid water. The liquid solution comes into equilibrium with pure ice at a lower temperature than pure water does. Consequently $\Delta T_f = iK_f m > 0$, so the solution freezes below water's freezing point. Dissociation increases the number of solute particles; for an ideally dilute KCl solution, i approaches 2.

Step 3: Conclusion (a) Endothermic mixing caused by disruption of ethanol hydrogen bonding

Quick Tip to Solve: For cooling on mixing compare intermolecular attractions; for KCl freezing count the dissolved ions.

produces cooling. (b) Dissolved KCl ions cause freezing-point depression.

Quick Tip to Solve: For cooling on mixing compare intermolecular attractions; for KCl freezing count the dissolved ions.

8(a). Write balanced chemical equations for the following processes:

(a) Cl_2 is passed through slaked lime.

(b) SO_2 gas is passed through an aqueous solution of Fe(III) salt. [2 marks]

Solution:

Concept:

- Chlorine reacts with dry slaked lime, $Ca(OH)_2$, to form bleaching powder, conventionally represented as $CaOCl_2$.
- Sulfur dioxide acts as a reducing agent in aqueous solution: sulfur is oxidised from $+4$ to $+6$, while Fe^{3+} is reduced to Fe^{2+}.

Step 1: Write the reaction with slaked lime The balanced equation for preparation of bleaching powder is

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O.$$

The product is calcium oxychloride (bleaching powder). There is one calcium atom, two oxygen atoms, two hydrogen atoms and two chlorine atoms on each side. The conventional formula $CaOCl_2$ is the standard school representation of bleaching powder.

Step 2: Balance the reduction of an aqueous Fe(III) salt The oxidation and reduction half-equations are

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-,$$
$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}.$$

Adding and cancelling electrons gives the required ionic equation:

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+.$$

Both atoms and total charge are balanced. This ionic form applies regardless of the spectator anion of the Fe(III) salt.

Step 3: Conclusion (a) $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$. (b) $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$.

Quick Tip to Solve: SO2 loses two electrons on forming sulfate, so pair it with two Fe(III) ions, each gaining one electron.

OR

8(b). (a) Write two poisonous gases prepared from chlorine gas.

(b) Why does Cu^{2+} solution give blue colour on reaction with ammonia? [2 marks]

Solution:

Concept:

- Chlorine is used to prepare chlorine-containing poisonous compounds such as phosgene and mustard gas.
- Ammonia acts as a ligand: it donates a lone pair to Cu^{2+}, forming a coordination complex with a characteristic deep-blue colour.

Step 1: Name two poisonous gases prepared from chlorine The two examples are phosgene, $COCl_2$, and mustard gas, $(ClCH_2CH_2)_2S$. Phosgene is carbonyl dichloride; mustard gas is bis(2-chloroethyl) sulfide. The name "mustard gas" is the customary name of this poisonous chemical. For example, formation of phosgene uses carbon monoxide and chlorine:

$$CO + Cl_2 \longrightarrow COCl_2.$$

Both examples contain chlorine and answer the requested names.

Step 2: Explain the blue colour with ammonia In excess ammonia, aqueous copper(II) ions form the deep-blue tetraamminecopper(II) complex. The ligand-exchange equation is

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O.$$

Ammonia donates its nitrogen lone pair to the metal ion. This changes the ligand environment and the energy separation of the copper d orbitals. Absorption of visible light in d–d transitions gives the characteristic intense blue appearance of the complex solution.

Step 3: Conclusion (a) Phosgene, $COCl_2$, and mustard gas, $(ClCH_2CH_2)_2S$. (b) Ammonia forms the deep-blue complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

Quick Tip to Solve: For Cu(II) with excess ammonia, name the deep-blue tetraammine complex and identify NH3 as the ligand.

9. Write structures of main compounds A and B in each of the following reactions:

(a) $C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd\text{-}BaSO_4} B$

(b) $CH_3CN \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} A \xrightarrow{Zn(Hg)/conc.\ HCl} B$ [2 marks]

Solution:

Concept:

- PCl_5 converts a carboxylic acid into its acyl chloride. Rosenmund reduction, $H_2/Pd - BaSO_4$, converts an acyl chloride into an aldehyde.
- A Grignard reagent adds to a nitrile and hydrolysis gives a ketone. Clemmensen reduction, $Zn(Hg)/\text{conc. HCl}$, replaces the carbonyl oxygen with two hydrogens.

Step 1: Find the structures in sequence (a) Benzoic acid first forms benzoyl chloride:

$$C_6H_5C(=O)OH + PCl_5 \longrightarrow C_6H_5C(=O)Cl + POCl_3 + HCl.$$

Thus A is $C_6H_5 - C(=O) - Cl$. The poisoned palladium catalyst then gives controlled reduction:

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

Therefore B is benzaldehyde, $C_6H_5 - C(=O) - H$. The catalyst prevents further reduction of the aldehyde.

Step 2: Find the structures in sequence (b) Methylmagnesium bromide adds one methyl group to the carbon of the nitrile. Acid hydrolysis of the intermediate gives propanone:

$$CH_3CN \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} CH_3 - C(=O) - CH_3.$$

Hence A is acetone (propanone), with three carbon atoms. Clemmensen reduction then changes $>C=O$ into $>CH_2$ without changing the carbon skeleton:

$$CH_3COCH_3 \xrightarrow{Zn(Hg)/conc.\ HCl} CH_3CH_2CH_3.$$

Therefore B is propane, $CH_3 - CH_2 - CH_3$.

Step 3: Conclusion (a) $A = C_6H_5 - C(=O) - Cl$; $B = C_6H_5 - C(=O) - H$. (b) $A = CH_3 - C(=O) - CH_3$; $B = CH_3 - CH_2 - CH_3$.

Quick Tip to Solve: Rosenmund stops at the aldehyde; a methyl Grignard adds one carbon to CH3CN before Clemmensen removes oxygen.

10(a). Define the following terms with a suitable example of each:

(a) Chelate complex

(b) Ambidentate ligand [2 marks]

Solution:

Concept:

- A ligand donates a lone pair from a donor atom to a central metal ion, forming a coordinate bond.
- Denticity is the number of donor atoms of one ligand that simultaneously bind to the same metal ion. Chelation and ambidentate behaviour describe different ways in which donor atoms can bind.

Step 1: Define a chelate complex and give an example A chelate complex contains a polydentate ligand attached to the same central metal ion through two or more donor atoms, thereby forming one or more rings containing the metal. For example, $[Co(en)_3]^{3+}$, where en is ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, is a chelate complex. Each en ligand coordinates through both nitrogen atoms and forms a five-membered ring with cobalt.

Step 2: Define an ambidentate ligand and give an example An ambidentate ligand has two different possible donor atoms, but binds through only one of them to a particular metal centre at a time. The nitrite ion, NO_2^-, can coordinate through nitrogen (nitro) or oxygen (nitrito). Thus it offers alternative donor atoms without acting as a bidentate chelating ligand in these modes.

Step 3: Conclusion A chelate complex has a ring formed by a polydentate ligand and the metal, as in $[Co(en)_3]^{3+}$. An ambidentate ligand can bind through either of two different donor atoms, as in NO_2^-.

Quick Tip to Solve: For chelation, count donor atoms binding simultaneously; for ambidentate ligands, identify the two alternative donor atoms.

OR

10(b). Using IUPAC norms, write the formulae for the following complexes:

(a) Tetraamminediaquacobalt(III) chloride

(b) Dibromidobis(ethane-1,2-diamine)platinum(IV) nitrate [2 marks]

Solution:

Concept:

- The coordination entity is written inside square brackets, and ions required for electrical neutrality are written outside the brackets.
- Ammine, aqua and ethane-1,2-diamine (en) are neutral ligands; bromido has charge -1. The Roman numeral specifies the metal's oxidation state.

Step 1: Form the cobalt coordination entity and balance its charge Tetraammine gives four NH_3 ligands and diaqua gives two H_2O ligands. All six are neutral, so cobalt(III) produces a coordination cation with charge $+3$:

$$[Co(NH_3)_4(H_2O)_2]^{3+}.$$

Quick Tip to Solve: First calculate the charge inside the square brackets; use that charge to count chloride or nitrate counter-ions outside them.

Chloride is the counter-ion, not a ligand inside the brackets. Three Cl^- ions are required to neutralise this cation, giving $[Co(NH_3)_4(H_2O)_2]Cl_3$.

Step 2: Form the platinum coordination entity and add nitrate ions Dibromido means two Br^- ligands, and bis(ethane-1,2-diamine) means two neutral en ligands. Platinum(IV) contributes $+4$, so the coordination entity has charge

$$+4 + 2(-1) + 2(0) = +2.$$

Two nitrate counter-ions, each $NO_3{}^-$, balance this charge. Hence the salt formula is $[PtBr_2(en)_2](NO_3)_2$. Each en ligand is bidentate, so the two en ligands and two bromido ligands provide six donor atoms in total.

Step 3: Conclusion (a) $[Co(NH_3)_4(H_2O)_2]Cl_3$; (b) $[PtBr_2(en)_2](NO_3)_2$, with en = ethane-1,2-diamine.

Quick Tip to Solve: First calculate the charge inside the square brackets; use that charge to count chloride or nitrate counter-ions outside them.

11. (a) Using valence bond theory, write the hybridisation and magnetic character of the complex $[Fe(CN)_6]^{4-}$. (Atomic no. of Fe = 26)

(b) Write the electronic configuration of d^6 on the basis of crystal field theory when

(i) $\Delta_o < P$ and

(ii) $\Delta_o > P$. [2 marks]

Solution:

Concept:

- In valence bond theory, an octahedral inner-orbital complex uses d^2sp^3 hybridisation. Its magnetic character depends on the number of unpaired electrons.
- In an octahedral crystal field, the lower t_{2g} and upper e_g levels are separated by Δ_o. Compare this splitting with the pairing energy P to decide between high-spin and low-spin configurations.

Step 1: Determine the iron oxidation state and hybridisation Let the oxidation state of iron in $[Fe(CN)_6]^{4-}$ be x. Each cyanide ion carries charge -1, so

$$x + 6(-1) = -4 \quad \Rightarrow \quad x = +2.$$

Iron has atomic number 26, with configuration $[Ar]\,3d^64s^2$. Removing the two $4s$ electrons gives Fe^{2+} with $3d^6$. Cyanide is a strong-field ligand and causes these six electrons to pair in three of the five $3d$ orbitals. The remaining two vacant $3d$ orbitals, one $4s$ and three $4p$ orbitals undergo d^2sp^3 hybridisation. All electrons are paired, so the octahedral complex is diamagnetic.

