CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-1-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) All questions are compulsory.

(ii) Section A : 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(a). Why are medicines more effective in colloidal state? [1 mark]

Solution:

Concept:

- Colloidal particles have a large surface area relative to their volume because their size is very small.
- The effectiveness of a medicine depends in part on how readily it is absorbed and brought into contact with the affected tissues.

Step 1: Identify the effect of small particle size For the same amount of medicine, subdivision into colloidal particles greatly increases the total exposed surface area. More of the medicine can therefore interact with the surrounding biological medium.

Step 2: Relate surface area to absorption The larger exposed area facilitates absorption and assimilation of the medicine by the body, so it can act more effectively at the required site.

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

Quick Tip to Solve: Link colloidal size to large surface area, then explicitly connect the surface area to easier absorption.

OR

1(b). What is the difference between an emulsion and a gel? [1 mark]

Solution:

Concept:

- A colloid is described by the physical states of its dispersed phase and its dispersion medium.
- The dispersed phase consists of the distributed particles or droplets; the dispersion medium is the continuous surrounding phase.

Step 1: Classify an emulsion In an emulsion, both phases are liquids: droplets of one liquid are dispersed in another liquid with which it does not mix completely. Milk is a familiar example.

Step 2: Classify a gel In a gel, the dispersed phase is liquid and the dispersion medium is solid. The solid network holds the liquid and gives the system its jelly-like form; jelly is a familiar example.

Step 3: Conclusion An emulsion is a liquid dispersed in a liquid, whereas a gel is a liquid dispersed in a solid.

Quick Tip to Solve: Keep the order dispersed phase first, medium second: emulsion is liquid/liquid; gel is liquid/solid.

2. Arrange the following in increasing order of base strength in gas phase:

$(C_2H_5)_3N,\ C_2H_5NH_2,\ (C_2H_5)_2NH$ [1 mark]

Solution:

Concept:

- An amine acts as a base by donating the lone pair on nitrogen to a proton.
- In the gas phase, electron donation by alkyl groups (the positive inductive effect) increases basic strength; aqueous solvation does not control this order.

Step 1: Compare the number of ethyl groups Ethylamine, $C_2H_5NH_2$, has one electron-donating ethyl group. Diethylamine, $(C_2H_5)_2NH$, has two, while triethylamine, $(C_2H_5)_3N$, has three.

Step 2: Apply the gas-phase trend Increasing the number of ethyl groups raises electron density on nitrogen and stabilises the protonated form. Thus proton acceptance becomes more favourable from the primary to the secondary to the tertiary amine.

Step 3: Conclusion The increasing order of basic strength is

$$C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N.$$

Quick Tip to Solve: Underline gas phase before ranking: for these ethylamines, increasing alkyl substitution increases basic strength.

3. Why conductivity of silicon increases on doping with phosphorus? [1 mark]

Solution:

Concept:

- Silicon has four valence electrons, whereas phosphorus has five valence electrons.
- Electrical conductivity rises when the number of mobile charge carriers in a semiconductor increases.

Step 1: Count the electrons used in bonding A phosphorus atom replacing a silicon atom uses four of its five valence electrons to form covalent bonds with four neighbouring silicon atoms. The fifth electron is not needed to complete these bonds.

Step 2: Identify the additional carrier This extra electron is only weakly bound and can readily become mobile in the crystal. Phosphorus therefore supplies donor electrons, increasing the concentration of electrons available to carry current.

Step 3: Conclusion Doping silicon with phosphorus increases conductivity by providing extra mobile electrons and produces an n-type semiconductor.

Quick Tip to Solve: Compare valence counts: phosphorus has one more electron than silicon, so the added carriers are electrons.

4(a). What is the basic structural difference between glucose and fructose? [1 mark]

Solution:

Concept:

- Glucose and fructose are both monosaccharides containing six carbon atoms.
- Their basic structural distinction is the type and position of the carbonyl group in the open-chain form.

Step 1: Identify the group in glucose Open-chain glucose contains a terminal aldehyde group, $-\mathrm{CHO}$, at carbon 1. Its condensed structure is $\mathrm{CHO}-(\mathrm{CHOH})_4-\mathrm{CH_2OH}$, so glucose is classified as an aldohexose.

Step 2: Identify the group in fructose Open-chain fructose contains a ketone group at carbon 2. Its condensed structure is $\mathrm{CH_2OH}-\mathrm{CO}-(\mathrm{CHOH})_3-\mathrm{CH_2OH}$, so fructose is classified as a ketohexose.

Step 3: Conclusion Glucose is an aldohexose (aldehyde group at C-1), whereas fructose is a ketohexose (ketone group at C-2) in their open-chain forms.

Quick Tip to Solve: Use the open-chain structures for this comparison: terminal carbonyl means aldehyde; internal carbonyl means ketone.

OR

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

Solution:

Concept:

- Lactose is a disaccharide made from one galactose unit and one glucose unit.
- Hydrolysis uses water to cleave the glycosidic linkage joining the two monosaccharide units.

Step 1: Identify the linked units Lactose contains a β-(1$\rightarrow$4) glycosidic linkage from the galactose unit to the glucose unit. Breaking this linkage releases the two component sugars.

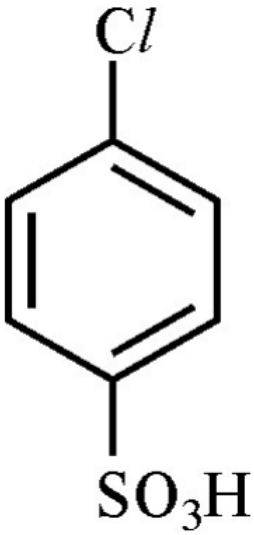
Step 2: Write the hydrolysis reaction On hydrolysis, each mole of lactose gives one mole each of D-galactose and D-glucose:

$$\underset{\text{lactose}}{\mathrm{C_{12}H_{22}O_{11}}} + \mathrm{H_2O} \longrightarrow \underset{\text{D-galactose}}{\mathrm{C_6H_{12}O_6}} + \underset{\text{D-glucose}}{\mathrm{C_6H_{12}O_6}}.$$

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

Quick Tip to Solve: Remember lactose as galactose plus glucose; do not confuse its products with the glucose and fructose from sucrose.

5. Write IUPAC name of the given compound: [1 mark]



Solution:

Concept:

- The sulfonic acid group, $-SO_3H$, is the principal functional group here and determines the parent name benzenesulfonic acid.
- The ring carbon bearing the principal group is numbered 1; other substituents receive locants relative to it.

Step 1: Choose and number the parent Take the benzene ring bearing $-SO_3H$ as benzenesulfonic acid. Assign carbon 1 to the ring carbon bonded to the sulfur atom of the sulfonic acid group.

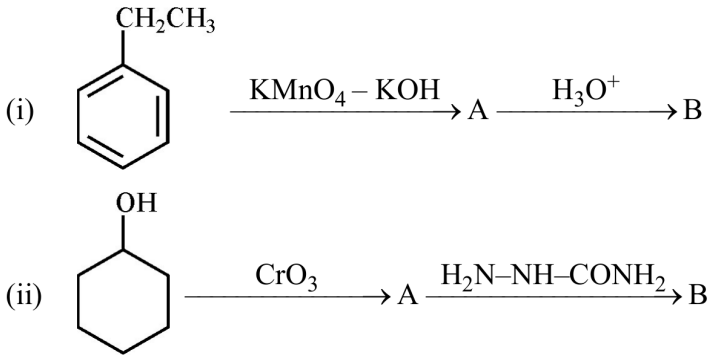
Step 2: Locate the chloro substituent The chlorine atom, Cl, is attached to the ring carbon directly opposite carbon 1. It therefore occupies carbon 4, the para position, and is named with the prefix 4-chloro.

Step 3: Conclusion The IUPAC name is 4-chlorobenzenesulfonic acid.

Quick Tip to Solve: Give the sulfonic acid group carbon 1 first; a substituent opposite it on benzene always has locant 4.

Section B (14 marks)

6. Write structures of compounds A and B in each of the following reactions: [2 marks]

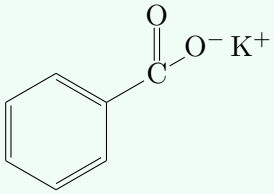


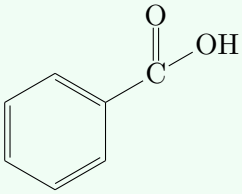
Solution:

Concept:

- Alkaline permanganate oxidises an alkylbenzene having a benzylic hydrogen to a benzoate salt; acidification gives benzoic acid.
- Chromium trioxide oxidises a secondary alcohol to a ketone. Semicarbazide, $H_2N{-}NH{-}CO{-}NH_2$, condenses with a carbonyl group to form $C{=}N{-}NH{-}CO{-}NH_2$.

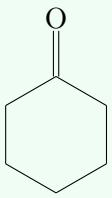
Step 1: (i) Oxidise ethylbenzene, then acidify The starting side chain is $-CH_2CH_3$. Its benzylic carbon has hydrogen atoms, so oxidation with $KMnO_4/KOH$ converts the side chain into $-COO^-K^+$, irrespective of its original length. Thus A is potassium benzoate and B is benzoic acid. Their structures are:

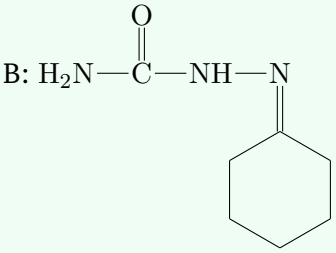
A: 

B: 

Acidification protonates the carboxylate ion; it does not change the benzene ring.

Step 2: (ii) Oxidise cyclohexanol and form its semicarbazone Cyclohexanol is a secondary alcohol. Oxidation changes the ring carbon bearing $-OH$ into a carbonyl carbon without breaking the six-membered ring. A is cyclohexanone. The terminal $-NH_2$ group of semicarbazide reacts with its carbonyl group, eliminating water. B is cyclohexanone semicarbazone:

A: 

B: 

The $-NH{-}CO{-}NH_2$ portion remains attached to the imine nitrogen.

Step 3: Conclusion (i) A: potassium benzoate, C_6H_5COOK; B: benzoic acid, C_6H_5COOH.

(ii) A: cyclohexanone; B: cyclohexanone semicarbazone, with the ring carbon bonded as

Quick Tip to Solve: Keep the six-membered ring intact in part (ii); replace C=O by C=N-NH-CO-NH2 for the semicarbazone.

$C{=}N{-}NH{-}CO{-}NH_2$.

Quick Tip to Solve: Keep the six-membered ring intact in part (ii); replace C=O by C=N-NH-CO-NH2 for the semicarbazone.

7. For a reaction

$$2\,H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2\,H_2O + O_2$$

the proposed mechanism is as given below:

(1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ **(slow)**

(2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ **(fast)**

(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 determines the rate of a multistep reaction. Its reactant concentrations give the rate-law factors.
- The overall order is the sum of the exponents in the rate law; it is not read from the balanced overall equation.

Step 1: (i) Obtain the rate law from the slow step Step (1), $H_2O_2 + I^- \longrightarrow H_2O + IO^-$, is slow and involves one peroxide species and one iodide ion. Its elementary rate expression is therefore

$$r = k[H_2O_2][I^-].$$

Here k is the rate constant at the specified temperature and the brackets denote molar concentrations. The fast second step consumes the intermediate IO^-, so that intermediate does not appear in the required rate law.

