CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-3-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) **All** questions are compulsory.

(ii) 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.

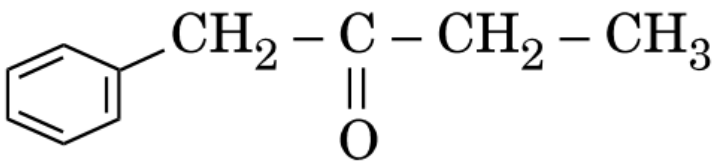
(v) Section D : Questions number **25 to 27** are long answer questions and carry **5 marks** each.

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



Solution:

Concept:

- The parent chain must include the ketone carbonyl carbon, and its numbering gives the carbonyl group the lowest possible locant.
- A benzene ring attached as a substituent is called phenyl, C_6H_5-.

Step 1: Identify the parent chain The structure is $C_6H_5CH_2COCH_2CH_3$. The four-carbon chain containing the carbonyl group is the parent. Thus the parent is a butanone, with the benzene ring treated as a phenyl substituent.

Step 2: Number from the phenyl end Numbering from the $C_6H_5CH_2-$ end puts the carbonyl group at carbon 2 and the phenyl group at carbon 1. Numbering from the other end would put the carbonyl at carbon 3, so it is rejected. Combine the substituent locant with the ketone parent name.

Step 3: Conclusion The IUPAC name is 1-phenylbutan-2-one.

Quick Tip to Solve: Choose the four-carbon chain containing the carbonyl carbon and number it to give the carbonyl locant 2.

2. Why is chloroform kept in dark coloured bottles? [1 mark]

Solution:

Concept:

- Chloroform, $CHCl_3$, undergoes slow oxidation in air in the presence of light.
- The oxidation product phosgene, $COCl_2$, is highly poisonous.

Step 1: Identify the harmful reaction Light promotes the oxidation of chloroform by atmospheric oxygen. The balanced reaction is

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl.$$

The carbonyl chloride formed is called phosgene.

Step 2: Relate the bottle colour to storage A dark coloured bottle reduces the light reaching chloroform and therefore suppresses this light-promoted oxidation. This limits the formation of poisonous phosgene during storage; the bottle colour is a protective measure against the chemical change.

Quick Tip to Solve: For chloroform storage, link dark glass to exclusion of light and prevention of poisonous phosgene formation.

Step 3: Conclusion Chloroform is kept in dark coloured bottles to prevent its light-promoted oxidation by air to poisonous phosgene, $COCl_2$.

Quick Tip to Solve: For chloroform storage, link dark glass to exclusion of light and prevention of poisonous phosgene formation.

3(a). Write IUPAC name of the complex $[Co(en)_2Cl_2]^+$. [1 mark]

Solution:

Concept:

- Ethane-1,2-diamine, en, is neutral; each chlorido ligand has charge -1.
- Name ligands alphabetically before the metal, ignoring multiplicative prefixes when deciding the order.

Step 1: Determine the oxidation state Let the oxidation state of cobalt be x. For $[Co(en)_2Cl_2]^+$, the two neutral en ligands contribute zero charge and the two chlorido ligands contribute -2:

$$x + 2(0) + 2(-1) = +1 \quad \Rightarrow \quad x = +3.$$

Step 2: Assemble the name Chlorido comes before ethane-1,2-diamine alphabetically. Two chlorido ligands give dichlorido; two ethane-1,2-diamine ligands require the prefix bis with parentheses. Because the complex is cationic, retain the metal name cobalt and append its oxidation state as (III).

Step 3: Conclusion The IUPAC name is dichloridobis(ethane-1,2-diamine)cobalt(III) ion.

Quick Tip to Solve: Ignore di and bis for alphabetical order: chlorido precedes ethane-1,2-diamine; neutral en leaves cobalt in state $+3$.

OR

3(b). Using IUPAC norms, write the formula of Sodium tetrachloridonickelate(II). [1 mark]

Solution:

Concept:

- Nickelate(II) denotes a complex containing nickel in oxidation state $+2$.
- Each chlorido ligand contributes -1, while sodium is the counter-ion Na^+.

Step 1: Find the charge on the complex Tetrachlorido means that four chloride ligands surround nickel. With nickel in oxidation state $+2$, the complex charge is

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

Thus the coordination entity is $[NiCl_4]^{2-}$, consistent with the anionic metal name nickelate.

Step 2: Balance the ionic charges Two sodium ions, each with charge $+1$, are required to neutralise

Quick Tip to Solve: Calculate $+2$ minus four ligand charges first; the resulting -2 complex needs two sodium counter-ions.

one complex ion of charge -2. Keep all four chlorido ligands inside the square brackets, and write the sodium ions outside the brackets as the counter-ions of the salt.

Step 3: Conclusion The formula is $\boxed{Na_2[NiCl_4]}$.

Quick Tip to Solve: Calculate +2 minus four ligand charges first; the resulting -2 complex needs two sodium counter-ions.

4(a). What is the difference between a glycosidic linkage and a peptide linkage? [1 mark]

Solution:

Concept:

- A glycosidic linkage joins monosaccharide units in carbohydrates through an oxygen atom.
- A peptide linkage is an amide bond, $-CO-NH-$, joining amino-acid residues in proteins.

Step 1: Describe the glycosidic linkage A glycosidic linkage is a $C-O-C$ bond formed by condensation involving hydroxyl groups of monosaccharides, including the anomeric hydroxyl group of one unit. It joins sugar residues, as in disaccharides and polysaccharides.

Step 2: Describe the peptide linkage A peptide linkage forms when the carboxyl group of one amino acid reacts with the amino group of another, eliminating water. The resulting $-CO-NH-$ bond joins amino-acid residues in peptides and proteins. Thus both are condensation linkages, but they join different building units through different bond groups.

Step 3: Conclusion A glycosidic linkage is an oxygen bridge between sugar units; a peptide linkage is the $-CO-NH-$ bond between amino-acid residues.

Quick Tip to Solve: Associate glycosidic with sugar units and an oxygen bridge; associate peptide with amino acids and the CO-NH group.

OR

4(b). What is the difference between Nucleotide and Nucleoside? [1 mark]

Solution:

Concept:

- A nucleoside consists of a nitrogenous base joined to a pentose sugar by an N-glycosidic bond.
- A nucleotide contains the base-sugar unit together with a phosphate group attached to the sugar.

Step 1: Identify a nucleoside The two components of a nucleoside are a nitrogenous base and a pentose sugar, which may be ribose or 2-deoxyribose. For example, adenine joined to ribose forms adenosine. No phosphate group is present in the nucleoside.

Step 2: Identify the additional component of a nucleotide When a phosphate group is esterified to a hydroxyl group of the sugar in a nucleoside, a nucleotide is obtained. Thus adenosine monophosphate contains adenine, ribose and phosphate. The extra phosphate group is the compositional distinction

Quick Tip to Solve: List the components: base plus sugar gives a nucleoside; adding phosphate gives a nucleotide.

asked for here.

Step 3: Conclusion Nucleoside = nitrogenous base + pentose sugar; nucleotide = nitrogenous base + pentose sugar + phosphate group.

Quick Tip to Solve: List the components: base plus sugar gives a nucleoside; adding phosphate gives a nucleotide.

5. Arrange the following in increasing order of their acidic character:
Ethanol, Phenol, Water [1 mark]

Solution:

Concept:

- Acidity increases when the conjugate base formed by loss of H^+ is more stable.
- The ethyl group has an electron-releasing inductive effect; the phenoxide ion is stabilised by resonance.

Step 1: Compare ethanol with water Ethanol forms ethoxide ion, $C_2H_5O^-$, while water forms hydroxide ion, OH^-. The electron-releasing ethyl group increases electron density on the negatively charged oxygen of ethoxide and destabilises it relative to hydroxide. Hence ethanol is less acidic than water.

Step 2: Compare phenol with the other two Phenol forms phenoxide ion. Its negative charge is delocalised by resonance between oxygen and the aromatic ring, stabilising the conjugate base. Ethoxide and hydroxide lack this aromatic resonance stabilisation. Phenol therefore loses a proton more readily than either ethanol or water.

Step 3: Conclusion The increasing order of acidic character is

$$\boxed{\text{Ethanol} < \text{Water} < \text{Phenol}}.$$

Quick Tip to Solve: Compare conjugate bases: ethyl destabilises ethoxide by its +I effect, while resonance stabilises phenoxide.

Section B (14 marks)

6. (a) Out of 0.1 molal aqueous solution of glucose and 0.1 molal aqueous solution of KCl, which one will have higher boiling point and why?

(b) Predict whether van't Hoff factor, (i) is less than one or greater than one in the following:

(i) CH_3COOH dissolved in water

(ii) CH_3COOH dissolved in benzene [2 marks]

Solution:

Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent ebullioscopic constant and m the molality.
- The factor i is the ratio of the actual number of solute particles to the number expected without association or dissociation. Dissociation increases it; association decreases it.

Step 1: Compare the two boiling points Both solutions have water as solvent and the same molality, $m = 0.1\,\text{mol kg}^{-1}$. Thus K_b and m are identical. Glucose remains as molecules and has $i = 1$. KCl dissociates as $\text{KCl} \rightarrow \text{K}^+ + \text{Cl}^-$, producing more solute particles, so its $i > 1$ (approximately 2 for ideal complete dissociation). Therefore its boiling-point elevation is greater.

Step 2: Predict association or dissociation of acetic acid In water, acetic acid partially ionises:

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+.$$

The number of solute particles increases, giving $i > 1$. In benzene, hydrogen bonding causes dimer formation:

$$2\text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2.$$

Two molecules form one particle, so the particle count falls and $i < 1$.

Step 3: Conclusion (a) The 0.1 molal KCl solution has the higher boiling point. (b) For acetic acid, (i) $i > 1$ in water and (ii) $i < 1$ in benzene.

Quick Tip to Solve: At equal molality in the same solvent, compare particle numbers: dissociation raises i; dimerisation lowers it.

7(a). What happens when AgCl is doped with $CdCl_2$? What is the name of this defect? [2 marks]

Solution:

Concept:

- An impurity defect arises when foreign ions occupy sites in an ionic crystal. Electrical neutrality must still be maintained.
- A divalent dopant replacing a monovalent cation introduces one extra positive charge, compensated by a vacancy at another monovalent cation site.

Step 1: Replace silver ions with cadmium ions When AgCl is crystallised in the presence of CdCl_2, some Cd^{2+} ions occupy sites normally occupied by Ag^+. Each cadmium ion has charge $+2$, whereas a

Quick Tip to Solve: Count charge before counting sites: one Cd^{2+} replaces two Ag^+, leaving one site vacant.

silver ion has charge $+1$. Merely replacing one silver ion by one cadmium ion would introduce an excess positive charge.

Step 2: Maintain neutrality by forming a vacancy To compensate, one additional Ag^+ site remains vacant for each Cd^{2+} incorporated. In effect, two silver ions, with total charge $+2$, are replaced by one cadmium ion and one vacant cation site, still giving total charge $+2$. Thus the number of cation vacancies equals the number of cadmium ions introduced. The chloride sublattice remains occupied; this is an impurity defect involving cation vacancies.

