CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/2 (Foreign)

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) Questions number **1 to 8** are very short-answer questions and carry **1** mark each.
(iii) Questions number **9 to 18** are short-answer questions and carry **2** marks each.
(iv) Questions number **19 to 27** are also short-answer questions and carry **3** marks each.
(v) Questions number **28 to 30** are long-answer questions and carry **5** marks each.
(vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. On what principle is the method of zone refining of metals based? [1 mark]

Solution:

Concept:

- Zone refining exploits the unequal solubility of impurities in the solid and molten states of a metal.
- The impurities are more soluble in the melt than in the solid metal.

Step 1: Compare the two phases When an impure molten metal solidifies, the solid that separates contains less impurity because impurities preferentially remain in the liquid phase.

Step 2: Apply the principle A narrow molten zone is moved slowly along a metal rod. As pure metal crystallises behind the moving zone, impurities remain in the melt and are carried towards one end. Repeated passes concentrate the impurities at that end, which is cut off.

Step 3: Conclusion Zone refining is based on the greater solubility of impurities in molten metal than in solid metal.

Quick Tip to Solve: Remember the direction: impurities stay in the moving melt; pure solid is left behind.

2. Name the temperature above which the formation of micelles takes place. [1 mark]

Solution:

Concept:

- Micelles are aggregates of surfactant molecules formed under suitable concentration and temperature conditions.
- The characteristic minimum temperature for micelle formation is the Kraft temperature, denoted by T_K.

Step 1: Identify the temperature The characteristic temperature above which a surfactant can form micelles in solution is known as the Kraft temperature.

Step 2: Distinguish temperature from concentration Micelle formation also requires the surfactant concentration to exceed the critical micelle concentration (CMC). The CMC is a concentration threshold, whereas this question asks for the temperature threshold, so the required name is Kraft temperature.

Step 3: Conclusion The temperature is the **Kraft temperature** (T_K).

Quick Tip to Solve: Keep the two thresholds distinct: Kraft temperature is a temperature; CMC is a concentration.

3. Arrange the following in the increasing order of their basic character:

NH_3, PH_3, AsH_3, SbH_3, BiH_3 [1 mark]

Solution:

Concept:

- A base accepts a proton by donating an available lone pair of electrons.
- For group 15 hydrides, the basic character decreases on moving down the group from NH_3 to BiH_3.

Step 1: Use the group trend The central atom becomes larger down group 15 and its lone pair becomes more diffuse. Its ability to donate the lone pair to a proton decreases, so the hydrides become progressively weaker bases.

Step 2: Reverse for increasing order The decreasing order is $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. To give the increasing order requested, place the least basic hydride first and ammonia last.

Step 3: Conclusion

$$\boxed{BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3}$$

Quick Tip to Solve: First recall that ammonia is the strongest base in this list, then write the order from weakest to strongest.

4. What type of isomerism is exhibited by the following complex:

$[Co(NH_3)_5SO_4]Cl$ [1 mark]

Solution:

Concept:

- Ionisation isomers exchange a coordinated anion with a counter-ion outside the coordination sphere.
- They have the same overall composition but give different ions when dissolved in water.

Step 1: Locate the anions In $[Co(NH_3)_5SO_4]Cl$, sulphate is coordinated to cobalt inside the square brackets, whereas chloride is the counter-ion outside the coordination sphere.

Step 2: Exchange their positions Exchanging these anions gives $[Co(NH_3)_5Cl]SO_4$. The original complex releases chloride ions in water, while this isomer releases sulphate ions. The overall composition is unchanged, but the ionisation behaviour differs.

Step 3: Conclusion The complex exhibits **ionisation isomerism**; its ionisation isomer is $[Co(NH_3)_5Cl]SO_4$.

Quick Tip to Solve: For ionisation isomerism, look for an anionic ligand inside the brackets and a different anion outside.

5. Express the relationship between atomic radius (r) and the edge length (a) of the f.c.c. unit cell. [1 mark]

Solution:

Concept:

- In a face-centred cubic (f.c.c.) unit cell, atoms touch along a face diagonal.
- For a cube of edge length a, the face diagonal is $\sqrt{2}a$, where r denotes the atomic radius.

Step 1: Count the radii along the diagonal A face diagonal passes through the centre of a corner atom, the face-centred atom, and the diagonally opposite corner atom. The touching distance is $r + 2r + r = 4r$.

Step 2: Equate the two expressions The geometric face diagonal and the total touching distance describe the same length. Therefore, $\sqrt{2}a = 4r$. Dividing by four gives the radius in terms of the edge length.

Step 3: Conclusion

$$\boxed{r = \frac{a}{2\sqrt{2}} = \frac{\sqrt{2}a}{4}} \quad \text{or} \quad \boxed{a = 2\sqrt{2}r}.$$

Quick Tip to Solve: For f.c.c., use the face diagonal: two corner radii plus the diameter of the face-centred atom give four radii.

6. Which of the two is more basic and why?

CH_3NH_2 or NH_3 [1 mark]

Solution:

Concept:

- Basic strength depends on the availability of the nitrogen lone pair for bonding to a proton.
- A methyl group has a positive inductive ($+I$) effect and releases electron density towards nitrogen.

Step 1: Compare electron donation In CH_3NH_2, the methyl group pushes electron density towards nitrogen through its $+I$ effect. In NH_3, there is no alkyl group to provide this additional electron donation.

Step 2: Relate electron density to basicity The increased electron density makes the nitrogen lone pair in methylamine more available for accepting H^+. Methylamine therefore accepts a proton more readily than ammonia, forming the methylammonium ion, $CH_3NH_3^+$.

Step 3: Conclusion $\boxed{CH_3NH_2}$ is more basic than NH_3 because the methyl group increases electron density on nitrogen by its $+I$ effect.

Quick Tip to Solve: When comparing methylamine with ammonia, identify the electron-releasing methyl group before judging lone-pair availability.

7. Name the compound which on polymerisation gives neoprene. [1 mark]

Solution:

Concept:

- Neoprene is an addition polymer obtained from a substituted conjugated diene.
- Chloroprene is 2-chlorobuta-$1,3$-diene, with formula $CH_2 = C(Cl) - CH = CH_2$.

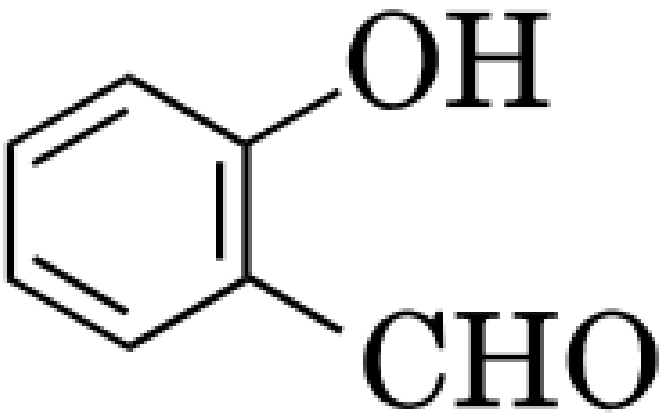
Step 1: Identify the monomer The monomer must contain two conjugated carbon-carbon double bonds and a chlorine substituent on carbon 2. This compound is called chloroprene.

Step 2: Relate the monomer to neoprene During addition polymerisation, chloroprene molecules join predominantly by 1,4-addition. The polymer has the repeating unit $[-CH_2 - C(Cl) = CH - CH_2-]_n$, which identifies it as neoprene.

Step 3: Conclusion The compound is **chloroprene (2-chlorobuta-1,3-diene)**.

Quick Tip to Solve: Remember neoprene by its chlorine-containing diene monomer: chloroprene.

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



Solution:

Concept:

- The aldehyde group $-CHO$ has priority over the hydroxyl group for selecting the principal functional group.
- A benzene ring bearing $-CHO$ is named using benzaldehyde as the parent; the attached ring carbon is numbered 1.

Step 1: Select the parent compound The structure contains a benzene ring with an aldehyde group and a hydroxyl group. Retain benzaldehyde as the parent name, while expressing the hydroxyl group by the prefix hydroxy.

Step 2: Locate the hydroxyl substituent The hydroxyl group lies on the ring carbon immediately next to the carbon bonded to $-CHO$. Numbering from the aldehyde-bearing ring carbon gives the hydroxyl group locant 2, the lowest possible locant.

Quick Tip to Solve: Give the aldehyde priority and number the adjacent hydroxyl-bearing carbon as 2.

Step 3: Conclusion The IUPAC name is **2-hydroxybenzaldehyde**.

Quick Tip to Solve: Give the aldehyde priority and number the adjacent hydroxyl-bearing carbon as 2.

9. Write the role of the following:

(i) CO in the purification of nickel

(ii) Graphite rod in the electrometallurgy of aluminium [2 marks]

Solution:

Concept:

- In the Mond process, carbon monoxide selectively converts nickel into a volatile metal carbonyl.
- In electrolytic extraction of aluminium, oxidation occurs at the graphite anode and reduction of Al^{3+} occurs at the cathode.

Step 1: Role of CO in nickel purification Carbon monoxide reacts with impure nickel at about 330–350 K to form volatile nickel tetracarbonyl:

$$Ni + 4CO \longrightarrow Ni(CO)_4.$$

The carbonyl vapour separates from nonvolatile impurities. Heating it to about 450–470 K decomposes it, depositing pure nickel and regenerating CO:

$$Ni(CO)_4 \longrightarrow Ni + 4CO.$$

Step 2: Role of the graphite rod The graphite rod acts as the conducting anode in the electrolytic cell. Oxide ions are discharged there: $2O^{2-} \longrightarrow O_2 + 4e^-$. The oxygen reacts with hot carbon to form mainly carbon dioxide, with some carbon monoxide. Hence the graphite anodes are consumed and require periodic replacement.

