CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/1 (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. What is the function of collectors in the froth floatation process for the concentration of ores?

[1 mark]

Solution:

Concept:

- Collectors selectively increase the non-wettability of sulphide ore particles by water in froth floatation.
- An ore particle with a hydrophobic surface attaches readily to an air bubble and rises with the froth.

Step 1: Identify the surface change A collector, such as a xanthate, associates with the surface of the sulphide ore particles. It makes their surface more water-repellent, so they are preferentially wetted by oil rather than by water.

Step 2: Relate the change to separation When air is blown through the suspension, the treated ore particles attach to the bubbles and are carried into the froth. The water-wetted gangue remains behind. Thus collectors help the valuable ore enter the froth selectively.

Step 3: Conclusion Collectors enhance the non-wettability of ore particles by water, enabling them to attach to air bubbles and rise in the froth.

Quick Tip to Solve: Remember: a collector makes ore water-repellent; a froth stabiliser keeps the froth from collapsing.

2. What type of forces are responsible for the occurrence of physisorption? [1 mark]

Solution:

Concept:

- Physisorption is the accumulation of an adsorbate on an adsorbent surface through weak intermolecular attraction.
- No new chemical bond is required between the adsorbate and the surface in physical adsorption.

Step 1: Identify the interaction An adsorbate molecule is attracted to the adsorbent surface by weak van der Waals forces. These include dispersion interactions and, where applicable, interactions involving molecular dipoles.

Step 2: Connect the interaction to physisorption These weak attractions hold molecules at the surface without forming the strong chemical bonds characteristic of chemisorption. Consequently, physical adsorption is generally reversible and has a comparatively low enthalpy of adsorption.

Step 3: Conclusion Weak van der Waals forces are responsible for physisorption.

Quick Tip to Solve: Use the word physical as the cue for weak van der Waals attraction, rather than chemical bond formation.

3. Why is the single N−N bond weaker than the single P−P bond? [1 mark]

Solution:

Concept:

- The strength of a single bond depends on both bonding attraction and repulsion between nonbonding electron pairs.
- Nitrogen is smaller than phosphorus, so lone pairs on adjacent bonded nitrogen atoms approach more closely.

Step 1: Compare the sizes of the atoms In a single N–N bond, each nitrogen atom has a small size and carries a lone pair in its common three-bonded state. The short interatomic distance brings the nonbonding electron clouds on the adjacent atoms close together.

Step 2: Explain the reduction in bond strength The resulting lone-pair–lone-pair repulsion is strong and destabilises the N–N single bond. Phosphorus atoms are larger, so the lone pairs on adjacent phosphorus atoms are farther apart and repel one another less strongly in the P–P bond.

Step 3: Conclusion The single N–N bond is weaker because the small nitrogen atoms produce greater lone-pair repulsion than occurs between the larger phosphorus atoms in a P–P bond.

Quick Tip to Solve: For this single-bond comparison, focus on lone-pair repulsion; do not apply the exceptional strength of the nitrogen triple bond.

4. What type of isomerism is shown by the following complex:
$[Co(NH_3)_6][Cr(CN)_6]$ [1 mark]

Solution:

Concept:

- Coordination isomerism occurs in salts containing both complex cations and complex anions.
- It arises through redistribution of ligands between the two metal coordination spheres, with overall composition unchanged.

Step 1: Identify the two coordination spheres In $[Co(NH_3)_6][Cr(CN)_6]$, the cation is $[Co(NH_3)_6]^{3+}$, while the anion is $[Cr(CN)_6]^{3-}$. Both ions contain a central metal surrounded by ligands.

Step 2: Recognise the ligand redistribution Interchanging the ligand sets between cobalt and chromium gives the coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$. The total numbers of metal atoms and ligands remain the same, but their distribution between the complex ions changes.

Step 3: Conclusion The complex shows coordination isomerism.

Quick Tip to Solve: When both the cation and anion are coordination complexes, check for interchange of their ligands.

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

Solution:

Concept:

- In an ideal body-centred cubic unit cell, atoms touch along the body diagonal.
- The body diagonal of a cube of edge length a is $\sqrt{3}a$.

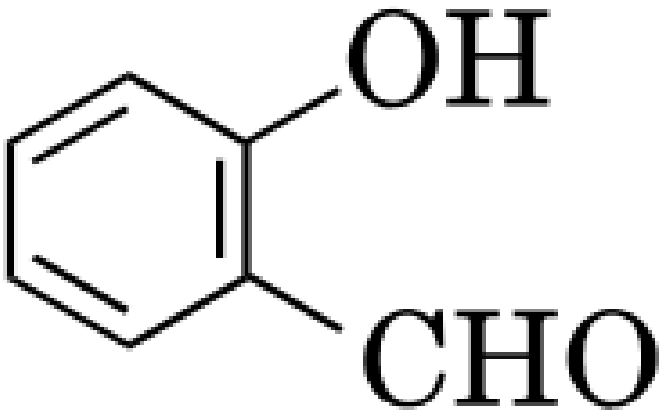
Step 1: Identify the line of contact Along a body diagonal, a corner atom touches the body-centred atom, which in turn touches the opposite corner atom. The distance between each corner centre and the body centre is $2r$, where r is the atomic radius.

Step 2: Equate the geometric and atomic lengths The complete body diagonal therefore spans $r + 2r + r = 4r$. From cube geometry its length is $\sqrt{a^2 + a^2 + a^2} = \sqrt{3}a$. Equating these two expressions gives $4r = \sqrt{3}a$. The edge itself is not the direction of contact in b.c.c.

Step 3: Conclusion $\boxed{r = \frac{\sqrt{3}}{4}a}$, or equivalently $a = \frac{4r}{\sqrt{3}}$.

Quick Tip to Solve: For b.c.c., use the body diagonal: its three-atom contact length is four radii.

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



Solution:

Concept:

- An aldehyde group has naming priority over a phenolic hydroxyl group.
- For a benzaldehyde parent, the ring carbon bonded to the formyl group is numbered 1.

Step 1: Select the parent compound The displayed structure contains a benzene ring bearing a formyl group, $-\mathrm{CHO}$, and a hydroxyl group, $-\mathrm{OH}$. The aldehyde is the principal functional group, so benzaldehyde is the parent name and the hydroxyl group is expressed by the prefix hydroxy.

Step 2: Number the hydroxyl substituent Assign position 1 to the ring carbon attached to the formyl group. The hydroxyl group is attached to the immediately adjacent ring carbon, so its locant is 2.

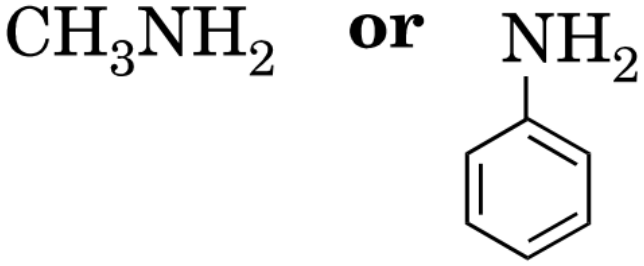
Quick Tip to Solve: Treat the CHO-bearing ring carbon as position 1; an adjacent OH then receives locant 2.

Choosing the numbering direction that gives the lowest locant therefore produces the prefix 2-hydroxy.

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

Quick Tip to Solve: Treat the CHO-bearing ring carbon as position 1; an adjacent OH then receives locant 2.

7. Which of the two is more basic and why? [1 mark]



Solution:

Concept:

- Basicity depends on how readily the nitrogen lone pair can accept a proton, H^+.
- An alkyl group donates electron density by the $+I$ effect, whereas conjugation with a benzene ring delocalises the nitrogen lone pair.

Step 1: Examine methylamine In CH_3NH_2, the methyl group exerts a positive inductive effect and increases electron density on nitrogen. Its lone pair remains localised and is readily available for bonding to a proton.

Step 2: Compare with aniline In $C_6H_5NH_2$, the nitrogen lone pair participates in resonance with the benzene ring. Delocalisation reduces its availability for protonation, so aniline accepts a proton less readily than methylamine.

Step 3: Conclusion $\boxed{CH_3NH_2 \text{ is more basic than } C_6H_5NH_2}$, because its lone pair is more readily available for protonation.

Quick Tip to Solve: Compare lone-pair availability: an alkyl group donates by induction, while a benzene ring delocalises the nitrogen lone pair.

8. Name the two components of α-glucose which constitute starch. [1 mark]

Solution:

Concept:

- Starch is a plant storage polysaccharide built from α-D-glucose units.
- Its two constituent polysaccharides differ mainly in whether their glucose chains are unbranched or branched.