Step 3: Conclusion Doping AgCl with $CdCl_2$ creates one Ag^+-site vacancy per Cd^{2+} incorporated. This is an impurity defect (a cation-vacancy defect).

Quick Tip to Solve: Count charge before counting sites: one Cd^{2+} replaces two Ag^+, leaving one site vacant.

OR

7(b). What type of defect is shown by NaCl in
(a) stoichiometric defects, and
(b) non-stoichiometric defects? [2 marks]

Solution:

Concept:

- Stoichiometric defects preserve the chemical formula and the cation-to-anion ratio of the crystal.
- Non-stoichiometric defects change the relative amounts of metal and non-metal. An electron trapped at an anion vacancy is called an F-centre.

Step 1: Identify the stoichiometric defect NaCl shows a Schottky defect: equal numbers of Na^+ and Cl^- ions are absent from their normal lattice sites. Removing equal positive and negative charges keeps the crystal electrically neutral, and the ratio of sodium ions to chloride ions remains $1:1$. The vacant sites lower the density of the crystal. NaCl has ions of comparable size and a high coordination number, favouring this vacancy-type defect.

Step 2: Identify the non-stoichiometric defect NaCl can show a metal-excess defect due to anion vacancies, for example on heating in sodium vapour. Some chloride-ion sites become vacant, and electrons occupy these sites to preserve electrical neutrality. These electron-filled anion vacancies are F-centres and impart a yellow colour to the crystal. The excess of metal relative to chloride makes this a non-stoichiometric defect; it is different from equal cation and anion vacancies in a Schottky defect.

Step 3: Conclusion (a) Stoichiometric: Schottky defect. (b) Non-stoichiometric: metal-excess defect due to anion vacancies containing electrons (F-centres).

Quick Tip to Solve: For NaCl, pair vacancies mean Schottky; an electron in a chloride vacancy means a metal-excess F-centre defect.

8(a). Complete and balance the following equations:

(a) NH_3 (excess) + Cl_2 $\rightarrow$

(b) XeF_6 + $2H_2O$ $\rightarrow$ [2 marks]

Solution:

Concept:

- The products of chlorine with ammonia depend on which reagent is in excess. Excess ammonia gives nitrogen and ammonium chloride.
- Controlled hydrolysis of XeF_6 replaces each pair of fluorine atoms by one oxygen atom, producing two HF molecules per water molecule used.

Step 1: Balance chlorine reacting with excess ammonia Chlorine oxidises some ammonia to nitrogen, while additional ammonia combines with the hydrogen chloride formed to give ammonium chloride. The balanced equation is

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl.$$

Nitrogen atoms balance as $8 = 2+6$, hydrogen as $24 = 6 \times 4$, and chlorine as $6 = 6$. Because ammonia is in excess, the product is not nitrogen trichloride, which is associated with excess chlorine.

Step 2: Balance hydrolysis with two molecules of water The specified two molecules of water replace four of the six fluorine atoms in XeF_6, leaving xenon dioxydifluoride:

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF.$$

Xenon is balanced one to one, oxygen two to two, hydrogen four to four, and fluorine six to $2 + 4$. This is partial hydrolysis; complete hydrolysis to XeO_3 would require three water molecules instead.

Step 3: Conclusion (a) $8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$. (b) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$.

Quick Tip to Solve: Check the reagent condition first: excess ammonia gives N_2, and two waters convert XeF_6 to XeO_2F_2.

OR

8(b). Write balanced chemical equations involved in the following reactions:

(a) XeF_4 reacts with SbF_5.

(b) Ag is heated with PCl_5. [2 marks]

Solution:

Concept:

- A strong Lewis acid such as SbF_5 can accept a fluoride ion; XeF_4 can supply that ion to form an ionic adduct.
- On heating, phosphorus pentachloride can chlorinate silver: phosphorus is reduced from $+5$ to $+3$, while silver is oxidised from 0 to $+1$.

Step 1: Transfer fluoride from xenon tetrafluoride Antimony pentafluoride accepts one fluoride ion

Quick Tip to Solve: Let SbF_5 take one fluoride; for silver, balance the two-electron reduction of phosphorus using two Ag atoms.

from xenon tetrafluoride. The resulting ions are $[XeF_3]^+$ and $[SbF_6]^-$:

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-.$$

There is one xenon and one antimony atom on each side. The total number of fluorine atoms is nine on each side, and the product has zero net charge. This is fluoride transfer rather than a change in the oxidation state of xenon.

Step 2: Balance the reaction of heated silver Silver reacts with PCl_5 to form silver chloride and phosphorus trichloride:

$$2Ag + PCl_5 \xrightarrow{\Delta} 2AgCl + PCl_3.$$

Two silver atoms each lose one electron. Phosphorus gains two electrons as its oxidation state falls from $+5$ in PCl_5 to $+3$ in PCl_3. Thus two silver atoms are required per molecule of pentachloride; the five chlorine atoms divide between two AgCl units and one PCl_3 molecule.

Step 3: Conclusion (a) $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$. (b) $2Ag + PCl_5 \xrightarrow{\Delta} 2AgCl + PCl_3$.

Quick Tip to Solve: Let SbF_5 take one fluoride; for silver, balance the two-electron reduction of phosphorus using two Ag atoms.

9. Write any two oxoacids of sulphur and draw their structures. [2 marks]

Solution:

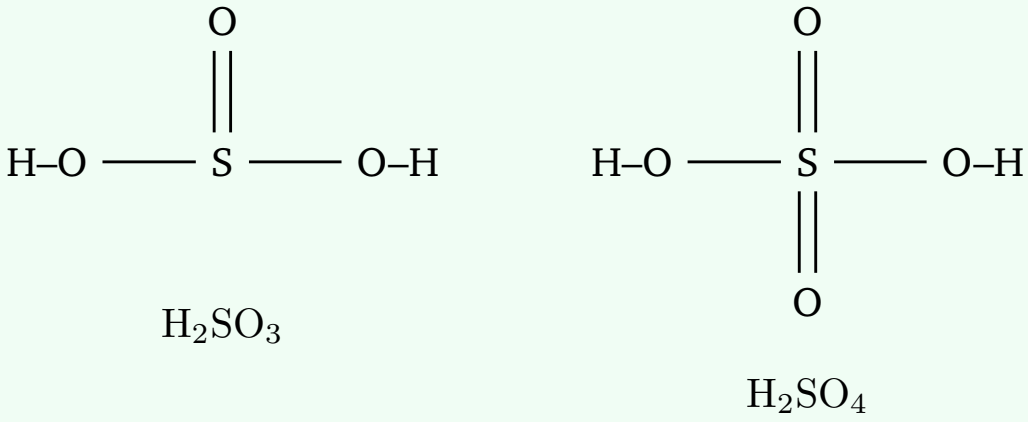
Concept:

- Oxoacids contain oxygen along with hydrogen and the central element. In sulphur oxoacids, the ionisable hydrogen atoms are bonded to oxygen as hydroxyl groups.
- Two examples are sulphurous acid, H_2SO_3, and sulphuric acid, H_2SO_4. Their structures differ by one terminal oxygen atom.

Step 1: Sulphurous acid Sulphurous acid has the formula H_2SO_3. Its conventional structural formula is $HO - S(=O) - OH$: sulphur is attached to two hydroxyl groups and one doubly bonded oxygen. Sulphur has oxidation state $+4$, since $2(+1) + x + 3(-2) = 0$.

Step 2: Sulphuric acid Sulphuric acid has the formula H_2SO_4. Its conventional structural formula is $HO - S(=O)_2 - OH$: sulphur is attached to two hydroxyl groups and two doubly bonded oxygen atoms. Its oxidation state is $+6$, since $2(+1) + x + 4(-2) = 0$. The drawings below show every oxygen and both O-H groups explicitly.

Quick Tip to Solve: Draw both acidic hydrogens on oxygen; count three oxygens for sulphurous acid and four for sulphuric acid.



Conventional structures of sulphurous acid (left) and sulphuric acid (right)

Step 3: Conclusion Two oxoacids are sulphurous acid, H_2SO_3, and sulphuric acid, H_2SO_4, with the structures shown.

Quick Tip to Solve: Draw both acidic hydrogens on oxygen; count three oxygens for sulphurous acid and four for sulphuric acid.

10. Write the name of two fuels other than hydrogen used in fuel cell. Write two advantages of fuel cell over an ordinary cell. [2 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy through electrode reactions.
- Fuel is oxidised at the anode and an oxidant, usually oxygen, is reduced at the cathode. Continuous supply distinguishes its operation from an ordinary cell containing a finite stock of reactants.

Step 1: Name two fuels Methanol, CH_3OH, and methane, CH_4, are two fuels other than hydrogen used in fuel cells. Both can serve as sources of chemical energy for electricity generation; their carbon-containing products depend on the fuel-cell chemistry and operating conditions.

Step 2: State two advantages First, a fuel cell has high energy-conversion efficiency because chemical energy is converted directly into electrical energy. Second, it can deliver electricity continuously as long as fuel and oxidant are supplied and products are removed. An ordinary cell has a limited amount of reactants inside it and must be replaced or, if rechargeable, recharged after those reactants are depleted.

Step 3: Conclusion Methanol and methane are suitable examples. Two advantages are high energy-conversion efficiency and continuous operation with an external supply of reactants.

Quick Tip to Solve: Link continuous operation to continuous fuel and oxidant supply; a fuel cell cannot operate without fresh reactants.

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

(a) $C_6H_5NH_2 \xrightarrow{\text{conc. } H_2SO_4} A \xrightarrow{\text{heat, } 453\text{–}473\,K} B$.

(b) $C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} A \xrightarrow{(CH_3CO)_2O/\text{pyridine}} B$. [2 marks]

Solution:

Concept:

- Aniline forms anilinium salts with strong acids. Heating aniline with concentrated sulphuric acid at 453–473 K ultimately produces sulphanilic acid, with the sulphonic acid group para to the amino group.
- Hofmann bromamide degradation converts $RCONH_2$ to RNH_2, removing the carbonyl carbon. Acetic anhydride then acetylates a primary amine to an amide.

Step 1: Reaction (a): salt formation followed by sulphonation Concentrated sulphuric acid protonates aniline. Therefore the first compound is anilinium hydrogen sulphate:

$$A = [C_6H_5NH_3]^+[HSO_4]^-.$$

On heating at the stated temperature, the product is sulphanilic acid (4-aminobenzenesulphonic acid):

$$B = \text{p-}H_2N - C_6H_4 - S(=O)_2 - OH.$$

Here the amino group and sulphonic acid group occupy positions 1 and 4 on the benzene ring. The acid is commonly represented in its zwitterionic form, $\text{p-}^+H_3N - C_6H_4 - SO_3^-$, due to internal proton transfer.

Step 2: Reaction (b): degradation followed by acetylation Benzamide reacts with $Br_2/NaOH$ by Hofmann bromamide degradation. Loss of its carbonyl carbon gives aniline, so $A = C_6H_5 - NH_2$. The benzene ring remains intact. Aniline then reacts with acetic anhydride in pyridine; an amino hydrogen is replaced by an acetyl group. Thus B is acetanilide:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5 - NH - C(=O) - CH_3 + CH_3COOH.$$

Step 3: Conclusion (a) A: $[C_6H_5NH_3]^+[HSO_4]^-$; B: $\text{p-}H_2N - C_6H_4 - SO_3H$.
(b) A: $C_6H_5NH_2$; B: $C_6H_5 - NH - C(=O) - CH_3$.