Step 2: Fill the split orbitals for the two d-six cases When $\Delta_o < P$, occupying an upper orbital costs less energy than pairing. Electrons occupy all five orbitals before the sixth pairs in t_{2g}, giving the high-spin configuration $t_{2g}^4e_g^2$ with four unpaired electrons. When $\Delta_o > P$, pairing in the lower orbitals costs less energy than promotion. All six electrons fill the three t_{2g} orbitals in pairs, giving the

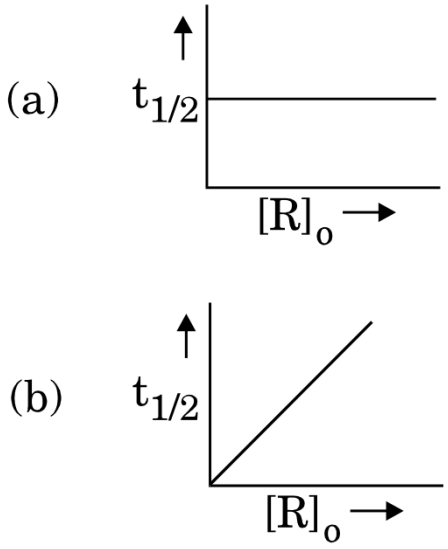
Quick Tip to Solve: Find the metal ion's d-electron count before filling orbitals; weak splitting gives high spin, while strong splitting favours pairing.

low-spin configuration $t_{2g}^6 e_g^0$, with no unpaired electrons.

Step 3: Conclusion (a) $[Fe(CN)_6]^{4-}$ has d^2sp^3 hybridisation and is diamagnetic. (b) For d^6: (i) $\Delta_o < P$: $t_{2g}^4 e_g^2$; (ii) $\Delta_o > P$: $t_{2g}^6 e_g^0$.

Quick Tip to Solve: Find the metal ion's d-electron count before filling orbitals; weak splitting gives high spin, while strong splitting favours pairing.

12. Define order of reaction. Predict the order of reaction in the given graphs: where $[R]_0$ is the initial concentration of reactant and $t_{1/2}$ is half-life. [2 marks]



Solution:

Concept:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law. For $r = k[A]^m[B]^n$, the overall order is $m + n$; it is not generally obtained from stoichiometric coefficients.
- Half-life $t_{1/2}$ is the time for a reactant concentration to fall from its initial value $[R]_0$ to $[R]_0/2$. Its dependence on $[R]_0$ identifies the order when temperature and the rate constant k are fixed.

Step 1: Interpret the horizontal graph in part (a) In graph (a), the half-life remains constant as the initial concentration increases. For a first-order reaction, the integrated rate law gives

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

This expression contains no $[R]_0$. The concentration-independent half-life therefore produces the horizontal line shown in graph (a).

Step 2: Interpret the rising straight line in part (b) In graph (b), half-life is directly proportional to initial concentration, and the straight line passes through the origin. For a zero-order reaction,

Quick Tip to Solve: Read the half-life dependence: constant half-life means first order, while half-life directly proportional to initial concentration means zero order.

$[R] = [R]_0 - kt$. At the half-life, substituting $[R] = [R]_0/2$ gives

$$\frac{[R]_0}{2} = [R]_0 - kt_{1/2} \quad \Rightarrow \quad t_{1/2} = \frac{[R]_0}{2k}.$$

Thus a plot of $t_{1/2}$ against $[R]_0$ is a straight line through the origin with slope $1/(2k)$, identifying graph (b) as zero order.

Step 3: Conclusion Reaction order is the sum of concentration exponents in the experimental rate law. Graph (a) represents a first-order reaction, while graph (b) represents a zero-order reaction.

Quick Tip to Solve: Read the half-life dependence: constant half-life means first order, while half-life directly proportional to initial concentration means zero order.

Section C (36 marks)

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

(b) Why is adsorption exothermic in nature?

(c) Write Freundlich adsorption isotherm for gases at high pressure. [3 marks]

Solution:

Concept:

- An emulsion is a colloidal dispersion of one liquid in another immiscible liquid. The dispersed phase consists of the droplets; the dispersion medium is the continuous surrounding liquid.
- Adsorption binds particles to a surface. For spontaneous adsorption, $\Delta G = \Delta H - T\Delta S < 0$, where ΔH is the enthalpy change and ΔS is the entropy change.
- Freundlich's relation is $x/m = kp^{1/n}$, where x is the mass adsorbed, m is the mass of adsorbent, p is gas pressure and k, n are constants at a fixed temperature.

Step 1: Identify the two phases in milk (a) Milk is a liquid-in-liquid emulsion. Tiny droplets of liquid fat form the dispersed phase, while water forms the dispersion medium. The fat droplets are distributed throughout the continuous aqueous phase rather than forming a molecular solution.

Step 2: Explain the heat released during adsorption (b) The surface particles of an adsorbent have residual attractive forces. When adsorbate particles attach to the surface, these forces are satisfied and the surface energy decreases, releasing heat. Also, the adsorbed particles have less freedom of movement, so $\Delta S < 0$. Therefore, for spontaneous adsorption, ΔH must be sufficiently negative to make $\Delta G = \Delta H - T\Delta S$ negative. Hence adsorption is exothermic, with $\Delta H < 0$.

Step 3: Apply the high-pressure limiting form (c) At high gas pressure, the available adsorption sites become effectively saturated, so the amount adsorbed per unit mass no longer increases with pressure. In the limiting Freundlich form, $1/n = 0$, giving

$$\frac{x}{m} = kp^0 = k.$$

Thus x/m is independent of pressure in this limit; it remains constant at the fixed temperature.

Quick Tip to Solve: For milk, name the droplets first (fat) and the continuous liquid second (water). For high-pressure adsorption, use saturation to set the pressure exponent to zero.

Step 4: Conclusion (a) Dispersed phase: liquid fat; dispersion medium: water. (b) Adsorption lowers surface energy and releases heat, so $\Delta H < 0$. (c) At high pressure, $x/m = kp^0 = k$.

Quick Tip to Solve: For milk, name the droplets first (fat) and the continuous liquid second (water). For high-pressure adsorption, use saturation to set the pressure exponent to zero.

14. The following data were obtained for the reaction:

A + 2B $\longrightarrow$ C

Experiment	[A]/M	[B]/M	Initial rate of formation of C /M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(a) Find the order of reaction with respect to A and B.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k). [3 marks]

Solution:

Concept:

- The initial-rate law is $r = k[A]^a[B]^b$, where r is the rate of formation of C, a, b are the partial orders and k is the rate constant at a fixed temperature.
- Compare experiments with one concentration held fixed to find the exponent of the other concentration. The overall order is $a + b$; it need not equal the sum of stoichiometric coefficients.
- A valid rate law must give the same $k = r/([A]^a[B]^b)$ for every experiment conducted under identical conditions. Rate in M min^{-1} gives a third-order constant in M^{-2} min^{-1}.

Step 1: Determine the order with respect to A (a) Compare experiments 1 and 3, where $[B] = 0.3\,\text{M}$ is unchanged. Doubling $[A]$ from 0.2 to $0.4\,\text{M}$ increases the rate by a factor of four:

$$\frac{r_3}{r_1} = \frac{1.68 \times 10^{-1}}{4.2 \times 10^{-2}} = 4 = \left(\frac{0.4}{0.2}\right)^a = 2^a.$$

Hence the pair gives $a = 2$.

Step 2: Determine the order with respect to B Compare experiments 2 and 4, where $[A] = 0.1\,\text{M}$ is unchanged. The concentration of B and the rate both increase fourfold:

$$\frac{r_4}{r_2} = \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4 = \left(\frac{0.4}{0.1}\right)^b = 4^b.$$

Therefore $b = 1$. (b) These independent comparisons give the rate law $r = k[A]^2[B]$ and overall order $2 + 1 = 3$.

Quick Tip to Solve: Use experiments 1 and 3 for A, and 2 and 4 for B. After finding the orders, check k from both pairs to detect the inconsistency in this table.

Step 3: Calculate and check the rate constant (c) Substitution of experiment 1 gives

$$k_1 = \frac{4.2 \times 10^{-2}}{(0.2)^2(0.3)} = 3.5\,\mathrm{M}^{-2}\ \mathrm{min}^{-1}.$$

Experiment 3 gives the same value. However, substituting experiment 2 gives

$$k_2 = \frac{6.0 \times 10^{-3}}{(0.1)^2(0.1)} = 6.0\,\mathrm{M}^{-2}\ \mathrm{min}^{-1},$$

and experiment 4 also gives $6.0\,\mathrm{M}^{-2}\ \mathrm{min}^{-1}$. Thus the printed data are internally inconsistent: the partial orders inferred from the fixed-concentration pairs cannot produce one common rate constant for all four experiments. Using experiment 1 yields $k = 3.5\,\mathrm{M}^{-2}\ \mathrm{min}^{-1}$, but a unique value compatible with the entire table does not exist.

Step 4: Conclusion The fixed-concentration comparisons give order 2 in A, order 1 in B, $r = k[A]^2[B]$, and overall order 3. Experiments 1 and 3 yield $k = 3.5\,\mathrm{M}^{-2}\ \mathrm{min}^{-1}$; experiments 2 and 4 yield $6.0\,\mathrm{M}^{-2}\ \mathrm{min}^{-1}$. Therefore no single rate constant fits all the printed data.

Quick Tip to Solve: Use experiments 1 and 3 for A, and 2 and 4 for B. After finding the orders, check k from both pairs to detect the inconsistency in this table.

15. Write the name and principle of the method used for refining of (a) Tin, (b) Copper, (c) Nickel.

[3 marks]

Solution:

Concept:

- Refining removes impurities from a crude metal by exploiting a difference in physical or chemical behaviour between the metal and its impurities.
- Liquation separates a low-melting metal from higher-melting impurities. Electrolytic refining transfers the metal from an impure anode to a pure cathode through a suitable electrolyte.
- Vapour-phase refining forms a volatile compound of the metal, separates it from nonvolatile impurities, and decomposes it to recover the pure metal.

Step 1: Refine tin by liquation (a) Tin is refined by liquation. Its principle is the difference in melting points: tin has a lower melting point than the accompanying infusible impurities. The impure tin is heated on a sloping hearth to a temperature sufficient to melt tin while leaving these impurities solid. Molten tin flows down the slope and is collected; the solid impurities remain behind on the hearth.

