

CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-1-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) All questions are compulsory.
- (ii) Section A : Q. no. 1 to 5 are very short-answer questions and carry 1 mark each.
- (iii) Section B : Q. no. 6 to 12 are short-answer questions and carry 2 marks each.
- (iv) Section C : Q. no. 13 to 24 are also short-answer questions and carry 3 marks each.
- (v) Section D : Q. no. 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 log tables if necessary. Use of calculators is not allowed.

Section A (5 marks)

1. Arrange the following in decreasing order of solubility in water:

$(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{NH}$, CH_3NH_2

[1 mark]

Solution:

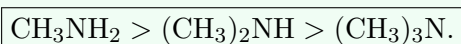
Concept:

- Lower aliphatic amines dissolve in water because their nitrogen atoms can form hydrogen bonds with water molecules.
- The polar amino group favours hydration, whereas an alkyl group is hydrophobic; more alkyl groups make hydration less favourable.

Step 1: Compare the amino groups Methylamine, CH_3NH_2 , has two N–H bonds; dimethylamine, $(\text{CH}_3)_2\text{NH}$, has one; trimethylamine, $(\text{CH}_3)_3\text{N}$, has none. All three can accept hydrogen bonds through the nitrogen lone pair, but their ability to donate them decreases in this order.

Step 2: Compare the hydrocarbon portions The number of methyl groups increases from one to three. The increasing nonpolar portion opposes dissolution in water. Thus, among these three amines, methylamine is hydrated most favourably and trimethylamine least favourably.

Step 3: Conclusion The decreasing order of solubility in water is



Quick Tip to Solve: For these methylamines, compare both the N–H bonds and the increasing hydrophobic methyl groups.

2. What type of stoichiometric defect is shown by ZnS and why?

[1 mark]

Solution:

Concept:

- A stoichiometric defect preserves the chemical composition and electrical neutrality of an ionic crystal.
- In a Frenkel defect, a small ion leaves its normal lattice site and occupies an interstitial site, creating a vacancy–interstitial pair.

Step 1: Identify the relative ion sizes In ZnS, the Zn^{2+} cation is much smaller than the S^{2-} anion. This large size difference allows a zinc ion to occupy an interstitial position in the crystal.

Step 2: Explain the displacement A Zn^{2+} ion can leave its regular site and move into an interstitial site. No ion leaves the crystal, so the numbers of zinc and sulphide ions remain unchanged. Hence the 1 : 1 composition, electrical neutrality and density are preserved.

Step 3: Conclusion ZnS shows a Frenkel defect because its small Zn^{2+} ions can move into interstitial sites, leaving vacancies at their original positions.

Quick Tip to Solve: Link Frenkel defects to a small cation entering an interstitial site; the displaced ion stays inside the crystal.

3. Write one stereochemical difference between S_N1 and S_N2 reactions.

[1 mark]

Solution:

Concept:

- Stereochemistry describes the spatial arrangement of groups around a reacting centre.
- For substitution at a chiral carbon, the intermediate or direction of attack determines whether configuration is retained, inverted or racemised.

Step 1: Consider the S_N1 pathway An S_N1 reaction proceeds through a planar carbocation intermediate. The nucleophile can attack either face of this intermediate, producing both configurations. A chiral substrate therefore undergoes racemisation, often with some excess of inversion.

Step 2: Consider the S_N2 pathway An S_N2 reaction occurs in one concerted step. The nucleophile attacks from the side opposite the leaving group, so the spatial arrangement at the reacting chiral centre is inverted. This is called Walden inversion.

Step 3: Conclusion At a chiral reacting centre, S_N1 gives racemisation, whereas S_N2 gives inversion of configuration.

Quick Tip to Solve: Associate a planar carbocation with attack on both faces, and backside attack with inversion.

4(a). Why are medicines more effective in colloidal state?

[1 mark]

Solution:

Concept:

- Colloidal particles are very small and have a large surface area per unit mass.
- A larger exposed surface increases contact between a dispersed medicinal substance and the medium in which it acts.

Step 1: Relate particle size to surface area When a medicinal substance is divided into colloidal particles, a given quantity presents a much larger total surface area than it does as a few large particles. More of the substance is therefore exposed to the surrounding medium.

Step 2: Connect surface area with effectiveness The increased surface available for contact facilitates the absorption and assimilation of the medicine by the body. Consequently, the medicinal substance can act more effectively in the colloidal state.

Step 3: Conclusion Medicines are more effective in the colloidal state because their large surface area facilitates absorption and assimilation by the body.

Quick Tip to Solve: For a colloidal medicine, connect smaller particles to larger surface area and hence easier absorption.

4(b). What is the difference between an emulsion and a gel?

[1 mark]

Solution:

Concept:

- A colloid is classified by the physical states of its dispersed phase and dispersion medium.
- The dispersed phase is distributed through the continuous dispersion medium; the two roles must be stated in the correct order.

Step 1: Identify an emulsion In an emulsion, both the dispersed phase and the dispersion medium are liquids. Tiny droplets of one liquid are dispersed in another liquid with which it is immiscible. Milk is a familiar example of an emulsion.

Step 2: Identify a gel In a gel, the dispersed phase is a liquid and the dispersion medium is a solid. The liquid is held within the solid framework, giving the system a semisolid character. Jelly is a familiar example of a gel.

Step 3: Conclusion An emulsion is liquid in liquid, whereas a gel is liquid in solid. Thus, their dispersion media differ.

Quick Tip to Solve: Write dispersed phase first and medium second: emulsion = liquid/liquid; gel = liquid/solid.

5(a). What is the basic structural difference between glucose and fructose?

[1 mark]

Solution:

Concept:

- Glucose and fructose are monosaccharides with the molecular formula $C_6H_{12}O_6$.
- Their basic structural difference is identified from the carbonyl functional group in their open-chain forms.

Step 1: Identify the group in glucose Open-chain glucose has six carbon atoms and a terminal aldehyde group, $-CHO$, at carbon 1. It is therefore an aldohexose. Its open-chain structure may be written as $CHO - (CHOH)_4 - CH_2OH$.

Step 2: Identify the group in fructose Open-chain fructose also has six carbon atoms, but it contains a ketone group, $>C=O$, at carbon 2. It is therefore a ketohexose. Its open-chain structure is $CH_2OH - CO - (CHOH)_3 - CH_2OH$.

Step 3: Conclusion Glucose is an aldohexose, whereas fructose is a ketohexose. Their open-chain forms contain an aldehyde and a ketone group, respectively.

Quick Tip to Solve: Use the open-chain carbonyl group: glucose has terminal CHO ; fructose has $C=O$ at carbon 2.

5(b). Write the products obtained after hydrolysis of lactose.

[1 mark]

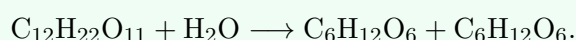
Solution:

Concept:

- Lactose is a disaccharide formed from two monosaccharide units joined through a glycosidic linkage.
- Hydrolysis uses water to break this linkage and releases the constituent monosaccharides.

Step 1: Identify the units in lactose Lactose contains one D-galactose unit and one D-glucose unit. A β -(1 $\rightarrow$ 4) glycosidic linkage joins the galactose unit to the glucose unit.

Step 2: Write the hydrolysis reaction On hydrolysis with dilute acid or the enzyme lactase, the glycosidic bond is cleaved:



The two monosaccharide products are D-galactose and D-glucose, obtained in a 1 : 1 molar ratio.

Step 3: Conclusion The products of lactose hydrolysis are D-galactose and D-glucose.

Quick Tip to Solve: Remember lactose as galactose plus glucose; do not confuse it with sucrose, which yields fructose.

Section B (14 marks)

6. When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (A). Compound (A) disproportionates in acidic solution to give purple compound (B). An alkaline solution of compound (B) oxidises KI to compound (C) whereas an acidified solution of compound (B) oxidises KI to (D). Identify (A), (B), (C), and (D).

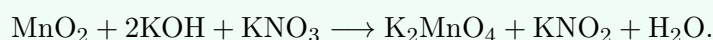
[2 marks]

Solution:

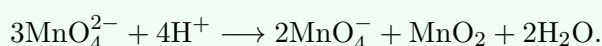
Concept:

- Fusion of manganese dioxide with an alkali and an oxidising agent converts manganese from oxidation state +4 to +6, producing green manganate ions, MnO_4^{2-} .
- Manganate disproportionates in acid to permanganate, MnO_4^- , and manganese dioxide. The product of iodide oxidation by permanganate depends on the medium.

Step 1: Identify the green and purple compounds The fusion reaction is



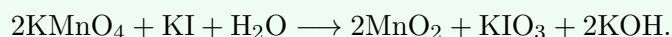
Thus the dark green compound (A) is potassium manganate. In acidic solution,



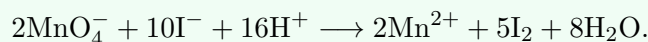
Quick Tip to Solve: Track the medium: alkaline permanganate gives iodate from KI , while acidified permanganate liberates iodine.

The purple compound (B) is potassium permanganate, KMnO_4 .

Step 2: Identify the iodide oxidation products In alkaline medium, iodide is oxidised to iodate:



Hence (C) is potassium iodate. In acidic medium, iodide is oxidised to iodine:



Here iodine changes from -1 to 0 , whereas in iodate it reaches $+5$.

Step 3: Conclusion (A) = K_2MnO_4 , potassium manganate; (B) = KMnO_4 , potassium permanganate; (C) = KIO_3 , potassium iodate; (D) = I_2 , iodine.

Quick Tip to Solve: Track the medium: alkaline permanganate gives iodate from KI, while acidified permanganate liberates iodine.

7. State Henry's law and write its two applications.

[2 marks]

Solution:

Concept:

- At constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas above the liquid.
- Henry's law is expressed as $p = K_H x$, where p is the gas's partial pressure, x its mole fraction in the solution, and K_H the Henry's law constant for that gas and solvent at the specified temperature.

Step 1: State the law in usable form Since $x = p/K_H$, increasing the gas pressure increases the amount dissolved when temperature is fixed. It is the partial pressure of the gas concerned that determines its solubility; for a gas mixture, the total pressure alone is insufficient.

Step 2: Give two applications **Carbonated beverages:** Soft drinks and soda water are bottled under high carbon dioxide pressure. This increases the solubility of CO_2 . When the bottle is opened, the pressure falls and the excess dissolved gas escapes as bubbles.

Deep-sea diving: At high underwater pressure, more nitrogen from breathing air dissolves in a diver's blood. Rapid ascent lowers the pressure and can release nitrogen bubbles, causing the bends. Helium-oxygen breathing mixtures reduce nitrogen uptake, and controlled ascent allows dissolved gas to leave gradually.

Step 3: Conclusion Henry's law is $p = K_H x$ at fixed temperature. Two applications are carbonation of beverages and the selection of breathing mixtures and controlled ascent procedures for deep-sea divers.

Quick Tip to Solve: Explain each application using the same chain: higher partial pressure means more dissolved gas; lowering it releases gas.

8(a). Write IUPAC name of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]$. Draw structures of geometrical isomers for this complex. [2 marks]

Solution:

Concept:

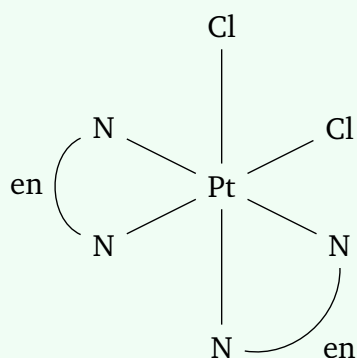
- Ethane-1,2-diamine, abbreviated en, is a neutral bidentate ligand: its two nitrogen donor atoms occupy two adjacent coordination sites. Each chlorido ligand carries charge -1 .
- The coordination number counts donor atoms. Two en ligands supply four donors and two chlorido ligands supply two more, giving six-coordinate, octahedral geometry. Two identical chlorido ligands can occupy adjacent (cis) or opposite (trans) sites.