Quick Tip to Solve: In Hofmann degradation delete only the amide carbonyl carbon; in acetylation retain the nitrogen and attach COCH3 to it.

12. Account for the following:

(a) Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.

(b) On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali. [2 marks]

Solution:

Concept:

- Gabriel synthesis forms a carbon-nitrogen bond by nucleophilic substitution of a halide with the phthalimide anion. Aryl halides resist the substitution needed in this synthesis.
- In the benzenesulphonyl chloride (Hinsberg) test, solubility in alkali depends on whether the sulphonamide product retains an acidic N-H hydrogen.

Step 1: (a) Limitation of Gabriel synthesis The phthalimide anion readily displaces halide from suitable alkyl halides, giving an N-alkylphthalimide that yields a primary amine on hydrolysis. Preparing an aromatic primary amine would require the corresponding reaction with an aryl halide. Its carbon-halogen bond has partial double-bond character due to resonance and the halogen-bearing carbon is sp^2-hybridised. Aryl halides therefore do not undergo the required ordinary nucleophilic substitution with potassium phthalimide. Hence this method is unsuitable for preparing aromatic primary amines.

Step 2: (b) Different sulphonamide products A primary amine gives $C_6H_5SO_2NHR$, which retains an N-H bond. The electron-withdrawing sulphonyl group makes that hydrogen acidic; alkali removes it to form a soluble ionic salt:

$$C_6H_5SO_2NHR + OH^- \longrightarrow C_6H_5SO_2NR^- + H_2O.$$

A secondary amine gives $C_6H_5SO_2NR_2$. This product has no N-H hydrogen, cannot form the corresponding salt with alkali, and remains insoluble in alkali.

Step 3: Conclusion (a) Aryl halides do not undergo the substitution required for Gabriel synthesis.
(b) The primary-amine product forms a soluble salt through its acidic N-H group; the secondary-amine product lacks that group.

Quick Tip to Solve: After adding SO2C6H5 to nitrogen, count the N-H bonds remaining: one permits salt formation, while zero prevents it.

Section C (36 marks)

13. (a) Following reaction takes place in the cell:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Calculate $\Delta_r G^\circ$ of the reaction.

[Given: $E^\circ_{(Zn^{2+}/Zn)} = -0.76$ V, $E^\circ_{(Ag^+/Ag)} = 0.80$ V, 1 F = 96,500 C mol^{-1}]

(b) How can you determine limiting molar conductivity, (Λ_m°) for strong electrolyte and weak electrolyte? [3 marks]

Solution:

Concept:

- The standard Gibbs energy change is related to the standard cell potential by $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- Limiting molar conductivity Λ°_m is the molar conductivity at infinite dilution. Strong electrolytes permit graphical extrapolation, whereas weak electrolytes require Kohlrausch's law of independent migration of ions.

Step 1: (a) Identify the electron transfer and use the supplied potentials Zinc is oxidised according to $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$, so $n = 2$. The silver species is reduced at the cathode. Taking the supplied silver electrode potential for the numerical calculation gives

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - (-0.76) = 1.56\,\text{V}.$$

Hence

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96500 \times 1.56 \\ &= -301080\,\text{J mol}^{-1} \\ &= -301.08\,\text{kJ mol}^{-1}.\end{aligned}$$

Strictly, the supplied silver potential is for Ag^+/Ag; the written silver-oxide reaction requires the $\text{Ag}_2\text{O}/\text{Ag}, \text{OH}^-$ potential. The numerical result uses the supplied value.

Step 2: (b) Determine the value for a strong electrolyte At several low concentrations measure conductivity and calculate Λ_m. Plot Λ_m against $\sqrt{c}$, where c is concentration. For a strong electrolyte, the dilute-solution relation is $\Lambda_m = \Lambda^\circ_m - A\sqrt{c}$. Extrapolating its straight line to $\sqrt{c} = 0$ gives the intercept Λ°_m.

Step 3: (b) Determine the value for a weak electrolyte Increasing ionisation on dilution makes the plot curved, so use Kohlrausch's law to combine strong-electrolyte values:

$$\begin{aligned}\Lambda^\circ_m(\text{CH}_3\text{COOH}) = \Lambda^\circ_m(\text{HCl}) &\\ + \Lambda^\circ_m(\text{CH}_3\text{COONa}) &\\ - \Lambda^\circ_m(\text{NaCl}).&\end{aligned}$$

Sodium and chloride contributions cancel, leaving hydrogen and acetate contributions.

Step 4: Conclusion Using the supplied potentials, $\Delta_r G^\circ = -301.08\,\text{kJ mol}^{-1}$. Obtain Λ°_m for strong electrolytes by extrapolation to zero concentration and for weak electrolytes by Kohlrausch's law.

Quick Tip to Solve: Count electrons from zinc oxidation first; for conductivity, extrapolate strong electrolytes and cancel common ions for weak electrolytes.

14(a). Define the following with a suitable example, of each:

(a) Coagulation

(b) Multimolecular colloid

(c) Gel [3 marks]

Solution:

Concept:

- A colloid has a dispersed phase distributed through a dispersion medium; the dispersed particles are larger than ordinary molecules but do not settle readily under gravity.
- Coagulation describes destabilisation of a sol. Multimolecular colloids are classified by particle formation, whereas gels are classified by the physical states of the dispersed phase and medium.

Step 1: (a) Coagulation Coagulation is the aggregation of colloidal particles into larger particles that separate as a precipitate. Adding an electrolyte can neutralise the charge responsible for stabilising a lyophobic sol. Once the repulsion between particles is reduced, they come together and settle. For example, adding sodium chloride solution to a negatively charged arsenic sulphide sol causes coagulation: the Na^+ ions act as the oppositely charged ions.

Step 2: (b) Multimolecular colloid A multimolecular colloid is formed when many atoms or small molecules aggregate to give particles of colloidal dimensions. The individual atoms or molecules are smaller than colloidal particles, and their aggregates are held together by van der Waals forces. Gold sol is an example: each colloidal particle consists of an aggregate of many gold atoms. Sulphur sol is another example, with aggregates containing many S_8 molecules.

Step 3: (c) Gel A gel is a colloidal system in which the dispersed phase is a liquid and the dispersion medium is a solid. The solid forms a network that retains the liquid, giving a jelly-like, semisolid material. Jelly is a suitable example; cheese is another common example. Thus a gel differs from a sol, in which a solid is dispersed in a liquid medium.

Step 4: Conclusion Coagulation is precipitation by aggregation, as in arsenic sulphide sol with added electrolyte; a multimolecular colloid contains atomic or molecular aggregates, as in gold sol; a gel is liquid dispersed in a solid, as in jelly.

Quick Tip to Solve: For each definition, give one example immediately; remember gel as liquid in solid and sol as solid in liquid.

OR

14(b). (a) Out of starch and ferric hydroxide sol, which one can easily be coagulated and why?
(b) What is observed when an emulsion is centrifuged?
(c) What is the role of promoters and poisons in catalysis? [3 marks]

Solution:

Concept:

- Lyophobic sols have little affinity for their dispersion medium and depend mainly on particle charge for stability. Lyophilic sols are additionally stabilised by strong solvation of their particles.
- An emulsion contains droplets of one liquid dispersed in another immiscible liquid. Promoters enhance catalytic activity, while poisons reduce or destroy that activity.

Step 1: (a) Compare starch and ferric hydroxide sols Ferric hydroxide sol is more easily coagulated. It is lyophobic, and its stability mainly depends on the electrical charge on the colloidal particles. An appropriate electrolyte neutralises this charge, allowing the particles to aggregate and precipitate. Starch sol is lyophilic: its particles have strong affinity for water and are protected by a hydration layer as well as charge. Consequently, starch sol resists coagulation much more strongly and ordinarily requires a large amount of electrolyte or removal of its hydration layer.

Step 2: (b) Centrifuge an emulsion On centrifugation, an emulsion separates into its constituent liquid layers. The rapid rotation promotes separation of phases of different densities, breaking the apparently uniform dispersion into two distinct layers. For example, centrifugation separates the cream-rich portion from milk. This separation of an emulsion is called demulsification.

Step 3: (c) State the roles of promoters and poisons Promoters are substances that increase the activity of a catalyst. For example, molybdenum acts as a promoter for the iron catalyst in the Haber process for manufacturing ammonia. Catalytic poisons are substances that decrease or destroy the activity of a catalyst, commonly by occupying its active sites and preventing reactants from adsorbing there. For example, arsenic compounds poison platinum used in the oxidation of sulphur dioxide in the contact process. Thus promoters help a catalyst perform more effectively, whereas poisons inhibit its function.

Step 4: Conclusion Ferric hydroxide sol coagulates more easily because it is lyophobic; centrifugation separates an emulsion into liquid layers; promoters increase catalytic activity and poisons decrease or destroy it.

Quick Tip to Solve: Link easier coagulation to weak solvation; distinguish a promoter from a poison by whether catalyst activity rises or falls.

15. (a) An element crystallises in bcc lattice with a cell edge of 3×10^{-8} cm. The density of the element is 6.89 g cm^{-3}. Calculate the molar mass of the element. ($N_A = 6.022 \times 10^{23}$ mol^{-1})

(b) What type of semiconductor is obtained when

(i) Ge is doped with In?

(ii) Si is doped with P? [3 marks]

Solution:

Concept:

- For a cubic unit cell, $\rho = \dfrac{ZM}{N_A a^3}$, where Z is the number of atoms per cell, M the molar mass, a the cell edge and N_A Avogadro's constant.
- A body-centred cubic lattice has $Z = 8(1/8) + 1 = 2$. A trivalent dopant in a group 14 crystal produces holes, whereas a pentavalent dopant supplies extra electrons.

Step 1: (a) Relate the unit-cell mass to its volume The eight corner atoms contribute one atom in total and the body-centre atom contributes one more. Therefore, the mass of one bcc unit cell is $2M/N_A$. Its volume is

$$a^3 = (3 \times 10^{-8})^3 = 27 \times 10^{-24}\ \text{cm}^3.$$

Since density is mass divided by volume, rearranging gives $M = \rho a^3 N_A/2$.

Step 2: Substitute the data consistently Use centimetres for the edge because the given density is in g cm^{-3}:

$$M = \frac{6.89 \times 27 \times 10^{-24} \times 6.022 \times 10^{23}}{2} = 56.0136\ \text{g mol}^{-1}.$$

The factors of cm^3 cancel, leaving the required molar-mass unit.

Step 3: (b) Identify the majority charge carriers (i) Ge has four valence electrons, while In has three. An In atom cannot complete all four covalent bonds with neighbouring Ge atoms without accepting an electron. The resulting mobile holes are the majority carriers, so the doped crystal is p-type.

(ii) Si has four valence electrons, while P has five. Four of the P electrons participate in bonding and the fifth is available for conduction. Electrons are the majority carriers, so the doped crystal is n-type.

Step 4: Conclusion (a) The molar mass is approximately 56.0 g mol^{-1}. (b) Ge doped with In gives a p-type semiconductor; Si doped with P gives an n-type semiconductor.