Step 2: (ii) Find the overall order The exponent of $[H_2O_2]$ is 1, and the exponent of $[I^-]$ is also 1. Hence the reaction is first order in each species and its overall order is $1 + 1 = 2$. Although two peroxide molecules occur in the net equation, that stoichiometric coefficient does not imply second order in peroxide.

Step 3: (iii) Identify the rate-determining step Step (1) is the rate-determining step because it is slower than step (2). Iodide is consumed in the first step and regenerated in the second, making it a catalyst. A catalyst can occur in the rate law even though it cancels from the overall equation.

Step 4: Conclusion $r = k[H_2O_2][I^-]$; overall order $= 2$; rate-determining step: step (1).

Quick Tip to Solve: Read concentration powers from the slow elementary step, then add those powers to obtain the overall order.

8. Write two differences between an ideal solution and a non-ideal solution. [2 marks]

Solution:

Concept:

- For component i, Raoultś law is $p_i = x_i p_i^\circ$, where x_i is its mole fraction and p_i° its pure-component vapour pressure at the same temperature.
- Ideal mixing leaves the average intermolecular interactions effectively unchanged; non-ideal mixing changes their strength.

Step 1: Difference 1: compliance with Raoult's law An ideal solution obeys Raoultś law for every component over the entire range of composition. For a binary ideal solution,

$$p_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ.$$

A non-ideal solution deviates from this law. Its actual vapour pressure may be greater than the ideal value (positive deviation) or less than the ideal value (negative deviation). Thus the distinction concerns the whole composition range, not just one measured composition.

Step 2: Difference 2: thermodynamic changes on mixing For an ideal solution, the enthalpy and volume changes on mixing are zero:

$$\Delta H_{\text{mix}} = 0, \qquad \Delta V_{\text{mix}} = 0.$$

For a non-ideal solution these changes are generally nonzero. Unlike-molecule attractions differ from like-molecule attractions, so mixing can absorb or release heat and cause expansion or contraction. Weaker unlike attractions usually produce positive deviation; stronger unlike attractions produce negative deviation.

Step 3: Conclusion Ideal: obeys Raoultś law at all compositions, with $\Delta H_{\text{mix}} = \Delta V_{\text{mix}} = 0$.

Non-ideal: deviates from Raoultś law, with generally nonzero enthalpy and volume changes on mixing.

Quick Tip to Solve: Compare the same two properties for both solution types: vapour-pressure law and changes on mixing.

9. 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:

- Manganate(VI), MnO_4^{2-}, is green; permanganate(VII), MnO_4^-, is purple.
- Permanganate oxidises iodide differently in different media: strongly alkaline conditions give iodate, whereas acidic conditions give iodine.

Quick Tip to Solve: Use the colours to distinguish manganate from permanganate, then check the medium before choosing the iodide oxidation product.

Step 1: Identify the green compound and its disproportionation product Oxidative fusion of MnO_2 with potassium hydroxide gives potassium manganate, A = K_2MnO_4. The nitrate supplies the oxidising action:

$$MnO_2 + 2\,KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O.$$

In acid, manganate disproportionates: manganese in oxidation state +6 forms both +7 and +4 products,

$$3\,MnO_4^{2-} + 4\,H^+ \longrightarrow 2\,MnO_4^- + MnO_2 + 2\,H_2O.$$

The purple compound B is potassium permanganate, $KMnO_4$.

Step 2: Identify the iodide oxidation products in the two media In alkaline solution, iodide is oxidised to iodate, so C is potassium iodate, KIO_3:

$$2\,MnO_4^- + I^- + H_2O \longrightarrow 2\,MnO_2 + IO_3^- + 2\,OH^-.$$

Iodine changes from oxidation state -1 in iodide to +5 in iodate. In acidic solution, the product is elemental iodine, D = I_2:

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O.$$

Here iodine changes from -1 to 0, while manganese changes from +7 to +2. Potassium ions are spectators in these ionic equations.

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: Use the colours to distinguish manganate from permanganate, then check the medium before choosing the iodide oxidation product.

10(a). Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex. [2 marks]

Solution:

Concept:

- In naming a coordination entity, list ligand names alphabetically before the metal name. Neutral NH_3 is ammine and Cl^- is chlorido.
- An octahedral complex of the form $[MA_4B_2]$ has two geometrical isomers: cis, with the two B ligands adjacent, and trans, with them opposite.

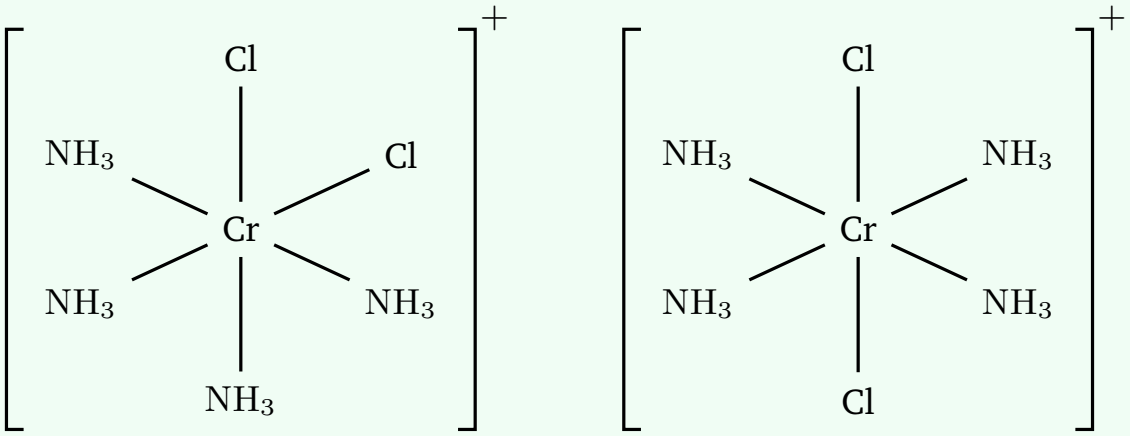
Step 1: Determine the oxidation state and name Let chromium have oxidation state x. The four ammine ligands are neutral and the two chlorido ligands each contribute -1, so

$$x + 4(0) + 2(-1) = +1 \quad \Rightarrow \quad x = +3.$$

Use tetraammine before dichlorido because alphabetical order ignores the prefixes tetra and di. The entity is cationic, so the metal retains the name chromium, followed by (III).

Quick Tip to Solve: For an octahedral MA_4B_2 complex, place the two identical B ligands adjacent for cis and opposite for trans.

Step 2: Place the ligands in an octahedral arrangement The six donor atoms occupy the vertices of an octahedron. In the cis structure, the two chlorido ligands subtend 90° at Cr; in the trans structure, they subtend 180°. The remaining four positions are occupied by ammine ligands. Rotating either structure does not produce another distinct geometrical isomer.



cis: Cl–Cr–Cl $= 90^\circ$ trans: Cl–Cr–Cl $= 180^\circ$

Octahedral cis and trans isomers; opposite equatorial sites lie on the same diagonal through Cr.

Step 3: Conclusion The IUPAC name is **tetraamminedichloridochromium(III) ion**. Its two geometrical isomers are **cis** and **trans**, as drawn above.

Quick Tip to Solve: For an octahedral MA_4B_2 complex, place the two identical B ligands adjacent for cis and opposite for trans.

OR

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

(i) Pentaamminenitrito-O-cobalt(III) chloride

(ii) Potassium tetracyanidonickelate(II) [2 marks]

Solution:

Concept:

- Write the metal and its attached ligands inside square brackets; counter-ions outside the brackets make the entire compound electrically neutral.
- Ammine (NH_3) is neutral, whereas nitrito (NO_2^-) and cyanido (CN^-) each carry charge -1. Nitrito-O specifies bonding through oxygen.

Step 1: Build the pentaamminenitrito-O-cobalt(III) chloride formula Cobalt(III) has charge $+3$. Five neutral ammine ligands contribute no charge, and one nitrito ligand contributes -1. Therefore the complex ion has charge

$$+3 + 5(0) - 1 = +2.$$

Quick Tip to Solve: Use ONO for nitrito-O, then calculate the bracketed ion's charge before adding chloride or potassium counter-ions.

Write the oxygen-bound nitrito ligand as ONO, giving $[Co(NH_3)_5(ONO)]^{2+}$. Two chloride counter-ions are required to balance this charge; chloride is not inside the coordination sphere.

Step 2: Build the potassium tetracyanidonickelate(II) formula Nickel(II) contributes $+2$, while four cyanido ligands contribute -4. Hence the complex ion is

$$[Ni(CN)_4]^{2-}, \qquad +2+4(-1)=-2.$$

Each potassium ion is K^+, so two potassium ions are needed per complex anion. The ending nickelate is consistent with the negatively charged coordination entity.

Step 3: Conclusion (i) $\boxed{[Co(NH_3)_5(ONO)]Cl_2}$.

(ii) $\boxed{K_2[Ni(CN)_4]}$.

Quick Tip to Solve: Use ONO for nitrito-O, then calculate the bracketed ion's charge before adding chloride or potassium counter-ions.

11. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is

(i) diamagnetic

(ii) more stable

(iii) outer orbital complex and

(iv) low spin complex?

(Atomic no. of Co = 27) [2 marks]

Solution:

Concept:

- Co has configuration $[Ar]3d^7 4s^2$; both complexes contain Co^{3+}, with configuration $3d^6$. Unpaired electrons cause paramagnetism, while an all-paired configuration is diamagnetic.
- In an octahedral field, a high-spin d^6 ion has configuration $t_{2g}^4 e_g^2$, whereas a low-spin d^6 ion has $t_{2g}^6 e_g^0$. Chelating ligands generally enhance complex stability.

Step 1: Compare electron pairing and orbital use In $[CoF_6]^{3-}$, fluoride is a weak-field ligand. The $3d^6$ electrons remain high spin, with four unpaired electrons. This is a paramagnetic, outer-orbital complex with sp^3d^2 hybridisation using the outer $4d$ orbitals.

In $[Co(C_2O_4)_3]^{3-}$, oxalate produces sufficient splitting for pairing in the Co(III) ion. The configuration is t_{2g}^6, with no unpaired electrons. It is a diamagnetic, low-spin, inner-orbital complex with d^2sp^3 hybridisation.

Step 2: Compare stability using chelation Each oxalate ion is bidentate and binds through two oxygen donor atoms, forming a chelate ring with cobalt. Three oxalate ligands occupy all six coordination positions. The chelate effect makes this complex more stable than the fluoride complex, whose six ligands are monodentate.

Step 3: Conclusion (i) Diamagnetic: $[Co(C_2O_4)_3]^{3-}$.

(ii) More stable: $[Co(C_2O_4)_3]^{3-}$.

Quick Tip to Solve: For these Co(III), d^6 complexes, connect fluoride with high spin and outer orbitals, and oxalate with pairing and chelation.

(iii) Outer orbital: $[CoF_6]^{3-}$.
(iv) Low spin: $[Co(C_2O_4)_3]^{3-}$.

Quick Tip to Solve: For these Co(III), d^6 complexes, connect fluoride with high spin and outer orbitals, and oxalate with pairing and chelation.

12(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 produces xenon, hydrogen fluoride and oxygen. Balance the atoms of each element, including the oxygen released from water.
- Hot concentrated hydrochloric acid reacts with manganese dioxide in a redox reaction: Mn(IV) is reduced to Mn(II), while chloride ions are oxidised to chlorine gas.