Step 1: Determine the oxidation state and IUPAC name The printed complex is neutral. If the oxidation state of platinum is z , charge balance gives

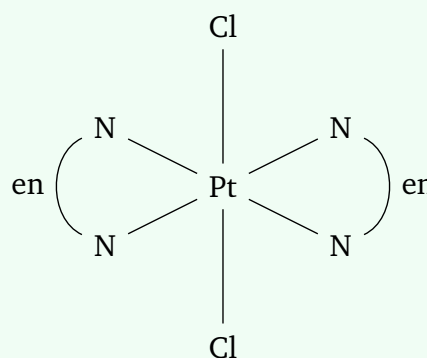
$$z + 2(0) + 2(-1) = 0, \quad z = +2.$$

Ligands are named alphabetically, ignoring multiplicative prefixes: chlorido precedes ethane-1,2-diamine. Since the latter ligand name already contains a numerical prefix, two such ligands are indicated by *bis*. The name is **dichloridobis(ethane-1,2-diamine)platinum(II)**.

Step 2: Construct the two geometrical isomers In the cis isomer the two Cl donors are adjacent, with $\angle \text{Cl} - \text{Pt} - \text{Cl} = 90^\circ$. In the trans isomer they are opposite, with $\angle \text{Cl} - \text{Pt} - \text{Cl} = 180^\circ$. In the structures below each curved connection labelled en joins the two nitrogen atoms of one chelating ligand; each such pair occupies adjacent octahedral positions. The four N donors belong to two $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ molecules.



cis: 90° between Cl ligands



trans: 180° between Cl ligands

Octahedral cis and trans structures; curved en links denote the two chelate ligands.

Step 3: Conclusion The complex is dichloridobis(ethane-1,2-diamine)platinum(II). Its two geometrical isomers are cis- $[\text{Pt}(\text{en})_2\text{Cl}_2]$ and trans- $[\text{Pt}(\text{en})_2\text{Cl}_2]$, as drawn.

Quick Tip to Solve: Count donor atoms before choosing geometry: two bidentate en ligands plus two chlorido ligands give six sites, not four.

8(b). Using IUPAC norms write the formulae for the following:

(i) Hexaamminecobalt(III) sulphate

(ii) Potassium trioxalatochromate(III)

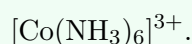
[2 marks]

Solution:

Concept:

- A coordination formula encloses the metal and its coordinated ligands within square brackets. Counterions outside the brackets balance the charge on the complex ion.
- Ammine NH_3 is neutral, oxalato $\text{C}_2\text{O}_4^{2-}$ carries charge -2 , and sulphate SO_4^{2-} also carries charge -2 . The Roman numeral specifies the metal's oxidation state.

Step 1: Write hexaamminecobalt(III) sulphate Hexaammine means six NH_3 ligands coordinated to cobalt. Cobalt(III) has oxidation state $+3$, so the complex ion is



Sulphate is SO_4^{2-} . Two complex cations supply charge $+6$ and three sulphate anions supply -6 , giving the neutral formula $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$.

Step 2: Write potassium trioxalatochromate(III) Three oxalato ligands surround chromium(III). The charge of this complex is

$$+3 + 3(-2) = -3.$$

Thus the anion is $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$. Three potassium ions, each carrying $+1$, are needed for electrical neutrality, so the compound is $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$.

Step 3: Conclusion (i) Hexaamminecobalt(III) sulphate: $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$.

(ii) Potassium trioxalatochromate(III): $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$.

Quick Tip to Solve: First calculate the charge inside each bracket; then choose counterion subscripts so that the total charge is zero.

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

(i) XeF_2 undergoes hydrolysis.

(ii) MnO_2 is heated with conc. HCl .

[2 marks]

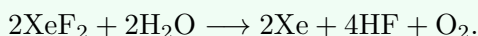
Solution:

Concept:

- Hydrolysis of xenon difluoride forms xenon, hydrogen fluoride and oxygen; the products must conserve each kind of atom.
- Manganese dioxide oxidises chloride ions of concentrated hydrochloric acid to chlorine, while manganese is reduced from $+4$ to $+2$.

Quick Tip to Solve: In the manganese reaction, reserve two chlorides for MnCl_2 and two for Cl_2 before balancing HCl and water.

Step 1: (i) Balance the hydrolysis of xenon difluoride Xenon difluoride reacts with water to liberate xenon and oxygen, with fluorine appearing as hydrogen fluoride:



There are two xenon atoms, four fluorine atoms, four hydrogen atoms and two oxygen atoms on each side. Thus oxygen is released as the diatomic molecule rather than as an oxide of xenon.

Step 2: (ii) Balance the reaction with concentrated hydrochloric acid On heating, the reaction is



Two chloride ions supply the two electrons accepted by manganese and form chlorine; the other two chloride ions form manganese(II) chloride. Four hydrogen ions combine with the two oxide oxygen atoms to give two water molecules.

Step 3: Conclusion (i) $2\text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2$.

(ii) $\text{MnO}_2 + 4\text{HCl} \xrightarrow{\Delta} \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$.

Quick Tip to Solve: In the manganese reaction, reserve two chlorides for MnCl_2 and two for Cl_2 before balancing HCl and water.

OR

9(b). Arrange the following in order of property indicated for each set:

(i) H_2O , H_2S , H_2Se , H_2Te — increasing acidic character

(ii) HF , HCl , HBr , HI — decreasing bond enthalpy

[2 marks]

Solution:

Concept:

- For group 16 hydrides, increasing central-atom size down the group lengthens and weakens the E – H bond, making proton release easier.
- Bond enthalpy is the energy needed to break a gaseous bond. The H – X bond becomes longer and weaker from fluorine to iodine.

Step 1: (i) Compare the acidic character of the hydrides The central atom increases in size in the sequence $\text{O} < \text{S} < \text{Se} < \text{Te}$. Its bond with hydrogen therefore becomes progressively weaker. The tendency of the hydride to release a proton increases down the group, so the required increasing order is

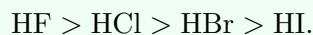


The bond-strength trend dominates this comparison; water is the least acidic member even though oxygen is the most electronegative atom in this set.

Step 2: (ii) Compare the hydrogen-halogen bond enthalpies Fluorine is the smallest halogen, and its bond with hydrogen is the shortest and strongest. Increasing halogen size from chlorine through

Quick Tip to Solve: Down each group the H-element bond weakens: acidity rises for group 16 hydrides, while bond enthalpy falls for hydrogen halides.

bromine to iodine produces a longer bond with less effective overlap. Hence, the decreasing order of bond enthalpy is



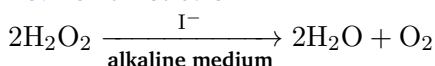
This is an order of energy required to break the bond, so the weakest bond must be placed last.

Step 3: Conclusion (i) Increasing acidic character: $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$.

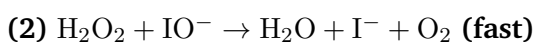
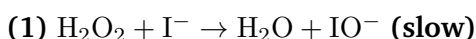
(ii) Decreasing bond enthalpy: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$.

Quick Tip to Solve: Down each group the H-element bond weakens: acidity rises for group 16 hydrides, while bond enthalpy falls for hydrogen halides.

10. For a reaction



the proposed mechanism is as given below:



(i) Write rate law for the reaction.

(ii) Write the overall order of reaction.

(iii) Out of steps (1) and (2), which one is rate determining step?

[2 marks]

Solution:

Concept:

- The slow elementary step controls the reaction rate. Its molecular reactants determine the concentration factors in the rate law.
- The overall order is the sum of the powers of reactant concentrations in the rate law; it need not equal the stoichiometric coefficient in the overall equation.

Step 1: (i) Write the rate law from the slow step Step (1), $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$, is slow and elementary. One molecule of hydrogen peroxide reacts with one iodide ion in this step. Consequently,

$$r = k[\text{H}_2\text{O}_2][\text{I}^-],$$

where k is the rate constant and square brackets denote molar concentration. The intermediate IO^- does not appear because it is a product of this slow step.

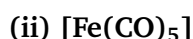
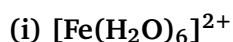
Step 2: (ii) Determine the overall order Each concentration in the rate expression has exponent one, so the reaction is first order in hydrogen peroxide and first order in iodide. Adding these powers gives the overall order, $1 + 1 = 2$. The iodide catalyst affects the rate even though it is regenerated and cancels from the overall chemical equation.

Step 3: (iii) Identify the rate-determining step Step (1) is the rate-determining step because it is slower than step (2). The rapid second step consumes the intermediate as it is formed; it cannot make the supply of that intermediate from step (1) faster.

Step 4: Conclusion (i) $r = k[\text{H}_2\text{O}_2][\text{I}^-]$; (ii) overall order = 2; (iii) step (1) is rate determining.

Quick Tip to Solve: Read the reactants of the labelled slow elementary step; do not infer the rate law from $2\text{H}_2\text{O}_2$ in the net equation.

11. Write the hybridization and magnetic character of following complexes:



(Atomic no. of Fe = 26)

[2 marks]

Solution:

Concept:

- Iron has ground-state configuration $[\text{Ar}]3d^64s^2$. Remove the $4s$ electrons first when forming Fe^{2+} .
- Weak-field water gives a high-spin complex, whereas strong-field carbon monoxide causes electron pairing. Unpaired electrons cause paramagnetism; fully paired electrons give diamagnetism.

Step 1: (i) Analyse the hexaaquairon(II) ion Each water ligand is neutral, so iron in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has oxidation state +2 and configuration $3d^6$. Water does not cause the pairing needed to vacate two inner $3d$ orbitals. Six outer orbitals, one $4s$, three $4p$ and two $4d$, therefore give sp^3d^2 hybridisation and an octahedral complex. The high-spin configuration has four unpaired electrons, so the complex is paramagnetic.

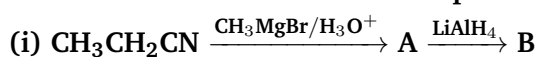
Step 2: (ii) Analyse iron pentacarbonyl CO is neutral, so iron in $[\text{Fe}(\text{CO})_5]$ has oxidation state zero. In the valence-bond description, the strong-field CO ligands pair the eight valence electrons into four $3d$ orbitals, leaving one $3d$ orbital available. This orbital, one $4s$ and three $4p$ orbitals form five dsp^3 hybrid orbitals with trigonal-bipyramidal geometry. All electrons are paired, so the complex is diamagnetic.

Step 3: Conclusion (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: sp^3d^2 , paramagnetic (four unpaired electrons).

(ii) $[\text{Fe}(\text{CO})_5]$: dsp^3 , diamagnetic (no unpaired electrons).

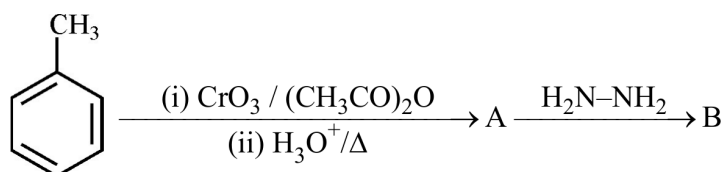
Quick Tip to Solve: Check the charge first: the aqua complex contains Fe(II), but neutral $\text{Fe}(\text{CO})_5$ contains Fe(0); then compare ligand field strengths.