Step 3: Conclusion (i) CO forms volatile $Ni(CO)_4$, enabling purification of nickel. (ii) The graphite rod serves as the anode and reacts with the oxygen liberated there.

Quick Tip to Solve: Link CO with volatile nickel carbonyl, and graphite with the oxygen-producing anode.

10. Complete the following equations:

(i) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow$ [2 marks]

Solution:

Concept:

- Balance redox equations by conserving both atoms and total electric charge.
- In acidic medium, balance oxygen with H_2O, hydrogen with H^+, and charge with electrons.

Step 1: Complete the permanganate-nitrite reaction Permanganate is reduced from Mn(VII) to Mn(II),

Quick Tip to Solve: After balancing atoms, compare net charge on both sides to catch a missing coefficient.

while nitrite is oxidised from N(III) to N(V). The half-reactions are

$$\mathrm{MnO_4^- + 8H^+ + 5}e^- \longrightarrow \mathrm{Mn^{2+} + 4H_2O},$$
$$\mathrm{NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2}e^-.$$

Multiply them by 2 and 5, respectively, and cancel electrons, water and hydrogen ions. This yields the printed coefficients on the reactant side.

Step 2: Complete the dichromate reduction Each chromium atom is reduced from oxidation state +6 to +3. Two chromium atoms therefore accept six electrons and form $2\mathrm{Cr^{3+}}$. The seven oxygen atoms form seven water molecules using the fourteen hydrogen ions already shown. The total charge is +6 on each side, confirming the balance.

Step 3: Conclusion

$$\text{(i)}\quad \mathrm{2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O},$$
$$\text{(ii)}\quad \mathrm{Cr_2O_7^{2-} + 14H^+ + 6}e^- \longrightarrow \mathrm{2Cr^{3+} + 7H_2O}.$$

Quick Tip to Solve: After balancing atoms, compare net charge on both sides to catch a missing coefficient.

11. Write the state of hybridization, shape and IUPAC name of the complex $[Ni(CN)_4]^{2-}$. (Atomic no. of Ni = 28) [2 marks]

Solution:

Concept:

- The oxidation state of the metal is found by equating the sum of its charge and ligand charges to the charge on the complex. Each cyanido ligand, $\mathrm{CN^-}$, has charge -1.
- Cyanide is a strong-field ligand. In a four-coordinate d^8 nickel(II) complex it pairs the $3d$ electrons, allowing inner-orbital dsp^2 hybridisation.

Step 1: Find the oxidation state and electronic configuration Let the oxidation state of Ni be x. Then $x + 4(-1) = -2$, so $x = +2$. Neutral Ni has configuration $[\mathrm{Ar}]3d^8 4s^2$; loss of the two $4s$ electrons gives $\mathrm{Ni^{2+}}$: $[\mathrm{Ar}]3d^8$.

Step 2: Determine hybridisation, shape and name The strong-field $\mathrm{CN^-}$ ligands cause pairing in the $3d$ subshell, leaving one $3d$ orbital available. This orbital, one $4s$ and two $4p$ orbitals form four dsp^2 hybrid orbitals directed towards the corners of a square. The complex is therefore square planar. Since the coordination entity is anionic, nickel is named nickelate; four cyanido ligands give the prefix tetracyanido, followed by the metal oxidation state (II).

Step 3: Conclusion Hybridisation: $\boxed{dsp^2}$; shape: $\boxed{\text{square planar}}$;
IUPAC name: tetracyanidonickelate(II).

Quick Tip to Solve: First obtain Ni(II), hence a d8 ion; strong-field cyanide then identifies the square-planar dsp2 complex.

12. Write chemical equations when

(i) methyl chloride is treated with $AgNO_2$.

(ii) bromobenzene is treated with CH_3Cl in the presence of anhydrous $AlCl_3$. [2 marks]

Solution:

Concept:

- The nitrite ion is an ambident nucleophile: it can bond through nitrogen or oxygen. Covalent silver nitrite favours attack through nitrogen and forms a nitroalkane.
- In electrophilic aromatic substitution, bromine is deactivating but ortho/para directing because its lone pair participates in resonance with the benzene ring.

Step 1: (i) Reaction of methyl chloride with silver nitrite Methyl chloride gives nitromethane with silver nitrite. The new bond is between the methyl carbon and nitrogen, not oxygen:

$$CH_3Cl + AgNO_2 \longrightarrow CH_3NO_2 + AgCl.$$

Thus the organic product is a nitro compound; methyl nitrite, CH_3ONO, is not the product expected with $AgNO_2$.

Step 2: (ii) Friedel–Crafts methylation of bromobenzene Anhydrous $AlCl_3$ activates methyl chloride for electrophilic substitution. Bromobenzene gives ortho- and para-bromotoluene:

$$C_6H_5Br + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} oBrC_6H_4CH_3 + HCl,$$

$$C_6H_5Br + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} pBrC_6H_4CH_3 + HCl.$$

These equations describe the two alternative substitution products of the reaction mixture. The para product is favoured because it has less steric crowding than the ortho product.

Step 3: Conclusion (i) CH_3NO_2 (nitromethane); (ii) ortho- and para-bromotoluene, with para as the major product.

Quick Tip to Solve: AgNO2 gives the nitro linkage C–N; for bromobenzene retain Br and put the incoming methyl group ortho or para.

13. Name the reagents used in the following reactions:

(i) Nitration of phenol to 2,4,6-trinitrophenol

(ii) Butanal to Butanol

(iii) Friedel–Crafts acetylation of anisole

(iv) Oxidation of primary alcohol to aldehyde [2 marks]

Solution:

Concept:

- A reagent must match the required change: nitration introduces NO_2, reduction converts an aldehyde into a primary alcohol, and controlled oxidation reverses that change.

Quick Tip to Solve: To stop primary-alcohol oxidation at an aldehyde, choose anhydrous PCC instead of a strong aqueous oxidant.

- Friedel–Crafts acetylation introduces CH_3CO- on an aromatic ring using an acetylating reagent and anhydrous $AlCl_3$.

Step 1: (i) Nitration of phenol Use concentrated nitric acid, conc. HNO_3. The strongly activating hydroxyl group allows substitution at both ortho positions and the para position, producing 2,4,6-trinitrophenol (picric acid). Dilute nitric acid would instead give mainly mononitrated phenols.

Step 2: (ii) Reduction of butanal Use sodium borohydride, $NaBH_4$, followed by hydrolysis. It reduces the aldehyde group of $CH_3CH_2CH_2CHO$ to CH_2OH, giving butan-1-ol. $LiAlH_4$ followed by water is also suitable.

Step 3: (iii) Acetylation of anisole Use acetyl chloride, CH_3COCl, in the presence of anhydrous $AlCl_3$. The Lewis acid generates the acetyl electrophile, which substitutes on the activated anisole ring. Acetic anhydride with anhydrous $AlCl_3$ is an alternative.

Step 4: (iv) Controlled oxidation of a primary alcohol Use pyridinium chlorochromate (PCC) in an anhydrous solvent such as dichloromethane. PCC oxidises RCH_2OH to $RCHO$ while avoiding further oxidation to the carboxylic acid under these conditions.

Step 5: Conclusion (i) Concentrated HNO_3; (ii) $NaBH_4$, then hydrolysis;
(iii) CH_3COCl with anhydrous $AlCl_3$; (iv) PCC.

Quick Tip to Solve: To stop primary-alcohol oxidation at an aldehyde, choose anhydrous PCC instead of a strong aqueous oxidant.

14. (a) Which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism and why?

$CH_3-CH_2-CH(Br)-CH_3$ and $CH_3-CH_2-CH_2-CH_2-Br$

(b) Racemisation occurs in S_N1 reactions. Why? [2 marks]

Solution:

Concept:

- An S_N2 reaction is a single-step substitution involving backside attack of the nucleophile. Less crowding around the carbon bearing the halogen increases its reaction rate.
- An S_N1 reaction proceeds through a planar, sp^2-hybridised carbocation. Attack on its two faces can give products of opposite configuration.

Step 1: (a) Compare the two bromides $CH_3CH_2CH(Br)CH_3$, 2-bromobutane, is secondary, whereas $CH_3CH_2CH_2CH_2Br$, 1-bromobutane, is primary. With the same leaving group Br and otherwise comparable conditions, the primary bromide offers less steric obstruction to backside attack. Its S_N2 transition state is therefore easier to form than that of the secondary bromide.

Step 2: (b) Explain racemisation For an optically active substrate undergoing S_N1, the carbon–halogen bond first breaks to produce a planar carbocation. The original tetrahedral configuration at that carbon is lost. The nucleophile may then approach either face: attack on one face gives retention and attack on the other gives inversion. Formation of both enantiomers causes racemisation and loss of optical purity. In practice, the departing ion may partially shield one face, so the two products need

Quick Tip to Solve: Count alkyl groups on the carbon bonded to Br for SN2; for SN1 racemisation, identify the planar carbocation.

not form in exactly equal amounts.

Step 3: Conclusion (a) $\boxed{CH_3CH_2CH_2CH_2Br}$ reacts faster by S_N2 because it is less sterically hindered. (b) Attack on both faces of the planar carbocation produces both enantiomers and causes racemisation.

Quick Tip to Solve: Count alkyl groups on the carbon bonded to Br for SN2; for SN1 racemisation, identify the planar carbocation.

15. Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

[2 marks]

Solution:

Concept:

- An alcohol reacts with hydrogen bromide by protonation of its hydroxyl oxygen followed by nucleophilic substitution. Protonation changes the poor leaving group $-OH$ into water, a good leaving group.
- Ethanol is a primary alcohol. Bromide ion attacks its primary carbon by the S_N2 mechanism; a free primary ethyl carbocation is not formed.