Step 2: Refine copper electrolytically (b) Copper is refined by electrolytic refining. An impure copper slab is the anode, a thin sheet of pure copper is the cathode, and acidified copper sulphate solution is the electrolyte. On passing current, copper dissolves from the anode and an equivalent amount of pure copper deposits at the cathode:

$$\text{Anode:}\quad \mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{e}^-$$
$$\text{Cathode:}\quad \mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Cu}.$$

Quick Tip to Solve: Match tin with melting, copper with anode-to-cathode transfer, and nickel with the volatile carbonyl. For nickel, state both carbonyl formation and its decomposition.

Less reactive impurities such as silver and gold do not dissolve and collect as anode mud. More reactive impurities dissolve but remain in solution under the refining conditions, rather than depositing with copper.

Step 3: Refine nickel by the Mond process (c) Nickel is refined by the Mond process, a vapour-phase refining method. Its principle is selective formation and subsequent thermal decomposition of volatile nickel tetracarbonyl. Impure nickel is treated with carbon monoxide at about 330–350 K:

$$\mathrm{Ni} + 4\,\mathrm{CO} \longrightarrow \mathrm{Ni(CO)_4}.$$

The volatile carbonyl separates from the nonvolatile impurities. It is then heated to about 450–470 K, where it decomposes:

$$\mathrm{Ni(CO)_4} \longrightarrow \mathrm{Ni} + 4\,\mathrm{CO}.$$

Pure nickel is deposited and carbon monoxide is released.

Step 4: Conclusion (a) Tin: liquation, based on its lower melting point than the impurities. (b) Copper: electrolytic refining, based on anodic dissolution and selective cathodic deposition. (c) Nickel: Mond process, based on formation of volatile $\mathrm{Ni(CO)_4}$ followed by thermal decomposition to pure nickel.

Quick Tip to Solve: Match tin with melting, copper with anode-to-cathode transfer, and nickel with the volatile carbonyl. For nickel, state both carbonyl formation and its decomposition.

16. Give reasons for the following:

(a) Transition metals show variable oxidation states.

(b) E° value for (Zn^{2+}/Zn) is negative while that of (Cu^{2+}/Cu) is positive.

(c) Higher oxidation state of Mn with fluorine is +4 whereas with oxygen is +7. [3 marks]

Solution:

Concept:

- The energies of the outer ns and penultimate $(n-1)d$ orbitals of transition metals are comparable, allowing electrons from both to participate in bonding.
- A standard reduction potential reflects the overall energy balance of atomisation, ionisation and hydration; a positive value favours reduction relative to the standard hydrogen electrode.
- Oxygen can stabilise very high oxidation states through multiple bonding, whereas fluorine forms only single bonds to the metal.

Step 1: Explain the variable oxidation states in part (a) In transition elements, the energy difference between the ns and $(n-1)d$ orbitals is small. Consequently, besides the outer ns electrons, different numbers of d electrons can be used in bond formation. Loss or sharing of different numbers of these electrons gives several oxidation states. For example, manganese has configuration $[\mathrm{Ar}]3d^5 4s^2$; its two $4s$ electrons and varying numbers of $3d$ electrons can participate, giving oxidation states such as $+2$, $+4$ and $+7$.

Step 2: Compare the reduction potentials in part (b) Oxidation of a solid metal to its aqueous divalent

Quick Tip to Solve: For the fluoride versus oxide comparison, use oxygen's ability to form multiple bonds; electronegativity alone does not explain the highest oxidation state.

ion requires atomisation and two ionisation steps, while hydration of the ion releases energy. For zinc, the comparatively favourable overall balance and the stable filled $3d^{10}$ configuration of Zn^{2+} favour formation of the aqueous ion. Thus zinc readily undergoes oxidation, and the reverse reduction $Zn^{2+} + 2\,e^- \longrightarrow Zn$ has a negative standard potential.

For copper, the sum of atomisation and ionisation energies is high and is not sufficiently compensated by hydration energy. Formation of $Cu^{2+}(aq)$ from copper is therefore less favourable; the reverse reduction $Cu^{2+} + 2\,e^- \longrightarrow Cu$ has a positive standard potential. These signs are measured relative to the standard hydrogen electrode, whose potential is zero.

Step 3: Explain the role of oxygen in part (c) Fluorine forms only single bonds with manganese, limiting the highest oxidation state in its fluoride to $+4$, as in MnF_4. Oxygen can form multiple bonds with manganese and thereby stabilise the higher oxidation state $+7$, as in Mn_2O_7. In that oxide, seven oxygen atoms contribute a total oxidation number of -14, so the two manganese atoms together contribute $+14$, or $+7$ each. The distinction arises from bonding ability, even though fluorine is more electronegative than oxygen.

Step 4: Conclusion (a) Comparable ns and $(n-1)d$ orbital energies permit variable electron participation. (b) The overall energy balance favours zinc oxidation but copper reduction, giving negative and positive reduction potentials respectively. (c) Multiple bonding with oxygen stabilises Mn in $+7$, while its fluoride reaches $+4$.

Quick Tip to Solve: For the fluoride versus oxide comparison, use oxygen's ability to form multiple bonds; electronegativity alone does not explain the highest oxidation state.

17. An element X with an atomic mass of 81 u has density 10.2 g cm^{-3}. If the volume of unit cell is 2.7 $\times$ 10^{-23} cm^3, identify the type of cubic unit cell. (Given: N_A = 6.022 $\times$ 10^{23} mol^{-1}) [3 marks]

Solution:

Concept:

- The mass of one unit cell is ZM/N_A, where Z is the number of atoms per cell, M is the molar mass and N_A is Avogadro's constant.
- Density is mass per unit volume, so $\rho = ZM/(N_A V)$, with V the unit-cell volume. Simple cubic, body-centred cubic and face-centred cubic cells have $Z = 1, 2, 4$, respectively.

Step 1: Express the atom count using density The given atomic mass of 81 u corresponds to molar mass $M = 81\,\text{g mol}^{-1}$. Use $\rho = 10.2\,\text{g cm}^{-3}$ and $V = 2.7 \times 10^{-23}\,\text{cm}^3$. Since the volume is already supplied, we need not calculate the lattice edge. Rearranging the density expression gives

$$Z = \frac{\rho V N_A}{M}.$$

The product ρV is the mass of one cell; multiplying by N_A/M converts that mass to its number of constituent atoms.

Step 2: Substitute the values and calculate Keep centimetres and grams throughout so that the given

Quick Tip to Solve: When cell volume is given directly, use $Z = \rho V N_A/M$ and match the result to $1, 2, 4$; do not spend time finding the edge length.

density and cell volume have consistent units:

$$\begin{aligned} Z &= \frac{10.2 \times (2.7 \times 10^{-23}) \times (6.022 \times 10^{23})}{81} \\ &= \frac{10.2 \times 2.7 \times 6.022}{81} \\ &= \frac{165.84588}{81} \\ &= 2.04748 \approx 2. \end{aligned}$$

The factors 10^{-23} and 10^{23} cancel. The small departure from an integer reflects the approximate input values; the allowed cubic-cell atom counts are discrete.

Step 3: Match the atom count with the cubic cell A body-centred cubic cell has eight corner atoms and one atom entirely inside the cell at its centre. Each corner atom is shared among eight neighbouring cells, giving

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

This matches the calculated count. A simple cubic cell has only one effective atom, and a face-centred cubic cell has four, so neither matches the given data.

Step 4: Conclusion The number of atoms per unit cell is approximately 2; hence element X has a body-centred cubic (bcc) unit cell.

Quick Tip to Solve: When cell volume is given directly, use $Z = \rho V N_A/M$ and match the result to $1, 2, 4$; do not spend time finding the edge length.

18. A solution containing 1.9 g per 100 mL of KCl (M = 74.5 g mol^{-1}) is isotonic with a solution containing 3 g per 100 mL of urea (M = 60 g mol^{-1}). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature. [3 marks]

Solution:

Concept:

- Osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature. Isotonic solutions have equal osmotic pressures.
- Urea is a non-electrolyte, so $i_{\text{urea}} = 1$. For $\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$, one formula unit gives two ions, and $i = 1 + \alpha$, where α is the degree of dissociation.

Step 1: Calculate the molarity of each solution Each given mass is dissolved to make $100\,\text{mL} = 0.100\,\text{L}$ of solution. Convert the masses to moles using their respective molar masses:

$$C_{\text{KCl}} = \frac{1.9/74.5}{0.100} = 0.25503\,\text{mol L}^{-1},$$
$$C_{\text{urea}} = \frac{3/60}{0.100} = 0.500\,\text{mol L}^{-1}.$$

Urea remains as molecules in solution, whereas dissociation of potassium chloride increases the

Quick Tip to Solve: For isotonic solutions of equal volume, compare their mole amounts directly; then for a salt giving two ions, obtain the dissociation fraction from $\alpha = i - 1$.

number of dissolved particles.

Step 2: Use isotonicity to obtain the van't Hoff factor At the same temperature, equal osmotic pressures give

$$i_{\mathrm{KCl}} C_{\mathrm{KCl}} RT = C_{\mathrm{urea}} RT.$$

Cancel the common factors R and T. Retaining the mass ratio rather than prematurely rounding the molarities,

$$\begin{aligned} i_{\mathrm{KCl}} &= \frac{C_{\mathrm{urea}}}{C_{\mathrm{KCl}}} \\ &= \frac{3/60}{1.9/74.5} \\ &= \frac{3 \times 74.5}{60 \times 1.9} = 1.96053. \end{aligned}$$

The equal solution volumes cancel in this ratio. A value between 1 and 2 is consistent with partial dissociation into two ions.

Step 3: Relate particle count to dissociation Starting with one mole of KCl, a fraction α dissociates. The solution then contains $1 - \alpha$ mole of undissociated solute and α mole of each ion. The total number of moles of solute particles is

$$(1 - \alpha) + \alpha + \alpha = 1 + \alpha.$$

Thus

$$\alpha = i - 1 = 1.96053 - 1 = 0.96053, \qquad 100\alpha = 96.053\%.$$

Step 4: Conclusion The degree of dissociation of KCl is $\boxed{\alpha \approx 0.961}$, corresponding to approximately $\boxed{96.1\%}$ dissociation.

Quick Tip to Solve: For isotonic solutions of equal volume, compare their mole amounts directly; then for a salt giving two ions, obtain the dissociation fraction from $\alpha = i - 1$.