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



(ii)

[2 marks]



Solution:

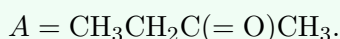
Concept:

- A nitrile reacts with a Grignard reagent to give an imine salt, which yields a ketone on acidic hydrolysis. Lithium aluminium hydride reduces a ketone to a secondary alcohol.
- Chromium trioxide in acetic anhydride gives a protected aldehyde from toluene; hydrolysis releases

Quick Tip to Solve: Hydrazine alone forms the hydrazone; look for base and heat before treating a carbonyl reaction as Wolff-Kishner reduction.

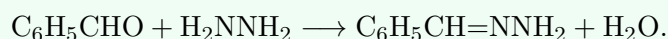
benzaldehyde. Hydrazine condenses with a carbonyl group to form a hydrazone.

Step 1: (i) Identify the ketone and its reduction product The methyl group of CH_3MgBr adds to the carbon atom of the nitrile group in $\text{CH}_3\text{CH}_2\text{CN}$. Acidic hydrolysis converts that group into a carbonyl, giving butan-2-one:



Reduction with LiAlH_4 , followed by work-up, converts the ketone carbonyl into $-\text{CH}(\text{OH})-$, without changing the four-carbon skeleton. The second compound is thus butan-2-ol, with structure $B = \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.

Step 2: (ii) Identify the aldehyde and its hydrazone Toluene is oxidised by CrO_3 in acetic anhydride to benzylidene diacetate, $\text{C}_6\text{H}_5\text{CH}(\text{OCOCH}_3)_2$. Acidic hydrolysis on heating releases benzaldehyde, so $A = \text{C}_6\text{H}_5\text{C}(=\text{O})\text{H}$. Its carbonyl group then condenses with the printed reagent, hydrazine:



Thus B is benzaldehyde hydrazone. The oxygen of the carbonyl is replaced by $=\text{N}-\text{NH}_2$; conversion to a methylene group would require the additional basic, heated Wolff-Kishner conditions.

Step 3: Conclusion (i) $A = \text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_3$, $B = \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.

(ii) $A = \text{C}_6\text{H}_5\text{C}(=\text{O})\text{H}$, $B = \text{C}_6\text{H}_5\text{CH}=\text{N}-\text{NH}_2$.

Quick Tip to Solve: Hydrazine alone forms the hydrazone; look for base and heat before treating a carbonyl reaction as Wolff-Kishner reduction.

Section C (36 marks)

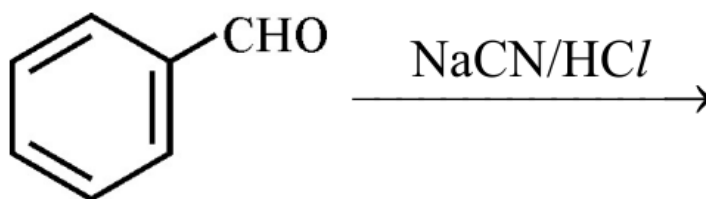
13(a). Complete the following reactions:

(i) The reaction shown in the figure.

(ii) $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Cd} + 2\text{CH}_3\text{COCl} \longrightarrow$

(iii) $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) Br}_2/\text{Red P}_4}$

[3 marks]



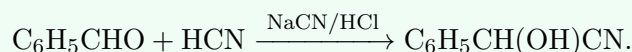
Solution:

Concept:

- Cyanide adds to the electrophilic carbonyl carbon of an aldehyde; protonation gives a cyanohydrin bearing both $-\text{OH}$ and $-\text{CN}$ on that carbon.
- A dialkylcadmium reagent converts an acyl chloride into a ketone. In the Hell-Volhard-Zelinsky reaction, bromine and red phosphorus replace an alpha hydrogen of a carboxylic acid by bromine.

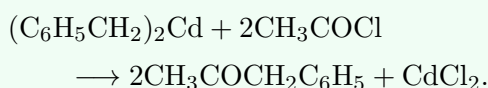
Quick Tip to Solve: Track the original carbonyl carbon: HCN adds across $\text{C}=\text{O}$, cadmium gives a ketone, and HVZ replaces only the alpha hydrogen.

Step 1: (i) Form the cyanohydrin of benzaldehyde The figure shows benzaldehyde with NaCN/HCl, which generates hydrogen cyanide. Cyanide attacks the carbonyl carbon and the resulting alkoxide is protonated:



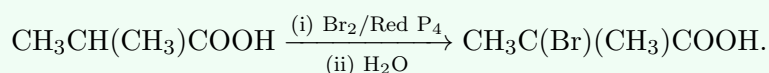
The product is benzaldehyde cyanohydrin, also called mandelonitrile. The phenyl group remains attached to the original carbonyl carbon.

Step 2: (ii) Replace the acyl chloride chlorine by a benzyl group Each benzyl group $\text{C}_6\text{H}_5\text{CH}_2-$ of dibenzylcadmium combines with the acetyl group of one acetyl chloride molecule:



This gives the ketone 1-phenylpropan-2-one; the carbonyl group is retained.

Step 3: (iii) Brominate the alpha carbon of the acid In 2-methylpropanoic acid, the carbon adjacent to $-\text{COOH}$ has one hydrogen. The given reagents replace this hydrogen by bromine, followed by hydrolysis to regenerate the acid:



Thus bromination occurs at the alpha carbon, not at either methyl group.

Step 4: Conclusion The products are (i) $\text{C}_6\text{H}_5\text{CH(OH)CN}$, (ii) two molecules of $\text{CH}_3\text{COCH}_2\text{C}_6\text{H}_5$ with CdCl_2 , and (iii) $(\text{CH}_3)_2\text{CBrCOOH}$, 2-bromo-2-methylpropanoic acid.

Quick Tip to Solve: Track the original carbonyl carbon: HCN adds across $\text{C}=\text{O}$, cadmium gives a ketone, and HVZ replaces only the alpha hydrogen.

OR

13(b). Write chemical equations for the following reactions:

(i) Propanone is treated with dilute Ba(OH)_2 .

(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl .

(iii) Benzoyl chloride is hydrogenated in presence of Pd/BaSO_4 .

[3 marks]

Solution:

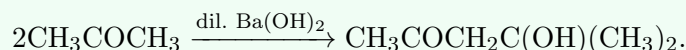
Concept:

- A ketone containing alpha hydrogen undergoes base-catalysed aldol addition to give a beta-hydroxy ketone.
- Clemmensen reduction, using Zn(Hg)/conc. HCl , converts a carbonyl group to $-\text{CH}_2-$. Rosenmund reduction uses $\text{H}_2/\text{Pd/BaSO}_4$ to convert an acyl chloride into an aldehyde.

Step 1: (i) Aldol addition of propanone Dilute Ba(OH)_2 removes an alpha hydrogen from propanone. The resulting enolate attacks a second propanone molecule, and protonation produces diacetone

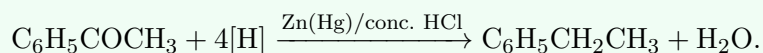
Quick Tip to Solve: Dilute base joins two propanone molecules; Zn(Hg)/HCl removes carbonyl oxygen, while Rosenmund reduction stops at an aldehyde.

alcohol, 4-hydroxy-4-methylpentan-2-one:



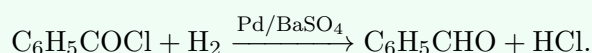
The product retains one carbonyl group and gains a beta-hydroxyl group. Heating can dehydrate it to mesityl oxide, but heating is not specified here, so the required product is the beta-hydroxy ketone.

Step 2: (ii) Clemmensen reduction of acetophenone Zinc amalgam and concentrated hydrochloric acid reduce the carbonyl group of acetophenone to a methylene group without changing the benzene ring:



The organic product is ethylbenzene. Here [H] denotes reducing hydrogen supplied by the reaction conditions.

Step 3: (iii) Rosenmund reduction of benzoyl chloride Hydrogen over palladium supported on barium sulphate selectively reduces the acyl chloride to benzaldehyde:



The moderated catalyst permits the reaction to stop at the aldehyde stage instead of further reduction to benzyl alcohol.

Step 4: Conclusion The products are (i) diacetone alcohol, $\text{CH}_3\text{COCH}_2\text{C(OH)(CH}_3)_2$; (ii) ethylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$; and (iii) benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

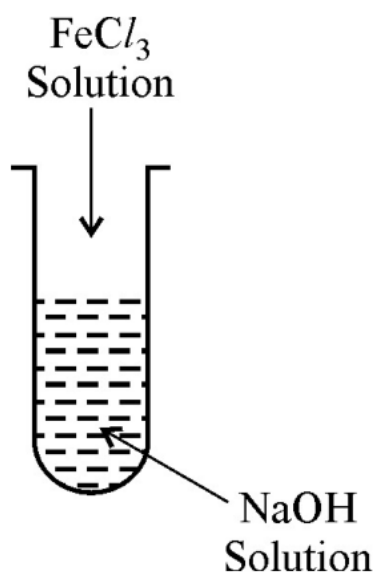
Quick Tip to Solve: Dilute base joins two propanone molecules; Zn(Hg)/HCl removes carbonyl oxygen, while Rosenmund reduction stops at an aldehyde.

14. (i) What is the role of activated charcoal in gas mask?

(ii) A colloidal sol is prepared by the given method in figure. What is the charge on hydrated ferric oxide colloidal particles formed in the test tube? How is the sol represented?

(iii) How does chemisorption vary with temperature?

[3 marks]



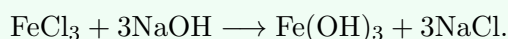
Solution:

Concept:

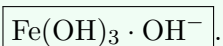
- Adsorption concentrates gas molecules at a solid surface. Activated charcoal has a large surface area because of its porous structure.
- Colloidal particles acquire charge by preferential adsorption of ions from the surrounding medium. Chemisorption involves chemical bond formation and generally needs activation energy.

Step 1: (i) Role of charcoal in a gas mask Activated charcoal adsorbs poisonous gases and vapours on its extensive internal surface as contaminated air passes through the mask. These substances are retained on the charcoal surface, reducing their concentration in the air reaching the wearer. The relevant process is surface adsorption, rather than absorption throughout the bulk of charcoal.

Step 2: (ii) Charge and representation of the ferric hydroxide sol The figure shows ferric chloride solution being added to sodium hydroxide solution, so hydrated ferric oxide forms in a medium containing excess hydroxide ions:



The freshly formed $\text{Fe}(\text{OH})_3$ particles preferentially adsorb OH^- ions from this medium and therefore acquire a negative charge. The sol is represented as



More generally, its charged particles can be written $\{[\text{Fe}(\text{OH})_3]_n \cdot x\text{OH}^-\}^{x-}$, with Na^+ as counterions. The direction of addition matters: the receiving solution in the printed figure is NaOH.

Step 3: (iii) Effect of temperature on chemisorption At low temperature chemisorption is often slow because gas molecules lack the energy needed to cross the activation barrier for bond formation. Initially, increasing temperature increases chemisorption by helping molecules overcome this barrier. At sufficiently high temperature, the exothermic nature of adsorption favours desorption, so the extent of chemisorption decreases. Thus the usual trend is an initial rise to a maximum, followed by a fall at higher temperature.

