

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-1-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 2 hours

Maximum Marks: 35

General Instructions

- (i) This question paper contains **12** questions. **All** questions are compulsory.
- (ii) This question paper is divided into **three** Sections – **Section A, B and C**.
- (iii) **Section - A** Q. Nos. **1 to 3** are very short answer type questions carrying **2** marks each.
- (iv) **Section - B** Q. Nos. **4 to 11** are short answer type questions carrying **3** marks each.
- (v) **Section - C** Q. No. **12** is case based question carrying **5** marks.
- (vi) Use of log tables and calculators is NOT allowed.

Section A (6 marks)

1. (a) A reaction is second order in X and first order in Y. How is the rate affected when the concentrations of both X and Y are doubled?

(b) Write the units of 'k' for

(i) zero order reaction

(ii) first order reaction

[2 marks]

Solution:

Concept:

- Reaction order specifies the power of concentration in the rate law. For second order in X and first order in Y, the rate is $r = k[X]^2[Y]$, where k is the rate constant at a fixed temperature.
- Rate has units $\text{mol L}^{-1} \text{s}^{-1}$. For overall order n , the units of k are $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$.

Step 1: (a) Substitute the doubled concentrations Initially, $r = k[X]^2[Y]$. Doubling both reactant concentrations while keeping temperature unchanged gives

$$r' = k(2[X])^2(2[Y]) = 2^2 \times 2 k[X]^2[Y].$$

Thus $r'/r = 8$. The two concentration effects multiply; they are not added. The overall order is three, although the order with respect to X alone is two.

Step 2: (b) Obtain the units from the rate law For a zero order reaction, $r = k[A]^0 = k$; hence k has the same units as rate, namely $\text{mol L}^{-1} \text{s}^{-1}$. For a first order reaction, $r = k[A]$, so

$$[k] = \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}.$$

The concentration units cancel only in the first order case.

Step 3: Conclusion (a) The rate becomes 8 times its initial value. (b) The units of k are (i) $\text{mol L}^{-1} \text{s}^{-1}$ for zero order and (ii) s^{-1} for first order.

Quick Tip to Solve: Multiply each concentration-change factor raised to its own order; obtain units of k by dividing rate units by concentration to the overall order.

2. Out of the following pairs, predict with reason which will allow greater conduction of electricity:

(i) 1 M CH_3COOH solution or 0.1 M CH_3COOH solution on dilution.

(ii) Copper wire at 27 °C or Copper wire at 50 °C.

[2 marks]

Solution:

Concept:

- Acetic acid is a weak electrolyte: $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$. Dilution increases its degree of ionisation and therefore its molar conductivity, Λ_m .
- Metallic conduction occurs through electrons. Heating a metal increases lattice vibrations, scatter-

Quick Tip to Solve: Identify whether conductivity is measured per unit volume or per mole: dilution decreases specific conductivity but increases molar conductivity.

ing the electrons more strongly and increasing electrical resistance.

Step 1: (i) Compare the acid solutions on dilution In the dilution comparison, the 0.1 M acetic acid solution has a higher degree of ionisation than the 1 M solution. More of each mole of acid produces mobile ions, so its molar conductivity is greater. This is the sense of greater conduction associated with dilution of a weak electrolyte. The distinction between molar and specific conductivity is essential: dilution reduces the number of ions per unit volume, so specific conductivity κ decreases even though Λ_m increases. If conduction is compared for equal cell dimensions, the 1 M solution has the greater conductance; the dilution answer 0.1 M refers to molar conductivity.

Step 2: (ii) Compare copper at the two temperatures Copper wire at 27°C permits greater conduction than at 50°C, for identical wire dimensions. At the higher temperature, stronger lattice vibrations obstruct electron motion more frequently. The resistance therefore increases and conductance, its reciprocal, decreases. Unlike electrolytes, the metal does not gain additional charge carriers through increased ionisation on heating.

Step 3: Conclusion (i) On dilution, 0.1 M CH_3COOH has greater molar conductivity because its ionisation increases; for specific conductivity or equal-cell conductance, 1 M is greater. (ii) Copper at 27°C conducts better because its resistance is lower.

Quick Tip to Solve: Identify whether conductivity is measured per unit volume or per mole: dilution decreases specific conductivity but increases molar conductivity.

3. Arrange the following compounds as directed: (any Two)

(i) In decreasing order of basic strength in aqueous solution: $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$

(ii) In increasing order of solubility in water: $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$

(iii) In decreasing order of their pK_b values: $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{NH}_2$, NH_3

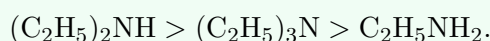
[2 marks]

Solution:

Concept:

- Basic strength depends on the availability of the nitrogen lone pair and the stability of the conjugate acid. In water, the electron-releasing inductive effect, solvation and steric hindrance all contribute.
- Amines dissolve in water by hydrogen bonding. A larger nonpolar hydrocarbon group opposes dissolution. Also, $pK_b = -\log K_b$: a weaker base has a larger pK_b .