Quick Tip to Solve: For bcc use two atoms per cell; compare dopant valency with four to identify holes or extra electrons.

16. A solution 0.1 M of Na_2SO_4 is dissolved to the extent of 95%. What would be its osmotic pressure at 27°C? (R = 0.0821 L atm K^{-1} mol^{-1}) [3 marks]

Solution:

Concept:

- The osmotic pressure of an electrolyte solution is $\pi = iCRT$, where C is its formula-unit molarity, T the absolute temperature, R the gas constant and i the van't Hoff factor.

Quick Tip to Solve: For sodium sulphate use three ions, calculate $i = 1 + 2\alpha$, and convert Celsius to kelvin before multiplying.

- If each formula unit produces n ions and the degree of dissociation is α, then $i = 1 + (n-1)\alpha$, because dissociation increases the number of dissolved particles.

Step 1: Count the ions formed by sodium sulphate Sodium sulphate dissociates according to

$$\mathrm{Na_2SO_4} \longrightarrow 2\mathrm{Na^+} + \mathrm{SO_4^{2-}}.$$

Thus, one dissociated formula unit gives three ions, so $n = 3$. The stated 95 percent dissociation corresponds to $\alpha = 0.95$. Starting with one mole of formula units, the undissociated amount is $1 - \alpha$ mole and the ionic amount is 3α mole.

Step 2: Calculate the effective particle concentration The total particle amount relative to the initial formula-unit amount is

$$i = (1-\alpha) + 3\alpha = 1 + 2\alpha = 1 + 2(0.95) = 2.90.$$

Hence the effective concentration for osmotic pressure is $iC = 2.90(0.1) = 0.290\,\text{mol L}^{-1}$. Complete dissociation would give $i = 3$, but that is not appropriate for the specified degree of dissociation.

Step 3: Apply the osmotic-pressure equation Convert the temperature to kelvin: $T = 27 + 273 = 300\,\text{K}$. Using the given value of R,

$$\begin{aligned}\pi &= 2.90 \times 0.1 \times 0.0821 \times 300 \\ &= 7.1427\,\text{atm}.\end{aligned}$$

Molarity in mol L^{-1} and R in L atm $\text{K}^{-1}\text{mol}^{-1}$ leave pressure in atmospheres.

Step 4: Conclusion The osmotic pressure of the solution at 27°C is approximately $7.14\,\text{atm}$.

Quick Tip to Solve: For sodium sulphate use three ions, calculate $i = 1 + 2\alpha$, and convert Celsius to kelvin before multiplying.

17(a). Write down the reactions taking place in blast furnace related to the metallurgy of iron in the temperature range 500 K – 800 K. What is the role of limestone in the metallurgy of iron? [3 marks]

Solution:

Concept:

- In the cooler region of the blast furnace, carbon monoxide acts as the reducing agent for iron oxides. Oxygen is removed from the oxides and carbon monoxide is oxidised to carbon dioxide.
- Limestone, $\mathrm{CaCO_3}$, is a flux. It produces basic calcium oxide, which combines with acidic silica gangue to form a fusible slag.

Step 1: Write the reductions occurring at 500–800 K The reactions of iron oxides with carbon monoxide in this temperature range are

$$\begin{aligned}3\mathrm{Fe_2O_3} + \mathrm{CO} &\longrightarrow 2\mathrm{Fe_3O_4} + \mathrm{CO_2}, \\ \mathrm{Fe_3O_4} + 4\mathrm{CO} &\longrightarrow 3\mathrm{Fe} + 4\mathrm{CO_2}, \\ \mathrm{Fe_2O_3} + \mathrm{CO} &\longrightarrow 2\mathrm{FeO} + \mathrm{CO_2}.\end{aligned}$$

Quick Tip to Solve: Keep the two roles distinct: CO removes oxygen from iron oxides, while CaO from limestone removes silica as slag.

These balanced equations represent the reduction of haematite and other iron oxides by CO. In each equation the oxygen removed from the oxide appears in carbon dioxide. The reactions describe the relevant reduction pathways, rather than three steps that must all occur consecutively for each iron atom.

Step 2: Explain the action of limestone On heating in the furnace, limestone decomposes:

$$\mathrm{CaCO_3} \xrightarrow{\Delta} \mathrm{CaO} + \mathrm{CO_2}.$$

The calcium oxide formed is a basic oxide. It reacts with silica, the acidic impurity accompanying the ore:

$$\mathrm{CaO} + \mathrm{SiO_2} \longrightarrow \mathrm{CaSiO_3}.$$

Calcium silicate forms a molten slag. It separates from the molten iron and can be removed, thereby eliminating silica gangue from the metal. Thus limestone supplies the flux; it is not the reducing agent for the iron oxide.

Step 3: Conclusion At 500–800 K, CO reduces iron oxides as shown in the three equations above. Limestone removes silica impurity by producing CaO, which forms calcium silicate slag, $\mathrm{CaSiO_3}$.

Quick Tip to Solve: Keep the two roles distinct: CO removes oxygen from iron oxides, while CaO from limestone removes silica as slag.

OR

17(b). What happens when

(a) Silver is leached with NaCN in the presence of air?

(b) Copper matte is charged into silica lined converter and hot air blast is blown?

(c) NaCN is added in an ore containing PbS and ZnS during concentration by froth floatation method?

[3 marks]

Solution:

Concept:

- Cyanide leaching dissolves silver as the soluble dicyanidoargentate(I) complex, $[\mathrm{Ag(CN)_2}]^-$, in the presence of oxygen.
- In a converter, air oxidises sulphides in copper matte; silica combines with basic iron(II) oxide to form slag. Copper(I) sulphide and copper(I) oxide then undergo self-reduction.
- A depressant prevents one sulphide mineral from joining the froth, permitting selective separation of mixed sulphide ores.

Step 1: (a) Silver undergoes cyanide leaching Silver dissolves in aqueous sodium cyanide when air supplies the oxygen required for oxidation. A soluble silver(I) cyanide complex is formed:

$$4\mathrm{Ag} + 8\mathrm{NaCN} + \mathrm{O_2} + 2\mathrm{H_2O} \longrightarrow 4\mathrm{Na[Ag(CN)_2]} + 4\mathrm{NaOH}.$$

Thus silver passes into the leach solution as sodium dicyanidoargentate(I); oxygen acts as the oxidising

Quick Tip to Solve: In the PbS-ZnS mixture, remember that NaCN depresses ZnS; in the converter, pair FeO with silica and Cu2O with Cu2S.

agent, while cyanide stabilises silver(I) by complex formation.

Step 2: (b) Copper matte yields blister copper Copper matte contains mainly Cu_2S and FeS. The hot air blast oxidises iron sulphide, and the resulting iron(II) oxide reacts with the silica lining to give iron silicate slag:

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2,$$
$$FeO + SiO_2 \longrightarrow FeSiO_3.$$

Some copper(I) sulphide is oxidised to copper(I) oxide. This oxide reacts with the remaining sulphide, producing metallic copper by self-reduction:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2,$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2.$$

The escaping sulphur dioxide produces a blistered surface on cooling, hence the product is called blister copper.

Step 3: (c) Sodium cyanide depresses zinc sulphide Sodium cyanide acts as a depressant for ZnS, preventing it from being carried up by the froth. Consequently, only PbS is preferentially carried into the froth and collected, while ZnS remains behind. This permits separation of the two sulphides during concentration.

Step 4: Conclusion (a) Silver dissolves as $Na[Ag(CN)_2]$. (b) Iron is removed as $FeSiO_3$ slag and copper matte is converted into blister copper. (c) $NaCN$ depresses ZnS, allowing PbS to float.

Quick Tip to Solve: In the PbS-ZnS mixture, remember that NaCN depresses ZnS; in the converter, pair FeO with silica and Cu2O with Cu2S.

18. Give reasons for the following:

(a) Acidic character decreases from N_2O_3 to Bi_2O_3.

(b) All the P−Cl bonds in PCl_5 are not equivalent.

(c) HF is a weaker acid than HCl in an aqueous solution. [3 marks]

Solution:

Concept:

- Within a group, increasing metallic character generally decreases the acidic character and increases the basic character of the element's oxides.
- Molecular PCl_5 has trigonal bipyramidal geometry: two axial bonds and three equatorial bonds experience different bond-pair repulsions.
- The acid strength of a hydrogen halide in water depends on its tendency to ionise; breaking the hydrogen-halogen bond is a key factor.

Step 1: (a) Oxide acidity decreases down group 15 From nitrogen to bismuth, atomic size and metallic character increase, while electronegativity and non-metallic character generally decrease. Non-metal oxides are predominantly acidic, whereas oxides become more basic as metallic character increases. Therefore the acidic character of the trioxides decreases down the group, from acidic N_2O_3

Quick Tip to Solve: For these three reasons, identify the controlling factor first: metallic character, axial 90-degree repulsions, and hydrogen-halogen bond strength.

towards basic Bi_2O_3. The trend follows the changing nature of the element even though its oxidation state in these oxides remains $+3$.

Step 2: (b) Axial and equatorial bonds have different environments In the trigonal bipyramidal molecule PCl_5, the three equatorial P–Cl bonds lie in one plane at 120° to one another. The two axial bonds are perpendicular to that plane. Each axial bond pair experiences three 90° repulsions from the equatorial bond pairs, while each equatorial bond pair experiences only two 90° repulsions from the axial bond pairs. Hence the axial bonds suffer greater repulsion and are longer and weaker than the equatorial bonds. Thus all five P–Cl bonds are not equivalent.

Step 3: (c) HF ionises less readily than HCl in water The H–F bond is much stronger than the H–Cl bond because fluorine is very small. Its high bond dissociation enthalpy makes ionisation of HF less favourable, despite its high bond polarity. Consequently HF undergoes only partial ionisation in aqueous solution:

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-.$$

HCl, with its weaker H–Cl bond, ionises essentially completely in water. Therefore HF produces fewer hydronium ions at comparable concentration and is the weaker acid.

Step 4: Conclusion Increasing metallic character explains the decrease in oxide acidity from N_2O_3 to Bi_2O_3; greater repulsion makes axial P–Cl bonds longer and weaker; the stronger H–F bond makes HF weaker than HCl in water.

Quick Tip to Solve: For these three reasons, identify the controlling factor first: metallic character, axial 90-degree repulsions, and hydrogen-halogen bond strength.

19(a). Write the structures of monomers used to obtain the following polymers:

(a) Natural rubber

(b) PVC

(c) Nylon-6,6 [3 marks]

Solution:

Concept:

- A monomer is the small molecule from which a polymer's repeating structure is built. Addition polymerisation uses unsaturated monomers without eliminating small molecules.
- Nylon-6,6 is a condensation polymer of a diamine and a dicarboxylic acid. Their functional groups form amide links, $-CO-NH-$, with elimination of water.

Step 1: (a) Monomer of natural rubber Natural rubber is cis-1,4-polyisoprene. Its monomer is isoprene, whose systematic name is 2-methylbuta-1,3-diene. The structural formula is

$$CH_2 = C(CH_3) - CH = CH_2.$$

This conjugated diene contains a methyl group on carbon 2. Its 1,4-addition polymerisation leaves a double bond in each repeat unit; the cis arrangement of the polymer chains is characteristic of natural rubber.