Step 4: Conclusion Activated charcoal removes poisonous gases by adsorption. The illustrated preparation gives a negatively charged sol, $\text{Fe}(\text{OH})_3 \cdot \text{OH}^-$. Chemisorption generally increases initially with temperature and decreases at sufficiently high temperature.

Quick Tip to Solve: For a sol's charge, identify the solution already in the test tube: excess NaOH supplies adsorbed hydroxide ions and gives a negative sol.

15. A 4% solution (w/w) of sucrose ($M = 342 \text{ g mol}^{-1}$) in water has a freezing point of 271.15 K. Calculate the freezing point of 5% glucose ($M = 180 \text{ g mol}^{-1}$) in water.

(Given: Freezing point of pure water = 273.15 K)

[3 marks]

Solution:

Concept:

- Freezing-point depression obeys $\Delta T_f = K_f m$, where m is the molality and K_f is the molal depression constant of the solvent.
- Sucrose and glucose are non-electrolytes, so their van't Hoff factors are $i = 1$. For the same solvent, the ratio of depressions equals the ratio of molalities.
- A mass percentage refers to the mass of solute in 100 g of solution. The solvent mass is therefore the solution mass minus the solute mass.

Step 1: Obtain the sucrose molality and freezing-point depression Take 100 g of the sucrose solution. It contains 4 g of sucrose and 96 g = 0.096 kg of water. Hence

$$m_s = \frac{4/342}{0.096} = 0.12183 \text{ mol kg}^{-1}.$$

The measured depression is

$$\Delta T_{f,s} = 273.15 - 271.15 = 2.00 \text{ K}.$$

This measurement supplies the solvent constant needed for comparison, so no separately tabulated value of K_f is required.

Step 2: Calculate the glucose depression using the same solvent Take 100 g of the glucose solution. It contains 5 g of glucose and 95 g = 0.095 kg of water. Thus

$$m_g = \frac{5/180}{0.095} = 0.29240 \text{ mol kg}^{-1}.$$

Since both solutes remain as molecules in water, divide the two freezing-point-depression equations:

$$\begin{aligned}\Delta T_{f,g} &= \Delta T_{f,s} \frac{m_g}{m_s} \\ &= 2.00 \times \frac{5 \times 342 \times 96}{180 \times 95 \times 4} \\ &= 4.80 \text{ K}.\end{aligned}$$

The larger glucose molality produces a larger depression. Subtract this depression from the freezing point of pure water to obtain the solution's freezing point.

Step 3: Conclusion The freezing point of the glucose solution is $T_{f,g} = 273.15 - 4.80 = \boxed{268.35 \text{ K}}$.

Quick Tip to Solve: For these mass percentages use 96 g and 95 g of water, respectively; cancel the common solvent constant by taking the molality ratio.

16. An element crystallizes in fcc lattice with a cell edge of 300 pm. The density of the element is 10.8 g cm^{-3} . Calculate the number of atoms in 108 g of the element. [3 marks]

Solution:

Concept:

- A face-centred cubic (fcc) unit cell contains $Z = 4$ atoms: the eight corner atoms contribute one atom in total and the six face-centred atoms contribute three atoms.
- For a cubic unit cell, its volume is a^3 , where a is the edge length. Its mass is ρa^3 , where ρ is the density.
- The number of atoms in a sample is the number of complete unit-cell equivalents multiplied by the number of atoms per cell.

Step 1: Express the unit-cell volume in cubic centimetres The density is given in g cm^{-3} , so express the edge length in centimetres. Since $1 \text{ pm} = 10^{-10} \text{ cm}$,

$$a = 300 \times 10^{-10} \text{ cm} = 3.00 \times 10^{-8} \text{ cm}.$$

Cubing the entire edge length gives

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

Both the numerical factor and the power of ten must be cubed when computing the volume.

Step 2: Find the number of unit cells represented by the sample The mass associated with one unit cell is

$$m_{\text{cell}} = \rho a^3 = 10.8 \times 2.70 \times 10^{-23} = 2.916 \times 10^{-22} \text{ g}.$$

Therefore the 108 g sample contains

$$n_{\text{cells}} = \frac{108}{2.916 \times 10^{-22}} = 3.7037 \times 10^{23}$$

unit-cell equivalents. This calculation uses the sample mass divided by the mass per cell; it does not require a separately known molar mass.

Step 3: Apply the fcc atom count Counting shared atoms correctly, the number of atoms per fcc cell is

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

Consequently, multiply the number of cells by four:

$$N = 4(3.7037 \times 10^{23}) = 1.48148 \times 10^{24}.$$

Step 4: Conclusion The number of atoms in 108 g of the element is 1.48×10^{24} atoms.

Quick Tip to Solve: Use the direct relation $N = 4$ times sample mass divided by density times the cube of the edge; first convert the edge from pm to cm.

17. How will you convert the following:

(i) Impure Nickel to pure Nickel

(ii) Zinc blende to Zinc metal

(iii) $[\text{Ag}(\text{CN})_2]^-$ to Ag

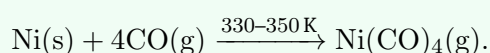
[3 marks]

Solution:

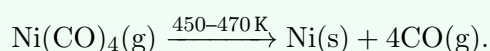
Concept:

- Mond's process refines nickel through formation of a volatile carbonyl followed by its thermal decomposition, which deposits pure nickel.
- A sulphide ore is roasted in excess air to form its oxide. Zinc oxide can then be reduced with coke at high temperature.
- A more reactive metal can displace silver from its cyanide complex. Zinc is oxidised while silver(I) is reduced to silver metal.

Step 1: (i) Refine impure nickel by Mond's process Pass carbon monoxide over impure nickel at 330–350 K. Nickel forms volatile nickel tetracarbonyl, whereas the impurities are left behind:

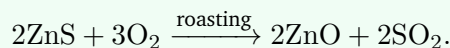


Separate the carbonyl vapour from the non-volatile impurities and heat it to 450–470 K:

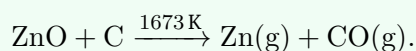


Thermal decomposition deposits pure nickel and releases carbon monoxide, which can be reused.

Step 2: (ii) Convert zinc blende into zinc metal Zinc blende is ZnS . First roast the concentrated sulphide ore in excess air so that it becomes zinc oxide:

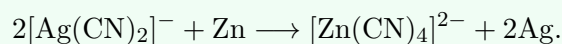


Next heat the oxide with coke at about 1673 K:



Zinc is produced as vapour at this temperature; cool and condense it to collect zinc metal. Roasting first makes the sulphide suitable for reduction by carbon through its oxide.

Step 3: (iii) Recover silver from its cyanide complex Add zinc to the solution containing dicyanidoargentate(I). Zinc, being more reactive than silver, reduces silver(I) to metallic silver and itself forms a cyanide complex:



Each zinc atom supplies two electrons and therefore liberates two silver atoms. The equation conserves all four cyanide ligands and has total charge -2 on each side.

Step 4: Conclusion Use Mond's process for nickel, roasting followed by coke reduction for zinc blende, and displacement with zinc to recover silver from $[\text{Ag}(\text{CN})_2]^-$.

Quick Tip to Solve: Remember the sequence: nickel through its volatile carbonyl, zinc sulphide through its oxide, and silver cyanide complex through displacement by zinc.

18. Give reasons for the following:

(i) The transition metals generally form coloured compounds.

(ii) E° value for ($\text{Mn}^{3+}|\text{Mn}^{2+}$) is highly positive than that for ($\text{Cr}^{3+}|\text{Cr}^{2+}$) couple.

(iii) The chemistry of actinoids elements is not so smooth as that of the lanthanoids.

[3 marks]

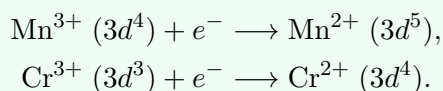
Solution:

Concept:

- Ligands split the five metal d orbitals into groups of different energies; absorption of visible light can promote an electron between these levels.
- A more positive standard reduction potential E° indicates a greater tendency for the oxidised species to accept an electron. The stability of the resulting electronic configuration is important.
- Actinoid valence orbitals $5f$, $6d$ and $7s$ have comparable energies, so their electrons can participate in bonding in different ways.

Step 1: (i) Explain the colour of transition-metal compounds Transition-metal ions generally have partially filled d orbitals. In the field of surrounding ligands, these orbitals split into sets with different energies. An electron can absorb a suitable wavelength from visible light and undergo a $d-d$ transition to a higher-energy orbital. The light transmitted or reflected therefore lacks the absorbed colour and the compound appears in the complementary colour. Ions with d^0 or d^{10} configurations do not show this mechanism, which explains the word “generally” in the question.

Step 2: (ii) Compare the manganese and chromium couples The relevant configurations and reductions are



Reduction of Mn^{3+} produces the especially stable half-filled $3d^5$ configuration of Mn^{2+} , so this reduction is strongly favoured. In contrast, Cr^{3+} has the stable $3d^3$ configuration (t_{2g}^3 in an octahedral field); its reduction to $3d^4$ is less favourable. Consequently, $E^\circ(\text{Mn}^{3+}/\text{Mn}^{2+})$ is much more positive than $E^\circ(\text{Cr}^{3+}/\text{Cr}^{2+})$.

Step 3: (iii) Explain the less regular chemistry of actinoids The small energy differences between $5f$, $6d$ and $7s$ orbitals allow variable numbers of electrons to take part in bonding. Actinoids therefore exhibit a wider and less regular range of oxidation states than lanthanoids, whose chemistry is dominated by the +3 state. The changing participation of $5f$ electrons makes trends in actinoid compounds less uniform; their radioactivity also complicates their study.

Step 4: Conclusion (i) Colour generally arises from visible-light absorption in $d-d$ transitions. (ii) Reduction to stable half-filled Mn^{2+} is favoured, whereas stable Cr^{3+} resists reduction. (iii) Comparable valence-orbital energies give actinoids a wider, less regular range of oxidation states.

Quick Tip to Solve: Write both ion configurations before comparing reduction potentials: formation of d^5 favours manganese reduction, while the stability of d^3 opposes chromium reduction.

19(a). (i) What type of drug is used in sleeping pills?

(ii) What type of detergents are used in toothpastes?

(iii) Why the use of alitame as artificial sweetener is not recommended?

[3 marks]

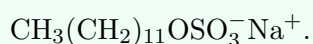
Solution:

Concept:

- Tranquillisers act on the central nervous system and are used to reduce anxiety or induce sleep, depending on the drug and dose.
- Detergents are classified by the charge on their active cleansing ion: anionic detergents have a negatively charged hydrophilic group.
- An artificial sweetener must permit accurate control of sweetness when added to food.

Step 1: (i) Identify the drug class used in sleeping pills Sleeping pills contain tranquilliser drugs, particularly those with sedative or hypnotic action. They depress central nervous system activity and help induce sleep. Barbiturates, such as veronal, are examples of the class used for this purpose in the textbook classification. Thus the requested drug type is a tranquilliser.

Step 2: (ii) Identify the detergent class used in toothpastes Anionic detergents are used in toothpastes. A common example is sodium lauryl sulphate, also called sodium dodecyl sulphate:



Its long hydrocarbon chain is the hydrophobic part, while the negatively charged sulphate-containing head is hydrophilic. This detergent helps disperse material and produce foam during cleaning; its active cleansing species is an anion, which determines the classification.

Step 3: (iii) Explain the difficulty with alitame Alitame is a high-potency artificial sweetener, approximately 2000 times as sweet as sucrose. Because such a small quantity produces substantial sweetness, it is difficult to control the sweetness of food when using it: even a slight excess can make the food much sweeter than intended. This difficulty in controlling the dose, rather than poor sweetness or thermal instability, is the textbook reason that its use is not recommended in this context.

