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

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. Out of NaCl and AgCl, which one shows Frenkel defect and why? [1 mark]

Solution:

Concept:

- A Frenkel defect occurs when a small ion leaves its normal lattice site and occupies an interstitial site.
- A vacancy and an interstitial ion are produced together, so stoichiometry and density remain unchanged.

Step 1: Compare the ion sizes In $AgCl$, the Ag^+ ion is much smaller than the Cl^- ion. The small cation can therefore fit into an interstitial space in the crystal.

Step 2: Identify the defect An Ag^+ ion can move from its normal lattice position to an interstitial site, leaving a vacancy behind. In $NaCl$, the cation is not sufficiently small relative to the anion for this displacement to be favoured.

Step 3: Conclusion $\boxed{AgCl}$ shows Frenkel defect because its small Ag^+ ions can occupy interstitial sites.

Quick Tip to Solve: For Frenkel defect, look for a small cation compared with the anion; AgCl is a standard example.

2. Arrange the following in increasing order of boiling points:
$(CH_3)_3N$, C_2H_5OH, $C_2H_5NH_2$ [1 mark]

Solution:

Concept:

- Boiling requires overcoming intermolecular attractions; stronger hydrogen bonding generally raises the boiling point.
- A hydrogen bonded to nitrogen or oxygen can act as a hydrogen-bond donor; an oxygen atom is more electronegative than nitrogen.

Step 1: Compare trimethylamine with ethylamine Trimethylamine, $(CH_3)_3N$, has no $N-H$ bond and cannot form hydrogen bonds with other trimethylamine molecules. Ethylamine, $C_2H_5NH_2$, has $N-H$ bonds and forms intermolecular hydrogen bonds, so it has the higher boiling point.

Step 2: Compare ethylamine with ethanol Ethanol, C_2H_5OH, forms stronger intermolecular hydrogen bonds through its $O-H$ group than ethylamine does through $N-H$. Its boiling point is therefore the highest of these three compounds.

Step 3: Conclusion The increasing order is

$$\boxed{(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH}.$$

Quick Tip to Solve: First check for an N-H or O-H bond: a tertiary amine lacks a hydrogen-bond donor.

3(a). Why are medicines more effective in colloidal state? [1 mark]

Solution:

Concept:

- Colloidal particles have a large surface area in relation to their volume.
- A larger exposed surface provides greater contact between the dispersed substance and its surroundings.

Step 1: Relate particle size to exposed surface When a medicinal substance is dispersed into fine colloidal particles, the total exposed surface area becomes large for the same amount of substance. More of the medicine is thus available at the surface for interaction.

Step 2: Explain the increased effectiveness The large surface area allows the medicine to come into extensive contact with body tissues and facilitates its absorption and assimilation. Consequently, a medicinal substance can act more effectively when administered in colloidal form.

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

Quick Tip to Solve: Connect the small particle size to large surface area, then to better absorption of the medicine.

OR

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

Solution:

Concept:

- Colloids are classified using the physical states of their dispersed phase and dispersion medium.
- The dispersed phase is the distributed component; the dispersion medium is the phase in which it is distributed.

Step 1: Describe an emulsion An emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are liquids. One liquid is distributed as tiny droplets in the other; milk is a familiar example of an emulsion.

Step 2: Describe a gel A gel is a colloidal system in which the dispersed phase is liquid and the dispersion medium is solid. The liquid is retained within a solid network, giving a semisolid form; jelly is an example. The key distinction is therefore the state of the dispersion medium.

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

Quick Tip to Solve: Compare the dispersion medium: liquid for an emulsion, solid for a gel; the dispersed phase is liquid in both.

4. Define ambident nucleophile with an example. [1 mark]

Solution:

Concept:

- A nucleophile donates an electron pair to an electron-deficient centre to form a covalent bond.
- An ambident nucleophile possesses two alternative donor atoms, through either of which it can attack.

Step 1: State the defining feature An ambident nucleophile can attack an electrophile through either of two different atoms. It normally forms a bond through one of these atoms in a given reaction; the term does not mean that both atoms must bond simultaneously.

Step 2: Give a specific example The cyanide ion, CN^-, is an ambident nucleophile because attack can occur through its carbon atom or its nitrogen atom. With an alkyl group R, bonding through carbon produces $R - C \equiv N$, whereas bonding through nitrogen produces $R - N \equiv C$.

Step 3: Conclusion An ambident nucleophile has two alternative sites of attack; CN^-, which can attack through carbon or nitrogen, is an example.

Quick Tip to Solve: Name both possible donor atoms in your example; two atoms in an ion alone do not establish ambident behaviour.

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

Solution:

Concept:

- An aldose contains an aldehyde group in its open-chain form; a ketose contains a ketone group.
- Both glucose and fructose are hexoses and have molecular formula $C_6H_{12}O_6$.

Step 1: Identify the group in glucose In its open-chain structure, glucose has a terminal aldehyde group, $-CHO$, at carbon 1. It is therefore classified as an aldohexose: a six-carbon monosaccharide containing an aldehyde functional group.

Step 2: Identify the group in fructose In its open-chain structure, fructose has an internal ketone group, $> C = O$, at carbon 2. It is therefore a ketohexose. Although the two sugars have the same molecular formula, the type and position of their carbonyl group differ.

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

Quick Tip to Solve: Remember the open-chain carbonyl positions: glucose C-1, fructose C-2.

OR

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

Solution:

Concept:

- Lactose is a disaccharide formed from one galactose unit and one glucose unit.
- Hydrolysis uses water to break the glycosidic linkage and release the constituent monosaccharides.

Step 1: Identify the constituent units Lactose contains a D-galactose residue joined to a D-glucose residue through a β-(1$\rightarrow$4) glycosidic linkage. These are the two sugar units that are recovered when the bond joining them is hydrolysed.

Step 2: Write the hydrolysis reaction Water cleaves the glycosidic linkage, yielding one molecule of each constituent sugar per molecule of lactose:

$$\text{Lactose} + \text{H}_2\text{O} \longrightarrow \text{D-glucose} + \text{D-galactose}.$$

The products are monosaccharides; neither sucrose nor fructose is a constituent of lactose.

Step 3: Conclusion The hydrolysis products of lactose are $\boxed{\text{D-glucose and D-galactose}}$.

Quick Tip to Solve: Associate lactose with glucose plus galactose; sucrose instead gives glucose plus fructose.

Section B (14 marks)

6(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 means reaction with water. Xenon difluoride gives xenon, hydrogen fluoride and oxygen on complete hydrolysis.
- In a redox reaction, atoms and charge must balance. Hot concentrated hydrochloric acid is oxidised to chlorine by manganese dioxide.

Step 1: (i) Hydrolysis of xenon difluoride Write the products as xenon, hydrogen fluoride and oxygen, then balance fluorine and hydrogen using water. The balanced equation is

$$2\text{XeF}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2.$$

Both sides contain two xenon atoms, four fluorine atoms, four hydrogen atoms and two oxygen atoms. Xenon is reduced from oxidation state $+2$ to zero; oxygen in water is oxidised from -2 to zero.

Step 2: (ii) Heating manganese dioxide with concentrated HCl Manganese dioxide forms man-

Quick Tip to Solve: For hot MnO2 and HCl, reserve two chloride ions for MnCl2 and two for Cl2; this fixes the coefficient of HCl as four.

ganese(II) chloride, water and chlorine:

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

Manganese changes from $+4$ to $+2$, while two chloride ions lose electrons to form chlorine. Of the four chloride ions supplied, two remain in manganese chloride and two form chlorine gas.

Step 3: Conclusion $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$;
$MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + 2H_2O + Cl_2$.

Quick Tip to Solve: For hot MnO2 and HCl, reserve two chloride ions for MnCl2 and two for Cl2; this fixes the coefficient of HCl as four.

OR

6(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, acidity in aqueous solution increases as the central atom becomes larger and the E–H bond becomes weaker down the group.
- The bond enthalpy of a hydrogen halide is the energy needed to break one mole of H–X bonds in the gaseous state. Increasing halogen size increases bond length and weakens the bond.

Step 1: (i) Increasing acidic character From oxygen to tellurium, the size of the group 16 atom increases. Its bond with hydrogen becomes progressively weaker, so the hydride releases a proton more readily. Thus the sequence, from least acidic to most acidic, is

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

The weakening of the E–H bond controls this trend despite the decreasing electronegativity of the central atom.

Step 2: (ii) Decreasing bond enthalpy The H–F bond is the shortest and strongest of these hydrogen-halogen bonds. Down the group, the larger halogen atoms give longer bonds and poorer orbital overlap with hydrogen. Therefore the energy needed to break the bond decreases in the sequence

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

This is the requested order of bond enthalpy; it is not the order of acid strength in water.

Step 3: Conclusion (i) $H_2O < H_2S < H_2Se < H_2Te$.
(ii) $HF > HCl > HBr > HI$.

Quick Tip to Solve: Down each group, the bond to hydrogen weakens: this raises hydride acidity but lowers hydrogen-halide bond enthalpy.

7. State Raoult's law for a solution containing volatile components. Write two characteristics of the solution which obeys Raoult's law at all concentrations. [2 marks]

Solution:

Concept:

- Raoult's law relates a volatile component's partial vapour pressure to its mole fraction in the liquid solution at a fixed temperature.
- An ideal solution obeys this law throughout the composition range because unlike and like intermolecular attractions are approximately equal.

Step 1: State the law for volatile components For each volatile component i,

$$p_i = x_i p_i^\circ,$$

where p_i is its partial vapour pressure, x_i is its mole fraction in the solution, and p_i° is the vapour pressure of the pure component at the same temperature. For a binary solution, $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$. Consequently, the total vapour pressure is $p = p_A + p_B$.

Step 2: Give two characteristics of an ideal solution A solution that obeys this law at every concentration is an ideal solution. Its two characteristics are:

(1) The enthalpy change on mixing is zero: $\Delta H_{\text{mix}} = 0$. No heat is absorbed or evolved on mixing.

(2) The volume change on mixing is zero: $\Delta V_{\text{mix}} = 0$. The final volume equals the sum of the component volumes before mixing. These properties follow from the similarity of unlike and like intermolecular interactions.