Step 1: Balance the hydrolysis of xenon difluoride Each XeF_2 supplies one xenon atom and two fluorine atoms, so it yields Xe and $2HF$. One water molecule supplies the two hydrogen atoms required for this HF, leaving half a molecule of oxygen. Multiplying throughout by two gives integer coefficients:

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

Both sides contain two Xe, four F, four H and two O atoms.

Step 2: Balance the reaction of manganese dioxide with concentrated HCl The two oxygen atoms form two water molecules, requiring four hydrogen atoms from four HCl molecules. Two chloride ions form $MnCl_2$, and the other two form Cl_2:

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

The HCl is concentrated. Mn changes from $+4$ to $+2$, gaining two electrons, while two chloride ions lose two electrons in forming chlorine; the electron balance agrees with the atom balance.

Step 3: Conclusion (i) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$.
(ii) $MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$, using concentrated HCl.

Quick Tip to Solve: Remember oxygen as a product of XeF2 hydrolysis; in the MnO2 reaction, four HCl supply both the chloride salt and chlorine gas.

OR

12(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, acidic character depends on the ease of releasing a proton. The strength of the bond between hydrogen and the central atom decreases down the group.
- Bond enthalpy is the energy required to break one mole of gaseous bonds. For hydrogen halides, increasing halogen size increases bond length and generally weakens the hydrogen-halogen bond.

Step 1: Compare the acidic character of group 16 hydrides From oxygen to tellurium, the central atom becomes larger and the overlap with the hydrogen orbital becomes less effective. Thus the bond to hydrogen weakens down the group, making proton release progressively easier. Although oxygen is the most electronegative of these elements, bond strength controls this down-group trend: water is the least acidic and hydrogen telluride is the most acidic of the given hydrides.

Step 2: Compare the hydrogen-halogen bond enthalpies Fluorine is the smallest halogen in this set, so the $H-F$ bond is shortest and strongest. On moving through chlorine and bromine to iodine, the bond becomes longer and weaker. Hence successively less energy is needed to break the bond; $H-I$ has the lowest bond enthalpy. The requested order here is decreasing, opposite to the increasing order requested for acidity.

Step 3: Conclusion (i) Increasing acidic character:

$$H_2O < H_2S < H_2Se < H_2Te.$$

(ii) Decreasing bond enthalpy:

$$HF > HCl > HBr > HI.$$

Quick Tip to Solve: Moving down either group weakens the bond to hydrogen: acidity increases, but bond enthalpy decreases. Check the requested direction before writing each order.

Section C (36 marks)

13. 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:

- An fcc unit cell contains $Z = 4$ atoms: the eight corner atoms each contribute $1/8$, and the six face-centred atoms each contribute $1/2$.
- For a cubic unit cell of edge a, its volume is a^3. A sample of mass w and density ρ occupies volume

Quick Tip to Solve: Use $N = Zw/(\rho a^3)$ directly with $Z = 4$ for fcc, and convert picometres to centimetres before cubing the cell edge.

$V = w/\rho$; dividing this by a^3 gives the number of unit cells.

Step 1: Convert the cell edge and calculate the cell volume Since the density is given in $\mathrm{g\,cm^{-3}}$, use centimetres for the edge length. As $1\,\mathrm{pm} = 10^{-10}\,\mathrm{cm}$,

$$\begin{aligned} a &= 300 \times 10^{-10} = 3.00 \times 10^{-8}\,\mathrm{cm}, \\ a^3 &= (3.00 \times 10^{-8})^3 \\ &= 27.0 \times 10^{-24} = 2.70 \times 10^{-23}\,\mathrm{cm^3}. \end{aligned}$$

The power of ten must be cubed along with the numerical factor.

Step 2: Find the number of unit cells in the sample The volume occupied by $108\,\mathrm{g}$ of the element is

$$V = \frac{w}{\rho} = \frac{108\,\mathrm{g}}{10.8\,\mathrm{g\,cm^{-3}}} = 10.0\,\mathrm{cm^3}.$$

Therefore the number of unit cells in the sample is

$$n_{\mathrm{cells}} = \frac{V}{a^3} = \frac{10.0}{2.70 \times 10^{-23}} = 3.7037 \times 10^{23}.$$

The volume units cancel, leaving a count of cells.

Step 3: Convert the cell count to an atom count Each fcc cell contains

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

atoms. Hence multiply the cell count by four:

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

This calculation uses density and the unit-cell geometry directly, so the molar mass and Avogadro constant are not needed separately.

Step 4: Conclusion The number of atoms in $108\,\mathrm{g}$ of the element is

$$\boxed{N \approx 1.48 \times 10^{24}\ \text{atoms.}}$$

Quick Tip to Solve: Use $N = Zw/(\rho a^3)$ directly with $Z = 4$ for fcc, and convert picometres to centimetres before cubing the cell edge.

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

(Given: Freezing point of pure water = 273.15 K) [3 marks]

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = K_f m$ for a non-electrolyte, where K_f is the solvent's molal depression constant and m is the number of moles of solute per kilogram of solvent.
- Sucrose and glucose do not dissociate in water, so their van't Hoff factors are both $i = 1$. For the same solvent, the ratio of freezing-point depressions equals the ratio of molalities.
- A mass percentage refers to the mass of the whole solution. Thus a 4% solution has $4\,\text{g}$ solute in $100\,\text{g}$ solution, leaving $96\,\text{g}$ solvent.

Step 1: Obtain the depression and molality for sucrose Take $100\,\text{g}$ of sucrose solution. It contains $4\,\text{g}$ sucrose and $96\,\text{g} = 0.096\,\text{kg}$ water. Therefore

$$\Delta T_{f,\text{s}} = 273.15 - 271.15 = 2.00\,\text{K},$$
$$m_{\text{s}} = \frac{4/342}{0.096} = 0.12183\,\text{mol kg}^{-1}.$$

Use the sucrose measurement to calibrate the depression for this question; no tabulated value of K_f is required.

Step 2: Calculate the glucose molality A $100\,\text{g}$ sample of 5% glucose solution contains $5\,\text{g}$ glucose and $95\,\text{g} = 0.095\,\text{kg}$ water. Its molality is

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

The solvent mass differs from that in the sucrose sample; replacing either solvent mass by $100\,\text{g}$ would be incorrect for the stated mass percentages.

Step 3: Compare the depressions and subtract from the pure-water value Dividing the two equations $\Delta T_f = K_f m$ cancels the common solvent constant:

$$\frac{\Delta T_{f,\text{g}}}{\Delta T_{f,\text{s}}} = \frac{(5/180)/0.095}{(4/342)/0.096}$$
$$= \frac{5 \times 342 \times 96}{180 \times 4 \times 95} = 2.4,$$
$$\Delta T_{f,\text{g}} = 2.00 \times 2.4 = 4.80\,\text{K}.$$

Freezing-point depression is a positive temperature difference, so subtract it from the freezing point of pure water: $T_{f,\text{g}} = 273.15 - 4.80\,\text{K}$. The larger glucose molality correctly produces a lower freezing point.

Step 4: Conclusion The freezing point of the 5% glucose solution is

$$\boxed{T_{f,\text{g}} = 268.35\,\text{K}.}$$

Quick Tip to Solve: On a $100\,\text{g}$ solution basis, use $96\,\text{g}$ and $95\,\text{g}$ of water, then take the molality ratio so that K_f cancels.

15. The decomposition of NH_3 on platinum surface is zero order reaction. If rate constant (k) is 4 $\times$ 10^{-3} 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 disappearance rate of the reactant is independent of its concentration: $-d[A]/dt = k$, where $[A]$ is the reactant concentration, t is time and k is the rate constant.
- Integrating gives $[A]_t = [A]_0 - kt$, so the time for a specified concentration decrease is $t = ([A]_0 - [A]_t)/k$. Here $[A]_0$ and $[A]_t$ denote the initial and remaining concentrations.

Step 1: Select the integrated zero-order equation The question explicitly states zero-order decomposition on the platinum surface. Hence the concentration of ammonia decreases linearly with time:

$$[\mathrm{NH_3}]_t = [\mathrm{NH_3}]_0 - kt.$$

The supplied units $\mathrm{M\,s^{-1}}$ for k are consistent with concentration lost per unit time. A logarithmic concentration ratio is used for first-order kinetics and is not applicable here.

Step 2: Determine the concentration consumed The initial concentration is $0.100\,\mathrm{M}$, while the concentration remaining at the required time is $0.064\,\mathrm{M}$. Their positive difference is

$$[\mathrm{NH_3}]_0 - [\mathrm{NH_3}]_t = 0.100 - 0.064 = 0.036\,\mathrm{M}.$$

Use this concentration decrease in the numerator, rather than the final concentration alone.

Step 3: Substitute into the time expression and check Rearranging the integrated equation gives

$$t = \frac{0.036\,\mathrm{M}}{4 \times 10^{-3}\,\mathrm{M\,s^{-1}}} = \frac{0.036}{0.004}\,\mathrm{s} = 9\,\mathrm{s}.$$

Concentration units cancel to leave seconds. As a check, the concentration after this time is

$$0.100 - (4 \times 10^{-3})(9) = 0.064\,\mathrm{M},$$

exactly the required remaining concentration. The time is positive because the concentration has decreased and the rate constant is positive.

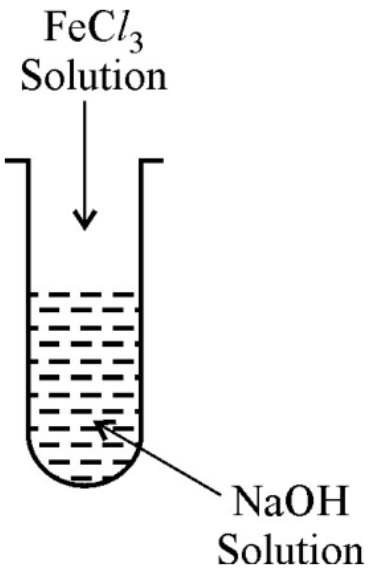
Step 4: Conclusion The required time for the ammonia concentration to decrease from $0.100\,\mathrm{M}$ to $0.064\,\mathrm{M}$ is $\boxed{9\,\mathrm{s}}$.

Quick Tip to Solve: For zero order, divide the concentration lost, $0.100 - 0.064$, by k; do not use a logarithm or divide the remaining concentration by k.

16. (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 molecules at a solid surface; a porous adsorbent offers a large surface area.
- A freshly formed colloidal particle preferentially adsorbs suitable ions present in excess, acquiring their charge.
- Chemisorption involves chemical bond formation and usually requires activation energy; adsorption itself is generally exothermic.

Step 1: Explain the action of activated charcoal (i) Activated charcoal in a gas mask adsorbs poisonous gases and vapours on its large, porous surface. Thus harmful gaseous impurities are retained while the air passes through the mask. Its effectiveness follows from its high surface area, which supplies many adsorption sites.