Quick Tip to Solve: In nylon-6,6, count both carboxyl carbons: adipic acid has four CH2 groups but six carbons overall, while the diamine has six CH2 groups.

Step 2: (b) Monomer of PVC PVC stands for polyvinyl chloride. Its monomer is vinyl chloride, also called chloroethene, with structure

$$CH_2 = CH - Cl.$$

During addition polymerisation the carbon-carbon double bond opens and produces the repeating unit $[-CH_2 - CH(Cl)-]$. The chlorine atom remains attached to a chain carbon, so the monomer must contain a chlorine substituent on ethene.

Step 3: (c) The two monomers of nylon-6,6 Nylon-6,6 is prepared from hexamethylenediamine (hexane-1,6-diamine) and adipic acid (hexanedioic acid). Their structures are, respectively,

$$H_2N - (CH_2)_6 - NH_2,$$
$$HOOC - (CH_2)_4 - COOH.$$

The diamine has six carbon atoms between its two amino groups. The acid also has six carbons in total: four methylene carbons plus the two carboxyl carbons. Reaction of the amino and carboxyl groups forms the amide links of nylon-6,6, with water eliminated during condensation.

Step 4: Conclusion Natural rubber: $CH_2 = C(CH_3) - CH = CH_2$; PVC: $CH_2 = CHCl$; nylon-6,6: $H_2N - (CH_2)_6 - NH_2$ and $HOOC - (CH_2)_4 - COOH$.

Quick Tip to Solve: In nylon-6,6, count both carboxyl carbons: adipic acid has four CH2 groups but six carbons overall, while the diamine has six CH2 groups.

OR

19(b). Write the mechanism of free radical polymerisation of ethene. [3 marks]

Solution:

Concept:

- Free-radical addition polymerisation converts the double bonds of ethene into a saturated carbon chain without eliminating a small molecule.
- A peroxide initiator produces radicals by homolytic bond cleavage. Chain initiation, propagation and termination are the three stages; the dot denotes an unpaired electron.

Step 1: Chain initiation On heating, a peroxide initiator undergoes homolysis. Writing its organic group as R, the initiating steps are

$$RO{-}OR \xrightarrow{\Delta} 2RO^{\bullet},$$

$$RO^{\bullet} + CH_2{=}CH_2 \longrightarrow RO{-}CH_2{-}CH_2{}^{\bullet}.$$

The radical attacks the ethene double bond, creates a new sigma bond and leaves a radical at the end of the growing chain.

Step 2: Chain propagation The terminal radical adds successive ethene molecules. Each addition

Quick Tip to Solve: Put a radical dot at every growing chain end during propagation; remove both dots when two chains combine in termination.

consumes a double bond and regenerates a radical at the new chain end:

$$\mathrm{RO{-}CH_2{-}CH_2^{\bullet} + CH_2{=}CH_2} \longrightarrow \mathrm{RO{-}CH_2{-}CH_2{-}CH_2{-}CH_2^{\bullet}}.$$

Repetition builds a long chain containing many $-CH_2-CH_2-$ units, with the unpaired electron retained at its growing end.

Step 3: Chain termination Two growing chain radicals combine to form a covalent bond. If P and Q denote the remaining polymer-chain portions, this is represented by

$$\mathrm{P{-}CH_2{-}CH_2^{\bullet} + {}^{\bullet}CH_2{-}CH_2{-}Q \longrightarrow P{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}Q}.$$

Both unpaired electrons are paired in the new bond, so this chain no longer propagates.

Step 4: Conclusion Ethene forms polyethene by peroxide-initiated free-radical addition through initiation, propagation and termination. Its repeating unit is $[-CH_2-CH_2-]_n$.

Quick Tip to Solve: Put a radical dot at every growing chain end during propagation; remove both dots when two chains combine in termination.

20(a). Why are metal hydroxides better alternatives than sodium hydrogen carbonate in antacids?

(b) Why is aspirin used in the prevention of heart-attacks?

(c) Why antihistamines do not affect the secretion of acid in stomach? [3 marks]

Solution:

Concept:

- Antacids neutralise excess stomach acid. A desirable antacid controls acidity without making the stomach strongly alkaline.
- Aspirin inhibits platelet aggregation, whereas the action of antihistamines depends on which histamine-receptor type they block.

Step 1: (a) Metal hydroxides as antacids Sodium hydrogen carbonate is soluble and can make the stomach alkaline when used in excess; this can stimulate further acid secretion. Its reaction with acid also releases carbon dioxide:

$$\mathrm{NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2}.$$

Sparingly soluble metal hydroxides, such as magnesium hydroxide and aluminium hydroxide, neutralise excess acid without raising the pH above neutrality as readily. They therefore give better control of acidity. For example,

$$\mathrm{Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O}.$$

Step 2: (b) Role of aspirin Aspirin has an anti-blood-clotting action: it inhibits the aggregation of blood platelets. This reduces the formation of clots in coronary blood vessels. Since such a clot can

Quick Tip to Solve: For the antihistamine part, explicitly distinguish the allergy receptor H_1 from the gastric-acid receptor H_2.

obstruct the blood supply to the heart muscle, aspirin is used in the prevention of heart attacks in appropriate patients.

Step 3: (c) Receptor selectivity of antihistamines The usual antihistamines used against allergy block histamine at H_1 receptors. The receptors involved in stimulation of gastric acid secretion are a different type, namely H_2 receptors. Because drugs are selective for particular receptor structures, these antiallergic antihistamines do not block the gastric receptors and hence do not suppress acid secretion. Specific H_2-receptor antagonists are required for that action.

Step 4: Conclusion (a) Sparingly soluble metal hydroxides control excess acidity more effectively without readily making the stomach alkaline. (b) Aspirin reduces platelet aggregation and clot formation. (c) Antiallergic antihistamines act on H_1, whereas gastric acid secretion involves H_2 receptors.

Quick Tip to Solve: For the antihistamine part, explicitly distinguish the allergy receptor H_1 from the gastric-acid receptor H_2.

OR

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

(a) Tranquilizers

(b) Antibiotics

(c) Non-ionic detergents [3 marks]

Solution:

Concept:

- Drugs are classified by their biological action: tranquilizers act on the central nervous system, whereas antibiotics inhibit or destroy microorganisms.
- Detergents are classified by their hydrophilic groups. Non-ionic detergents contain polar groups but no ionic group in their molecular constitution.

Step 1: (a) Tranquilizers Tranquilizers are drugs used to treat stress and mild or severe mental disorders. They act on the central nervous system and can relieve anxiety or tension and produce a feeling of well-being. An example is diazepam, which is used to relieve anxiety. Thus the classification refers to the drug's effect on mental and nervous functions, rather than to an antibacterial or cleansing action.

Step 2: (b) Antibiotics Antibiotics are chemical substances produced by microorganisms, or their synthetic or semisynthetic counterparts, which in low concentrations inhibit the growth of or destroy other microorganisms by interfering with their metabolic processes. Penicillin is a suitable example; it acts against susceptible bacteria by interfering with bacterial cell-wall synthesis. An antibiotic may therefore be growth-inhibiting or microorganism-killing, depending on the substance and organism.

Step 3: (c) Non-ionic detergents Non-ionic detergents are cleansing agents whose molecules contain no ionic group. Their polar, non-ionic portions interact with water, while their long hydrocarbon portions interact with grease. An example is the condensation product of stearic acid and polyethylene

Quick Tip to Solve: Pair each definition immediately with one named example, and identify the absence of an ionic group when defining a non-ionic detergent.

glycol, with the general structure

$$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nH.$$

The long stearate chain is the hydrophobic part and the oxygen-containing polyethylene glycol portion is the hydrophilic part. No charged head group is needed for its cleansing action.

Step 4: Conclusion Suitable examples are: (a) diazepam, a tranquilizer; (b) penicillin, an antibiotic; and (c) the stearic acid-polyethylene glycol condensation product, a non-ionic detergent.

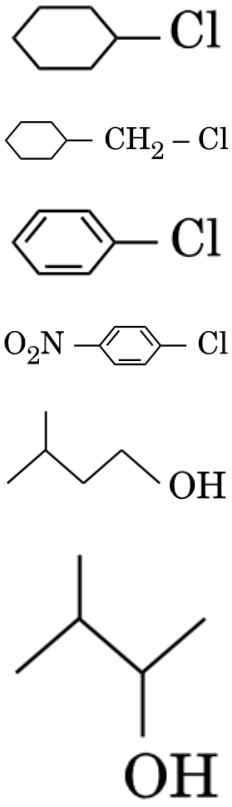
Quick Tip to Solve: Pair each definition immediately with one named example, and identify the absence of an ionic group when defining a non-ionic detergent.

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21. (a) Out of chlorocyclohexane ($C_6H_{11}-Cl$) and cyclohexylmethyl chloride ($C_6H_{11}-CH_2-Cl$), which one is more reactive towards S_N2 reaction and why?

(b) Out of C_6H_5-Cl and p-$O_2N-C_6H_4-Cl$, which one is more reactive towards nucleophilic substitution reaction and why?

(c) Out of $(CH_3)_2CH-CH_2-CH_2-OH$ and $(CH_3)_2CH-CH(OH)-CH_3$, which one is optically active and why? The printed structures are shown below in the order of parts (a), (b) and (c). [3 marks]



Solution:

Concept:

- An S_N2 reaction occurs by backside attack of a nucleophile. Less crowding around the carbon bearing the leaving group facilitates this attack.
- An electron-withdrawing nitro group at the ortho or para position activates an aryl halide towards nucleophilic substitution by stabilising the anionic intermediate.
- A tetrahedral carbon attached to four different groups is a chiral centre; a pure enantiomer of such a molecule can rotate plane-polarised light.

Step 1: (a) Compare the carbon bearing chlorine In chlorocyclohexane, the carbon bonded to chlorine is secondary and lies within the ring, so backside attack is sterically hindered. In $C_6H_{11}CH_2Cl$, chlorine is attached to a primary CH_2 carbon outside the ring. This carbon is less crowded and more accessible to a nucleophile. Therefore cyclohexylmethyl chloride undergoes S_N2 substitution more readily than chlorocyclohexane. The comparison is between two saturated alkyl chlorides, not between an aryl chloride and a benzyl chloride.

Step 2: (b) Examine the effect of the para nitro group In p-$O_2NC_6H_4Cl$, the strongly electron-withdrawing NO_2 group decreases electron density at the carbon bearing chlorine. On nucleophilic addition, the negative charge of the intermediate can be delocalised through the ring and onto the nitro group. This stabilisation facilitates substitution. Chlorobenzene has no such activating group; its carbon–chlorine bond also has partial double-bond character through resonance. Thus the para-nitro compound is more reactive towards nucleophilic substitution.

Step 3: (c) Identify a carbon with four different substituents The first alcohol, $(CH_3)_2CHCH_2CH_2OH$, has no chiral centre: its branched carbon bears two identical methyl groups and its other saturated carbons have repeated hydrogen substituents. In the second alcohol, $(CH_3)_2CHCH(OH)CH_3$, the carbon carrying OH is bonded to H, OH, CH_3 and $CH(CH_3)_2$, four different groups. Hence 3-methylbutan-2-ol is chiral and its individual enantiomers are optically active.

