

CBSE Class 12 Chemistry Question Paper 2010 with Solution PDF-Set 56/1 (Delhi)



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

1. Write a feature which will distinguish a metallic solid from an ionic solid.

[1 mark]

Solution:

Concept:

- Metallic solids contain delocalised electrons that can move through the solid lattice.
- In an ionic solid, charged ions are held at fixed lattice positions in the solid state.

Step 1: Identify the mobile particles In a metallic solid, valence electrons are free to move through the lattice. When a potential difference is applied, their directed movement carries electric current.

Step 2: Compare the solid states In an ionic solid, the ions cannot move freely while the lattice remains intact, so the solid does not conduct electricity. Its ions become mobile on melting or dissolving in water.

Step 3: Conclusion A metallic solid conducts electricity in the solid state, whereas an ionic solid does not.

Quick Tip to Solve: Compare conductivity in the solid state; molten ionic solids also conduct, so state the physical condition.

2. Define 'order of a reaction'.

[1 mark]

Solution:

Concept:

- The rate law expresses the experimentally determined dependence of reaction rate on reactant concentrations.
- For $r = k[A]^m[B]^n$, k is the rate constant and m, n are the partial orders.

Step 1: Write the rate expression Consider the rate law $r = k[A]^m[B]^n$. The exponents describe how changing each reactant concentration affects the rate while other conditions remain constant.

Step 2: Add the concentration powers The overall order is obtained by adding these exponents: $m + n$. The powers are determined experimentally; they need not equal the coefficients in the balanced chemical equation.

Step 3: Conclusion The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.

Quick Tip to Solve: Add the powers in the rate law, rather than the stoichiometric coefficients in the balanced equation.

3. What is an emulsion?

[1 mark]

Solution:

Concept:

- A colloid contains a dispersed phase distributed throughout a continuous dispersion medium.

- An emulsion is a liquid-in-liquid colloidal system made from two immiscible liquids.

Step 1: Identify the dispersed phase In an emulsion, one liquid is divided into fine droplets. These droplets form the dispersed phase, rather than dissolving molecularly in the other liquid.

Step 2: Identify the dispersion medium The second liquid is the continuous dispersion medium. The two liquids are immiscible; for example, milk contains tiny fat droplets dispersed in water and is an oil-in-water emulsion.

Step 3: Conclusion An emulsion is a colloidal dispersion of one liquid as fine droplets in another immiscible liquid.

Quick Tip to Solve: Remember liquid in liquid: an emulsion has both a liquid dispersed phase and a liquid dispersion medium.

4. Why does NO₂ dimerise?

[1 mark]

Solution:

Concept:

- NO₂ is an odd-electron molecule with an unpaired electron.
- Pairing unpaired electrons by bond formation can produce a more stable, closed-shell species.

Step 1: Count the valence electrons One NO₂ molecule has $5 + 2(6) = 17$ valence electrons. Since this total is odd, the molecule contains an unpaired electron and is paramagnetic.

Step 2: Pair the unpaired electrons Two NO₂ molecules combine by forming an N–N bond. The two unpaired electrons become paired in the dimer:



The resulting N₂O₄ has no unpaired electrons and is diamagnetic.

Step 3: Conclusion NO₂ dimerises to N₂O₄ to pair its unpaired electrons and form a more stable molecule.

Quick Tip to Solve: For an odd-electron molecule such as NO₂, look for dimerisation through pairing of unpaired electrons.

5. Give an example of linkage isomerism.

[1 mark]

Solution:

Concept:

- Linkage isomerism occurs when an ambidentate ligand coordinates through different donor atoms.
- The nitrite ion, NO₂[−], can attach to a metal through nitrogen or oxygen.

Step 1: Choose the ambidentate ligand Use NO₂[−], which has two possible donor atoms. Nitrogen coordination gives a nitro complex, whereas oxygen coordination gives a nitrito complex.

Step 2: Write the pair of isomers An example is $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$. In the first complex the metal is bonded to N; in the second it is bonded to O. The composition and oxidation state of cobalt remain unchanged.

Step 3: Conclusion $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ (N-bonded nitro) and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ (O-bonded nitrito) are linkage isomers.

Quick Tip to Solve: Use the same ambidentate ligand and change only its donor atom: nitrite can bind through N or O.

6. A solution of KOH hydrolyses $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. Which one of these is more easily hydrolysed? [1 mark]

Solution:

Concept:

- Hydrolysis of an alkyl chloride replaces Cl by OH to form an alcohol.
- In an ionisation-controlled substitution, a more stable carbocation forms more readily; secondary carbocations are more stable than primary ones.

Step 1: Classify the alkyl chlorides In $\text{CH}_3\text{CHClCH}_2\text{CH}_3$, the carbon carrying chlorine is attached to two carbon groups, so it is secondary. In $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, that carbon is attached to only one carbon group, so it is primary.

Step 2: Compare ease of hydrolysis In the usual comparison based on carbocation stability, ionisation of the secondary chloride gives the more stable secondary carbocation. Alkyl groups stabilise this positive charge by the inductive effect and hyperconjugation, making hydrolysis easier than for the primary chloride.

Step 3: Conclusion $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ (2-chlorobutane) is more easily hydrolysed.

Quick Tip to Solve: Identify the carbon bonded to chlorine; the secondary chloride gives a more stable carbocation than the primary chloride.

7. Draw the structural formula of 1-phenylpropan-1-one molecule. [1 mark]

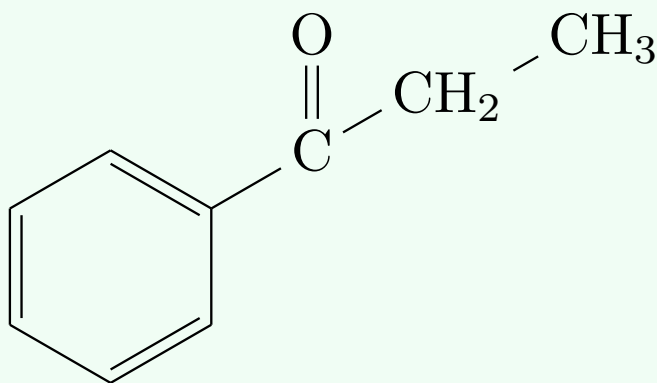
Solution:

Concept:

- The suffix propan-1-one specifies a three-carbon chain with its carbonyl carbon numbered 1.
- A phenyl substituent is the group C_6H_5^- , obtained by removing one hydrogen atom from benzene.

Step 1: Construct the parent chain Place the carbonyl group at carbon 1 of the three-carbon chain. The remaining two carbons form an ethyl group, $-\text{CH}_2-\text{CH}_3$, attached to that carbonyl carbon.

Step 2: Attach the phenyl group The prefix 1-phenyl places the benzene ring directly on carbon 1. Thus the carbonyl carbon has a double bond to oxygen and single bonds to the phenyl and ethyl groups; it has no hydrogen attached.



Structural formula of 1-phenylpropan-1-one

Step 3: Conclusion The required structural formula is $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3$, as drawn above.

Quick Tip to Solve: Attach phenyl directly to the carbonyl carbon; inserting a methylene group between them gives a different compound.

8. Give the IUPAC name of $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$.

[1 mark]

Solution:

Concept:

- The amino group is the principal functional group and receives the lowest possible locant.
- The longest chain contains four carbons and one carbon-carbon double bond; use the suffix amine and the infix en.

Step 1: Number from the amino end Number the chain from the carbon bonded to NH_2 . The amino group is then at carbon 1, while the double bond lies between carbons 3 and 4. Numbering from the alkene end would give the amino group locant 4, which is not preferred.

Step 2: Assemble the systematic name The four-carbon unsaturated parent is but-3-ene. Replace the terminal e by the suffix 1-amine, placing each locant immediately before the feature it specifies.

Step 3: Conclusion The IUPAC name is but-3-en-1-amine.

Quick Tip to Solve: In an unsaturated amine, choose numbering for the amino suffix before minimising the double-bond locant.

9. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type.

[2 marks]

Solution:

Concept:

- For an ideal binary solution, Raoult's law gives $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$, where x_i is liquid mole fraction and p_i° is pure-component vapour pressure.

- Deviation occurs when unlike-molecule attractions differ from the attractions between like molecules, changing their tendency to escape into vapour.

Step 1: Explain positive deviation Positive deviation means the partial vapour pressures, and hence the total vapour pressure, are higher than the Raoult's-law prediction. Unlike $A - B$ attractions are weaker than the original $A - A$ and $B - B$ attractions, so molecules escape more readily. Ethanol and acetone provide an example: acetone disrupts the hydrogen-bonded association of ethanol.

Step 2: Explain negative deviation Negative deviation means the partial and total vapour pressures are lower than the corresponding ideal values. Unlike $A - B$ attractions are stronger than the attractions in the separate liquids, so escape into vapour is hindered. Chloroform and acetone show this behaviour because the hydrogen of CHCl_3 forms a hydrogen bond with the carbonyl oxygen of acetone.

Step 3: Conclusion Weaker unlike interactions produce positive deviation (ethanol-acetone); stronger unlike interactions produce negative deviation (chloroform-acetone).

Quick Tip to Solve: Compare unlike attractions with like attractions: easier molecular escape raises vapour pressure and gives positive deviation.

10. A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when

10(i). the concentration of B alone is increased to three times

[2 marks total]

Solution:

Concept:

- For a reaction first order in A and second order in B , the rate law is $r = k[A][B]^2$. Here k is the rate constant at fixed temperature.
- When comparing rates at the same temperature, divide the new rate by the initial rate so that k cancels. The powers in the rate law determine the concentration effect.

Step 1: Triple the concentration of B alone Keep $[A]$ unchanged and replace $[B]$ by $3[B]$. Then

$$r_1 = k[A](3[B])^2 = 9k[A][B]^2 = 9r.$$

The factor is squared because the reaction is second order in B ; tripling its concentration does not merely triple the rate.

Step 2: Check the reasoning The unchanged concentration of A cancels from the rate ratio; only the squared concentration factor of B remains.

Step 3: Conclusion The rate becomes nine times its initial value: $r' = 9r$.

Quick Tip to Solve: For B alone, square its concentration multiplier because its order is two.

10(ii). the concentrations of A as well as B are doubled?

Solution:

Concept:

- For a reaction first order in A and second order in B, the rate law is $r = k[A][B]^2$. Here k is the rate constant at fixed temperature.
- When comparing rates at the same temperature, divide the new rate by the initial rate so that k cancels. The powers in the rate law determine the concentration effect.

