

CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-2-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



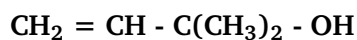
Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) All questions are compulsory.
- (ii) Questions number 1 to 5 are very short-answer questions and carry 1 mark each.
- (iii) Questions number 6 to 10 are short-answer questions and carry 2 marks each.
- (iv) Questions number 11 to 22 are also short-answer questions and carry 3 marks each.
- (v) Question number 23 is a value based question and carries 4 marks.
- (vi) Questions number 24 to 26 are long-answer questions and carry 5 marks each.
- (vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Write the IUPAC name of the following compound:



[1 mark]

Solution:

Concept:

- The parent chain must contain the carbon bearing the principal functional group, $-\text{OH}$, and the carbon-carbon double bond.
- Number the chain to give the hydroxyl group the lowest locant; the alkene is indicated by en and the alcohol by ol.

Step 1: Select the parent chain The longest chain containing both the hydroxyl-bearing carbon and the double bond has four carbons. It can be written as $\text{CH}_3 - \text{C}(\text{OH})(\text{CH}_3) - \text{CH} = \text{CH}_2$. One methyl group belongs to this four-carbon parent chain; the other is a substituent.

Step 2: Assign the locants Numbering from the methyl end puts the hydroxyl group at carbon 2, the methyl substituent at carbon 2, and the double bond between carbons 3 and 4. Numbering from the alkene end would put the principal hydroxyl group at carbon 3, so that direction is rejected.

Step 3: Conclusion The IUPAC name is 2-methylbut-3-en-2-ol.

Quick Tip to Solve: Choose numbering by the hydroxyl locant before comparing the double-bond locant.

2. Among the isomers of pentane (C_5H_{12}), write the one which on photochemical chlorination yields a single monochloride.

[1 mark]

Solution:

Concept:

- Photochemical chlorination replaces a hydrogen atom by chlorine through a free-radical substitution reaction.
- A single monochloride results when every hydrogen in the molecule is chemically equivalent by symmetry.

Step 1: Compare the pentane isomers Pentane and 2-methylbutane contain hydrogen atoms in different chemical environments. Replacing hydrogens at inequivalent positions therefore produces more than one constitutional monochloride.

Step 2: Identify the symmetric isomer In 2,2-dimethylpropane, $\text{C}(\text{CH}_3)_4$, the central carbon has no hydrogen and is bonded to four identical methyl groups. All twelve hydrogen atoms are equivalent. Replacing any one of them gives the same compound, $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$.

Step 3: Conclusion The required isomer is 2,2-dimethylpropane (neopentane).

Quick Tip to Solve: Look for equivalent hydrogen positions, not merely equivalent carbon atoms.

3. Arrange the following hydrides of Group-16 elements in the decreasing order of their acidic strength:

H₂O, H₂S, H₂Se, H₂Te

[1 mark]

Solution:

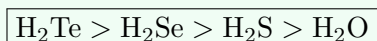
Concept:

- Acidic strength of a hydride measures its tendency to release H⁺.
- Down Group 16, the size of the central atom increases and the hydrogen-element bond becomes weaker.

Step 1: Apply the bond-strength trend From oxygen to tellurium, the increasing atomic size reduces effective overlap with the hydrogen orbital. The H – E bond, where E is the Group-16 element, becomes progressively easier to break.

Step 2: Convert the trend to acidic strength The weaker bond favours proton release. Acidic strength therefore increases down the group: water is the weakest of these hydrides and hydrogen telluride is the strongest. The requested decreasing order must begin with H₂Te, rather than with the most electronegative element.

Step 3: Conclusion



Quick Tip to Solve: For Group-16 hydrides, follow decreasing bond strength down the group to rank acidity.

4. What is the formula of a compound in which the element P forms hcp lattice and atoms of Q occupy 2/3rd of octahedral voids?

[1 mark]

Solution:

Concept:

- A close-packed lattice containing N atoms has N octahedral voids.
- The empirical formula follows from the simplest whole-number ratio of the numbers of atoms present.

Step 1: Count the occupied octahedral voids Let the hcp lattice contain N atoms of P. The total number of octahedral voids is then N , irrespective of the choice of a large representative portion of the lattice. Since Q occupies two-thirds of these voids, the number of Q atoms is $2N/3$.

Step 2: Reduce the atomic ratio The ratio is

$$\text{P} : \text{Q} = N : \frac{2N}{3} = 3 : 2.$$

For example, three P atoms provide three octahedral voids, of which two are occupied by Q. The occupancy fraction must be applied to the octahedral-void count, not to the tetrahedral-void count.

Step 3: Conclusion The formula is P_3Q_2 .

Quick Tip to Solve: For close packing, use one octahedral void per lattice atom, then clear the fraction.

5. What is the role of desorption in the process of catalysis?

[1 mark]

Solution:

Concept:

- In heterogeneous catalysis, reactants adsorb on the catalyst surface and react at its active sites.
- Desorption is the release of adsorbed species from the surface into the surrounding phase.

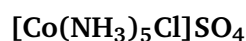
Step 1: Release the products After adsorbed reactants have reacted, the product molecules must leave the catalyst surface. Desorption releases these products so they can be collected or carried away from the reaction region.

Step 2: Regenerate the active sites The departure of product molecules frees the sites they occupied. Fresh reactant molecules can then adsorb and undergo another catalytic cycle. If products remained strongly attached, they would block the surface and reduce the available active sites, slowing further reaction even though the catalyst itself is not consumed.

Step 3: Conclusion Desorption removes products from the catalyst surface and frees active sites for continued catalysis.

Quick Tip to Solve: Connect product removal to the availability of fresh adsorption sites in the next cycle.

6. (a) Write the IUPAC name of the isomer of the following complex:



(b) Write the formula for the following:

Diamminechloridonitrito-N-platinum(II)

[2 marks]

Solution:

Concept:

- Ionisation isomers exchange a coordinated anionic ligand with a counter-ion outside the coordination sphere.
- Ammonia is a neutral ligand; chlorido and nitrito each have charge -1 , while sulfato has charge -2 .
- Nitrito-N denotes coordination of the NO_2^- ligand through its nitrogen atom.

Step 1: Find and name the ionisation isomer in part (a) In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, the complex cation has charge $+2$; hence cobalt has oxidation state $+3$. Exchange coordinated Cl^- with the external SO_4^{2-} ion to obtain $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$. Its complex ion has charge $+1$, with cobalt still in oxidation state $+3$. Name the neutral ammonia ligands as ammine, the coordinated sulfate as sulfato, and the counter-ion as chloride.

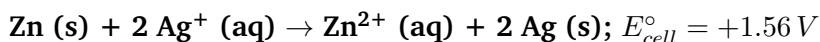
Step 2: Construct the formula in part (b) Diammine supplies two NH_3 ligands; chlorido supplies one Cl^- ligand, and nitrito-N supplies one nitrogen-bonded NO_2^- ligand. Platinum(II) contributes charge $+2$, exactly balancing the two anionic ligands. The complex is therefore neutral and needs no counter-ion. Put all four ligands inside the coordination brackets, writing NO_2 to indicate the nitrogen-bonded ligand.

Quick Tip to Solve: For an ionisation isomer swap the coordinated anion and counter-ion, then recheck the metal oxidation state.

Step 3: Conclusion (a) Pentaamminesulfatocobalt(III) chloride, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$.
(b) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$.

Quick Tip to Solve: For an ionisation isomer swap the coordinated anion and counter-ion, then recheck the metal oxidation state.

7. In a galvanic cell, the following cell reaction occurs:



(a) Is the direction of flow of electrons from zinc to silver or silver to zinc?

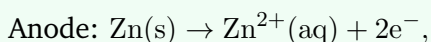
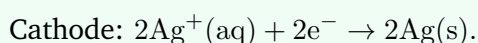
(b) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions? [2 marks]

Solution:

Concept:

- In a galvanic cell, oxidation releases electrons at the anode and reduction consumes electrons at the cathode. Electrons travel through the external circuit from anode to cathode.
- The half-reactions identify which dissolved ions are formed and which are consumed; their concentrations change accordingly as the cell discharges.

Step 1: (a) Identify the electrodes and electron flow The given spontaneous reaction has zinc losing electrons and silver ions gaining them:



Zinc is therefore the anode and silver is the cathode. The electrons released by zinc pass through the connecting wire towards the silver electrode, where they reduce silver ions. The positive standard cell potential is consistent with this direction of the spontaneous cell reaction.

Step 2: (b) Track the ion concentrations Zinc metal dissolves at the anode, producing Zn^{2+} ions, so their concentration increases. At the cathode, Ag^+ ions are removed from solution by deposition as silver metal, so their concentration decreases. For every mole of zinc oxidised, one mole of zinc ions is formed and two moles of silver ions are consumed, as shown by the balanced cell reaction.

Step 3: Conclusion (a) Electrons flow from zinc to silver through the external circuit. (b) $[\text{Zn}^{2+}]$ increases and $[\text{Ag}^+]$ decreases as the cell functions.

Quick Tip to Solve: Write the oxidation half-reaction first: the metal releasing electrons tells you both the electron-flow origin and the ion concentration that increases.

8. In the following ions:

Mn^{3+} , V^{3+} , Cr^{3+} , Ti^{4+}

(Atomic no.: Mn = 25, V = 23, Cr = 24, Ti = 22)

(a) Which ion is most stable in an aqueous solution?

(b) Which ion is the strongest oxidizing agent?

(c) Which ion is colourless?

(d) Which ion has the highest number of unpaired electrons?

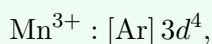
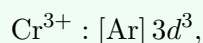
[2 marks]

Solution:

Concept:

- To obtain a transition-metal ion's electronic configuration, remove the $4s$ electrons before the $3d$ electrons. Aqueous ions of these metals normally form octahedral hydrated complexes.
- The d^3 configuration has particular stability in an octahedral field. A d^0 ion has no electrons available for $d-d$ transitions, while an oxidising ion is readily reduced by accepting an electron.

Step 1: Compare the electronic configurations Using the given atomic numbers and removing the outer electrons gives



(a) Cr^{3+} is the most stable in aqueous solution. Its octahedral d^3 arrangement, t_{2g}^3 , has one electron in each of the three lower-energy orbitals, giving substantial crystal-field stabilisation.

Step 2: Identify the oxidising, colourless and most unpaired ion (b) Mn^{3+} is the strongest oxidising agent among these ions. It readily accepts an electron to form Mn^{2+} , whose $3d^5$ configuration is especially stable because the five d orbitals are half-filled.

(c) Ti^{4+} is colourless: its $3d^0$ configuration permits no $d-d$ transition.

(d) For the ordinary aqueous ions, the respective numbers of unpaired electrons are 4, 2, 3, 0 in the order given. The high-spin $3d^4$ ion Mn^{3+} therefore has the highest number, four. Notice that part (d) asks about the supplied ion, not the Mn^{2+} formed on reduction.