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

(a) Nylon-6,6

(b) Bakelite

(c) Buna-S [3 marks]

Solution:

Concept:

- A monomer is a small molecule that combines repeatedly with other monomer molecules to form a polymer. Identify its functional groups and carbon skeleton, not merely its molecular formula.
- Nylon-6,6 and Bakelite are condensation polymers, whereas Buna-S is an addition copolymer formed from two different unsaturated monomers.

Step 1: (a) Monomers of Nylon-6,6 The two monomers are hexamethylenediamine (hexane-1,6-

Quick Tip to Solve: Count both carboxyl carbon atoms in adipic acid; the S in Buna-S identifies styrene as its second monomer.

diamine) and adipic acid (hexanedioic acid). Their condensed structures are

$$H_2N-(CH_2)_6-NH_2 \quad \text{and} \quad HOOC-(CH_2)_4-COOH.$$

The diamine has six carbon atoms and two terminal amino groups; the diacid also has six carbon atoms, including the two carboxyl carbon atoms. Their reaction forms amide linkages with elimination of water. Thus the two six-carbon monomers account for the name Nylon-6,6.

Step 2: (b) Monomers of Bakelite Bakelite is obtained from phenol and formaldehyde (methanal). The structures are

$$C_6H_5-OH \quad \text{and} \quad H-C(=O)-H.$$

In phenol, the hydroxyl group is bonded directly to a carbon of the benzene ring. Formaldehyde supplies methylene bridges between phenolic rings, ultimately producing the cross-linked phenol-formaldehyde polymer.

Step 3: (c) Monomers of Buna-S Buna-S is the copolymer of buta-1,3-diene and styrene (phenylethene). Their structures are

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

Buta-1,3-diene has two conjugated carbon-carbon double bonds, while styrene has a vinyl group attached to a benzene ring. These unsaturated groups participate in addition copolymerisation to give the synthetic rubber Buna-S.

Step 4: Conclusion Nylon-6,6: $H_2N-(CH_2)_6-NH_2$ and $HOOC-(CH_2)_4-COOH$; Bakelite: C_6H_5OH and $H-C(=O)-H$; Buna-S: $CH_2=CH-CH=CH_2$ and $C_6H_5-CH=CH_2$.

Quick Tip to Solve: Count both carboxyl carbon atoms in adipic acid; the S in Buna-S identifies styrene as its second monomer.

OR

19(b). (a) Write one example each of

(i) Thermoplastic polymer

(ii) Elastomers

(b) Arrange the following polymers in the increasing order of their intermolecular forces:

Polythene, Nylon-6,6, Buna-S

(c) Which factor provides crystalline nature to a polymer like Nylon? [3 marks]

Solution:

Concept:

- Thermoplastic polymers have linear or slightly branched chains and soften on heating. Elastomers have weak attractions between chains and a few cross-links, allowing stretching followed by recovery.
- In the standard classification by intermolecular forces, elastomers have weaker attractions than

Quick Tip to Solve: Classify the three polymers first: rubber, thermoplastic, fibre; then place their intermolecular forces in that order.

thermoplastics, while fibres such as Nylon-6,6 have stronger attractions, including hydrogen bonding.

Step 1: (a) Give an example of each class (i) A thermoplastic polymer is polythene. Its chains can slide past one another on heating, so it can be softened and remoulded repeatedly.

(ii) An elastomer is Buna-S, the synthetic rubber made from buta-1,3-diene and styrene. Its chains can uncoil when stretched and return towards their original arrangement when the stress is removed. These examples distinguish a remouldable plastic from an elastic rubber.

Step 2: (b) Arrange the intermolecular forces Buna-S is an elastomer, polythene is a thermoplastic, and Nylon-6,6 is a fibre. Buna-S has weak interchain attractions that permit extension. Polythene has intermediate intermolecular forces in this classification. The amide groups of Nylon-6,6 form strong hydrogen bonds between neighbouring chains. Therefore, the increasing order is

$$\text{Buna-S} < \text{Polythene} < \text{Nylon-6,6}.$$

This is an ordering of the attractions between polymer chains, rather than of the covalent bonds within an individual chain.

Step 3: (c) Explain the crystalline nature of Nylon Strong intermolecular hydrogen bonding between the amide groups provides crystalline nature to Nylon. A hydrogen attached to nitrogen in one chain is attracted to the carbonyl oxygen in a neighbouring chain, represented as $\mathrm{N{-}H\cdots O{=}C}$. The repeated amide groups permit many such interchain contacts. These attractions hold chains close together in an ordered arrangement and promote efficient packing, producing crystalline regions within the polymer.

Step 4: Conclusion (a) Thermoplastic: polythene; elastomer: Buna-S. (b) Buna-S $<$ Polythene $<$ Nylon-6,6. (c) Strong intermolecular hydrogen bonding between amide groups promotes the ordered packing responsible for Nylon's crystalline nature.

Quick Tip to Solve: Classify the three polymers first: rubber, thermoplastic, fibre; then place their intermolecular forces in that order.

20. Among all the isomers of molecular formula C_4H_9Br, identify

(a) the one isomer which is optically active.

(b) the one isomer which is highly reactive towards S_N2.

(c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH. [3 marks]

Solution:

Concept:

- A tetrahedral carbon bonded to four different groups is a stereogenic centre. Its two enantiomers can show optical activity when present separately or in an unequal mixture.
- An $\mathrm{S_N2}$ reaction involves backside attack on the carbon bearing the leaving group; less steric hindrance favours faster reaction.
- Alcoholic KOH promotes elimination of a hydrogen from a carbon adjacent to the carbon bearing

Quick Tip to Solve: Draw all four skeletons: test four different groups for chirality, crowding for SN2, and adjacent hydrogens for elimination.

bromine. Removal of HBr creates a carbon-carbon double bond.

Step 1: List the four constitutional isomers The four isomers of C_4H_9Br are:

1-bromobutane: $CH_3CH_2CH_2CH_2Br$;

2-bromobutane: $CH_3CH(Br)CH_2CH_3$;

1-bromo-2-methylpropane: $(CH_3)_2CHCH_2Br$;

2-bromo-2-methylpropane: $(CH_3)_3CBr$.

Comparing these four structures answers each part directly.

Step 2: (a) Identify the optically active isomer In 2-bromobutane, carbon 2 is attached to four different groups: Br, H, CH_3 and C_2H_5. It is therefore a stereogenic centre, so 2-bromobutane is the isomer capable of optical activity. The other three structures have no carbon bonded to four different groups. An individual enantiomer is optically active; a racemic mixture of 2-bromobutane has no net optical rotation.

Step 3: (b) Identify the most reactive isomer towards SN2 1-Bromobutane is the most reactive towards S_N2. Its bromine-bearing carbon is primary and the carbon chain is unbranched, giving relatively unhindered backside access. Although 1-bromo-2-methylpropane is also primary, branching at the adjacent carbon impedes attack. The secondary carbon of 2-bromobutane is more hindered, while the tertiary carbon of 2-bromo-2-methylpropane strongly obstructs an S_N2 attack.

Step 4: (c) Identify the pair with the same elimination product 1-Bromo-2-methylpropane and 2-bromo-2-methylpropane both give 2-methylpropene on heating with alcoholic KOH:

$$(CH_3)_2CHCH_2Br + KOH \xrightarrow[\Delta]{\text{alcohol}} CH_2{=}C(CH_3)_2 + KBr + H_2O,$$

$$(CH_3)_3CBr + KOH \xrightarrow[\Delta]{\text{alcohol}} CH_2{=}C(CH_3)_2 + KBr + H_2O.$$

In the first structure, the adjacent central carbon supplies the hydrogen. In the second, all three adjacent methyl groups are equivalent, so elimination from any of them gives the same alkene. The unbranched bromobutanes instead yield unbranched butenes.

Step 5: Conclusion (a) 2-Bromobutane. (b) 1-Bromobutane. (c) 1-Bromo-2-methylpropane and 2-bromo-2-methylpropane; both form 2-methylpropene, $CH_2{=}C(CH_3)_2$.

Quick Tip to Solve: Draw all four skeletons: test four different groups for chirality, crowding for SN2, and adjacent hydrogens for elimination.

21(a). Pick out the odd one from the following on the basis of their medicinal properties:
Equanil, Seconal, Bithional, Luminal
(b) What type of detergents are used in dishwashing liquids?
(c) Why is the use of aspartame limited to cold foods? [3 marks]

Solution:

Concept:

- Drugs are classified by their therapeutic action. Tranquillisers act on the nervous system, whereas antiseptics inhibit or kill microorganisms on living tissues.
- Non-ionic detergents have uncharged hydrophilic groups. Their molecules contain both a water-attracting portion and an oil-attracting portion.
- An artificial sweetener must remain chemically stable under the conditions in which a food is prepared or stored.

Step 1: (a) Compare the medicinal properties Equanil, Seconal and Luminal belong to the tranquilliser class in the textbook classification. These drugs act on the central nervous system. Bithional is an antiseptic and therefore has a different medicinal action: it inhibits microorganisms instead of belonging to this group of nervous-system drugs. Hence Bithional is the odd one out on the stated basis.

Step 2: (b) Identify the detergent used in dishwashing liquids Dishwashing liquids use non-ionic detergents. The polar, hydrophilic part of a non-ionic detergent does not carry an ionic charge. Together with the hydrophobic part of the molecule, it enables greasy material to be dispersed in water and removed during washing. Thus the required classification is non-ionic, rather than anionic or cationic.

Step 3: (c) Explain the temperature restriction for aspartame Aspartame is an artificial sweetener that is unstable at cooking temperatures. On heating, it decomposes and loses its sweetening action. Consequently it is suitable for cold foods and drinks, where the temperatures do not cause this thermal decomposition. The restriction follows from its lack of heat stability, rather than from insufficient sweetness.

Step 4: Conclusion (a) Bithional is the odd one out because it is an antiseptic. (b) Non-ionic detergents are used in dishwashing liquids. (c) Aspartame is limited to cold foods because it decomposes on heating and loses its sweetness.

Quick Tip to Solve: Classify each drug by its action first; for a sweetener used in cooking, check heat stability before comparing sweetness.

OR

21(b). Define the following terms with a suitable example of each:

(a) Antibiotics

(b) Antiseptics

(c) Anionic detergents [3 marks]

Solution:

Concept:

- Antibiotics act against microorganisms at low concentrations by killing them or inhibiting their growth.
- Antiseptics are antimicrobial substances suitable for application to living tissues, such as skin or wounds.
- An anionic detergent has a negatively charged hydrophilic group and a long hydrocarbon chain that forms its hydrophobic part.