Step 4: Conclusion (a) $C_6H_{11}CH_2Cl$ is more reactive in S_N2. (b) p-$O_2NC_6H_4Cl$ is more reactive towards nucleophilic substitution. (c) The second alcohol, 3-methylbutan-2-ol, is optically active because its hydroxyl-bearing carbon is asymmetric.

Quick Tip to Solve: First locate the carbon bonded to chlorine for steric comparison; for chirality, list all four groups on the carbon bearing OH rather than counting branches alone.

22. What happens when

(a) Sodium phenoxide is treated with CH_3Cl?

(b) $CH_2{=}CH{-}CH_2{-}OH$ is oxidised by PCC?

(c) Phenol is treated with CH_3COCl/anhydrous $AlCl_3$?

Write chemical equations in support of your answer. [3 marks]

Solution:

Concept:

- Williamson ether synthesis couples an alkoxide or phenoxide ion with a primary alkyl halide through nucleophilic substitution.
- Pyridinium chlorochromate (PCC) is a mild oxidising agent that converts a primary alcohol into an aldehyde without further oxidation to a carboxylic acid under the usual anhydrous conditions.
- The hydroxyl group activates the phenol ring towards electrophilic substitution and directs an entering acyl group to the ortho and para positions.

Step 1: (a) Form anisole by Williamson synthesis The phenoxide oxygen acts as the nucleophile and displaces chloride from methyl chloride in an S_N2 reaction. Because the alkyl halide is methyl chloride, steric hindrance is minimal. The product is anisole (methoxybenzene), an ether:

$$C_6H_5ONa + CH_3Cl \longrightarrow C_6H_5OCH_3 + NaCl.$$

The new bond is between phenoxide oxygen and the methyl carbon; the aromatic carbon–oxygen bond remains intact.

Step 2: (b) Oxidise the primary allylic alcohol The $-CH_2OH$ group in prop-2-en-1-ol is oxidised to $-CHO$. PCC leaves the carbon–carbon double bond unchanged, so the product is prop-2-enal (acrolein):

$$CH_2{=}CHCH_2OH + [O] \xrightarrow{PCC} CH_2{=}CHCHO + H_2O.$$

Here $[O]$ denotes an oxygen equivalent supplied by the oxidant. The oxidation stops at the aldehyde rather than producing acrylic acid.

Step 3: (c) Acylate the phenol ring Acetyl chloride in the presence of anhydrous aluminium chloride introduces an acetyl group, $-COCH_3$, into the activated aromatic ring. The $-OH$ group directs substitution to the ortho and para positions, giving 2-hydroxyacetophenone and 4-hydroxyacetophenone. The para product is favoured because it has less steric crowding. The two alternative substitution equations are

$$C_6H_5OH + CH_3COCl \xrightarrow{\text{anhyd.}\ AlCl_3} \text{o-}HOC_6H_4COCH_3 + HCl,$$

$$C_6H_5OH + CH_3COCl \xrightarrow{\text{anhyd.}\ AlCl_3} \text{p-}HOC_6H_4COCH_3 + HCl.$$

Each equation represents formation of one positional isomer, not simultaneous formation of two products from one molecule.

Step 4: Conclusion (a) Anisole is formed. (b) The allylic alcohol yields prop-2-enal. (c) Phenol undergoes ring acetylation to give ortho- and para-hydroxyacetophenone, with the para isomer favoured.

Quick Tip to Solve: Track the reacting site: phenoxide oxygen gives an ether, PCC changes only the primary alcohol group to CHO, and acetyl chloride with aluminium chloride introduces COCH3 on the phenol ring.

23. (a) Give one chemical test as an evidence to show that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.

(b) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why? (Atomic no. of Ni = 28)

(c) Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (i) strong field ligand, and (ii) weak field ligand. (Atomic no. of Fe = 26) [3 marks]

Solution:

Concept:

- Ionisation isomers exchange a coordinated anion and a counter-ion. Free counter-ions can be identified by precipitation tests.
- Paramagnetism requires unpaired electrons. Count d electrons after finding the metal oxidation state.
- An octahedral field splits the d orbitals into lower t_{2g} and higher e_g sets. The splitting energy Δ_o relative to pairing energy P determines spin state.

Step 1: (a) Test for free sulphate ions Add aqueous barium chloride to separate aqueous solutions. $[Co(NH_3)_5Cl]SO_4$ releases free $SO_4{}^{2-}$ ions, so it gives a white precipitate of barium sulphate:

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

In $[Co(NH_3)_5(SO_4)]Cl$, sulphate is inside the coordination sphere and is not released as a free ion in this test; no immediate barium sulphate precipitate forms. These different free ions establish ionisation isomerism.

Step 2: (b) Count the d electrons in each nickel complex In $[NiCl_4]^{2-}$, let nickel have oxidation state x. Then $x + 4(-1) = -2$, so $x = +2$. Nickel(II) has configuration $3d^8$. Weak-field chloride gives two unpaired electrons (paramagnetic), with occupancy $e^4t_2^4$. In $Ni(CO)_4$, carbon monoxide is neutral, so nickel is in oxidation state zero. Strong-field CO causes pairing and redistribution to give a filled $3d^{10}$ set. All electrons are paired, so it is diamagnetic.

Step 3: (c) Fill the octahedral levels for iron(III) Iron(III) has $3d^5$ configuration after removing two 4s electrons and one 3d electron from neutral iron. With a strong-field ligand, $\Delta_o > P$, so electrons pair in the lower set before occupying the upper set:

$$(t_{2g})^5(e_g)^0 \quad \text{(low spin, one unpaired electron)}.$$

With a weak-field ligand, $\Delta_o < P$, so electrons occupy all five orbitals singly before pairing:

$$(t_{2g})^3(e_g)^2 \quad \text{(high spin, five unpaired electrons)}.$$

Step 4: Conclusion (a) Free sulphate gives white $BaSO_4$ only in the first salt. (b) The chloride complex has two unpaired electrons; the carbonyl has none. (c) Strong field: $t_{2g}^5e_g^0$; weak field: $t_{2g}^3e_g^2$.

Quick Tip to Solve: For magnetic comparisons, find the oxidation state before the d count: Ni(II) is d8, Ni(0) in its carbonyl is d10, and Fe(III) is d5 before octahedral splitting.

24. Define the following terms with a suitable example of each:

(a) Tertiary structure of protein

(b) Essential amino acids

(c) Disaccharides [3 marks]

Solution:

Concept:

- A protein's structure describes the arrangement of its polypeptide chain; tertiary structure is the overall three-dimensional folding of a single chain.
- Essential amino acids are required by the body but must be supplied in the diet. Disaccharides are carbohydrates which yield two monosaccharide units on hydrolysis.

Step 1: (a) Define tertiary structure and give an example The tertiary structure of a protein is the overall three-dimensional shape produced by further folding and coiling of its polypeptide chain, including the arrangement of its secondary structural regions in space. It is stabilised by interactions between side chains, such as hydrogen bonds, disulphide linkages, ionic attractions and hydrophobic interactions. For example, myoglobin has a compact globular tertiary structure formed by folding one polypeptide chain. This folding produces the specific shape needed for the protein's biological activity.

Step 2: (b) Define essential amino acids and give an example Essential amino acids are those amino acids which the human body cannot synthesise in adequate amounts and therefore must obtain from food. For example, valine is an essential amino acid; lysine and leucine are other examples. The word essential refers to the need for a dietary supply, rather than implying that other amino acids are unnecessary for making proteins.

Step 3: (c) Define disaccharides and give an example Disaccharides are carbohydrates which on hydrolysis give two monosaccharide units. The two units are joined through a glycosidic linkage formed by elimination of a water molecule. For example, sucrose is a disaccharide which hydrolyses to one molecule each of glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6.$$

Here the two products are glucose and fructose respectively. The monosaccharides may be identical, as in maltose, or different, as in sucrose.

Step 4: Conclusion Suitable examples are myoglobin for tertiary protein structure, valine for essential amino acids and sucrose for disaccharides.

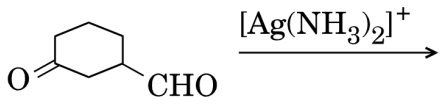
Quick Tip to Solve: Pair each definition with its key idea: overall folding, dietary supply, and two monosaccharide units on hydrolysis.

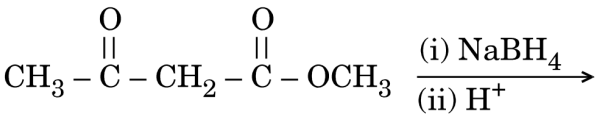
Section D (15 marks)

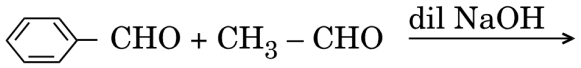
25(a). Predict the main product of the following reactions (i), (ii) and (iii), shown in the first figure below.

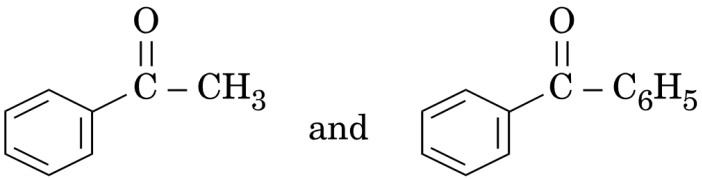
(b) Give a simple chemical test to distinguish between the two compounds shown in the second figure below.

(c) Why is alpha (α) hydrogen of carbonyl compounds acidic in nature? [5 marks]

(i) 

(ii) 

(iii) 



Solution:

Concept:

- Tollens' reagent oxidises an aldehyde group to a carboxylate group in alkaline solution, while an ordinary ketone group remains unchanged. Acidification converts the carboxylate into the corresponding carboxylic acid.
- $NaBH_4$ reduces ketones to secondary alcohols but normally leaves an ester group unchanged. Cross aldol reaction involves an enolate donor and a carbonyl acceptor.
- A methyl ketone, $RCOCH_3$, gives the iodoform test. Acidity of an α-hydrogen follows from resonance stabilisation of the enolate formed on its removal.

Step 1: (a)(i) Oxidise only the aldehyde group The printed substrate is a cyclohexanone ring bearing a formyl group at the third ring carbon, namely 3-oxocyclohexanecarbaldehyde. Tollens' reagent oxidises its $-CHO$ group to $-COO^-$, depositing metallic silver, while the ketonic carbonyl within the ring is retained. Thus the product in the alkaline reaction medium is 3-oxocyclohexanecarboxylate; after acidification it is 3-oxocyclohexanecarboxylic acid. The selective oxidation is represented by

$$RCHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow RCOO^- + 2\,Ag + 4\,NH_3 + 2\,H_2O,$$

where R denotes the unchanged 3-oxocyclohexyl group. The ring ketone is not reduced or oxidised by this test.

Step 2: (a)(ii) Reduce the ketone without reducing the ester The starting compound contains a

Quick Tip to Solve: Check each functional group separately: Tollens' reagent selects the aldehyde, borohydride selects the ketone, and the iodoform test selects the methyl ketone.

ketone group and an ester group. Sodium borohydride supplies hydride to the ketonic carbonyl; the acid work-up protonates the resulting alkoxide. The ester group is retained:

$$CH_3COCH_2COOCH_3 \xrightarrow[(ii)\,H^+]{(i)\,NaBH_4} CH_3CH(OH)CH_2COOCH_3.$$

The product is methyl 3-hydroxybutanoate. Formation of a secondary alcohol at the ketone carbon, rather than complete reduction of both carbonyl groups, is the key selectivity here.