Step 3: Conclusion (a) Cr^{3+} ; (b) Mn^{3+} ; (c) Ti^{4+} ; (d) Mn^{3+} , with four unpaired electrons.

Quick Tip to Solve: List the four d-electron counts first: d^3 signals aqueous stability, d^0 colourlessness, and Mn^{3+} gains an electron to reach d^5 .

9(a). Do the following conversions in not more than two steps:

(a) Propene to Acetone

(b) Propanoic acid to 2-hydroxypropanoic acid

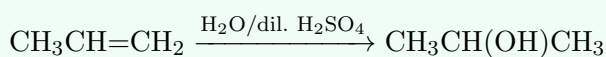
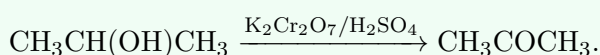
[2 marks]

Solution:

Concept:

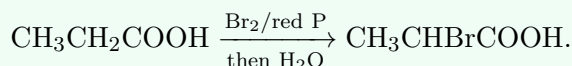
- Acid-catalysed hydration of propene follows Markovnikov addition, producing the secondary alcohol propan-2-ol. Oxidation of a secondary alcohol produces a ketone without changing its carbon skeleton.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen. Hydrolysis of the resulting alpha-halo acid replaces the halogen by a hydroxyl group.

Step 1: (a) Convert propene to acetone in two steps First hydrate propene with water in the presence of dilute sulphuric acid. The hydroxyl group attaches to the middle carbon, giving propan-2-ol. Then oxidise this secondary alcohol with acidified potassium dichromate:

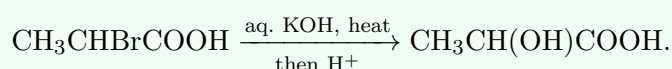


The intermediate is a secondary alcohol, so its oxidation gives acetone rather than an aldehyde. Both transformations retain the three-carbon chain.

Step 2: (b) Convert propanoic acid to 2-hydroxypropanoic acid Brominate propanoic acid at its alpha carbon using bromine and red phosphorus, followed by water work-up. This gives 2-bromopropanoic acid by the Hell-Volhard-Zelinsky reaction:



Heat this alpha-bromo acid with aqueous alkali to replace bromine by hydroxyl; acidification of the carboxylate gives the required free acid:



These are two synthetic steps, each including its work-up. Carbon 2 is the carbon adjacent to the carboxyl group, which is why alpha substitution gives the requested product.

Step 3: Conclusion (a) Propene $\rightarrow$ propan-2-ol $\rightarrow$ acetone. (b) Propanoic acid $\rightarrow$ 2-bromopropanoic acid $\rightarrow$ 2-hydroxypropanoic acid, using the reagents shown above.

Quick Tip to Solve: For an alpha-hydroxy acid, first introduce an alpha halogen by Br₂/red P, then replace that halogen by OH with aqueous alkali and acidify.

9(b). Write the reaction involved in the following:

(a) Etard reaction

(b) Wolff-Kishner reduction

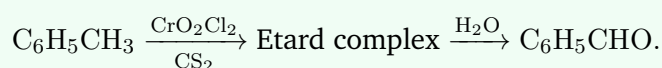
[2 marks]

Solution:

Concept:

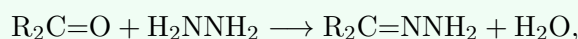
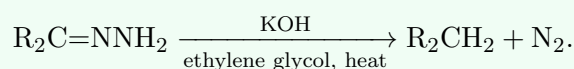
- The Etard reaction selectively oxidises the methyl side chain of an aromatic compound to an aldehyde using chromyl chloride, followed by hydrolysis of the intermediate complex.
- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone to a methylene group by hydrazine and strong base on heating. Nitrogen gas is liberated in the reduction.

Step 1: (a) Write the Etard reaction Treat toluene with chromyl chloride, CrO_2Cl_2 , in an inert solvent such as carbon disulphide. An Etard complex is formed; hydrolysis gives benzaldehyde:

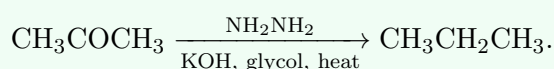


The side-chain methyl group becomes an aldehyde group while the benzene ring is retained. Naming both chromyl chloride and the hydrolytic work-up distinguishes this reaction from ordinary vigorous oxidation of toluene to benzoic acid.

Step 2: (b) Write the Wolff-Kishner reduction An aldehyde or ketone reacts with hydrazine, NH_2NH_2 , to form a hydrazone. Heating with potassium hydroxide in a high-boiling solvent such as ethylene glycol reduces the carbonyl carbon to a methylene group:



Here R represents an organic group; one substituent may be hydrogen for an aldehyde. For example, acetone gives propane:



Step 3: Conclusion Etard reaction: toluene $\rightarrow$ benzaldehyde using CrO_2Cl_2 in CS_2 , then hydrolysis. Wolff-Kishner reduction: $>\text{C}=\text{O} \rightarrow >\text{CH}_2$ using hydrazine and KOH in ethylene glycol on heating.

Quick Tip to Solve: Remember the distinguishing reagents: chromyl chloride followed by water for Etard; hydrazine, KOH and heat for Wolff-Kishner.

10. State Raoult's law for a solution containing non-volatile solute. What type of deviation from Raoult's law is shown by a solution of chloroform and acetone and why? [2 marks]

Solution:

Concept:

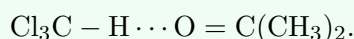
- For a solution containing a non-volatile solute, only the solvent contributes to the vapour pressure. Raoult's law relates its partial vapour pressure to its mole fraction.
- Stronger attractions between unlike molecules decrease their tendency to escape into the vapour and produce a negative deviation from Raoult's law.

Step 1: State Raoult's law At a given temperature, the vapour pressure of the solvent over the solution is directly proportional to its mole fraction in the solution:

$$p_1 = x_1 p_1^0.$$

Here p_1 is the solvent vapour pressure over the solution, p_1^0 is the vapour pressure of the pure solvent at the same temperature, and x_1 is its mole fraction. Since the solute is non-volatile, the total vapour pressure of this solution is p_1 .

Step 2: Explain the chloroform-acetone mixture Chloroform and acetone show negative deviation. On mixing, the hydrogen atom of chloroform forms a hydrogen bond with the oxygen atom of the carbonyl group of acetone:



These chloroform-acetone attractions are stronger than the attractions between molecules in the pure liquids. Consequently, molecules escape less readily into the vapour, and the observed vapour pressure is lower than the value predicted by Raoult's law.

Step 3: Conclusion Raoult's law is $p_1 = x_1 p_1^0$. The chloroform-acetone solution shows negative deviation because hydrogen bonding strengthens the attraction between unlike molecules.

Quick Tip to Solve: Identify the new attraction on mixing: stronger unlike-molecule attraction means lower vapour pressure and negative deviation.

11. Write the names and structures of the monomers of the following polymers:

(a) Bakelite

(b) PVC

(c) Buna-S

[3 marks]

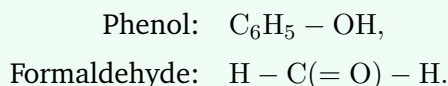
Solution:

Concept:

- A monomer is a small molecule that joins with other monomer molecules to form a polymer. The monomers must be identified from the chemical structure of the polymer.
- Bakelite is a condensation polymer of phenol and methanal. PVC is an addition polymer of chloroethene, whereas Buna-S is a copolymer of a conjugated diene and styrene.

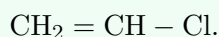
Quick Tip to Solve: Remember that the S in Buna-S means styrene; Bakelite needs both phenol and formaldehyde, while PVC has only vinyl chloride.

Step 1: (a) Monomers of Bakelite The two monomers are phenol and formaldehyde (methanal). Their condensed structural formulae are



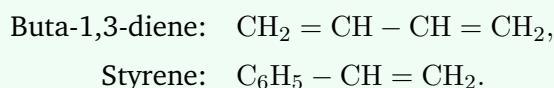
In phenol, the OH group is attached directly to a benzene ring, represented by C_6H_5 . Methanal has a carbonyl carbon bonded to two hydrogen atoms. Condensation links phenol rings through methylene bridges; further cross-linking produces Bakelite.

Step 2: (b) Monomer of PVC The monomer is vinyl chloride, also called chloroethene:



Its carbon-carbon double bond opens during addition polymerisation, giving the repeating unit $[-\text{CH}_2 - \text{CH}(\text{Cl})-]_n$. Thus chlorine is attached to one of the two carbon atoms of the monomer, rather than being a separate reactant.

Step 3: (c) Monomers of Buna-S The two monomers are buta-1,3-diene and styrene (phenylethene). Their condensed structural formulae are



Buta-1,3-diene has two conjugated double bonds. Styrene has a vinyl group attached to a benzene ring. Their copolymerisation gives the synthetic rubber Buna-S; the letter S identifies styrene as the second monomer.

Step 4: Conclusion Bakelite: phenol $\text{C}_6\text{H}_5 - \text{OH}$ and methanal $\text{H} - \text{C}(=\text{O}) - \text{H}$. PVC: chloroethene $\text{CH}_2 = \text{CH} - \text{Cl}$. Buna-S: buta-1,3-diene $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ and styrene $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$.

Quick Tip to Solve: Remember that the S in Buna-S means styrene; Bakelite needs both phenol and formaldehyde, while PVC has only vinyl chloride.

12. (a) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o > P$.

(b) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic whereas $[\text{NiCl}_4]^{2-}$ is paramagnetic. Give reason. (At. no. of Ni = 28) [3 marks]

Solution:

Concept:

- Crystal field splitting removes the degeneracy of the five metal d orbitals. The energy gap between the resulting sets is the crystal field splitting energy.
- Electrons occupy orbitals according to the relative sizes of the splitting energy Δ_o and the pairing energy P . Unpaired electrons cause paramagnetism; a complex with all electrons paired is diamagnetic.

Quick Tip to Solve: Determine the metal oxidation state first: both complexes contain d8 nickel(II), but ligand strength and geometry change their unpaired-electron counts.

Step 1: (a) Define the splitting energy and fill the orbitals Crystal field splitting energy is the energy difference between the two sets of d orbitals produced by the ligand field. In an octahedral field, the lower-energy set is t_{2g} and the higher-energy set is e_g ; their separation is denoted by Δ_o . For a d^4 ion with $\Delta_o > P$, pairing an electron in the lower set costs less energy than promoting it to the upper set. The fourth electron therefore pairs in a t_{2g} orbital:



This is the low-spin configuration. The t_{2g} occupancy is one pair and two singly occupied orbitals, so two electrons remain unpaired.

Step 2: (b) Identify the nickel ion Each cyanide or chloride ligand has charge -1 . In both complexes, if the nickel oxidation state is x , then $x + 4(-1) = -2$, giving $x = +2$. Neutral nickel has configuration $[\text{Ar}]3d^8 4s^2$; loss of the two $4s$ electrons gives $\text{Ni}^{2+} = [\text{Ar}]3d^8$.