Quick Tip to Solve: Remember amylose as the essentially linear starch component and amylopectin as the branched component.

Step 1: Identify the unbranched component Amylose is the essentially linear component of starch. Its α-D-glucose units are joined through $\alpha(1\rightarrow4)$ glycosidic linkages, and the chain adopts a helical form.

Step 2: Identify the branched component Amylopectin is the branched component. It contains $\alpha(1\rightarrow4)$ linkages along the chains and $\alpha(1\rightarrow6)$ linkages at branch points. Both components are polymers of the glucose units named in the question.

Step 3: Conclusion The two components constituting starch are $\boxed{\text{amylose and amylopectin}}$.

Quick Tip to Solve: Remember amylose as the essentially linear starch component and amylopectin as the branched component.

9. 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 molar mass, Q is charge, n is electrons required per metal ion and F is the Faraday constant.
- The charge passed is $Q = It$, with current I in amperes and time t in seconds.

Step 1: Write the cathode process Nickel nitrate provides Ni^{2+} ions. At the cathode, reduction occurs:

$$Ni^{2+} + 2e^- \longrightarrow Ni(s).$$

Thus one mole of nickel requires two moles of electrons, so $n = 2$. The platinum electrode is inert and does not supply nickel.

Step 2: Calculate the charge and deposited mass Convert the given time before using the current:

$$t = 20 \times 60 = 1200\,\text{s}, \qquad Q = 5.0 \times 1200 = 6000\,\text{C}.$$

Hence

$$m = \frac{58.7 \times 6000}{2 \times 96500}\,\text{g} = 1.82487\,\text{g}.$$

The factor of two in the denominator accounts for the divalent nickel ion; using one electron per ion would double the predicted mass.

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

Quick Tip to Solve: Write the metal-ion reduction first: nickel(II) needs two electrons, and convert minutes to seconds before calculating charge.

10. 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 $t_{1/2}$ is the time required for the concentration of a reactant to decrease to half its initial value.
- Let $[A]_0$ denote initial concentration, $[A]_t$ concentration after time t, and k the rate constant for the stated reaction order.

Step 1: Obtain the zero-order expression For a zero-order reaction the integrated rate law is

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

At the half-life, $[A]_t = [A]_0/2$. Substituting gives

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

Thus zero-order half-life is directly proportional to the initial concentration.

Step 2: Obtain the first-order expression For a first-order reaction,

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

Putting $[A]_t = [A]_0/2$ gives $kt_{1/2} = \ln 2$. Therefore

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

The initial concentration cancels, so the first-order half-life is independent of it.

Step 3: Conclusion Half-life is the time for the reactant concentration to fall to half its initial value. The expressions are (i) zero order: $\boxed{t_{1/2} = [A]_0/(2k)}$; (ii) first order: $\boxed{t_{1/2} = 0.693/k}$.

Quick Tip to Solve: Set the remaining concentration equal to half the initial concentration in the integrated rate law; do not confuse half-life with complete consumption.

11. Write the chemical reactions involved in the extraction of silver from silver ore. [2 marks]

Solution:

Concept:

- Silver is extracted from argentite, Ag_2S, by cyanide leaching followed by displacement with zinc.
- Cyanide forms the soluble dicyanidoargentate(I) complex $[Ag(CN)_2]^-$; zinc reduces complexed silver(I) to silver metal.

Quick Tip to Solve: Use two cyanide ligands per silver(I) ion, and remember that one zinc atom precipitates two silver atoms from the leach solution.

Step 1: Leach the silver ore with cyanide Treat the crushed silver sulphide ore with dilute aqueous sodium cyanide. Silver enters solution as a soluble complex:

$$\mathrm{Ag_2S} + 4\mathrm{NaCN} \rightleftharpoons 2\mathrm{Na[Ag(CN)_2]} + \mathrm{Na_2S}.$$

The reaction expresses complex formation: each silver(I) ion binds two cyanide ions. Formation of the soluble complex separates the silver-bearing species from insoluble material.

Step 2: Recover metallic silver using zinc Add zinc to the cyanide leach solution. Zinc, being more readily oxidised, displaces silver:

$$2\mathrm{Na[Ag(CN)_2]} + \mathrm{Zn} \longrightarrow \mathrm{Na_2[Zn(CN)_4]} + 2\mathrm{Ag}.$$

Here zinc changes from oxidation state zero to $+2$, supplying two electrons, while two silver(I) ions each gain one electron to form silver metal. Both atoms and charge are conserved.

Step 3: Conclusion The extraction involves cyanide leaching of $\mathrm{Ag_2S}$ to form $\mathrm{Na[Ag(CN)_2]}$, followed by zinc displacement to obtain $\boxed{\mathrm{Ag(s)}}$.

Quick Tip to Solve: Use two cyanide ligands per silver(I) ion, and remember that one zinc atom precipitates two silver atoms from the leach solution.

12(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:

- Allotropes are different structural forms of the same element in the same physical state. The two important crystalline forms of sulphur are rhombic sulphur (α-sulphur) and monoclinic sulphur (β-sulphur).
- The transition temperature of these two forms is approximately $370\,\mathrm{K}$; their relative stability reverses across this temperature.

Step 1: Identify the stable room-temperature allotrope At ordinary room temperature, about $298\,\mathrm{K}$, rhombic sulphur is the stable form. Both crystalline allotropes contain puckered $\mathrm{S_8}$ rings, but the rings are packed differently in their crystals. Thus their different stability does not mean that they contain different elements.

Step 2: Describe the change on heating When rhombic sulphur is heated above $370\,\mathrm{K}$, it changes into monoclinic sulphur. Monoclinic sulphur is the stable crystalline form above the transition temperature, up to its melting point. This is an allotropic transformation; the immediate change asked here is not decomposition or a chemical reaction with another substance.

Step 3: Conclusion The allotropes are rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature and changes to monoclinic sulphur on heating above $370\,\mathrm{K}$.

Quick Tip to Solve: Remember the temperature boundary: rhombic below $370\,\mathrm{K}$, monoclinic above it.

OR

12(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 key contact-process equilibrium is $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, an exothermic reaction accompanied by a decrease in gas molecules.
- Successive acid dissociation removes protons from species of increasingly negative charge; removal of the second proton is therefore less favourable.

Step 1: (i) State the contact-process conditions A low temperature and high pressure favour the equilibrium yield of SO_3. In practice, use about $720\,K$ (approximately $450\,^\circ C$), a pressure of about $2\,bar$, a V_2O_5 catalyst and excess oxygen. The moderate temperature provides a useful reaction rate with good conversion. The catalyst speeds attainment of equilibrium without changing its position. Absorb the product in concentrated sulphuric acid to form oleum and then dilute it to obtain sulphuric acid.

Step 2: (ii) Compare the two acid dissociations The first dissociation, $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$, is essentially complete in water. The second, $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$, removes a proton from an already negatively charged ion. The proton is held more strongly by electrostatic attraction, so this step is much less extensive.

Step 3: Conclusion Use the stated contact-process conditions with V_2O_5. Since the second proton must be removed from HSO_4^-, its ionisation is much harder and $K_{a2} \ll K_{a1}$.

Quick Tip to Solve: Distinguish favourable equilibrium conditions from the practical temperature needed for an adequate rate.

13. Complete the following equations:

(i) $2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow$

(ii) $Cr_2O_7^{2-} + 2OH^- \rightarrow$ [2 marks]

Solution:

Concept:

- In acidic medium, permanganate is reduced from Mn(+7) to Mn(+2); sulphide is oxidised from S(−2) to elemental sulphur.
- Addition of alkali converts orange dichromate into yellow chromate. Chromium remains in oxidation state +6, so this second conversion is not a redox reaction.

Step 1: (i) Complete the acidic permanganate reaction The half-reactions are

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Quick Tip to Solve: Check both atoms and total ionic charge; in alkali dichromate changes to chromate without changing chromium oxidation state.

and

$$S^{2-} \rightarrow S + 2e^{-}.$$

Multiply the first by 2 and the second by 5 to cancel ten electrons. The completed equation is

$$\boxed{2MnO_4^- + 5S^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O}.$$

The net charge on each side is $+4$; oxygen and hydrogen also balance.

Step 2: (ii) Complete the dichromate reaction with alkali Hydroxide shifts the dichromate–chromate equilibrium towards chromate. Balancing oxygen and hydrogen gives

$$\boxed{Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O}.$$

There are two chromium atoms, nine oxygen atoms and two hydrogen atoms on each side. The charge is -4 on each side, confirming the coefficients.