Step 2: Identify the ion adsorbed in the test tube (ii) The figure shows ferric chloride solution being added to sodium hydroxide solution. Hydrated ferric oxide, represented as ferric hydroxide, is formed:

$$\mathrm{FeCl_3 + 3\,NaOH \longrightarrow Fe(OH)_3 + 3\,NaCl.}$$

As the particles form in excess alkali, they preferentially adsorb OH^- ions. Hence they acquire a negative charge. The sol is represented as

$$\mathrm{Fe(OH)_3 \,/\, OH^-},$$

with Na^+ ions acting as counter-ions in the surrounding solution. The slash denotes adsorption of

Quick Tip to Solve: For the sign of a sol, identify the solution already in the test tube: excess alkali supplies adsorbed OH^-, giving a negative sol.

hydroxide ions on the colloidal particle, not a chemical division operation.

Step 3: Describe the temperature dependence (iii) At low temperature chemisorption is slow because molecules cannot readily cross the activation-energy barrier. Initially, increasing temperature increases chemisorption by helping molecules form chemical bonds with the surface. Beyond a suitable temperature, further heating decreases the extent of adsorption because desorption is favoured for an exothermic adsorption process.

Step 4: Conclusion Activated charcoal adsorbs harmful gases. The hydrated ferric oxide sol is negatively charged and represented as $Fe(OH)_3 / OH^-$. Chemisorption initially increases with temperature and then decreases at higher temperature.

Quick Tip to Solve: For the sign of a sol, identify the solution already in the test tube: excess alkali supplies adsorbed OH^-, giving a negative sol.

17. (i) Write the role of 'CO' in the purification of nickel.
(ii) What is the role of silica in the extraction of copper?
(iii) What type of metals are generally extracted by electrolytic method? [3 marks]

Solution:

Concept:

- In vapour-phase refining, the metal forms a volatile compound that is separated and then decomposed to give pure metal.
- A flux reacts with an impurity to form an easily removable slag; an acidic flux removes a basic oxide impurity.
- Highly electropositive metals are obtained by electrolytic reduction of their molten compounds, with metal ions gaining electrons at the cathode.

Step 1: State the role of carbon monoxide in nickel refining (i) In Mond's process, carbon monoxide acts as the ligand that converts impure nickel into volatile nickel tetracarbonyl at about 330–350 K:

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

The volatile carbonyl is separated from the non-volatile impurities and heated to about 450–470 K. It decomposes, depositing pure nickel and regenerating carbon monoxide:

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

Thus carbon monoxide enables the separation through formation of a volatile complex.

Step 2: Identify the function of silica (ii) Silica acts as an acidic flux during the extraction of copper. Iron present as an impurity is oxidised to basic ferrous oxide. Silica combines with this oxide to produce fusible iron silicate slag:

$$\mathrm{FeO} + \mathrm{SiO_2} \longrightarrow \mathrm{FeSiO_3}.$$

Quick Tip to Solve: Link each reagent to its product: carbon monoxide gives volatile nickel carbonyl, whereas silica gives iron silicate slag.

The slag separates from the copper-containing material and can be removed. Silica therefore removes the iron oxide impurity.

Step 3: Identify the metals requiring electrolysis (iii) Highly reactive, strongly electropositive metals, such as sodium, potassium, calcium, magnesium and aluminium, are generally extracted by electrolysis of their molten salts or molten oxide mixtures. Their compounds are too stable for ordinary chemical reduction by carbon. At the cathode a metal cation accepts electrons:

$$\mathrm{M}^{n+} + n\mathrm{e}^- \longrightarrow \mathrm{M}.$$

A molten electrolyte is used because, for these reactive metals, water would interfere with metal deposition from an aqueous solution.

Step 4: Conclusion Carbon monoxide forms volatile $Ni(CO)_4$ in nickel refining; silica removes FeO as $FeSiO_3$ slag; highly electropositive metals are extracted by electrolytic reduction.

Quick Tip to Solve: Link each reagent to its product: carbon monoxide gives volatile nickel carbonyl, whereas silica gives iron silicate slag.

18. Give reasons for the following:

(i) Transition metals form alloys.

(ii) Mn_2O_3 is basic whereas Mn_2O_7 is acidic.

(iii) Eu^{2+} is a strong reducing agent. [3 marks]

Solution:

Concept:

- Alloy formation is favoured when constituent metals have similar atomic radii and can occupy sites in the same metallic lattice.
- For a metal with several oxidation states, the basic character of its oxides generally decreases and acidic character increases as the oxidation state rises.
- A reducing agent donates electrons and is itself oxidised. The trivalent state is the characteristic stable oxidation state of lanthanoids.

Step 1: Relate alloy formation to atomic size (i) Transition metals have similar atomic sizes and often similar crystal structures. An atom of one transition metal can therefore replace an atom of another in its metallic lattice without causing a large distortion. Their compatible metallic bonding allows them to form substitutional solid solutions, or alloys; a familiar example is an iron-nickel alloy.

Step 2: Compare the oxidation states of manganese (ii) Taking oxygen as -2, the oxidation states of manganese are obtained from charge neutrality:

$$\mathrm{Mn_2O_3}: \quad 2x + 3(-2) = 0, \quad x = +3,$$
$$\mathrm{Mn_2O_7}: \quad 2x + 7(-2) = 0, \quad x = +7.$$

Quick Tip to Solve: Calculate the metal's oxidation state before classifying its oxide, and write electron loss explicitly when explaining a reducing agent.

In the lower oxidation state, the oxide is more ionic and behaves as a base, reacting with acids:

$$Mn_2O_3 + 6\,H^+ \longrightarrow 2\,Mn^{3+} + 3\,H_2O.$$

The higher oxidation state strongly polarises the oxygen electron cloud, producing a covalent acidic oxide. Thus Mn_2O_7 is the acid anhydride of permanganic acid:

$$Mn_2O_7 + H_2O \longrightarrow 2\,HMnO_4.$$

Step 3: Explain the reducing action of divalent europium (iii) Although Eu^{2+} has the half-filled configuration $[Xe]4f^7$, it readily loses an electron to form Eu^{3+} in aqueous solution:

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

The overall energetic balance, including the stronger hydration of the tripositive ion, favours oxidation to the characteristic trivalent lanthanoid state. The electron released reduces another species, so Eu^{2+} acts as a strong reducing agent. Half-filled-shell stability alone does not determine the aqueous redox behaviour.

Step 4: Conclusion Similar atomic sizes favour alloys; manganese's lower $+3$ oxide is basic whereas its higher $+7$ oxide is acidic; Eu^{2+} is strongly reducing because it is readily oxidised to Eu^{3+}.

Quick Tip to Solve: Calculate the metal's oxidation state before classifying its oxide, and write electron loss explicitly when explaining a reducing agent.

19(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 a small molecule from which a polymer is formed. Identify the functional groups that link together when writing its structure.
- Nylon-6,6 is a polyamide, glyptal is a polyester, and Buna-S is an addition copolymer of a diene and styrene.

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

$$H_2N - (CH_2)_6 - NH_2 \quad \text{hexamethylenediamine,}$$
$$HOOC - (CH_2)_4 - COOH \quad \text{adipic acid.}$$

Both monomers contain six carbon atoms. The amino and carboxyl groups react with elimination of water to form the amide links of the polymer.

Quick Tip to Solve: For Nylon-6,6 count six carbons in each monomer, including the two carboxyl carbons of adipic acid.

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

$$\begin{aligned} &HO - CH_2 - CH_2 - OH && \text{ethylene glycol,} \\ &1,2 - C_6H_4(COOH)_2 && \text{phthalic acid.} \end{aligned}$$

The two carboxyl groups of phthalic acid occupy adjacent positions on the benzene ring. Condensation between hydroxyl and carboxyl groups produces ester links.

Step 3: (iii) Monomers of Buna-S Buna-S is obtained by copolymerisation of buta-1,3-diene and styrene (phenylethene):

$$\begin{aligned} &CH_2 = CH - CH = CH_2 && \text{buta-1,3-diene,} \\ &C_6H_5 - CH = CH_2 && \text{styrene.} \end{aligned}$$

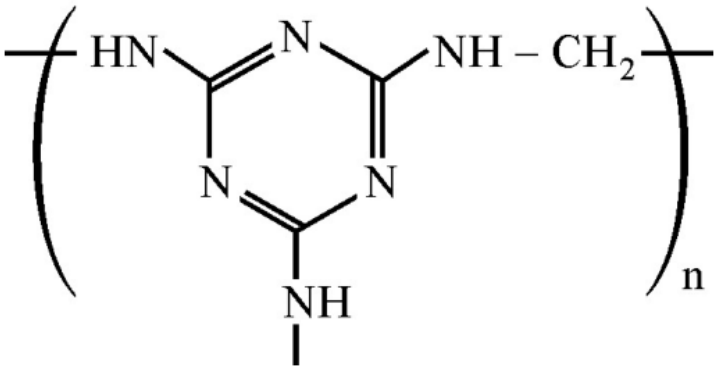
Both supply unsaturated bonds for addition polymerisation; styrene contributes the phenyl substituent to the rubber chain.

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: For Nylon-6,6 count six carbons in each monomer, including the two carboxyl carbons of adipic acid.

OR

19(b). (i) Is $\{CH_2\text{-}CH(CH_3)\}_n$ 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 formed from a single species of monomer, whereas a copolymer is formed from two or more different monomer species.
- Condensation polymers are identified from their characteristic linking groups. Vulcanisation

Quick Tip to Solve: Identify the alternating nitrogen-carbon ring first: a triazine ring linked through amino groups points to melamine-formaldehyde resin.

introduces sulphur cross-links between rubber chains.

Step 1: (i) Classify the given polymer The repeating unit is $[-CH_2 - CH(CH_3)-]$, obtained by opening the double bond of propene, $CH_2 = CH - CH_3$. Thus the polymer is polypropene (polypropylene). Every repeating unit comes from the same monomer, propene; the methyl side group does not represent a second monomer. Hence it is a homopolymer.

Step 2: (ii) Identify the monomers of the illustrated polymer The figure contains a 1,3,5-triazine ring with amino-derived groups and methylene bridges. It is melamine-formaldehyde resin. Its monomers are melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde (methanal).

$$\text{Melamine: } C_3N_3(NH_2)_3,$$
$$\text{Formaldehyde: } H - C(=O) - H.$$

In melamine, the six-membered ring has alternating carbon and nitrogen atoms, and each ring carbon bears an amino group. Formaldehyde reacts with these amino groups; subsequent condensation produces the methylene-linked resin shown in the question.

Step 3: (iii) Explain the role of sulphur During vulcanisation, sulphur forms cross-links at reactive sites associated with the double bonds in polyisoprene chains. These sulphur bridges connect neighbouring chains and restrict their slipping past one another. Consequently, rubber becomes stronger, more elastic and more resistant to wear and temperature changes. Its excessive softness and stickiness are reduced; after deformation the linked chains can return towards their original arrangement.

Step 4: Conclusion (i) The polymer is a homopolymer of propene. (ii) The monomers are melamine and formaldehyde. (iii) Sulphur creates cross-links between rubber chains, improving strength and elasticity.

Quick Tip to Solve: Identify the alternating nitrogen-carbon ring first: a triazine ring linked through amino groups points to melamine-formaldehyde resin.

20(a). (i) Why bithional is added in soap?
(ii) Why magnesium hydroxide is a better antacid than sodium bicarbonate?
(iii) Why soaps are biodegradable whereas detergents are non-biodegradable? [3 marks]

Solution:

Concept:

- An antiseptic inhibits or destroys microorganisms on living tissue; adding one to soap gives the soap an antiseptic action.
- An antacid neutralises excess stomach acid. Biodegradability depends on whether microorganisms can break down the molecular structure.