Step 4: Conclusion (i) Tranquillisers with sedative or hypnotic action are used in sleeping pills. (ii) Toothpastes use anionic detergents, for example sodium lauryl sulphate. (iii) Alitame's very high sweetening power makes the sweetness of food difficult to control.

Quick Tip to Solve: Link each use to its defining property: tranquilliser to sleep, negatively charged detergent head to toothpaste, and alitame's high potency to difficult sweetness control.

19(b). Define the following terms with a suitable example in each:

(i) Broad-spectrum antibiotics

(ii) Disinfectants

(iii) Cationic detergents

[3 marks]

Solution:

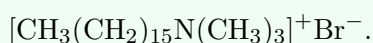
Concept:

- The spectrum of an antibiotic is the range of microorganisms against which it is effective.
- Disinfectants are antimicrobial chemicals used on inanimate objects; their normal disinfecting concentrations are unsuitable for living tissues.
- A cationic detergent contains a positively charged surface-active ion with a long hydrocarbon chain and a hydrophilic ionic head.

Step 1: (i) Broad-spectrum antibiotics Broad-spectrum antibiotics are antibiotics that kill or inhibit a wide range of bacteria, including both Gram-positive and Gram-negative bacteria. Their defining feature is the breadth of their antibacterial activity, rather than simply the strength of the medicine. Chloramphenicol is a suitable example of a broad-spectrum antibiotic; tetracycline is another accepted example.

Step 2: (ii) Disinfectants Disinfectants are chemical substances that kill or inhibit microorganisms and are applied to non-living objects or surfaces, such as floors, drains and instruments. At the concentrations used for disinfection, they are generally too harmful to be applied to living tissues. A 1% solution of phenol is an example of a disinfectant. This contrasts with an antiseptic, which is suitable for application to living tissue at its prescribed concentration.

Step 3: (iii) Cationic detergents Cationic detergents are usually quaternary ammonium salts in which the positively charged ion contains a long hydrocarbon chain and provides the surface-active cleansing action. Cetyltrimethylammonium bromide is a suitable example:



The long alkyl chain is hydrophobic, while the quaternary ammonium head is hydrophilic and positively charged. The bromide ion is the counter-ion; the detergent is classified as cationic because the active surface-active species is the positive ion.

Step 4: Conclusion (i) Broad-spectrum antibiotics act against a wide range of bacteria; example: chloramphenicol. (ii) Disinfectants destroy or inhibit microorganisms on inanimate objects; example: 1% phenol solution. (iii) Cationic detergents have a positively charged surface-active ion; example: cetyltrimethylammonium bromide.

Quick Tip to Solve: Give both the defining property and a named example for each term; for detergents, classify the charge on the long-chain surface-active ion.

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

(i) Nylon-6,6

(ii) Glyptal

(iii) Buna-S

[3 marks]

Solution:

Concept:

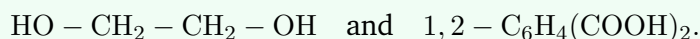
- A monomer is the small molecule from which a polymer is formed. Condensation polymers need monomers with two reactive functional groups.
- Nylon-6,6 contains amide linkages, glyptal contains ester linkages, and Buna-S is an addition copolymer of a diene and a vinyl compound.

Step 1: (i) Monomers of Nylon-6,6 Nylon-6,6 is obtained by condensation of hexamethylenediamine (hexane-1,6-diamine) and adipic acid (hexanedioic acid). Their structures are



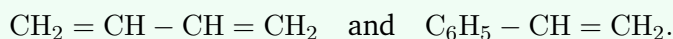
The amino and carboxyl groups react with elimination of water to form amide, $-\text{CO} - \text{NH}-$, linkages. Each monomer has six carbon atoms, explaining the two sixes in the name.

Step 2: (ii) Monomers of glyptal Glyptal is prepared from ethylene glycol (ethane-1,2-diol) and phthalic acid (benzene-1,2-dicarboxylic acid):



In the phthalic acid structure, the two $-\text{COOH}$ groups occupy adjacent positions on the benzene ring. The alcohol and acid groups condense to produce ester linkages.

Step 3: (iii) Monomers of Buna-S Buna-S is formed by copolymerisation of buta-1,3-diene and styrene (phenylethene). Their structures are



Both monomers supply carbon-carbon double bonds for addition polymerisation; the letter S identifies the styrene component of this synthetic rubber.

Step 4: Conclusion Nylon-6,6: hexamethylenediamine and adipic acid; glyptal: ethylene glycol and phthalic acid; Buna-S: buta-1,3-diene and styrene, with the structures given above.

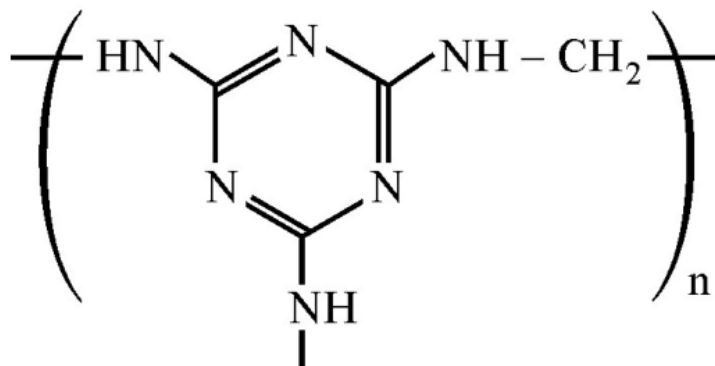
Quick Tip to Solve: Match the linkage to the monomers: amide means diamine plus diacid; ester means diol plus diacid; Buna-S contains styrene.

20(b). (i) Is $\{\text{CH}_2\text{-CH}(\text{CH}_3)\}_n$ a homopolymer or copolymer? Give reason.

(ii) Write the monomers of the following polymer:

(iii) What is the role of Sulphur in vulcanization of rubber?

[3 marks]

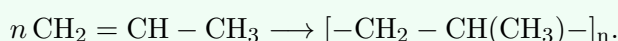


Solution:

Concept:

- A homopolymer is made from one kind of monomer; a copolymer is made from two or more different kinds of monomer.
- Condensation of melamine with formaldehyde gives a cross-linked thermosetting resin. Vulcanisation similarly introduces cross-links between rubber chains, improving their mechanical properties.

Step 1: (i) Classify the given polymer The repeating unit $[-\text{CH}_2 - \text{CH}(\text{CH}_3)-]_n$ is that of polypropene (polypropylene). It is a homopolymer because all its repeating units are obtained from just one kind of monomer, propene:



The methyl side group is already present in propene; it does not indicate a second monomer.

Step 2: (ii) Identify the monomers from the printed structure The nitrogen-containing six-membered ring with three amino-derived substituents identifies melamine-formaldehyde resin. Its monomers are melamine (2,4,6-triamino-1,3,5-triazine), $\text{C}_3\text{N}_3(\text{NH}_2)_3$, and formaldehyde (methanal), $\text{H} - \text{C}(=\text{O}) - \text{H}$. Melamine has an alternating carbon-nitrogen ring, with an $-\text{NH}_2$ group on each ring carbon. Formaldehyde supplies the methylene groups linking amino groups on different melamine units during condensation. Thus the ring comes from melamine and the $-\text{CH}_2-$ bridges come from formaldehyde.

Step 3: (iii) Explain the action of sulphur When rubber is heated with sulphur, sulphur forms cross-links between its polyisoprene chains at reactive sites associated with the carbon-carbon double bonds. These sulphur bridges restrict the slipping of adjacent chains, reduce plasticity and stickiness, and increase tensile strength, elasticity and resistance to wear and temperature changes. The network therefore helps stretched rubber recover its original shape.

Quick Tip to Solve: Count the kinds of starting monomer, not the kinds of atoms; recognise the triazine ring as melamine and the methylene bridge as formaldehyde-derived.

Step 4: Conclusion (i) The polymer is a homopolymer of propene. (ii) The monomers are melamine and formaldehyde. (iii) Sulphur forms cross-links between rubber chains, making rubber stronger and more elastic and durable.

Quick Tip to Solve: Count the kinds of starting monomer, not the kinds of atoms; recognise the triazine ring as melamine and the methylene bridge as formaldehyde-derived.

- 21. (i) Out of $(\text{CH}_3)_3\text{C-Br}$ and $(\text{CH}_3)_3\text{C-I}$, which one is more reactive towards $\text{S}_{\text{N}}1$ and why?**
(ii) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.
(iii) Why dextro and laevo-rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation? [3 marks]

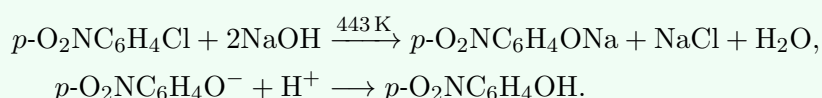
Solution:

Concept:

- In an $\text{S}_{\text{N}}1$ reaction the slow step is ionisation of the carbon-halogen bond to form a carbocation; easier departure of the leaving group increases the rate.
- A para nitro group activates an aryl halide towards nucleophilic substitution. Enantiomers have identical physical properties in an achiral environment, apart from opposite optical rotations.

Step 1: (i) Compare the tertiary alkyl halides Both compounds form the same tertiary carbocation, $(\text{CH}_3)_3\text{C}^+$, so carbocation stability does not distinguish them. The carbon-iodine bond is weaker and breaks more readily than the carbon-bromine bond; iodide is also a better leaving group than bromide. Hence tert-butyl iodide, $(\text{CH}_3)_3\text{C-I}$, undergoes the rate-determining ionisation more readily and is more reactive towards $\text{S}_{\text{N}}1$.

Step 2: (ii) Replace chlorine and then acidify Heating para-nitrochlorobenzene with aqueous sodium hydroxide at 443 K replaces chlorine by the oxygen-containing group, giving sodium para-nitrophenoxide in the alkaline medium. Acidification protonates this ion to give para-nitrophenol (4-nitrophenol):



The para nitro group withdraws electrons and stabilises the anionic intermediate of the substitution.

Step 3: (iii) Explain why distillation does not resolve the isomers Dextro- and laevo-rotatory butan-2-ol are enantiomers, that is, non-superimposable mirror images with opposite configurations at the carbon bearing $-\text{OH}$. They have identical boiling points and vapour pressures in an ordinary achiral environment. Fractional distillation separates liquids using differences in volatility, so it cannot separate these two enantiomers. Their opposite directions of optical rotation do not produce a boiling-point difference.

Step 4: Conclusion (i) $(\text{CH}_3)_3\text{C-I}$ is more reactive because its C-I bond ionises more easily. (ii) The final product is para-nitrophenol. (iii) The two butan-2-ol enantiomers have identical boiling points and cannot be resolved by fractional distillation.

Quick Tip to Solve: For the same alkyl group, compare leaving groups in $\text{S}_{\text{N}}1$; for enantiomers, remember that opposite optical rotations do not imply different boiling points.

22. Write equations of the following reactions:

(i) Acetylation of aniline

(ii) Coupling reaction

(iii) Carbyl amine reaction

[3 marks]

Solution:

Concept:

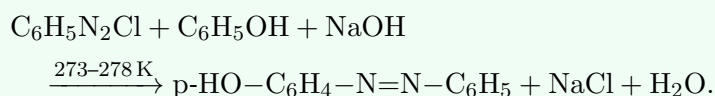
- Acetylation replaces one hydrogen of the amino group by an acetyl group, $\text{CH}_3\text{CO}-$, giving an amide.
- Aromatic diazonium salts undergo azo coupling with activated aromatic rings. A primary amine reacts with chloroform and alcoholic potassium hydroxide to form an isocyanide.