Step 3: Conclusion Raoult's law is $p_i = x_i p_i^\circ$ for every volatile component. An ideal solution has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$.

Quick Tip to Solve: Keep partial pressure and total pressure distinct: apply $p_i = x_i p_i^\circ$ to each component, then add the partial pressures.

8. For a reaction

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

the proposed mechanism is as given below:

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

(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ **(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:

- For an elementary step, its rate law follows from the reactants participating in that step. A slow step controls the rate of the overall reaction.

Quick Tip to Solve: Read the slow elementary step to obtain the concentration powers; do not infer them from the overall peroxide equation.

- The overall order is the sum of the exponents of the concentrations in the rate law; it need not equal the sum of coefficients in the overall balanced equation.

Step 1: (i) Rate law The slow elementary step is

$$H_2O_2 + I^- \longrightarrow H_2O + IO^-.$$

It involves one hydrogen peroxide molecule and one iodide ion. Therefore its rate, and hence the reaction rate, depends on the first power of each concentration:

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

where k is the rate constant. The intermediate IO^- does not enter this rate law because it is produced by the slow step.

Step 2: (ii) Overall order and (iii) controlling step The powers of $[H_2O_2]$ and $[I^-]$ are both one. Adding them gives the overall order $1 + 1 = 2$. Step (1) is the rate-determining step because it is slow; the fast second step consumes its intermediate as it is formed. Iodide is regenerated in step (2), so it is a catalyst, but a catalyst concentration can still occur in a rate law.

Step 3: Conclusion (i) $r = k[H_2O_2][I^-]$.

(ii) The overall order is 2.

(iii) Step (1), the slow step, is rate determining.

Quick Tip to Solve: Read the slow elementary step to obtain the concentration powers; do not infer them from the overall peroxide equation.

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. Manganate disproportionates in acidic solution.
- The oxidation product of iodide depends on the medium: alkaline permanganate forms iodate, whereas acidified permanganate liberates iodine.

Step 1: Identify the green and purple manganese compounds Fusion oxidises manganese(IV) to manganese(VI):

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

Thus (A) is potassium manganate, K_2MnO_4. On acidification,

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

Quick Tip to Solve: Use green for manganate and purple for permanganate; then check the medium before choosing iodate or iodine.

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

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

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

Thus (C) is potassium iodate, KIO_3. In acidic medium, iodide gives iodine:

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

Hence (D) is I_2. Each equation conserves both atoms and total charge.

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 green for manganate and purple for permanganate; then check the medium before choosing iodate or iodine.

10(a). Write IUPAC name of the complex $[Pt(en)_2Cl_2]$. Draw structures of geometrical isomers for this complex. [2 marks]

Solution:

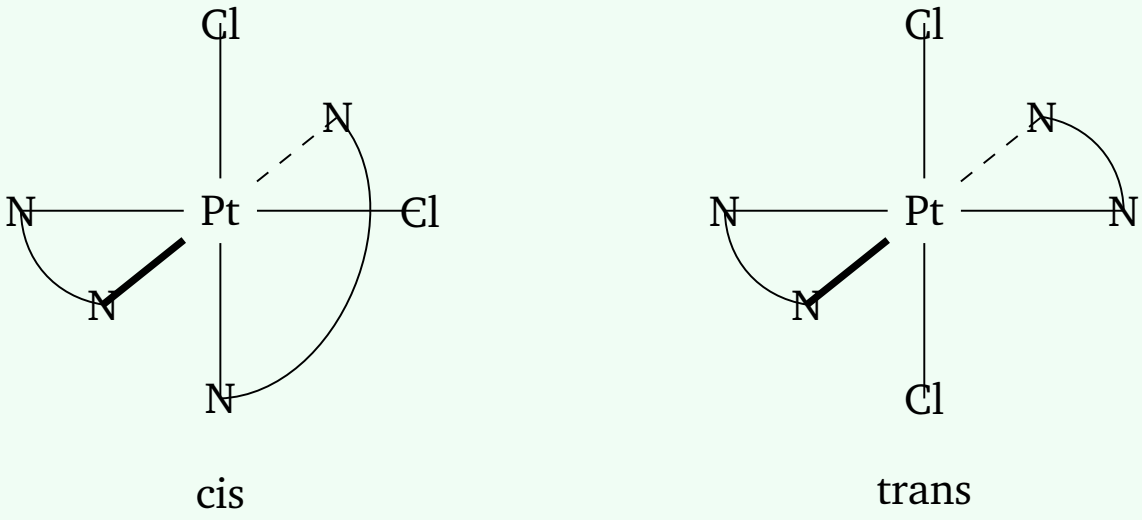
Concept:

- Ethane-1,2-diamine (en) is a neutral bidentate ligand; each molecule binds through two nitrogen donor atoms. Chlorido is a monodentate ligand of charge -1.
- For the neutral complex, platinum has oxidation state $x + 2(0) + 2(-1) = 0$, so $x = +2$. Two en ligands and two chlorido ligands give coordination number six and an octahedral arrangement.

Step 1: Name the complex Ligands are named alphabetically, ignoring multiplicative prefixes. Thus chlorido precedes ethane-1,2-diamine. Use dichlorido for two chloride ligands and bis(ethane-1,2-diamine) for two bidentate ligands. The metal name remains platinum because the coordination entity is neutral; its oxidation state is written as (II).

Step 2: Place the chlorido ligands The two geometrical isomers differ in the relative positions of the chlorido ligands: in the cis isomer their Pt–Cl bonds are adjacent, at $90°$, whereas in the trans isomer they are opposite, at $180°$. In each sketch, the curved links join the two nitrogen donors belonging to one en ligand; each en occupies adjacent octahedral positions.

Quick Tip to Solve: Count donor atoms, not ligand molecules: two en ligands supply four coordination sites.



Octahedral cis and trans isomers; each curved N–N link represents one en ligand.

Step 3: Conclusion The IUPAC name is dichloridobis(ethane-1,2-diamine)platinum(II). Its geometrical isomers are cis-$[Pt(en)_2Cl_2]$ and trans-$[Pt(en)_2Cl_2]$, shown above.

Quick Tip to Solve: Count donor atoms, not ligand molecules: two en ligands supply four coordination sites.

OR

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

(i) Hexaamminecobalt(III) sulphate

(ii) Potassium trioxalatochromate(III) [2 marks]

Solution:

Concept:

- Construct the coordination entity from the metal and ligands, then balance its charge with the counter-ions. Ammine, NH_3, is neutral; oxalato, $C_2O_4^{2-}$, carries charge -2.
- The Roman numeral specifies the metal oxidation state. Sulphate is SO_4^{2-}, while potassium supplies K^+. The total formula must be electrically neutral.

Step 1: (i) Hexaamminecobalt(III) sulphate Six neutral ammonia ligands surround Co^{3+}, giving the complex cation $[Co(NH_3)_6]^{3+}$. The smallest neutral combination contains two such cations and three sulphate anions, since $2(+3) + 3(-2) = 0$. Therefore the formula is $[Co(NH_3)_6]_2(SO_4)_3$.

Step 2: (ii) Potassium trioxalatochromate(III) Three oxalato ligands around chromium(III) give complex charge $+3 + 3(-2) = -3$. The entity is therefore $[Cr(C_2O_4)_3]^{3-}$; three potassium ions are required to neutralise it. Oxalate is bidentate, so these three ligands occupy six coordination sites.

Step 3: Conclusion (i) $\boxed{[Co(NH_3)_6]_2(SO_4)_3}$.

(ii) $\boxed{K_3[Cr(C_2O_4)_3]}$.

Quick Tip to Solve: First calculate the charge inside the brackets; balance counter-ions only afterwards.

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

(i) paramagnetic

(ii) more stable

(iii) inner orbital complex and

(iv) high spin complex

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

Solution:

Concept:

- Cobalt has atomic number 27: $\mathrm{Co} = [Ar]3d^7 4s^2$. In both complexes its oxidation state is $+3$, so Co^{3+} has a $3d^6$ configuration.
- Fluoride is a weak-field ligand, whereas en is a stronger-field bidentate ligand. Weak-field octahedral d^6 is high spin; stronger-field d^6 can be low spin.

Step 1: Compare spin and magnetic behaviour In $[\mathrm{CoF_6}]^{3-}$, weak-field fluoride does not pair the electrons in the lower set before the upper set is occupied. The configuration is $t_{2g}^4 e_g^2$, with four unpaired electrons. Hence this complex is paramagnetic and high spin. In $[\mathrm{Co(en)_3}]^{3+}$, the stronger field produces $t_{2g}^6 e_g^0$, with all electrons paired.

Step 2: Compare orbital use and stability Pairing in the en complex leaves two vacant inner $3d$ orbitals available for d^2sp^3 hybridisation, so it is an inner orbital octahedral complex. The fluoride complex uses outer d orbitals, giving sp^3d^2 hybridisation. The en complex is also more stable because its three bidentate ligands form chelate rings; the chelate effect favours its formation relative to a complex of monodentate fluoride ligands.

Step 3: Conclusion (i) Paramagnetic: $[\mathrm{CoF_6}]^{3-}$.

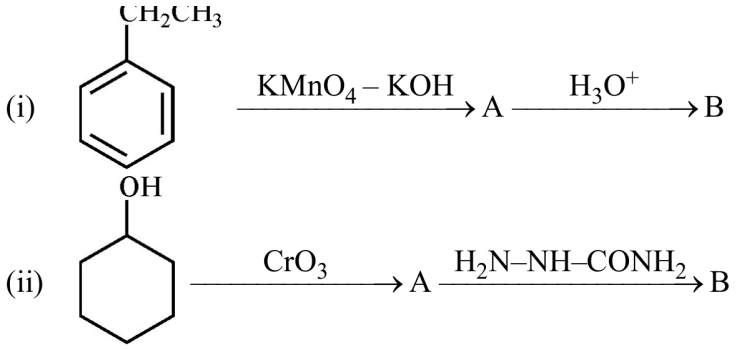
(ii) More stable: $[\mathrm{Co(en)_3}]^{3+}$.

(iii) Inner orbital: $[\mathrm{Co(en)_3}]^{3+}$.