Step 1: (a) Define antibiotics and give an example Antibiotics are chemical substances produced by microorganisms that, in low concentrations, kill other microorganisms or inhibit their growth. The term also includes related substances obtained wholly or partly by chemical synthesis. Penicillin is a suitable example of an antibiotic. The definition concerns action against microorganisms; it does not describe a general pain-relieving drug.

Step 2: (b) Define antiseptics and give an example Antiseptics are chemical substances that kill microorganisms or prevent their growth and can be applied to living tissues, including skin, cuts and wounds. Dettol is an example; its antiseptic ingredients include chloroxylenol. Suitability for living tissues distinguishes this use from the use of disinfectants on inanimate objects such as floors and instruments.

Step 3: (c) Define anionic detergents and give an example Anionic detergents are cleansing agents in which the hydrophilic, detergent-active part is a negatively charged ion. They commonly include sodium salts of sulphonated long-chain alcohols or hydrocarbons. A suitable example is sodium lauryl sulphate, also called sodium dodecyl sulphate:

$$CH_3(CH_2)_{11}OSO_3^- \, Na^+.$$

The long hydrocarbon chain is hydrophobic, while the negatively charged sulphate head is hydrophilic. The anion, rather than the sodium counterion, contains the long chain and supplies the detergent action.

Step 4: Conclusion Antibiotics kill or inhibit microorganisms at low concentrations, for example penicillin. Antiseptics are antimicrobials applied to living tissues, for example Dettol. Anionic detergents have a negatively charged detergent-active ion, for example sodium lauryl sulphate.

Quick Tip to Solve: Pair each definition immediately with an example; identify anionic detergents by the charge on the long-chain active ion.

22(a). What are the products of hydrolysis of maltose?

(b) What type of bonding provides stability to α-helix structure of protein?

(c) Name the vitamin whose deficiency causes pernicious anaemia. [3 marks]

Solution:

Concept:

- A disaccharide yields its constituent monosaccharides when its glycosidic linkage is hydrolysed.
- The secondary structure of a protein describes the regular arrangement of its polypeptide backbone. Hydrogen bonds can stabilise this arrangement without changing the peptide sequence.
- Vitamins are required in small quantities for normal body functions, and a deficiency can cause a characteristic disorder.

Step 1: (a) Hydrolyse maltose Maltose contains two glucose units joined through an $\alpha(1 \rightarrow 4)$ glycosidic linkage. Hydrolysis cleaves this linkage by the addition of water, releasing two molecules of D-glucose:

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

Thus glucose is the only monosaccharide product. Fructose is not obtained from maltose; it is a constituent of sucrose.

Step 2: (b) State the bonding that stabilises the alpha-helix The α-helix is stabilised by intramolecular hydrogen bonds between peptide groups of the same polypeptide chain. A carbonyl oxygen, $\mathrm{C = O}$, of one peptide group forms a hydrogen bond with the hydrogen of an $\mathrm{N - H}$ group farther along that chain, conventionally four residues ahead. The regular sequence of these hydrogen bonds holds the chain in its helical arrangement. Peptide bonds form the backbone, but the requested stabilising interaction is hydrogen bonding.

Step 3: (c) Identify the deficient vitamin The vitamin whose deficiency causes pernicious anaemia is vitamin $\mathrm{B_{12}}$, also called cobalamin. This is the specific vitamin-deficiency association requested. It should not be confused with vitamin C deficiency, associated with scurvy, or vitamin D deficiency, associated with rickets.

Step 4: Conclusion (a) Maltose gives two molecules of D-glucose on hydrolysis. (b) Intramolecular hydrogen bonding stabilises the α-helix. (c) Deficiency of vitamin $\mathrm{B_{12}}$ causes pernicious anaemia.

Quick Tip to Solve: Recall maltose as glucose plus glucose, and connect the alpha-helix to hydrogen bonds within one polypeptide chain.

OR

22(b). Define the following terms:

(a) Invert sugar

(b) Native protein

(c) Nucleotide [3 marks]

Solution:

Concept:

- Hydrolysis splits a glycosidic bond by adding water; sucrose yields equal amounts of glucose and fructose.
- A protein's biological activity depends on its specific folded conformation. Nucleic acids are polymers of nucleotides.

Step 1: (a) Define invert sugar Invert sugar is the equimolar mixture of D-glucose and D-fructose obtained by hydrolysis of sucrose, using dilute acid or the enzyme invertase:

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

The two products are glucose and fructose, respectively. Sucrose is dextrorotatory, but its hydrolysis mixture is laevorotatory because the negative rotation of fructose exceeds the positive rotation of glucose. This reversal of the sign of optical rotation is called inversion.

Step 2: (b) Define native protein A native protein is a protein in its naturally occurring, correctly folded and biologically active state. Its characteristic secondary and tertiary structures, and quaternary structure where present, are intact. For example, an enzyme in its native conformation has the active-site shape required for its activity. Heat or a change in pH may disrupt this conformation and cause denaturation without breaking the primary peptide chain.

Step 3: (c) Define nucleotide A nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group. The base and sugar together constitute a nucleoside; addition of phosphate gives a nucleotide. The sugar is ribose in RNA and 2-deoxyribose in DNA. Adenosine monophosphate is an example of a nucleotide. Nucleotides join through phosphodiester bonds to form nucleic-acid chains.

Step 4: Conclusion (a) Invert sugar: the glucose-fructose mixture produced by sucrose hydrolysis. (b) Native protein: the naturally folded, biologically active protein. (c) Nucleotide: nitrogenous base + pentose sugar + phosphate.

Quick Tip to Solve: Remember: nucleoside has base + sugar; adding phosphate makes a nucleotide. Invert sugar is named for the reversal of optical rotation.

23. (a) Give reasons:

(i) Benzoic acid is a stronger acid than acetic acid.

(ii) Methanal is more reactive towards nucleophilic addition reaction than ethanal.

(b) Give a simple chemical test to distinguish between propanal and propanone. [3 marks]

Solution:

Concept:

- An acid is stronger when loss of H^+ gives a more stable conjugate base; electron withdrawal favours acidity.
- Nucleophiles attack the electrophilic carbonyl carbon. Electron donation and steric hindrance reduce its susceptibility to attack.
- Aldehydes are readily oxidised by Tollens' reagent, whereas ordinary ketones are not.

Step 1: (a)(i) Compare the acidity of benzoic and acetic acids In acetic acid, the methyl group exerts an electron-releasing $+I$ effect. It increases electron density in the carboxylate group and destabilises the acetate ion relative to benzoate. In benzoic acid, the phenyl group has an electron-withdrawing inductive effect relative to a methyl group and favours formation of the benzoate ion. Consequently, benzoic acid loses H^+ more readily and is the stronger acid. Both conjugate bases have resonance delocalisation within the carboxylate group; merely saying that only benzoate has resonance would be incorrect.

Step 2: (a)(ii) Compare nucleophilic addition Methanal, $HCHO$, has two small hydrogen atoms bonded to the carbonyl carbon. Ethanal, CH_3CHO, has an electron-donating methyl group. Its $+I$ effect lowers the partial positive charge on the carbonyl carbon, so nucleophilic attack is less favourable. The methyl group also offers more steric hindrance than hydrogen. Methanal therefore undergoes nucleophilic addition more readily for both electronic and steric reasons.

Step 3: (b) Apply Tollens' test Warm each compound separately with freshly prepared Tollens' reagent (ammoniacal silver nitrate). Propanal produces a silver mirror as it is oxidised to propanoate, but propanone gives no silver mirror:

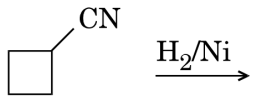
$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

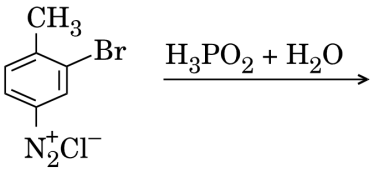
Thus, the positive silver-mirror observation identifies propanal, while a negative test identifies propanone.

Step 4: Conclusion Benzoic acid is stronger because phenyl withdraws electrons compared with methyl. Methanal has greater carbonyl electrophilicity and less steric hindrance. Tollens' reagent gives a silver mirror with propanal but none with propanone.

Quick Tip to Solve: For the two reactivity comparisons, check inductive effects first; for carbonyl addition also check crowding around the carbonyl carbon.

24(a). Complete the following reactions: [3 marks]

(a) 

(b) 

(c) 

Solution:

Concept:

- Nitrile hydrogenation gives $R - CH_2NH_2$, retaining the nitrile carbon.
- Hypophosphorous acid replaces an aromatic diazonium group by hydrogen with evolution of nitrogen.
- Primary amines react with chloroform and alcoholic potassium hydroxide to form isocyanides in the carbylamine reaction.

Step 1: (a) Reduce cyclobutanecarbonitrile With $c - C_4H_7$ denoting cyclobutyl, hydrogenation gives cyclobutylmethanamine:

$$c - C_4H_7 - CN + 2H_2 \xrightarrow{Ni} c - C_4H_7 - CH_2NH_2.$$

The ring stays intact; the nitrile carbon becomes the methylene carbon outside it.

Step 2: (b) Replace the diazonium group by hydrogen H_3PO_2 replaces the diazonium group by hydrogen. Bromine and methyl retain their adjacent positions, giving 2-bromotoluene:

$$ArN_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl.$$

Here Ar is the 3-bromo-4-methylphenyl group, numbered from the diazonium carbon; ArH is *o*-bromotoluene.

Step 3: (c) Carry out the carbylamine reaction The starting compound is benzylamine, $C_6H_5CH_2NH_2$, a primary amine. Heating it with chloroform and ethanolic KOH gives benzyl isocyanide:

$$C_6H_5CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{ethanol, heat}} C_6H_5CH_2N \equiv C + 3KCl + 3H_2O.$$

Step 4: Conclusion The organic products are (a) cyclobutylmethanamine, $c - C_4H_7CH_2NH_2$; (b) 2-bromotoluene; and (c) benzyl isocyanide, $C_6H_5CH_2N \equiv C$.

Quick Tip to Solve: Retain the nitrile carbon in (a), replace only the diazonium group in (b), and attach the benzyl group to nitrogen in the isocyanide product of (c).

OR

24(b). How do you convert the following:

(a) N-phenylethanamide to p-bromoaniline

(b) Benzene diazonium chloride to nitrobenzene

(c) Benzoic acid to aniline [3 marks]

Solution:

Concept:

- The acetyl group protects the amino group of aniline during bromination. The $-NHCOCH_3$ group directs substitution mainly to the para position; hydrolysis subsequently restores $-NH_2$.
- A diazonium group can be replaced by a nitro group by treating the diazonium fluoroborate with sodium nitrite in the presence of copper.
- Hofmann bromamide degradation converts an amide $RCONH_2$ into RNH_2, with loss of the carbonyl carbon.