Step 1: (i) Acetylation of aniline Treat aniline with acetic anhydride to obtain acetanilide:



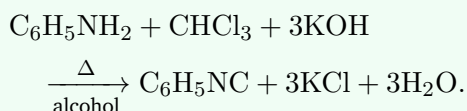
The amino group is acetylated; the benzene ring remains unchanged. The product is an amide, also called N-phenylethanamide.

Step 2: (ii) Coupling reaction Benzene diazonium chloride couples with phenol in a cold, weakly alkaline medium to give predominantly p-hydroxyazobenzene:



The two aromatic rings are joined through the azo linkage, $-\text{N}=\text{N}-$. Phenol activates its ring and coupling occurs mainly at its para position.

Step 3: (iii) Carbylamine reaction Heating aniline, a primary amine, with chloroform and alcoholic potassium hydroxide gives phenyl isocyanide:



The isocyanide has an offensive smell. This reaction is a test for primary amines; secondary and tertiary amines do not give this test.

Step 4: Conclusion The products are (i) acetanilide, (ii) p-hydroxyazobenzene in the coupling example, and (iii) phenyl isocyanide.

Quick Tip to Solve: In the carbylamine equation, remember three KOH and write the product as RNC, not RCN.

23. The decomposition of NH_3 on platinum surface is zero order reaction. If rate constant (k) is $4 \times 10^{-3} \text{ Ms}^{-1}$, how long will it take to reduce the initial concentration of NH_3 from 0.1 M to 0.064 M. [3 marks]

Solution:

Concept:

- For a zero order reaction, the rate of disappearance of the reactant is constant: $-d[A]/dt = k$, where $[A]$ is its concentration and k is the rate constant.
- Integration gives $[A]_t = [A]_0 - kt$, with $[A]_0$ the initial concentration and $[A]_t$ its value after time t . The units of k are concentration per unit time.

Step 1: Identify the concentration decrease The given zero order decomposition has

$$[\text{NH}_3]_0 = 0.100 \text{ M}, \quad [\text{NH}_3]_t = 0.064 \text{ M}.$$

Hence the amount of ammonia consumed per unit volume is

$$\Delta[\text{NH}_3] = 0.100 - 0.064 = 0.036 \text{ M}.$$

The platinum surface provides the catalyst; the stated zero order law specifies that the concentration decreases linearly with time under these conditions.

Step 2: Apply the integrated zero order rate law Rearranging the integrated law and substituting the given rate constant,

$$\begin{aligned} t &= \frac{[\text{NH}_3]_0 - [\text{NH}_3]_t}{k} \\ &= \frac{0.100 - 0.064}{4 \times 10^{-3}} \frac{\text{M}}{\text{Ms}^{-1}} \\ &= \frac{0.036}{0.004} \text{ s} = 9 \text{ s}. \end{aligned}$$

The concentration units cancel, leaving seconds. As a check, in this interval the decrease kt is $0.004 \times 9 = 0.036 \text{ M}$, exactly the required decrease. A logarithmic concentration ratio would apply to a first order reaction and is not used here.

Step 3: Conclusion The required time for ammonia to decrease from 0.100 M to 0.064 M is 9 s.

Quick Tip to Solve: For zero order kinetics, divide the concentration lost by k ; do not use a logarithm or multiply by the stoichiometric coefficient.

24(a). Define the following with a suitable example in each:

(i) Oligosaccharides

(ii) Denaturation of protein

(iii) Vitamins

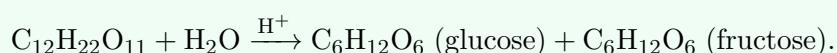
[3 marks]

Solution:

Concept:

- Carbohydrates are classified partly by the number of monosaccharide units obtained on hydrolysis; a glycosidic linkage joins the sugar units.
- The biological activity of a protein depends on its native folded structure. Vitamins are organic micronutrients required for normal growth and health.

Step 1: (i) Oligosaccharides Oligosaccharides are carbohydrates that yield two to ten monosaccharide units on hydrolysis. Their monosaccharide residues are joined by glycosidic linkages. For example, sucrose is a disaccharide and therefore an oligosaccharide. Hydrolysis of one molecule of sucrose produces one molecule each of D-glucose and D-fructose:



Step 2: (ii) Denaturation of protein Denaturation is the loss of a protein's native conformation and biological activity due to a physical change such as heating or a chemical change such as a change in pH. Secondary and tertiary structures are disrupted while the primary structure, that is, the amino acid sequence held by peptide bonds, remains intact. For example, egg white coagulates on boiling because its protein, albumin, becomes denatured. This illustrates a change in protein folding rather than hydrolysis into amino acids.

Step 3: (iii) Vitamins Vitamins are organic compounds needed in small amounts in the diet to maintain normal growth and health. The body generally cannot synthesize them in sufficient amounts, so adequate dietary supply is required. For example, vitamin C (ascorbic acid) is a water-soluble vitamin obtained from foods such as citrus fruits and amla. Its deficiency causes scurvy. Vitamins serve essential physiological functions but are not required as bulk sources of energy.

Step 4: Conclusion Suitable examples are sucrose for an oligosaccharide, coagulation of egg white on boiling for protein denaturation, and ascorbic acid for a vitamin.

Quick Tip to Solve: Distinguish denaturation from hydrolysis: denaturation destroys the native fold but preserves the protein's primary amino acid sequence.

24(b). Write the reactions involved when D-glucose is treated with the following reagents:

(i) Br₂ water

(ii) H₂N-OH

(iii) (CH₃CO)₂O

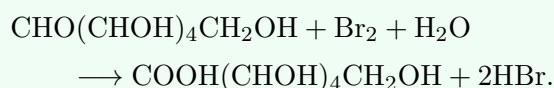
[3 marks]

Solution:

Concept:

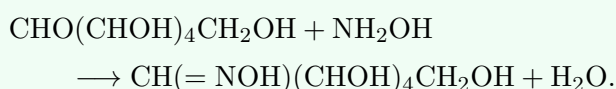
- The open-chain form of D-glucose is CHO(CHOH)₄CH₂OH. It contains an aldehyde group and five hydroxyl groups.
- Bromine water mildly oxidises an aldehyde to a carboxylic acid; hydroxylamine forms an oxime, while acetic anhydride acetylates hydroxyl groups.

Step 1: (i) Reaction with bromine water Bromine water oxidises the terminal aldehyde group to a carboxyl group, giving D-gluconic acid. The terminal primary alcohol group is not oxidised by this mild reagent:



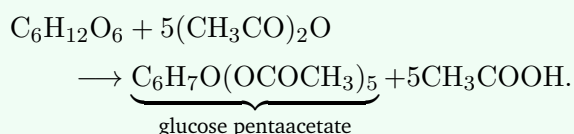
Thus the six-carbon skeleton is retained and bromine water is decolourised.

Step 2: (ii) Reaction with hydroxylamine Hydroxylamine reacts with the aldehyde group by condensation. One molecule of water is eliminated and glucose oxime is formed:



The formation of the C = NOH group provides evidence for a carbonyl group in glucose.

Step 3: (iii) Reaction with acetic anhydride Each of the five hydroxyl groups undergoes acetylation: its hydrogen is replaced by COCH₃. Glucose therefore forms glucose pentaacetate on treatment with excess acetic anhydride:



Pentaacetate formation establishes the presence of five alcoholic hydroxyl groups; the formula here represents the acetylated product without implying a free aldehyde group.

Step 4: Conclusion The products are (i) D-gluconic acid, (ii) glucose oxime and (iii) glucose pentaacetate, respectively.

Quick Tip to Solve: Match each reagent to its target: bromine water oxidises CHO, hydroxylamine forms an oxime, and acetic anhydride acetylates all five OH groups.

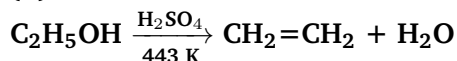
Section D (15 marks)

25(a). How do you convert the following:

(i) Phenol to Anisole

(ii) Ethanol to Propan-2-ol

(b) Write mechanism of the following reaction:



(c) Why phenol undergoes electrophilic substitution more easily than benzene?

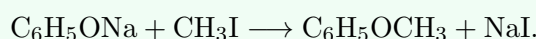
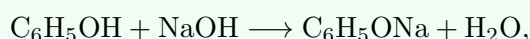
[5 marks]

Solution:

Concept:

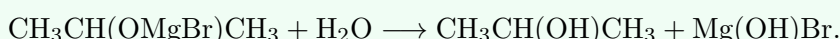
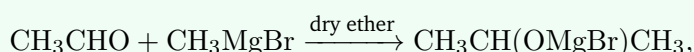
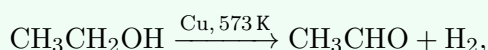
- Williamson synthesis forms an ether by reaction of a phenoxide or alkoxide ion with a suitable primary alkyl halide.
- A Grignard reagent RMgX adds its alkyl group to a carbonyl carbon; hydrolysis of the resulting magnesium alkoxide gives an alcohol.
- Concentrated sulphuric acid catalyses dehydration of ethanol at 443 K. Resonance donation from the oxygen lone pair activates phenol towards electrophiles.

Step 1: (a)(i) Convert phenol into anisole First treat phenol with aqueous sodium hydroxide to form sodium phenoxide. Then react the phenoxide with methyl iodide:



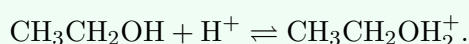
Phenoxide attacks the methyl carbon and displaces iodide in the Williamson ether synthesis. The product $\text{C}_6\text{H}_5\text{OCH}_3$ is anisole.

Step 2: (a)(ii) Convert ethanol into propan-2-ol Pass ethanol vapour over heated copper at 573 K to obtain ethanal. Add methylmagnesium bromide in dry ether, followed by acidic hydrolysis:



The Grignard step adds one carbon to the two-carbon aldehyde and produces the required secondary alcohol. Water must be excluded until this addition is complete because it destroys the Grignard reagent.

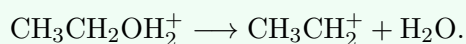
Step 3: (b) Acid-catalysed dehydration of ethanol In the standard stepwise acid-catalysed mechanism, oxygen first accepts a proton. This converts the poor leaving group $-\text{OH}$ into a water molecule:



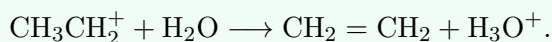
The protonated alcohol then loses water in the slow step, represented by formation of the ethyl

Quick Tip to Solve: To lengthen ethanol by one carbon and obtain a secondary alcohol, first make ethanal and then add a methyl Grignard reagent; keep the addition step dry.

carbocation:



Water removes a proton from the adjacent carbon; the electrons of that carbon-hydrogen bond form the carbon-carbon double bond:



Acid is regenerated, so it acts as a catalyst. At 443 K, the net reaction is elimination of water from ethanol to give ethene.

Step 4: (c) Explain the greater reactivity of phenol In phenol, a lone pair on oxygen is delocalised into the benzene ring by resonance, giving a positive mesomeric effect. Its resonance contributors increase electron density especially at the ortho and para positions. The electron-rich ring attracts an electrophile more readily, and resonance donation also stabilises the positively charged intermediate formed during electrophilic substitution. Although oxygen withdraws electrons inductively, its resonance donation predominates in this reaction. Benzene has no hydroxyl group to provide this extra donation, so phenol undergoes electrophilic substitution more easily.