Step 1: Protonate the hydroxyl group The oxygen lone pair accepts a proton from HBr, while the H–Br bond electrons go to bromine. This gives the ethyloxonium ion and bromide nucleophile:

$$CH_3CH_2OH + HBr \rightleftharpoons CH_3CH_2OH_2^+ + Br^-.$$

The positive charge is on oxygen.

Step 2: Substitute bromide for water The bromide ion attacks the carbon bonded to oxygen from the side opposite the C–O bond. Formation of the C–Br bond and cleavage of the C–O bond occur together, with the latter bond pair returning to oxygen:

$$Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.$$

Thus water leaves in the substitution step, producing bromoethane.

Step 3: Conclusion The mechanism is protonation of ethanol followed by S_N2 displacement of water by Br^-, yielding CH_3CH_2Br.

Quick Tip to Solve: For a primary alcohol, protonate OH first and show direct bromide attack; do not draw a free primary carbocation.

16. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?
(Given: At. mass of Ni = 58.7 g mol^{-1}, 1 F = 96500 C mol^{-1}) [2 marks]

Solution:

Concept:

- Faraday's law gives $m = MQ/(nF)$, where m is deposited mass, M the molar mass, $Q = It$ the charge and n the electrons required per metal ion.
- Nickel nitrate supplies Ni^{2+}, so cathodic reduction is $Ni^{2+} + 2e^- \rightarrow Ni(s)$; hence $n = 2$.

Step 1: Calculate the charge passed Convert the time to seconds because the current is in amperes:

$$t = 20 \times 60 = 1200\,\text{s}.$$

Therefore,

$$Q = It = (5.0\,\text{A})(1200\,\text{s}) = 6000\,\text{C}.$$

This is the total charge delivered during the electrolysis.

Step 2: Calculate the nickel deposited Two moles of electrons deposit one mole of nickel. Thus

$$n(\text{Ni}) = \frac{Q}{2F} = \frac{6000}{2 \times 96500}\,\text{mol}.$$

Using $M = 58.7\,\text{g mol}^{-1}$,

$$m = \frac{58.7 \times 6000}{2 \times 96500} = 1.8249\,\text{g} \approx 1.82\,\text{g}.$$

The factor two follows from the nickel ion charge; platinum serves as the inert electrode.

Step 3: Conclusion The mass of nickel deposited at the cathode is $\boxed{1.82\,\text{g}}$ (approximately).

Quick Tip to Solve: Write the cathode half-reaction first: the charge on the metal ion supplies the divisor in Faraday's law.

17. Define half-life of a reaction. Write the expression of half-life for
(i) zero order reaction and
(ii) first order reaction. [2 marks]

Solution:

Concept:

- The half-life $t_{1/2}$ of a reaction is the time required for the concentration of a reactant to decrease to half of its initial value: $[A] = [A]_0/2$.
- Here $[A]_0$ is the initial reactant concentration and k is the rate constant for the stated reaction order.

Quick Tip to Solve: Set the remaining concentration equal to half the initial concentration in the integrated rate law to avoid interchanging the formulae.

Step 1: (i) Half-life of a zero order reaction The integrated rate law is

$$[A] = [A]_0 - kt.$$

At the half-life, substitute $[A] = [A]_0/2$ and $t = t_{1/2}$:

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

A zero order half-life therefore increases in direct proportion to the initial concentration.

Step 2: (ii) Half-life of a first order reaction The integrated first order rate law is

$$kt = \ln \frac{[A]_0}{[A]}.$$

On putting $[A] = [A]_0/2$,

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

In this case the initial concentration cancels, so the half-life is independent of the initial concentration.

Step 3: Conclusion Half-life is the time for a reactant concentration to become half its initial value. It is $\boxed{[A]_0/(2k)}$ for zero order and $\boxed{0.693/k}$ for first order.

Quick Tip to Solve: Set the remaining concentration equal to half the initial concentration in the integrated rate law to avoid interchanging the formulae.

18(a). Name the two most important allotropes of sulphur. Which one of the two is stable at room temperature? What happens when the stable form is heated above 370 K? [2 marks]

Solution:

Concept:

- The two most important allotropes of sulphur are rhombic sulphur (α-sulphur) and monoclinic sulphur (β-sulphur). Both contain puckered S_8 rings, but their crystal arrangements differ.
- The transition temperature between these crystalline forms is approximately 369 K (usually rounded to 370 K). Stability depends on which side of this temperature the sample is kept.

Step 1: Identify the room-temperature stable form At room temperature, which is below the transition temperature, rhombic sulphur is the stable allotrope. Monoclinic sulphur is stable above the transition temperature and below its melting point; when kept at room temperature, it slowly converts into the rhombic form.

Step 2: Heat the stable form above 370 K On heating rhombic sulphur above about 370 K, it changes into monoclinic sulphur, the stable solid form in that temperature region:

$$\alpha\text{-sulphur (rhombic)} \xrightarrow{\text{above } 370\,\text{K}} \beta\text{-sulphur (monoclinic)}.$$

This is an allotropic transformation involving a change in crystal structure, not the formation of a new

Quick Tip to Solve: Remember rhombic below the transition temperature and monoclinic above it; the change is between two crystalline forms of sulphur.

chemical element.

Step 3: Conclusion The allotropes are rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature and changes into monoclinic sulphur when heated above $370\,\text{K}$.

Quick Tip to Solve: Remember rhombic below the transition temperature and monoclinic above it; the change is between two crystalline forms of sulphur.

OR

18(b). (i) Write the conditions to maximize the yield of H_2SO_4 by contact process.
(ii) Why is $K_{a2} << K_{a1}$ for H_2SO_4 in water? [2 marks]

Solution:

Concept:

- The contact process involves the reversible, exothermic oxidation $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. The number of gaseous moles decreases from three to two.
- For successive ionisations, K_{a1} describes proton loss from neutral H_2SO_4, whereas K_{a2} describes proton loss from HSO_4^-.

Step 1: (i) Conditions for the contact process By Le Chateliers principle, a lower temperature and higher pressure favour the formation of SO_3, because the forward reaction is exothermic and reduces gaseous moles. In practice, a temperature of about $720\,\text{K}$, a pressure of about $2\,\text{bar}$, and a V_2O_5 catalyst give an economical high yield at an adequate rate. The catalyst speeds attainment of equilibrium without changing its position. The SO_3 is absorbed in concentrated sulphuric acid to form oleum, which is then diluted to obtain H_2SO_4.

Step 2: (ii) Compare the two acid dissociations The first ionisation is almost complete in water:

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-.$$

In the second ionisation,

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-},$$

the proton must be removed from an already negatively charged ion. Its electrostatic attraction for the proton makes removal much harder than removal from neutral H_2SO_4. Consequently the second dissociation is much less extensive.

Step 3: Conclusion (i) Use about $720\,\text{K}$, $2\,\text{bar}$, and V_2O_5. (ii) Proton removal from HSO_4^- is more difficult; hence $K_{a2} \ll K_{a1}$.

Quick Tip to Solve: Distinguish the low temperature favoured by equilibrium from the moderate temperature used for a useful reaction rate.

19. After the ban on plastic bags, students of one school decided to create awareness among the people about the harmful effects of plastic bags on the environment and the Yamuna river. To make it more impactful, they organized a rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save the Yamuna river.

After reading the above passage, answer the following questions:

(i) What values are shown by the students?

(ii) What are biodegradable polymers? Give one example.

(iii) Is polythene a homopolymer or copolymer? [3 marks]

Solution:

Concept:

- Biodegradation is the breakdown of a material by biological agents such as microorganisms and their enzymes.
- A homopolymer is formed from only one type of monomer; a copolymer is formed from two or more different monomer types.

Step 1: (i) Values demonstrated by the students The students show environmental awareness, social responsibility and concern for the health of the Yamuna river. Joining other schools demonstrates cooperation and teamwork. Distributing paper bags shows initiative and a practical commitment to replacing harmful plastic bags, while their pledge shows responsible citizenship and concern for future generations.

Step 2: (ii) Biodegradable polymers and an example Biodegradable polymers are polymers that can be decomposed by microorganisms through enzyme-catalysed reactions into simpler products. A standard example is PHBV, poly(β-hydroxybutyrate-co-β-hydroxyvalerate). Its ester linkages can undergo biological degradation. The term describes susceptibility to biological breakdown, rather than merely breaking into smaller visible pieces.

Step 3: (iii) Classify polythene Polythene is produced by addition polymerisation of ethene alone:

$$n\,CH_2{=}CH_2 \longrightarrow [-CH_2 - CH_2-]_n.$$

Since all its repeating units come from a single monomer type, ethene, it is a homopolymer. The two carbon atoms in each repeat unit do not make it a copolymer.

Step 4: Conclusion The values include environmental concern, cooperation and social responsibility. Biodegradable polymers undergo microbial decomposition; PHBV is an example. Polythene is a homopolymer.

Quick Tip to Solve: Count the distinct starting monomers, rather than the atoms in a repeat unit, when classifying a polymer.

20. Define the following terms:

(a) Polysaccharides

(b) Amino acids

(c) Enzymes [3 marks]

Solution:

Concept:

- A biochemical definition should state both the defining chemical feature and the role or behaviour that distinguishes the class.
- Polysaccharides are classified by hydrolysis products; amino acids by functional groups; enzymes by their catalytic action.

Step 1: (a) Polysaccharides Polysaccharides are high molecular mass carbohydrates consisting of many monosaccharide units joined by glycosidic linkages. On complete hydrolysis they yield a large number of monosaccharide molecules. Starch and cellulose, for example, yield glucose on hydrolysis. Thus, they differ from disaccharides, which yield only two monosaccharide units per molecule.