Step 1: Double both concentrations Replace $[A]$ by $2[A]$ and $[B]$ by $2[B]$. Thus

$$r_2 = k(2[A])(2[B])^2 = 2 \times 4 k[A][B]^2 = 8r.$$

The first-order reactant contributes a factor of two, while the second-order reactant contributes a factor of four.

Step 2: Check the reasoning The concentration effects multiply: A contributes 2^1 and B contributes 2^2 , with the rate constant unchanged.

Step 3: Conclusion The rate becomes eight times its initial value: $r' = 8r$.

Quick Tip to Solve: When both concentrations double, multiply their individual rate factors 2 and 4.

11. The rate constant for a reaction of zero order in A is $0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M? [2 marks]

Solution:

Concept:

- For a zero-order reaction, the rate is constant: $-d[A]/dt = k$, where $[A]$ is reactant concentration.
- The integrated rate equation is $[A]_t = [A]_0 - kt$, so $t = ([A]_0 - [A]_t)/k$. The units of k are concentration per unit time.

Step 1: Find the concentration decrease The initial concentration is $[A]_0 = 0.10 \text{ mol L}^{-1}$, and the required final concentration is $[A]_t = 0.075 \text{ mol L}^{-1}$. Therefore,

$$\Delta[A] = [A]_0 - [A]_t = 0.10 - 0.075 = 0.025 \text{ mol L}^{-1}.$$

Use the amount consumed, rather than the final concentration alone, in the integrated equation.

Step 2: Substitute into the zero-order equation With $k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$,

$$t = \frac{0.025 \text{ mol L}^{-1}}{0.0030 \text{ mol L}^{-1} \text{ s}^{-1}} = 8.33 \text{ s}.$$

The concentration units cancel, leaving seconds. A logarithmic rate equation is unnecessary because the reaction is zero order, not first order.

Step 3: Conclusion The required time is approximately 8.3 s.

Quick Tip to Solve: For zero order, divide concentration consumed by the constant rate; do not use a concentration ratio or logarithm.

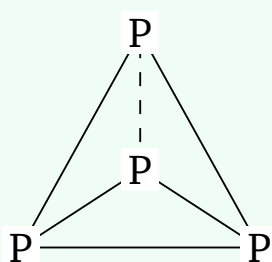
12. Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why? [2 marks]

Solution:

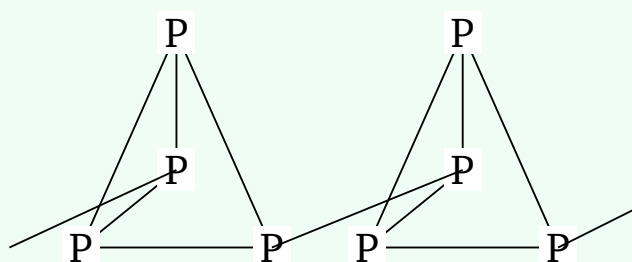
Concept:

- White phosphorus consists of discrete tetrahedral P_4 molecules; each phosphorus atom forms three covalent bonds.
- Red phosphorus has a polymeric network of linked phosphorus units. Bond-angle strain affects the relative reactivity of these allotropes.

Step 1: Draw the structures The first drawing shows all six P-P edges of a tetrahedral P_4 molecule. The second is a schematic segment of polymeric red phosphorus: opened tetrahedral units link through P-P bonds, and the terminal bonds indicate continuation of the network. It is not made of separate P_4 molecules.



White: discrete P_4



Red: linked polymeric units

White phosphorus and a schematic segment of polymeric red phosphorus

Step 2: Compare their reactivity In white phosphorus the P-P-P bond angles are only 60° , producing considerable angular strain. Red phosphorus has a less strained polymeric structure and is more stable. Consequently, the bonds in white phosphorus react more readily, whereas red phosphorus is comparatively less reactive.

Step 3: Conclusion White phosphorus is more reactive than red phosphorus because its tetrahedral P_4 molecules have highly strained 60° bond angles.

Quick Tip to Solve: Count six edges in the white phosphorus tetrahedron, then link the opened units for red phosphorus.

13. Explain the following observations:

13(i). Generally there is an increase in density of elements from titanium ($Z = 22$) to copper ($Z = 29$) in the first series of transition elements. [2 marks total]

Solution:

Concept:

- Density is mass per unit volume: $\rho = M/V_m$, where M is molar mass and V_m is molar volume.
- An increase in mass alone is not the whole explanation.

Step 1: Explain the general density trend From titanium to copper, atomic mass generally increases. At the same time, increasing effective nuclear charge tends to contract atomic size, so atomic or molar volume generally decreases. The increase in the numerator and decrease in the denominator of $\rho = M/V_m$ together explain the general rise in density. The statement describes an overall trend; it does not require a perfectly uniform increase at every successive element.

Step 2: Check the reasoning An increase in mass alone is not the whole explanation. The general contraction of atomic volume reinforces it in the density ratio.

Step 3: Conclusion Density generally increases because atomic mass rises while atomic volume generally decreases.

Quick Tip to Solve: Use density equals molar mass divided by molar volume, and examine both factors.

13(ii). Transition elements and their compounds are generally found to be good catalysts in chemical reactions.

Solution:

Concept:

- A catalyst provides a reaction pathway with lower activation energy. Transition metals can use variable oxidation states and surface adsorption to facilitate such pathways.
- The metal or its compound is regenerated after the intermediate steps.

Step 1: Explain catalytic activity Transition elements exhibit variable oxidation states because their outer ns and $(n-1)d$ electrons have comparable energies. Their compounds can therefore form intermediates and undergo oxidation-state changes during a catalytic cycle, returning to the original state at its end. Finely divided transition metals also adsorb reactants on their surfaces, bringing molecules together and weakening reacting bonds. These effects lower the activation energy.

Step 2: Check the reasoning The metal or its compound is regenerated after the intermediate steps. Its role is to lower the activation barrier, without changing the equilibrium constant.

Step 3: Conclusion Variable oxidation states, intermediate formation and surface adsorption explain their catalytic activity.

Quick Tip to Solve: Connect variable oxidation states to intermediate formation and a lower activation energy.

14. Name the following coordination compounds according to IUPAC system of nomenclature:

14(i). $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$

[2 marks total]

Solution:

Concept:

- Name ligands alphabetically, followed by the metal and its oxidation state in Roman numerals. Name the counter-ion after the complex cation.
- NH_3 , H_2O and ethane-1,2-diamine are neutral ligands; each chlorido ligand has charge -1 .

Step 1: Name the cobalt compound The two chloride ions outside the brackets show that the complex ion has charge +2. If cobalt has oxidation state x , then $x - 1 = +2$, so $x = +3$. The four ammine ligands, one aqua ligand and one chlorido ligand are written in the alphabetical order ammine, aqua, chlorido; the multiplicative prefix tetra does not affect this order. Thus the name is tetraammineaquachloridocobalt(III) chloride.

Step 2: Check the reasoning The complex is a cation, so the metal retains the name cobalt. The external chloride ions are named last as chloride, without a numerical prefix.

Step 3: Conclusion Tetraammineaquachloridocobalt(III) chloride.

Quick Tip to Solve: Use the two external chloride ions to get complex charge +2, then cobalt oxidation state +3.

14(ii). $[\text{CrCl}_2(\text{en})_2]\text{Cl}$, (en = ethane-1,2-diamine)

Solution:

Concept:

- Name ligands alphabetically, followed by the metal and its oxidation state in Roman numerals. Name the counter-ion after the complex cation.
- NH_3 , H_2O and ethane-1,2-diamine are neutral ligands; each chlorido ligand has charge -1 .

Step 1: Name the chromium compound The single external chloride ion makes the complex cation singly positive. Hence $x - 2 = +1$, giving chromium oxidation state +3. There are two chlorido ligands and two neutral bidentate ethane-1,2-diamine ligands. Use bis for the two ligands whose name already contains numerical locants, and alphabetize chlorido before ethane-1,2-diamine. The name is dichloridobis(ethane-1,2-diamine)chromium(III) chloride. The chloride outside the brackets is named separately and is not a coordinated ligand.

Step 2: Check the reasoning The ligand en is neutral even though it binds through two nitrogen atoms. Thus two coordinated chlorido ligands contribute charge -2 , not -4 .

Step 3: Conclusion Dichloridobis(ethane-1,2-diamine)chromium(III) chloride.

Quick Tip to Solve: Treat en as neutral and use bis for two ethane-1,2-diamine ligands.

15. Illustrate the following reactions giving a chemical equation for each:

15(i). Kolbe's reaction

[2 marks total]

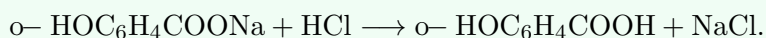
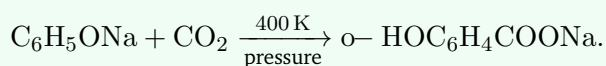
Solution:

Concept:

- In the phenol chapter, Kolbe's reaction is the carboxylation of sodium phenoxide with carbon dioxide, followed by acidification.
- The major product has OH and COOH at adjacent ring positions.

Step 1: Illustrate Kolbe's reaction Sodium phenoxide is heated with carbon dioxide under pressure at

about 400 K. The ortho carboxylation product is sodium salicylate; acidification produces salicylic acid (2-hydroxybenzoic acid):



The hydroxyl group and carboxyl group occupy adjacent positions on the benzene ring.

Step 2: Check the reasoning The major product has OH and COOH at adjacent ring positions. Acidification is necessary to convert the sodium carboxylate into the free carboxylic acid.

Step 3: Conclusion Kolbe reaction carboxylates sodium phenoxide to give salicylic acid after acidification.

Quick Tip to Solve: Write carbon dioxide under pressure first, then acidify sodium salicylate.

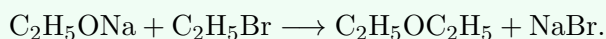
15(ii). Williamson synthesis

Solution:

Concept:

- Williamson synthesis forms an ether by reaction of a sodium alkoxide with a suitable alkyl halide through nucleophilic substitution.
- The oxygen atom in the ether comes from the alkoxide.

Step 1: Illustrate Williamson synthesis For example, sodium ethoxide reacts with bromoethane to form ethoxyethane (diethyl ether):



The ethoxide ion acts as the nucleophile and displaces bromide from the primary alkyl halide. A primary halide favours substitution and therefore gives a good ether yield.

Step 2: Check the reasoning The oxygen atom in the ether comes from the alkoxide. Bromide leaves from the alkyl halide and combines with sodium to form sodium bromide.

Step 3: Conclusion Sodium ethoxide and bromoethane form ethoxyethane and sodium bromide.