Step 1: (i) Purpose of bithional in soap Bithional is added to soap for its antiseptic properties. It inhibits the growth of bacteria on the skin and thereby reduces the unpleasant odour caused by bacterial action. Its role is to provide germ-inhibiting action in addition to the cleansing action of the soap.

Quick Tip to Solve: For biodegradability, compare the hydrocarbon chain structures instead of merely comparing the cleansing action of soap and detergent.

Step 2: (ii) Compare the two antacids Magnesium hydroxide is sparingly soluble and therefore neutralises excess hydrochloric acid gradually without raising the stomach pH excessively. Sodium bicarbonate is soluble; an excessive amount can make the stomach alkaline and stimulate further acid secretion. Their neutralisation reactions are

$$\mathrm{Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O},$$
$$\mathrm{NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2}.$$

Magnesium hydroxide also avoids the carbon dioxide evolved by bicarbonate, which can cause discomfort. Thus it provides gentler control of excess acidity.

Step 3: (iii) Explain biodegradability Soaps are sodium or potassium salts of long-chain fatty acids. Their generally straight hydrocarbon chains can be degraded by microorganisms, so soaps are biodegradable. The non-biodegradable synthetic detergents referred to here contain highly branched hydrocarbon chains. Microorganisms cannot readily attack and break down these branched structures, so such detergents persist in the environment. The key distinction is the chain structure: detergents with straight chains can be biodegradable, so non-biodegradability is characteristic of the branched-chain detergents in this comparison.

Step 4: Conclusion Bithional imparts antiseptic action; magnesium hydroxide controls acidity gradually without excessive alkalinity; soaps biodegrade because of their straight chains, while highly branched detergent chains resist microbial degradation.

Quick Tip to Solve: For biodegradability, compare the hydrocarbon chain structures instead of merely comparing the cleansing action of soap and detergent.

OR

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

(i) Antibiotics

(ii) Artificial sweeteners

(iii) Analgesics [3 marks]

Solution:

Concept:

- Drugs are classified by the biological function they perform: antibiotics act against microorganisms, while analgesics relieve pain.
- Artificial sweeteners provide a sweet taste as substitutes for sucrose; their usefulness depends on their sweetness and the energy they supply.

Step 1: (i) Define antibiotics and give an example Antibiotics are chemical substances produced wholly or partly by chemical synthesis which, in low concentrations, kill microorganisms or inhibit their growth by interfering with their metabolic processes. Many antibiotics were originally obtained from microorganisms such as moulds and bacteria. For example, penicillin is an antibiotic which inhibits bacterial cell-wall synthesis. Thus, its relevant action is against bacteria rather than merely

Quick Tip to Solve: Pair each term with its main function first: antibiotic—microbial growth, artificial sweetener—sweet taste, analgesic—pain relief. Then attach one standard example.

relieving the symptoms of an infection.

Step 2: (ii) Define artificial sweeteners and give an example Artificial sweeteners are synthetic substances used to impart sweetness to food and beverages in place of sugar. They are usually much sweeter than sucrose, so only a small amount is needed. For example, saccharin is an artificial sweetener. It is not metabolised by the body to provide food energy, making it a non-nutritive sweetening agent. The defining property here is the sweet taste it provides as a sugar substitute.

Step 3: (iii) Define analgesics and give an example Analgesics are drugs that reduce or abolish pain without causing loss of consciousness, mental confusion, incoordination or paralysis, or other disturbances of the nervous system. For example, aspirin is a non-narcotic analgesic. It relieves pain and also has fever-reducing and anti-inflammatory actions. The pain-relieving action identifies it as an analgesic; an analgesic need not kill the microorganism that may have caused an illness.

Step 4: Conclusion Suitable examples are: (i) antibiotic—penicillin; (ii) artificial sweetener—saccharin; and (iii) analgesic—aspirin.

Quick Tip to Solve: Pair each term with its main function first: antibiotic—microbial growth, artificial sweetener—sweet taste, analgesic—pain relief. Then attach one standard example.

21. Write the structures of main products when benzene diazonium chloride reacts with the following reagents:

(i) CuCN

(ii) CH_3CH_2OH

(iii) KI [3 marks]

Solution:

Concept:

- In substitution reactions of benzene diazonium chloride, $C_6H_5N_2{}^+Cl^-$, the diazonium group is replaced and stable nitrogen gas, N_2, is released.
- Cuprous cyanide replaces the diazonium group by $-CN$; ethanol reduces it to hydrogen; iodide replaces it by iodine. In the condensed structures below, $C_6H_5{}^-$ represents a phenyl ring.

Step 1: (i) Replace the diazonium group using cuprous cyanide Reaction with $CuCN$ is a Sandmeyer reaction. The cyanide group becomes attached to the benzene ring through its carbon atom, giving benzonitrile:

$$C_6H_5N_2Cl + CuCN \longrightarrow C_6H_5{-}C{\equiv}N + N_2 + CuCl.$$

The main organic product has the condensed structure $C_6H_5{-}C{\equiv}N$. It is a nitrile, not an isocyanide, since the ring is bonded to carbon rather than nitrogen of the introduced group.

Step 2: (ii) Reduce the diazonium group with ethanol Ethanol acts as a reducing agent and replaces the diazonium group by hydrogen. Ethanol itself is oxidised to ethanal during the reaction:

$$C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow C_6H_5{-}H + N_2 + CH_3CHO + HCl.$$

Quick Tip to Solve: Keep the phenyl ring unchanged and replace only the diazonium group: $CuCN$ gives $-CN$, ethanol gives $-H$, and KI gives $-I$.

The main product derived from the diazonium salt is benzene, C_6H_6, represented structurally as $C_6H_5{-}H$. In this reaction ethanol does not introduce an ethoxy group into the ring.

Step 3: (iii) Replace the diazonium group with iodide Potassium iodide supplies iodide ions, which replace the diazonium group to give iodobenzene:

$$C_6H_5N_2Cl + KI \longrightarrow C_6H_5{-}I + N_2 + KCl.$$

Thus, the product structure is $C_6H_5{-}I$, with iodine bonded directly to the aromatic ring. Unlike the corresponding copper-assisted preparation of chloro- or bromobenzene, this iodide replacement does not require a cuprous halide catalyst.

Step 4: Conclusion The main organic products are (i) benzonitrile, $C_6H_5{-}C{\equiv}N$; (ii) benzene, $C_6H_5{-}H$; and (iii) iodobenzene, $C_6H_5{-}I$.

Quick Tip to Solve: Keep the phenyl ring unchanged and replace only the diazonium group: $CuCN$ gives $-CN$, ethanol gives $-H$, and KI gives $-I$.

22. (i) Out of $(CH_3)_3C$-Br and $(CH_3)_3C$-I, which one is more reactive towards S_N1 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:

- The rate-determining step of an S_N1 reaction is ionisation of the carbon-halogen bond to form a carbocation. With the same carbocation, the better leaving group gives the faster reaction.
- A nitro group at the ortho or para position activates an aryl halide towards nucleophilic substitution by stabilising the negatively charged intermediate.
- Enantiomers have identical physical properties, including boiling points, in an achiral environment; they rotate plane-polarised light through equal angles in opposite directions.

Step 1: (i) Compare the leaving groups Both $(CH_3)_3C{-}Br$ and $(CH_3)_3C{-}I$ form the same tertiary butyl carbocation on ionisation:

$$(CH_3)_3C{-}X \longrightarrow (CH_3)_3C^+ + X^-, \qquad X = Br \text{ or } I.$$

Their carbocation stabilities are therefore the same. The $C{-}I$ bond is weaker than the $C{-}Br$ bond, and I^- is a better leaving group than Br^-. Hence, tert-butyl iodide ionises more readily and is more reactive towards S_N1.

Step 2: (ii) Identify the product after acidification The para nitro group facilitates replacement of chlorine by hydroxyl on heating with aqueous sodium hydroxide at $443\,K$. In the alkaline reaction mixture the product is present as sodium 4-nitrophenoxide. Acidification protonates the phenoxide

Quick Tip to Solve: When two halides form the same carbocation, compare leaving groups. For an alkaline phenol preparation, check whether acidification is specified before naming the final product.

ion to give 4-nitrophenol, also called p-nitrophenol:

$$\text{p-NO}_2\text{–C}_6\text{H}_4\text{–Cl} + 2\,\text{NaOH} \longrightarrow \text{p-NO}_2\text{–C}_6\text{H}_4\text{–ONa} + \text{NaCl} + \text{H}_2\text{O},$$
$$\text{p-NO}_2\text{–C}_6\text{H}_4\text{–ONa} + \text{HCl} \longrightarrow \text{p-NO}_2\text{–C}_6\text{H}_4\text{–OH} + \text{NaCl}.$$

The hydroxyl and nitro groups occupy para positions on the benzene ring.

Step 3: (iii) Explain why fractional distillation fails Butan-2-ol, $\text{CH}_3\text{–CH(OH)–CH}_2\text{–CH}_3$, has one asymmetric carbon attached to four different groups. Its dextro- and laevo-rotatory forms are enantiomers. Fractional distillation separates substances through differences in their boiling points and relative volatilities. These two enantiomers have identical boiling points and vapour pressures under ordinary achiral conditions, so neither becomes enriched by ordinary fractional distillation. Their opposite optical rotations do not provide a boiling-point difference.

Step 4: Conclusion (i) $(\text{CH}_3)_3\text{C–I}$ is more reactive because iodide is the better leaving group. (ii) The final product is p-nitrophenol, $\text{p-NO}_2\text{–C}_6\text{H}_4\text{–OH}$. (iii) The two butan-2-ol enantiomers cannot be resolved by ordinary fractional distillation because their boiling points are identical.

Quick Tip to Solve: When two halides form the same carbocation, compare leaving groups. For an alkaline phenol preparation, check whether acidification is specified before naming the final product.

23(a). Differentiate between the following:

(i) Amylose and Amylopectin

(ii) Peptide linkage and Glycosidic linkage

(iii) Fibrous proteins and Globular proteins [3 marks]

Solution:

Concept:

- Polysaccharides differ in the way their monosaccharide units are linked and whether their chains have branches.
- A peptide linkage joins amino acids through an amide group, whereas a glycosidic linkage joins sugar units through oxygen.
- Protein shape and intermolecular interactions determine whether a protein is fibrous or globular and influence its solubility.

Step 1: Compare amylose and amylopectin **(i) Amylose** is the water-soluble component of starch. It consists of long, unbranched chains of α-D-glucose units joined by $\alpha(1 \to 4)$ glycosidic linkages; these chains can form helices. **Amylopectin** is the water-insoluble component of starch. Its chains have $\alpha(1 \to 4)$ linkages, but branches arise through $\alpha(1 \to 6)$ linkages. Thus, the decisive structural difference is absence or presence of branching.

Step 2: Distinguish the two linkages **(ii) A peptide linkage**, –CO–NH–, forms by condensation between the carboxyl group of one amino acid and the amino group of another, with loss of water. It is the characteristic linkage in proteins. **A glycosidic linkage**, C–O–C, joins two monosaccharide units through an oxygen atom, with elimination of water between appropriate hydroxyl groups. It is

Quick Tip to Solve: For each pair, give its defining structural difference first: branching, the atoms in the linkage, or the overall shape of the protein.

found in disaccharides and polysaccharides such as starch.