Step 3: Conclusion (i) Products: $2Mn^{2+} + 5S + 8H_2O$. (ii) Products: $2CrO_4^{2-} + H_2O$, with the reactant coefficients as printed.

Quick Tip to Solve: Check both atoms and total ionic charge; in alkali dichromate changes to chromate without changing chromium oxidation state.

14. Write the state of hybridization, shape and IUPAC name of the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) [2 marks]

Solution:

Concept:

- Fluoride is a weak-field ligand. In the valence-bond description it does not cause pairing of the $3d$ electrons of cobalt(III).
- Six monodentate ligands give coordination number six. An outer-orbital octahedral complex uses sp^3d^2 hybridisation.

Step 1: Find the oxidation state and electronic configuration If cobalt has oxidation state x, then $x + 6(-1) = -3$, so $x = +3$. Neutral cobalt has configuration $[Ar]\,3d^7 4s^2$; removal of the two $4s$ electrons and one $3d$ electron gives Co^{3+} : $[Ar]\,3d^6$. With weak-field fluoride, this is a high-spin arrangement with four unpaired electrons.

Step 2: Assign hybridisation, shape and the name Because the $3d$ electrons do not pair to leave two vacant inner d orbitals, the complex uses the outer $4d$ orbitals together with $4s$ and $4p$ orbitals. Its hybridisation is therefore sp^3d^2, and the six Co–F bonds have octahedral geometry. Name the six fluoride ligands as hexafluorido; since the coordination entity is an anion, the metal takes the ending cobaltate. The oxidation state is written as (III).

Step 3: Conclusion Hybridisation: $\boxed{sp^3d^2}$; shape: $\boxed{\text{octahedral}}$; IUPAC name: hexafluoridocobaltate(III) ion (traditionally, hexafluorocobaltate(III)).

Quick Tip to Solve: For this weak-field fluoride complex, keep cobalt(III) high spin and use the outer-orbital hybridisation.

15. Write chemical equations when

(i) ethyl chloride is treated with aqueous KOH.

(ii) chlorobenzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$. [2 marks]

Solution:

Concept:

- Aqueous hydroxide ions replace the halogen in a haloalkane by nucleophilic substitution, producing an alcohol.
- Chlorine deactivates the benzene ring but directs electrophilic substitution to the ortho and para positions.

Step 1: (i) Reaction of ethyl chloride In aqueous KOH, hydroxide acts as a nucleophile. It replaces chloride at the saturated carbon atom of ethyl chloride:

$$CH_3CH_2Cl + KOH(aq) \longrightarrow CH_3CH_2OH + KCl.$$

The organic product is ethanol. The aqueous condition favours substitution; alcoholic KOH with heating would favour elimination instead.

Step 2: (ii) Acylation of chlorobenzene Acetyl chloride in the presence of anhydrous aluminium chloride introduces the acetyl group, $-COCH_3$, at positions ortho and para to chlorine:

$$C_6H_5Cl + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} o\text{–}\ ClC_6H_4COCH_3 + HCl,$$

$$C_6H_5Cl + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} p\text{–}\ ClC_6H_4COCH_3 + HCl.$$

These represent the two substitution products of Friedel–Crafts acylation; the para isomer is the major product because it is less sterically hindered.

Step 3: Conclusion The products are (i) ethanol and (ii) ortho- and para-chloroacetophenone, with the para isomer predominant.

Quick Tip to Solve: Identify the solvent first: aqueous KOH gives substitution, whereas acetyl chloride introduces an acetyl group onto the ring.

16. (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 occurs by concerted backside attack, so crowding around the carbon bearing the leaving group lowers its rate.
- An S_N1 reaction proceeds through a trigonal planar, sp^2-hybridised carbocation intermediate.

Step 1: (a) Compare steric hindrance The second compound, $CH_3CH_2CH_2CH_2Br$ (1-bromobutane), reacts faster by the S_N2 mechanism. Its bromine-bearing carbon is primary and is therefore more accessible to backside attack by a nucleophile. The first compound, $CH_3CH_2CH(Br)CH_3$ (2-bromobutane), has a secondary carbon at the reaction centre. Its larger surrounding alkyl groups obstruct the incoming nucleophile. Since both compounds have bromide as the leaving group, their different steric hindrance determines this comparison.

Step 2: (b) Explain racemisation In an S_N1 reaction of an optically active substrate, the leaving group first departs to form a planar carbocation. The nucleophile can attack this intermediate from either face. Attack from one face gives retention of configuration, while attack from the opposite face gives inversion. Thus both enantiomeric products are formed, causing racemisation. Equal attack from the two faces gives an optically inactive racemic mixture.

Step 3: Conclusion (a) 1-Bromobutane reacts faster by S_N2. (b) Attack on either face of the planar carbocation produces both enantiomers.

Quick Tip to Solve: For an SN2 comparison with the same leaving group, inspect the substitution level of the carbon bonded directly to the halogen.

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17. Write the mechanism of the following reaction:

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

[2 marks]

Solution:

Concept:

- The hydroxyl group of an alcohol is a poor leaving group; protonation converts it into water, a good leaving group.
- Ethanol is a primary alcohol. Bromide attacks the primary carbon by an S_N2 displacement of water.

Step 1: Protonate ethanol Hydrogen bromide supplies a proton and bromide ion. A lone pair on the oxygen atom of ethanol accepts the proton, forming the ethyloxonium ion:

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

Quick Tip to Solve: For a primary alcohol, first make water the leaving group, then show bromide attacking as the C–O bond breaks.

The electron pair on oxygen forms the new O–H bond, while the H–Br bond pair goes to bromine. Protonation activates the alcohol because the group that can now leave is neutral water rather than hydroxide ion.

Step 2: Displace water by bromide The bromide ion attacks the carbon bonded to oxygen from the back side. At the same time, the C–O bond breaks and its electron pair goes to oxygen:

$$\mathrm{Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.}$$

This concerted nucleophilic substitution forms bromoethane. A separate ethyl carbocation is not required because it would be very unstable; the primary carbon permits direct attack by bromide.

Step 3: Conclusion Protonation followed by S_N2 displacement converts ethanol into bromoethane, with water as the other product.

Quick Tip to Solve: For a primary alcohol, first make water the leaving group, then show bromide attacking as the C–O bond breaks.

18. Name the reagents used in the following reactions:

(i) Bromination of phenol to 2,4,6-tribromophenol

(ii) Butan-2-one to Butan-2-ol

(iii) Friedel–Crafts alkylation of anisole

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

Solution:

Concept:

- Choose a reagent according to the functional-group change: electrophilic bromination, carbonyl reduction, aromatic alkylation or complete oxidation.
- Primary alcohols require sufficiently strong oxidation conditions to proceed beyond the aldehyde to the carboxylic acid.

Step 1: (i) Bromination of phenol Use bromine water, $\mathrm{Br_2(aq)}$, at room temperature. The strongly activating hydroxyl group causes substitution at both ortho positions and the para position, giving a white precipitate of 2,4,6-tribromophenol. A Lewis-acid catalyst is unnecessary.

Step 2: (ii) Reduction of butan-2-one Use sodium borohydride, $\mathrm{NaBH_4}$, followed by hydrolysis. It reduces the ketone carbonyl group to a secondary alcohol, giving butan-2-ol. Lithium aluminium hydride followed by hydrolysis is also suitable.

Step 3: (iii) Alkylation of anisole Use an alkyl halide such as methyl chloride, $\mathrm{CH_3Cl}$, in the presence of anhydrous $\mathrm{AlCl_3}$. These are Friedel–Crafts alkylation conditions; anisole gives ortho- and para-alkylated products.

Step 4: (iv) Oxidation to a carboxylic acid Use acidified potassium dichromate, $\mathrm{K_2Cr_2O_7/H_2SO_4}$, with heating under reflux and sufficient oxidant. These conditions oxidise the primary alcohol through the aldehyde to the carboxylic acid. Acidified potassium permanganate is another suitable strong oxidant.

Quick Tip to Solve: For complete oxidation of a primary alcohol, choose excess strong oxidant and reflux so that oxidation continues past the aldehyde.

Step 5: Conclusion (i) Bromine water; (ii) $NaBH_4$, then hydrolysis; (iii) CH_3Cl/anhydrous $AlCl_3$; (iv) acidified $K_2Cr_2O_7$, heat under reflux.