Step 3: Compare the ligand fields and magnetic behaviour CN^- is a strong-field ligand. In $[\text{Ni}(\text{CN})_4]^{2-}$, the large square-planar splitting allows the eight d electrons to occupy the four lower d orbitals as pairs, leaving the highest-energy $d_{x^2-y^2}$ orbital empty. The complex is square planar (dsp^2 in the hybridisation description), has no unpaired electrons and is diamagnetic. Cl^- is a weak-field ligand. $[\text{NiCl}_4]^{2-}$ is tetrahedral (sp^3), with the d^8 crystal-field configuration $e^4 t_2^4$. The lower e set is filled, while the four electrons in the three t_2 orbitals occupy them as one pair and two single electrons. These two unpaired electrons make the chloride complex paramagnetic.

Step 4: Conclusion Crystal field splitting energy is the energy gap between the ligand-split d -orbital sets. For octahedral d^4 with $\Delta_o > P$, the configuration is $t_{2g}^4 e_g^0$. Square-planar $[\text{Ni}(\text{CN})_4]^{2-}$ has all electrons paired, whereas tetrahedral $[\text{NiCl}_4]^{2-}$ has two unpaired electrons.

Quick Tip to Solve: Determine the metal oxidation state first: both complexes contain d8 nickel(II), but ligand strength and geometry change their unpaired-electron counts.

13. What happens when

- $(\text{CH}_3)_3\text{C} - \text{OH}$ is treated with Cu at 573 K ,
- Anisole is treated with $\text{CH}_3\text{Cl}/\text{anhydrous AlCl}_3$,
- Phenol is treated with Zn dust?

Write chemical equations in support of your answer.

[3 marks]

Solution:

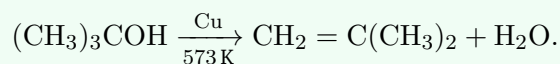
Concept:

- Alcohol vapours passed over heated copper at 573 K behave according to the class of alcohol. Tertiary alcohols undergo dehydration to an alkene because the carbon carrying $-\text{OH}$ has no hydrogen for dehydrogenation.
- The $-\text{OCH}_3$ group in anisole activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- Zinc dust removes oxygen from phenol on heating, forming benzene; zinc itself is converted into

Quick Tip to Solve: First identify the alcohol class: a tertiary alcohol over hot copper gives an alkene, while anisole directs an incoming methyl group to ortho and para positions.

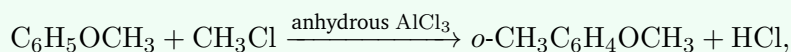
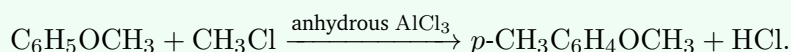
zinc oxide.

Step 1: (a) Dehydration of tert-butyl alcohol The given alcohol is tertiary: its carbon bonded to $-OH$ is bonded to three methyl groups. On treatment with copper at 573 K, it loses water to give 2-methylpropene. A hydrogen from a neighbouring methyl group and the hydroxyl group are eliminated:



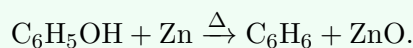
It does not give a ketone by dehydrogenation, because there is no hydrogen on the carbon bearing the hydroxyl group.

Step 2: (b) Friedel–Crafts methylation of anisole Methyl chloride in the presence of anhydrous aluminium chloride introduces a methyl group into the activated ring. Both ortho- and para-methylanisole are formed, with the para product predominating because it suffers less steric crowding:



These equations represent the two alternative substitution products, not simultaneous products from one molecule of anisole.

Step 3: (c) Reduction of phenol by zinc dust Heating phenol with zinc dust gives benzene. Zinc takes up the oxygen of the hydroxyl group as zinc oxide, while the aromatic ring remains intact:



Step 4: Conclusion (a) tert-Butyl alcohol gives 2-methylpropene and water; (b) anisole gives ortho- and para-methylanisole, predominantly the para isomer; (c) phenol gives benzene and zinc oxide.

Quick Tip to Solve: First identify the alcohol class: a tertiary alcohol over hot copper gives an alkene, while anisole directs an incoming methyl group to ortho and para positions.

14. Account for the following:

(a) Eu^{2+} is a strong reducing agent.

(b) Orange colour of dichromate ion changes to yellow in alkaline medium.

(c) $E^\circ(M^{2+}/M)$ values for transition metals show irregular variation.

[3 marks]

Solution:

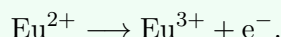
Concept:

- A reducing agent donates electrons and is itself oxidised. The common and favourable oxidation state of the lanthanoids in aqueous solution is +3.
- Chromate and dichromate ions exist in a pH-dependent equilibrium: chromate is yellow, whereas dichromate is orange.
- The standard reduction potential $E^\circ(M^{2+}/M)$ depends on the overall energy change between the

Quick Tip to Solve: For the dichromate colour change, write the equilibrium and remove hydrogen ions with alkali; for electrode potentials, consider all three energy contributions together.

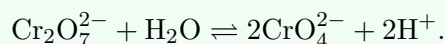
metal and its aqueous divalent ion, including atomisation, ionisation and hydration.

Step 1: (a) Reducing behaviour of europium(II) Europium(II) readily loses an electron to form europium(III), the common trivalent state of a lanthanoid:



By donating this electron to another species, Eu^{2+} reduces that species and is therefore a strong reducing agent. Its half-filled $4f^7$ configuration does not prevent this oxidation: the overall energetics in water favour the trivalent state.

Step 2: (b) Conversion of dichromate into chromate The equilibrium between the two oxyanions can be written as



In alkaline medium, hydroxide ions remove hydrogen ions as water. The equilibrium consequently shifts towards chromate. The net reaction is



Since dichromate is orange and chromate is yellow, the solution changes from orange to yellow. Chromium remains in oxidation state +6, so this is an equilibrium conversion rather than a redox reaction.

Step 3: (c) Irregular standard electrode potentials Formation of $\text{M}^{2+}(\text{aq})$ from solid metal involves atomisation, removal of two electrons and hydration. The energy contributions are thus atomisation enthalpy, the first two ionisation enthalpies and hydration enthalpy. These contributions do not vary uniformly across a transition series. In particular, changing d-electron configurations and the extra stability of certain configurations affect the ionisation energies. The combined free-energy change therefore varies irregularly, giving irregular values of $E^{\circ}(\text{M}^{2+}/\text{M})$.

Step 4: Conclusion Europium(II) oxidises to europium(III); alkali forms yellow chromate; and the combined energy contributions cause irregular electrode potentials.

Quick Tip to Solve: For the dichromate colour change, write the equilibrium and remove hydrogen ions with alkali; for electrode potentials, consider all three energy contributions together.

15. Define the following terms:

(a) Antiseptic

(b) Cationic detergent

(c) Broad spectrum antibiotic

[3 marks]

Solution:

Concept:

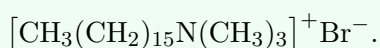
- Antimicrobial substances can be classified by their site of application or by the range of microorganisms against which they act.

Quick Tip to Solve: Match each definition to its distinguishing feature: living tissue for antiseptics, a positive organic ion for cationic detergents, and a wide bacterial range for broad spectrum antibiotics.

- Detergents contain a long hydrophobic hydrocarbon chain and a hydrophilic ionic group. The charge on the detergent's active organic ion determines whether it is cationic or anionic.

Step 1: (a) Antiseptic An antiseptic is a chemical substance that kills microorganisms or inhibits their growth and can be applied to living tissues, such as wounds, cuts and diseased skin, to prevent infection. The defining feature is its suitability for living tissue at the concentration used. Disinfectants, in contrast, are generally used on non-living objects such as floors and instruments. Tincture of iodine is an example of an antiseptic; it is a solution containing iodine in an alcohol–water mixture.

Step 2: (b) Cationic detergent A cationic detergent is a detergent whose surface-active organic ion is positively charged. Such detergents are commonly quaternary ammonium salts with a long hydrocarbon chain, together with a counter-ion such as chloride or bromide. For example, cetyltrimethylammonium bromide has the formula



Here the long hydrocarbon chain forms the hydrophobic part and the positively charged ammonium group forms the hydrophilic part. The organic cation, rather than the bromide counter-ion, supplies the detergent action. Many cationic detergents also have germicidal properties.

Step 3: (c) Broad spectrum antibiotic A broad spectrum antibiotic is an antibiotic that kills or inhibits the growth of a wide range of bacteria, including both Gram-positive and Gram-negative bacteria. The term describes the range of susceptible bacteria. It distinguishes these antibiotics from narrow spectrum antibiotics, which act against a relatively limited group of bacteria. Chloramphenicol is a standard example of a broad spectrum antibiotic. The definition does not imply that an antibiotic is effective against every microorganism or against viruses.

Step 4: Conclusion Antiseptics control microorganisms on living tissues; cationic detergents contain a positively charged surface-active organic ion; and broad spectrum antibiotics act against a wide range of Gram-positive and Gram-negative bacteria.

Quick Tip to Solve: Match each definition to its distinguishing feature: living tissue for antiseptics, a positive organic ion for cationic detergents, and a wide bacterial range for broad spectrum antibiotics.

16. The electrical resistance of a column of 0.05 M KOH solution of diameter 1 cm and length 45.5 cm is $4.55 \times 10^3 \Omega$. Calculate its molar conductivity. [3 marks]

Solution:

Concept:

- For a solution column, resistivity is $\rho = RA/l$, so conductivity is $\kappa = l/(RA)$. Here R is resistance, l is column length and A is its cross-sectional area.
- For concentration c expressed in mol L^{-1} , molar conductivity is $\Lambda_m = 1000\kappa/c$ when κ is in S cm^{-1} .

Step 1: Calculate the area of the solution column The column is cylindrical. Its diameter is $d = 1 \text{ cm}$,

Quick Tip to Solve: First halve the diameter to find the radius; then use centimetres throughout and apply $\Lambda_m = 1000\kappa/c$.

hence its radius is $r = d/2 = 0.5$ cm. Therefore,

$$A = \pi r^2 = \pi(0.5)^2 = 0.7854 \text{ cm}^2.$$

The supplied length is $l = 45.5$ cm, and the resistance is $R = 4.55 \times 10^3 \Omega$. The radius, rather than the diameter, must be squared when finding the area.

Step 2: Find conductivity from resistance The conductance is $G = 1/R$, and multiplying it by the cell constant l/A gives conductivity:

$$\begin{aligned}\kappa &= \frac{l}{RA} \\ &= \frac{45.5}{(4.55 \times 10^3)(0.7854)} \\ &= 1.2732 \times 10^{-2} \text{ S cm}^{-1}.\end{aligned}$$

Keeping length in centimetres and area in square centimetres ensures that the conductivity has the required centimetre-based unit.