(iv) High spin: $[\mathrm{CoF_6}]^{3-}$.

Quick Tip to Solve: For Co(III), start with six d electrons; weak-field fluoride leaves four unpaired.

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



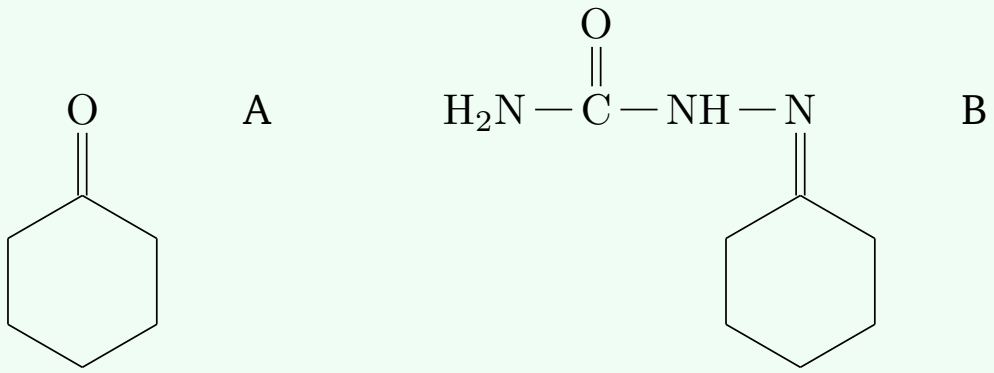
Solution:

Concept:

- Alkaline permanganate oxidises an alkyl side chain having a benzylic hydrogen to the benzoate salt. Acidification converts the carboxylate into the corresponding carboxylic acid.
- Chromium trioxide oxidises a secondary alcohol to a ketone. Semicarbazide condenses with a carbonyl compound to give its semicarbazone with loss of water.

Step 1: (i) Oxidation of ethylbenzene The printed substrate is ethylbenzene, $C_6H_5CH_2CH_3$. Its benzylic carbon has hydrogen atoms, so oxidation with $KMnO_4/KOH$ converts the entire side chain into a carboxylate group attached to the unchanged benzene ring. Thus $A = C_6H_5C(=O)O^-K^+$, potassium benzoate. On adding H_3O^+, protonation gives $B = C_6H_5C(=O)OH$, benzoic acid.

Step 2: (ii) Oxidation and condensation of cyclohexanol The hydroxyl-bearing ring carbon is bonded to two other carbon atoms, so cyclohexanol is secondary. Oxidation gives cyclohexanone (A); the six-membered carbon ring remains intact. Semicarbazide reacts through its terminal amino group. Condensation replaces the ketone oxygen by $=N-NH-C(=O)-NH_2$, giving cyclohexanone semicarbazone (B) and water. The structures shown below retain all six carbons in the original ring.



Products A and B in reaction (ii).

Step 3: Conclusion (i) $A = C_6H_5C(=O)O^-K^+$; $B = C_6H_5C(=O)OH$.

(ii) A is cyclohexanone and B is cyclohexanone semicarbazone, with the structures shown above.

Quick Tip to Solve: In alkaline oxidation write the carboxylate first; the acid appears only after acidification.

Section C (36 marks)

13. 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:

- A zero-order reaction has rate independent of reactant concentration: $-d[A]/dt = k$, where $[A]$ is reactant concentration and k is the rate constant.
- Its integrated law is $[A]_t = [A]_0 - kt$, with $[A]_0$ the initial concentration and $[A]_t$ the concentration at time t. Thus concentration decreases linearly with time.

Step 1: Identify the concentration decrease The question explicitly states that ammonia decomposition on platinum follows zero-order kinetics. Therefore no logarithmic concentration ratio is needed. The initial and final concentrations are $0.100\,\text{M}$ and $0.064\,\text{M}$, respectively. The amount consumed per litre is their positive difference:

$$[\text{NH}_3]_0 - [\text{NH}_3]_t = 0.100 - 0.064 = 0.036\,\text{mol L}^{-1}.$$

The rate constant is $4 \times 10^{-3}\,\text{mol L}^{-1}\text{s}^{-1}$, so it gives the concentration decrease per second directly for this zero-order reaction.

Step 2: Apply the integrated zero-order rate law Rearrange the integrated law and substitute the given values:

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

Concentration divided by concentration per second leaves seconds, as required. Checking the result, $kt = 0.004 \times 9 = 0.036\,\text{M}$; hence $[\text{NH}_3]_t = 0.100 - 0.036 = 0.064\,\text{M}$, agreeing with the question. The calculation uses the concentration loss of ammonia itself, so no additional stoichiometric factor is required.

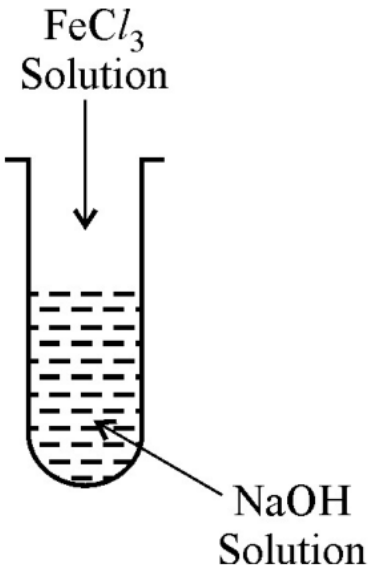
Step 3: Conclusion The required time is $\boxed{9\,\text{s}}$.

Quick Tip to Solve: For zero order, divide the concentration decrease by k; use the difference of concentrations, not their logarithmic ratio.

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

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

(iii) How does chemisorption vary with temperature? [3 marks]



Solution:

Concept:

- Adsorption concentrates substances on a solid surface. Activated charcoal has a large surface area and adsorbs harmful gases and vapours.
- Colloidal particles acquire charge by preferential adsorption of ions from the dispersion medium. The excess electrolyte in the preparation determines the sign of the charge.
- Chemisorption involves chemical bond formation and commonly requires activation energy; temperature affects both the rate of adsorption and the adsorption equilibrium.

Step 1: Explain the role of charcoal in the gas mask (i) Activated charcoal acts as an adsorbent. Its porous structure provides a very large surface area on which poisonous gases and vapours are adsorbed as contaminated air passes through the mask. Thus it removes these harmful substances from the air before inhalation. This is a surface process: the gases accumulate on charcoal, rather than simply being absorbed throughout its bulk.

Step 2: Determine the charge and representation of the sol (ii) The printed figure shows ferric chloride solution being added to sodium hydroxide solution in the test tube. Hydrated ferric oxide, conventionally represented as $\mathrm{Fe(OH)_3}$, forms:

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

Since the particles form in the sodium hydroxide medium, they preferentially adsorb $\mathrm{OH^-}$ ions. Consequently the colloidal particles are negatively charged. The sol is represented as

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

Quick Tip to Solve: Read which reagent is already in the test tube: FeCl3 added to NaOH gives OH- adsorption and a negatively charged sol.

Here $Fe(OH)_3$ denotes the colloidal particle and OH^- denotes its adsorbed, charge-determining ion. Sodium ions act as counter-ions in the surrounding medium.

Step 3: Describe the temperature dependence of chemisorption (iii) Chemisorption initially increases with increasing temperature because adsorbate molecules gain sufficient energy to overcome the activation-energy barrier for chemical bond formation with the surface. It reaches a maximum and then decreases at higher temperatures: adsorption is generally exothermic, so higher temperature favours desorption and reduces the equilibrium amount adsorbed. Thus the expected trend is an initial increase followed by a decrease, rather than a decrease throughout as is usual for physisorption.

Step 4: Conclusion (i) Activated charcoal adsorbs poisonous gases and vapours. (ii) The sol is negatively charged and represented by $Fe(OH)_3/OH^-$. (iii) Chemisorption initially increases with temperature, reaches a maximum and then decreases.

Quick Tip to Solve: Read which reagent is already in the test tube: FeCl3 added to NaOH gives OH- adsorption and a negatively charged sol.

15. 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 $Z = 8(1/8) + 6(1/2) = 4$ atoms: corner atoms are shared by eight cells and face-centred atoms by two cells.
- For a cubic unit cell, the volume is a^3, where a is its edge. A sample of mass m and density ρ occupies volume m/ρ, giving $N = Zm/(\rho a^3)$ atoms.

Step 1: Convert the cell edge and calculate cell volume The density is expressed in g cm^{-3}, so convert the edge length to centimetres before cubing. Since $1\,\text{pm} = 10^{-10}\,\text{cm}$,

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

The exponent is multiplied by three when the edge is cubed. The fcc arrangement contributes four atoms to each such cell after accounting for the sharing of boundary atoms.

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

$$V = \frac{m}{\rho} = \frac{108\,\text{g}}{10.8\,\text{g cm}^{-3}} = 10\,\text{cm}^3.$$

Hence the number of unit cells is

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

This ratio is dimensionless, since both numerator and denominator are volumes in cubic centimetres.

Quick Tip to Solve: Convert pm to cm before cubing; then multiply sample volume divided by cell volume by four for an fcc lattice.

Step 3: Convert the cell count to an atom count Each fcc cell contributes four atoms, so

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

As a check, the mass of one unit cell is $\rho a^3 = 10.8(2.70 \times 10^{-23}) = 2.916 \times 10^{-22}$ g. Dividing the sample mass by this cell mass gives the same cell count, which must again be multiplied by four. Avogadro's constant is unnecessary because the cell count directly determines the atom count.

Step 4: Conclusion The number of atoms in 108 g of the element is approximately $\boxed{1.48 \times 10^{24} \text{ atoms}}$.

Quick Tip to Solve: Convert pm to cm before cubing; then multiply sample volume divided by cell volume by four for an fcc lattice.

16. 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 obeys $\Delta T_f = K_f m$, where m is the moles of solute per kilogram of solvent and K_f is the cryoscopic constant of water.
- Sucrose and glucose are non-electrolytes with van't Hoff factor unity. A w/w percentage gives solute mass per 100 g of solution; the remaining mass is water.