Quick Tip to Solve: For complete oxidation of a primary alcohol, choose excess strong oxidant and reflux so that oxidation continues past the aldehyde.

19. (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:

- Stoichiometric defects preserve the cation-to-anion ratio and electrical neutrality of an ionic crystal.
- Doping introduces charge carriers; magnetic behaviour depends on the relative alignment of magnetic moments.

Step 1: (i) Identify the defect in KCl KCl shows a Schottky defect. Equal numbers of K^+ and Cl^- ions are missing from their normal lattice sites. This is favoured because the cation and anion have comparable sizes and the crystal has a high coordination number. Losing ions in equal numbers preserves both the 1:1 composition and electrical neutrality, although the density decreases.

Step 2: (ii) Determine the semiconductor produced by As Silicon has four valence electrons, whereas arsenic has five. Four electrons of each substituted As atom form covalent bonds with neighbouring Si atoms. The fifth electron is available for conduction. Thus As acts as a donor and produces an n-type semiconductor, with electrons as the majority carriers.

Step 3: (iii) Distinguish molecular and network solids Solid CO_2 is a molecular solid: discrete carbon dioxide molecules are held together by intermolecular forces. In contrast, SiO_2 forms an extended covalent network, rather than a lattice of separate molecules.

Step 4: (iv) Compare magnetic ordering Ferromagnetic substances make better magnets. Their magnetic moments align parallel in domains, producing a large resultant magnetisation. Ferrimagnetic substances have oppositely aligned unequal moments, so partial cancellation reduces the resultant magnetic moment compared with parallel alignment.

Step 5: Conclusion (i) Schottky defect; (ii) n-type semiconductor; (iii) CO_2; (iv) ferromagnetic substances.

Quick Tip to Solve: Count the dopant's valence electrons: five in As supplies an extra electron to four-valent Si.

20. (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 reactants directly into electrical energy.
- The standard cell potential is related to the equilibrium constant by $E^\circ_{cell} = (2.303RT/nF)\log K$, where n is the number of transferred electrons.

Step 1: (i) State two advantages of the hydrogen-oxygen fuel cell First, it can operate continuously as long as hydrogen and oxygen are supplied; unlike an ordinary cell with a fixed internal supply of reactants, it need not stop when that initial supply is exhausted. Second, its reaction product is water, so its operation does not generate polluting combustion products or spent electrode materials as ordinary cells can. The overall cell reaction is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l).$$

Step 2: (ii) Determine the electron transfer number In the printed reaction, A is oxidised from oxidation state zero to $+2$, while B^{2+} is reduced to B. The half-reactions are

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

Hence $n = 2$, irrespective of the identities of A and B.

Step 3: Calculate the standard cell potential Using the standard room-temperature relation at $298\,K$,

$$\begin{aligned} E^\circ_{cell} &= \frac{0.0591}{n}\log K_c \\ &= \frac{0.0591}{2}\log 10 \\ &= 0.02955\,V. \end{aligned}$$

Here $\log 10 = 1$. The positive value agrees with $K_c > 1$, meaning that products are favoured for the reaction as written under standard conditions.

Step 4: Conclusion The fuel cell permits continuous operation and produces water with minimal pollution. At $298\,K$, $\boxed{E^\circ_{cell} \approx 0.0296\,V}$.

Quick Tip to Solve: Find n from the oxidation-state change before substituting K; here A loses two electrons, so divide by 2.

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

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

Calculate the rate constant.

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

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0·4
2	100	0·7

Solution:

Concept:

- For a first-order reaction, $k = (2.303/t)\log(p_0/p_A)$, where p_A is the remaining reactant's partial pressure at time t.
- At constant volume and temperature, gas pressure is proportional to the number of moles. For one gaseous reactant forming two gaseous products, $p_A = 2p_0 - P_t$.

Step 1: Express the pressures using the reaction stoichiometry Initially only SO_2Cl_2 is present, with pressure $p_0 = 0.4$ atm. Let x atm be the pressure equivalent of the amount decomposed after 100 s. For

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g),$$

the partial pressures become $p_0 - x$, x and x, respectively. Their sum is $P_t = p_0 + x$, because each mole decomposed increases the total amount of gas by one mole.

Step 2: Calculate the remaining reactant's partial pressure The measured total pressure is 0.7 atm, so

$$x = P_t - p_0 = 0.7 - 0.4 = 0.3\,\text{atm}.$$

Thus

$$p_{SO_2Cl_2} = p_0 - x = 0.4 - 0.3 = 0.1\,\text{atm}.$$

Equivalently, $p_{SO_2Cl_2} = 2p_0 - P_t = 0.8 - 0.7$. The total pressure cannot itself be used as the reactant pressure, since it includes both products.

Step 3: Apply the first-order integrated rate law At the same volume and temperature the concentra-

Quick Tip to Solve: For SO2Cl2 decomposing into two gases, first calculate the remaining reactant pressure as twice the initial pressure minus the total pressure.

tion ratio equals the reactant partial-pressure ratio. Hence

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

The ratio inside the logarithm is dimensionless, and the inverse-time unit follows from dividing by the elapsed time.

Step 4: Conclusion The rate constant is $\boxed{k = 1.39 \times 10^{-2}\,\text{s}^{-1}}$.

Quick Tip to Solve: For SO2Cl2 decomposing into two gases, first calculate the remaining reactant pressure as twice the initial pressure minus the total pressure.

22. (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:

- Adsorption is accumulation of a gas at a solid surface. The Freundlich isotherm relates the mass adsorbed per unit mass of adsorbent to gas pressure at a fixed temperature.
- A colloid has a dispersed phase distributed in a continuous dispersion medium. Electrolytes can coagulate a charged colloid by neutralising its charge.

Step 1: (a) Freundlich adsorption isotherm At a fixed temperature, the empirical relation for adsorption of a gas on a solid is

$$\frac{x}{m} = kp^{1/n},$$

where x is the mass of gas adsorbed, m is the mass of solid adsorbent, p is the equilibrium pressure of the gas, and k and n are constants for the particular gas and adsorbent at that temperature. Usually $0 < 1/n < 1$. Equivalently, $\log(x/m) = \log k + (1/n)\log p$. This relation describes adsorption over a limited pressure range.

Step 2: (b) Phases present in butter Butter is a water-in-oil emulsion: fine droplets of water are distributed through a continuous fat or oil phase. Hence its dispersed phase is water (liquid), while its dispersion medium is fat or oil, which is semisolid in butter. Classifying the emulsion by its continuous phase avoids confusing butter with an oil-in-water emulsion such as milk.

Step 3: (c) Formation of a delta River water carries fine, negatively charged clay particles as a colloidal dispersion. Sea water contains dissolved electrolytes. Their positively charged ions neutralise the charge on the clay particles, decreasing the electrostatic repulsion that keeps the particles dispersed.

Quick Tip to Solve: Identify an emulsion by the continuous phase: butter has continuous fat, so it is water-in-oil.

The particles consequently coagulate into larger aggregates and settle at the river mouth. Continued deposition of this coagulated material forms a delta.

Step 4: Conclusion (a) $x/m = kp^{1/n}$. (b) Dispersed phase: water; dispersion medium: fat or oil. (c) Sea-water electrolytes coagulate colloidal clay, causing deposition at the river mouth.

Quick Tip to Solve: Identify an emulsion by the continuous phase: butter has continuous fat, so it is water-in-oil.

23(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:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its commonly formed oxidation states.
- The similar energies of ns and $(n-1)d$ electrons allow several oxidation states; unpaired d electrons cause paramagnetism.

Step 1: (a) Oxidation states of lanthanoids The characteristic and most common oxidation state of lanthanoids is $+3$. Some members also exhibit $+2$ and $+4$, when these states gain additional stability from empty, half-filled or fully filled $4f$ subshells. For example, Eu^{2+} has $4f^7$, Yb^{2+} has $4f^{14}$, and Ce^{4+} has $4f^0$. Thus the expected oxidation states are $+2, +3, +4$, with $+3$ predominant across the series.

Step 2: (b) Two characteristics of transition elements First, transition elements generally exhibit variable oxidation states because both the outer ns and inner $(n-1)d$ electrons can participate in bonding; iron, for example, forms Fe^{2+} and Fe^{3+}. Second, many of their atoms and ions are paramagnetic because their partially filled d subshells contain unpaired electrons. The magnitude of the magnetic moment depends on the number of unpaired electrons. These are general characteristics, so they need not occur in every ion of every transition element.