Step 2: (b) Amino acids Amino acids are organic compounds containing both an amino group $(-NH_2)$ and a carboxyl group $(-COOH)$. The amino acids obtained from proteins are mainly α-amino acids, in which both groups are attached to the same carbon atom:

$$H_2N - CH(R) - COOH.$$

Here R is the side chain, which varies between amino acids. Glycine has $R = H$.

Step 3: (c) Enzymes Enzymes are biological catalysts produced by living cells; most are globular proteins. They increase the rates of biochemical reactions by providing a pathway of lower activation energy, without being consumed in the overall reaction. They are usually highly specific for a substrate or reaction. For example, invertase catalyses the hydrolysis of sucrose into glucose and fructose.

Step 4: Conclusion Polysaccharides yield many monosaccharides on hydrolysis; amino acids contain amino and carboxyl groups; enzymes are biological catalysts, generally proteins.

Quick Tip to Solve: For each definition, give the defining feature first, then one example to make the distinction precise.

21. (i) Define Antihistamine with an example.

(ii) Which one of the following drugs is an antibiotic: Morphine, Equanil, Chloramphenicol, Aspirin.

(iii) Why is use of aspartame limited to cold food and drink? [3 marks]

Solution:

Concept:

- Antihistamines oppose the effects of histamine by blocking its action at histamine receptors; they are used to treat allergic reactions.
- Antibiotics inhibit the growth of, or destroy, disease-causing microorganisms. Aspartame is an

Quick Tip to Solve: Classify each drug by its therapeutic action before choosing the antibiotic; for aspartame, connect cold use to thermal instability.

artificial sweetener whose stability decreases on heating.

Step 1: Define an antihistamine and give an example Histamine released during an allergic response produces effects such as sneezing, a running nose and irritation. An antihistamine is a drug that blocks the action of histamine at its receptor sites and thereby relieves these allergic symptoms. Brompheniramine is an example; terfenadine is another acceptable example. Such a drug antagonises histamine rather than acting as an antibiotic.

Step 2: Identify the antibiotic Chloramphenicol is the antibiotic among the four named drugs. It is a broad-spectrum antibiotic that inhibits bacterial protein synthesis. Morphine is a narcotic analgesic used for pain relief, Equanil is a tranquilliser, and aspirin is a non-narcotic analgesic and antipyretic. Thus these three belong to different therapeutic classes and do not answer the antibiotic part.

Step 3: Explain the temperature restriction on aspartame Aspartame is the methyl ester of the dipeptide formed from aspartic acid and phenylalanine. It is unstable at cooking temperatures and decomposes on heating, so it loses its desired sweetening action. Consequently its use as a sweetener is restricted to cold foods and soft drinks, where substantial thermal decomposition is avoided.

Step 4: Conclusion (i) An antihistamine blocks histamine action; example: brompheniramine. (ii) Chloramphenicol is the antibiotic. (iii) Aspartame decomposes on heating, so it is used in cold foods and drinks.

Quick Tip to Solve: Classify each drug by its therapeutic action before choosing the antibiotic; for aspartame, connect cold use to thermal instability.

22. Give the structures of A, B and C in the following reactions:

(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\,K]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$ [3 marks]

Solution:

Concept:

- With ionic cyanide, nucleophilic substitution gives a nitrile, adding one carbon to the alkyl chain. Reduction of a nitrile gives a primary amine.
- Hofmann bromamide degradation converts an amide into a primary amine with one fewer carbon. The carbylamine reaction converts a primary amine into an isocyanide.

Step 1: Identify A and B in sequence (i) Potassium cyanide attacks methyl bromide through carbon, giving ethanenitrile (acetonitrile), not an isocyanide. Reduction converts its nitrile carbon into a methylene group:

$$CH_3Br + KCN \longrightarrow CH_3C \equiv N + KBr,$$

$$CH_3C \equiv N + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2NH_2.$$

Thus A has the structure $CH_3C \equiv N$ and B is ethanamine, $CH_3CH_2NH_2$.

Step 2: Complete sequence (i) with nitrous acid An aliphatic primary amine reacts with nitrous acid to give the corresponding alcohol, with nitrogen evolution. The intermediate aliphatic diazonium

Quick Tip to Solve: Track carbons: KCN adds one carbon, Hofmann degradation removes the carbonyl carbon, and carbylamine gives an N-linked isocyanide.

species is unstable even at the stated temperature.

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O.$$

Therefore C is ethanol, CH_3CH_2OH; the carbon skeleton remains two carbons long.

Step 3: Identify A and B in sequence (ii) Acetic acid first forms ammonium ethanoate with ammonia; heating dehydrates this salt to ethanamide.

$$CH_3COOH + NH_3 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Thus A is $CH_3C(=O)NH_2$. Hofmann degradation then removes the carbonyl carbon:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Hence B is methylamine, CH_3NH_2.

Step 4: Complete sequence (ii) using the carbylamine reaction Methylamine is a primary amine and undergoes the carbylamine reaction with chloroform and alkali:

$$CH_3NH_2 + CHCl_3 + 3NaOH \longrightarrow CH_3N \equiv C + 3NaCl + 3H_2O.$$

C is methyl isocyanide, $CH_3N \equiv C$. Its methyl group is attached to nitrogen, which distinguishes this product from the nitrile in sequence (i).

Step 5: Conclusion (i) $A = CH_3C \equiv N$, $B = CH_3CH_2NH_2$, $C = CH_3CH_2OH$. (ii) $A = CH_3CONH_2$, $B = CH_3NH_2$, $C = CH_3N \equiv C$.

Quick Tip to Solve: Track carbons: KCN adds one carbon, Hofmann degradation removes the carbonyl carbon, and carbylamine gives an N-linked isocyanide.

23. (i) What type of stoichiometric defect is shown by KCl and why?
(ii) What type of semiconductor is formed when silicon is doped with As?
(iii) Which one of the following is an example of molecular solid: CO_2 or SiO_2
(iv) What type of substances would make better magnets, ferromagnetic or ferrimagnetic? [3 marks]

Solution:

Concept:

- A Schottky defect consists of equal numbers of cation and anion vacancies in an ionic crystal; electrical neutrality and stoichiometry remain unchanged.
- Group 15 dopants supply donor electrons to silicon. Molecular solids contain discrete molecules, while ferromagnetism involves parallel alignment of magnetic moments.

Step 1: Identify the stoichiometric defect in KCl KCl shows a Schottky defect. In this defect, equal numbers of K^+ and Cl^- ions are absent from their normal lattice sites, leaving paired vacancies. The two ions have sufficiently comparable sizes and the crystal has high coordination, conditions

Quick Tip to Solve: For As-doped silicon count the extra valence electron; for magnetic solids compare parallel alignment with partial antiparallel cancellation.

favouring Schottky disorder rather than displacement of a small cation to an interstitial site. The 1:1 composition and electrical neutrality are preserved, while density decreases.

Step 2: Determine the semiconductor obtained with arsenic Arsenic has five valence electrons, whereas silicon has four. When an As atom replaces a Si atom, four electrons form covalent bonds with neighbouring silicon atoms. The fifth electron can enter the conduction band readily and acts as an extra charge carrier. Electrons are therefore the majority carriers, so the doped crystal is an n-type semiconductor.

Step 3: Distinguish the two solids Solid CO_2 is a molecular solid: it contains discrete carbon dioxide molecules held together by intermolecular dispersion forces. In SiO_2, silicon and oxygen atoms are joined in a continuous covalent network. Consequently SiO_2 is a covalent network solid, and CO_2 is the required molecular-solid example.

Step 4: Compare magnetic alignment Ferromagnetic substances make better magnets in this comparison. Their magnetic moments align parallel within domains, producing a large resultant magnetisation when the domains are aligned. In ferrimagnetic substances, moments on different sets of sites align antiparallel with unequal magnitudes. They have a nonzero resultant, but partial cancellation reduces the net magnetic moment compared with parallel alignment.

Step 5: Conclusion (i) Schottky defect, favoured by the comparable ionic sizes and high coordination of KCl. (ii) n-type semiconductor. (iii) CO_2. (iv) Ferromagnetic substances.

Quick Tip to Solve: For As-doped silicon count the extra valence electron; for magnetic solids compare parallel alignment with partial antiparallel cancellation.

24. (i) Write two advantages of $H_2 - O_2$ fuel cell over ordinary cell.
(ii) Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.

$$A(s) + B^{2+}(aq) \rightleftharpoons A^{2+}(aq) + B(s)$$

[3 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.
- The standard cell potential and equilibrium constant are related by $E^\circ_{cell} = (0.0591/n)\log K$ at $298\,K$, where n is the number of electrons transferred.

Step 1: (i) State two advantages of the hydrogen-oxygen fuel cell First, it is environmentally clean: hydrogen reacts with oxygen to form water, so the operating cell does not release polluting combustion products. Second, it can provide electricity continuously as long as hydrogen and oxygen are supplied and the product water is removed. An ordinary cell has a finite internal supply of reactants and becomes exhausted. The fuel cell therefore need not be discarded or recharged merely because its original reactants have been used up.

Step 2: (ii) Identify the electron transfer and calculate the potential For the printed reaction, the

Quick Tip to Solve: Count the two electrons from $A \to A^{2+}$ before inserting n; $\log 10 = 1$.

half-reactions are

$$\mathrm{A(s)} \rightarrow \mathrm{A^{2+}(aq)} + 2\mathrm{e^-}, \qquad \mathrm{B^{2+}(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{B(s)}.$$

Thus $n = 2$, not one. Using the standard room-temperature value $T = 298\,\mathrm{K}$,

$$E^\circ_{\text{cell}} = \frac{0.0591}{2}\log 10 = \frac{0.0591}{2}(1) = 0.02955\,\mathrm{V}.$$

The positive sign agrees with $K_c > 1$: the forward cell reaction is favoured under standard conditions. Pure solids do not appear in the equilibrium quotient.