Step 1: Calculate the sucrose molality and observed depression Take 100 g of the sucrose solution: sucrose has mass 4 g and water has mass $100 - 4 = 96$ g. Hence,

$$m_s = \frac{4/342}{96/1000} = 0.12183 \,\text{mol kg}^{-1}.$$

Its observed depression is $\Delta T_{f,s} = 273.15 - 271.15 = 2.00\,\text{K}$. This supplied value establishes the solvent constant for the calculation, so a separately memorised value is unnecessary.

Step 2: Compare the glucose and sucrose depressions In 100 g of the glucose solution, glucose has mass 5 g and water has mass 95 g. Thus,

$$m_g = \frac{5/180}{95/1000} = 0.29240 \,\text{mol kg}^{-1}.$$

Since both solutions contain the same solvent, their depressions are proportional to their molalities:

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

Subtract the calculated depression from the freezing point of pure water: $T_{f,g} = 273.15 - 4.80 = 268.35\,\text{K}$. Using solvent mass, rather than solution mass, is essential in both molalities.

Step 3: Conclusion The freezing point of the 5% (w/w) glucose solution is $\boxed{268.35\,\text{K}}$.

Quick Tip to Solve: Subtract the solute mass from 100 g to obtain solvent mass, then compare depressions to cancel the common solvent constant.

17. (a) Name the method of refining which is

(i) used to obtain semiconductor of high purity,

(ii) used to obtain low boiling metal.

(b) Write chemical reactions taking place in the extraction of copper from Cu_2S. [3 marks]

Solution:

Concept:

- Refining separates impurities by using differences in solubility between liquid and solid metal, or differences in volatility.
- Copper extraction from Cu_2S involves partial oxidation to Cu_2O, followed by self-reduction between the oxide and the remaining sulphide.

Step 1: (a)(i) Refining a semiconductor to high purity The method is zone refining, used for semiconductors such as silicon and germanium. Impurities are more soluble in the molten material than in its solid. A narrow molten zone moves along a rod; pure material crystallises behind it while impurities move with the melt towards one end. Repeating the operation concentrates impurities at that end, which is removed.

Step 2: (a)(ii) Refining a low-boiling metal The method is distillation. A volatile metal such as zinc is heated until it vaporises; non-volatile impurities remain behind. The metal vapour is then cooled and condensed to obtain purified metal. This method uses the relatively low boiling point of the metal compared with that of the impurities.

Step 3: (b) Reactions in copper extraction On heating copper(I) sulphide in air, part of it is oxidised to copper(I) oxide:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2.$$

The oxide reacts with the remaining sulphide without an external reducing agent:

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2.$$

This second reaction is self-reduction (auto-reduction). Sulphur leaves as sulphur dioxide, and metallic copper is formed.

Step 4: Conclusion (a) The methods are (i) zone refining and (ii) distillation. (b) Partial oxidation of Cu_2S, followed by self-reduction of Cu_2O with the remaining sulphide, gives copper through the balanced equations above.

Quick Tip to Solve: Remember the sequence sulphide to oxide to metal; copper sulphide itself reduces the oxide in the second reaction.

18. Give reasons for the following:

(i) Transition elements and their compounds act as catalysts.

(ii) E° value for ($Mn^{2+}|Mn$) is negative whereas for ($Cu^{2+}|Cu$) is positive.

(iii) Actinoids show irregularities in their electronic configurations. [3 marks]

Solution:

Concept:

- Transition metals have accessible oxidation states and orbitals that enable interactions with reactants; these can provide a reaction pathway with lower activation energy.
- A standard electrode potential for M^{2+}/M refers to reduction of the aqueous ion. Its value reflects atomisation, ionisation and hydration contributions, relative to the standard hydrogen electrode.
- Electronic configurations depend on the relative energies of available orbitals; closely spaced orbital energies permit competing electron arrangements.

Step 1: (i) Catalytic activity Transition elements and their compounds exhibit variable oxidation states, allowing them to form intermediate compounds with reactants and then return to their original state. Their partially filled d orbitals also help bind reactants. On a metal surface, adsorption brings reactants together and weakens their bonds. These effects provide an alternative pathway of lower activation energy, increasing the reaction rate without consuming the catalyst overall.

Step 2: (ii) Opposite signs of the manganese and copper potentials The aqueous Mn^{2+} ion has an especially stable half-filled $3d^5$ configuration. Together with hydration, this favours formation of the ion from the metal and makes its reverse reduction unfavourable relative to hydrogen; hence $E^\circ(Mn^{2+}/Mn)$ is negative. For copper, the energy needed for atomisation and ionisation to form Cu^{2+} is not compensated by its hydration energy. Oxidation of copper to the aqueous ion is therefore unfavourable relative to hydrogen, while reduction of the ion is favoured; its standard reduction potential is positive. The potential depends on the complete energy balance, not ionisation alone.

Step 3: (iii) Irregular actinoid configurations The $5f$, $6d$ and $7s$ subshells in actinoids have comparable energies. Small changes in nuclear charge and electron interactions alter their relative energies, so electrons can occupy competing arrangements. Consequently, the configurations do not follow a simple regular pattern of adding every successive electron only to $5f$.

Step 4: Conclusion Catalysis arises from variable oxidation states and reactant binding; the potential signs reflect the energy balance and the stability of aqueous Mn^{2+}; actinoid irregularities arise from closely spaced $5f$, $6d$ and $7s$ energies.

Quick Tip to Solve: Read an electrode potential as reduction of the aqueous ion; explain its sign using the full energy balance and ion stability.

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:

- Monomers are the small molecules that join to form a polymer. Condensation polymers require reactive groups on both ends of their monomers.
- Addition copolymers are formed from two different unsaturated monomers by opening their carbon-carbon double bonds.

Step 1: (i) Monomers of Nylon-6,6 Nylon-6,6 is a polyamide obtained from hexamethylenediamine and adipic acid. Their structures are

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

The amino groups react with carboxyl groups to form amide linkages with elimination of water. Each monomer has six carbon atoms, which accounts for the designation 6,6.

Step 2: (ii) Monomers of Glyptal Glyptal is the polyester formed from ethylene glycol and phthalic acid. The monomer structures are

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

In phthalic acid the two carboxyl groups are attached to adjacent carbon atoms of the benzene ring. Reaction of hydroxyl and carboxyl groups forms ester linkages with loss of water.

Step 3: (iii) Monomers of Buna-S Buna-S is an addition copolymer of 1,3-butadiene and styrene. Their structures are

$$\begin{aligned} &CH_2=CH-CH=CH_2 \quad &&\text{(1,3-butadiene)},\\ &C_6H_5-CH=CH_2 \quad &&\text{(styrene)}. \end{aligned}$$

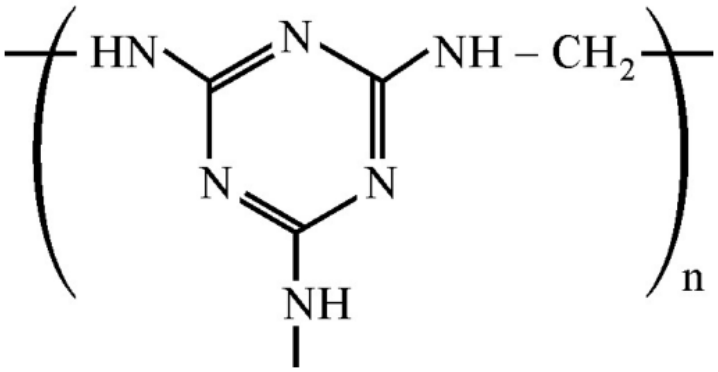
Both monomers contain carbon-carbon double bonds that participate in polymerisation. The letter S identifies the styrene component of the rubber.

Step 4: Conclusion The required pairs are: Nylon-6,6 – hexamethylenediamine and adipic acid; Glyptal – ethylene glycol and phthalic acid; Buna-S – 1,3-butadiene and styrene, with the structures given above.

Quick Tip to Solve: Match the linkage to the monomers: amide needs diamine plus diacid, ester needs diol plus diacid, and Buna-S includes styrene.

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 one kind of monomer; a copolymer is formed from two or more different kinds of monomer.
- Condensation polymerisation joins monomers through reactive functional groups. Vulcanisation introduces cross-links between rubber chains.

Step 1: (i) Identify the polymer and its monomer The given repeating unit is $[-CH_2 - CH(CH_3)-]_n$, which represents polypropene (polypropylene). Its monomer is propene, $CH_2 = CH - CH_3$. Opening the double bond in many propene molecules joins them into a chain while retaining a methyl group on every second backbone carbon. Since only one kind of monomer, propene, is used, the polymer is a homopolymer.

Step 2: (ii) Identify the monomers of the illustrated resin The displayed polymer contains a nitrogen-containing six-membered ring with exocyclic amino groups joined through methylene bridges. This is melamine-formaldehyde resin. Its monomers are melamine (2,4,6-triamino-1,3,5-triazine), $C_3N_3(NH_2)_3$, and formaldehyde (methanal), $H - CHO$. Melamine has three amino groups attached to the alternating carbon atoms of the triazine ring. These amino groups react with formaldehyde during condensation to produce bridges connecting the melamine units.

Step 3: (iii) Explain the role of sulphur During vulcanisation, sulphur forms cross-links between the long polyisoprene chains of natural rubber at reactive sites associated with their double bonds. These sulphur bridges reduce unrestricted sliding of one chain over another. Thus the rubber gains strength and elasticity and becomes less sticky and less sensitive to temperature changes.

Step 4: Conclusion (i) Polypropene is a homopolymer of propene. (ii) The resin is made from melamine and formaldehyde. (iii) Sulphur cross-links rubber chains, improving strength, elasticity and temperature resistance.

Quick Tip to Solve: Count the different starting monomers to classify the polymer; identify the triazine ring to recognise melamine-formaldehyde resin.

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

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

(iii) Why the use of alitame as artificial sweetener is not recommended? [3 marks]

Solution:

Concept:

- Drugs are classified according to their therapeutic action. Tranquillisers act on the nervous system and may be used to induce sleep.
- Detergents are classified as anionic, cationic or non-ionic according to the electrical character of their active part in solution.
- A very intense artificial sweetener requires careful control of the amount added to food.