Step 3: Convert conductivity to molar conductivity The concentration is $c = 0.05 \text{ mol L}^{-1}$. Since one litre contains 1000 cm^3 , use the factor 1000 in the molar-conductivity formula:

$$\Lambda_m = \frac{1000\kappa}{c} = \frac{1000(1.2732 \times 10^{-2})}{0.05} = 254.6 \text{ S cm}^2 \text{ mol}^{-1}.$$

Step 4: Conclusion The molar conductivity of the KOH solution is $\Lambda_m \approx 254.6 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: First halve the diameter to find the radius; then use centimetres throughout and apply $\Lambda_m = 1000\kappa/c$.

17(a). Define the following terms with an example in each:

(a) Lyophobic colloids

(b) Homogeneous catalysis

(c) O/W emulsion

[3 marks]

Solution:

Concept:

- A colloid has a dispersed phase distributed through a dispersion medium. Lyophobic behaviour describes weak affinity between these two phases.
- Catalysis is homogeneous when reactants and catalyst occupy the same phase. In an emulsion, one liquid is dispersed as droplets in another immiscible liquid.

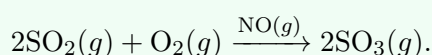
Step 1: (a) Lyophobic colloids Lyophobic colloids are colloidal systems in which the dispersed phase has little or no affinity for the dispersion medium. They do not form simply by mixing the two components and normally require special preparation methods. Because their particles are not strongly solvated, their stability commonly depends on the electrical charge carried by the particles; a suitable electrolyte can coagulate them.

Quick Tip to Solve: For O/W emulsions, read the first letter as the droplet phase and the second as the continuous dispersion medium.

Example: a gold sol in water is a lyophobic colloid. Gold particles constitute the dispersed phase and water is the dispersion medium. This contrasts with substances such as starch that show appreciable affinity for water.

Step 2: (b) Homogeneous catalysis Homogeneous catalysis is catalysis in which the catalyst and the reactants are present in the same phase. The phase criterion, rather than whether the substances have identical chemical composition, determines the classification.

Example: oxidation of gaseous sulphur dioxide by gaseous oxygen in the presence of gaseous nitric oxide is homogeneous catalysis:



Both reactants and the catalyst are gases; nitric oxide facilitates the reaction and is regenerated in the catalytic cycle.

Step 3: (c) Oil-in-water emulsion An oil-in-water, or O/W, emulsion is a colloidal system in which oil is the dispersed phase and water is the dispersion medium. Thus, small oil droplets are distributed throughout a continuous aqueous phase; the two liquids do not form a true molecular solution.

Example: milk is an O/W emulsion in which liquid fat droplets are dispersed in an aqueous medium. The order O/W identifies the droplet phase first and the continuous phase second.

Step 4: Conclusion Lyophobic colloids have little affinity between their phases, for example gold sol; homogeneous catalysis has reactants and catalyst in one phase, for example gaseous SO_2 oxidation using NO; an O/W emulsion contains oil droplets in water, for example milk.

Quick Tip to Solve: For O/W emulsions, read the first letter as the droplet phase and the second as the continuous dispersion medium.

OR

17(b). Write three differences between Physisorption and Chemisorption.

[3 marks]

Solution:

Concept:

- Adsorption is accumulation of a substance, the adsorbate, at the surface of another substance, the adsorbent. Physical and chemical adsorption differ in the interaction holding the adsorbate on that surface.
- Physisorption involves weak intermolecular forces, whereas chemisorption involves formation of chemical bonds between the adsorbate and the adsorbent surface.

Step 1: 1. Nature of the attractive forces In physisorption, molecules are held to the surface by weak van der Waals forces, without the formation of a new chemical bond. In chemisorption, the adsorbate forms chemical bonds with atoms at the adsorbent surface. Thus, the defining distinction is physical attraction versus chemical bond formation. For example, molecular hydrogen can be physically held on a suitable surface, whereas its chemical adsorption on a metal may involve dissociation and

Quick Tip to Solve: Remember the chain: weak physical attraction allows many combinations and layers; chemical bonding requires specific surface sites.

bonding of hydrogen atoms to that surface.

Step 2: 2. Specificity towards the adsorbate Physisorption is generally non-specific: the van der Waals attraction operates between many different adsorbate and adsorbent combinations. Its extent still depends on properties such as surface area and the ease of liquefaction of the gas.

Chemisorption is highly specific because chemical bond formation requires a suitable chemical affinity between the adsorbate and the surface. A surface that chemically adsorbs one gas need not chemically adsorb another gas under the same conditions.

Step 3: 3. Number of adsorbed layers Physisorption may form multiple layers. After the first layer forms on the solid surface, further adsorbate molecules can attach through intermolecular attractions to molecules already adsorbed.

Chemisorption normally forms a single molecular or atomic layer. Chemical bonds form at available surface sites, and once those sites are occupied, additional molecules cannot continue the same bonding process to build successive layers. The layer distinction follows directly from the different kinds of interaction.

Step 4: Conclusion The three differences are: physisorption uses van der Waals forces, is generally non-specific and may be multilayer; chemisorption uses chemical bonds, is highly specific and is normally restricted to a monolayer.

Quick Tip to Solve: Remember the chain: weak physical attraction allows many combinations and layers; chemical bonding requires specific surface sites.

18. A solution of glucose (Molar mass = 180 g mol^{-1}) in water has a boiling point of 100.20°C . Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are $1.86 \text{ K kg mol}^{-1}$ and $0.512 \text{ K kg mol}^{-1}$ respectively. [3 marks]

Solution:

Concept:

- For a dilute solution, elevation of boiling point is $\Delta T_b = iK_b m$, where m is molality, K_b is the molal elevation constant and i is the van't Hoff factor.
- Depression of freezing point is $\Delta T_f = iK_f m$. Glucose is a non-electrolyte and neither dissociates nor associates in water, so $i = 1$.
- For the same solution the molality is unchanged; hence $\Delta T_f / \Delta T_b = K_f / K_b$. Pure water boils at 100.00°C and freezes at 0.00°C at normal atmospheric pressure.

Step 1: Calculate the elevation of boiling point The boiling-point elevation is the difference between the boiling points of the solution and pure solvent, rather than the solution's absolute boiling point:

$$\Delta T_b = 100.20 - 100.00 = 0.20 \text{ K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius.

Quick Tip to Solve: Use $\Delta T_f = (K_f / K_b) \Delta T_b$ for the same solution, then subtract this depression from 0°C .

Step 2: Determine the molality and freezing-point depression Using the boiling-point elevation gives

$$m = \frac{\Delta T_b}{K_b} = \frac{0.20}{0.512} = 0.390625 \text{ mol kg}^{-1}.$$

This same molality determines the freezing-point depression:

$$\Delta T_f = K_f m = 1.86(0.390625) = 0.7265625 \text{ K}.$$

The given molar mass of glucose is unnecessary here because the boiling-point data already determine the molality; no mass of solute or solvent needs to be calculated.

Step 3: Apply the depression to pure water's freezing point Dissolved glucose lowers the freezing point. Therefore subtract the positive depression from the freezing point of pure water:

$$T_f(\text{solution}) = 0.00 - 0.7265625 = -0.7265625 \text{ }^{\circ}\text{C}.$$

The negative sign is physically consistent with a solution freezing below the pure solvent.

Step 4: Conclusion The freezing point of the glucose solution is approximately $-0.73 \text{ }^{\circ}\text{C}$.

Quick Tip to Solve: Use $\Delta T_f = (K_f/K_b)\Delta T_b$ for the same solution, then subtract this depression from $0 \text{ }^{\circ}\text{C}$.

19. (a) Write the principle of Zone refining.

(b) What is the role of collectors in froth floatation process? Give an example of a collector.

(c) Write the name of a reducing agent to obtain Fe from Fe_2O_3 at low temperature.

[3 marks]

Solution:

Concept:

- Zone refining separates impurities by their greater solubility in the molten metal than in its solid phase.
- Froth floatation separates sulphide ore from gangue by differences in wetting: sulphide particles preferentially attach to air bubbles when their surfaces are water-repellent.
- A reducing agent removes oxygen from a metal oxide. For iron oxide in the low-temperature region of a blast furnace, carbon monoxide is an effective reducing agent.

Step 1: (a) State and explain the principle of zone refining The principle is that impurities are more soluble in the molten state than in the solid state of the metal. A narrow molten zone is produced by a moving heater along a rod of impure metal. As the heater advances, relatively pure metal crystallises behind it, while impurities remain preferentially in the moving molten zone. Repeated passes concentrate the impurities at one end of the rod, which is then cut off. This method is used when highly pure materials, such as semiconductor-grade silicon or germanium, are required.

Step 2: (b) Explain the collector's role and give an example Collectors enhance the non-wettability of sulphide ore particles by water. They adsorb on the ore surface and make it hydrophobic, so the particles attach to air bubbles and rise with the froth; the water-wetted gangue remains behind. An

Quick Tip to Solve: Link zone refining to impurity solubility, a collector to hydrophobic ore surfaces, and low-temperature iron reduction to CO.

example is **sodium ethyl xanthate**, $C_2H_5OCS_2Na$. Xanthates are collectors, whereas a froth stabiliser has the separate task of keeping the froth stable enough for removal.

Step 3: (c) Identify the low-temperature reducing agent for iron oxide Carbon monoxide, CO , reduces Fe_2O_3 in the lower-temperature region of iron extraction. It accepts oxygen and is oxidised to carbon dioxide. The overall reduction may be written as



In the furnace this reduction proceeds through lower oxides of iron. Carbon monoxide, rather than direct reduction by coke in this temperature region, is the required answer.

Step 4: Conclusion (a) Impurities are more soluble in molten metal than in solid metal. (b) Collectors make sulphide ore water-repellent; sodium ethyl xanthate is an example. (c) The reducing agent is CO , carbon monoxide.

Quick Tip to Solve: Link zone refining to impurity solubility, a collector to hydrophobic ore surfaces, and low-temperature iron reduction to CO .

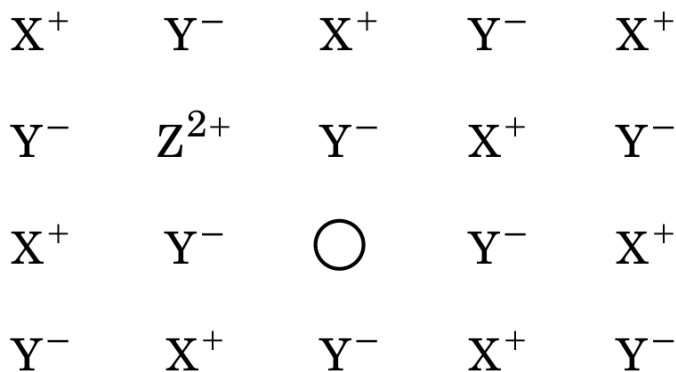
20. (a) What is the radius of sodium atom if it crystallises in bcc structure with the cell edge of 400 pm?