Step 5: Conclusion Phenol gives anisole by Williamson synthesis. Ethanol gives propan-2-ol via ethanal and methylmagnesium bromide. Acid-catalysed dehydration at 443 K gives ethene, and oxygen lone-pair resonance donation accounts for phenol's enhanced electrophilic substitution.

Quick Tip to Solve: To lengthen ethanol by one carbon and obtain a secondary alcohol, first make ethanal and then add a methyl Grignard reagent; keep the addition step dry.

OR

25(b). (a) Account for the following:

- (i) o-nitrophenol is more steam volatile than p-nitrophenol.
(ii) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butylmethylether.

(b) Write the reaction involved in the following:

- (i) Reimer-Tiemann reaction
(ii) Friedel-Crafts Alkylation of Phenol

(c) Give simple chemical test to distinguish between Ethanol and Phenol.

[5 marks]

Solution:

Concept:

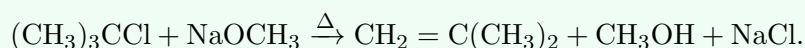
- Hydrogen bonding controls molecular association: intramolecular hydrogen bonding acts within one molecule, whereas intermolecular hydrogen bonding joins different molecules and raises the energy needed for vaporisation.
- A tertiary alkyl halide is sterically hindered towards $\text{S}_{\text{N}}2$ substitution; a strong base on heating can remove a β -hydrogen to give an alkene by elimination.

Quick Tip to Solve: Link ortho nitrophenol with an internal hydrogen bond, tertiary halide plus hot alkoxide with elimination, and phenol identification with neutral ferric chloride.

- The –OH group activates the phenol ring towards electrophilic substitution at its ortho and para positions. Phenols also give a characteristic colour with neutral ferric chloride.

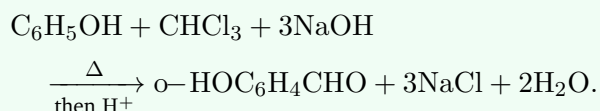
Step 1: (a)(i) Compare hydrogen bonding in the nitrophenols In *o*-nitrophenol, the adjacent –OH and –NO₂ groups form an intramolecular hydrogen bond. This reduces association between different molecules. In *p*-nitrophenol, the groups are too far apart for such an internal bond, so intermolecular hydrogen bonding produces associated molecules. More energy is needed to separate these molecules into vapour. Thus the ortho isomer has greater vapour pressure and is more readily carried over with steam than the para isomer.

Step 2: (a)(ii) Explain elimination from tert-butyl chloride The carbon bonded to chlorine is tertiary and is surrounded by three methyl groups. Backside attack by methoxide, needed for Williamson ether synthesis through S_N2, is strongly hindered. Methoxide instead acts as a strong base and removes a hydrogen from an adjacent methyl group while chloride leaves. Heating favours this elimination:



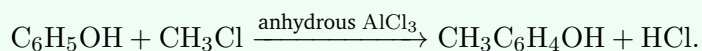
The double bond therefore forms between the carbon originally bearing chlorine and a neighbouring methyl carbon.

Step 3: (b)(i) Write the Reimer–Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, followed by acidification. A formyl group is introduced mainly at the ortho position, giving salicylaldehyde (2-hydroxybenzaldehyde). The overall equation, including work-up to the neutral product, is



Dichlorocarbene, :CCl₂, generated in the alkaline medium, is the electrophilic species. A small amount of the para isomer can also form.

Step 4: (b)(ii) Write Friedel–Crafts alkylation of phenol For example, methyl chloride in the presence of anhydrous aluminium chloride introduces a methyl group into the activated ring at the ortho and para positions:



Here CH₃C₆H₄OH represents the mixture of 2-methylphenol (*o*-cresol) and 4-methylphenol (*p*-cresol). The directing effect follows from resonance donation of the oxygen lone pair into the ring.

Step 5: (c) Distinguish ethanol from phenol Add a few drops of freshly prepared neutral aqueous ferric chloride solution separately to the two samples. Phenol gives a violet colour due to formation of a coloured iron(III)–phenolate complex. Ethanol gives no characteristic violet colour. The observation therefore identifies the phenol sample directly. Use neutral ferric chloride for this test; simple effervescence with sodium metal would not distinguish the samples because both compounds react with sodium.

Step 6: Conclusion *o*-Nitrophenol is more steam volatile because it has intramolecular rather than intermolecular hydrogen bonding. Heated tert-butyl chloride and sodium methoxide give 2-methylpropene by elimination. Reimer–Tiemann formylation gives mainly salicylaldehyde, and

Quick Tip to Solve: Link ortho nitrophenol with an internal hydrogen bond, tertiary halide plus hot alkoxide with elimination, and phenol identification with neutral ferric chloride.

Friedel–Crafts methylation gives *o*- and *p*-cresol. Neutral FeCl_3 gives a violet colour with phenol and no such colour with ethanol.

Quick Tip to Solve: Link ortho nitrophenol with an internal hydrogen bond, tertiary halide plus hot alkoxide with elimination, and phenol identification with neutral ferric chloride.

26(a). Give reasons for the following:

(i) Sulphur in vapour state shows paramagnetic behaviour.

(ii) N–N bond is weaker than P–P bond.

(iii) Ozone is thermodynamically less stable than oxygen.

(b) Write the name of gas released when Cu is added to

(i) dilute HNO_3 and

(ii) conc. HNO_3

[5 marks]

Solution:

Concept:

- Paramagnetic species contain unpaired electrons. At high temperature sulphur vapour contains S_2 molecules whose electronic structure is analogous to that of O_2 .
- Lone-pair repulsion can weaken a single covalent bond. Thermodynamic stability depends on Gibbs energy, $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the enthalpy and entropy changes and T is absolute temperature.
- Nitric acid oxidises copper to copper(II) nitrate and is itself reduced. The nitrogen-containing reduction product depends on the acid concentration.

Step 1: (a)(i) Explain the paramagnetism of sulphur vapour At high temperatures, sulphur vapour contains diatomic S_2 molecules. Each sulphur atom contributes six valence electrons, so S_2 has twelve valence electrons, like O_2 . After the lower molecular orbitals are filled, two electrons occupy the two degenerate antibonding π^* orbitals singly, according to Hund's rule. These two unpaired electrons cause the molecules to be attracted by a magnetic field, so the vapour exhibits paramagnetic behaviour. The explanation concerns the diatomic high-temperature species, rather than assuming that every molecular form of sulphur has unpaired electrons.

Step 2: (a)(ii) Compare the N–N and P–P single bonds Nitrogen atoms are small. The lone pairs on two directly bonded nitrogen atoms consequently lie close together and repel one another strongly. This lone-pair–lone-pair repulsion weakens the N–N single bond. Phosphorus atoms are larger, so their lone pairs are farther apart and the corresponding repulsion is smaller; the P–P single bond is therefore stronger. This comparison is specifically between single bonds: it does not imply that the $\text{N} \equiv \text{N}$ triple bond in nitrogen gas is weak.

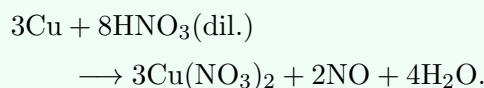
Step 3: (a)(iii) Explain the lower thermodynamic stability of ozone Ozone is an energetic form of oxygen and its conversion to ordinary oxygen is exothermic:



Quick Tip to Solve: Remember dilute nitric acid gives colourless NO, which browns in air; concentrated nitric acid gives brown NO_2 directly. Compare N–N and P–P as single bonds.

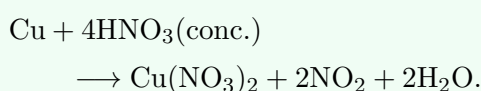
The number of gas molecules also increases from two to three, and the entropy change is positive. Hence $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is negative for this decomposition under ordinary conditions. Oxygen is therefore the thermodynamically favoured product, while ozone is thermodynamically less stable. Ozone can nevertheless persist for a time because the rate of a reaction is a separate kinetic question.

Step 4: (b)(i) Identify the gas with dilute nitric acid Copper reacts with dilute nitric acid to release nitric oxide, NO, a colourless gas. The balanced reaction is



Nitrogen is reduced from oxidation state +5 in nitrate to +2 in NO. On contact with air, this colourless gas becomes brown because $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. The gas initially released by the dilute-acid reaction is still NO.

Step 5: (b)(ii) Identify the gas with concentrated nitric acid Copper reacts with concentrated nitric acid to release nitrogen dioxide, NO₂, directly as a reddish-brown gas:



Here nitrogen is reduced from +5 to +4. In both acid concentrations copper is oxidised from 0 to +2; the difference lies in the reduction product of nitric acid, rather than in the oxidation state of the copper salt.

Step 6: Conclusion Sulphur vapour is paramagnetic because high-temperature S₂ has two unpaired electrons. Stronger lone-pair repulsion makes N–N weaker than P–P. Ozone decomposes favourably and exothermically to oxygen. Copper gives nitric oxide, NO, with dilute HNO₃, and nitrogen dioxide, NO₂, with concentrated HNO₃.

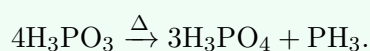
Quick Tip to Solve: Remember dilute nitric acid gives colourless NO, which browns in air; concentrated nitric acid gives brown NO₂ directly. Compare N–N and P–P as single bonds.

- 26(b).** (a) (i) Write the disproportionation reaction of H_3PO_3 .
 (ii) Draw the structure of XeF_4 .
 (b) Account for the following:
 (i) Although Fluorine has less negative electron gain enthalpy yet F_2 is strong oxidizing agent.
 (ii) Acidic character decreases from N_2O_3 to Bi_2O_3 in group 15.
 (c) Write a chemical reaction to test sulphur dioxide gas. Write chemical equation involved. [5 marks]

Solution:**Concept:**

- Disproportionation is simultaneous oxidation and reduction of the same element in one substance. Oxidation numbers identify both changes.
- VSEPR theory counts bonding and lone electron pairs around the central atom. Six electron-pair domains give an octahedral arrangement; two opposite lone pairs leave a square planar molecular shape.
- Oxidising power in water depends on the complete reduction process, including bond dissociation, electron gain and hydration. Oxide acidity generally falls as metallic character increases.

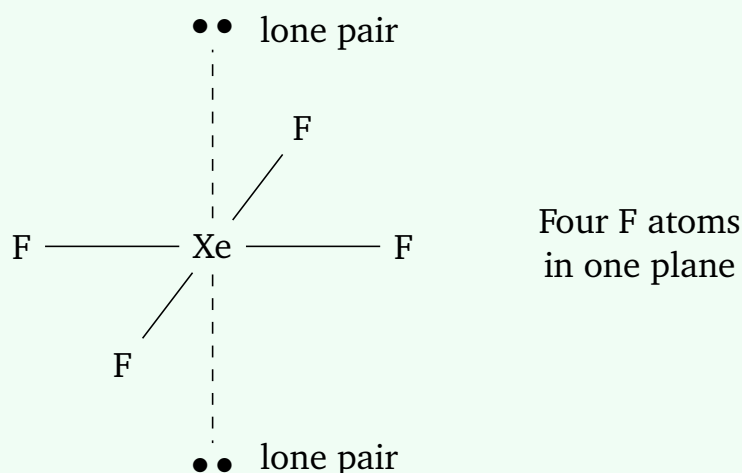
Step 1: (a)(i) Disproportionation of phosphorous acid On heating, phosphorous acid gives phosphoric acid and phosphine:



Phosphorus has oxidation number +3 in H_3PO_3 . It rises to +5 in H_3PO_4 and falls to -3 in PH_3 . Thus three phosphorus atoms each lose two electrons, while one gains six electrons; oxidation and reduction occur together.