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

Step 4: Conclusion (a) $+2, +3, +4$, chiefly $+3$. (b) Variable oxidation states and paramagnetic behaviour. (c) Zn, because both Zn and Zn^{2+} have completely filled $3d^{10}$ subshells.

Quick Tip to Solve: Test both the neutral atom and its common ions for a partly filled d subshell; a d-zero ion alone does not exclude Sc.

OR

23(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:

- Half-filled d^5 configurations have additional stability associated with exchange energy and symmetrical occupation of the five orbitals.
- Atomization enthalpy measures the energy needed to separate a metal into gaseous atoms. Colour in aqueous transition-metal ions commonly arises from d-d transitions between ligand-field-split levels.

Step 1: (a) Resistance of manganese(II) to oxidation For manganese, Mn^{2+} has configuration $[Ar]3d^5$, while Mn^{3+} is $[Ar]3d^4$. Oxidation of Mn^{2+} removes an electron from the particularly stable half-filled d^5 subshell. In contrast, Fe^{2+} is $[Ar]3d^6$, and oxidation produces Fe^{3+}, which is $[Ar]3d^5$. Thus oxidation of iron(II) attains the stable half-filled configuration, whereas oxidation of manganese(II) destroys it. This explains the greater resistance of manganese(II) compounds to oxidation to the +3 state.

Step 2: (b) Low atomization enthalpy of zinc Zinc has configuration $[Ar]3d^{10}4s^2$. Its completely filled $3d$ subshell has no unpaired electrons available to strengthen metallic bonding. Relative to the other 3d-series metals, whose partly filled d subshells contribute more strongly to interatomic bonding, metallic bonding in zinc is weak. Therefore less energy is required to separate the solid into individual gaseous atoms, and zinc has the lowest enthalpy of atomization in this series. A filled subshell does not mean that zinc has no metallic bonding; it explains its comparatively weak bonding.

Step 3: (c) Colour of the aqueous ions Sc^{3+} has configuration $[Ar]3d^0$. It has no d electron that can undergo a transition between the split d levels in an aqueous complex, so it is colourless. Ti^{3+}, however, has configuration $[Ar]3d^1$. Water ligands split the d orbitals into different energy levels; absorption of visible light promotes its electron from a lower to a higher level. This d-d absorption makes the solution appear coloured.

Step 4: Conclusion (a) Mn^{2+} retains stable d^5, whereas oxidation of Fe^{2+} yields stable d^5. (b) Zn has weak metallic bonding owing to its filled $3d^{10}$ subshell. (c) Sc^{3+} is d^0; Ti^{3+} is d^1 and permits visible-light d-d absorption.

Quick Tip to Solve: Write each ionic d configuration first: Mn(II) d5, Fe(II) d6, Sc(III) d0 and Ti(III) d1.

24. 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:

- Potassium cyanide substitutes a halogen by $-C \equiv N$; its carbon enters the product chain. Reduction of a nitrile converts $-C \equiv N$ to $-CH_2NH_2$.
- A primary aliphatic amine reacts with nitrous acid to give an alcohol. Hofmann bromamide degradation converts an amide into a primary amine with one carbon fewer; the carbylamine reaction converts a primary amine into an isocyanide.

Step 1: (i) Identify the nitrile and its reduction product Cyanide attacks through carbon, giving ethanenitrile:

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

Thus A is $CH_3C \equiv N$. Reduction with lithium aluminium hydride gives:

$$CH_3C \equiv N + 4[H] \longrightarrow CH_3CH_2NH_2.$$

Hence B is ethanamine, $CH_3CH_2NH_2$.

Step 2: (i) React ethanamine with nitrous acid The unstable aliphatic diazonium intermediate loses nitrogen and gives ethanol:

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

Therefore C in the first sequence is CH_3CH_2OH.

Step 3: (ii) Identify the three products Heating ammonium ethanoate, formed from the acid and ammonia, gives ethanamide:

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

Thus A is $CH_3C(=O)NH_2$. Bromine and potassium hydroxide cause Hofmann degradation:

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

Hence B is methylamine, CH_3NH_2. Its reaction with chloroform and sodium hydroxide gives methyl isocyanide:

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

The methyl group is bonded to nitrogen.

Step 4: Conclusion (i) A: $CH_3C \equiv N$, B: $CH_3CH_2NH_2$, C: CH_3CH_2OH.
(ii) A: $CH_3C(=O)NH_2$, B: CH_3NH_2, C: $CH_3N \equiv C$.

Quick Tip to Solve: KCN adds a carbon; Hofmann degradation removes the carbonyl carbon. The isocyanide has an R–N bond.

25. Define the following terms:

(a) Anomers

(b) Denaturation of proteins

(c) Essential amino acids [3 marks]

Solution:

Concept:

- Ring formation in a monosaccharide produces an anomeric carbon, derived from the carbonyl carbon of its open-chain form.
- Protein function depends on its native three-dimensional structure. Human nutrition must supply amino acids that the body cannot synthesise adequately.

Step 1: (a) Define anomers Anomers are cyclic stereoisomers of a carbohydrate that differ in configuration only at the anomeric carbon. This carbon is the former carbonyl carbon: C-1 in glucose, an aldose, and C-2 in fructose, a ketose. For example, α-D-glucopyranose and β-D-glucopyranose differ in the orientation of the hydroxyl group at C-1; the configurations of the other stereocentres remain unchanged. Thus the term is more specific than simply calling two sugars stereoisomers.

Step 2: (b) Define denaturation of proteins Denaturation is the loss of the native spatial structure and biological activity of a protein under physical or chemical influences, such as heating or a change in pH. The interactions maintaining its secondary and tertiary structures are disrupted, while its primary structure, the amino-acid sequence linked by peptide bonds, remains intact. Coagulation of egg white on boiling is an example. Denaturation is therefore different from hydrolysis, which breaks peptide bonds.

Step 3: (c) Define essential amino acids Essential amino acids are amino acids that the human body cannot synthesise, or cannot synthesise in sufficient amounts to meet its requirements, and must therefore obtain through the diet. Valine, leucine and lysine are examples. The word essential refers to their dietary requirement; it does not imply that the amino acids the body can synthesise are unimportant for protein formation.

Step 4: Conclusion Anomers differ only at the anomeric carbon; denaturation destroys native protein structure and activity without changing the primary sequence; essential amino acids must be supplied by the diet.

Quick Tip to Solve: Associate each definition with its deciding feature: anomeric carbon, loss of native folding, and dietary supply, respectively.

26. (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:

- Drugs are classified by their biological action. Histamine mediates allergic responses, while antibiotics act against susceptible microorganisms.
- An artificial sweetener must remain chemically stable under the conditions in which food is prepared and served; heating can destroy a heat-sensitive sweetener.

Step 1: (i) Define an antihistamine and give an example Antihistamines are drugs that oppose the action of histamine by blocking its receptors. In the treatment of allergies they prevent histamine from producing effects such as sneezing, itching and a running nose. They do not act by removing an infectious organism; their role is to reduce histamine-mediated symptoms. Brompheniramine is an example of an antihistamine used for allergic conditions.

Step 2: (ii) Identify the antibiotic Chloramphenicol is the antibiotic among the four listed drugs. It inhibits bacterial protein synthesis and therefore acts against susceptible bacteria. The alternatives belong to other classes: morphine is a narcotic analgesic, Equanil is a tranquilliser, and aspirin is a non-narcotic analgesic with antipyretic action. Their principal uses do not make them antibiotics. Thus classification by therapeutic action selects chloramphenicol uniquely.

Step 3: (iii) Explain the temperature restriction for aspartame Aspartame is an artificial sweetener based on the methyl ester of the dipeptide formed from aspartic acid and phenylalanine. It is unstable at cooking temperatures and decomposes on heating, so the original sweetening compound is no longer retained effectively. Its sweetness is consequently lost or reduced. It is therefore used in cold foods and drinks, for which heating-induced decomposition is avoided, rather than as a sweetener for cooking.

Step 4: Conclusion (i) An antihistamine blocks histamine action; brompheniramine is an example. (ii) Chloramphenicol is the antibiotic. (iii) Aspartame decomposes on heating and loses its sweetening effectiveness.

Quick Tip to Solve: Separate the three ideas: antihistamine blocks histamine, chloramphenicol is antibacterial, and aspartame requires low-temperature use because it is heat-sensitive.

27. 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:

- Biodegradable polymers undergo breakdown by biological agents such as microorganisms and their enzymes, forming simpler substances.
- A homopolymer is formed from a single type of monomer; a copolymer is formed from two or more different monomers.