Step 3: (a)(iii) Carry out the crossed aldol reaction Benzaldehyde has no α-hydrogen, so acetaldehyde provides the enolate. This attacks the benzaldehyde carbonyl and, after protonation, gives the crossed aldol $C_6H_5CH(OH)CH_2CHO$. Loss of water gives the conjugated main condensation product, cinnamaldehyde (3-phenylprop-2-enal):

$$C_6H_5CHO + CH_3CHO \xrightarrow{dil\cdot\,NaOH} C_6H_5CH(OH)CH_2CHO$$
$$\xrightarrow{-H_2O} C_6H_5CH{=}CHCHO.$$

The first product is the β-hydroxy aldehyde; dehydration is favoured by conjugation of the double bond with the phenyl ring and aldehyde group.

Step 4: (b) Apply the iodoform test Warm each compound separately with iodine and aqueous sodium hydroxide. Acetophenone, $C_6H_5COCH_3$, contains the methyl-ketone group and produces a yellow precipitate of iodoform, CHI_3:

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

Benzophenone, $C_6H_5COC_6H_5$, lacks the $-COCH_3$ group and does not produce the yellow precipitate. This positive versus negative observation distinguishes the two ketones.

Step 5: (c) Explain the acidity of alpha hydrogen Removal of a hydrogen from the carbon adjacent to the carbonyl group forms an enolate ion. Its negative charge is delocalised between the α-carbon and the electronegative oxygen:

$$RCOCH_2^- \longleftrightarrow RC(O^-){=}CH_2.$$

The electron-withdrawing inductive effect of the carbonyl group also assists removal of the proton. Resonance stabilisation of the conjugate base makes an α-hydrogen more acidic than a hydrogen in an ordinary alkane. A hydrogen on a remote carbon cannot produce this same carbonyl-stabilised enolate.

Step 6: Conclusion (a) The products are the 3-oxocyclohexanecarboxylate (acid on acidification), $CH_3CH(OH)CH_2COOCH_3$, and cinnamaldehyde via the crossed aldol. (b) Only acetophenone gives yellow iodoform. (c) α-Hydrogen is acidic because its removal gives a resonance-stabilised enolate ion.

Quick Tip to Solve: Check each functional group separately: Tollens' reagent selects the aldehyde, borohydride selects the ketone, and the iodoform test selects the methyl ketone.

OR

25(b). **(a) Write the main product formed when propanal reacts with the following reagents:**
(i) 2 moles of CH_3OH in presence of dry HCl
(ii) Dilute NaOH
(iii) H_2N-NH_2 followed by heating with KOH in ethylene glycol
(b) Arrange the following compounds in increasing order of their property as indicated:
(i) $F-CH_2COOH$, O_2N-CH_2COOH, CH_3COOH, HCOOH — acid character
(ii) Acetone, Acetaldehyde, Benzaldehyde, Acetophenone — reactivity towards addition of HCN

[5 marks]

Solution:

Concept:

- An aldehyde reacts with two molecules of an alcohol in dry acid to form an acetal. Dilute alkali causes aldol addition when an alpha hydrogen is present; Wolff-Kishner reduction replaces the carbonyl oxygen by two hydrogen atoms.
- Acid strength increases when electron-withdrawing groups stabilise the carboxylate ion. Nucleophilic addition of HCN is favoured by a more electrophilic, less hindered carbonyl carbon; conjugation with a phenyl ring lowers its electrophilicity.

Step 1: (a)(i) Acetal formation Propanal first forms a hemiacetal with methanol; further reaction with methanol in the presence of dry HCl gives the acetal, 1,1-dimethoxypropane:

$$CH_3CH_2CHO + 2CH_3OH \xrightarrow{\text{dry HCl}} CH_3CH_2CH(OCH_3)_2 + H_2O.$$

Both methoxy groups are attached to the original carbonyl carbon.

Step 2: (a)(ii) Aldol addition Propanal has alpha hydrogen atoms. In dilute NaOH, its enolate attacks the carbonyl carbon of another propanal molecule and forms the beta-hydroxy aldehyde, 3-hydroxy-2-methylpentanal:

$$2CH_3CH_2CHO \xrightarrow{\text{dil. NaOH}} CH_3CH_2CH(OH)CH(CH_3)CHO.$$

The question specifies dilute alkali without subsequent heating, so the main product is the aldol addition product; dehydration to an unsaturated aldehyde is not required here.

Step 3: (a)(iii) Wolff-Kishner reduction Hydrazine first forms the hydrazone. Heating it with KOH in ethylene glycol reduces the carbonyl group to a methylene group, giving propane:

$$CH_3CH_2CHO + H_2NNH_2 \longrightarrow CH_3CH_2CH{=}NNH_2 + H_2O,$$
$$CH_3CH_2CH{=}NNH_2 \xrightarrow[\text{ethylene glycol}]{\text{KOH, }\Delta} CH_3CH_2CH_3 + N_2.$$

Step 4: (b)(i) Increasing acid character The order is

$$CH_3COOH < HCOOH < FCH_2COOH < O_2NCH_2COOH.$$

Quick Tip to Solve: For propanal's aldol product, retain one terminal CHO and put the new OH on the beta carbon; do not dehydrate unless heating is specified.

The methyl group's electron-releasing inductive effect destabilises the acetate ion relative to formate, so acetic acid is weaker than formic acid. Fluorine and the nitro group withdraw electron density through sigma bonds and stabilise the conjugate base. The stronger electron-withdrawing effect of the nitro group makes nitroacetic acid the strongest of these acids.

Step 5: (b)(ii) Increasing reactivity towards HCN The required order is

$$\text{Acetophenone} < \text{Benzaldehyde} < \text{Acetone} < \text{Acetaldehyde}.$$

Cyanide attacks the electrophilic carbonyl carbon. Phenyl conjugation reduces the positive character of this carbon, lowering the reactivity of aromatic carbonyl compounds. The additional methyl group and greater crowding make acetophenone less reactive than benzaldehyde. Among the aliphatic compounds, acetaldehyde has only one electron-releasing alkyl group and less steric hindrance than acetone, so it reacts most readily.

Step 6: Conclusion (a) The products are (i) $CH_3CH_2CH(OCH_3)_2$, (ii) $CH_3CH_2CH(OH)CH(CH_3)CHO$, and (iii) propane. (b) The increasing orders are (i) acetic acid $<$ formic acid $<$ fluoroacetic acid $<$ nitroacetic acid; (ii) acetophenone $<$ benzaldehyde $<$ acetone $<$ acetaldehyde.

Quick Tip to Solve: For propanal's aldol product, retain one terminal CHO and put the new OH on the beta carbon; do not dehydrate unless heating is specified.

26(a). Account for the following:

(i) Manganese shows maximum number of oxidation states in 3d series.

(ii) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(iii) Ti^{4+} is colourless whereas V^{4+} is coloured in an aqueous solution.

(b) Write the chemical equations for the preparation of $KMnO_4$ from MnO_2. Why does purple colour of acidified permanganate solution decolourise when it oxidises Fe^{2+} to Fe^{3+}? [5 marks]

Solution:

Concept:

- The similar energies of the $3d$ and $4s$ orbitals permit transition elements to use different numbers of valence electrons in bonding. Half-filled d^5 and appropriate d^3 configurations confer extra stability.
- A positive standard reduction potential indicates a favourable reduction under standard conditions. Colour in many aqueous transition-metal ions arises from visible-light absorption during transitions between ligand-field-split d orbitals.
- Manganese dioxide is oxidised in alkaline medium to manganate(VI), then to permanganate(VII). In acid, permanganate gains five electrons to become Mn^{2+}.

Step 1: (a)(i) Oxidation states of manganese Manganese has the ground-state configuration $[Ar]\,3d^5 4s^2$. Its two $4s$ and five $3d$ electrons have sufficiently similar energies to participate in bonding. Consequently, different numbers of these seven valence electrons can be involved, giving the large range of oxidation states from $+2$ to $+7$. Thus manganese exhibits the maximum number of oxidation states in the first transition series.

Quick Tip to Solve: Track manganese's oxidation states as $+4$ to $+6$ to $+7$ in preparation, but $+7$ to $+2$ in acidic titration; one permanganate oxidises five ferrous ions.

Step 2: (a)(ii) Comparison of standard reduction potentials The relevant changes are

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

Reduction of $\mathrm{Mn^{3+}}$ gives the particularly stable half-filled $3d^5$ configuration of $\mathrm{Mn^{2+}}$, and is strongly favoured. In contrast, $\mathrm{Cr^{3+}}$ itself has a stable $3d^3$ configuration (t_{2g}^3 in an octahedral aqueous complex), which is disturbed on reduction to $\mathrm{Cr^{2+}}$. Hence $E^\circ(\mathrm{Mn^{3+}}/\mathrm{Mn^{2+}})$ is much more positive than $E^\circ(\mathrm{Cr^{3+}}/\mathrm{Cr^{2+}})$.

Step 3: (a)(iii) Colour of the aqueous ions Titanium has configuration $[\mathrm{Ar}]3d^2 4s^2$, so $\mathrm{Ti^{4+}}$ is $3d^0$. It has no d electron to undergo a d-d transition and its aqueous solution is colourless. Vanadium has configuration $[\mathrm{Ar}]3d^3 4s^2$, so $\mathrm{V^{4+}}$ is $3d^1$. Its d electron can absorb visible light and move between the split d levels in the aqueous complex, making the solution coloured.

Step 4: (b) Preparation of potassium permanganate Fuse manganese dioxide with KOH in the presence of oxygen. Green potassium manganate forms:

$$2\mathrm{MnO_2} + 4\mathrm{KOH} + \mathrm{O_2} \xrightarrow{\Delta} 2\mathrm{K_2MnO_4} + 2\mathrm{H_2O}.$$

Oxidise the manganate solution electrolytically to purple permanganate. At the anode,

$$\mathrm{MnO_4^{2-}} \longrightarrow \mathrm{MnO_4^-} + \mathrm{e^-}.$$

Including the cathodic evolution of hydrogen, the overall chemical equation is

$$2\mathrm{K_2MnO_4} + 2\mathrm{H_2O} \xrightarrow{\text{electrolysis}} 2\mathrm{KMnO_4} + 2\mathrm{KOH} + \mathrm{H_2}.$$

Manganese thus changes successively from $+4$ to $+6$ to $+7$.

Step 5: (b) Decolourisation during oxidation of ferrous ions In acidified solution, purple $\mathrm{MnO_4^-}$ oxidises $\mathrm{Fe^{2+}}$ to $\mathrm{Fe^{3+}}$, while it is reduced to $\mathrm{Mn^{2+}}$:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5\mathrm{Fe^{2+}} \longrightarrow \mathrm{Mn^{2+}} + 5\mathrm{Fe^{3+}} + 4\mathrm{H_2O}.$$

The $\mathrm{Mn^{2+}}$ ions are very pale pink and appear practically colourless in dilute solution. Therefore, the purple permanganate colour disappears as long as sufficient $\mathrm{Fe^{2+}}$ remains to consume the added permanganate. After all the ferrous ions are oxidised, excess permanganate gives a persistent faint pink colour.