Step 1: Brominate the protected amine and hydrolyse (a) N-phenylethanamide is acetanilide, $C_6H_5NHCOCH_3$. Treat it with bromine in glacial acetic acid. The major product is p-bromoacetanilide because para substitution is less sterically hindered than ortho substitution:

$$C_6H_5NHCOCH_3 + Br_2 \xrightarrow{CH_3COOH} \text{p-}BrC_6H_4NHCOCH_3 + HBr.$$

Hydrolyse the acetyl group by heating with aqueous acid, then neutralise to obtain the free amine. The overall hydrolysis is

$$\text{p-}BrC_6H_4NHCOCH_3 + H_2O \xrightarrow[\text{heat}]{H^+} \text{p-}BrC_6H_4NH_2 + CH_3COOH.$$

Protecting the amino group prevents the extensive bromination that occurs when aniline itself is treated with bromine water.

Step 2: Replace the diazonium group by a nitro group (b) First treat benzene diazonium chloride with fluoroboric acid to form benzene diazonium fluoroborate:

$$C_6H_5N_2Cl + HBF_4 \longrightarrow C_6H_5N_2BF_4 + HCl.$$

Heat the fluoroborate with aqueous sodium nitrite in the presence of copper. Nitrogen is liberated and the diazonium group is replaced by $-NO_2$:

$$C_6H_5N_2BF_4 + NaNO_2 \xrightarrow[\text{heat}]{Cu} C_6H_5NO_2 + N_2 + NaBF_4.$$

Sodium nitrite supplies the nitro group in this substitution; heating the fluoroborate alone would instead favour fluorobenzene.

Step 3: Form benzamide and carry out Hofmann degradation (c) Convert benzoic acid into benzoyl

Quick Tip to Solve: Retain the acetyl protection until bromination is complete; for benzoic acid to aniline, first make the amide so Hofmann degradation can remove exactly the carbonyl carbon.

chloride using thionyl chloride, then react the acid chloride with excess ammonia:

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl,$$
$$C_6H_5COCl + 2\,NH_3 \longrightarrow C_6H_5CONH_2 + NH_4Cl.$$

Treat benzamide with bromine and aqueous sodium hydroxide, warming the mixture:

$$C_6H_5CONH_2 + Br_2 + 4\,NaOH \longrightarrow C_6H_5NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O.$$

The phenyl group migrates during this degradation, and the carbonyl carbon is removed. Thus the seven-carbon acid gives the six-carbon amine.

Step 4: Conclusion (a) Acetanilide $\longrightarrow$ p-bromoacetanilide $\longrightarrow$ p-bromoaniline. (b) Benzene diazonium chloride $\longrightarrow$ its fluoroborate $\longrightarrow$ nitrobenzene. (c) Benzoic acid $\longrightarrow$ benzoyl chloride $\longrightarrow$ benzamide $\longrightarrow$ aniline.

Quick Tip to Solve: Retain the acetyl protection until bromination is complete; for benzoic acid to aniline, first make the amide so Hofmann degradation can remove exactly the carbonyl carbon.

Section D (15 marks)

25(a). Give equations of the following reactions:

(i) Phenol is treated with conc. HNO_3.

(ii) Propene is treated with B_2H_6 followed by H_2O_2/OH^-.

(iii) Sodium t-butoxide is treated with CH_3Cl.

(b) How will you distinguish between butan-1-ol and butan-2-ol?

(c) Arrange the following in increasing order of acidity:

Phenol, ethanol, water [5 marks]

Solution:

Concept:

- Phenol strongly activates its benzene ring towards electrophilic substitution at the ortho and para positions. Concentrated nitric acid gives 2,4,6-trinitrophenol.
- Hydroboration followed by oxidation hydrates an alkene with anti-Markovnikov orientation. Williamson ether synthesis joins an alkoxide to a suitable alkyl halide by S_N2 substitution.
- The iodoform test identifies the $CH_3CH(OH)^-$ group in an alcohol because it oxidises to a methyl ketone and then forms yellow CHI_3.
- Acid strength depends on the stability of the conjugate base: resonance stabilises phenoxide, whereas an electron-releasing ethyl group destabilises ethoxide relative to hydroxide.

Step 1: Write the nitration reaction of phenol (a)(i) Concentrated nitric acid nitrates all three activated positions of phenol, giving 2,4,6-trinitrophenol, also called picric acid:

$$C_6H_5OH + 3\,HNO_3 \xrightarrow{\text{conc.}} C_6H_2(NO_2)_3OH + 3\,H_2O.$$

The three nitro groups occupy positions 2, 4 and 6 relative to the hydroxyl group. This distinguishes the concentrated-acid reaction from nitration with dilute nitric acid, which gives mainly the mono-nitro products.

Step 2: Apply hydroboration followed by oxidation to propene (a)(ii) Diborane adds across the double bond so that boron bonds to the less substituted terminal carbon. Repetition of the addition produces a trialkylborane:

$$6\,CH_3CH{=}CH_2 + B_2H_6 \longrightarrow 2\,(CH_3CH_2CH_2)_3B.$$

Oxidation with hydrogen peroxide in alkaline medium replaces each carbon-boron bond with a carbon-oxygen bond:

$$(CH_3CH_2CH_2)_3B + 3\,H_2O_2 \xrightarrow{OH^-} 3\,CH_3CH_2CH_2OH + B(OH)_3.$$

Thus the alcohol obtained is propan-1-ol. The hydroxyl group ends up on the terminal carbon, following anti-Markovnikov orientation; rearrangement does not occur.

Step 3: Form the ether by Williamson synthesis (a)(iii) The oxygen atom of sodium tert-butoxide

Quick Tip to Solve: Locate the hydroxyl-bearing carbon before choosing a reaction: terminal propene hydration by hydroboration gives propan-1-ol, while only butan-2-ol has the methyl carbinol group needed for iodoform.

attacks the methyl carbon of chloromethane, displacing chloride:

$$(CH_3)_3CONa + CH_3Cl \longrightarrow (CH_3)_3COCH_3 + NaCl.$$

The product is 2-methoxy-2-methylpropane, commonly called methyl tert-butyl ether. The halide is methyl chloride, which is suitable for S_N2 attack even though the alkoxide is bulky. Methyl chloride has no beta carbon, so beta-elimination cannot compete in this reaction.

Step 4: Distinguish the two butanols using the iodoform test (b) Warm each alcohol with iodine and aqueous sodium hydroxide. Butan-2-ol contains $CH_3CH(OH)^-$, so it gives a yellow precipitate of iodoform. Its overall reaction is

$$CH_3CH(OH)CH_2CH_3 + 4\,I_2 + 6\,NaOH \longrightarrow CH_3CH_2COONa + CHI_3\downarrow + 5\,NaI + 5\,H_2O.$$

Butan-1-ol, $CH_3CH_2CH_2CH_2OH$, lacks this group and gives no yellow precipitate. On oxidation it gives butanal rather than a methyl ketone, so the required iodoform-producing intermediate is absent.

Step 5: Compare the conjugate bases to order acidity (c) Phenol loses a proton to give phenoxide, in which the negative charge is delocalised by resonance over oxygen and the aromatic ring. Water gives hydroxide; ethanol gives ethoxide, whose negative charge remains largely on oxygen. The electron-releasing ethyl group increases the electron density on the ethoxide oxygen and makes this ion less stable than hydroxide. Ethanol therefore loses a proton less readily than water, whereas phenoxide resonance makes phenol the strongest acid of the three.

Step 6: Conclusion (a) The products are (i) 2,4,6-trinitrophenol, (ii) propan-1-ol and (iii) 2-methoxy-2-methylpropane. (b) Butan-2-ol gives yellow iodoform with iodine and alkali; butan-1-ol gives no precipitate. (c) The increasing order of acidity is

$$\boxed{\text{ethanol} < \text{water} < \text{phenol}}.$$

Quick Tip to Solve: Locate the hydroxyl-bearing carbon before choosing a reaction: terminal propene hydration by hydroboration gives propan-1-ol, while only butan-2-ol has the methyl carbinol group needed for iodoform.

OR

25(b). (a) How can you obtain Phenol from (i) Cumene, (ii) Benzene sulphonic acid, (iii) Benzene diazonium chloride?

(b) Write the structure of the major product obtained from dinitration of 3-methylphenol.

(c) Write the reaction involved in Kolbe's reaction. [5 marks]

Solution:

Concept:

- Phenol can be prepared by oxidation and acidic cleavage of cumene, by alkaline fusion of benzene sulphonic acid, or by hydrolysis of benzene diazonium chloride.
- The $-OH$ and $-CH_3$ groups are activating, ortho-para directing groups. In 3-methylphenol, both favour positions 2, 4 and 6, but position 2 is sterically crowded between them.
- In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure and is then acidified to form salicylic acid, with $-COOH$ ortho to $-OH$.

Step 1: (a)(i) Obtain phenol from cumene Pass air through cumene (isopropylbenzene) to oxidise it to cumene hydroperoxide. Acidic cleavage of this peroxide yields phenol and acetone:

$$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2OOH$$

$$C_6H_5C(CH_3)_2OOH \xrightarrow{H^+} C_6H_5OH + CH_3COCH_3$$

The hydroperoxide is the necessary intermediate; acetone is the coproduct of the cleavage.

Step 2: (a)(ii) Obtain phenol from benzene sulphonic acid First neutralise benzene sulphonic acid with sodium hydroxide to obtain sodium benzene sulphonate:

$$C_6H_5SO_3H + NaOH \longrightarrow C_6H_5SO_3Na + H_2O$$

Fuse this salt with molten sodium hydroxide at $623\,K$. The sulphonate group is replaced to form sodium phenoxide:

$$C_6H_5SO_3Na + 2\,NaOH \xrightarrow{623\,K} C_6H_5ONa + Na_2SO_3 + H_2O$$

Acidification liberates phenol:

$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl$$

Step 3: (a)(iii) Obtain phenol from benzene diazonium chloride Warm an aqueous solution of benzene diazonium chloride. Hydrolysis replaces the diazonium group with hydroxyl, and nitrogen gas is evolved:

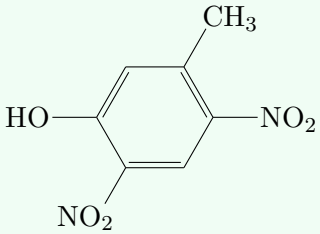
$$C_6H_5N_2Cl + H_2O \xrightarrow{warm} C_6H_5OH + N_2\uparrow + HCl$$

Thus warming with water directly gives phenol; alkaline fusion is unnecessary for this route.