Quick Tip to Solve: Choose a primary alkyl halide for Williamson synthesis to favour substitution over elimination.

16. How are the following conversions carried out?

16(i). Benzyl chloride to benzyl alcohol

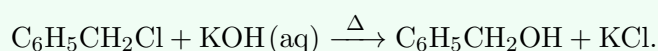
[2 marks total]

Solution:

Concept:

- An aqueous hydroxide replaces chlorine in benzyl chloride by nucleophilic substitution, giving benzyl alcohol.
- The benzylic carbon retains its carbon skeleton and acquires the OH group.

Step 1: Convert benzyl chloride by hydrolysis Heat benzyl chloride with aqueous potassium hydroxide. The hydroxide ion substitutes for chloride at the benzylic carbon, while the benzene ring remains unchanged:



Use aqueous alkali because the required transformation is replacement of chlorine by hydroxyl.

Step 2: Check the reasoning The benzylic carbon retains its carbon skeleton and acquires the OH group. Aqueous alkali supplies the hydroxide required for hydrolysis.

Step 3: Conclusion Heat benzyl chloride with aqueous KOH to obtain benzyl alcohol.

Quick Tip to Solve: Use aqueous KOH to replace benzylic chlorine by hydroxyl without changing the benzene ring.

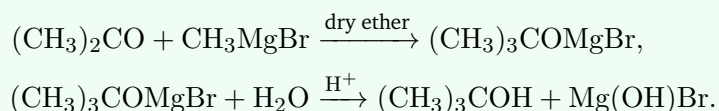
16(ii). Methyl magnesium bromide to 2-methylpropan-2-ol

Solution:

Concept:

- A Grignard reagent adds its alkyl group to the carbonyl carbon of a ketone; subsequent acidic hydrolysis gives a tertiary alcohol. The reaction must first be performed in dry ether.
- The new carbon-carbon bond joins the Grignard methyl group to the carbonyl carbon.

Step 1: Add methylmagnesium bromide to propanone, then hydrolyse The target tertiary alcohol has three methyl groups bonded to the carbon carrying the hydroxyl group. Propanone supplies two methyl groups, and methylmagnesium bromide supplies the third. Add propanone to the Grignard reagent in dry ether, and then carry out acidic hydrolysis:



Water is introduced only after addition, since it would otherwise destroy the Grignard reagent.

Step 2: Check the reasoning The new carbon-carbon bond joins the Grignard methyl group to the carbonyl carbon. Hydrolysis then protonates the alkoxide oxygen to give the tertiary alcohol.

Step 3: Conclusion Use propanone in dry ether, followed by acidic hydrolysis, to form 2-methylpropan-2-ol.

Quick Tip to Solve: Choose propanone to supply two methyl groups; the Grignard reagent supplies the third.

Explain the following terms:

17(i). Invert sugar

[2 marks total]

Solution:

Concept:

- Sucrose hydrolyses into equal molar amounts of glucose and fructose.
- The optical rotation of the hydrolysis mixture determines the term invert sugar.

Step 1: Identify the mixture Invert sugar is the equimolar mixture of D-glucose and D-fructose obtained by hydrolysis of sucrose with dilute acid or invertase.

Step 2: Explain the inversion Sucrose is dextrorotatory, whereas its hydrolysis mixture is laevorotatory. The negative rotation of fructose is greater in magnitude than the positive rotation of glucose, so the sign of rotation reverses. This reversal is called inversion.

Step 3: Conclusion Invert sugar is the equimolar glucose-fructose mixture formed by sucrose hydrolysis, whose optical rotation is opposite in sign to that of sucrose.

Quick Tip to Solve: Connect invert sugar with inversion of optical rotation after hydrolysis of sucrose.

17(ii). Polypeptides

Solution:

Concept:

- A peptide linkage is the amide bond $-\text{CO} - \text{NH}-$ joining amino-acid residues.
- Condensation of many amino acids produces a polypeptide chain.

Step 1: Identify the building units Polypeptides are chains containing many α -amino-acid residues. Successive residues are joined through peptide linkages, rather than merely being mixed together.

Step 2: Explain formation of the linkages The carboxyl group of one amino acid reacts with the amino group of another, eliminating water and forming a $-\text{CO} - \text{NH}-$ bond. Repetition of this condensation produces a long chain containing many peptide bonds.

Step 3: Conclusion Polypeptides are long chains of amino-acid residues linked together by peptide bonds.

Quick Tip to Solve: Identify the repeated $-\text{CO} - \text{NH}-$ linkage when defining a polypeptide.

OR

17(b). Name the products of hydrolysis of sucrose. Why is sucrose not a reducing sugar?

[2 marks]

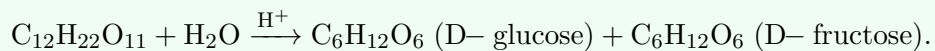
Solution:

Concept:

- Sucrose hydrolyses to an equimolar mixture of D-glucose and D-fructose.

- A reducing sugar needs a free anomeric group that permits ring opening to a reactive carbonyl form. A glycosidic bond that engages both anomeric centres prevents this opening.

Step 1: Identify the hydrolysis products On heating sucrose with dilute mineral acid, or using the enzyme invertase, its glycosidic linkage is hydrolysed. One molecule each of D-glucose and D-fructose is obtained:



Thus the products are present in equal molar amounts; hydrolysis breaks the linkage joining the two monosaccharide units.

Step 2: Explain the non-reducing nature of sucrose In sucrose, the glycosidic linkage joins the anomeric carbon C-1 of the glucose unit to the anomeric carbon C-2 of the fructose unit. Both anomeric hydroxyl groups are involved in this linkage, so there is no free hemiacetal or hemiketal group. Consequently, intact sucrose cannot open its rings to give a free aldehydic or ketonic group and does not reduce Tollens' reagent or Fehling's solution. Its hydrolysis products can be reducing sugars even though sucrose itself is non-reducing.

Step 3: Conclusion Sucrose yields D-glucose and D-fructose on hydrolysis. It is non-reducing because its glycosidic linkage involves the anomeric carbons of both units, leaving no free anomeric group.

Quick Tip to Solve: For reducing ability, check whether an anomeric carbon remains free; sucrose locks both glucose C-1 and fructose C-2.

18. What are essential and non-essential amino acids in human food? Give one example of each type. [2 marks]

Solution:

Concept:

- Essentiality of an amino acid refers to whether the human body can synthesise enough of it to meet its needs; it does not describe its chemical importance.
- Essential amino acids must be supplied by food, whereas non-essential amino acids can normally be synthesised by the body.

Step 1: Define essential amino acids and give an example Essential amino acids are those that the human body cannot synthesise in sufficient amounts to satisfy its requirements. They must therefore be obtained through dietary proteins. For example, valine is an essential amino acid. Digestion of food proteins supplies amino acids that the body uses for synthesis of its own proteins, so dietary provision of these essential amino acids is necessary.

Step 2: Define non-essential amino acids and give an example Non-essential amino acids are those that the human body can normally synthesise in adequate amounts. Therefore, they need not all be supplied separately in the diet. For example, glycine is a non-essential amino acid. The term non-essential refers only to the absence of an obligatory dietary supply under normal conditions; these amino acids still have important roles in proteins and metabolism.

Step 3: Conclusion Essential amino acids must be supplied in food; an example is valine. Non-essential amino acids can normally be synthesised by the human body; an example is glycine.

Quick Tip to Solve: Remember valine as essential and glycine as non-essential; classify them by the body's ability to synthesise them.

19. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and 8 F^- ions and that Ca^{2+} ions are arranged in a fcc lattice. The F^- ions fill all the tetrahedral holes in the face centred cubic lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3} . Use this information to calculate Avogadro's number. (Molar mass of $\text{CaF}_2 = 78.08 \text{ g mol}^{-1}$) [3 marks]

Solution:

Concept:

- The number of formula units per unit cell, Z , counts complete stoichiometric units, not the total number of ions.
- For a cubic unit cell of edge a , density $\rho = \frac{ZM}{N_A a^3}$, where M is molar mass and N_A is Avogadro's constant.

Step 1: Count formula units in the unit cell One formula unit of CaF_2 contains one Ca^{2+} ion and two F^- ions. The cell contains 4 calcium ions and 8 fluoride ions, hence $Z = 4$. This also agrees with the fcc arrangement: the calcium contribution is $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$, and its eight tetrahedral holes contain the eight fluoride ions. The total of 12 ions must not be used as Z .

Step 2: Calculate the volume and mass of one unit cell The edge is already in centimetres, matching the density unit. Thus

$$a^3 = (5.46 \times 10^{-8})^3 = 1.62771336 \times 10^{-22} \text{ cm}^3.$$

Therefore, the mass of one cell is

$$m_{\text{cell}} = \rho a^3 = 3.18(1.62771336 \times 10^{-22}) = 5.17612848 \times 10^{-22} \text{ g}.$$

Step 3: Calculate Avogadro's constant The same cell contains four formula units, so its mass is $4M/N_A$. Equating the two expressions and rearranging gives

$$N_A = \frac{ZM}{\rho a^3} = \frac{4 \times 78.08}{5.17612848 \times 10^{-22}} = 6.03385 \times 10^{23} \text{ mol}^{-1}.$$

The units reduce to $(\text{g mol}^{-1})/\text{g} = \text{mol}^{-1}$.

Step 4: Conclusion Avogadro's constant calculated from the data is $N_A \approx 6.03 \times 10^{23} \text{ mol}^{-1}$.

Quick Tip to Solve: For fluorite, use four CaF_2 formula units per cell; counting all twelve ions gives an incorrect factor of three.

20. A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (B.P. of pure benzene = 80.10°C and K_b for benzene = 2.53°C kg mol⁻¹) [3 marks]

Solution:

Concept:

- Boiling-point elevation is $\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = K_b m$, where m is the molality of a dilute solution of a nonvolatile nonelectrolyte.
- Molality is moles of solute per kilogram of solvent: $m = \frac{w_2/M_2}{w_1/1000}$, for masses w_1, w_2 in grams and solute molar mass M_2 .

Step 1: Find the elevation in boiling point The boiling point increases on dissolving methyl salicylate. Use the difference between the two temperatures, not the absolute boiling temperature:

$$\Delta T_b = 80.31 - 80.10 = 0.21^\circ\text{C}.$$

A temperature interval of 0.21 °C is also 0.21 K. The solute is treated as a molecular nonelectrolyte, so no dissociation factor is required.