(b) Examine the given defective crystal:

(i) Write the term used for this type of defect.

(ii) What is the result when XY crystal is doped with divalent (Z^{2+}) impurity?

[3 marks]



Solution:

Concept:

- In a body-centred cubic (bcc) unit cell, atoms touch along the body diagonal. For cell edge a and atomic radius r , $\sqrt{3}a = 4r$.
- An impurity defect occurs when foreign ions enter an ionic crystal. Charge neutrality may require vacancies when an impurity ion has a different charge from the host ion it replaces.
- In XY , the ions are X^+ and Y^- . One substitutional Z^{2+} and one vacant cation site together replace two X^+ ions without changing the total charge.

Quick Tip to Solve: For bcc, use the body diagonal $4r = \sqrt{3}a$; for divalent doping of a monovalent cation lattice, count one cation vacancy per impurity ion.

Step 1: (a) Relate the bcc body diagonal to the atomic radius The length of the body diagonal is $\sqrt{3}a$. Along it, one corner atom touches the body-centred atom, which touches the opposite corner atom. The distance between the two corner centres is therefore $r + 2r + r = 4r$. Thus

$$r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4}(400 \text{ pm}) = 100\sqrt{3} \text{ pm} \approx 173.2 \text{ pm}.$$

The relation for a face-centred cubic structure is different and must not be used for the given bcc sodium crystal.

Step 2: (b)(i) Identify the defect shown by the crystal The printed crystal contains a foreign divalent ion Z^{2+} on a site normally occupied by X^+ , together with an empty cation site, shown by the circle. It therefore exhibits an **impurity defect**, specifically a substitutional impurity accompanied by a cation vacancy. The vacancy is associated with compensation for the impurity's greater positive charge; the drawing does not show the paired cation and anion vacancies characteristic of a Schottky defect.

Step 3: (b)(ii) Explain the result of doping with the divalent ion Each Z^{2+} substitutes for one X^+ , adding one extra unit of positive charge at that site. Another X^+ must be absent to balance that excess, producing one cation vacancy for each incorporated Z^{2+} . The charge balance is

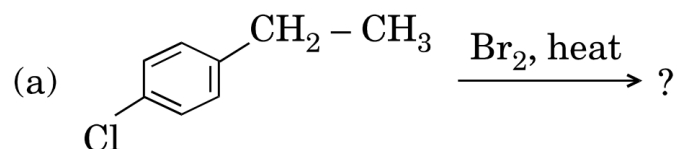
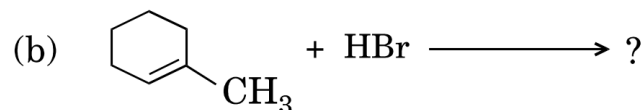
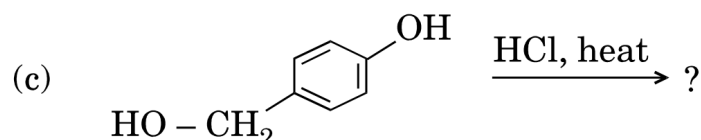
$$2(+1) = (+2) + 0.$$

Thus the number of cation vacancies equals the number of divalent impurity ions, and the crystal remains electrically neutral. The anion sublattice need not acquire a corresponding vacancy for this charge-compensation mechanism.

Step 4: Conclusion (a) $r = 100\sqrt{3} \text{ pm} \approx 173.2 \text{ pm}$. (b)(i) The crystal shows an impurity defect. (ii) One cation vacancy is created per Z^{2+} ion incorporated, maintaining electrical neutrality.

Quick Tip to Solve: For bcc, use the body diagonal $4r = \sqrt{3}a$; for divalent doping of a monovalent cation lattice, count one cation vacancy per impurity ion.

21. Draw the structures of the major monohalo product for each of the following reactions: [3 marks]

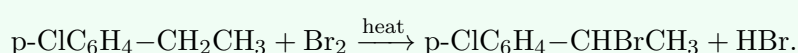


Solution:

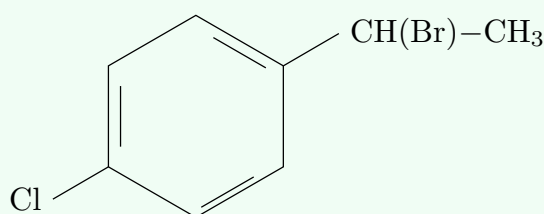
Concept:

- Bromination with Br_2 and heat proceeds by free-radical substitution. In an alkylbenzene, a benzylic hydrogen is preferentially replaced because the benzylic radical is resonance-stabilised.
- Addition of HBr to an unsymmetrical alkene without peroxide follows Markovnikov's rule: hydrogen adds so that the more stable carbocation is formed, and bromide then attacks that carbon.
- HCl replaces the hydroxyl group of a benzyl alcohol by chlorine. A phenolic C–OH bond resists this substitution because it has partial double-bond character through resonance.

Step 1: (a) Brominate the benzylic carbon The substrate is para-chloroethylbenzene. Its side chain is $-\text{CH}_2\text{CH}_3$, so the carbon directly attached to the benzene ring has two benzylic hydrogens. Under heat, Br_2 produces radicals; removal of a benzylic hydrogen gives the resonance-stabilised radical $\text{p-ClC}_6\text{H}_4-\text{CH}^\bullet-\text{CH}_3$. Bromination at the terminal methyl group would instead involve a less stable primary radical. Therefore, replacement occurs mainly at the benzylic position:



The chlorine already attached to the ring remains present. The structure below shows the major product, 1-(1-bromoethyl)-4-chlorobenzene.

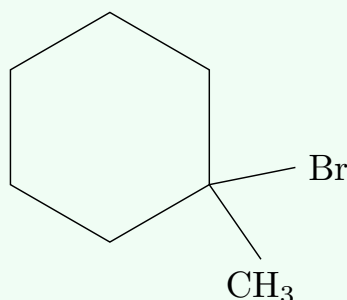


(a) 1-(1-Bromoethyl)-4-chlorobenzene

Step 2: (b) Apply Markovnikov addition The alkene is 1-methylcyclohexene. Addition of hydrogen to the less substituted carbon of the double bond leaves a tertiary carbocation on the carbon bearing the

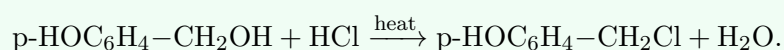
Quick Tip to Solve: First identify the reaction site: heat with bromine selects a benzylic hydrogen, HBr adds across the double bond, and HCl changes the alcoholic hydroxyl group while leaving the phenolic group intact.

methyl group. The reverse direction would give a less stable secondary carbocation. Bromide attacks the tertiary carbocation, placing Br and CH₃ on the same ring carbon. The double bond becomes a single bond and the major product is 1-bromo-1-methylcyclohexane, drawn below. No peroxide is indicated, so anti-Markovnikov addition does not apply.

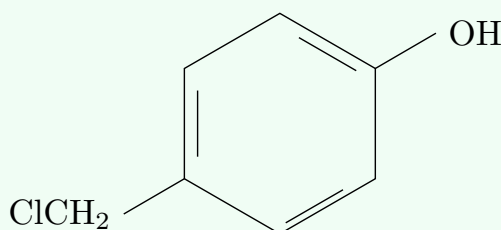


(b) 1-Bromo-1-methylcyclohexane

Step 3: (c) Replace the benzylic hydroxyl group The substrate contains both a phenolic hydroxyl group and a benzyl-alcohol group, –CH₂OH, para to one another. On treatment with hot HCl, protonation of the alcoholic hydroxyl group makes water a good leaving group. Substitution by chloride gives –CH₂Cl. The hydroxyl group directly attached to the aromatic ring remains unchanged because its carbon-oxygen bond has partial double-bond character and the aromatic carbon does not undergo ordinary alcohol substitution. Thus,



The product is 4-(chloromethyl)phenol, shown below.



(c) 4-(Chloromethyl)phenol

Step 4: Conclusion The major products are:

- (a) $p\text{-ClC}_6\text{H}_4\text{-CHBrCH}_3$;
- (b) 1-bromo-1-methylcyclohexane;
- (c) $p\text{-HOC}_6\text{H}_4\text{-CH}_2\text{Cl}$.

Quick Tip to Solve: First identify the reaction site: heat with bromine selects a benzylic hydrogen, HBr adds across the double bond, and HCl changes the alcoholic hydroxyl group while leaving the phenolic group intact.

22. Give reasons:

(a) Propanone is less reactive than ethanal towards nucleophilic addition reactions.

(b) $\text{O}_2\text{N}-\text{CH}_2-\text{COOH}$ has lower pK_a value than CH_3COOH .

(c) $(\text{CH}_3)_2\text{CH}-\text{CHO}$ undergoes aldol condensation whereas $(\text{CH}_3)_3\text{C}-\text{CHO}$ does not.

[3 marks]

Solution:

Concept:

- Nucleophilic addition depends on the electrophilicity and accessibility of the carbonyl carbon. Alkyl groups donate electron density through the positive inductive effect and also create steric hindrance.
- Acid strength depends on the stability of the conjugate base. An electron-withdrawing group stabilises a carboxylate ion, increasing K_a and lowering $\text{pK}_a = -\log_{10} K_a$.
- An aldehyde or ketone must have an α -hydrogen to undergo the usual aldol reaction. The α -carbon is the carbon adjacent to the carbonyl carbon; removal of its hydrogen produces a resonance-stabilised enolate.

Step 1: (a) Compare the two carbonyl groups Propanone, CH_3COCH_3 , has two methyl groups attached to its carbonyl carbon, whereas ethanal, CH_3CHO , has one methyl group and one hydrogen. The two methyl groups in propanone donate more electron density by the positive inductive effect, reducing its carbonyl carbon's partial positive charge and hence its attraction for a nucleophile. Moreover, two methyl groups hinder the approach of the nucleophile more than one methyl group and a small hydrogen atom do. These electronic and steric effects together make propanone less reactive towards nucleophilic addition.

Step 2: (b) Compare conjugate-base stability Nitroacetic acid gives the conjugate base $\text{O}_2\text{N}-\text{CH}_2-\text{COO}^-$, while ethanoic acid gives CH_3COO^- . The nitro group has a strong negative inductive effect: it withdraws electron density through sigma bonds and stabilises the negative charge of the carboxylate group. In contrast, the methyl group of ethanoic acid exerts a positive inductive effect and tends to destabilise that negative charge. Nitroacetic acid is therefore the stronger acid. Consequently,

$$K_a(\text{O}_2\text{N}-\text{CH}_2-\text{COOH}) > K_a(\text{CH}_3\text{COOH}),$$

and, because $\text{pK}_a = -\log_{10} K_a$, its pK_a is lower.