Step 4: (b) Identify and write the dinitration product Number the ring of 3-methylphenol with $-OH$ at carbon 1 and $-CH_3$ at carbon 3. Both groups direct incoming nitro groups towards carbons 2, 4

Quick Tip to Solve: For dinitration of m-cresol, mark the positions favoured by both groups, then exclude carbon 2 because it is crowded between OH and methyl; place the nitro groups at 4 and 6.

and 6. Carbon 2 lies between the two substituents and is less accessible because of steric crowding. Dinitration therefore introduces $-NO_2$ at carbons 4 and 6. The major product has the following structure:



With the phenolic carbon numbered 1 and the direction chosen to give the methyl group position 3, this is 3-methyl-4,6-dinitrophenol. It retains the hydroxyl and methyl groups of the starting material.

Step 5: (c) Write Kolbe's reaction Treat sodium phenoxide with carbon dioxide at $400\,K$ under 4–7 atm pressure. Carboxylation occurs mainly at an ortho position, forming sodium salicylate. Acidify the salt to obtain salicylic acid (2-hydroxybenzoic acid):

$$C_6H_5ONa + CO_2 \xrightarrow[4\text{-}7\ atm]{400\,K} o\text{-}HOC_6H_4COONa$$

$$o\text{-}HOC_6H_4COONa + HCl \longrightarrow o\text{-}HOC_6H_4COOH + NaCl$$

The prefix *o* specifies that the hydroxyl and carboxyl groups are adjacent on the benzene ring.

Step 6: Conclusion (a) Cumene gives phenol through its hydroperoxide; benzene sulphonic acid gives phenol through alkaline fusion and acidification; benzene diazonium chloride gives phenol by warm-water hydrolysis. (b) The major product is 3-methyl-4,6-dinitrophenol. (c) Kolbe's reaction converts sodium phenoxide into salicylic acid via carbon dioxide treatment and acidification.

Quick Tip to Solve: For dinitration of m-cresol, mark the positions favoured by both groups, then exclude carbon 2 because it is crowded between OH and methyl; place the nitro groups at 4 and 6.

26(a). Account for the following:

(i) Tendency to show -3 oxidation state decreases from N to Bi in group 15.

(ii) Acidic character increases from H_2O to H_2Te.

(iii) F_2 is more reactive than ClF_3, whereas ClF_3 is more reactive than Cl_2.

(b) Draw the structure of (i) XeF_2, (ii) $H_4P_2O_7$. [5 marks]

Solution:

Concept:

- Down a group, increasing atomic size usually decreases electronegativity and weakens bonds to hydrogen. The stability of a negative oxidation state depends on the tendency to attract electrons; hydride acidity depends mainly on the ease of breaking the element–hydrogen bond.
- Interhalogen compounds have bonds between two different halogens. Their reactivity relative to the parent halogens is explained by bond strength, with fluorine being the exceptional highly reactive halogen.

Quick Tip to Solve: For these trends, identify the controlling factor first: electron attraction for -3 oxidation state, E-H bond strength for acidity, and halogen bond strength for reactivity. In the acid structure, count four OH groups and one P-O-P bridge.

- In VSEPR theory, both bond pairs and lone pairs around the central atom determine electron-pair arrangement. Molecular shape describes the positions of atoms only. A structural formula for an oxoacid must distinguish terminal oxygen, hydroxyl groups and bridging oxygen.

Step 1: (a)(i) Explain the decreasing tendency to show the -3 oxidation state Group 15 elements have the valence configuration ns^2np^3. They can attain a noble-gas valence configuration by gaining three electrons, giving oxidation state -3. From nitrogen to bismuth, atomic size increases and electronegativity decreases. The attraction for additional electrons therefore decreases, and the heavier elements become more metallic. Consequently, the tendency to form compounds in the -3 oxidation state decreases down the group. This concerns the tendency to gain electrons, rather than the number of valence electrons, which remains five throughout the group.

Step 2: (a)(ii) Explain the increasing acidity of group 16 hydrides On moving from oxygen to tellurium, the central atom becomes larger, the $E-H$ bond becomes longer, and its bond dissociation enthalpy decreases, where E denotes the group 16 element. Thus, the bond is progressively easier to break and the hydride releases H^+ more readily. This bond-strength effect explains why acidity increases even though the electronegativity of the central atom decreases. The acidic-character order is

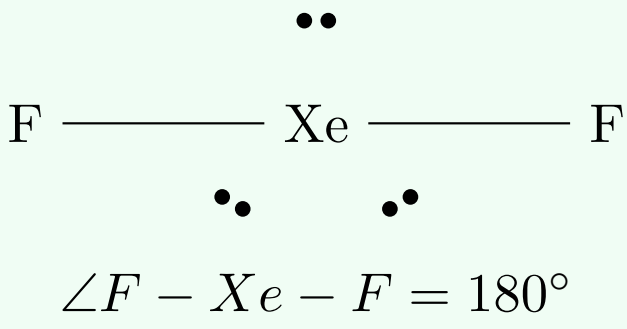
$$\mathrm{H_2O} < \mathrm{H_2S} < \mathrm{H_2Se} < \mathrm{H_2Te}.$$

Step 3: (a)(iii) Compare fluorine, chlorine trifluoride and chlorine The $F-F$ bond is unusually weak because the small fluorine atoms bring their nonbonding electron pairs close together, causing strong lone-pair repulsions. Together with fluorine's very high electronegativity, this accounts for the exceptional reactivity of F_2, which exceeds that of ClF_3. The $Cl-F$ bonds in the interhalogen ClF_3 are weaker than the $Cl-Cl$ bond in Cl_2 and are more easily broken in reactions. Therefore, ClF_3 is more reactive than Cl_2. The order asked for is

$$\mathrm{F_2} > \mathrm{ClF_3} > \mathrm{Cl_2}.$$

Step 4: (b)(i) Draw and explain the structure of xenon difluoride Xenon in XeF_2 has two bond pairs and three lone pairs, making five electron-pair domains. Their arrangement is trigonal bipyramidal. The three lone pairs occupy equatorial positions, where they experience fewer 90° interactions, and the two fluorine atoms occupy the two axial positions. The resulting molecular shape is linear, with an $F-Xe-F$ angle of 180°. The conventional CBSE hybridisation description is sp^3d; the diagram shows the linear atomic skeleton and the three lone pairs on xenon schematically.

Quick Tip to Solve: For these trends, identify the controlling factor first: electron attraction for -3 oxidation state, E-H bond strength for acidity, and halogen bond strength for reactivity. In the acid structure, count four OH groups and one P-O-P bridge.

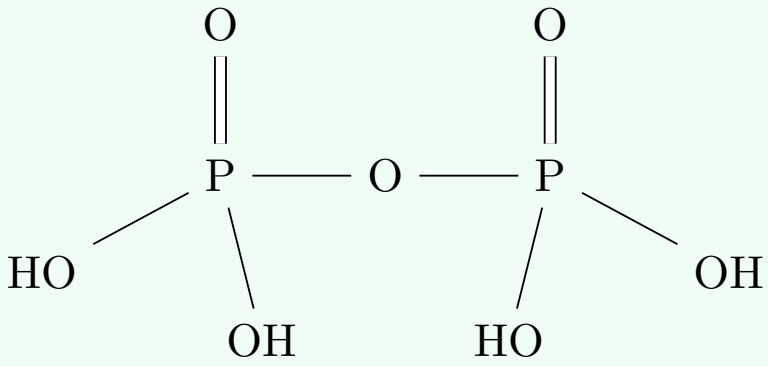


$$\angle F - Xe - F = 180^\circ$$

Linear XeF2 skeleton; the three pairs of dots indicate xenon's lone pairs schematically.

Step 5: (b)(ii) Draw the structure of pyrophosphoric acid Pyrophosphoric acid, $H_4P_2O_7$, consists of two phosphorus centres connected through one bridging oxygen, giving a $P - O - P$ linkage. Each phosphorus bears one terminal doubly bonded oxygen and two hydroxyl groups. Thus, the acid contains four $P - OH$ groups, two terminal oxygen atoms and one bridging oxygen: seven oxygen atoms in all. Each phosphorus is tetrahedrally surrounded by oxygen atoms; the planar drawing below records the bonding connections. The condensed structural formula is

$$(\mathrm{HO})_2\mathrm{P}(=\mathrm{O}) - \mathrm{O} - \mathrm{P}(=\mathrm{O})(\mathrm{OH})_2.$$



Bonding structure of H4P2O7, showing four hydroxyl groups and the oxygen bridge.

Step 6: Conclusion (a) The -3 state becomes less favoured as electronegativity decreases; hydride acidity increases as $E - H$ bonds weaken; the reactivity order is $F_2 > ClF_3 > Cl_2$. (b) XeF_2 is linear with three lone pairs on Xe, and $H_4P_2O_7$ has two $P(=O)(OH)_2$ units joined by one oxygen bridge.

Quick Tip to Solve: For these trends, identify the controlling factor first: electron attraction for -3 oxidation state, E-H bond strength for acidity, and halogen bond strength for reactivity. In the acid structure, count four OH groups and one P-O-P bridge.

OR

26(b). (a) Give one example to show the anomalous reaction of fluorine.

(b) What is the structural difference between white phosphorus and red phosphorus?

(c) What happens when XeF_6 reacts with NaF?

(d) Why is H_2S a better reducing agent than H_2O?

(e) Arrange the following acids in the increasing order of their acidic character: HF, HCl, HBr and HI [5 marks]

Solution:

Concept:

- Fluorine has exceptionally high electronegativity and is a powerful oxidising agent. Its compounds show fluorine in the oxidation state -1.
- The bonding and structure of phosphorus allotropes explain their different reactivities. A strained discrete molecule differs from a polymeric network.
- A weaker hydrogen-element bond is more easily broken. Down a group, this helps explain both reducing behaviour of hydrides and acid strength in water.

Step 1: (a) An anomalous reaction of fluorine Fluorine oxidises water to oxygen, whereas chlorine and bromine react with water to give a hydrohalic acid and a hypohalous acid. The fluorine reaction is

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2.$$

Oxygen in water changes from oxidation state -2 to 0, while fluorine changes from 0 to -1. This illustrates fluorine's unusually strong oxidising action and its inability to form a positive oxidation state like the heavier halogens.