Step 3: Compare fibrous and globular proteins **(iii) Fibrous proteins** contain polypeptide chains arranged in elongated, fibre-like structures; the chains are held together by interactions such as hydrogen bonds and disulphide bonds. They are generally insoluble in water and perform structural functions, as in keratin and myosin. **Globular proteins** have chains folded into compact, roughly spherical structures. They are usually water-soluble and commonly perform metabolic functions; insulin and albumin are examples.

Step 4: Conclusion Amylose is unbranched while amylopectin is branched; peptide bonds join amino acids while glycosidic bonds join sugars; fibrous proteins are elongated and generally insoluble, whereas globular proteins are compact and usually soluble.

Quick Tip to Solve: For each pair, give its defining structural difference first: branching, the atoms in the linkage, or the overall shape of the protein.

OR

23(b). Write chemical reactions to show that open structure of D-glucose contains the following:

(i) Straight chain

(ii) Five alcohol groups

(iii) Aldehyde as carbonyl group [3 marks]

Solution:

Concept:

- Chemical reactions identify the carbon skeleton and functional groups in the open-chain form of D-glucose, $CHO-(CHOH)_4-CH_2OH$.
- Prolonged heating with hydriodic acid reduces glucose to a hydrocarbon; acetylation counts its free hydroxyl groups; mild oxidation distinguishes an aldehyde from a ketone.

Step 1: Establish the straight carbon chain **(i)** On prolonged heating with excess hydriodic acid, glucose gives n-hexane:

$$C_6H_{12}O_6 + 14\,HI \xrightarrow{\Delta} CH_3(CH_2)_4CH_3 + 6\,H_2O + 7\,I_2.$$

Formation of the unbranched six-carbon hydrocarbon shows that the six carbon atoms in glucose are connected in a straight chain. The oxygen-containing groups are removed during this reduction while the carbon skeleton is retained.

Step 2: Identify five alcoholic hydroxyl groups **(ii)** Acetylation of glucose with acetic anhydride gives glucose pentaacetate:

$$C_6H_{12}O_6 + 5\,(CH_3CO)_2O \longrightarrow C_6H_7O(OCOCH_3)_5 + 5\,CH_3COOH.$$

Each free hydroxyl group forms one acetate ester group, $-OCOCH_3$. Formation of the pentaacetate therefore demonstrates the presence of five hydroxyl groups. Since glucose is stable, the five hydroxyl

Quick Tip to Solve: Match each structural claim to a diagnostic product: straight chain to n-hexane, five hydroxyl groups to pentaacetate, and aldehyde to gluconic acid.

groups are associated with five different carbon atoms in the usual open-chain structure.

Step 3: Identify the aldehyde carbonyl group **(iii)** Bromine water oxidises glucose to gluconic acid:

$$\mathrm{CHO{-}(CHOH)_4{-}CH_2OH + Br_2 + H_2O}$$

$$\longrightarrow \mathrm{COOH{-}(CHOH)_4{-}CH_2OH + 2\,HBr.}$$

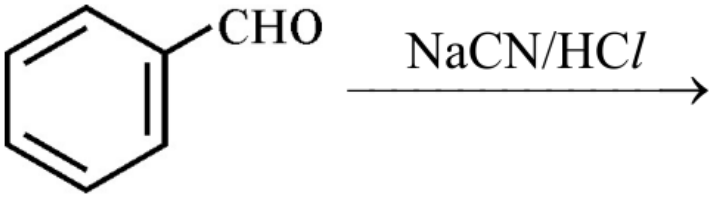
Bromine water is a mild oxidising agent: it converts the terminal $-\mathrm{CHO}$ group into $-\mathrm{COOH}$, leaving the alcoholic groups unchanged. A ketonic carbonyl does not undergo this mild oxidation. Hence the carbonyl group in open-chain glucose is aldehydic.

Step 4: Conclusion Formation of n-hexane establishes a straight six-carbon chain, formation of glucose pentaacetate establishes five alcoholic hydroxyl groups, and oxidation to gluconic acid establishes an aldehyde group.

Quick Tip to Solve: Match each structural claim to a diagnostic product: straight chain to n-hexane, five hydroxyl groups to pentaacetate, and aldehyde to gluconic acid.

24(a). Complete the following reactions:

(i)



(ii) $(\mathrm{C_6H_5CH_2)_2Cd + 2\,CH_3COCl \longrightarrow}$

(iii) $\mathrm{CH_3{-}CH(CH_3){-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2/\textbf{Red } P_4}}$ [3 marks]

Solution:

Concept:

- Cyanide adds to the electrophilic carbon atom of a carbonyl group; protonation of the resulting alkoxide forms a cyanohydrin.
- Dialkylcadmium reagents convert acyl chlorides into ketones by transferring an organic group to the acyl carbon.
- The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine using bromine and red phosphorus, followed by hydrolysis.

Step 1: Complete the cyanohydrin formation **(i)** $\mathrm{NaCN/HCl}$ supplies hydrogen cyanide. Cyanide addition to benzaldehyde followed by protonation gives:

$$\mathrm{C_6H_5CHO + HCN \xrightarrow{NaCN/HCl} C_6H_5CH(OH)CN.}$$

The product is benzaldehyde cyanohydrin, also called mandelonitrile. Both $-\mathrm{OH}$ and $-\mathrm{CN}$ attach to

Quick Tip to Solve: Track the reactive carbon: add OH and CN at the aldehyde carbon, replace acyl chloride's Cl by benzyl, and replace the acid's alpha H by Br.

the original carbonyl carbon.

Step 2: Form the ketone from the acyl chloride **(ii)** Dibenzylcadmium transfers one benzyl group, $C_6H_5CH_2^-$, to each molecule of acetyl chloride:

$$(C_6H_5CH_2)_2Cd + 2\,CH_3COCl$$

$$\longrightarrow 2\,CH_3COCH_2C_6H_5 + CdCl_2.$$

The ketone is 1-phenylpropan-2-one. Both benzyl groups are used, giving two ketone molecules and one molecule of $CdCl_2$.

Step 3: Brominate the alpha carbon of the acid **(iii)** In 2-methylpropanoic acid, the carbon next to $-COOH$ has one hydrogen. This alpha hydrogen is replaced by bromine in the Hell–Volhard–Zelinsky reaction:

$$(CH_3)_2CHCOOH + Br_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) Red } P_4} (CH_3)_2C(Br)COOH + HBr.$$

Hydrolysis restores $-COOH$, giving 2-bromo-2-methylpropanoic acid.

Step 4: Conclusion The products are (i) $C_6H_5CH(OH)CN$, (ii) $2\,CH_3COCH_2C_6H_5 + CdCl_2$, and (iii) $(CH_3)_2C(Br)COOH$, with HBr as the by-product in (iii).

Quick Tip to Solve: Track the reactive carbon: add OH and CN at the aldehyde carbon, replace acyl chloride's Cl by benzyl, and replace the acid's alpha H by Br.

OR

24(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 an alpha hydrogen undergoes aldol addition with dilute base, forming a beta-hydroxy ketone.
- Clemmensen reduction converts a carbonyl group to a methylene group using amalgamated zinc and concentrated hydrochloric acid.
- Rosenmund reduction converts an acyl chloride to an aldehyde using hydrogen and poisoned palladium supported on barium sulphate.

Step 1: (i) Aldol addition of propanone Propanone has alpha hydrogens. Dilute $Ba(OH)_2$ generates an enolate, which attacks the carbonyl carbon of another propanone molecule. Protonation gives diacetone alcohol, or 4-hydroxy-4-methylpentan-2-one:

$$2CH_3COCH_3 \xrightarrow{\text{dilute } Ba(OH)_2} CH_3COCH_2C(OH)(CH_3)_2.$$

Quick Tip to Solve: Identify the reagent first: dilute base gives an aldol addition product, Zn(Hg)/HCl removes carbonyl oxygen, and Pd/BaSO4 stops acyl chloride reduction at the aldehyde.

This is the beta-hydroxy ketone obtained under the stated dilute-base conditions. Dehydration to an unsaturated ketone requires an additional heating step, which the question does not specify.

Step 2: (ii) Clemmensen reduction of acetophenone The carbonyl group of acetophenone is reduced to $-CH_2-$, while the benzene ring remains intact. The product is ethylbenzene:

$$C_6H_5COCH_3 + 4[H] \xrightarrow{Zn(Hg)/\text{conc. HCl}} C_6H_5CH_2CH_3 + H_2O.$$

Here [H] denotes reducing equivalents supplied by the zinc and acid system; it is not free molecular hydrogen.

Step 3: (iii) Rosenmund reduction of benzoyl chloride The poisoned catalyst limits hydrogenation to the aldehyde stage. Benzoyl chloride therefore gives benzaldehyde, with hydrogen chloride as the other product:

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

The carbonyl group is retained in the aldehyde; this reagent does not convert the substrate to ethylbenzene or benzyl alcohol under the stated conditions.

Step 4: Conclusion The respective organic products are $CH_3COCH_2C(OH)(CH_3)_2$ (diacetone alcohol), $C_6H_5CH_2CH_3$ (ethylbenzene), and C_6H_5CHO (benzaldehyde).

Quick Tip to Solve: Identify the reagent first: dilute base gives an aldol addition product, Zn(Hg)/HCl removes carbonyl oxygen, and Pd/BaSO4 stops acyl chloride reduction at the aldehyde.

Section D (15 marks)

25(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:

- Paramagnetism results from unpaired electrons: such species are attracted by an external magnetic field.
- Single-bond strength depends on effective orbital overlap and repulsion between the lone pairs on adjacent atoms.
- Thermodynamic stability is judged by Gibbs energy. A reaction with negative ΔG is thermodynamically favourable.
- Nitric acid oxidises copper to copper(II); the nitrogen-containing reduction product depends on the acid concentration.

Quick Tip to Solve: For copper and nitric acid, remember dilute gives colourless NO and concentrated gives brown NO2; distinguish the gas first formed from NO2 produced later in air.

Step 1: (a)(i) Paramagnetism of sulphur vapour At high temperature, sulphur vapour contains S_2 molecules. Like O_2, each S_2 molecule has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons cause attraction towards a magnetic field, so the vapour shows paramagnetic behaviour. The explanation is the electronic configuration of the diatomic species present in the vapour, rather than a general magnetic property of solid sulphur.

Step 2: (a)(ii) Relative strengths of N-N and P-P single bonds Nitrogen atoms are small, so the lone pairs on adjacent nitrogen atoms lie close together in an N-N single bond. Strong lone-pair–lone-pair repulsion weakens this bond. Phosphorus atoms are larger and their lone pairs are farther apart, making this repulsion smaller in a P-P single bond. Consequently, the N-N single bond is weaker than the P-P single bond. This comparison concerns single bonds; it does not concern the very strong triple bond in N_2.

Step 3: (a)(iii) Thermodynamic instability of ozone Ozone decomposes to oxygen by an exothermic reaction:

$$2O_3(g) \longrightarrow 3O_2(g), \qquad \Delta H^\circ < 0.$$

The number of gas molecules also increases, giving a positive entropy change. Hence $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is negative for this decomposition under ordinary conditions. Conversion to oxygen is therefore thermodynamically favourable, which makes ozone less stable than oxygen. Thermodynamic favourability does not by itself specify how fast the decomposition occurs.