Step 2: Find the molality and amount of solute Using the given boiling-point elevation constant,

$$m = \frac{\Delta T_b}{K_b} = \frac{0.21}{2.53} = 0.08300395 \text{ mol kg}^{-1}.$$

The solvent mass is 99.0 g = 0.0990 kg. Hence the amount of solute is

$$n_2 = m \times 0.0990 = 0.00821739 \text{ mol}.$$

Only the benzene mass belongs in this molality calculation; the mass of the whole solution is not used.

Step 3: Calculate molar mass The molar mass is the solute mass divided by its amount:

$$M_2 = \frac{1.25}{0.00821739} = 152.116 \text{ g mol}^{-1}.$$

Equivalently, direct substitution gives

$$M_2 = \frac{K_b w_2 1000}{\Delta T_b w_1} = \frac{2.53 \times 1.25 \times 1000}{0.21 \times 99.0}.$$

Both methods give the same value; retaining extra digits during the calculation avoids premature rounding.

Step 4: Conclusion The molar mass of methyl salicylate is approximately 152 g mol⁻¹.

Quick Tip to Solve: Use the 0.21 degree rise and 0.0990 kg of benzene; never substitute the boiling point or total solution mass.

21. What is the difference between multi molecular and macromolecular colloids? Give one example of each type. How are associated colloids different from these two types of colloids? [3 marks]

Solution:

Concept:

- Colloids have dispersed particles of colloidal dimensions, approximately 1–1000 nm; their classification here depends on how these particles are formed.
- A colloidal particle may be an aggregate of many small species, one giant molecule, or a concentration-dependent aggregate called a micelle.

Step 1: Multimolecular colloids In a multimolecular colloid, a large number of atoms or small molecules aggregate together to form a particle of colloidal size. The individual atoms or molecules are smaller than colloidal dimensions, and are held together in the aggregate by weak intermolecular forces. Thus each dispersed particle contains many distinct small species. For example, a gold sol contains colloidal aggregates of gold atoms; sulphur sol is another example.

Step 2: Macromolecular colloids In a macromolecular colloid, the molecule itself is so large that its dimensions fall in the colloidal range. Each dispersed particle is essentially one giant molecule, rather than an aggregate of small molecules. Such substances form colloidal solutions in a suitable solvent. Starch in water is an example; proteins and cellulose are other macromolecular substances. The essential distinction from a multimolecular colloid is therefore the size and identity of the individual molecular unit.

Step 3: Associated colloids Associated colloids behave as ordinary electrolytes at low concentrations, but their ions or molecules associate into micelles above the critical micelle concentration (CMC), at a suitable temperature. For soaps, micelle formation also requires a temperature above the Kraft temperature. Soap, such as sodium stearate in water, is an example. Its hydrophobic hydrocarbon tails gather inside the micelle while hydrophilic ionic heads face water. Unlike a macromolecular colloid, no single giant molecule constitutes the particle; unlike an ordinary multimolecular sol, micelle formation is characteristic only beyond the concentration threshold.

Step 4: Conclusion Multimolecular colloids contain aggregates of small species (gold sol); macromolecular colloids contain giant molecules (starch). Associated colloids, such as soap solutions, form micelles above the CMC under suitable temperature conditions.

Quick Tip to Solve: Identify whether the dispersed particle is many small species, one giant molecule, or a micelle formed above the CMC.

Describe how the following changes are brought about:

22(i). Pig iron into steel

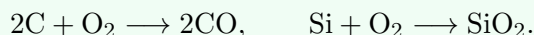
[3 marks total]

Solution:

Concept:

- Steel manufacture removes excess carbon and other impurities from pig iron by controlled oxidation, followed by adjustment of composition.
- Control the oxidation so that excess carbon is removed without converting all of the iron into oxide.

Step 1: (i) Convert pig iron into steel Blow oxygen through molten pig iron in a basic oxygen converter. Excess carbon is oxidised to gaseous carbon monoxide or carbon dioxide; silicon, manganese and other impurities are also oxidised. For example,



Added lime removes acidic oxide impurities in the slag, for example $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$. The carbon content is adjusted to the required steel composition; suitable alloying elements may also be added.

Step 2: Check the reasoning Control the oxidation so that excess carbon is removed without converting all of the iron into oxide. Slag separation and composition adjustment produce the required steel.

Step 3: Conclusion Controlled oxidation removes excess carbon and impurities from pig iron to produce steel.

Quick Tip to Solve: For pig iron to steel, remove excess carbon and acidic impurities, then adjust composition.

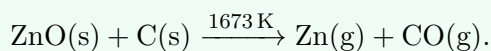
22(ii). Zinc oxide into metallic zinc

Solution:

Concept:

- Carbon can reduce zinc oxide to zinc at sufficiently high temperature.
- At the reduction temperature, zinc leaves the furnace as vapour.

Step 1: (ii) Reduce zinc oxide Heat ZnO with coke at about 1673 K:



Zinc is formed as vapour because the reaction temperature exceeds its boiling point. Cool and condense this vapour to obtain metallic zinc, separating it from the solid residue.

Step 2: Check the reasoning At the reduction temperature, zinc leaves the furnace as vapour. Condensation is therefore an essential final step in obtaining the metal rather than leaving it in the gaseous state.

Step 3: Conclusion Heat zinc oxide with coke and condense the resulting zinc vapour.

Quick Tip to Solve: Write carbon reduction of ZnO, followed by cooling because zinc forms as vapour.

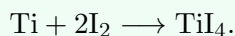
22(iii). Impure titanium into pure titanium

Solution:

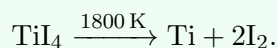
Concept:

- The van Arkel process purifies titanium by forming and decomposing a volatile iodide.
- The volatile iodide separates titanium from non-volatile impurities.

Step 1: (iii) Refine titanium In the van Arkel process, heat impure titanium with iodine in an evacuated vessel at about 523 K. Volatile titanium tetraiodide forms, leaving non-volatile impurities behind:



Pass this vapour over an electrically heated tungsten filament at about 1800 K. The iodide decomposes and pure titanium deposits on the filament:



Liberated iodine can participate again in iodide formation.

Step 2: Check the reasoning The volatile iodide separates titanium from non-volatile impurities. Its decomposition deposits the pure metal and releases iodine, completing the refining cycle.

Step 3: Conclusion Use the van Arkel process: form volatile TiI_4 , then decompose it on a hot filament.

Quick Tip to Solve: Show both titanium iodide formation and decomposition to explain purification.

OR

Describe the role of

22(i). NaCN in the extraction of gold from gold ore

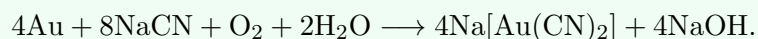
[3 marks total]

Solution:

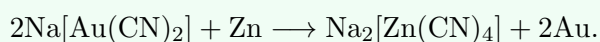
Concept:

- Cyanide extracts gold by forming a soluble coordination complex in the presence of oxygen; zinc subsequently displaces the dissolved gold.
- The role of cyanide is complex formation and leaching, not direct displacement of gold.

Step 1: (i) Sodium cyanide in gold extraction Dilute aqueous NaCN leaches gold from its ore in the presence of air. Gold is oxidised and stabilised as the soluble dicyanidoaurate(I) complex:



Gold is then recovered from the leach solution by displacement with zinc:



Step 2: Check the reasoning The role of cyanide is complex formation and leaching, not direct displacement of gold. Oxygen enables dissolution; zinc is used subsequently to recover the metal.

Step 3: Conclusion NaCN leaches gold as soluble dicyanidoaurate(I), from which zinc displaces gold.

Quick Tip to Solve: Keep the roles distinct: oxygen oxidises, cyanide complexes, and zinc recovers gold.

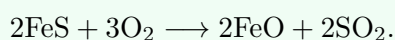
22(ii). SiO₂ in the extraction of copper from copper matte

Solution:

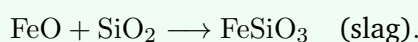
Concept:

- Silica is an acidic flux that reacts with basic iron(II) oxide to form iron silicate slag.
- Silica is the acidic flux and iron(II) oxide is the basic impurity.

Step 1: (ii) Silica in copper extraction When copper matte is blown with air, iron sulphide is preferentially oxidised to iron(II) oxide:



Added silica acts as an acidic flux. It reacts with the basic FeO to form fusible iron silicate slag, which can be separated from the copper-containing material:



Step 2: Check the reasoning Silica is the acidic flux and iron(II) oxide is the basic impurity. Their reaction converts the impurity into separable iron silicate slag rather than reducing copper directly.

Step 3: Conclusion SiO₂ removes FeO as iron silicate slag, FeSiO₃.

Quick Tip to Solve: Pair acidic silica with basic FeO and write the iron silicate slag equation.

22(iii). Iodine in the refining of zirconium

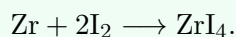
Write chemical equations for the involved reactions.

Solution:

Concept:

- Iodine converts zirconium into a volatile iodide for separation from non-volatile impurities.
- The metal is transported as a volatile iodide while non-volatile impurities remain behind.

Step 1: (iii) Iodine in zirconium refining In the van Arkel process, impure zirconium reacts with iodine to form volatile zirconium tetraiodide:



On a hot tungsten filament the iodide decomposes, depositing pure zirconium:



Step 2: Check the reasoning The metal is transported as a volatile iodide while non-volatile impurities remain behind. Pure zirconium deposits when the iodide reaches the much hotter filament.

Step 3: Conclusion Iodine refines zirconium through formation and thermal decomposition of volatile ZrI₄.

Quick Tip to Solve: For iodine refining, give a volatile iodide formation equation and its reverse on a hot filament.

23. How would you account for the following?

23(i). The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) series. [3 marks total]

Solution:

Concept:

- Poor shielding by 4f electrons increases effective nuclear attraction across the lanthanoids and causes lanthanoid contraction.
- The crucial shielding electrons are in the 4f subshell, which fills before the 5d series.

Step 1: (i) Similar radii of corresponding 4d and 5d elements The lanthanoid series intervenes before the 5d transition series. Across the lanthanoids, electrons enter the 4f subshell, whose electrons shield the nuclear charge poorly. The increasing effective nuclear charge therefore contracts the electron cloud; this is lanthanoid contraction. The contraction largely compensates for the size increase expected from the additional electron shell in a 5d atom. Consequently, corresponding 4d and 5d metals have almost equal atomic radii, as illustrated by zirconium and hafnium.

Step 2: Check the reasoning The crucial shielding electrons are in the 4f subshell, which fills before the 5d series. Their poor shielding offsets the size increase expected down a group.

Step 3: Conclusion Lanthanoid contraction makes corresponding 4d and 5d atomic radii nearly equal.