Step 1: (i) Drug used in sleeping pills Tranquillisers are the class of drugs used in sleeping pills. In particular, barbiturates such as veronal are sleep-inducing drugs. They depress the activity of the central nervous system, producing a calming effect and helping to induce sleep. The required classification is therefore a tranquilliser; an antibiotic would act against microorganisms and an analgesic would primarily relieve pain.

Step 2: (ii) Detergent used in toothpaste Anionic detergents are used in toothpastes. A common example is sodium lauryl sulphate (sodium dodecyl sulphate), with the structure

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

Its active detergent ion has a negatively charged sulphate end and a long hydrocarbon tail. The tail associates with oily material while the ionic end interacts with water, helping cleaning and foaming. The sodium ion is the counter-ion; it does not make the detergent cationic. Anionic detergents differ from non-ionic detergents, whose active molecules do not bear an ionic charge.

Step 3: (iii) Limitation of alitame Alitame is a high-potency artificial sweetener, approximately 2000 times sweeter than sucrose. Consequently, the amount needed to obtain the desired sweetness is extremely small. Controlling the sweetness of food while using alitame is difficult, since a small error in its quantity can produce excessive sweetness. This difficulty in controlling sweetness is the reason asked for in this question; the answer does not require attributing toxicity to alitame.

Step 4: Conclusion (i) Tranquillisers, such as sleep-inducing barbiturates, are used in sleeping pills. (ii) Anionic detergents are used in toothpastes. (iii) Alitame's very high sweetness makes the sweetness of food difficult to control.

Quick Tip to Solve: For toothpaste remember sodium lauryl sulphate is anionic; for alitame connect high potency directly to difficulty controlling sweetness.

OR

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

(i) Broad-spectrum antibiotics

(ii) Disinfectants

(iii) Cationic detergents [3 marks]

Solution:

Concept:

- Antibiotics are chemical substances that kill microorganisms or inhibit their growth; their spectrum describes the range of bacteria against which they act.
- Disinfectants are antimicrobial chemicals used on non-living objects. In cationic detergents, the organic cation is the cleansing part.

Step 1: (i) Broad-spectrum antibiotics Broad-spectrum antibiotics kill or inhibit a wide range of both Gram-positive and Gram-negative bacteria. Thus, their action is not restricted to one small group of bacteria. Chloramphenicol is a suitable example; it acts against a broad range of bacterial infections. Ampicillin is another example of this category.

Step 2: (ii) Disinfectants Disinfectants are chemicals that destroy microorganisms and are applied to inanimate objects such as floors, drains and instruments. They are generally unsuitable for direct application to living tissues at the concentrations used for disinfection. A suitable example is a 1 per cent phenol solution, which acts as a disinfectant. This differs from antiseptics, which are used on living tissues.

Step 3: (iii) Cationic detergents Cationic detergents are usually quaternary ammonium salts of amines with chloride, bromide or acetate counter-ions. The positively charged organic ion contains the long hydrocarbon chain and is the active cleansing component. For example, cetyltrimethylammonium bromide has the formula

$$[CH_3(CH_2)_{15}N(CH_3)_3]^+ Br^-.$$

Its long hydrocarbon tail interacts with grease, while the charged head interacts with water.

Step 4: Conclusion Examples: broad-spectrum antibiotic—chloramphenicol; disinfectant—1 per cent phenol solution; cationic detergent—cetyltrimethylammonium bromide.

Quick Tip to Solve: For each definition, name the distinguishing feature first and then give one matching example; for cationic detergents identify the positive organic ion.

21. (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:

- In an S_N1 reaction, the rate-determining step is ionisation of the carbon-halogen bond to form a carbocation.
- A para nitro group activates an aryl halide towards nucleophilic substitution. Enantiomers have identical physical properties in an achiral environment, apart from the direction of optical rotation.

Step 1: (i) Compare the leaving groups $(CH_3)_3C-I$ is more reactive towards S_N1 than $(CH_3)_3C-Br$. Both substrates produce the same tertiary carbocation, so carbocation stability is the same. The C-I bond is weaker than the C-Br bond and breaks more readily. Also, iodide is a better leaving group than bromide. Hence the slow ionisation step is faster for tert-butyl iodide.

Step 2: (ii) Identify the substitution product On heating with aqueous NaOH at $443\,K$, the chlorine atom of p-nitrochlorobenzene is replaced by an oxygen-containing group, giving sodium p-nitrophenoxide in alkaline medium. Acidification protonates the phenoxide to form **4-nitrophenol (p-nitrophenol)**. The nitro group at the para position stabilises the intermediate in nucleophilic aromatic substitution. The sequence is

$$p\text{-}NO_2C_6H_4Cl \xrightarrow[443\,K]{\text{aq. NaOH}} p\text{-}NO_2C_6H_4ONa \xrightarrow{H^+} p\text{-}NO_2C_6H_4OH.$$

Step 3: (iii) Explain the separation difficulty The dextro- and laevo-rotatory forms of butan-2-ol are enantiomers. In an achiral environment they have identical boiling points and vapour pressures. Fractional distillation separates substances through differences in volatility or boiling point, so it cannot resolve these enantiomers. Their equal and opposite optical rotations do not provide a boiling-point difference.

Step 4: Conclusion (i) tert-Butyl iodide is more reactive. (ii) The final product is 4-nitrophenol. (iii) The enantiomers have identical boiling points, so fractional distillation cannot separate them.

Quick Tip to Solve: When both halides give the same carbocation, compare leaving groups; for optical isomers, remember that opposite rotation does not imply different boiling points.

22. An aromatic compound 'A' on heating with Br_2 and KOH forms a compound 'B' of molecular formula C_6H_7N which on reacting with $CHCl_3$ and alcoholic KOH produces a foul smelling compound 'C'. Write the structures and IUPAC names of compounds A, B and C. [3 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ into RNH_2, removing the carbonyl carbon from the organic product.
- The carbylamine reaction of a primary amine with chloroform and alcoholic KOH gives a foul-smelling isocyanide $R - N \equiv C$.

Step 1: Identify compound B from its formula and reaction The molecular formula C_6H_7N, together with the positive carbylamine reaction, identifies B as the aromatic primary amine $C_6H_5 - NH_2$. Its IUPAC name is **benzenamine** (aniline). The six-membered benzene ring bears the amino group directly; the formula accounts for five ring hydrogens and two amino hydrogens.

Step 2: Work backwards to compound A Heating A with bromine and KOH is Hofmann bromamide degradation. The amide that gives benzenamine must have a $-CONH_2$ group attached to the phenyl group. Thus A is $C_6H_5 - C(=O) - NH_2$, named **benzamide** (benzenecarboxamide). The balanced reaction is

$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

A contains seven carbon atoms, while B contains six, as required by the degradation.

Step 3: Identify the foul-smelling compound C Benzenamine reacts with chloroform and alcoholic KOH to form $C_6H_5 - N \equiv C$. C is **isocyanobenzene** (phenyl isocyanide). In an isocyanide the phenyl group is bonded to nitrogen, not to the terminal carbon. The reaction is

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O.$$

The alcoholic medium and heating give the characteristic foul-smelling carbylamine product.

Step 4: Conclusion A: $C_6H_5CONH_2$, benzamide; B: $C_6H_5NH_2$, benzenamine; C: $C_6H_5N \equiv C$, isocyanobenzene.

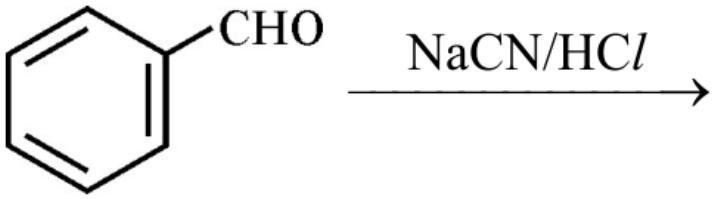
Quick Tip to Solve: Work backwards from the primary amine: add a carbonyl carbon to obtain its parent amide, then write the carbylamine product with the ring bonded to nitrogen.

23(a). Complete the following reactions:

(i)

(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \rightarrow$

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



Solution:

Concept:

- Cyanide adds nucleophilically to a carbonyl group; protonation of the resulting alkoxide gives a cyanohydrin containing $-OH$ and $-CN$ on the same carbon.
- Dialkylcadmium reagents convert acid chlorides into ketones. The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine.

Step 1: (i) Formation of benzaldehyde cyanohydrin The printed aromatic aldehyde is benzaldehyde. Sodium cyanide and hydrochloric acid provide HCN and cyanide for addition across its carbonyl group:

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

Cyanide attacks the electrophilic carbonyl carbon, and the oxygen is protonated. The aldehydic hydrogen remains attached; the product is benzaldehyde cyanohydrin (mandelonitrile).

Step 2: (ii) Formation of a ketone using dibenzylcadmium Each benzyl group, $C_6H_5CH_2-$, replaces chloride in one molecule of acetyl chloride. Thus the balanced equation is

$$(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow 2CH_3COCH_2C_6H_5 + CdCl_2.$$

The acetyl carbonyl is retained and becomes bonded to the benzyl carbon. Cadmium reagents stop at the ketone stage, giving 1-phenylpropan-2-one; the product is not acetophenone because the transferred group contains an intervening CH_2.

Step 3: (iii) Bromination at the alpha carbon In 2-methylpropanoic acid, the carbon next to $COOH$ bears one hydrogen. Bromine and red phosphorus replace precisely this alpha hydrogen; hydrolysis restores the acid group:

$$CH_3CH(CH_3)COOH + Br_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) red P}} CH_3C(Br)(CH_3)COOH + HBr.$$

The product is 2-bromo-2-methylpropanoic acid. Bromination occurs at the alpha carbon, not at a methyl group.

Step 4: Conclusion The products are benzaldehyde cyanohydrin, 1-phenylpropan-2-one and 2-bromo-2-methylpropanoic acid, respectively.

Quick Tip to Solve: Circle the alpha hydrogen before applying HVZ, and retain the benzyl CH2 group when using dibenzylcadmium.