Step 2: (b) Compare the phosphorus structures White phosphorus consists of separate tetrahedral P_4 molecules: each phosphorus atom is bonded to the other three vertices of the tetrahedron. The 60° bond angles produce considerable strain. Red phosphorus has a polymeric structure in which phosphorus tetrahedral units are linked together in an extended network. It therefore lacks the same isolated, highly strained molecular arrangement and is less reactive than white phosphorus.

Step 3: (c) Reaction of xenon hexafluoride with sodium fluoride Xenon hexafluoride accepts a fluoride ion from sodium fluoride and forms sodium heptafluoroxenate(VI):

$$XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-.$$

Here XeF_6 acts as a Lewis acid and F^- is the Lewis base. Xenon remains in oxidation state $+6$; this is fluoride addition rather than a redox reaction.

Step 4: (d) Explain the stronger reducing action of hydrogen sulphide Sulphur is larger than oxygen, so the $S-H$ bond is weaker than the $O-H$ bond. Hydrogen sulphide is therefore less thermally stable and can be oxidised more readily than water. Sulphur at oxidation state -2 can readily lose electrons, for example forming elemental sulphur at oxidation state 0. Thus H_2S is a better reducing agent than H_2O.

Step 5: (e) Arrange the hydrohalic acids From fluorine to iodine, the halogen atom becomes larger

Quick Tip to Solve: For hydrohalic acids and group-16 hydrides, compare hydrogen-element bond strength down the group; electronegativity alone gives the wrong acid-strength prediction for HF.

and the $H-X$ bond becomes longer and weaker. The release of H^+ in water consequently becomes easier down the group. HF has a particularly strong $H-F$ bond, which makes it the weakest of these acids despite fluorine's high electronegativity.

Step 6: Conclusion Fluorine oxidises water to O_2; white phosphorus is molecular P_4, whereas red phosphorus is polymeric. XeF_6 and NaF form $Na[XeF_7]$. The weaker $S-H$ bond makes H_2S more reducing. The increasing acid-strength order is $\boxed{HF < HCl < HBr < HI}$.

Quick Tip to Solve: For hydrohalic acids and group-16 hydrides, compare hydrogen-element bond strength down the group; electronegativity alone gives the wrong acid-strength prediction for HF.

27(a). The conductivity of 0.001 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate the dissociation constant if Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}.

(b) Write Nernst equation for the reaction at 25°C:

2 Al(s) + 3 Cu^{2+}(aq) $\longrightarrow$ 2 Al^{3+}(aq) + 3 Cu(s)

(c) What are secondary batteries? Give an example. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in $S\,cm^{-1}$ and concentration c is in $mol\,L^{-1}$. For a weak electrolyte, its degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- For a weak monoprotic acid, $K_a = c\alpha^2/(1-\alpha)$. The denominator accounts for the acid that remains undissociated.
- At 25°C, the Nernst equation is $E_{cell} = E^\circ_{cell} - (0.0591/n)\log_{10} Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: (a) Calculate molar conductivity and dissociation The given concentration and conductivity are $c = 0.001\,mol\,L^{-1}$ and $\kappa = 4.95 \times 10^{-5}\,S\,cm^{-1}$. Thus

$$\Lambda_m = \frac{1000(4.95 \times 10^{-5})}{0.001} = 49.5\,S\,cm^2\,mol^{-1}.$$

Using the limiting molar conductivity,

$$\alpha = \frac{49.5}{390.5} = 0.12676.$$

About 12.7% of the acetic acid is dissociated at this concentration.

Step 2: (a) Obtain the acid dissociation constant For the equilibrium $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$,

Quick Tip to Solve: First convert conductivity to molar conductivity using the factor 1000. For the Nernst equation, count six transferred electrons and use ion coefficients as powers in the quotient.

the equilibrium concentrations of both ions are $c\alpha$, and that of undissociated acid is $c(1-\alpha)$. Therefore,

$$\begin{aligned} K_a &= \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} \\ &= \frac{c\alpha^2}{1-\alpha} = \frac{0.001(0.12676)^2}{1-0.12676} \\ &\approx 1.84 \times 10^{-5}. \end{aligned}$$

Retaining $1-\alpha$ is appropriate here, since α is not negligibly small. In the concentration convention, the result is $1.84 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$.

Step 3: (b) Write the Nernst equation for the aluminium-copper reaction The oxidation and reduction half-reactions are

$$\mathrm{2Al \longrightarrow 2Al^{3+} + 6}e^-$$
$$\mathrm{3Cu^{2+}} + 6e^- \longrightarrow \mathrm{3Cu}.$$

Hence $n = 6$. Aluminium and copper are pure solids, so they are omitted from the reaction quotient. The coefficients of the dissolved ions become powers:

$$Q = \frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Cu^{2+}}]^3}.$$

In this customary concentration expression, ionic concentrations are taken relative to the standard concentration $1\,\mathrm{mol\,L^{-1}}$. Therefore at $25^\circ\mathrm{C}$,

$$E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \frac{0.0591\,\mathrm{V}}{6}\log_{10}\frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Cu^{2+}}]^3}.$$

Step 4: (c) Define secondary batteries and give an example Secondary batteries are rechargeable electrochemical batteries. During discharge they deliver electrical energy through a chemical reaction. Passing an external electric current in the opposite direction during charging reverses the discharge reaction and regenerates the active materials, allowing repeated use. The lead storage battery used in automobiles is an example: its discharge products can be converted back into lead and lead dioxide on charging.

Step 5: Conclusion (a) $\boxed{K_a \approx 1.84 \times 10^{-5}}$. (b) $E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \frac{0.0591\,\mathrm{V}}{6}\log_{10}\frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Cu^{2+}}]^3}$. (c) Secondary batteries can be recharged by reversing their discharge reaction; a lead storage battery is an example.

Quick Tip to Solve: First convert conductivity to molar conductivity using the factor 1000. For the Nernst equation, count six transferred electrons and use ion coefficients as powers in the quotient.

OR

27(b). (a) Represent the cell in which the following reaction takes place:

2 Al(s) + 3 Ni^{2+} (0.1 M) $\longrightarrow$ 2 Al^{3+} (0.01 M) + 3 Ni(s)

Calculate its emf if $E^\circ_{cell} = 1.41$ V.

(b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ°_m) for weak electrolyte? [5 marks]

Solution:

Concept:

- A galvanic cell is written with its oxidation electrode (anode) on the left and reduction electrode (cathode) on the right. A single vertical line separates phases and a double line denotes the salt bridge.
- The Nernst equation at 298 K is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- Molar conductivity Λ_m is conductivity per mole of electrolyte. At infinite dilution, each ion contributes independently to Λ°_m, according to Kohlrausch's law.

Step 1: (a) Identify the electrodes and represent the cell Aluminium is oxidised, while nickel ions are reduced. The balanced half-reactions are

$$\text{Anode: } 2\text{Al}(s) \longrightarrow 2\text{Al}^{3+}(aq) + 6e^-,$$
$$\text{Cathode: } 3\text{Ni}^{2+}(aq) + 6e^- \longrightarrow 3\text{Ni}(s).$$

Thus $n = 6$. With the concentrations specified in the question, the cell notation is

$$\text{Al}(s)\,|\,\text{Al}^{3+}(0.01\,\text{M})\,\|\,\text{Ni}^{2+}(0.1\,\text{M})\,|\,\text{Ni}(s).$$

Electrons flow through the external circuit from the aluminium electrode to the nickel electrode.

Step 2: (a) Calculate the reaction quotient and emf For the overall reaction, the aqueous concentrations are raised to their stoichiometric coefficients. Neither metal appears in the quotient because it is a pure solid:

$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(0.01)^2}{(0.1)^3} = 0.1.$$

Applying the Nernst equation at the standard textbook temperature 298 K,

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6}\log(0.1) \\ &= 1.41 - \frac{0.0591}{6}(-1) \\ &= 1.41985\,\text{V} \approx 1.420\,\text{V}. \end{aligned}$$

Since $Q < 1$, the logarithmic term is negative, so the emf exceeds the standard emf. This provides a check on the sign of the correction.

Step 3: (b) Explain the effect of increasing concentration For a strong electrolyte, molar conductivity

Quick Tip to Solve: Balance the half-reactions before choosing n: here six electrons are transferred, and the solid metals must be omitted from Q.

decreases gradually as concentration increases. Strong electrolytes are almost completely dissociated; increasing concentration strengthens interionic attractions, which reduce ionic mobility. At low concentrations the variation is represented by

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{c},$$

where c is concentration and A is a positive constant for the electrolyte and solvent at a fixed temperature. For a weak electrolyte, molar conductivity also decreases with increasing concentration, but its change is much more pronounced and nonlinear. Increasing concentration lowers its degree of dissociation, so fewer ions are available per mole. Conversely, dilution increases dissociation markedly and hence increases molar conductivity sharply.

Step 4: (b) Obtain limiting molar conductivity of a weak electrolyte A weak electrolyte does not give a straight-line Λ_m versus $\sqrt{c}$ plot that can be extrapolated reliably to zero concentration. Its limiting value is obtained using Kohlrausch's law of independent migration of ions:

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ,$$

where λ_+° and λ_-° are limiting ionic molar conductivities and ν_+, ν_- are the numbers of the respective ions per formula unit. For example, limiting conductivities of three strong electrolytes give that of acetic acid:

$$\begin{aligned}\Lambda_m^\circ(\mathrm{CH_3COOH}) = {} & \Lambda_m^\circ(\mathrm{HCl}) \\ & + \Lambda_m^\circ(\mathrm{CH_3COONa}) \\ & - \Lambda_m^\circ(\mathrm{NaCl}).\end{aligned}$$

On adding the ionic contributions, those of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ cancel, leaving the required sum for $\mathrm{H^+}$ and $\mathrm{CH_3COO^-}$. The strong-electrolyte limiting values can be obtained by extrapolating their low-concentration plots.

Step 5: Conclusion (a) The cell is $\mathrm{Al|Al^{3+}(0.01\,M)||Ni^{2+}(0.1\,M)|Ni}$, with emf $\boxed{1.420\,\mathrm{V}}$ at $298\,\mathrm{K}$. (b) Molar conductivity decreases with increasing concentration for both electrolytes, gradually for strong electrolytes and more sharply for weak electrolytes. A weak electrolyte's Λ_m° is found using Kohlrausch's law.

Quick Tip to Solve: Balance the half-reactions before choosing n: here six electrons are transferred, and the solid metals must be omitted from Q.