Step 1: Identify the values shown by the students The students show environmental awareness, social responsibility, cooperation and concern for public welfare. Their rally spreads awareness of the harm caused by discarded plastic bags, while distributing paper bags provides a practical alternative. Joining hands with other schools demonstrates teamwork, and their pledge shows commitment to protecting the Yamuna river.

Step 2: Define biodegradable polymers and give an example Biodegradable polymers are polymers that can be decomposed by microorganisms or enzymes into simpler, environmentally compatible products. One example is poly(beta-hydroxybutyrate-co-beta-hydroxyvalerate), abbreviated PHBV. Its biodegradable nature distinguishes it from persistent conventional plastic waste.

Step 3: Classify polythene Polythene is a homopolymer because it is produced by addition polymerisation of only one monomer, ethene:

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

The repeated units all originate from ethene; no second monomer is required. Thus the fact that polythene is non-biodegradable does not make it a copolymer: classification by monomer composition and classification by biodegradability are different.

Step 4: Conclusion (i) Environmental awareness, responsibility and cooperation. (ii) Polymers decomposed by biological agents; example: PHBV. (iii) Polythene is a homopolymer.

Quick Tip to Solve: Classify a polymer by counting the different monomers used, not by whether it degrades in the environment.

28(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 the partial vapour pressure of each volatile component to its mole fraction in the liquid solution at the same temperature.
- For component i, $p_i = x_i p_i^0$, where p_i^0 is its pure-liquid vapour pressure.

Step 1: State the law for each volatile component 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 at the same temperature. For a binary solution,

$$p_A = x_A p_A^0, \qquad p_B = x_B p_B^0.$$

Here $x_A + x_B = 1$; the pressures p_A^0 and p_B^0 must refer to the temperature of the solution.

Step 2: Identify the solution obeying the law A solution obeying Raoult's law over the entire concentration range at all temperatures is called an ideal solution. For such a binary solution the total vapour pressure is

$$p_{\text{total}} = x_A p_A^0 + x_B p_B^0.$$

The defining condition applies separately to each volatile component, not merely to the total pressure.

Step 3: Conclusion Raoult's law is $p_i = x_i p_i^0$. A solution obeying it at all concentrations and temperatures is an ideal solution.

Quick Tip to Solve: Write a separate partial-pressure equation for each volatile component before adding the pressures.

28(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 $\Delta T_b = iK_b m$, where m is molality and i is the van't Hoff factor accounting for solute particles.
- For complete dissociation, $CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$, so one formula unit gives three ions and $i = 3$.

Step 1: Account for the electrolyte particles Calcium chloride is a strong electrolyte. Taking its dissociation in water as complete, as required when no degree of dissociation is supplied,

$$CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq).$$

There are three moles of ions per mole of dissolved calcium chloride, giving $i = 3$. Using $i = 1$ would ignore the increase in particle number caused by dissociation.

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

Step 2: Calculate the molality The amount of calcium chloride is

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

The solvent mass is $200\,\text{g} = 0.200\,\text{kg}$, hence

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

Molality uses the mass of water, not the total mass of the solution.

Step 3: Obtain the boiling point elevation Substitute the molality and van't Hoff factor:

$$\begin{aligned}\Delta T_b &= 3 \times 0.512 \times 0.45045\,\text{K} \\ &= 0.69189\,\text{K} \approx 0.692\,\text{K}.\end{aligned}$$

The positive sign means that the solution boils at a higher temperature than pure water. A temperature interval in kelvin has the same numerical value as an interval in degrees Celsius.

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

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

OR

28(a). Define the following terms:

(i) Azeotrope

(ii) Osmotic pressure

(iii) Colligative properties [3 marks]

Solution:

Concept:

- An azeotrope concerns the liquid-vapour equilibrium of a mixture; osmotic pressure concerns solvent flow through a semipermeable membrane.
- Colligative properties depend on the number of dissolved solute particles relative to solvent particles, rather than the chemical identity of the solute.

Step 1: (i) 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. On boiling, the two components therefore distil together without a change in their relative proportions. Consequently, its components cannot be separated by fractional distillation. Such mixtures arise from sufficiently large positive or negative deviations from Raoult's law.

Step 2: (ii) Osmotic pressure Osmotic pressure, π, is the minimum excess pressure that must be applied on the solution side to prevent the net flow of solvent into it through a semipermeable

Quick Tip to Solve: For an azeotrope state both constant boiling and equal liquid-vapour compositions; for osmotic pressure specify pressure on the solution side.

membrane. The membrane permits solvent molecules to pass but not solute particles. For a dilute solution, $\pi = CRT$, where C is its molar concentration, R is the gas constant and T is the absolute temperature.

Step 3: (iii) Colligative properties Colligative properties are properties of dilute solutions which depend on the number of solute particles present relative to the number of solvent particles, and not on the nature of the solute. They are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. Dissociation or association changes these properties because it changes the particle count.

Step 4: Conclusion An azeotrope is a constant-boiling mixture with identical liquid and vapour compositions; osmotic pressure stops osmosis; colligative properties depend on the relative number of solute particles.

Quick Tip to Solve: For an azeotrope state both constant boiling and equal liquid-vapour compositions; for osmotic pressure specify pressure on the solution side.

28(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 means $9.8\,\text{g}$ of solute per $100\,\text{g}$ of solution, not per $100\,\text{mL}$.
- Molarity is $M = n/V$, where n is the number of moles of solute and V is the solution volume in litres. Density converts solution mass into solution volume.

Step 1: Choose a convenient mass and calculate moles Take $100\,\text{g}$ of the solution. Since its concentration is 9.8% by mass, the mass of dissolved sulphuric acid is $9.8\,\text{g}$. Using its given molar mass,

$$n(\text{H}_2\text{SO}_4) = \frac{9.8\,\text{g}}{98\,\text{g mol}^{-1}} = 0.100\,\text{mol}.$$

The remaining mass is solvent; it is the total solution mass that must be used with the given density.

Step 2: Convert the solution mass to volume and calculate molarity With density $\rho = 1.02\,\text{g mL}^{-1}$, the volume of this solution is

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

Hence

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

Molarity counts moles of the acid formula units; its ionisation does not multiply the analytical molarity.

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

Quick Tip to Solve: For mass percent w and density d in g per mL, use M = 10dw divided by the molar mass; always check that the volume is in litres.

29(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 increasingly stabilises the lower oxidation state down group 15; for bismuth the $+3$ state is more stable than $+5$.
- Nitrogen obeys the octet restriction, whereas phosphorus can form a hypervalent pentachloride. A non-oxidising acid supplies hydrogen ions but does not oxidise iron to its higher oxidation state.

Step 1: (i) Strong oxidising action of bismuth(V) Bismuth is a heavy group 15 element. Its $6s^2$ electron pair has a strong tendency to remain non-bonding, which is called the inert-pair effect. Thus the $+3$ oxidation state is more stable than the $+5$ state. Bismuth(V) readily gains two electrons to form bismuth(III):

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

By accepting electrons it oxidises another substance, so bismuth in the $+5$ state acts as a strong oxidising agent.

Step 2: (ii) Existence of phosphorus pentachloride Phosphorus can accommodate more than eight electrons in its valence shell and form five bonds to chlorine in $\mathrm{PCl_5}$. In the usual school description it has available vacant $3d$ orbitals for expansion of its octet. Nitrogen is a second-period element with only $2s$ and $2p$ valence orbitals and no $2d$ orbitals. It cannot accommodate ten valence-shell electrons in five ordinary covalent bonds; hence $\mathrm{NCl_5}$ is not known.

Step 3: (iii) Formation of iron(II) chloride with hydrochloric acid Hydrochloric acid is a non-oxidising acid. Iron displaces hydrogen from it and forms the stable iron(II) salt under these conditions:

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

The acid does not provide an oxidising agent capable of converting the resulting $\mathrm{Fe^{2+}}$ to $\mathrm{Fe^{3+}}$. Furthermore, any iron(III) ions in contact with excess iron would be reduced:

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

Thus the chloride obtained is $\mathrm{FeCl_2}$, rather than $\mathrm{FeCl_3}$.

Step 4: Conclusion The reasons are: greater stability of Bi(III) due to the inert-pair effect; the octet restriction on nitrogen; and the non-oxidising nature of HCl, which gives iron(II) chloride.

Quick Tip to Solve: Link oxidising strength to reduction into the more stable state, and distinguish the non-oxidising acid HCl from oxidising acids.