Quick Tip to Solve: For similar 4d and 5d sizes, identify the intervening 4f filling and lanthanoid contraction.

23(ii). The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ couple or $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.

Solution:

Concept:

- A reduction potential reflects the relative stability of the oxidised and reduced ions. Half-filled d^5 and appropriately stabilised d^3 configurations help explain the trends.
- A highly positive reduction potential indicates favourable reduction.

Step 1: (ii) More positive reduction potential of the manganese couple The relevant reduction is $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$. Here Mn^{3+} is $3d^4$, whereas Mn^{2+} has the especially stable half-filled $3d^5$ configuration. Reduction to this stable ion is strongly favoured, making the reduction potential highly positive. In contrast, Cr^{3+} has a stable $3d^3$ configuration; its reduction to Cr^{2+} , $3d^4$, loses this stability. Also, Fe^{3+} is already half-filled $3d^5$, whereas Fe^{2+} is $3d^6$. Thus the manganese reduction gains a half-filled configuration while the iron reduction loses one, explaining the much greater positive value for manganese.

Step 2: Check the reasoning A highly positive reduction potential indicates favourable reduction. Manganese gains the special half-filled stability in its reduced ion, unlike the chromium and iron comparisons.

Step 3: Conclusion Reduction of Mn^{3+} produces especially stable half-filled $3d^5$ Mn^{2+} , giving a

strongly positive potential.

Quick Tip to Solve: Compare the d-electron counts before and after reduction; manganese changes from d^4 to d^5 .

23(iii). The highest oxidation state of a metal is exhibited in its oxide or fluoride.

Solution:

Concept:

- Oxygen and fluorine are small, strongly electronegative elements that stabilise high positive oxidation states of metals by strong bonding.
- Strong metal-ligand bonds compensate for the energetic cost of producing a high formal oxidation state.

Step 1: (iii) Highest oxidation states in oxides and fluorides Oxygen and fluorine have high electronegativities and small sizes, so they form strong bonds with metals and stabilise large positive oxidation states. Fluorine stabilises these states through strong metal-fluorine bonds, while oxygen can additionally form multiple bonds with a metal. For example, manganese attains +7 in Mn_2O_7 , chromium attains +6 in CrO_3 , and vanadium attains +5 in VF_5 . Such strong bonding makes high oxidation states accessible in their oxides or fluorides.

Step 2: Check the reasoning Strong metal-ligand bonds compensate for the energetic cost of producing a high formal oxidation state. Oxygen can further stabilise such states through multiple bonding.

Step 3: Conclusion Highly electronegative oxygen and fluorine stabilise high oxidation states through strong bonding.

Quick Tip to Solve: Link high oxidation state to strong bonds with small, highly electronegative oxygen or fluorine.

24(i). State one use each of DDT and iodoform.

[3 marks total]

Solution:

Concept:

- DDT is an organochlorine insecticide, whereas iodoform has been used as an antiseptic.
- These uses distinguish an insect-control compound from an antiseptic.

Step 1: State the uses DDT is used as an insecticide to control insects such as mosquitoes. Iodoform, CHI_3 , is used as an antiseptic for dressing wounds. Its antiseptic action is associated with the liberation of iodine; the liberated iodine provides the antiseptic action.

Step 2: Check the reasoning These uses distinguish an insect-control compound from an antiseptic. Iodoform has the formula CHI_3 ; its antiseptic effect is attributed to iodine released from it.

Step 3: Conclusion DDT is an insecticide; iodoform has been used as an antiseptic for wound dressings.

Quick Tip to Solve: Associate DDT with insect control and iodoform with antiseptic dressings.

Which compound in the following couples will react faster in S_N2 displacement and why?

24(ii)(a). 1-Bromopentane or 2-bromopentane

Solution:

Concept:

- An S_N2 reaction is a single-step nucleophilic substitution involving backside attack at the carbon bonded to the leaving group. Steric crowding at this carbon reduces the reaction rate.
- For comparable alkyl halides with the same leaving group, the usual reactivity order is primary > secondary $\gg$ tertiary.

Step 1: Compare the two bromopentanes In 1-bromopentane, bromine is attached to a primary carbon, while in 2-bromopentane it is attached to a secondary carbon. The primary carbon offers less steric hindrance to backside attack by the nucleophile. Consequently, 1-bromopentane reacts faster in S_N2 displacement. Both compounds have bromide as the leaving group, so the difference is principally due to their substitution at the reacting carbon.

Step 2: Check the reasoning The leaving group is the same in both compounds. Compare steric crowding at the carbon directly attached to bromine rather than the overall chain length.

Step 3: Conclusion 1-Bromopentane reacts faster in S_N2 displacement because it is primary and less hindered.

Quick Tip to Solve: Identify whether the bromine-bearing carbon is primary or secondary before comparing rates.

24(ii)(b). 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane

Solution:

Concept:

- An S_N2 reaction is a single-step nucleophilic substitution involving backside attack at the carbon bonded to the leaving group. Steric crowding at this carbon reduces the reaction rate.
- For comparable alkyl halides with the same leaving group, the usual reactivity order is primary > secondary $\gg$ tertiary.

Step 1: Compare the two methylbutanes 1-Bromo-2-methylbutane has a primary carbon bearing bromine, whereas 2-bromo-2-methylbutane has a tertiary carbon bearing bromine. Although branching next to the primary carbon slows attack somewhat, it is much less obstructed than the tertiary centre. Thus 1-bromo-2-methylbutane reacts faster. The tertiary halide is extremely resistant to the backside approach needed for an S_N2 reaction.

Step 2: Check the reasoning Branching next to the primary centre may slow its reaction, but the tertiary centre prevents effective backside approach much more strongly.

Step 3: Conclusion 1-Bromo-2-methylbutane reacts faster in S_N2 displacement than the tertiary halide.

Quick Tip to Solve: Count substituents on the Br-bearing carbon: primary remains far more accessible than tertiary.

25. In the following cases rearrange the compounds as directed:

25(i). In an increasing order of basic strength: $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2

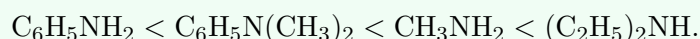
[3 marks total]

Solution:

Concept:

- Basic strength increases with the availability of the nitrogen lone pair for protonation. Alkyl groups donate electron density by the $+I$ effect, while conjugation with a benzene ring reduces lone-pair availability.
- In aqueous solution, both electron donation and solvation of the conjugate acid influence the basicity of aliphatic amines.

Step 1: Arrange part (i) in increasing basic strength The lone pair of aniline is delocalised into the benzene ring, making it less available for protonation. The two methyl groups on nitrogen increase electron density in $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, making it more basic than aniline. Aliphatic amines are stronger bases than these aromatic amines. Diethylamine is stronger than methylamine because of the electron donation of two ethyl groups and favourable solvation. Hence the increasing order is



Step 2: Check the reasoning Compare aromatic and aliphatic amines first, then compare the members within each class. Resonance decreases basicity, while alkyl donation increases it.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 < \text{CH}_3\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$.

Quick Tip to Solve: Place the aromatic amines before the aliphatic amines in increasing basic strength.

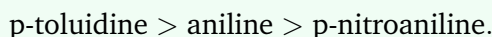
25(ii). In a decreasing order of basic strength: Aniline, p-nitroaniline and p-toluidine

Solution:

Concept:

- Basic strength increases with the availability of the nitrogen lone pair for protonation. Alkyl groups donate electron density by the $+I$ effect, while conjugation with a benzene ring reduces lone-pair availability.
- The amino nitrogen is the proton-accepting site.

Step 1: Arrange part (ii) in decreasing basic strength The para-methyl group in p-toluidine donates electron density and increases basicity relative to aniline. The para-nitro group withdraws electron density by inductive and resonance effects, decreasing availability of the nitrogen lone pair. Therefore,



Step 2: Check the reasoning The amino nitrogen is the proton-accepting site. A donor raises its electron density, whereas the strongly withdrawing nitro substituent reduces lone-pair availability.

Step 3: Conclusion p-toluidine > aniline > p-nitroaniline in decreasing basic strength.

Quick Tip to Solve: The para methyl group increases basicity, while the para nitro group decreases it.

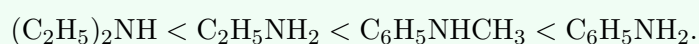
25(iii). In an increasing order of pK_b values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Solution:

Concept:

- Basic strength increases with the availability of the nitrogen lone pair for protonation. Alkyl groups donate electron density by the $+I$ effect, while conjugation with a benzene ring reduces lone-pair availability.
- $pK_b = -\log K_b$; therefore, a stronger base has a larger K_b and a smaller pK_b .
- In aqueous solution, both electron donation and solvation of the conjugate acid influence the basicity of aliphatic amines.

Step 1: Arrange part (iii) in increasing pK_b Diethylamine is a stronger aqueous base than ethylamine. Both are stronger than the aromatic amines. N-Methylaniline is more basic than aniline owing to the electron-donating methyl group attached to nitrogen. Since increasing pK_b means decreasing basic strength, the required order is



Step 2: Check the reasoning The numerical direction is opposite to base strength: because $pK_b = -\log K_b$, the strongest base must appear first in increasing pK_b .

Step 3: Conclusion $(C_2H_5)_2NH < C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$ in increasing pK_b .

Quick Tip to Solve: Arrange decreasing basic strength first; that sequence is increasing pK_b .

26. Give one example each of

26(i). addition polymers

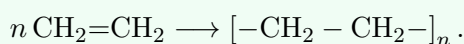
[3 marks total]

Solution:

Concept:

- Addition polymerisation joins unsaturated monomers without elimination of a small molecule.
- Each ethene monomer contributes both carbon atoms to the polymer chain.

Step 1: Give an addition polymer Polythene is an addition polymer formed by repeated addition of ethene molecules. The carbon-carbon double bond opens and the monomers join to form a long chain:



No small molecule is eliminated during formation of the chain.

Step 2: Check the reasoning Each ethene monomer contributes both carbon atoms to the polymer chain. Only the double bond opens; no water or other small molecule is lost.

Step 3: Conclusion Polythene is an addition polymer obtained from ethene.

Quick Tip to Solve: An alkene opening its double bond without eliminating a small molecule gives an addition polymer.

26(ii). condensation polymers

Solution:

Concept:

- Condensation polymerisation joins bifunctional or polyfunctional monomers with elimination of small molecules such as water.
- The repeating amide linkage identifies nylon as a polyamide.