OR

23(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:

- Ketones having an alpha hydrogen undergo aldol addition in dilute base, producing a beta-hydroxy ketone.
- Clemmensen reduction converts a carbonyl group to a methylene group using $\mathrm{Zn(Hg)/conc.\ HCl}$. Rosenmund reduction converts an acid chloride into an aldehyde using hydrogen and $\mathrm{Pd/BaSO_4}$.

Step 1: (i) Aldol addition of propanone Dilute barium hydroxide removes an alpha hydrogen from propanone. The resulting enolate adds to the carbonyl group of another propanone molecule and is then protonated:

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

The product is 4-hydroxy-4-methylpentan-2-one (diacetone alcohol), a beta-hydroxy ketone. Its six carbons come from the two three-carbon reactant molecules. With dilute base as specified, the addition product is written; heating would cause dehydration to an unsaturated ketone.

Step 2: (ii) Clemmensen reduction of acetophenone Acetophenone contains the group $\mathrm{C_6H_5COCH_3}$. Zinc amalgam and concentrated hydrochloric acid reduce its carbonyl group to $\mathrm{CH_2}$:

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

The benzene ring and the two-carbon side chain remain intact. The organic product is ethylbenzene; the reagent gives complete carbonyl deoxygenation rather than the secondary alcohol obtained with a mild hydride reducing agent.

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

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

Chloride is replaced by hydrogen and the carbonyl group is retained. The moderated catalyst limits further reduction, so the expected product is the aldehyde rather than benzyl alcohol. One molecule of hydrogen balances the aldehydic hydrogen and the hydrogen in HCl.

Step 4: Conclusion The organic products are (i) diacetone alcohol, (ii) ethylbenzene and (iii) benzaldehyde, with equations shown above.

Quick Tip to Solve: Match dilute base to aldol addition, Zn(Hg)/HCl to carbonyl deoxygenation, and Pd/BaSO4 to the aldehyde stage.

24(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:

- The properties of biomolecules depend on their monomer units, the bonds joining those units and the shape of their chains.
- Starch components are glucose polymers; peptide bonds join amino acids, whereas glycosidic bonds join monosaccharide units. Protein shape also affects water solubility and biological function.

Step 1: (i) Amylose and amylopectin Amylose is the essentially unbranched component of starch. Its alpha-D-glucose units are joined by $\alpha(1 \rightarrow 4)$ glycosidic linkages, and the chain adopts a helical form. It is the water-soluble component of starch and constitutes about 15–20 percent of it.

Amylopectin is the branched component. Its chains contain $\alpha(1 \rightarrow 4)$ linkages, with $\alpha(1 \rightarrow 6)$ linkages at branch points. It is the water-insoluble component and constitutes about 80–85 percent of starch. Thus branching, rather than a change of monomer, distinguishes the two.

Step 2: (ii) Peptide linkage and glycosidic linkage A peptide linkage is the amide bond $-\mathrm{CO}-\mathrm{NH}-$, formed by condensation of the carboxyl group of one amino acid with the amino group of another, eliminating water. It joins amino-acid residues in peptides and proteins.

A glycosidic linkage is the oxygen bridge $\mathrm{C}-\mathrm{O}-\mathrm{C}$ joining monosaccharide units. It forms by condensation involving the anomeric hydroxyl group of one sugar and a hydroxyl group of another, eliminating water. It occurs in disaccharides and polysaccharides, for example the $\alpha(1 \rightarrow 4)$ linkage in maltose. Hence the linked units and the type of bond differ.

Step 3: (iii) Fibrous proteins and globular proteins Fibrous proteins have long, thread-like chains arranged in fibres, often with chains running parallel and held together by hydrogen bonds and other interactions. They are generally insoluble in water and provide structural support; keratin in hair and collagen in connective tissue are examples.

Globular proteins have polypeptide chains folded into compact, approximately spherical shapes. They are generally soluble in water and commonly perform metabolic or regulatory functions. Insulin and many enzymes are examples. Their compact folding contrasts with the extended arrangement of fibrous proteins.

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 while globular proteins are compact and generally soluble.

Quick Tip to Solve: For each comparison state the structural difference first, then add the linked units, solubility or a suitable example.

OR

24(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:

- Reactions of glucose identify its carbon skeleton and functional groups: reduction with excess HI reveals the skeleton, acetylation counts hydroxyl groups, and mild oxidation identifies an aldehyde.
- The open-chain condensed formula is $CHO - (CHOH)_4 - CH_2OH$. The four secondary alcohol groups and one primary alcohol group give five hydroxyl groups in total.

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

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

The product is an unbranched six-carbon hydrocarbon. Since the oxygen-containing groups are reduced without changing the carbon skeleton, this shows that all six carbon atoms of glucose lie in a straight chain.

Step 2: (ii) Establish the five alcohol groups Glucose reacts with acetic anhydride to form glucose pentaacetate:

$$\begin{aligned} &C_6H_7O(OH)_5 + 5(CH_3CO)_2O \\ &\longrightarrow C_6H_7O(OCOCH_3)_5 \\ &\quad + 5CH_3COOH. \end{aligned}$$

Each hydroxyl group forms one acetate ester. Formation of a pentaacetate therefore establishes the presence of five alcoholic $-OH$ groups. Here the formula groups the five hydroxyl groups to show their acetylation; it does not assign an open-chain structure to the isolated pentaacetate.

Step 3: (iii) Identify the aldehyde carbonyl group Bromine water, a mild oxidising agent, oxidises glucose to gluconic acid:

$$\begin{aligned} &CHO - (CHOH)_4 - CH_2OH + Br_2 + H_2O \\ &\longrightarrow COOH - (CHOH)_4 - CH_2OH + 2HBr. \end{aligned}$$

Only the terminal $-CHO$ group becomes $-COOH$; the alcohol groups are retained. Aldehydes undergo this mild oxidation whereas ketones do not, so the carbonyl group is an aldehyde.

Step 4: Conclusion Normal hexane formation proves a straight six-carbon chain; pentaacetate formation proves five alcohol groups; oxidation by bromine water to gluconic acid proves an aldehyde group.

Quick Tip to Solve: Match each requested feature to its diagnostic reaction: HI for the skeleton, acetic anhydride for hydroxyl count, and bromine water for the aldehyde.

Section D (15 marks)

25(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 $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log_{10} Q$, where n is the number of transferred electrons and Q is the reaction quotient. Pure solid activities are unity.
- Conventional current in the external circuit flows opposite to electrons. An opposing external voltage reverses the spontaneous reaction only when it exceeds the actual cell emf at the given concentrations.

Step 1: Identify the electron transfer and reaction quotient The spontaneous electrode reactions are

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

Thus $n = 2$. Magnesium is the anode and copper is the cathode during spontaneous discharge. Omitting the pure solids from Q, and using the given molar concentrations as dilute-solution activities, gives

$$Q = \frac{[\mathrm{Mg^{2+}}]}{[\mathrm{Cu^{2+}}]} = \frac{0.001}{0.01} = 0.1, \qquad \log_{10} Q = -1.$$

Step 2: Calculate the emf at the specified concentrations Using the usual Nernst-equation temperature of 298 K,

$$E_{\text{cell}} = 2.71 - \frac{0.0591}{2}\log_{10}(0.1)$$
$$= 2.71 + 0.02955 = 2.73955\,\text{V}.$$

Since $Q < 1$, the concentration correction increases the emf above its standard value. This sign check is useful before deciding which source dominates the circuit.

Step 3: (i) Opposing potential less than 2.71 V If $E_{\text{ext}} < 2.71\,\text{V}$, it is also less than the actual cell emf 2.73955 V. The cell therefore continues its spontaneous reaction. Electrons flow from Mg to Cu through the external circuit, while conventional current flows from Cu to Mg through that circuit. Magnesium dissolves and copper is deposited.

Step 4: (ii) Opposing potential greater than 2.71 V The printed inequality alone is insufficient to give

Quick Tip to Solve: Calculate the actual Nernst emf first, then compare the opposing voltage with that value; remember that conventional current is opposite to electron flow.

one current direction because the calculated emf is greater than $2.71\,\text{V}$. The precise cases are:

$$\begin{aligned} 2.71 < E_{\text{ext}} < 2.73955\,\text{V}: &\quad \text{current from Cu to Mg,} \\ E_{\text{ext}} = 2.73955\,\text{V}: &\quad \text{no net current,} \\ E_{\text{ext}} > 2.73955\,\text{V}: &\quad \text{current from Mg to Cu.} \end{aligned}$$

These directions refer to conventional current in the external circuit. In the last case, the external source drives the reverse reaction: copper is oxidised and magnesium ions are reduced. Thus the usual intended reversal answer for part (ii), Mg to Cu, applies when the opposing potential exceeds the actual emf, not merely the standard emf.

Step 5: Conclusion $E_{\text{cell}} = 2.73955\,\text{V} \approx 2.74\,\text{V}$. For (i), conventional external current flows Cu to Mg. For (ii), current reverses to Mg to Cu only above $2.73955\,\text{V}$; it remains Cu to Mg below that threshold and is zero at equality.

Quick Tip to Solve: Calculate the actual Nernst emf first, then compare the opposing voltage with that value; remember that conventional current is opposite to electron flow.

OR

25(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.

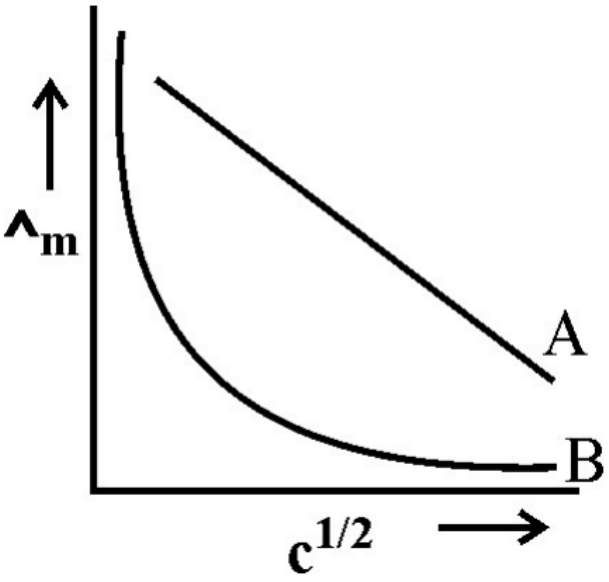
(Molar mass: Fe = 56 g mol^{-1}, Zn = 65.3 g mol^{-1}, 1F = 96500 C mol^{-1})

(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 law gives $m = MQ/(zF)$, where m is deposited mass, M is molar mass, z is the number of electrons required per metal ion and $Q = It$ is the charge passed. Cells in series receive the same charge.
- Both Fe^{2+} and Zn^{2+} require two electrons to form one metal atom. Their equivalent masses are therefore $M/2$.
- A strong electrolyte obeys $\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$ at low concentration. A weak electrolyte shows a strongly curved variation because its degree of ionisation increases on dilution.