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

(i) $XeOF_4$

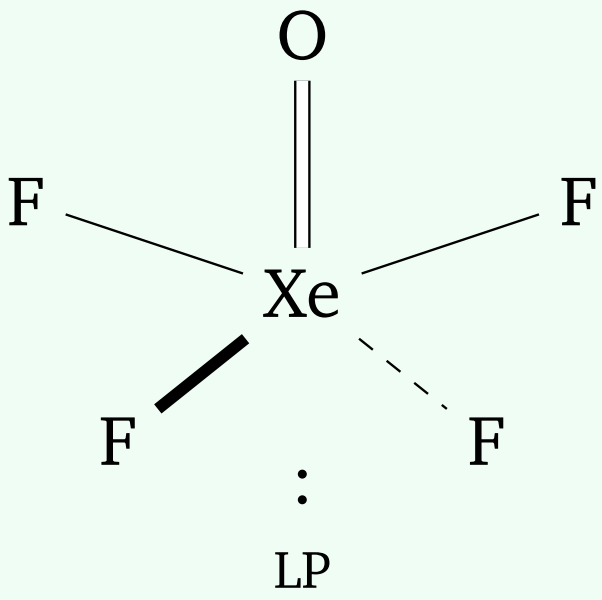
(ii) $HClO_4$ [2 marks]

Solution:

Concept:

- VSEPR theory counts a multiple bond as one electron domain. In $XeOF_4$, xenon has five bonding domains and one lone pair: an octahedral electron-pair arrangement gives a square-pyramidal molecular shape.
- In $HClO_4$, chlorine is bonded to four oxygen atoms in a tetrahedral arrangement. The hydrogen atom belongs to an $O-H$ group, not a direct chlorine-hydrogen bond.

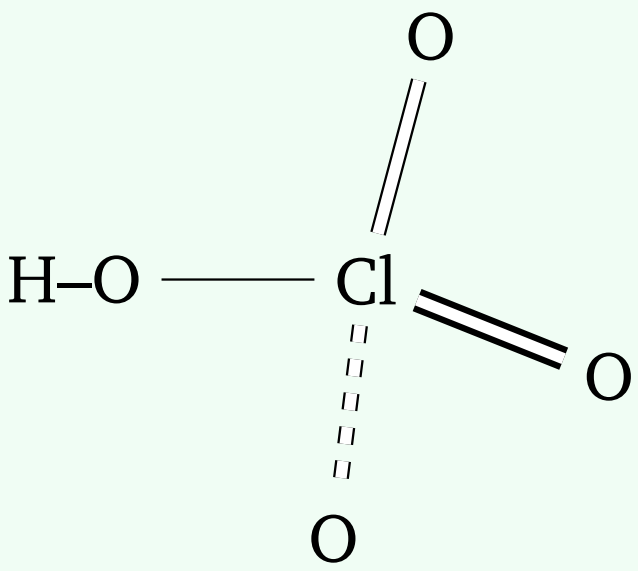
Step 1: (i) Structure of xenon oxytetrafluoride The xenon atom forms four $Xe-F$ single bonds and one $Xe=O$ double bond. Its remaining lone pair occupies the sixth octahedral position, opposite oxygen. Thus the four fluorine atoms form a square base, xenon lies at its centre, and oxygen occupies the axial position above it. The lone pair is shown below xenon; it is not an additional atom.



Square-pyramidal XeOF4; LP is opposite the axial oxygen.

Step 2: (ii) Structure of perchloric acid The conventional structure is $HO-Cl(=O)_3$: three oxygen atoms have double bonds to chlorine and the fourth is the hydroxyl oxygen. Four bonding directions around chlorine give tetrahedral geometry. The drawing shows connectivity with a bold bond and a dashed bond to indicate the three-dimensional arrangement; the two-dimensional bond angles are only a projection.

Quick Tip to Solve: Count the lone pair on Xe separately; in perchloric acid attach H to O.



Tetrahedral arrangement around chlorine in HClO4.

Step 3: Conclusion $XeOF_4$ is square pyramidal; $HClO_4$ has the tetrahedral structure $HO-Cl(=O)_3$.

Quick Tip to Solve: Count the lone pair on Xe separately; in perchloric acid attach H to O.

OR

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

(i) $H_2S_2O_8$

(ii) Red P_4 [2 marks]

Solution:

Concept:

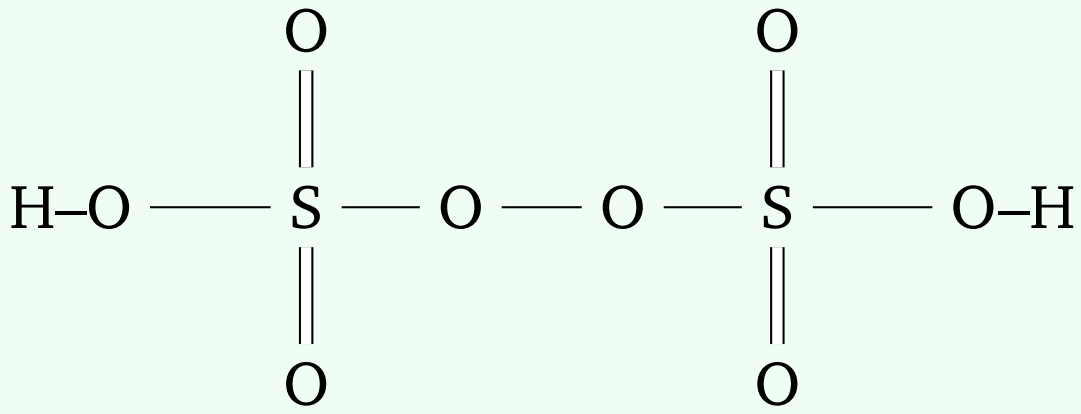
- Peroxodisulphuric acid, $H_2S_2O_8$, contains a peroxide linkage $-O-O-$ between two sulphur-containing groups.
- Red phosphorus has an extended polymeric structure. A standard structural representation links opened P_4 tetrahedral units through additional $P-P$ bonds; each phosphorus is bonded to three other phosphorus atoms.

Step 1: (i) Structure of peroxodisulphuric acid Join two $HO-S(=O)_2-$ groups through an $O-O$ single bond. The resulting connectivity is

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

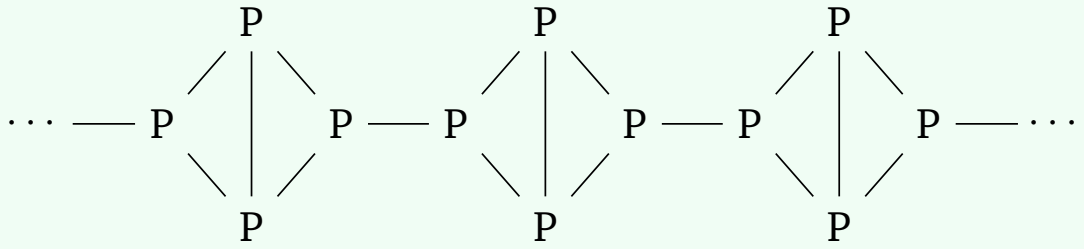
Each sulphur has two terminal double-bonded oxygens, one hydroxyl oxygen and one bridging peroxide oxygen. This accounts for both hydrogen atoms, both sulphur atoms and all eight oxygen atoms. The peroxide bond must not be replaced by an $S-O-S$ bridge.

Quick Tip to Solve: Preserve the O-O bond in H2S2O8; show linked opened units for red phosphorus.



Peroxodisulphuric acid with its central O-O linkage.

Step 2: (ii) Structure of red phosphorus The figure represents the extended network using linked opened tetrahedra. For each four-phosphorus unit, five internal $P-P$ bonds remain; the two terminal phosphorus atoms connect to neighbouring units. Every phosphorus therefore has three covalent bonds and a lone pair. The bonds crossing in this projection do not indicate an extra atom. The dots at the ends indicate continuation of the polymer. Red phosphorus is not made of discrete closed P_4 molecules, which characterize white phosphorus.



Polymeric representation of red phosphorus: linked opened P4 units.

Step 3: Conclusion The acid contains a central peroxide linkage, and red phosphorus has the polymeric structure shown.

Quick Tip to Solve: Preserve the O-O bond in H2S2O8; show linked opened units for red phosphorus.

29(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 molecule with all electrons paired is diamagnetic.
- Formation of noble-gas compounds depends on the energy required to remove or involve valence

Quick Tip to Solve: For phosphorus oxoacids, count direct P-H bonds for reduction and O-H bonds for basicity.

electrons.

- The reducing behaviour of phosphorus oxoacids is associated with their direct $P-H$ bonds.