Step 1: Give a condensation polymer Nylon-6,6 is a condensation polymer. It is obtained from hexamethylenediamine, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$, and adipic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$. Amine and carboxylic acid groups react to form amide linkages, $-\text{CO}-\text{NH}-$, with elimination of water. Its repeating unit may be represented as



Step 2: Check the reasoning The repeating amide linkage identifies nylon as a polyamide. Both monomers carry two functional groups, allowing repeated condensation to build a long chain.

Step 3: Conclusion Nylon-6,6 is a condensation polymer of hexamethylenediamine and adipic acid.

Quick Tip to Solve: For nylon-6,6 remember a diamine and a diacid, each containing six carbon atoms.

26(iii). copolymers

Solution:

Concept:

- A copolymer contains units derived from two different monomers; this classification concerns monomer identity rather than whether the reaction is addition or condensation.
- The term copolymer refers to the use of different monomer species.

Step 1: Give a copolymer Buna-S is a copolymer made from 1,3-butadiene and styrene. Its chain therefore contains structural units derived from both monomers. Here the two monomers are $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ and $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$. Buna-S is also called styrene-butadiene rubber. It is an addition copolymer, illustrating that the classifications in the question can overlap.

Step 2: Check the reasoning The term copolymer refers to the use of different monomer species. In Buna-S these are styrene and butadiene, rather than repeated units of a single monomer.

Step 3: Conclusion Buna-S, made from 1,3-butadiene and styrene, is a copolymer.

Quick Tip to Solve: Remember the S in Buna-S as styrene, the second monomer paired with butadiene.

27. What are analgesic medicines? How are they classified and when are they commonly recommended for use? [3 marks]

Solution:

Concept:

- Analgesics are medicines that reduce or abolish pain without causing loss of consciousness, mental confusion, incoordination or paralysis, or other disturbances of the nervous system.
- Analgesics are classified as non-narcotic (non-addictive) and narcotic (addictive) analgesics, according to their action and dependence-producing potential.

Step 1: Non-narcotic analgesics and their uses Aspirin and paracetamol are familiar non-narcotic analgesics. They relieve relatively mild pain, such as a headache or toothache, and are commonly recommended for ordinary aches and pains. Aspirin also relieves pain associated with inflammation, as in arthritis. These medicines can also reduce fever, so they are described as antipyretics. They do not produce the addiction characteristic of narcotic analgesics when used appropriately.

Step 2: Narcotic analgesics and their uses Morphine and its related drugs are narcotic analgesics. In medicinal doses they relieve severe pain and produce sleep; in larger doses they can cause stupor and unconsciousness. They are commonly recommended for severe pain, for example after an operation, in terminal cancer, or in cardiac pain. Because repeated use can cause dependence, their administration requires medical supervision. Their use is reserved for pain sufficiently severe to warrant their stronger action.

Step 3: Conclusion Analgesics relieve pain. Non-narcotic analgesics, such as aspirin and paracetamol, are used for ordinary mild pain and fever, whereas narcotic analgesics, such as morphine, are used under medical supervision for severe pain.

Quick Tip to Solve: Link each class to one example and the severity of pain: aspirin for ordinary pain; morphine for severe pain.

28(a). State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law. [5 marks total]

Solution:

Concept:

- Kohlrausch's law states that at infinite dilution each ion makes a definite, independent contribution to the molar conductivity of an electrolyte, irrespective of the other ion present.
- If an electrolyte gives ions with stoichiometric coefficients ν_+ and ν_- , its limiting molar conductivity is $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$, where λ_i^0 is the limiting ionic molar conductivity of ion i .

Step 1: (a) Apply the law to acetic acid At infinite dilution the ions of acetic acid contribute independently to conduction. Since one formula unit produces one hydrogen ion and one acetate ion, the required expression is

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \lambda^0(\text{H}^+) + \lambda^0(\text{CH}_3\text{COO}^-).$$

The statement concerns the limiting value at infinite dilution. Acetic acid is a weak electrolyte, so its molar conductivity changes markedly as dilution increases and its ionisation increases. We therefore obtain its limiting value from strong-electrolyte data using the independent contributions of the same ions.

Step 2: Check the reasoning For a general electrolyte, $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$, where ν_i counts each ion. The contribution of a given ion is independent of its counter-ion. In acetic acid, both coefficients are one, so no additional factors are needed.

Step 3: Conclusion $\Lambda_m^0(\text{CH}_3\text{COOH}) = \lambda^0(\text{H}^+) + \lambda^0(\text{CH}_3\text{COO}^-)$, by independent ionic migration at infinite dilution.

Quick Tip to Solve: At infinite dilution add the individual ionic contributions with their stoichiometric coefficients.

28(b). Calculate Λ_m^0 for acetic acid. Given that $\Lambda_m^0(\text{HCl}) = 426 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^0(\text{NaCl}) = 126 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^0(\text{CH}_3\text{COONa}) = 91 \text{ S cm}^2 \text{ mol}^{-1}$

Solution:

Concept:

- Kohlrausch's law states that at infinite dilution each ion makes a definite, independent contribution to the molar conductivity of an electrolyte, irrespective of the other ion present.
- If an electrolyte gives ions with stoichiometric coefficients ν_+ and ν_- , its limiting molar conductivity is $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$, where λ_i^0 is the limiting ionic molar conductivity of ion i .

Step 1: (b) Combine the given limiting conductivities Write each of the supplied strong-electrolyte values as a sum of ionic contributions:

$$\begin{aligned}\Lambda_m^0(\text{HCl}) &= \lambda^0(\text{H}^+) + \lambda^0(\text{Cl}^-), \\ \Lambda_m^0(\text{CH}_3\text{COONa}) &= \lambda^0(\text{CH}_3\text{COO}^-) + \lambda^0(\text{Na}^+), \\ \Lambda_m^0(\text{NaCl}) &= \lambda^0(\text{Na}^+) + \lambda^0(\text{Cl}^-).\end{aligned}$$

Add the first two expressions and subtract the third. The sodium and chloride contributions cancel exactly, leaving the hydrogen and acetate contributions required for acetic acid. Thus

$$\begin{aligned}\Lambda_m^0(\text{CH}_3\text{COOH}) &= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) \\ &= 426 + 91 - 126 \\ &= 391 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

All supplied values use the same conductivity units, so they can be combined directly without a unit conversion.

Step 2: Check the reasoning Check the combination by cancelling ions before arithmetic. Sodium and chloride cancel, leaving one hydrogen ion and one acetate ion; all conductivities use the same units.

Step 3: Conclusion $\Lambda_m^0(\text{CH}_3\text{COOH}) = 391 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Add the HCl and sodium acetate values, then subtract the NaCl value.

28(a). Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery. [5 marks total]

Solution:

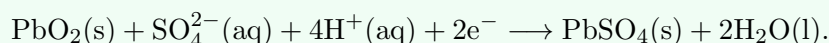
Concept:

- In a discharging lead storage battery, lead is oxidised at the negative anode and lead dioxide is reduced at the positive cathode; sulphuric acid is consumed.
- Balance atoms and charge in each half-reaction.

Step 1: (a) Write the battery half-reactions during discharge At the anode, lead loses two electrons and forms lead sulphate:

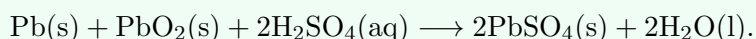


At the cathode, lead dioxide is reduced in acidic solution:



The electrons released by the lead electrode travel through the external circuit to the lead dioxide electrode. Both electrodes become coated with lead sulphate as discharge proceeds.

Step 2: (a) Obtain the overall battery reaction Add the two half-reactions and cancel the two electrons. Combining hydrogen and sulphate ions as sulphuric acid gives



Thus sulphuric acid concentration decreases during discharge. Charging reverses this overall reaction and regenerates the original electrode materials.

Step 3: Check the result Balance atoms and charge in each half-reaction. Both electrodes yield lead sulphate during discharge; two electrons cancel when the half-reactions are added.

Step 4: Conclusion $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$ is the overall discharge reaction.

Quick Tip to Solve: In discharge, both electrode materials become lead sulphate and sulphuric acid is consumed.

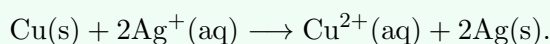
28(b). A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell. (Given $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$)

Solution:

Concept:

- The reduction potential determines the cathode. The Nernst equation at 298 K is $E = E^\circ - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- The calculated quotient is greater than one, consistently lowering the potential below its standard value.

Step 1: (b) Identify the copper-silver cell reaction Since $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V}$ exceeds $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34 \text{ V}$, silver ions are reduced and copper is oxidised:



Here $n = 2$, and

$$E_{\text{cell}}^\circ = 0.80 - 0.34 = 0.46 \text{ V}, \quad Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}.$$

Pure solid metals do not enter the reaction quotient because their activities are unity.

Step 2: (b) Apply the Nernst equation Using the usual room-temperature form of the Nernst equation, with concentrations in mol L^{-1} ,

$$0.422 = 0.460 - \frac{0.0591}{2} \log \frac{0.10}{[\text{Ag}^+]^2}.$$

Hence

$$\begin{aligned} \log \frac{0.10}{[\text{Ag}^+]^2} &= \frac{2(0.460 - 0.422)}{0.0591} = 1.286, \\ \frac{0.10}{[\text{Ag}^+]^2} &= 10^{1.286} \simeq 19.3, \\ [\text{Ag}^+] &= \sqrt{\frac{0.10}{19.3}} \simeq 0.0720 \text{ mol L}^{-1}. \end{aligned}$$

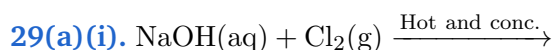
The quotient exceeds unity, so the measured cell potential is below the standard value, consistently with the given data.

Step 3: Check the result The calculated quotient is greater than one, consistently lowering the potential below its standard value. Keep the square on silver-ion concentration when solving.

Step 4: Conclusion $[\text{Ag}^+] \simeq 7.2 \times 10^{-2} \text{ mol L}^{-1}$.

Quick Tip to Solve: Balance two silver ions per copper atom before writing the Nernst reaction quotient.

Complete the following chemical equations:



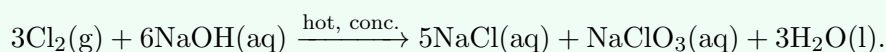
[5 marks total]

Solution:

Concept:

- Chlorine disproportionates in hot concentrated alkali to chloride and chlorate.
- The chlorine atoms balance as six on either side.

Step 1: (a)(i) Chlorine with hot concentrated sodium hydroxide The balanced equation is



Chlorine in oxidation state zero is reduced to chloride, -1 , and oxidised to chlorate, $+5$. Five chlorine atoms each gain one electron while one loses five electrons. This explains the chloride-to-chlorate ratio of five to one. The hot concentrated conditions favour chlorate formation.