Step 1: (a) Calculate the charge needed to deposit iron The cathode reaction in cell X is $Fe^{2+} + 2e^- \longrightarrow Fe$. The deposited amount of iron is

$$n_{Fe} = \frac{2.8}{56} = 0.050\,\text{mol}.$$

Hence 0.100 mol of electrons must pass through the cell. Thus

$$Q = n_{e^-}F = 0.100 \times 96500 = 9650\,\text{C}.$$

Using two electrons per iron ion is essential; the sulphate ion does not determine the electron requirement at the cathode.

Step 2: (a) Find the time and the zinc deposit The steady current is $I = 2\,\text{A} = 2\,\text{C s}^{-1}$. Therefore

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

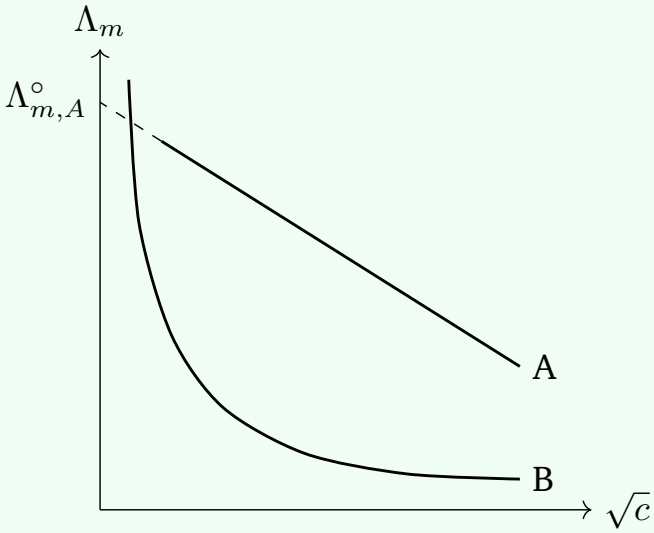
Cell Y is in series with cell X, so the same $9650\,\text{C}$ passes through it. Its cathode reaction is $Zn^{2+} + 2e^- \longrightarrow Zn$. Consequently,

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

Equivalently, equal charges and equal ionic valencies give equal amounts of deposited metal: $n_{Zn} = n_{Fe} = 0.050$ mol. Equal amounts do not imply equal masses, since their molar masses differ.

Step 3: (b)(i) Identify the two electrolytes Curve A is approximately a straight line with negative slope in the Λ_m versus $\sqrt{c}$ plot. It represents a strong electrolyte, which is essentially fully ionised. On dilution, reduced interionic interactions increase ionic mobility and hence its molar conductivity. Curve B is nonlinear and rises sharply as $\sqrt{c}$ approaches zero. It represents a weak electrolyte. Dilution greatly increases its ionisation, increasing the number of ions available per mole as well as their mobility. This accounts for the much steeper increase near zero concentration.

Quick Tip to Solve: In cells in series, compare equivalent masses: since both ions are divalent, multiply the iron mass by $65.3/56$ to find the zinc mass directly.



Strong electrolyte A extrapolates linearly to its limiting molar conductivity; weak electrolyte B has a curved variation.

Step 4: (b)(ii) Explain extrapolation to zero concentration For A, the straight line can be extrapolated to $\sqrt{c} = 0$. Its intercept on the Λ_m axis gives the limiting molar conductivity Λ°_m, corresponding to infinite dilution. For B, direct graphical extrapolation is unreliable because the curve is not linear and becomes very steep near zero concentration. Its limiting molar conductivity cannot be determined accurately by simply extending this measured curve. Instead, it is obtained using Kohlrausch's law of independent migration of ions, combining suitable limiting conductivities of strong electrolytes. Both electrolytes have a limiting molar conductivity; the distinction concerns how that limit can be determined.

Step 5: Conclusion (a) The current flowed for $\boxed{4825\,\text{s}}$, and $\boxed{3.265\,\text{g}}$ of zinc was deposited. (b) A is a strong electrolyte and B is a weak electrolyte. Extrapolation of A gives Λ°_m; direct extrapolation of B does not reliably give it.

Quick Tip to Solve: In cells in series, compare equivalent masses: since both ions are divalent, multiply the iron mass by $65.3/56$ to find the zinc mass directly.

26(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 an alkoxide or phenoxide ion with a primary alkyl halide.
- Oxidation of ethanol gives ethanal. Addition of methylmagnesium bromide to its carbonyl group followed by hydrolysis increases the carbon chain by one carbon and gives a secondary alcohol.
- Concentrated sulphuric acid catalyses dehydration of ethanol at $443\,\text{K}$. The hydroxyl group is protonated so that water can leave.
- The oxygen lone pair in phenol donates electron density into the benzene ring by resonance, activating especially the ortho and para positions.

Step 1: (a)(i) Convert phenol into anisole First form sodium phenoxide using sodium hydroxide. Then react it with methyl iodide:

$$\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O},$$
$$\text{C}_6\text{H}_5\text{ONa} + \text{CH}_3\text{I} \longrightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{NaI}.$$

Phenoxide attacks the methyl carbon and displaces iodide. The product $\text{C}_6\text{H}_5\text{OCH}_3$ is anisole; the methyl halide is suitable for this Williamson reaction.

Step 2: (a)(ii) Convert ethanol into propan-2-ol Oxidise ethanol under controlled conditions with pyridinium chlorochromate (PCC), stopping at ethanal. Treat ethanal with methylmagnesium bromide in dry ether and then hydrolyse the magnesium alkoxide:

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CH}_3\text{CHO},$$
$$\text{CH}_3\text{CHO} + \text{CH}_3\text{MgBr} \xrightarrow{\text{dry ether}} \text{CH}_3\text{CH(OMgBr)CH}_3,$$
$$\text{CH}_3\text{CH(OMgBr)CH}_3 \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{CH(OH)CH}_3.$$

The methyl group supplied by the Grignard reagent bonds to the carbonyl carbon. Hydrolysis supplies the hydroxyl proton, producing propan-2-ol. Dry ether is essential because moisture destroys the Grignard reagent.

Step 3: (b) Acid-catalysed dehydration of ethanol At $443\,\text{K}$, concentrated H_2SO_4 supplies the proton catalyst. The oxygen lone pair accepts a proton:

$$\text{CH}_3\text{CH}_2\text{OH} + \text{H}^+ \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}_2^+.$$

In the standard board-level stepwise representation, the protonated alcohol loses water, followed by

Quick Tip to Solve: To add one carbon while converting ethanol to a secondary alcohol, stop oxidation at ethanal and then add a methyl Grignard reagent before hydrolysis.

loss 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 adjacent C–H bond form the carbon-carbon double bond. The proton is regenerated, so the acid acts as a catalyst. For this primary alcohol, water departure and removal of the adjacent proton can occur together; the displayed ethyl cation is a formal intermediate in the textbook representation, not a stable species accumulating in solution.

Step 4: (c) Explain the greater reactivity of phenol In phenol, a lone pair on oxygen overlaps with the ring's conjugated π-electron system. Resonance donation increases electron density in the ring, particularly at the ortho and para positions. The ring therefore attracts an electrophile more strongly than benzene. Donation from oxygen also stabilises the positively charged intermediate formed during electrophilic substitution. Although oxygen exerts an electron-withdrawing inductive effect, its resonance donation predominates in ring substitution, so phenol reacts more readily than benzene.

Step 5: Conclusion Phenol gives anisole through sodium phenoxide and methyl iodide; ethanol gives propan-2-ol through ethanal and methylmagnesium bromide. Protonation, water elimination and proton loss give ethene, while oxygen's resonance donation explains phenol's greater electrophilic substitution reactivity.

Quick Tip to Solve: To add one carbon while converting ethanol to a secondary alcohol, stop oxidation at ethanal and then add a methyl Grignard reagent before hydrolysis.

OR

26(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, whereas intermolecular hydrogen bonding associates different molecules and reduces their volatility.
- A tertiary alkyl halide is sterically hindered towards the substitution needed for Williamson ether synthesis. A strong base favours elimination on heating.
- Phenol undergoes ortho formylation in the Reimer–Tiemann reaction and ortho/para alkylation because its hydroxyl group activates the ring.

Quick Tip to Solve: For nitrophenol volatility, distinguish hydrogen bonds within a molecule from bonds between molecules; only the latter strongly associate the molecules.

- Neutral ferric chloride gives a coloured complex with phenol and distinguishes it from ethanol.

Step 1: (a)(i) Compare the steam volatility of the nitrophenols In o-nitrophenol, the hydroxyl and nitro groups are adjacent. The hydroxyl hydrogen forms an intramolecular hydrogen bond with a nitro oxygen of the same molecule. This limits hydrogen bonding between separate molecules and hence molecular association. In p-nitrophenol, the groups are too far apart for this internal hydrogen bond, so intermolecular hydrogen bonding produces associated molecules. More energy is required to separate these molecules. Consequently, o-nitrophenol has greater volatility and is carried over with steam more readily than p-nitrophenol.

Step 2: (a)(ii) Explain formation of 2-methylpropene The carbon bonded to chlorine in tert-butyl chloride is tertiary and surrounded by three methyl groups. This crowding prevents the easy backside attack required for the S_N2 pathway of Williamson ether formation. Sodium methoxide is a strong base; on heating it removes a hydrogen from a neighbouring methyl group while chloride leaves, producing an alkene:

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

Thus dehydrohalogenation is favoured over substitution, and the main product is 2-methylpropene instead of tert-butyl methyl ether.