Step 3: (c) Locate the α -hydrogen In $(\text{CH}_3)_2\text{CH}-\text{CHO}$, the α -carbon is the CH carbon directly next to $-\text{CHO}$; it bears one hydrogen. A base can remove this α -hydrogen to form an enolate, which attacks the carbonyl carbon of another aldehyde molecule to form the aldol product. It therefore undergoes the aldol reaction. In $(\text{CH}_3)_3\text{C}-\text{CHO}$, the α -carbon is attached to three methyl groups and to the aldehyde carbon, so it has no hydrogen. It cannot form the required enolate and hence does not undergo self-aldol condensation. The hydrogens on its methyl groups are not α -hydrogens because those methyl carbons are not directly adjacent to the carbonyl carbon.

Step 4: Conclusion (a) Propanone has greater electron donation and steric hindrance at its carbonyl carbon. (b) The nitro group's negative inductive effect stabilises the conjugate base, lowering pK_a . (c) $(\text{CH}_3)_2\text{CHCHO}$ has an α -hydrogen, but $(\text{CH}_3)_3\text{CCHO}$ has none.

Quick Tip to Solve: For aldol questions, count hydrogens only on the carbon directly next to the carbonyl; for acidity questions, compare how substituents stabilise the carboxylate ion.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Veena, a class XII student, decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins-rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and students.

After reading the above passage, answer the following questions:

- (a) What are the values (at least two) displayed by Veena?
- (b) Which polysaccharide component of carbohydrates is commonly present in bread?
- (c) Write the two types of secondary structures of proteins.
- (d) Give two examples of water soluble vitamins.

[4 marks]

Solution:

Concept:

- Social responsibility and concern for others are shown when a person uses scientific awareness to take constructive action for the community's welfare.
- Starch is the main storage polysaccharide in cereals. It consists of amylose and amylopectin, both built from glucose units.
- The secondary structure of a protein is the regular local arrangement of its polypeptide backbone, stabilised by hydrogen bonding between peptide groups.
- Vitamins are classified by their solubility: the B-group vitamins and vitamin C are water soluble, whereas vitamins A, D, E and K are fat soluble.

Step 1: (a) Identify Veena's values from her actions Veena shows **concern for the health and welfare of others** because she wants to protect fellow students from the adverse effects described in the programme. She also shows **social responsibility and initiative**: she approaches the principal and seeks a practical improvement in the school canteen instead of keeping the information to herself. Her use of information to raise awareness also reflects scientific awareness. Any two of these values, supported by her actions in the passage, answer this part.

Step 2: (b) Identify the carbohydrate in bread Bread is generally made from cereal flour, such as wheat flour. Cereals store carbohydrate predominantly as **starch**, a polysaccharide composed of glucose units. Thus, the polysaccharide commonly present in bread is starch. Amylose and amylopectin are its constituent forms; the required name of the polysaccharide here is starch.

Step 3: (c) State the two secondary structures of proteins The two principal secondary structures are the α -**helix** and the β -**pleated sheet**. In the α -helix, the polypeptide backbone coils into a helix and hydrogen bonds occur within that chain. In a β -pleated sheet, extended backbone segments lie alongside one another and are held together by hydrogen bonds between neighbouring segments. These names describe backbone arrangements rather than the sequence of amino acids, which is the primary structure.

Step 4: (d) Give two water-soluble vitamins Two examples are **vitamin B₁ (thiamine)** and **vitamin C (ascorbic acid)**. Vitamin B₁ belongs to the water-soluble B group, and vitamin C is also water soluble.

Quick Tip to Solve: Link each value to an action in the passage; for the chemistry parts recall starch, the two backbone folds, and the water-soluble B and C vitamins.

Vitamins A, D, E and K belong to the fat-soluble group, so they would not be suitable examples for this part.

Step 5: Conclusion (a) Concern for others' health and social responsibility/initiative. (b) Starch. (c) α -helix and β -pleated sheet. (d) Vitamin B_1 and vitamin C.

Quick Tip to Solve: Link each value to an action in the passage; for the chemistry parts recall starch, the two backbone folds, and the water-soluble B and C vitamins.

24(a). Account for the following:

(i) BiH_3 is the strongest reducing agent in Group 15 elements hydrides.

(ii) Cl_2 acts as a bleaching agent.

(iii) Noble gases have very low boiling points.

(b) Draw the structures of the following:

(i) $\text{H}_4\text{P}_2\text{O}_7$

(ii) XeOF_4

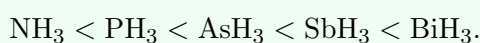
[5 marks]

Solution:

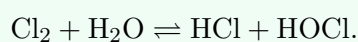
Concept:

- The reducing strength of Group 15 hydrides increases as the central atom–hydrogen bond becomes weaker down the group; the less stable hydride is more easily oxidised.
- Chlorine bleaches by oxidation in the presence of moisture. Noble-gas atoms are held together only by weak London dispersion forces.
- Pyrophosphoric acid contains two tetrahedral phosphorus centres joined by an oxygen bridge. VSEPR theory predicts the molecular shape from bonding domains and lone pairs around the central atom.

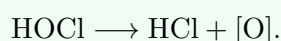
Step 1: (a)(i) Reducing strength of bismuthine Down Group 15, the atomic size increases and the overlap between the central atom's orbital and the hydrogen orbital becomes poorer. Consequently, the E – H bond strength and the thermal stability of EH_3 decrease. The Bi – H bond is the weakest in the series, so BiH_3 most readily supplies hydrogen and is itself oxidised. Thus the reducing character follows



Step 2: (a)(ii) Bleaching action of chlorine In moist conditions, chlorine reacts with water to form hydrochloric acid and hypochlorous acid:



Hypochlorous acid is an oxidising agent. Its action is conventionally represented as



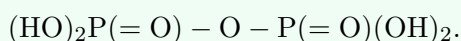
Here $[\text{O}]$ denotes an oxidising equivalent. It oxidises the coloured substance to a colourless product,

Quick Tip to Solve: Count four OH groups and one P–O–P bridge in pyrophosphoric acid; for XeOF_4 count the $\text{Xe}=\text{O}$ bond as one domain, then place the lone pair opposite O.

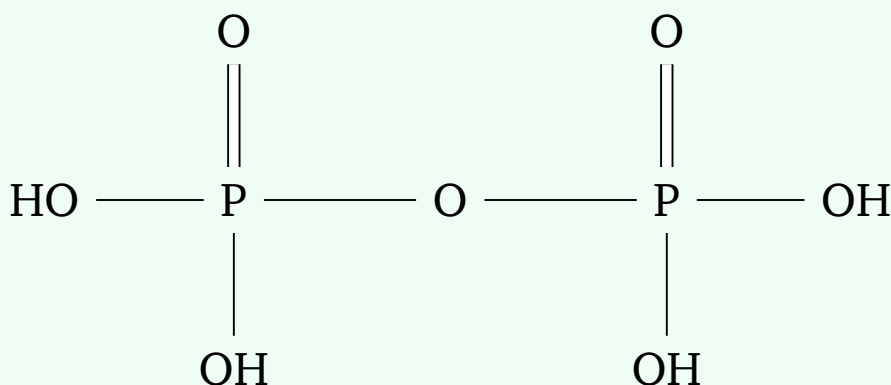
causing permanent bleaching. Moisture is therefore essential for chlorine's usual bleaching action.

Step 3: (a)(iii) Low boiling points of noble gases Noble gases exist as separate, electrically neutral atoms with closed valence shells. Their atoms have no permanent dipole moments and do not form hydrogen bonds. The attractive forces between them are only weak London dispersion forces, produced by temporary and induced dipoles. Little energy is needed to separate these atoms into the gaseous state, so their boiling points are very low. The boiling points nevertheless increase down the group because larger electron clouds are more polarisable.

Step 4: (b)(i) Structure of pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$ has the connectivity



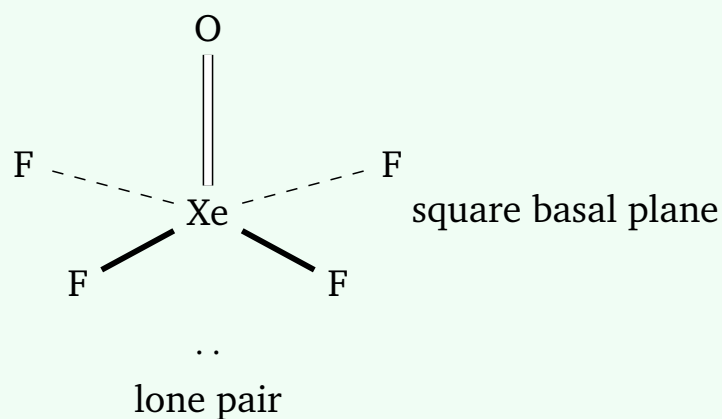
Each phosphorus is attached to one doubly bonded oxygen, two hydroxyl groups and the common bridging oxygen. Thus the drawing contains four O – H groups and seven oxygen atoms in all. The arrangement around each phosphorus centre is approximately tetrahedral; the connectivity diagram below is drawn in the plane for clarity.



Connectivity of pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$

Step 5: (b)(ii) Structure of xenon oxytetrafluoride In XeOF_4 , xenon has five bonding domains (four Xe – F bonds and one Xe = O domain) and one lone pair. The double bond counts as one VSEPR domain. Six domains give an octahedral electron-domain arrangement, conventionally described by sp^3d^2 hybridisation. The oxygen occupies one axial position and the lone pair the opposite axial position. The four fluorine atoms form a square basal plane, giving a square-pyramidal molecular shape.

Quick Tip to Solve: Count four OH groups and one P–O–P bridge in pyrophosphoric acid; for XeOF_4 count the Xe=O bond as one domain, then place the lone pair opposite O.



Square-pyramidal XeOF_4 ; the lone pair lies opposite axial oxygen

Step 6: Conclusion BiH_3 is the strongest reducing hydride because its $\text{Bi} - \text{H}$ bonds are weakest; moist chlorine bleaches by oxidation; noble gases boil at low temperatures because their interatomic dispersion forces are weak. $\text{H}_4\text{P}_2\text{O}_7$ has a $\text{P} - \text{O} - \text{P}$ bridge with two hydroxyl groups on each phosphorus, while XeOF_4 is square pyramidal with oxygen axial and the lone pair opposite it.

Quick Tip to Solve: Count four OH groups and one $\text{P} - \text{O} - \text{P}$ bridge in pyrophosphoric acid; for XeOF_4 count the $\text{Xe} = \text{O}$ bond as one domain, then place the lone pair opposite O.

OR

24(b). (a) Although nitrogen and chlorine have nearly same electronegativity yet nitrogen forms hydrogen bonding while chlorine does not. Why?

(b) What happens when F_2 reacts with water?

(c) Write the name of the gas evolved when Ca_3P_2 is dissolved in water.

(d) Write the formula of a noble gas species which is isostructural with IBr_2^- .