Step 3: Conclusion The fuel cell is clean and operates continuously with a sustained reactant supply. At 298 K, $\boxed{E^\circ_{\text{cell}} \approx +0.0296\,\mathrm{V}}$.

Quick Tip to Solve: Count the two electrons from $\mathrm{A} \rightarrow \mathrm{A^{2+}}$ before inserting n; $\log 10 = 1$.

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25. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Experiment 1: Time = 0 s, Total pressure = 0.4 atm

Experiment 2: Time = 100 s, Total pressure = 0.7 atm

Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010) [3 marks]

Solution:

Concept:

- For $\mathrm{SO_2Cl_2} \rightarrow \mathrm{SO_2} + \mathrm{Cl_2}$, each mole of reactant lost gives two moles of products; at fixed volume and temperature, partial pressure is proportional to amount.
- For a first-order reaction, $k = (2.303/t)\log(p_0/p_t)$, where p_t is the partial pressure of the undecomposed reactant.

Step 1: Find the pressure of undecomposed sulphuryl chloride Initially only $\mathrm{SO_2Cl_2}$ is present, so $p_0 = 0.4\,\mathrm{atm}$. Let $x\,\mathrm{atm}$ be the pressure corresponding to the amount decomposed after $100\,\mathrm{s}$. The partial pressures are then $0.4 - x$ for $\mathrm{SO_2Cl_2}$, x for $\mathrm{SO_2}$, and x for $\mathrm{Cl_2}$. Hence

$$P_t = (0.4 - x) + x + x = 0.4 + x = 0.7\,\mathrm{atm}.$$

Thus $x = 0.3\,\mathrm{atm}$ and the reactant pressure is

$$p_t = 0.4 - 0.3 = 0.1\,\mathrm{atm}.$$

Equivalently, $p_t = 2p_0 - P_t$.

Step 2: Apply the integrated first-order equation Pressure ratios can replace concentration ratios because the gas volume and temperature are fixed. Using the remaining reactant pressure rather than

Quick Tip to Solve: For one gaseous reactant forming two gaseous products, first calculate $p_{\text{reactant}} = 2P_0 - P_t$, then use the first-order formula.

the total pressure,

$$\begin{aligned} k &= \frac{2.303}{100\,\text{s}} \log \frac{0.4}{0.1} \\ &= \frac{2.303}{100\,\text{s}} \log 4 \\ &= \frac{2.303 \times 0.6021}{100}\,\text{s}^{-1} \\ &= 0.013866\,\text{s}^{-1}. \end{aligned}$$

The reactant has fallen to one-quarter of its initial amount, corresponding to two half-lives in the given interval; this is consistent with the calculated positive rate constant.

Step 3: Conclusion $\boxed{k \approx 1.387 \times 10^{-2}\,\text{s}^{-1}}$.

Quick Tip to Solve: For one gaseous reactant forming two gaseous products, first calculate $p_{\text{reactant}} = 2P_0 - P_t$, then use the first-order formula.

26. (a) Write the expression for the Freundlich adsorption isotherm for the adsorption of gases on solids, in the form of an equation.

(b) What are the dispersed phase and dispersion medium of butter?

(c) A delta is formed at the meeting place of sea and river water. Why? [3 marks]

Solution:

Concept:

- The Freundlich isotherm relates the mass of gas adsorbed per unit mass of adsorbent to gas pressure at a fixed temperature.
- An emulsion contains droplets of one liquid dispersed in another medium. Electrolytes can coagulate a colloid by neutralising the charge that stabilises its particles.

Step 1: (a) Write the Freundlich adsorption equation For a gas adsorbed on a solid at constant temperature,

$$\frac{x}{m} = kP^{1/n}, \qquad 0 < \frac{1}{n} < 1.$$

Here x is the mass of gas adsorbed, m is the mass of solid adsorbent, P is the equilibrium gas pressure, and k and n are constants for the particular gas-adsorbent pair at that temperature. Its logarithmic form is $\log(x/m) = \log k + (1/n)\log P$. This empirical relationship applies over an appropriate pressure range.

Step 2: (b) Identify the two phases of butter Butter is a water-in-oil emulsion. The dispersed phase is water, present as small droplets, and the dispersion medium is fat or oil, which forms the continuous phase. The names refer to the internal droplets and their surrounding medium, respectively; they must not be interchanged.

Step 3: (c) Explain delta formation River water carries fine clay particles as a colloidal dispersion. The particles carry charge and normally remain dispersed because of electrostatic repulsion. Sea water contains dissolved salts and supplies electrolyte ions. Counter-ions reduce or neutralise the charge on the clay particles, causing coagulation into larger aggregates. These aggregates settle near

Quick Tip to Solve: In water-in-oil butter, the first named liquid is the droplet phase; delta formation is electrolyte-induced coagulation, not adsorption.

the river mouth, and their continued deposition produces a delta.

Step 4: Conclusion $\boxed{x/m = kP^{1/n}}$; butter has water as dispersed phase and fat/oil as dispersion medium. Sea-water electrolytes coagulate river-water clay, causing sediment deposition and delta formation.

Quick Tip to Solve: In water-in-oil butter, the first named liquid is the droplet phase; delta formation is electrolyte-induced coagulation, not adsorption.

27(a). What are the different oxidation states exhibited by the lanthanoids?

(b) Write two characteristics of the transition elements.

(c) Which of the 3d-block elements may not be regarded as the transition elements and why? [3 marks]

Solution:

Concept:

- Lanthanoids lose the two outer 6s electrons and usually one more electron to form the characteristic $+3$ state; the relative stability of 4f configurations also permits other states.
- A transition element has an incompletely filled d subshell in its atom or in at least one of its cations. Being a d-block element alone does not establish this classification.

Step 1: (a) Oxidation states of lanthanoids The common and most stable oxidation state is $+3$. Some lanthanoids also exhibit $+2$ and $+4$, especially where loss or gain relative to the trivalent state gives an empty, half-filled or filled 4f subshell. For example, Eu^{2+} has $4f^7$, Yb^{2+} has $4f^{14}$, and Ce^{4+} has $4f^0$. Thus the oxidation states required are $+2, +3, +4$.

Step 2: (b) Two characteristic properties Transition elements show variable oxidation states because the ns and the $(n-1)d$ electrons have comparable energies and can participate in bonding. They also commonly form coloured ions: a partly filled d subshell permits electronic transitions between the d levels split by surrounding ligands, with absorption in the visible region. These are characteristic trends; individual ions with d^0 or d^{10} configurations may be colourless.

Step 3: (c) Identify the exception in the 3d block Zinc is not regarded as a transition element. Its atom has configuration $[Ar]3d^{10}4s^2$, and its usual ion, Zn^{2+}, has configuration $[Ar]3d^{10}$. Thus neither has an incompletely filled d subshell. Scandium, however, is a transition element because its neutral atom is $[Ar]3d^14s^2$, even though Sc^{3+} is d^0.

Step 4: Conclusion Lanthanoids exhibit $+2, +3, +4$, predominantly $+3$. Variable oxidation states and coloured-ion formation are two transition-element characteristics. Zn is excluded because its atom and usual cation have filled $3d^{10}$ subshells.

Quick Tip to Solve: Apply the definition to both the neutral atom and its cations: the empty d shell of Sc3+ does not exclude scandium.

OR

27(b). Assign suitable reasons for the following:

(a) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

(b) In the 3d series from Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of Zn is the lowest.

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. [3 marks]

Solution:

Concept:

- A half-filled d^5 configuration has extra stability. Oxidation removes an electron, so compare the d configurations before and after oxidation.
- Metallic bonding generally strengthens when more unpaired valence electrons participate; aqueous-ion colour depends on available visible-light electronic transitions.

Step 1: (a) Compare oxidation of manganese(II) and iron(II) Mn^{2+} has configuration $[Ar]3d^5$, whereas Mn^{3+} is $[Ar]3d^4$. Oxidation of Mn^{2+} therefore destroys the especially stable half-filled subshell and is relatively unfavourable. In contrast, Fe^{2+} is $[Ar]3d^6$, while Fe^{3+} is $[Ar]3d^5$. Its oxidation produces the stable half-filled configuration. Hence manganese(II) compounds resist oxidation to +3 more strongly than iron(II) compounds.

Step 2: (b) Explain the low atomization enthalpy of zinc Zinc has the closed-shell valence configuration $3d^{10}4s^2$, with no unpaired electrons. Its filled 3d subshell contributes little to the strong d-electron metallic bonding characteristic of the other members of the series. Consequently, zinc has comparatively weak interatomic metallic bonding, and relatively little energy is required to separate its solid into gaseous atoms. Its enthalpy of atomization is therefore the lowest in this 3d series.

Step 3: (c) Explain the aqueous-ion colours Sc^{3+} has configuration $[Ar]3d^0$; it has no d electron available for a d-d transition and is colourless in aqueous solution. Ti^{3+} has configuration $[Ar]3d^1$. Water ligands split the d levels, and the single d electron can absorb visible light to move from a lower to a higher level. The remaining transmitted light gives the ion its observed colour.

Step 4: Conclusion Mn^{2+} retains a stable d^5 configuration; Zn has weak metallic bonding associated with its filled $3d^{10}$ shell; Sc^{3+} is d^0, whereas coloured Ti^{3+} is d^1.

Quick Tip to Solve: Write the d-electron counts first: Mn2+ d5, Fe2+ d6, Fe3+ d5, Sc3+ d0 and Ti3+ d1.