Step 3: (b)(i) Write the Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. The main product is o-hydroxybenzaldehyde (salicylaldehyde); a small amount of the para isomer may also form. The net reaction, with acid work-up understood, is:

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow[\text{then acidify}]{\Delta} o\text{–}HOC_6H_4CHO + 3NaCl + 2H_2O.$$

Chloroform and base generate dichlorocarbene, which introduces a group at the activated ring; hydrolysis and work-up yield the aldehyde group ortho to hydroxyl.

Step 4: (b)(ii) Write Friedel–Crafts alkylation of phenol With an alkyl halide in the presence of anhydrous aluminium chloride, phenol gives ortho- and para-alkylphenols. For example, using methyl chloride:

$$C_6H_5OH + CH_3Cl \xrightarrow{\text{anhydrous } AlCl_3} o\text{–}CH_3C_6H_4OH + HCl,$$

$$C_6H_5OH + CH_3Cl \xrightarrow{\text{anhydrous } AlCl_3} p\text{–}CH_3C_6H_4OH + HCl.$$

These equations represent the two alternative positional products in the mixture, o-cresol and p-cresol. The hydroxyl group directs electrophilic substitution to the ortho and para positions; methyl replaces a ring hydrogen, while the hydroxyl group is retained.

Step 5: (c) Distinguish ethanol and phenol Add a few drops of neutral aqueous ferric chloride solution to separate samples. Phenol gives a violet colour because it forms a coloured iron(III)-phenolate complex. Ethanol does not give this violet colour. Hence the sample showing violet colour is phenol, while the sample without the characteristic colour is ethanol. Use neutral ferric chloride for the usual phenol test.

Step 6: Conclusion Intramolecular hydrogen bonding makes o-nitrophenol more steam volatile.

Quick Tip to Solve: For nitrophenol volatility, distinguish hydrogen bonds within a molecule from bonds between molecules; only the latter strongly associate the molecules.

Heated tert-butyl chloride undergoes elimination with methoxide. Reimer–Tiemann formylation gives mainly salicylaldehyde, alkylation gives ortho/para alkylphenols, and neutral ferric chloride identifies phenol by a violet colour.

Quick Tip to Solve: For nitrophenol volatility, distinguish hydrogen bonds within a molecule from bonds between molecules; only the latter strongly associate the molecules.

27(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 arises from unpaired electrons; a species with all electrons paired is diamagnetic.
- Single-bond strength depends on bonding attraction and repulsion between nonbonding electron pairs on neighbouring atoms.
- A thermodynamically unstable species tends to form a lower-energy product. Nitric acid acts as an oxidising acid, and its reduction product depends on its concentration.

Step 1: (a)(i) Explain the magnetism of sulphur vapour At high temperatures, sulphur vapour contains diatomic S_2 molecules. Like O_2, each S_2 molecule has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons give the molecule a net magnetic moment, so it is attracted by an applied magnetic field and is paramagnetic. The explanation refers to diatomic sulphur in the vapour state rather than the usual cyclic S_8 molecules of solid sulphur.

Step 2: (a)(ii) Compare the nitrogen and phosphorus single bonds Nitrogen has a much smaller atomic size than phosphorus. In an $N-N$ single bond, the lone pairs on the two small nitrogen atoms lie close together and exert strong lone-pair–lone-pair repulsion. This repulsion weakens the single bond. In the larger phosphorus atoms, the lone pairs are farther apart and their mutual repulsion is less severe, so the $P-P$ single bond is stronger. This comparison is specifically between single bonds; the very strong $N \equiv N$ triple bond is a different case.

Step 3: (a)(iii) Explain the relative stability of ozone Ozone has a higher energy than ordinary molecular oxygen. Its decomposition into oxygen releases heat:

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

The decomposition also increases the number of gas molecules and hence entropy. Thus both the enthalpy decrease and entropy increase favour conversion of ozone into oxygen, making $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ negative. Ozone is therefore thermodynamically less stable than oxygen. A favourable

Quick Tip to Solve: For copper with nitric acid, remember dilute acid gives colourless NO first, whereas concentrated acid gives brown NO2 directly.

decomposition need not be instantaneous, since its rate still depends on kinetic factors.

Step 4: (b)(i) Identify the gas with dilute nitric acid Copper is oxidised to copper(II) nitrate, while dilute nitric acid is reduced to nitric oxide, NO:

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

The gas initially evolved is colourless nitric oxide. It can subsequently turn brown in air because atmospheric oxygen oxidises it to nitrogen dioxide; this later change does not alter the identity of the initially released gas.

Step 5: (b)(ii) Identify the gas with concentrated nitric acid Concentrated nitric acid is reduced to nitrogen dioxide, NO_2, when it oxidises copper:

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

Nitrogen dioxide is the brown gas released directly in this reaction. In both reactions copper enters solution as Cu^{2+}; the different nitrogen oxides arise from the different reduction of nitric acid.

Step 6: Conclusion (a) Sulphur vapour is paramagnetic because S_2 has two unpaired electrons; strong lone-pair repulsion weakens $N - N$ compared with $P - P$; ozone decomposes favourably to lower-energy oxygen. (b) The gases are (i) nitric oxide, NO, with dilute acid and (ii) nitrogen dioxide, NO_2, with concentrated acid.

Quick Tip to Solve: For copper with nitric acid, remember dilute acid gives colourless NO first, whereas concentrated acid gives brown NO2 directly.

OR

27(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 phosphorous acid, H_3PO_3, phosphorus has oxidation state $+3$.
- VSEPR theory predicts geometry from bonding and lone pairs around the central atom; lone pairs repel more strongly than bonding pairs.
- Oxidising power in aqueous solution depends on the overall energy change, including bond dissociation, electron gain and hydration, rather than electron gain enthalpy alone.
- Increasing metallic character down a group makes the oxides progressively less acidic. Sulphur

Quick Tip to Solve: For xenon fluorides, count both bond pairs and remaining lone pairs before assigning the molecular shape; four bonds and two opposite lone pairs give square planar XeF4.

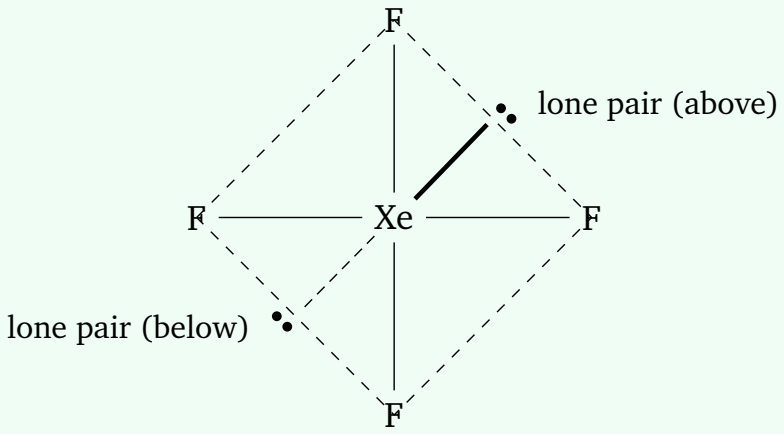
dioxide is a reducing agent and reduces acidified permanganate.

Step 1: (a)(i) Disproportionation of phosphorous acid On heating, phosphorous acid disproportionates:

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

Phosphorus changes from $+3$ to $+5$ in phosphoric acid (oxidation) and from $+3$ to -3 in phosphine (reduction). Three phosphorus atoms each lose two electrons, while one phosphorus atom gains six electrons; thus the electron balance agrees with the equation.

Step 2: (a)(ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four are used to form four Xe–F bonds, leaving two lone pairs on Xe. Thus there are six electron pairs around Xe, with an octahedral electron-pair arrangement (conventionally described by sp^3d^2 hybridisation). The two lone pairs occupy opposite positions to minimise repulsion. The four fluorine atoms lie in one plane around Xe, giving a square planar molecular shape with adjacent F–Xe–F angles of $90°$. The diagram shows the fluorine square in the page and the two lone pairs above and below that plane.



Square planar XeF4; opposite lone pairs lie perpendicular to the fluorine plane.

Step 3: (b)(i) Strong oxidising power of fluorine Fluorine's electron gain enthalpy is less negative than chlorine's because the incoming electron experiences strong repulsion in the compact $2p$ shell. Nevertheless, the aqueous reduction

$$F_2 + 2e^- \longrightarrow 2F^-(aq)$$

is highly favourable overall. The F–F bond has low bond dissociation enthalpy because of repulsion between lone pairs on the small neighbouring fluorine atoms. Also, the small fluoride ion has a very large negative hydration enthalpy. These contributions outweigh the less negative electron gain enthalpy, giving fluorine very strong oxidising power.

Step 4: (b)(ii) Decrease in acidity of group 15 oxides Down group 15, atomic size and metallic character increase, while electronegativity decreases. The oxides therefore become more ionic and more basic, and their acidic character decreases. N_2O_3 is acidic, As_2O_3 and Sb_2O_3 are amphoteric, and Bi_2O_3 is predominantly basic. The change reflects the increasing tendency of the central element to exhibit metallic behaviour.

Step 5: (c) Chemical test for sulphur dioxide Pass the gas through acidified potassium permanganate

Quick Tip to Solve: For xenon fluorides, count both bond pairs and remaining lone pairs before assigning the molecular shape; four bonds and two opposite lone pairs give square planar XeF4.

solution. Sulphur dioxide decolourises the purple solution by reducing MnO_4^- to Mn^{2+}, while it is oxidised to sulphate. The balanced equation is

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

Equivalently, the ionic equation is

$$2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+.$$

Step 6: Conclusion H_3PO_3 gives H_3PO_4 and PH_3 on disproportionation; XeF_4 is square planar with two opposite lone pairs. Fluorine's weak F–F bond and strongly exothermic fluoride hydration account for its oxidising power. Increasing metallic character decreases oxide acidity down group 15, and SO_2 decolourises acidified permanganate.

Quick Tip to Solve: For xenon fluorides, count both bond pairs and remaining lone pairs before assigning the molecular shape; four bonds and two opposite lone pairs give square planar XeF4.