Step 6: Conclusion Manganese's seven available valence electrons account for its wide oxidation-state range; the stability of $\mathrm{Mn^{2+}}$ and $\mathrm{Cr^{3+}}$ explains the potential comparison. $\mathrm{Ti^{4+}}$ is d^0, whereas $\mathrm{V^{4+}}$ is d^1. Alkaline oxidation followed by electrolytic oxidation produces $\mathrm{KMnO_4}$; its purple colour vanishes on reduction to $\mathrm{Mn^{2+}}$ during ferrous-ion oxidation.

Quick Tip to Solve: Track manganese's oxidation states as $+4$ to $+6$ to $+7$ in preparation, but $+7$ to $+2$ in acidic titration; one permanganate oxidises five ferrous ions.

OR

26(b). (a) Write one difference between transition elements and p-block elements with reference to variability of oxidation states.

(b) Why do transition metals exhibit higher enthalpies of atomization?

(c) Name an element of lanthanoid series which is well known to shown +4 oxidation state. Is it a strong oxidising agent or reducing agent?

(d) What is lanthanoid contraction? Write its one consequence.

(e) Write the ionic equation showing the oxidation of Fe(II) salt by acidified dichromate solution.

[5 marks]

Solution:

Concept:

- Transition elements can use both $(n-1)d$ and ns electrons in bonding, whereas the common oxidation states of p-block elements reflect the participation of ns and np electrons.
- Strong metallic bonding gives a high enthalpy of atomization, the enthalpy needed to form gaseous atoms from the solid metal.
- Poor shielding by $4f$ electrons produces lanthanoid contraction. Redox equations are balanced by conserving atoms and charge.

Step 1: (a) Compare variable oxidation states The oxidation states of transition elements commonly differ by one unit, for example iron exhibits $+2$ and $+3$. This is because the energies of the outer ns and inner $(n-1)d$ orbitals are comparable, allowing different numbers of electrons to participate in bonding. In contrast, the common variable oxidation states of p-block elements usually differ by two units, for example tin shows $+2$ and $+4$, corresponding to retention or participation of the ns^2 electron pair.

Step 2: (b) Explain the high enthalpy of atomization Transition metals have a large number of valence electrons, including unpaired d electrons, available for strong interatomic metallic bonding. Considerable energy is therefore required to separate the solid into individual gaseous atoms, so their enthalpies of atomization are generally high.

Step 3: (c) Identify the lanthanoid and its redox behaviour Cerium is well known for its $+4$ oxidation state. The Ce^{4+} ion is a strong oxidising agent because it readily accepts an electron to form the more stable $+3$ state:

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}.$$

In doing so, it oxidises the other reactant while itself being reduced.

Step 4: (d) Define lanthanoid contraction and give a consequence Lanthanoid contraction is the gradual decrease in atomic size and in the ionic radii of Ln^{3+} ions with increasing atomic number across the lanthanoid series. The added $4f$ electrons shield the increasing nuclear charge poorly, so the effective nuclear attraction increases. One consequence is that zirconium and hafnium have nearly equal atomic radii and consequently very similar chemical properties: the contraction largely offsets the size increase expected on entering the next transition series.

Step 5: (e) Balance oxidation by acidified dichromate Iron(II) loses one electron per ion, while one

Quick Tip to Solve: For dichromate in acid, remember the ratio: one dichromate ion consumes fourteen hydrogen ions and oxidises six iron(II) ions.

dichromate ion gains six electrons in acidic solution. The half-reactions are

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

Multiply the iron half-reaction by six and add. The resulting ionic equation is

$$\boxed{\mathrm{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}}}.$$

Both sides contain two Cr, seven O, fourteen H and six Fe atoms; the total charge on each side is $+24$.

Step 6: Conclusion Transition-element oxidation states commonly differ by one, while common p-block oxidation states differ by two. Strong metallic bonding explains the high atomization enthalpies. Cerium exhibits $+4$, and $\mathrm{Ce^{4+}}$ is a strong oxidising agent. Lanthanoid contraction explains the similar sizes of Zr and Hf. Acidified dichromate oxidises six $\mathrm{Fe^{2+}}$ ions per dichromate ion, as shown above.

Quick Tip to Solve: For dichromate in acid, remember the ratio: one dichromate ion consumes fourteen hydrogen ions and oxidises six iron(II) ions.

27(a). Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction?

(b) A first order reaction is 50% complete in 25 minutes. Calculate the time for 80% completion of the reaction. [5 marks]

Solution:

Concept:

- For the experimental rate law $r = k[A]^m[B]^n$, the overall order is $m + n$; the exponents are determined experimentally.
- Molecularity counts reacting species in one elementary step. It is a positive integer and is not defined for an overall complex reaction.
- For a first order reaction, $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t}$ and $t_{1/2} = \dfrac{0.693}{k}$, where $[A]_0$ and $[A]_t$ are initial and remaining reactant concentrations.

Step 1: (a) Define order and distinguish it from molecularity The order of a reaction is the sum of the powers of the concentrations of reactants in its experimentally determined rate law. For example, if $r = k[A]^m[B]^n$, then the overall order is $m + n$. Order may be zero, fractional or integral; it cannot generally be inferred from the balanced overall chemical equation.

Molecularity is the number of reacting species, such as atoms, ions or molecules, that participate together in an elementary reaction step. It is always a positive integer. A complex reaction occurs through several elementary steps, so molecularity is specified for each individual step and has no meaning for the overall complex reaction. The overall reaction nevertheless has an experimentally measurable order, governed by its mechanism and kinetic conditions; it need not equal the sum of the stoichiometric coefficients in the overall equation.

Step 2: (b) Find the first order rate constant A reaction that is 50% complete has consumed half of

Quick Tip to Solve: Convert percent completion to percent remaining before using the logarithm: eighty percent completion means a concentration ratio of five, not a ratio of 1.25.

its initial reactant. Therefore the given time is the half-life:

$$t_{1/2} = 25\,\text{min}.$$

The first order half-life is independent of the initial concentration, hence

$$k = \frac{0.693}{25} = 0.02772\,\text{min}^{-1}.$$

Keeping minutes as the time unit ensures that the final time is obtained directly in minutes.

Step 3: Calculate the time for eighty percent completion At 80% completion, 20% of the original reactant remains. Thus $[A]_t = 0.20[A]_0$ and the concentration ratio is $[A]_0/[A]_t = 5$. Substitution in the integrated first order equation gives

$$\begin{aligned} t_{80} &= \frac{2.303}{k}\log 5 \\ &= \frac{2.303 \times 0.6990}{0.02772} \\ &\simeq 58.1\,\text{min}. \end{aligned}$$

Equivalently, $t_{80}/t_{1/2} = \log 5/\log 2 = 0.6990/0.3010$, which gives $t_{80} \simeq 58.06\,\text{min}$. This is between two half-lives ($50\,\text{min}$, 75% completion) and three half-lives ($75\,\text{min}$, 87.5% completion), as expected. It is the total time from the start of the reaction.

Step 4: Conclusion Order is the sum of the concentration exponents in the experimental rate law. Molecularity is defined only for an elementary step, so an overall complex reaction has an order but no overall molecularity. The time for 80% completion is $\boxed{58.1\,\text{min}}$, approximately.

Quick Tip to Solve: Convert percent completion to percent remaining before using the logarithm: eighty percent completion means a concentration ratio of five, not a ratio of 1.25.

OR

27(b). (a) The decomposition of a hydrocarbon has value of rate constant as $2.5 \times 10^4\ \text{s}^{-1}$ at 27°C. At what temperature would rate constant be $7.5 \times 10^4\ \text{s}^{-1}$ if energy of activation is 19.147×10^3 J mol^{-1}?

(b) Write a condition under which a bimolecular reaction is kinetically first order. Give an example of such a reaction.

(Given: log 2 = 0.3010, log 3 = 0.4771, log 5 = 0.6990) [5 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A is the pre-exponential factor, E_a is activation energy, R is the gas constant and T is absolute temperature.
- For two temperatures with the same activation energy and pre-exponential factor, $\log(k_2/k_1) =$

Quick Tip to Solve: First take the ratio of the rate constants: the common power of ten cancels, leaving 3. Use 300 K in the Arrhenius equation and convert to Celsius only after solving for the final temperature.

$\frac{E_a}{2.303R}(1/T_1 - 1/T_2)$, where log denotes the common logarithm.

- A reaction involving two reacting species can show pseudo-first-order kinetics when one reactant is in such large excess that its concentration remains effectively constant during the reaction.

Step 1: (a) Express the given quantities in consistent units The initial absolute temperature is $T_1 = 27 + 273 = 300\,\text{K}$. The two rate constants are $k_1 = 2.5 \times 10^4\,\text{s}^{-1}$ and $k_2 = 7.5 \times 10^4\,\text{s}^{-1}$. Thus their ratio is

$$\frac{k_2}{k_1} = \frac{7.5 \times 10^4}{2.5 \times 10^4} = 3, \qquad \log \frac{k_2}{k_1} = 0.4771.$$

Use $E_a = 19.147 \times 10^3\,\text{J mol}^{-1}$ and $R = 8.314\,\text{J mol}^{-1}\text{K}^{-1}$, so that the energy units cancel consistently.

Step 2: (a) Apply the two-temperature Arrhenius equation Substitution gives

$$0.4771 = \frac{19.147 \times 10^3}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{T_2}\right).$$

The factor multiplying the brackets is approximately $1000\,\text{K}$. Hence

$$\begin{aligned} \frac{1}{300} - \frac{1}{T_2} &= 4.771 \times 10^{-4}\,\text{K}^{-1}, \\ \frac{1}{T_2} &= 0.0033333 - 0.0004771 \\ &= 0.0028562\,\text{K}^{-1}, \\ T_2 &\approx 350.1\,\text{K}. \end{aligned}$$

This is approximately $77.1\,^\circ\text{C}$. Since the activation energy is positive, increasing temperature increases the rate constant; the computed temperature is therefore consistent with the required threefold increase.

Step 3: (b) State the condition and illustrate the effective rate law Keep one reactant in very large excess so that the amount consumed is negligible compared with the amount initially present. For a rate law $r = k[A][B]$, effectively constant $[B]$ gives $r = k'[A]$, where $k' = k[B]$. The observed kinetics are then first order in A, although both species participate in the reaction. A standard example is the acid-catalysed hydrolysis of ethyl acetate in excess water:

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}.$$

With water in large excess and the acid catalyst concentration held fixed, their contributions are incorporated into the observed constant. The rate becomes $r = k'[\text{CH}_3\text{COOC}_2\text{H}_5]$. This behaviour is called a pseudo-first-order reaction.

Step 4: Conclusion (a) The required temperature is approximately $350\,\text{K}$, or $77\,^\circ\text{C}$. (b) A bimolecular reaction shows pseudo-first-order kinetics when one reactant is in large excess and remains effectively constant in concentration; hydrolysis of ethyl acetate in excess water at fixed acid concentration is an example.

Quick Tip to Solve: First take the ratio of the rate constants: the common power of ten cancels, leaving 3. Use 300 K in the Arrhenius equation and convert to Celsius only after solving for the final temperature.