Step 1: Explain sulphur vapour At high temperature, 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 a net magnetic moment, so the vapour is attracted by a magnetic field and exhibits paramagnetism.

Step 2: Compare helium and xenon Helium has the compact, completely filled $1s^2$ shell, extremely high ionisation enthalpy and very low polarizability. Its electrons are held too strongly for ordinary chemical compound formation. Xenon is much larger and has a substantially lower ionisation enthalpy; highly electronegative fluorine and oxygen can therefore form compounds with it. Thus no distinct ordinary chemical compound of helium is known, unlike xenon.

Step 3: Compare the phosphorus oxoacids The structures may be written as $HOP(O)H_2$ for H_3PO_2 and $(HO)_2P(O)H$ for H_3PO_3, where $P(O)$ denotes $P=O$. Hypophosphorous acid has two direct $P-H$ bonds whereas phosphorous acid has only one. Since reducing character is associated with these bonds, H_3PO_2 is the stronger reducing agent; the number of ionisable $O-H$ hydrogens does not determine this trend.

Step 4: Conclusion Sulphur vapour is paramagnetic because S_2 has unpaired electrons; helium resists compound formation because of its exceptionally stable shell; H_3PO_2 is more reducing because it has two $P-H$ bonds.

Quick Tip to Solve: For phosphorus oxoacids, count direct P-H bonds for reduction and O-H bonds for basicity.

30(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 hydrolysis converts the alkoxide into an alcohol.
- Clemmensen reduction converts an aldehyde or ketone carbonyl group into a methylene group.
- In crossed aldol condensation, ethanal supplies the enolate while benzaldehyde, which has no alpha hydrogen, serves as the electrophile.

Step 1: Reaction with methylmagnesium bromide The methyl group adds to the carbonyl carbon of ethanal in dry ether, producing a magnesium alkoxide. Subsequent acidic hydrolysis protonates the oxygen.

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

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

Quick Tip to Solve: For the crossed aldol product, retain the ethanal CHO end and place the benzaldehyde phenyl group at the other end.

The organic product is propan-2-ol, a secondary alcohol containing one more carbon atom than ethanal.

Step 2: Reduction with zinc amalgam and hydrochloric acid Zinc amalgam with concentrated hydrochloric acid gives Clemmensen reduction. The aldehyde group is reduced to a terminal methyl group without changing the carbon skeleton:

$$CH_3CHO + 4[H] \xrightarrow{\text{Zn(Hg)/conc. HCl}} CH_3CH_3 + H_2O.$$

The product is ethane; stopping at ethanol would correspond to a different type of carbonyl reduction.

Step 3: Crossed aldol reaction with benzaldehyde Dilute sodium hydroxide removes an alpha hydrogen from ethanal. Its enolate attacks benzaldehyde, giving the crossed aldol addition product, 3-hydroxy-3-phenylpropanal:

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

This beta-hydroxy aldehyde readily loses water to form the conjugated condensation product cinnamaldehyde, or 3-phenylprop-2-enal:

$$C_6H_5CH(OH)CH_2CHO \longrightarrow C_6H_5CH = CHCHO + H_2O.$$

Thus cinnamaldehyde is the customary final product reported for this crossed aldol condensation; the preceding equation identifies the addition intermediate.

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

Quick Tip to Solve: For the crossed aldol product, retain the ethanal CHO end and place the benzaldehyde phenyl group at the other end.

30(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; ordinary esters do not.
- Tollens reagent oxidises aliphatic aldehydes while depositing metallic silver; simple ketones give no silver mirror.

Step 1: Benzoic acid and ethyl benzoate Add aqueous sodium hydrogen carbonate to separate samples at room temperature. Benzoic acid produces brisk effervescence of carbon dioxide, while

Quick Tip to Solve: Choose a test with opposite observations: gas for the acid/ester pair and silver for the aldehyde/ketone pair.

ethyl benzoate gives no effervescence under these conditions:

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

The evolved gas turns limewater milky. This is an acid-base test and does not require heating or hydrolysis of the ester.

Step 2: Propanal and butan-2-one Warm separate samples gently with freshly prepared Tollens reagent in a water bath. Propanal gives a silver mirror (or a grey silver deposit) as it is oxidised to propanoate; butan-2-one gives no silver mirror.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\longrightarrow CH_3CH_2COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O.$$

The contrasting observation distinguishes the aldehyde from the ketone.

Step 3: Conclusion Use aqueous $NaHCO_3$: only benzoic acid releases CO_2. Use Tollens reagent: only propanal deposits silver.

Quick Tip to Solve: Choose a test with opposite observations: gas for the acid/ester pair and silver for the aldehyde/ketone pair.

OR

30(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 is a nucleophilic addition: cyanide attacks the electrophilic carbonyl carbon, followed by protonation.
- Electron donation and steric crowding reduce carbonyl reactivity; resonance delocalisation reduces the availability of a nitrogen lone pair.

Step 1: (i) Compare ethanal with propanone In CH_3CHO, the carbonyl carbon is attached to one methyl group and one hydrogen. In CH_3COCH_3, it is attached to two methyl groups. Methyl groups exert a positive inductive effect and donate electron density towards the carbonyl carbon. Thus the two methyl groups of propanone reduce its positive character more than the single methyl group of ethanal does. Consequently, attack by CN^- is less favourable in propanone. Moreover, two methyl groups cause greater steric hindrance to the incoming nucleophile than a methyl group and a small hydrogen atom. Both electronic and steric effects therefore favour faster HCN addition to ethanal.

Step 2: (ii) Identify the reactive amino group of semicarbazide Write semicarbazide as $H_2N-NH-C(=O)-NH_2$. The lone pair on the terminal $-NH_2$ directly bonded to the car-

Quick Tip to Solve: In semicarbazide, first locate the amino nitrogen bonded directly to C=O: its lone pair is delocalised and it does not form the C=N bond.

bonyl carbon is delocalised into the carbonyl group by resonance, as in an amide. It is therefore much less available for nucleophilic attack. The other terminal group, H_2N-NH-, has an available lone pair and attacks an aldehyde or ketone, followed by loss of water:

$$R_2C{=}O + H_2N{-}NH{-}CONH_2 \longrightarrow R_2C{=}N{-}NH{-}CONH_2 + H_2O.$$

Step 3: Conclusion Ethanal reacts more readily with HCN because its carbonyl carbon is more electrophilic and less hindered. Only the terminal hydrazino $-NH_2$ of semicarbazide forms the semicarbazone; the amide $-CONH_2$ group is resonance-deactivated.

Quick Tip to Solve: In semicarbazide, first locate the amino nitrogen bonded directly to C=O: its lone pair is delocalised and it does not form the C=N bond.

30(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 converts an acid chloride into an aldehyde using hydrogen over poisoned palladium.
- The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen.
- Cannizzaro reaction is disproportionation of an aldehyde lacking alpha hydrogen in concentrated alkali.

Step 1: (i) Rosenmund reduction Hydrogenate benzoyl chloride using palladium deposited on barium sulphate (a poisoned catalyst):

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

The acid chloride is reduced to benzaldehyde. The reduced activity of the poisoned catalyst allows the reaction to stop at the aldehyde stage rather than continuing to the corresponding primary alcohol.

Step 2: (ii) Hell–Volhard–Zelinsky reaction Ethanoic acid undergoes alpha bromination with bromine in the presence of a small amount of red phosphorus, followed by hydrolysis:

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

The product is bromoethanoic acid. The hydrogen on the carbon adjacent to the carboxyl group is replaced by bromine; an alpha hydrogen is essential for this reaction.

Step 3: (iii) Cannizzaro reaction Benzaldehyde has no alpha hydrogen and disproportionates on

Quick Tip to Solve: Check the substrate requirement: HVZ needs an alpha hydrogen, while Cannizzaro needs an aldehyde with no alpha hydrogen.

treatment with concentrated aqueous sodium hydroxide:

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

One molecule of benzaldehyde is oxidised to sodium benzoate while the other is reduced to benzyl alcohol. In the alkaline reaction mixture the oxidation product is the carboxylate salt; benzoic acid would be obtained only after acidification.

Step 4: Conclusion The equations illustrate acid chloride-to-aldehyde reduction, alpha bromination of a carboxylic acid, and aldehyde disproportionation into a carboxylate salt and a primary alcohol, respectively.

Quick Tip to Solve: Check the substrate requirement: HVZ needs an alpha hydrogen, while Cannizzaro needs an aldehyde with no alpha hydrogen.