(e) Complete the equation: $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO} \rightarrow ?$

[5 marks]

Solution:

Concept:

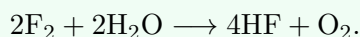
- Strong hydrogen bonding requires hydrogen attached to a highly electronegative, small atom and a lone pair on a neighbouring atom. Small atomic size concentrates the charge and permits a short, strong intermolecular interaction.
- Fluorine is a powerful oxidising agent: it can oxidise water to oxygen while being reduced to fluoride in hydrogen fluoride. Metal phosphides undergo hydrolysis to give phosphine.
- In VSEPR theory, a central atom with two bonding pairs and three lone pairs has a linear molecular shape. Nitric oxide can replace a coordinated water molecule to form a nitrosyl complex.

Step 1: (a) Compare nitrogen and chlorine as hydrogen-bonding atoms Similar electronegativities alone do not ensure similar hydrogen-bonding behaviour. Nitrogen is much smaller than chlorine, so its lone-pair electron density is concentrated in a smaller region. The hydrogen of an $\text{N} - \text{H}$ bond

Quick Tip to Solve: For an isostructural species, count bonding pairs and lone pairs on the central atom; both species here are linear because they have two bonding pairs and three lone pairs.

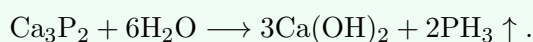
can approach a lone pair on another nitrogen closely, giving appreciable hydrogen bonding, as in ammonia. Chlorine has a much larger atomic size and more diffuse lone pairs, so its interaction with hydrogen is too weak to give the characteristic strong hydrogen bonding observed with nitrogen. Thus the decisive difference is atomic size and the resulting concentration of charge.

Step 2: (b) Write the reaction of fluorine with water Fluorine reacts vigorously with water to form hydrogen fluoride and liberate oxygen:



Fluorine changes its oxidation state from zero to -1 , whereas oxygen in water changes from -2 to zero. Thus water is oxidised and fluorine is reduced; the equation balances both atoms and the transfer of electrons.

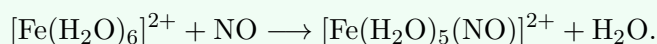
Step 3: (c) Identify the gas from calcium phosphide Calcium phosphide is hydrolysed by water, producing calcium hydroxide and phosphine gas:



The gas evolved is therefore phosphine, PH_3 . The equation also shows that each formula unit of calcium phosphide yields two molecules of phosphine.

Step 4: (d) Find a noble-gas species with the same molecular shape In IBr_2^- , the central iodine has eight valence-shell electrons available after including the negative charge. Two bonding pairs and three lone pairs give five electron-pair domains. The three lone pairs occupy equatorial positions in a trigonal-bipyramidal electron-pair arrangement, leaving the two I-Br bonds axial. Consequently, the ion is linear. Xenon difluoride, XeF_2 , likewise has two bonding pairs and three lone pairs on xenon and is linear. It is therefore isostructural with IBr_2^- .

Step 5: (e) Complete the nitrosyl-complex formation equation Nitric oxide replaces one water ligand of the hexaaquairon(II) ion. Five water ligands remain coordinated, and the displaced ligand appears as free water:



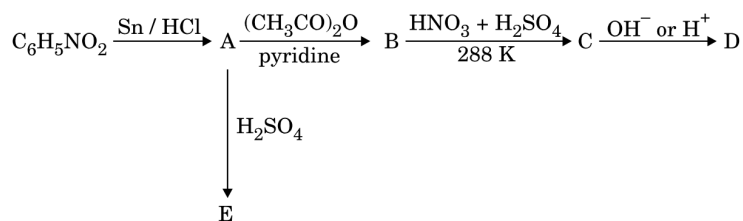
The nitrosyl complex formed is responsible for the brown ring in the nitrate test. Writing the liberated water balances the oxygen and hydrogen atoms as well as retaining the overall charge of $+2$.

Step 6: Conclusion (a) Nitrogen's smaller size favours strong hydrogen bonding; chlorine's larger size does not. (b) $2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{O}_2$. (c) Phosphine, PH_3 . (d) XeF_2 . (e) The products are $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+} + \text{H}_2\text{O}$.

Quick Tip to Solve: For an isostructural species, count bonding pairs and lone pairs on the central atom; both species here are linear because they have two bonding pairs and three lone pairs.

25(a). Write the structures of A, B, C, D and E in the following reactions:

[5 marks]

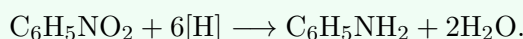


Solution:

Concept:

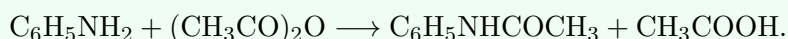
- Reduction changes an aromatic nitro group, $-\text{NO}_2$, into an amino group, $-\text{NH}_2$, without changing the benzene ring.
- Acetylation converts aniline into acetanilide. The protected amino group directs electrophilic substitution mainly to the para position because the ortho positions are more hindered.
- Hydrolysis removes the acetyl protecting group. Separately, the basic nitrogen of aniline accepts a proton from sulphuric acid to form an anilinium salt.

Step 1: Identify A by reduction of nitrobenzene Tin and hydrochloric acid reduce the nitro group of $\text{C}_6\text{H}_5\text{NO}_2$ to an amino group. The organic amine represented by A in the sequence is aniline, whose condensed structural formula is $\text{C}_6\text{H}_5 - \text{NH}_2$. The net reduction is



Here $[\text{H}]$ denotes reducing equivalents supplied by the reagent. In the acidic reaction mixture the amine is protonated; on isolation of the free amine, A is aniline.

Step 2: Identify B by acetylation of the amino group Aniline reacts with acetic anhydride in pyridine to form acetanilide. One hydrogen attached to nitrogen is replaced by the acetyl group, $-\text{COCH}_3$. Thus B has the structure $\text{C}_6\text{H}_5 - \text{NH} - \text{C}(=\text{O}) - \text{CH}_3$:



Acetylation protects the amino group before nitration; the product is an amide rather than an amino-substituted ketone.

Step 3: Identify C from nitration of acetanilide The mixture of nitric and sulphuric acids supplies the nitrating electrophile. At 288 K, nitration of B gives predominantly para-nitroacetanilide, with the nitro group opposite the acetamido group on the ring. Therefore C is

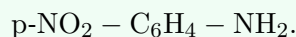


The $-\text{NHCOCH}_3$ group is ortho/para directing; the para product predominates because attack there encounters less steric hindrance. The minor ortho isomer is not the principal product represented by C.

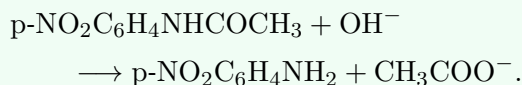
Step 4: Identify D by hydrolysis of the protecting group Acidic or alkaline hydrolysis cleaves the amide linkage of C and removes its acetyl group. The nitro group remains on the ring, so D is

Quick Tip to Solve: Follow each arrow from its own starting compound: protect the amino group before nitration, remove the acetyl group on hydrolysis, and protonate A for the separate sulphuric-acid branch.

para-nitroaniline:

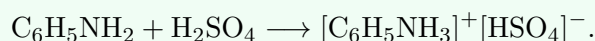


For example, the alkaline hydrolysis can be written as



Acid hydrolysis initially gives the protonated amine; neutralisation gives the free para-nitroaniline represented by D.

Step 5: Identify E from the separate acid-base reaction The downward arrow starts from A, not from B or C. Aniline accepts a proton from H_2SO_4 , producing anilinium hydrogensulphate:



Thus E consists of the anilinium cation, with three hydrogens attached to nitrogen, and the hydrogensulphate counter-ion. Further heating at 453–473 K can produce sulphanilic acid, but that heating condition is not shown on this arrow; the acid-base product is E.

Step 6: Conclusion A is aniline; B is acetanilide; C is para-nitroacetanilide; D is para-nitroaniline; and E is anilinium hydrogensulphate. Their condensed structures are given above, with the nitro and amino-derived groups para to each other in C and D.

Quick Tip to Solve: Follow each arrow from its own starting compound: protect the amino group before nitration, remove the acetyl group on hydrolysis, and protonate A for the separate sulphuric-acid branch.

OR

25(b). (a) Write the structures of the main products when benzene diazonium chloride reacts with the following reagents:

(i) CuCN

(ii) $\text{CH}_3\text{CH}_2\text{OH}$

(iii) Cu/HCl

(b) Arrange the following in the increasing order of their basic strength:

CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

(c) Write one chemical test to distinguish between Aniline and Ethyl amine.

[5 marks]

Solution:

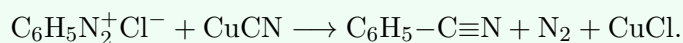
Concept:

- Benzene diazonium chloride contains the group $-\text{N}_2^+\text{Cl}^-$ attached to a phenyl ring. Replacement of the diazonium group liberates stable nitrogen gas.
- An amine accepts a proton using the nitrogen lone pair. Resonance delocalisation lowers its availability, whereas the electron-releasing inductive effect of alkyl groups increases basic strength.

Quick Tip to Solve: For diazonium substitutions, replace only the diazonium group: CuCN gives CN , ethanol gives H , and Cu/HCl gives Cl . In the basicity comparison, distinguish aniline from benzylamine by checking whether nitrogen is directly bonded to the aromatic ring.

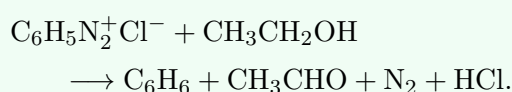
- For the usual aqueous comparison of simple methylamines, both the electron-releasing effect and hydration of the protonated amine matter; dimethylamine is more basic than methylamine.
- Aromatic primary amines form diazonium salts with nitrous acid at 273–278 K, whereas aliphatic primary amines evolve nitrogen and form alcohols.

Step 1: (a)(i) Reaction with copper(I) cyanide Copper(I) cyanide replaces the diazonium group with a cyano group in the Sandmeyer reaction:



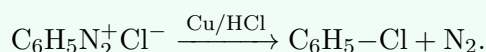
The main organic product is benzonitrile. Its structure has the benzene ring bonded to the carbon atom of $\text{—C}\equiv\text{N}$, so it is a nitrile rather than an isocyanide.

Step 2: (a)(ii) Reaction with ethanol Ethanol reduces the diazonium group, replacing it by hydrogen. Ethanol itself is oxidised to ethanal:



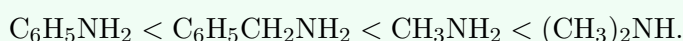
The main product derived from the diazonium salt is benzene, $\text{C}_6\text{H}_5\text{—H}$. Thus the reagent removes the diazonium substituent from the ring.

Step 3: (a)(iii) Reaction with copper and hydrochloric acid Copper powder and hydrochloric acid replace the diazonium group by chlorine in the Gattermann reaction:

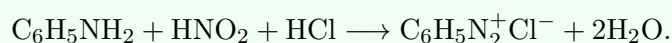


The main organic product is chlorobenzene, with chlorine directly attached to a carbon of the benzene ring.