Step 4: (b)(i) Copper with dilute nitric acid Dilute nitric acid oxidises copper and is reduced mainly to nitric oxide, NO, a colourless gas:

$$3Cu + 8HNO_3 \text{ (dilute)} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

On contact with air, the released nitric oxide can become brown because it reacts with oxygen to form NO_2. The gas initially produced by the stated dilute-acid reaction is nevertheless nitric oxide.

Step 5: (b)(ii) Copper with concentrated nitric acid With concentrated nitric acid, the nitrogen-containing reduction product is nitrogen dioxide, NO_2, a brown gas:

$$Cu + 4HNO_3 \text{ (concentrated)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O.$$

Copper forms copper(II) nitrate in both reactions, but the acid concentration changes the gaseous reduction product. Hydrogen gas is not the product of either reaction because nitric acid acts as an oxidising acid.

Step 6: Conclusion Sulphur vapour is paramagnetic because S_2 has two unpaired electrons. Strong lone-pair repulsion weakens the N-N single bond, and favourable decomposition makes ozone less stable than oxygen. Copper releases nitric oxide (NO) with dilute nitric acid and nitrogen dioxide (NO_2) with concentrated nitric acid.

Quick Tip to Solve: For copper and nitric acid, remember dilute gives colourless NO and concentrated gives brown NO2; distinguish the gas first formed from NO2 produced later in air.

OR

25(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 reactant. The oxidation number of phosphorus in H_3PO_3 is $+3$.
- VSEPR predicts shape from the bond pairs and lone pairs around the central atom. Six electron pairs have an octahedral arrangement; two opposite lone pairs leave four bonds in a square plane.
- Oxidising strength in aqueous solution depends on the total energetics of bond dissociation, electron gain and hydration, not on electron gain enthalpy alone.
- Increasing metallic character makes oxides less acidic. Sulphur dioxide is a reducing agent and reduces acidified permanganate to nearly colourless Mn^{2+}.

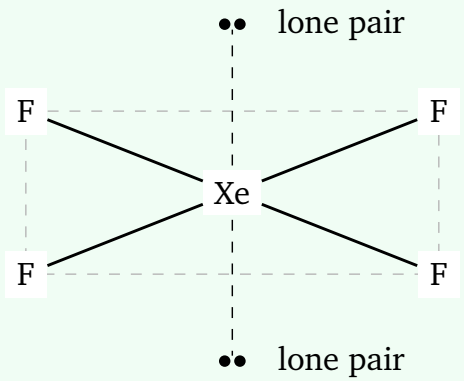
Step 1: (a)(i) Disproportionation of phosphorous acid On heating, phosphorous acid gives phosphoric acid and phosphine:

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3.$$

Phosphorus changes from $+3$ to $+5$ in H_3PO_4, so three phosphorus atoms each lose two electrons. The remaining phosphorus changes from $+3$ to -3 in PH_3, gaining six electrons. Thus the oxidation and reduction occur together and the electron changes balance.

Step 2: (a)(ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four participate in four Xe–F bonds and the remaining four form two lone pairs on xenon. There are therefore six electron pairs around Xe: four bond pairs and two lone pairs, conventionally described by sp^3d^2 hybridisation. The electron-pair arrangement is octahedral. The two lone pairs occupy opposite positions to minimise their repulsion, leaving all four fluorine atoms and Xe in one plane. The molecular shape is **square planar**, with adjacent F–Xe–F angles of 90° and opposite angles of 180°.

Quick Tip to Solve: Count both bond pairs and lone pairs for XeF4: six electron pairs give an octahedral arrangement, but two opposite lone pairs leave a square planar molecule.



Four F atoms and Xe in one plane

Square planar XeF4 shown in perspective; the two 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 very compact $2p$ shell strongly repels the incoming electron. Nevertheless, aqueous reduction involves the overall process

$$\mathrm{F_2(g) + 2}e^- \longrightarrow \mathrm{2F^-(aq)}.$$

The F–F bond has a low bond dissociation enthalpy because of strong lone-pair repulsions between the small fluorine atoms. Also, the very small fluoride ion has a highly negative hydration enthalpy. The low energy required to dissociate $\mathrm{F_2}$, together with the large energy released on hydrating $\mathrm{F^-}$, outweighs the less favourable electron gain enthalpy. Hence $\mathrm{F_2}$ is a very strong oxidising agent.

Step 4: (b)(ii) Decreasing acidity of group 15 oxides Down group 15, atomic size increases, electronegativity decreases and metallic character increases. The trioxides consequently become less covalent and more ionic, so their acidic character decreases from $\mathrm{N_2O_3}$ to $\mathrm{Bi_2O_3}$. Nitrogen trioxide is acidic, arsenic and antimony trioxides show amphoteric character, and bismuth trioxide is predominantly basic. This change follows the increasing metallic nature of the central element.

Step 5: (c) Chemical test for sulphur dioxide Pass the gas through potassium permanganate solution acidified with dilute sulphuric acid. Its purple colour is discharged because sulphur dioxide reduces permanganate to $\mathrm{Mn^{2+}}$, while sulphur is oxidised from $+4$ to $+6$:

$$\mathrm{2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4}.$$

Thus decolourisation of acidified permanganate provides the required chemical test for the reducing action of sulphur dioxide.

Step 6: Conclusion On heating, $\mathrm{4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3}$; $\mathrm{XeF_4}$ is square planar with two opposite lone pairs. Fluorine's weak F–F bond and highly exothermic fluoride hydration explain its strong oxidising power. Increasing metallic character reduces group 15 oxide acidity, and $\mathrm{SO_2}$ decolourises acidified $\mathrm{KMnO_4}$.

Quick Tip to Solve: Count both bond pairs and lone pairs for XeF4: six electron pairs give an octahedral arrangement, but two opposite lone pairs leave a square planar molecule.

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

$Mg_{(s)} + Cu^{2+}_{(0.01\ M)} \rightarrow Mg^{2+}_{(0.001\ M)} + Cu_{(s)}$

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 $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log_{10} Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- Electrons flow externally from anode to cathode; conventional current flows oppositely. An opposing voltage reverses current only when it exceeds the actual emf.

Step 1: Identify the electron transfer and reaction quotient Magnesium is oxidised and copper(II) ions are reduced:

$$\mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2e^-,$$
$$\mathrm{Cu^{2+}(aq)} + 2e^- \longrightarrow \mathrm{Cu(s)}.$$

Thus $n = 2$. Omitting pure solids from the reaction quotient,

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

Step 2: Substitute in the Nernst equation At the usual temperature of 298 K,

$$\begin{aligned} E_{\text{cell}} &= 2.71 - \frac{0.0591}{2}\log_{10}(0.1) \\ &= 2.71 - 0.02955(-1) \\ &= 2.73955\,\mathrm{V} \simeq 2.74\,\mathrm{V}. \end{aligned}$$

Since $Q < 1$, the concentration correction raises the emf.

Step 3: Current for part (i) For opposing voltage $E_{\text{ext}} < 2.71\,\mathrm{V}$, the cell emf is larger. Magnesium dissolves and copper is deposited. Electrons flow externally from Mg to Cu, so conventional current flows externally from Cu to Mg.

Step 4: Current for part (ii) The net driving voltage is $E_{\text{cell}} - E_{\text{ext}}$. Thus the actual reversal threshold is $2.73955\,\mathrm{V}$. The printed condition $E_{\text{ext}} > 2.71\,\mathrm{V}$ alone does not uniquely determine the direction:

- For $2.71 < E_{\text{ext}} < 2.73955\,\mathrm{V}$, conventional current still flows externally from Cu to Mg.
- At $E_{\text{ext}} = 2.73955\,\mathrm{V}$, there is no net current in the ideal cell.
- For $E_{\text{ext}} > 2.73955\,\mathrm{V}$, electrons flow from Cu to Mg; conventional current flows externally from Mg to Cu.

Step 5: Conclusion $\boxed{E_{\text{cell}} \simeq 2.74\,\mathrm{V}}$. (i) External conventional current: Cu to Mg. (ii) Reversal to Mg to Cu requires $E_{\text{ext}} > 2.73955\,\mathrm{V}$; the printed condition alone is insufficient.

Quick Tip to Solve: Form Q as magnesium-ion concentration divided by copper-ion concentration, then compare the opposing voltage with the calculated emf. Conventional current is opposite to electron flow.

OR

26(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.**

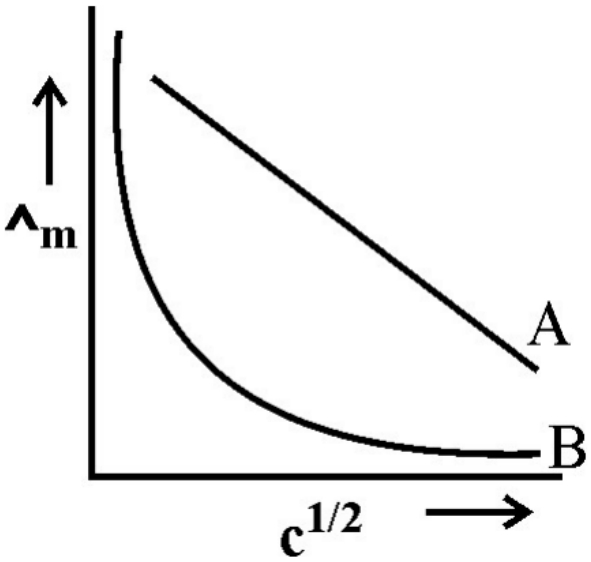
(Molar mass: Fe = 56 g mol^{-1}, Zn = 65.3 g mol^{-1}, 1F = 96500 C mol^{-1})

(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 first law gives $m = MQ/(nF)$, where m is deposited mass, M is molar mass, n is electrons required per metal ion, $Q = It$ is charge, and $F = 96500\,\text{C mol}^{-1}$.
- Cells connected in series carry the same current for the same time, so equal charge passes through them. Their deposited masses are proportional to their equivalent masses M/n.
- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$, where Λ_m° is limiting molar conductivity and K is a positive constant. Weak electrolytes show a nonlinear dependence because their degree of ionisation increases markedly on dilution.

Step 1: (a) Calculate the charge required for iron deposition In cell X, the cathode reaction is

$$Fe^{2+} + 2e^- \longrightarrow Fe.$$

Quick Tip to Solve: In series cells, compare M/n, not just molar masses. Here both ions need two electrons, so $m_{Zn} = m_{Fe}(65.3/56)$. In conductivity plots, only the strong-electrolyte straight line gives a reliable zero-concentration intercept.