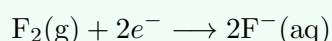
Step 2: (a)(ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four Xe-F bonds and two lone pairs give six electron-pair domains, conventionally described by sp^3d^2 hybridisation. The electron-pair geometry is octahedral. The two lone pairs occupy opposite positions to minimise repulsion, leaving four fluorine atoms in one square plane. Hence XeF_4 is square planar, with adjacent F-Xe-F angles of 90° and opposite angles of 180° .

Quick Tip to Solve: Count Xe's four bond pairs plus two lone pairs before drawing XeF_4 ; place the lone pairs opposite each other to leave a square plane of fluorine atoms.



Square planar XeF₄; the opposite axial lone pairs lie above and below the fluorine plane.

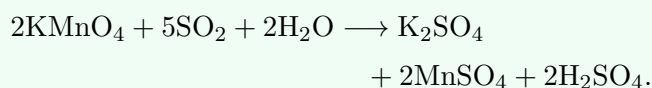
Step 3: (b)(i) Strong oxidising power of fluorine Fluorine has a less negative electron gain enthalpy than chlorine because its compact $2p$ shell produces stronger electron–electron repulsion for the incoming electron. Nevertheless, the reduction



is extremely favourable overall. The F–F bond has a low dissociation enthalpy, and the small fluoride ion has a very large negative hydration enthalpy. These factors more than compensate for the less negative electron gain enthalpy. Consequently, F_2 is a very strong oxidising agent in aqueous solution.

Step 4: (b)(ii) Decreasing acidity of group 15 oxides Down group 15, atomic size and metallic character increase, while electronegativity decreases. The oxides therefore become more ionic and less acidic: the acidic non-metal oxide N_2O_3 is at one end, whereas Bi_2O_3 is predominantly basic. The intermediate oxides show the gradual change toward amphoteric and then basic character. This explains the decrease in acidity from N_2O_3 to Bi_2O_3 .

Step 5: (c) Chemical test for sulphur dioxide Pass the gas through potassium permanganate solution acidified with dilute sulphuric acid. Sulphur dioxide reduces purple permanganate ions to nearly colourless Mn^{2+} , so the purple solution is decolourised. Sulphur dioxide itself is oxidised to sulphate:

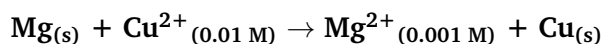


Manganese changes from +7 to +2, while sulphur changes from +4 to +6, accounting for the observed reduction of the reagent.

Step 6: Conclusion Heated H_3PO_3 disproportionates into H_3PO_4 and PH_3 ; XeF_4 is square planar. Fluorine's weak bond and strong fluoride hydration explain its oxidising strength. Increasing metallic character lowers oxide acidity down group 15, and SO_2 decolourises acidified potassium permanganate.

Quick Tip to Solve: Count Xe's four bond pairs plus two lone pairs before drawing XeF_4 ; place the lone pairs opposite each other to leave a square plane of fluorine atoms.

27(a). E°_{cell} for the given redox reaction is 2.71 V



Calculate E_{cell} for the reaction. Write the direction of flow of current when an external opposite potential applied is

(i) less than 2.71 V and

(ii) greater than 2.71 V

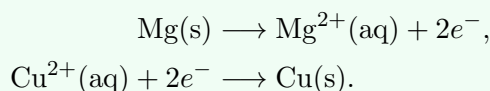
[5 marks]

Solution:

Concept:

- At 298 K, the Nernst equation 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. Conventional current in the external circuit flows opposite to electron flow. An opposing source reverses the reaction only when its potential exceeds the actual cell emf.

Step 1: Identify the electron transfer and reaction quotient The half-reactions are



Thus $n = 2$. Mg is the anode and Cu is the cathode. Omitting the solids,

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.001}{0.01} = 0.1.$$

Step 2: Apply the Nernst equation At 298 K, substitute $\log(0.1) = -1$:

$$\begin{aligned}E_{\text{cell}} &= 2.71 - \frac{0.0591}{2} \log(0.1) \\ &= 2.71 + 0.02955 \\ &= 2.73955 \text{ V} \simeq 2.74 \text{ V}.\end{aligned}$$

Step 3: Determine the current for an opposing potential below 2.71 V For an opposing potential $E_{\text{ext}} < 2.71 \text{ V}$, the cell still discharges since its emf is 2.73955 V. Electrons flow externally from Mg to Cu; conventional current flows externally from Cu to Mg.

Step 4: Compare the larger opposing potential with the actual emf For part (ii), compare with the actual emf. If $E_{\text{ext}} > 2.73955 \text{ V}$, the reaction reverses: electrons flow externally from Cu to Mg, and conventional current flows from Mg to Cu.

If $2.71 < E_{\text{ext}} < 2.73955 \text{ V}$, current still flows from Cu to Mg. At equality with the actual emf, current vanishes. Thus the printed lower bound alone does not specify a unique direction; reversal requires exceeding the actual emf.

Step 5: Conclusion $E_{\text{cell}} \simeq 2.74 \text{ V}$. (i) Conventional current flows externally from Cu to Mg. (ii) It reverses from Mg to Cu only above the actual emf 2.73955 V; between 2.71 V and that value it remains from Cu to Mg, and at equality it is zero.

Quick Tip to Solve: Exclude solid Mg and Cu from the reaction quotient, and compare the opposing voltage with the calculated emf before deciding whether current reverses.

27(b). (a) A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes FeSO_4 and ZnSO_4 until 2.8 g of Fe deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell Y.

(Molar mass: $\text{Fe} = 56 \text{ g mol}^{-1}$, $\text{Zn} = 65.3 \text{ g mol}^{-1}$, $1F = 96500 \text{ C mol}^{-1}$)

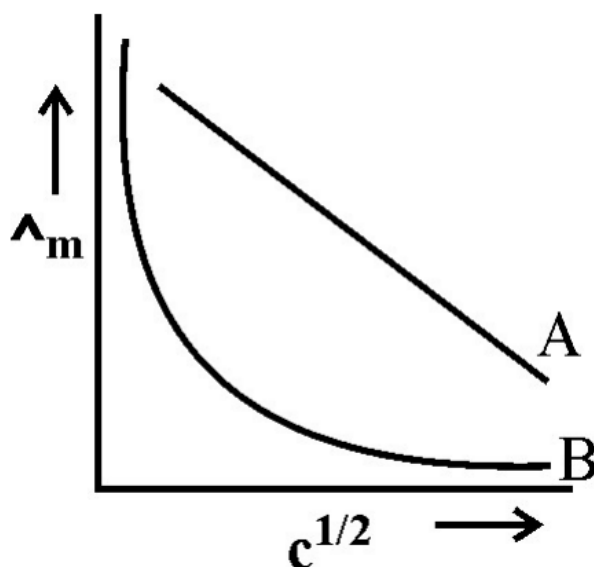
(b) In the plot of molar conductivity (Λ_m) vs square root of concentration ($c^{1/2}$), following curves are obtained for two electrolytes A and B:

Answer the following:

(i) Predict the nature of electrolytes A and B.

(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes A and B?

[5 marks]



Solution:

Concept:

- Faraday's law is $m = MQ/(nF)$, where m is deposited mass, M is molar mass, n is the number of electrons per metal ion and $Q = It$ is the charge passed.
- Cells connected in series receive the same charge. Both Fe^{2+} and Zn^{2+} require two electrons per deposited atom.
- A strong electrolyte follows $\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$ at low concentration. A weak electrolyte shows a strongly curved variation because its degree of ionisation increases on dilution.

Step 1: (a) Calculate the charge needed to deposit iron At the cathode of X, $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$. Hence depositing one mole of iron requires $2F$, and depositing $2.8/56 = 0.050 \text{ mol}$ requires

$$Q = \frac{2.8}{56} \times 2 \times 96500 = 9650 \text{ C}.$$

The factor of two is essential because the iron ion in FeSO_4 is divalent.

Quick Tip to Solve: In series, first calculate the common charge. When both metal ions have charge +2, the deposited masses are directly proportional to their molar masses.

Step 2: (a) Determine the current duration and zinc deposit The steady current is $I = 2\text{ A}$, so

$$t = \frac{Q}{I} = \frac{9650}{2} = 4825\text{ s} \approx 80.42\text{ min.}$$

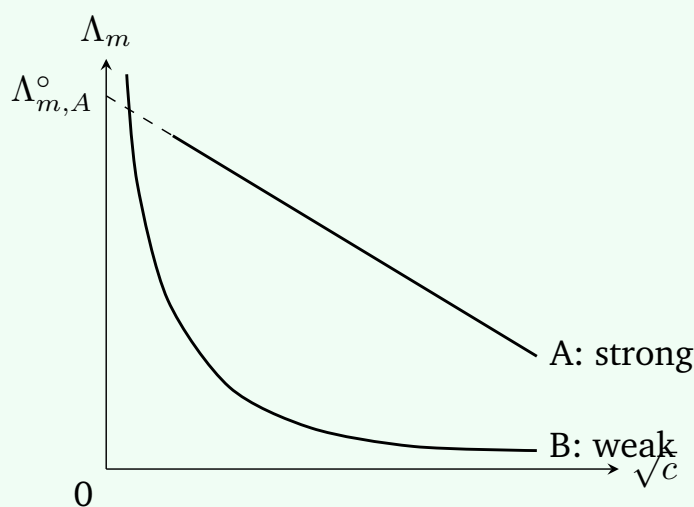
The same charge passes through Y, where $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$. Thus

$$m_{\text{Zn}} = \frac{65.3 \times 9650}{2 \times 96500} = 3.265\text{ g.}$$

Equivalently, equal electron requirements give equal deposited amounts in moles, so $m_{\text{Zn}} = (2.8/56) \times 65.3$.

Step 3: (b)(i) Identify the electrolytes from their curves A is a strong electrolyte: its molar conductivity decreases approximately linearly as $\sqrt{c}$ increases. It remains almost completely dissociated; dilution mainly reduces interionic interactions and increases ionic mobility. B is a weak electrolyte: its curve is distinctly nonlinear. On dilution, its ionisation increases substantially, producing a steep increase of Λ_m near zero concentration. The classification depends on the shape of each curve, not simply on which has the larger conductivity at a chosen concentration.

Step 4: (b)(ii) Explain extrapolation towards zero concentration For A, extend the straight line to $\sqrt{c} = 0$. The intercept on the Λ_m -axis gives its limiting molar conductivity, Λ_m° . For B, the sharp curvature at low concentration prevents a reliable direct graphical extrapolation to obtain Λ_m° . Its limiting molar conductivity nevertheless exists and can be calculated using Kohlrausch's law of independent migration of ions, from suitable strong electrolytes. It is incorrect to infer an infinite limiting conductivity merely from the steepness of the printed curve.



Schematic conductivity curves; the dashed extension of A locates its limiting intercept.

Step 5: Conclusion (a) The current flows for 4825 s and deposits 3.265 g of Zn. (b) A is a strong electrolyte and B is a weak electrolyte. Direct extrapolation gives Λ_m° for A, but is unreliable for B.

Quick Tip to Solve: In series, first calculate the common charge. When both metal ions have charge +2, the deposited masses are directly proportional to their molar masses.