28(a). Write the products formed when ethanal reacts with the following reagents:

(i) CH_3MgBr and then H_3O^+

(ii) Zn−Hg / conc. HCl

(iii) C_6H_5CHO in the presence of dilute NaOH [3 marks]

Solution:

Concept:

- A Grignard reagent adds its alkyl group to the carbonyl carbon; acidic work-up converts the magnesium alkoxide to an alcohol.

Quick Tip to Solve: For crossed aldol reactions, the aldehyde with alpha hydrogen supplies the enolate; retain its CHO group in the product.

- Clemmensen reduction converts an aldehyde carbonyl group $-CHO$ to $-CH_3$. An aldehyde with alpha hydrogen undergoes base-catalysed aldol addition.

Step 1: (i) Reaction with methylmagnesium bromide The methyl group of CH_3MgBr adds to the electrophilic carbonyl carbon of ethanal. The resulting magnesium alkoxide gives a secondary alcohol on hydrolysis:

$$CH_3CHO + CH_3MgBr \longrightarrow CH_3CH(OMgBr)CH_3$$

$$CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3.$$

The organic product is propan-2-ol; the carbon chain has gained one carbon from the reagent.

Step 2: (ii) Reaction with zinc amalgam and concentrated acid Zinc amalgam with concentrated hydrochloric acid performs Clemmensen reduction. It removes the carbonyl oxygen while converting the carbonyl carbon into a saturated carbon, without changing the carbon skeleton:

$$CH_3CHO \xrightarrow{Zn-Hg/\text{conc. } HCl} CH_3CH_3.$$

The product is ethane, rather than ethanol, because this reagent reduces the carbonyl group completely to a methylene-derived saturated group.

Step 3: (iii) Reaction with benzaldehyde and dilute alkali Ethanal has alpha hydrogens and supplies the enolate nucleophile; benzaldehyde has no alpha hydrogen and acts as the carbonyl acceptor. Crossed aldol addition gives the beta-hydroxy aldehyde:

$$CH_3CHO + C_6H_5CHO \xrightarrow{\text{dil. } NaOH} C_6H_5CH(OH)CH_2CHO.$$

This product is 3-hydroxy-3-phenylpropanal. On dehydration, the crossed aldol condensation product is cinnamaldehyde:

$$C_6H_5CH(OH)CH_2CHO \xrightarrow{-H_2O} C_6H_5CH{=}CHCHO.$$

Thus the commonly quoted final condensation product is 3-phenylprop-2-enal (cinnamaldehyde); the beta-hydroxy compound is the initial addition product.

Step 4: Conclusion The products are (i) propan-2-ol, $CH_3CH(OH)CH_3$; (ii) ethane, CH_3CH_3; (iii) the crossed aldol product $C_6H_5CH(OH)CH_2CHO$, which dehydrates to cinnamaldehyde, $C_6H_5CH{=}CHCHO$.

Quick Tip to Solve: For crossed aldol reactions, the aldehyde with alpha hydrogen supplies the enolate; retain its CHO group in the product.

28(b). Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Benzoic acid and Ethyl benzoate

(ii) Propanal and Butan-2-one [2 marks]

Solution:

Concept:

- Carboxylic acids liberate carbon dioxide from aqueous sodium hydrogen carbonate; esters do not give this immediate acid-base reaction.
- Tollens' reagent, ammoniacal silver nitrate, oxidises an aliphatic aldehyde to a carboxylate ion while silver ions are reduced to metallic silver. Ordinary ketones give no silver mirror.

Step 1: (i) Benzoic acid and ethyl benzoate Add aqueous sodium hydrogen carbonate separately to the samples. Benzoic acid gives brisk effervescence of carbon dioxide, which turns limewater milky. Ethyl benzoate gives no effervescence under these test conditions.

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2 \uparrow$$

Step 2: (ii) Propanal and butan-2-one Warm each sample gently with freshly prepared Tollens' reagent. Propanal gives a silver mirror on the clean test-tube wall; butan-2-one gives no silver mirror. The aldehyde group is oxidised, whereas the ketone group does not react under these conditions:

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$

$$\longrightarrow CH_3CH_2COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O.$$

Step 3: Conclusion Benzoic acid gives CO_2 with $NaHCO_3$, while ethyl benzoate does not. Propanal gives Tollens' silver-mirror test, while butan-2-one does not.

Quick Tip to Solve: Use bicarbonate to detect the acid, then Tollens' reagent to distinguish the aldehyde from the ketone.

OR

28(a). Account for the following:

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) There are two $-NH_2$ groups in semicarbazide ($H_2NNHCONH_2$). However, only one is involved in the formation of semicarbazone. [2 marks]

Solution:

Concept:

- Addition of HCN to a carbonyl compound begins with nucleophilic attack by CN^- on the electrophilic carbonyl carbon.
- Electron donation by alkyl groups reduces the positive character of the carbonyl carbon. Steric crowding also hinders nucleophilic attack.

Quick Tip to Solve: In semicarbazide, locate the amino nitrogen directly attached to C=O: its lone pair is tied up in resonance.

- A nitrogen lone pair delocalised into an adjacent carbonyl group is less available for nucleophilic attack than a localised lone pair.

Step 1: (i) Compare ethanal and propanone Ethanal, CH_3CHO, has one methyl group and one hydrogen attached to its carbonyl carbon, while propanone, CH_3COCH_3, has two methyl groups. The two electron-releasing methyl groups in propanone reduce the electrophilicity of its carbonyl carbon more strongly. They also cause greater steric hindrance to the approaching CN^- ion. Thus both electronic and steric factors favour faster HCN addition to ethanal.

Step 2: (ii) Identify the reactive amino group in semicarbazide In $H_2N-NH-C(=O)-NH_2$, the lone pair on the terminal $-NH_2$ group directly bonded to the carbonyl carbon is delocalised by resonance into that carbonyl group. It is therefore much less available for nucleophilic attack. The other terminal group, H_2N-NH-, has an available lone pair and attacks the aldehyde or ketone carbonyl carbon. Subsequent loss of water produces the semicarbazone linkage:

$$R_2C=O+H_2N-NH-CO-NH_2$$

$$\longrightarrow R_2C=N-NH-CO-NH_2+H_2O.$$

Step 3: Conclusion Ethanal is more reactive because its carbonyl carbon is more electrophilic and less hindered. Only the terminal hydrazino $-NH_2$ group of semicarbazide forms the semicarbazone.

Quick Tip to Solve: In semicarbazide, locate the amino nitrogen directly attached to C=O: its lone pair is tied up in resonance.

28(b). Write the chemical equation to illustrate each of the following name reactions:

(i) Rosenmund reduction

(ii) Hell–Volhard–Zelinsky reaction

(iii) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Rosenmund reduction selectively hydrogenates an acyl chloride to an aldehyde using palladium supported on barium sulphate.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by a halogen using halogen and red phosphorus.
- In the Cannizzaro reaction, an aldehyde without an alpha hydrogen undergoes disproportionation in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: (i) Rosenmund reduction For example, benzoyl chloride is hydrogenated over poisoned palladium supported on barium sulphate to give benzaldehyde:

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

The low-activity catalyst permits isolation of the aldehyde by suppressing further reduction to the

Quick Tip to Solve: Remember the three signatures: acyl chloride to aldehyde, alpha halogenation of an acid, and aldehyde disproportionation.

alcohol.

Step 2: (ii) Hell-Volhard-Zelinsky reaction For example, ethanoic acid reacts with bromine in the presence of red phosphorus, followed by hydrolysis, to give 2-bromoethanoic acid:

$$CH_3COOH + Br_2 \xrightarrow[\text{then } H_2O]{\text{red P}} BrCH_2COOH + HBr.$$

The bromine substitutes at the alpha carbon, the carbon immediately adjacent to the carboxyl group. An alpha hydrogen is required for this reaction.

Step 3: (iii) Cannizzaro reaction Benzaldehyde has no alpha hydrogen. On treatment with concentrated aqueous sodium hydroxide, two molecules disproportionate to sodium benzoate and benzyl alcohol:

$$2C_6H_5CHO + NaOH \xrightarrow{\text{conc. aq.}} C_6H_5COONa + C_6H_5CH_2OH.$$

One aldehyde molecule supplies the oxidised carboxylate product, while the other supplies the reduced alcohol; the equation accounts for both molecules.

Step 4: Conclusion The illustrated products are benzaldehyde in Rosenmund reduction, 2-bromoethanoic acid in the Hell-Volhard-Zelinsky reaction, and sodium benzoate with benzyl alcohol in the Cannizzaro reaction.

Quick Tip to Solve: Remember the three signatures: acyl chloride to aldehyde, alpha halogenation of an acid, and aldehyde disproportionation.

29(a). State Raoult's law for a solution containing volatile components. Name the solution which follows Raoult's law at all concentrations and temperatures. [2 marks]

Solution:

Concept:

- Raoult's law relates each volatile component's partial vapour pressure to its mole fraction in the liquid solution.
- For component i, $p_i = x_i p_i^\circ$, where p_i° is the vapour pressure of the pure component at the same temperature.

Step 1: State the law for each component At a given temperature, the partial vapour pressure of each volatile component of a solution equals the product of its mole fraction in the solution and its vapour pressure in the pure state. Thus, for a binary solution of volatile liquids A and B,

$$p_A = x_A p_A^\circ, \qquad p_B = x_B p_B^\circ.$$

Here $x_A + x_B = 1$. The law concerns the composition of the liquid phase; the two pure-component vapour pressures must be taken at the temperature of the solution.