Step 2: Check the reasoning The chlorine atoms balance as six on either side. The oxidised chlorine is chlorate, not hypochlorite, because the alkali is hot and concentrated.

Step 3: Conclusion $3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$.

Quick Tip to Solve: Hot concentrated alkali gives chlorate; cold dilute alkali would give hypochlorite.

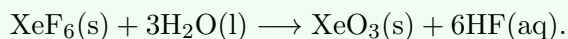
29(a)(ii). $\text{XeF}_6(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow$

Solution:

Concept:

- Complete hydrolysis replaces all xenon-fluorine bonds with xenon-oxygen bonds, releasing HF.
- Xenon remains in oxidation state +6.

Step 1: (a)(ii) Hydrolysis of xenon hexafluoride Complete hydrolysis gives xenon trioxide and hydrogen fluoride:



All six fluorine atoms leave as HF, and the three oxygen atoms from water form xenon trioxide. Xenon's oxidation state remains +6; this is hydrolysis rather than a redox reaction.

Step 2: Check the reasoning Xenon remains in oxidation state +6. Six fluorine atoms require six HF molecules, and three water molecules supply the required oxygen and hydrogen.

Step 3: Conclusion $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$.

Quick Tip to Solve: For complete hydrolysis replace all six F atoms and balance them as six HF.

How would you account for the following?

29(b)(i). The value of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen.

Solution:

Concept:

- Electron gain enthalpy depends on orbital size and electron-electron repulsion; compound formation enthalpy depends on the balance of bonds broken and formed.
- This is an exception to a simple size-only electron-affinity trend.

Step 1: (b)(i) Compare sulphur and oxygen electron gain enthalpies The incoming electron enters the compact $2p$ subshell in oxygen but the larger $3p$ subshell in sulphur. Oxygen's small size causes stronger repulsion between the incoming electron and the electrons already present. In sulphur, the added electron experiences less electron-electron repulsion in the more spacious orbital. Electron addition therefore releases more energy for sulphur: its electron gain enthalpy is more negative, or greater in magnitude with a negative sign, than that of oxygen.

Step 2: Check the reasoning This is an exception to a simple size-only electron-affinity trend. The

compact oxygen orbital increases electron repulsion enough to reduce the energy released.

Step 3: Conclusion Sulphur has a more negative electron gain enthalpy because its larger 3p orbital reduces electron repulsion.

Quick Tip to Solve: Compare oxygen 2p crowding with the more spacious sulphur 3p orbital.

29(b)(ii). NF_3 is an exothermic compound but NCl_3 is endothermic compound.

Solution:

Concept:

- Formation enthalpy compares the energy absorbed in breaking reactant bonds with the energy released in forming product bonds.
- Compare the net balance of bond breaking and formation, rather than electronegativity alone.

Step 1: (b)(ii) Explain the formation enthalpies of NF_3 and NCl_3 Forming these compounds from their elements requires breaking reactant bonds, including the strong nitrogen-nitrogen triple bond, and releases energy as nitrogen-halogen bonds form. The small fluorine atom forms strong N – F bonds; the total energy released on their formation exceeds the energy needed to break the reactant bonds. Thus $\Delta_f H^\circ(\text{NF}_3) < 0$. The N – Cl bonds are weaker, owing to less effective orbital overlap with the larger chlorine atom. Their formation does not compensate for the energy required to break reactant bonds, giving $\Delta_f H^\circ(\text{NCl}_3) > 0$.

Step 2: Check the reasoning Compare the net balance of bond breaking and formation, rather than electronegativity alone. Strong N–F bond formation provides the decisive energy release.

Step 3: Conclusion Strong N–F bonds make NF_3 formation exothermic; weaker N–Cl bonds leave NCl_3 formation endothermic.

Quick Tip to Solve: Explain formation enthalpy through energy needed to break bonds versus energy released on forming them.

29(b)(iii). ClF_3 molecule has a T-shaped structure and not a trigonal planar one.

Solution:

Concept:

- VSEPR theory counts both bond pairs and lone pairs around the central atom; lone pairs preferentially occupy positions with fewer strong repulsions.
- Molecular shape describes only the atom positions, not all electron pairs.

Step 1: (b)(iii) Explain the T shape of ClF_3 Chlorine has seven valence electrons. Forming three single bonds to fluorine leaves two lone pairs on chlorine, so there are five electron pairs around the central atom: AX_3E_2 . The electron-pair arrangement is trigonal bipyramidal, conventionally described using sp^3d hybridisation. Both lone pairs occupy equatorial positions to minimise the number of 90° repulsions. The three fluorine atoms then occupy two axial positions and one equatorial position, producing a T-shaped molecule. A trigonal planar molecular arrangement would ignore these two

lone pairs and is therefore incorrect.

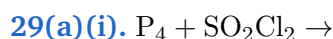
Step 2: Check the reasoning Molecular shape describes only the atom positions, not all electron pairs. Removing the two equatorial lone-pair positions from a trigonal bipyramid leaves a T.

Step 3: Conclusion ClF_3 is AX_3E_2 , with two equatorial lone pairs and a T-shaped molecular geometry.

Quick Tip to Solve: Count three bond pairs plus two lone pairs before choosing the molecular shape.

OR

Complete the following chemical reaction equations:



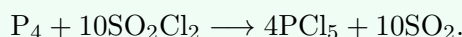
[5 marks total]

Solution:

Concept:

- Sulphuryl chloride, SO_2Cl_2 , acts as a chlorinating agent; phosphorus forms phosphorus pentachloride.
- Balance phosphorus first: four phosphorus atoms produce four pentachloride molecules.

Step 1: (a)(i) Chlorination of phosphorus The balanced reaction is



Each of the four phosphorus atoms forms five P-Cl bonds. The ten molecules of sulphuryl chloride supply twenty chlorine atoms, while their sulphur and oxygen leave as ten molecules of sulphur dioxide.

Step 2: Check the reasoning Balance phosphorus first: four phosphorus atoms produce four pentachloride molecules. These need twenty chlorine atoms, supplied by ten sulphuryl chloride molecules.

Step 3: Conclusion $\text{P}_4 + 10\text{SO}_2\text{Cl}_2 \longrightarrow 4\text{PCl}_5 + 10\text{SO}_2.$

Quick Tip to Solve: Four phosphorus atoms require twenty chlorine atoms for phosphorus pentachloride.



Solution:

Concept:

- Hydrolysis of XeF_4 is accompanied by disproportionation of xenon from oxidation state +4 to 0 and +6.
- Check oxygen carefully: twelve oxygen atoms become six in xenon trioxide and six in three oxygen molecules.

Step 1: (a)(ii) Hydrolysis of xenon tetrafluoride On hydrolysis, xenon tetrafluoride gives xenon

trioxide, xenon, hydrogen fluoride and oxygen:



The equation conserves six xenon atoms, twenty-four fluorine atoms and twenty-four hydrogen atoms. Its twelve oxygen atoms occur as six in xenon trioxide and six in oxygen gas. Xenon is both oxidised and reduced in this reaction.

Step 2: Check the reasoning Check oxygen carefully: twelve oxygen atoms become six in xenon trioxide and six in three oxygen molecules. Both elemental xenon and oxygen must appear.

Step 3: Conclusion $6\text{XeF}_4 + 12\text{H}_2\text{O} \longrightarrow 2\text{XeO}_3 + 4\text{Xe} + 24\text{HF} + 3\text{O}_2.$

Quick Tip to Solve: Include xenon, xenon trioxide and oxygen before balancing HF and water.

Explain the following observations giving appropriate reasons:

29(b)(i). The stability of +5 oxidation state decreases down the group in group 15 of the periodic table.

Solution:

Concept:

- The inert pair effect is the increasing reluctance of the valence ns^2 pair to participate in bonding down a group.
- The relative stabilisation is of the lower +3 state.

Step 1: (b)(i) Decreasing stability of the +5 state Group 15 elements have valence configuration ns^2np^3 . The +5 oxidation state involves all five valence electrons, whereas the +3 state leaves the ns^2 pair uninvolved. Down the group, the inert pair effect becomes more pronounced because inner d and f electrons shield poorly and the ns^2 pair is held relatively strongly. Consequently, the +3 state becomes more stable relative to +5, so the stability of the +5 state decreases.

Step 2: Check the reasoning The relative stabilisation is of the lower +3 state. Leaving the paired s electrons unused becomes increasingly favourable down the group.

Step 3: Conclusion The increasing inert pair effect stabilises +3 relative to +5 down group 15.

Quick Tip to Solve: For group 15, compare use of all five valence electrons with retention of the ns^2 pair.

29(b)(ii). Solid phosphorus pentachloride behaves as an ionic compound.

Solution:

Concept:

- A solid is ionic when its lattice consists of cations and anions held by electrostatic forces.
- The ionic formula combines equal numbers of singly charged cations and anions.

Step 1: (b)(ii) Ionic nature of solid phosphorus pentachloride In the solid state phosphorus pen-

tachloride exists as a lattice of tetrahedral $[\text{PCl}_4]^+$ cations and octahedral $[\text{PCl}_6]^-$ anions:



Thus the solid has ionic constituents even though an isolated gaseous PCl_5 molecule is covalent.

Step 2: Check the reasoning The ionic formula combines equal numbers of singly charged cations and anions. The resulting total composition is two phosphorus atoms and ten chlorine atoms.

Step 3: Conclusion Solid PCl_5 contains $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$ ions.

Quick Tip to Solve: Distinguish covalent gaseous phosphorus pentachloride from its ionic solid lattice.

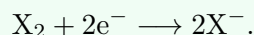
29(b)(iii). Halogens are strong oxidizing agents.

Solution:

Concept:

- An oxidising agent accepts electrons and is itself reduced; halogens readily form halide ions.
- An oxidising agent accepts electrons and is itself reduced.

Step 1: (b)(iii) Oxidising action of halogens Halogen atoms have valence configuration ns^2np^5 and need one electron to attain a stable noble-gas configuration. Their high electron affinity and favourable overall reduction energetics enable them to accept electrons from other substances:



The other substance loses electrons and is oxidised, while the halogen is reduced. This explains their strong oxidising action; in aqueous solution it generally decreases from fluorine to iodine.

Step 2: Check the reasoning An oxidising agent accepts electrons and is itself reduced. In the halogen half-reaction two atoms gain one electron each, forming two halide ions.

Step 3: Conclusion Halogens readily accept electrons to form halide ions and therefore oxidise other substances.

Quick Tip to Solve: Write $\text{X}_2 + 2\text{e}^- \longrightarrow 2\text{X}^-$ to show why the halogen acts as an oxidant.