Thus two moles of electrons deposit one mole of iron. The deposited amount of iron is

$$n(\text{Fe}) = \frac{2.8}{56} = 0.050\,\text{mol}.$$

The required amount of electrons is $2 \times 0.050 = 0.100\,\text{mol}$. Therefore the charge passed through each cell is

$$Q = 0.100 \times 96500 = 9650\,\text{C}.$$

Step 2: (a) Obtain the duration and zinc mass Using $Q = It$ with $I = 2\,\text{A} = 2\,\text{C s}^{-1}$,

$$t = \frac{Q}{I} = \frac{9650}{2} = 4825\,\text{s}.$$

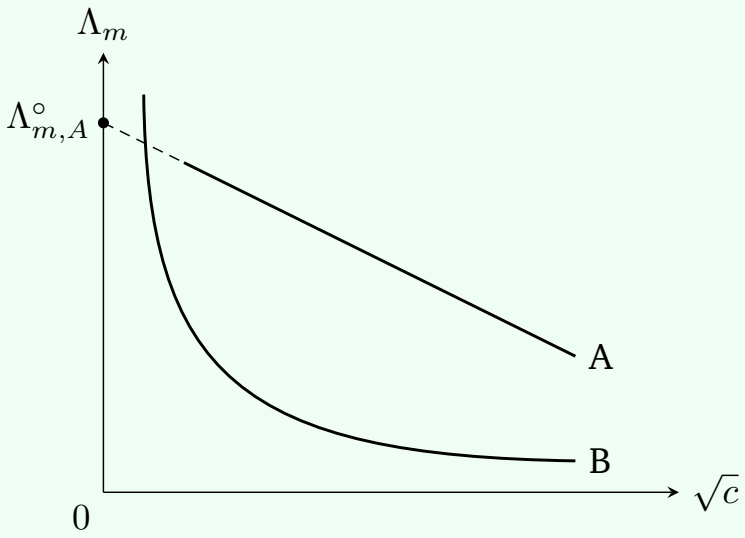
In cell Y, the cathode reaction is $\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$. The same $0.100\,\text{mol}$ of electrons passes through cell Y because the cells are in series. Thus

$$n(\text{Zn}) = \frac{0.100}{2} = 0.050\,\text{mol}, \qquad m(\text{Zn}) = 0.050 \times 65.3 = 3.265\,\text{g}.$$

Equivalently, both ions are divalent, so $m(\text{Zn})/m(\text{Fe}) = 65.3/56$. Equal charge gives equal amounts in moles here, but the masses differ because the molar masses differ.

Step 3: (b)(i) Identify electrolytes A and B A is a strong electrolyte: its approximately straight line has a negative slope in the Λ_m versus $\sqrt{c}$ plot. It is almost completely ionised, and the modest rise in molar conductivity on dilution is mainly due to reduced interionic interactions and increased ionic mobility.

B is a weak electrolyte: its curve rises sharply as concentration decreases. Dilution substantially increases its degree of ionisation, so many more ions become available per mole of electrolyte and Λ_m increases strongly. The sketch below indicates the two trends; its dotted line shows the valid linear extrapolation for A.



Conductivity trends and linear extrapolation for strong electrolyte A.

Quick Tip to Solve: In series cells, compare M/n, not just molar masses. Here both ions need two electrons, so $m_{\text{Zn}} = m_{\text{Fe}}(65.3/56)$. In conductivity plots, only the strong-electrolyte straight line gives a reliable zero-concentration intercept.

Step 4: (b)(ii) Explain the zero-concentration extrapolation 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 nonlinear curve cannot be reliably extrapolated to obtain Λ_m°. Its molar conductivity still tends to a finite limiting value at infinite dilution; it does not become infinite. The limitation is the graphical extrapolation method. Instead, its limiting molar conductivity is calculated using Kohlrausch's law of independent migration of ions,

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

where ν_+ and ν_- are the numbers of cations and anions in one formula unit, and λ_+°, λ_-° are their limiting ionic molar conductivities.

Step 5: Conclusion (a) The current flows for $\boxed{4825\,\text{s}}$ (about $80.4\,\text{min}$); the zinc deposited is $\boxed{3.265\,\text{g}}$. (b) A is a strong electrolyte and B is a weak electrolyte. Linear extrapolation gives Λ_m° for A; direct extrapolation is unsuitable for B, whose limiting molar conductivity is obtained using Kohlrausch's law.

Quick Tip to Solve: In series cells, compare M/n, not just molar masses. Here both ions need two electrons, so $m_{\text{Zn}} = m_{\text{Fe}}(65.3/56)$. In conductivity plots, only the strong-electrolyte straight line gives a reliable zero-concentration intercept.

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

(i) Phenol to Anisole

(ii) Ethanol to Propan-2-ol

(b) Write mechanism of the following reaction:

$\mathbf{C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O}$

(c) Why phenol undergoes electrophilic substitution more easily than benzene? [5 marks]

Solution:

Concept:

- Williamson synthesis forms an ether by the reaction of a phenoxide or alkoxide ion with a suitable primary alkyl halide.
- A Grignard reagent adds an alkyl group to a carbonyl carbon; hydrolysis of its addition product gives an alcohol.
- Concentrated sulphuric acid dehydrates ethanol at $443\,\text{K}$. Protonation converts its poor leaving group into water.
- The oxygen lone pair in phenol donates electron density into the aromatic ring by resonance, activating electrophilic substitution.

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

$$\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$$

Quick Tip to Solve: To turn ethanol into propan-2-ol, first make ethanal and add one methyl group with a Grignard reagent; direct dehydration cannot increase the carbon count.

$$C_6H_5ONa + CH_3I \longrightarrow C_6H_5OCH_3 + NaI$$

The phenoxide oxygen attacks the methyl carbon and displaces iodide in an S_N2 reaction. The ether formed is anisole (methoxybenzene); the benzene ring remains unchanged.

Step 2: (a)(ii) Increase the carbon chain by one carbon Dehydrogenate ethanol over heated copper at $573\,K$ to form ethanal:

$$CH_3CH_2OH \xrightarrow{Cu,\ 573\,K} CH_3CHO + H_2$$

Add methylmagnesium bromide in dry ether, then hydrolyse the magnesium alkoxide with dilute acid:

$$CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(OMgBr)CH_3$$

$$CH_3CH(OMgBr)CH_3 + H_2O \longrightarrow CH_3CH(OH)CH_3 + Mg(OH)Br$$

Addition of the methyl group changes the two-carbon aldehyde into the three-carbon secondary alcohol, propan-2-ol. Water must be excluded until the addition is complete because it destroys the Grignard reagent.

Step 3: (b) Write the acid-catalysed dehydration mechanism In the standard stepwise representation, ethanol first accepts a proton on oxygen:

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2{}^+$$

Protonation makes water a good leaving group. Loss of water is followed by removal of a proton from the adjacent carbon:

$$CH_3CH_2OH_2{}^+ \longrightarrow CH_3CH_2{}^+ + H_2O$$

$$CH_3CH_2{}^+ \longrightarrow CH_2{=}CH_2 + H^+$$

The electrons of the broken carbon–hydrogen bond form the carbon–carbon double bond. These equations give the conventional textbook representation; for a primary alcohol, water loss and removal of the adjacent proton can occur together without a long-lived free primary carbocation. Acid is regenerated, and at $443\,K$ the net reaction is dehydration to ethene:

$$CH_3CH_2OH \xrightarrow{\text{conc. } H_2SO_4,\ 443\,K} CH_2{=}CH_2 + H_2O$$

Step 4: (c) Explain the higher reactivity of phenol An oxygen lone pair overlaps with the ring's delocalised electron system. Its resonance donation increases electron density especially at the ortho and para positions. The electron-rich ring attracts an electrophile more readily than benzene does. Oxygen donation also stabilises the positively charged intermediate formed during ortho or para attack, lowering the activation barrier. Thus the resonance effect of the hydroxyl group activates the ring despite oxygen's electron-withdrawing inductive effect.

Step 5: Conclusion Phenol gives anisole through sodium phenoxide and methyl iodide; ethanol gives propan-2-ol through ethanal and methylmagnesium bromide followed by hydrolysis. Acid-catalysed dehydration gives ethene at $443\,K$, and resonance donation by the hydroxyl group makes phenol more reactive than benzene toward electrophilic substitution.

Quick Tip to Solve: To turn ethanol into propan-2-ol, first make ethanal and add one methyl group with a Grignard reagent; direct dehydration cannot increase the carbon count.

OR

27(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:

- Intramolecular hydrogen bonding occurs within one molecule; intermolecular hydrogen bonding associates separate molecules and decreases volatility.
- A tertiary alkyl halide reacts with a strong base mainly by elimination because its crowded carbon hinders S_N2 substitution.
- The hydroxyl group activates the aromatic ring of phenol and directs substitution mainly to the ortho and para positions.
- Phenol forms a coloured complex with neutral ferric chloride, whereas ethanol does not give this colour test.

Step 1: (a)(i) Compare the hydrogen bonding in the nitrophenols In ortho-nitrophenol, the hydroxyl group and nitro group are adjacent. The hydroxyl hydrogen forms an intramolecular hydrogen bond with an oxygen atom of the nitro group. Consequently, the molecules are less associated with one another and escape into the vapour more readily. In para-nitrophenol, the two groups are too far apart to form this intramolecular bond. Instead, intermolecular hydrogen bonds associate different molecules. More energy is needed to separate these molecules, so para-nitrophenol has lower volatility. Hence ortho-nitrophenol is more readily carried over with steam.

Step 2: (a)(ii) Explain elimination from tert-butyl chloride The carbon attached to chlorine in tert-butyl chloride is surrounded by three methyl groups. This steric crowding prevents the easy backside attack required for Williamson ether synthesis. Methoxide is a strong base and, on heating, removes a beta-hydrogen while chloride leaves, forming a double bond by elimination:

$$(CH_3)_3CCl + NaOCH_3 \xrightarrow{\text{heat}} (CH_3)_2C{=}CH_2 + CH_3OH + NaCl$$

Thus 2-methylpropene is the main product instead of tert-butyl methyl ether. For the ether, one would use tert-butoxide with a methyl halide, placing the less hindered carbon in the alkyl halide.

Step 3: (b)(i) Write the Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. A formyl group replaces a ring hydrogen mainly at the ortho position, producing salicylaldehyde (2-hydroxybenzaldehyde). The overall reaction, with acidification in the

Quick Tip to Solve: For steam volatility, check whether hydrogen bonding joins separate molecules. For Williamson synthesis, put the bulky group in the alkoxide and use an unhindered alkyl halide.

work-up, is:

$$C_6H_5OH + CHCl_3 + 3\,NaOH \xrightarrow[\text{then } H^+]{\text{heat}} C_6H_4(OH)CHO + 3\,NaCl + 2\,H_2O$$

Here the hydroxyl and aldehyde groups in the major product occupy adjacent ring positions. A small amount of the para isomer may also form.

Step 4: (b)(ii) Write a Friedel–Crafts alkylation of phenol For methylation, treat phenol with methyl chloride in the presence of anhydrous aluminium chloride. Methyl substitution occurs at the ortho and para positions relative to the hydroxyl group:

$$C_6H_5OH + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} C_6H_4(OH)CH_3 + HCl$$

The product notation represents the mixture of 2-methylphenol (ortho-cresol) and 4-methylphenol (para-cresol). Each substitution adds one methyl group to the ring while the hydroxyl group remains attached to it.

Step 5: (c) Distinguish ethanol from phenol Add a few drops of freshly prepared neutral ferric chloride solution to separate samples. Phenol gives a violet colour due to formation of a ferric phenolate complex. Ethanol gives no violet colour. This visible difference identifies phenol. The reagent should be neutral; reaction with sodium metal would not distinguish them because both can liberate hydrogen.

Step 6: Conclusion Intramolecular hydrogen bonding makes ortho-nitrophenol more steam volatile, while steric hindrance and strong basicity favour elimination from tert-butyl chloride. Reimer–Tiemann formylation gives mainly salicylaldehyde; Friedel–Crafts methylation gives ortho- and para-cresol. Neutral ferric chloride gives a violet colour with phenol but not ethanol.

Quick Tip to Solve: For steam volatility, check whether hydrogen bonding joins separate molecules. For Williamson synthesis, put the bulky group in the alkoxide and use an unhindered alkyl halide.