Step 2: Identify the solution An ideal solution obeys Raoult's law over the entire range of composition

Quick Tip to Solve: Write the law for each component separately before adding partial pressures to obtain the total pressure.

and temperature. For a binary ideal solution the total vapour pressure is

$$p = p_A + p_B = x_A p_A^\circ + x_B p_B^\circ.$$

Its unlike intermolecular interactions are comparable to the like interactions, so mixing has zero enthalpy change and zero volume change: $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$.

Step 3: Conclusion Raoult's law is $p_i = x_i p_i^\circ$ for each volatile component. The solution obeying it at all concentrations and temperatures is an **ideal solution**.

Quick Tip to Solve: Write the law for each component separately before adding partial pressures to obtain the total pressure.

29(b). Calculate the boiling point elevation for a solution prepared by adding 10 g of $CaCl_2$ to 200 g of water. (K_b for water = 0.512 K kg mol^{-1}, Molar mass of $CaCl_2$ = 111 g mol^{-1}) [3 marks]

Solution:

Concept:

- Boiling point elevation is a colligative property: $\Delta T_b = iK_b m$, where m is solute molality and i is the van't Hoff factor.
- An electrolyte contributes more particles on dissociation; complete dissociation of CaCl_2 gives three ions per formula unit.

Step 1: Calculate the molality The number of moles of calcium chloride is

$$n = \frac{10\,\text{g}}{111\,\text{g mol}^{-1}} = 0.09009\,\text{mol}.$$

The solvent is water of mass $200\,\text{g} = 0.200\,\text{kg}$. Molality uses the mass of solvent, rather than the mass of the whole solution. Therefore

$$m = \frac{0.09009}{0.200} = 0.45045\,\text{mol kg}^{-1}.$$

Step 2: Account for dissociation In water, taking calcium chloride to dissociate completely,

$$\text{CaCl}_2(\text{aq}) \longrightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}).$$

One mole of dissolved formula units produces one mole of calcium ions and two moles of chloride ions, hence three moles of solute particles. Thus $i = 3$. This particle count is needed because boiling point elevation depends on the total number of dissolved particles, rather than their chemical identity.

Step 3: Substitute into the elevation equation Using $K_b = 0.512\,\text{K kg mol}^{-1}$,

$$\begin{aligned}\Delta T_b &= iK_b m \\ &= 3 \times 0.512 \times 0.45045 \\ &= 0.69189\,\text{K}.\end{aligned}$$

Quick Tip to Solve: Count all ions from one formula unit: calcium chloride gives three particles, so multiply the non-electrolyte elevation by three.

The molality and the units of K_b cancel to leave kelvin. The positive sign means that the solution boils at a higher temperature than pure water under the same external pressure.

Step 4: Conclusion The boiling point elevation is $\boxed{\Delta T_b \approx 0.692\,\text{K}}$, taking complete dissociation of $CaCl_2$.

Quick Tip to Solve: Count all ions from one formula unit: calcium chloride gives three particles, so multiply the non-electrolyte elevation by three.

OR

29(a). Define the following terms:

(i) Azeotrope

(ii) Osmotic pressure

(iii) Colligative properties [3 marks]

Solution:

Concept:

- An azeotrope is characterised by equal liquid and vapour compositions at its boiling point.
- Osmotic pressure is defined through stopping solvent flow across a semipermeable membrane.
- Colligative properties depend on the number of solute particles relative to solvent, rather than the chemical identity of the solute.

Step 1: Define azeotrope An azeotrope is a liquid mixture which boils at a constant temperature and has the same composition in the vapour phase as in the liquid phase. Consequently, evaporation at the azeotropic composition does not enrich either component in the vapour, and the components cannot be completely separated by fractional distillation. Azeotropes occur for certain non-ideal solutions and may be minimum-boiling or maximum-boiling mixtures.

Step 2: Define osmotic pressure Osmotic pressure, denoted by π, is the minimum additional pressure that must be applied to a solution to prevent the net flow of solvent into it through a semipermeable membrane separating the solution from pure solvent. Such a membrane permits solvent molecules to pass but prevents solute particles from passing. For a dilute ideal solution, $\pi = CRT$, where C is the molar concentration, R is the gas constant and T is the absolute temperature.

Step 3: Define colligative properties Colligative properties are properties of dilute solutions that depend on the number of solute particles relative to the number of solvent molecules and not on the chemical nature of the solute. The four familiar examples are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. Dissociation or association changes the effective particle count and therefore changes the observed magnitude of these properties.

Step 4: Conclusion (i) An azeotrope boils with equal liquid and vapour compositions. (ii) Osmotic pressure is the minimum excess pressure needed to stop osmosis into a solution. (iii) Colligative properties depend on the relative number of solute particles, not their identity.

Quick Tip to Solve: For an azeotrope mention equal phase compositions; for osmotic pressure specify stopping solvent flow through a semipermeable membrane.

29(b). Calculate the molarity of 9.8% (w/w) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1}. (Molar mass of H_2SO_4 = 98 g mol^{-1}) [2 marks]

Solution:

Concept:

- Mass percentage specifies grams of solute in 100 g of solution. Molarity is the number of moles of solute per litre of solution: $M = n/V$.
- Density relates mass and volume by $V = m/\rho$; the volume used in molarity must be in litres.

Step 1: Choose a convenient mass of solution Take $100\,\text{g}$ of the solution. Since its concentration is 9.8% by mass, this sample contains $9.8\,\text{g}$ of H_2SO_4. Its amount is therefore

$$n = \frac{9.8\,\text{g}}{98\,\text{g mol}^{-1}} = 0.100\,\text{mol}.$$

The remaining mass belongs to water; it must not be used as the mass of the solution when applying the density.

Step 2: Convert the solution mass into volume and calculate molarity Using the given solution density,

$$V = \frac{100\,\text{g}}{1.02\,\text{g mL}^{-1}} = 98.039\,\text{mL} = 0.098039\,\text{L}.$$

Hence

$$M = \frac{0.100\,\text{mol}}{0.098039\,\text{L}} = 1.02\,\text{mol L}^{-1}.$$

The density is necessary because mass percentage alone does not directly specify the volume of solution.

Step 3: Conclusion The molarity of the sulphuric acid solution is $\boxed{1.02\,\text{mol L}^{-1}}$.

Quick Tip to Solve: For a mass percentage, start with 100 g of solution and convert that entire mass to volume using the density.

30(a). Account for the following:

(i) Bi is a strong oxidizing agent in the +5 state.

(ii) PCl_5 is known but NCl_5 is not known.

(iii) Iron dissolves in HCl to form $FeCl_2$ and not $FeCl_3$. [3 marks]

Solution:

Concept:

- The inert-pair effect stabilises the lower oxidation state of the heavier p-block elements.
- Bond formation depends on the valence-shell capacity and atomic size; oxidation by an acid also depends on the oxidising strength of that acid.

Step 1: (i) Oxidising behaviour of bismuth(V) Bismuth has the valence configuration $6s^2 6p^3$. The $6s^2$ electron pair tends to remain non-bonding because of the pronounced inert-pair effect. Consequently,

Quick Tip to Solve: Link each explanation to its cause: inert pair for Bi, valence-shell capacity for N/P, and non-oxidising acid for iron.

the $+3$ oxidation state is much more stable than $+5$. Bismuth in the $+5$ state readily gains two electrons and changes to the more stable $+3$ state:

$$\mathrm{Bi(V)} + 2\mathrm{e}^- \longrightarrow \mathrm{Bi(III)}.$$

Since it accepts electrons from another substance, it oxidises that substance and is a strong oxidising agent.

Step 2: (ii) Existence of phosphorus pentachloride Phosphorus belongs to the third period and can accommodate five bonds around itself, giving the familiar trigonal-bipyramidal structure of $\mathrm{PCl_5}$. In the conventional school-level description, phosphorus has vacant $3d$ orbitals available for expansion of its valence shell. Nitrogen, a second-period element, has no d orbitals in its valence shell and cannot expand its octet to accommodate five N–Cl bonds. Its small size further disfavors surrounding it with five chlorine atoms. Thus $\mathrm{PCl_5}$ is known but $\mathrm{NCl_5}$ is not.

Step 3: (iii) Product of iron with hydrochloric acid Hydrochloric acid is a non-oxidising acid: its hydrogen ions oxidise iron to $\mathrm{Fe^{2+}}$ while being reduced to hydrogen gas, but do not oxidise $\mathrm{Fe^{2+}}$ further to $\mathrm{Fe^{3+}}$. The reaction is

$$\mathrm{Fe} + 2\mathrm{HCl} \longrightarrow \mathrm{FeCl_2} + \mathrm{H_2}\uparrow.$$

In addition, any ferric ions in contact with excess iron would be reduced according to

$$\mathrm{Fe} + 2\mathrm{Fe^{3+}} \longrightarrow 3\mathrm{Fe^{2+}}.$$

Thus the chloride obtained is ferrous chloride.

Step 4: Conclusion Bi(V) is readily reduced to stable Bi(III); phosphorus can form a pentachloride whereas nitrogen cannot expand its octet; non-oxidising HCl produces $\mathrm{FeCl_2}$.

Quick Tip to Solve: Link each explanation to its cause: inert pair for Bi, valence-shell capacity for N/P, and non-oxidising acid for iron.