Step 4: (b) Compare the availability of the nitrogen lone pair Aniline is the weakest base in the list because its nitrogen lone pair is delocalised into the benzene ring by resonance, making proton acceptance less favourable. In benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, the intervening saturated $\text{—CH}_2\text{—}$ group prevents this direct conjugation, so it is more basic than aniline. However, the phenyl group exerts an electron-withdrawing inductive influence through the methylene group, so benzylamine is less basic than methylamine. The methyl group in methylamine releases electron density towards nitrogen. Dimethylamine has two such methyl groups, and their combined effect together with adequate hydration makes it the strongest of these bases in aqueous solution. The increasing order is therefore

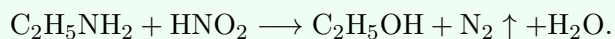


Step 5: (c) Apply the nitrous acid test Treat separate cold samples with freshly prepared nitrous acid, obtained from sodium nitrite and dilute hydrochloric acid, at 273–278 K. Aniline forms benzene diazonium chloride, which is stable at this low temperature:



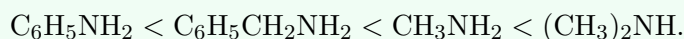
Quick Tip to Solve: For diazonium substitutions, replace only the diazonium group: CuCN gives CN, ethanol gives H, and Cu/HCl gives Cl. In the basicity comparison, distinguish aniline from benzylamine by checking whether nitrogen is directly bonded to the aromatic ring.

Ethylamine instead gives brisk nitrogen evolution and ethanol because its aliphatic diazonium intermediate decomposes immediately:



Thus immediate effervescence identifies ethylamine. To confirm aniline, couple its cold diazonium solution with alkaline β -naphthol: an orange-red azo dye forms. Keeping the mixture cold is essential because warming also decomposes the aromatic diazonium salt.

Step 6: Conclusion (a) The main products are (i) benzonitrile, $\text{C}_6\text{H}_5-\text{C}\equiv\text{N}$; (ii) benzene, $\text{C}_6\text{H}_5-\text{H}$; and (iii) chlorobenzene, $\text{C}_6\text{H}_5-\text{Cl}$. (b) Increasing basic strength:



(c) With cold nitrous acid, ethylamine immediately evolves nitrogen; aniline forms a diazonium salt that gives an orange-red azo dye on coupling with alkaline β -naphthol.

Quick Tip to Solve: For diazonium substitutions, replace only the diazonium group: CuCN gives CN , ethanol gives H , and Cu/HCl gives Cl . In the basicity comparison, distinguish aniline from benzylamine by checking whether nitrogen is directly bonded to the aromatic ring.

26(a). A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

(b) Predict the order of the reaction in the given plots:

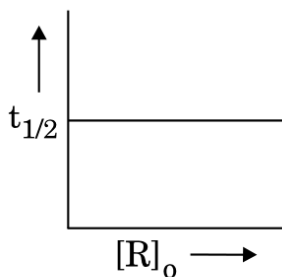
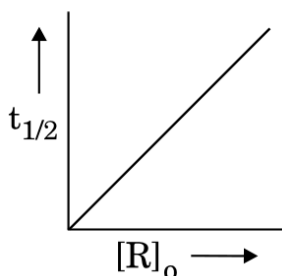
(i)

(ii)

where $[\text{R}]_0$ is the initial concentration of reactant.

(Given: $\log 2 = 0.3010$, $\log 4 = 0.6021$)

[5 marks]



Solution:

Concept:

- For a first-order reaction, the integrated rate law is $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial and remaining reactant concentrations and k is the rate constant.
- The half-life of a first-order reaction is $t_{1/2} = \frac{2.303 \log 2}{k}$; it is independent of the initial concentration.
- For a zero-order reaction, $[R]_t = [R]_0 - kt$, giving $t_{1/2} = \frac{[R]_0}{2k}$. Thus its half-life is directly proportional to the initial concentration.

Step 1: (a) Calculate the concentration remaining after 40 minutes Completion refers to the fraction of reactant consumed. If 75% has reacted, the remaining fraction is $100\% - 75\% = 25\%$. Therefore,

$$[R]_{40} = \frac{25}{100}[R]_0 = \frac{[R]_0}{4}, \quad \frac{[R]_0}{[R]_{40}} = 4.$$

The logarithmic rate expression uses the remaining concentration, rather than the amount consumed.

Step 2: (a) Obtain the rate constant and half-life Substituting the given time and $\log 4 = 0.6021$ into the first-order rate law,

$$k = \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6021}{40} = 0.03467 \text{ min}^{-1}.$$

Now use $\log 2 = 0.3010$:

$$\begin{aligned} t_{1/2} &= \frac{2.303 \log 2}{k} \\ &= \frac{40 \times 0.3010}{0.6021} = 19.997 \text{ min} \simeq 20 \text{ min}. \end{aligned}$$

This also follows because the remaining fraction $1/4 = (1/2)^2$ corresponds to two half-lives. The tiny difference from exactly 20 minutes results from rounding the supplied logarithms.

Step 3: (b)(i) Interpret the horizontal half-life plot In plot (i), the ordinate $t_{1/2}$ remains constant as the initial concentration $[R]_0$ increases. For first-order kinetics,

$$t_{1/2} = \frac{2.303 \log 2}{k},$$

which contains no initial-concentration term. At a fixed temperature, k is constant, so this equation predicts precisely the horizontal line shown. Hence plot (i) represents a first-order reaction.

Step 4: (b)(ii) Interpret the straight line through the origin Plot (ii) shows that the half-life increases linearly with $[R]_0$, and the line passes through the origin. For a zero-order reaction, putting $[R]_t = [R]_0/2$ in its integrated rate law gives

$$\frac{[R]_0}{2} = [R]_0 - kt_{1/2} \implies t_{1/2} = \frac{[R]_0}{2k}.$$

This is a straight-line relation with slope $1/(2k)$ and zero intercept. Thus plot (ii) represents a zero-order reaction; it is the dependence of half-life on concentration that identifies the order here.

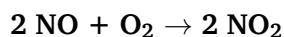
Quick Tip to Solve: For first-order kinetics, 75% completion leaves one-quarter of the reactant, so the elapsed time equals two half-lives. A constant half-life indicates first order; a half-life proportional to the initial concentration indicates zero order.

Step 5: Conclusion (a) $t_{1/2} \simeq 20 \text{ min}$. (b) Plot (i): first order; plot (ii): zero order.

Quick Tip to Solve: For first-order kinetics, 75% completion leaves one-quarter of the reactant, so the elapsed time equals two half-lives. A constant half-life indicates first order; a half-life proportional to the initial concentration indicates zero order.

OR

26(b). The following data were obtained for the reaction:



Experiment	[NO]/M	[O ₂]/M	Initial rate of formation of NO ₂ / M min ⁻¹
1	0.3	0.2	7.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

(a) Find the order of reaction with respect to NO and O₂.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k).

[5 marks]

Solution:

Concept:

- The initial-rate method determines reaction orders experimentally. Write $v = k[\text{NO}]^m[\text{O}_2]^n$, where v is the tabulated initial rate of formation of NO₂, m and n are the orders in the two reactants, and k is the rate constant for this rate law.
- Compare experiments in which one concentration is unchanged: dividing their rate laws cancels that concentration and k , leaving the concentration ratio raised to the unknown order. Reaction orders need not equal the stoichiometric coefficients.
- The overall order is $m + n$. For overall order p , the units of k are concentration^{1- p} time⁻¹, obtained by dividing rate units by the units of the concentration factors.

Step 1: (a) Determine the order with respect to NO Compare experiments 2 and 4, since both have $[\text{O}_2] = 0.1 \text{ M}$. The concentration of NO increases from 0.1 to 0.4 M, while the initial rate increases from 6.0×10^{-3} to $2.40 \times 10^{-2} \text{ M min}^{-1}$. Hence,

$$\frac{v_4}{v_2} = \left(\frac{[\text{NO}]_4}{[\text{NO}]_2} \right)^m, \quad \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \left(\frac{0.4}{0.1} \right)^m.$$

Thus $4 = 4^m$, so $m = 1$. At constant oxygen concentration, a fourfold increase in nitric oxide concentration gives a fourfold increase in rate; the reaction is first order with respect to NO.

Step 2: (a) Determine the order with respect to oxygen Compare experiments 1 and 3, since both have $[\text{NO}] = 0.3 \text{ M}$. The oxygen concentration doubles from 0.2 to 0.4 M, and the rate becomes four

Quick Tip to Solve: Compare experiments 2 and 4 for the NO order, and experiments 1 and 3 for the oxygen order. Keep the tabulated rate of formation definition when calculating k .

times as large:

$$\frac{v_3}{v_1} = \left(\frac{[\text{O}_2]_3}{[\text{O}_2]_1} \right)^n, \quad \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \left(\frac{0.4}{0.2} \right)^n.$$

Consequently, $4 = 2^n$, giving $n = 2$. The reaction is second order with respect to O_2 .

Step 3: (b) Write the rate law and find the overall order Insert the experimentally determined exponents into the assumed rate law. For the rate of formation specified in the table,

$$v = \frac{d[\text{NO}_2]}{dt} = k[\text{NO}][\text{O}_2]^2.$$

The overall order is the sum of the two exponents:

$$p = m + n = 1 + 2 = 3.$$

The balanced equation $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ alone cannot determine these exponents; the initial-rate data establish them.

Step 4: (c) Calculate the rate constant and check its units Using experiment 2 and the same tabulated rate definition throughout,

$$\begin{aligned} k &= \frac{v_2}{[\text{NO}]_2[\text{O}_2]_2^2} \\ &= \frac{6.0 \times 10^{-3}}{(0.1)(0.1)^2} \\ &= 6.0 \text{ M}^{-2} \text{ min}^{-1}. \end{aligned}$$

Since v has units M min^{-1} and the concentration product has units M^3 , the units of k are $\text{M}^{-2} \text{ min}^{-1}$, equivalently $\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$. Check with experiment 1: $6.0(0.3)(0.2)^2 = 0.072 \text{ M min}^{-1}$, agreeing with the given rate. Experiments 3 and 4 similarly give 0.288 and $0.0240 \text{ M min}^{-1}$. The constant therefore fits all four observations.

Step 5: Conclusion (a) Order with respect to NO : 1; with respect to O_2 : 2. (b) The rate law is $v = k[\text{NO}][\text{O}_2]^2$, and the overall order is 3. (c) $k = 6.0 \text{ M}^{-2} \text{ min}^{-1}$ for the tabulated rate of formation of NO_2 .

Quick Tip to Solve: Compare experiments 2 and 4 for the NO order, and experiments 1 and 3 for the oxygen order. Keep the tabulated rate of formation definition when calculating k .