30(a). Explain the mechanism of a nucleophilic attack on the carbonyl group of an aldehyde or a ketone. [5 marks total]

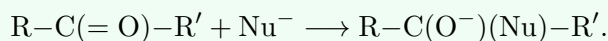
Solution:

Concept:

- The carbonyl bond is polar: oxygen is δ^- and carbon is δ^+ . A nucleophile donates an electron pair to the electrophilic carbonyl carbon.
- The nucleophile attacks carbon because the polar carbonyl bond makes carbon electrophilic.

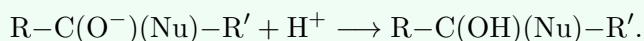
Step 1: (a) Nucleophilic attack and the tetrahedral intermediate Let the carbonyl compound be

$\text{R}-\text{C}(=\text{O})-\text{R}'$, where $\text{R}' = \text{H}$ for an aldehyde. The nucleophile Nu^- donates a lone pair to the carbonyl carbon. Simultaneously the carbon-oxygen π -electron pair shifts onto oxygen:



The carbon changes from trigonal planar sp^2 geometry to tetrahedral sp^3 geometry. The electron-pair movements are from the nucleophile to carbon, and from the carbonyl double bond to oxygen; oxygen is not the site of nucleophilic attack.

Step 2: (a) Protonation of the intermediate The negatively charged oxygen of the alkoxide intermediate accepts a proton from the medium:



This produces the nucleophilic addition product containing both the nucleophile and an OH group on the former carbonyl carbon. For a weak neutral nucleophile under acidic conditions, prior protonation of carbonyl oxygen increases the electrophilicity of carbon; attack is then followed by deprotonation.

Step 3: Check the result The nucleophile attacks carbon because the polar carbonyl bond makes carbon electrophilic. The pi electrons move to oxygen as the new carbon-nucleophile bond forms.

Step 4: Conclusion Attack at carbonyl carbon gives a tetrahedral alkoxide, which is protonated to the addition product.

Quick Tip to Solve: Track both electron movements: nucleophile to carbon and carbonyl pi bond to oxygen.

30(b). An organic compound (A) (molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid also produced (B). On dehydration (C) gives but-1-ene. Write the equations for the reactions involved.

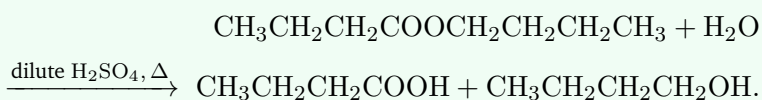
Solution:

Concept:

- Acid-catalysed ester hydrolysis gives a carboxylic acid and an alcohol. A primary alcohol oxidises to the corresponding carboxylic acid without changing its carbon skeleton.
- The ester contains four carbons in its acid residue and four in its alkyl residue.

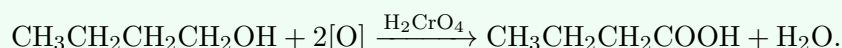
Step 1: (b) Identify the alcohol and acid Dehydration of alcohol (C) gives but-1-ene, and oxidation of (C) gives a carboxylic acid. Thus (C) is the primary alcohol butan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, rather than a secondary alcohol, which would oxidise to a ketone. Its oxidation product (B) is butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$. Since hydrolysis of (A) gives this acid and this alcohol, (A) is butyl butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. Its formula is $\text{C}_8\text{H}_{16}\text{O}_2$, in agreement with the question.

Step 2: (b) Write the hydrolysis equation The ester linkage cleaves on heating with dilute sulphuric acid:

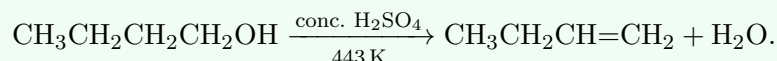


The products are (B) and (C), respectively; the acid acts as a catalyst.

Step 3: (b) Oxidation and dehydration of the alcohol Chromic acid oxidises the primary alcohol completely to the acid:



On dehydration, elimination of water from the terminal OH group and the adjacent carbon gives but-1-ene:



These reactions establish the same four-carbon chain in the alcohol, acid and alkene.

Step 4: Check the result The ester contains four carbons in its acid residue and four in its alkyl residue. Hydrolysis therefore gives the same four-carbon skeleton established independently by oxidation and dehydration.

Step 5: Conclusion (A) Butyl butanoate; (B) butanoic acid; (C) butan-1-ol.

Quick Tip to Solve: Identify the primary alcohol from oxidation and dehydration, then reconstruct its ester with the acid.

OR

Give chemical tests to distinguish between the following pairs of compounds:

30(a)(i). Ethanal and Propanal

[5 marks total]

Solution:

Concept:

- The iodoform test detects the $\text{CH}_3\text{CO}-$ group: ethanal gives a yellow precipitate of CHI_3 , whereas propanal does not.
- The test must distinguish the pair: both compounds respond to general aldehyde tests, but only ethanal possesses the required methyl-carbonyl arrangement.

Step 1: (a)(i) Distinguish ethanal and propanal Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3 , while propanal gives no such precipitate. The reaction for ethanal is



Ethanal has the required methyl group directly attached to its carbonyl carbon. Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, lacks this structural feature. Tests such as Tollens' test would not distinguish them because both are aldehydes.

Step 2: Check the reasoning The test must distinguish the pair: both compounds respond to general aldehyde tests, but only ethanal possesses the required methyl-carbonyl arrangement.

Step 3: Conclusion Ethanal gives yellow CHI_3 with iodine and alkali; propanal does not.

Quick Tip to Solve: Use iodoform rather than Tollens reagent because both compounds are aldehydes.

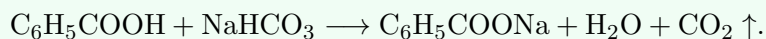
30(a)(ii). Phenol and Benzoic acid

Solution:

Concept:

- Carboxylic acids liberate carbon dioxide from aqueous sodium hydrogencarbonate; phenol is insufficiently acidic to do so.
- Gas evolution is the observation that identifies the carboxylic acid.

Step 1: (a)(ii) Distinguish phenol and benzoic acid Add aqueous sodium hydrogencarbonate to separate samples. Benzoic acid produces brisk effervescence of carbon dioxide:



Phenol gives no effervescence because it is weaker than carbonic acid and cannot displace carbon dioxide from hydrogencarbonate. Thus gas evolution identifies benzoic acid.

Step 2: Check the reasoning Gas evolution is the observation that identifies the carboxylic acid. Phenol does not release carbon dioxide from aqueous sodium hydrogencarbonate.

Step 3: Conclusion Benzoic acid effervesces with NaHCO_3 ; phenol does not.

Quick Tip to Solve: Use bicarbonate to distinguish the stronger carboxylic acid from phenol.

How will you bring about the following conversions?

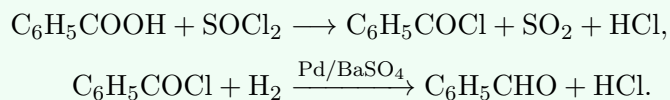
30(b)(i). Benzoic acid to benzaldehyde

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride to an aldehyde. Aldol condensation joins two ethanal molecules, while reduction followed by dehydration converts a ketone to an alkene.
- Direct strong reduction of the acid can overshoot to an alcohol.

Step 1: (b)(i) Convert benzoic acid to benzaldehyde First convert benzoic acid to benzoyl chloride using thionyl chloride. Then perform Rosenmund reduction with hydrogen over palladium supported on barium sulphate:



The deactivated catalyst allows reduction to stop at the aldehyde stage.

Step 2: Check the reasoning Direct strong reduction of the acid can overshoot to an alcohol. Conversion to the acyl chloride followed by a deactivated hydrogenation catalyst stops at benzaldehyde.

Step 3: Conclusion Convert benzoic acid to benzoyl chloride with SOCl_2 , then use $\text{H}_2/\text{Pd}-\text{BaSO}_4$.

Quick Tip to Solve: Use Rosenmund reduction of the acid chloride to stop at the aldehyde stage.

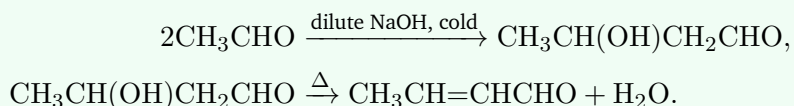
30(b)(ii). Ethanal to but-2-enal

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride to an aldehyde. Aldol condensation joins two ethanal molecules, while reduction followed by dehydration converts a ketone to an alkene.
- Two two-carbon molecules form the four-carbon product.

Step 1: (b)(ii) Convert ethanal to but-2-enal Treat ethanal with dilute aqueous sodium hydroxide in the cold. Two ethanal molecules undergo aldol addition to give 3-hydroxybutanal. Heat the aldol to eliminate water and form but-2-enal:



Ethanal has alpha hydrogen atoms, which permit aldol formation; dehydration gives the conjugated unsaturated aldehyde.

Step 2: Check the reasoning Two two-carbon molecules form the four-carbon product. The aldol first contains an OH group and then loses water to form the conjugated double bond.

Step 3: Conclusion Aldol addition of ethanal followed by dehydration gives but-2-enal.

Quick Tip to Solve: Write the four-carbon hydroxyaldehyde before eliminating water to form but-2-enal.

30(b)(iii). Propanone to propene

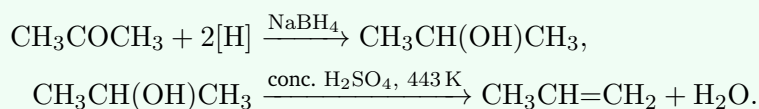
Give complete reaction in each case.

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride to an aldehyde. Aldol condensation joins two ethanal molecules, while reduction followed by dehydration converts a ketone to an alkene.
- The carbon skeleton remains unchanged throughout.

Step 1: (b)(iii) Convert propanone to propene Reduce propanone with sodium borohydride, followed by aqueous work-up, to obtain propan-2-ol. Dehydrate the alcohol by heating with concentrated sulphuric acid:



Here $[\text{H}]$ denotes reducing equivalents. Reduction changes the carbonyl group to an alcohol without altering the carbon skeleton; dehydration then creates the double bond.

Step 2: Check the reasoning The carbon skeleton remains unchanged throughout. Reduction supplies the alcohol intermediate, whose dehydration removes water to generate the alkene.

Step 3: Conclusion Reduce propanone to propan-2-ol, then dehydrate with hot concentrated sulphuric acid.

Quick Tip to Solve: First convert the ketone to an alcohol; then eliminate water to obtain propene.