30(b). Draw the structures of the following:

(i) $\mathrm{XeOF_4}$

(ii) $\mathrm{HClO_4}$ [2 marks]

Solution:

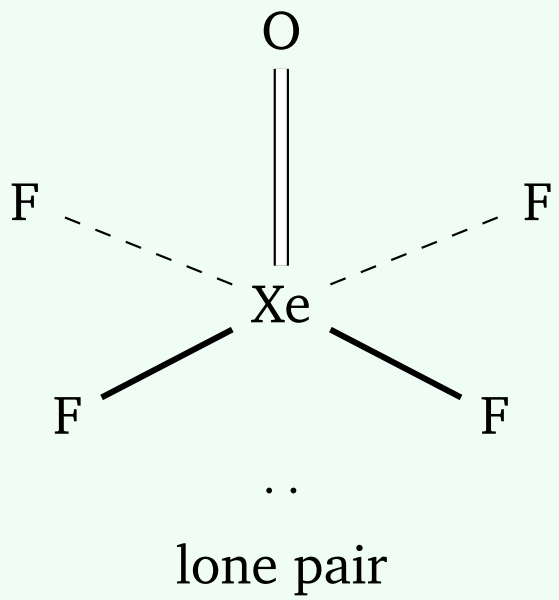
Concept:

- In VSEPR theory, each bond direction, whether single or multiple, counts as one electron domain; lone pairs also occupy electron domains.
- $\mathrm{XeOF_4}$ has five bonding domains and one lone pair on Xe. $\mathrm{HClO_4}$ has four oxygen atoms bonded around its central chlorine atom.

Step 1: (i) Xenon oxytetrafluoride Xenon is bonded to four fluorine atoms by single bonds and to oxygen by a double bond. One lone pair remains on Xe. Thus six electron domains have an octahedral

Quick Tip to Solve: Count the Xe lone pair as the sixth octahedral position, and always attach the acidic hydrogen of HClO4 to oxygen.

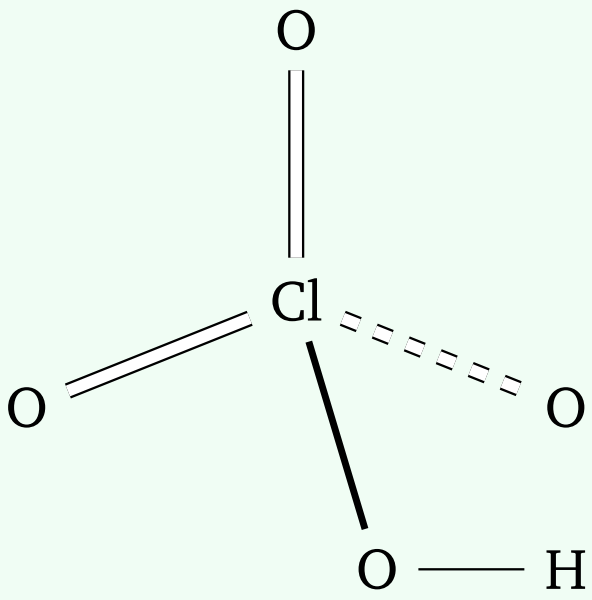
arrangement: the oxygen and lone pair lie opposite each other, while the four fluorine atoms form a square plane. Omitting the lone-pair position gives a square-pyramidal molecular shape. The Xe=O bond is perpendicular to the plane containing the four Xe–F bonds.



Square-pyramidal structure of XeOF4; the lone pair is opposite oxygen.

Step 2: (ii) Perchloric acid The usual structural formula is $HO-Cl(=O)_3$. Chlorine is at the centre, with three terminal oxygen atoms conventionally shown as double bonded and one hydroxyl oxygen single bonded. Hydrogen is attached to oxygen, not directly to chlorine. There are four Cl–O bond directions and no lone pair on the central chlorine in this representation, so the arrangement of oxygen atoms around chlorine is tetrahedral. The drawing below explicitly distinguishes the O–H bond from the Cl–O bonds.

Quick Tip to Solve: Count the Xe lone pair as the sixth octahedral position, and always attach the acidic hydrogen of HClO4 to oxygen.



Structure of HClO4; the four oxygen directions around Cl are tetrahedral.

Step 3: Conclusion $XeOF_4$ is square pyramidal, with an axial Xe=O bond and an opposite lone pair. $HClO_4$ has tetrahedral oxygen coordination around Cl and the connectivity $HO-Cl(=O)_3$.

Quick Tip to Solve: Count the Xe lone pair as the sixth octahedral position, and always attach the acidic hydrogen of HClO4 to oxygen.

OR

30(a). Draw the structures of the following:

(i) $H_2S_2O_8$

(ii) Red P_4 [2 marks]

Solution:

Concept:

- Peroxodisulphuric acid contains a peroxide linkage, $O-O$, joining two sulphur-containing groups. Each sulphur is bonded tetrahedrally to four oxygen atoms.
- Red phosphorus has a polymeric structure: P_4 tetrahedral units are linked through phosphorus-phosphorus bonds after opening a bond in each unit.

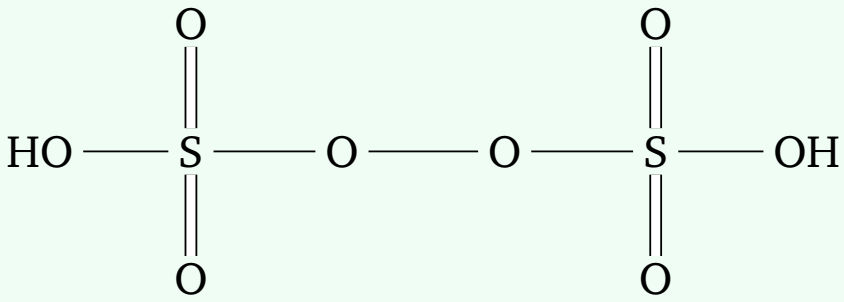
Step 1: (i) Structure of peroxodisulphuric acid The connectivity is

$$HO-S(=O)_2-O-O-S(=O)_2-OH.$$

Each sulphur has two terminal oxo groups, one hydroxyl oxygen and one oxygen of the peroxide bridge. Thus the eight oxygen atoms comprise four oxo oxygens, two hydroxyl oxygens and two

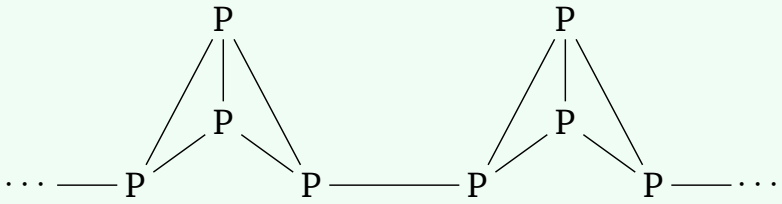
Quick Tip to Solve: For the acid, count all eight oxygen atoms and place an O-O bond between the sulphur groups; for red phosphorus show linked units.

peroxide oxygens; the two hydrogen atoms belong to the hydroxyl groups.



Peroxodisulphuric acid: the central O-O bond is the peroxide linkage.

Step 2: (ii) Structure of red phosphorus Red phosphorus consists of linked phosphorus units in an extended polymeric network. The drawing shows a representative chain segment of linked, opened P_4 tetrahedral units. Each phosphorus has three single bonds and one lone pair; the bonds continuing at the ends extend into the polymer. Red phosphorus is therefore represented by a network rather than by an isolated intact tetrahedral molecule.



Representative linked units in polymeric red phosphorus; end bonds continue into the network.

Step 3: Conclusion The required structures are the peroxide-bridged structure of $H_2S_2O_8$ and the polymeric structure of red phosphorus shown above.

Quick Tip to Solve: For the acid, count all eight oxygen atoms and place an O-O bond between the sulphur groups; for red phosphorus show linked units.

30(b). Account for the following:

(i) Sulphur in vapour state exhibits paramagnetism.

(ii) Unlike xenon, no distinct chemical compound of helium is known.

(iii) H_3PO_2 is a stronger reducing agent than H_3PO_3. [3 marks]

Solution:

Concept:

- Paramagnetism arises from unpaired electrons; a species with all electrons paired is diamagnetic.
- Formation of noble-gas compounds depends on the energy needed to disturb the stable electronic configuration.
- The reducing character of phosphorus oxyacids is associated with hydrogen atoms directly bonded to phosphorus, i.e. P-H bonds.

Quick Tip to Solve: Draw the oxyacid connectivity before counting P-H bonds: the molecular formula alone does not distinguish P-H from O-H hydrogens.

Step 1: (i) Paramagnetism of sulphur vapour At high temperature, sulphur vapour contains S_2 molecules. These have a molecular-orbital electronic arrangement analogous to that of O_2, with two unpaired electrons in the degenerate antibonding π^* orbitals. The unpaired electrons cause attraction in a magnetic field, explaining the paramagnetism of sulphur vapour. The explanation concerns the diatomic species present in the vapour.

Step 2: (ii) Absence of distinct helium compounds Helium has the compact, completely filled $1s^2$ shell. Its very high ionisation enthalpy and very small size make removal or sharing of its electrons energetically unfavourable. Xenon is larger, has less tightly held outer electrons and has a much lower ionisation enthalpy. Consequently, strongly electronegative elements such as fluorine can form compounds with xenon, whereas helium does not form the corresponding ordinary stable compounds.

Step 3: (iii) Relative reducing character of the oxyacids Hypophosphorous acid has the structure $H_2P(=O)(OH)$, containing two P-H bonds. Phosphorous acid has the structure $HP(=O)(OH)_2$, containing only one P-H bond. Since reducing character is associated with P-H bonds, H_3PO_2 is the stronger reducing agent. Its phosphorus is in oxidation state $+1$, compared with $+3$ in H_3PO_3, and can undergo a greater increase in oxidation state on oxidation to $+5$. The hydrogens in O-H groups determine basicity, not this comparison of reducing character.

Step 4: Conclusion Sulphur vapour is paramagnetic because of unpaired electrons in S_2; helium resists compound formation because of its exceptionally stable compact shell; and H_3PO_2 reduces more strongly because it has two P-H bonds rather than one.

Quick Tip to Solve: Draw the oxyacid connectivity before counting P-H bonds: the molecular formula alone does not distinguish P-H from O-H hydrogens.