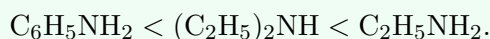
Step 1: (i) Decreasing basic strength in aqueous solution For ethyl-substituted amines, the aqueous order is



Diethylamine combines a strong electron-releasing effect with effective solvation of its conjugate acid. Triethylamine has a greater inductive effect but poorer solvation and more steric hindrance than the secondary amine. In this ethyl series, its inductive effect still makes it stronger than ethylamine. An order based only on the number of alkyl groups neglects the aqueous medium.

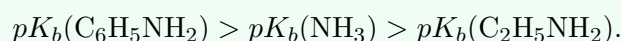
Quick Tip to Solve: For aqueous ethylamines remember secondary greater than tertiary greater than primary; reverse the basic-strength order when comparing pK_b .

Step 2: (ii) Increasing solubility in water The required order is



Ethylamine has the smallest nonpolar group and can form hydrogen bonds with water effectively. Diethylamine contains two ethyl groups and a larger hydrophobic portion. Aniline has a large phenyl group, making its interaction with water least favourable among these three compounds despite the presence of an amino group.

Step 3: (iii) Decreasing values of pK_b Ethylamine is more basic than ammonia because the ethyl group increases electron density on nitrogen. Aniline is weaker than ammonia because its nitrogen lone pair is delocalised into the benzene ring and is less available for protonation. Thus the basic-strength order is ethylamine greater than ammonia greater than aniline. Since pK_b varies oppositely to basic strength, the requested order is



Step 4: Conclusion (i) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$.

(ii) $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$.

(iii) $pK_b(\text{C}_6\text{H}_5\text{NH}_2) > pK_b(\text{NH}_3) > pK_b(\text{C}_2\text{H}_5\text{NH}_2)$. Any two of these arrangements may be written as requested.

Quick Tip to Solve: For aqueous ethylamines remember secondary greater than tertiary greater than primary; reverse the basic-strength order when comparing pK_b .

Section B (24 marks)

4(a). (i) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.

(ii) Using valence bond theory, predict the hybridization and magnetic character of $[\text{Ni}(\text{CN})_4]^{2-}$. (Atomic number of Ni = 28)

(iii) Write the formula of the following complex using IUPAC norms: Dichloridobis(ethane-1,2-diamine)cobalt(III)

[3 marks]

Solution:

Concept:

- In an octahedral field, the three t_{2g} orbitals lie below the two e_g orbitals. The splitting energy Δ_o competes with the electron-pairing energy P .
- Strong-field ligands can pair the metal's d electrons; valence bond theory then identifies the vacant orbitals used for hybridization. Magnetic character depends on unpaired electrons.
- A complex ion's charge equals the metal oxidation state plus the ligand charges. Ethane-1,2-diamine, abbreviated en, is neutral and bidentate; chlorido is Cl^- .

Step 1: (i) Distribute the four electrons in the octahedral levels Since $\Delta_o < P$, promotion to an e_g

Quick Tip to Solve: For a named complex, count ligand charges before adding a superscript: two neutral en ligands do not change the charge of Co(III).

orbital costs less energy than pairing in a t_{2g} orbital. The first three electrons singly occupy the three t_{2g} orbitals, and the fourth singly occupies an e_g orbital. Thus the high-spin distribution is $t_{2g}^3 e_g^1$, with four unpaired electrons. Pairing to give $t_{2g}^4 e_g^0$ would instead correspond to $\Delta_o > P$.

Step 2: (ii) Apply valence bond theory to the nickel complex In $[\text{Ni}(\text{CN})_4]^{2-}$, four cyanido ligands contribute charge -4 , so nickel is in oxidation state $+2$. Neutral nickel has configuration $[\text{Ar}]3d^8 4s^2$, and Ni^{2+} has $[\text{Ar}]3d^8$. The strong-field CN^- ligands pair the eight $3d$ electrons into four orbitals, leaving one $3d$ orbital vacant. That orbital, one $4s$ and two $4p$ orbitals form four dsp^2 hybrids directed towards the corners of a square. All electrons are paired, so the square-planar complex is diamagnetic.

Step 3: (iii) Translate the IUPAC name into a formula Cobalt(III) supplies Co^{3+} ; dichlorido specifies two coordinated Cl^- ligands, and bis(ethane-1,2-diamine) specifies two neutral en ligands. The charge of the coordination entity is $+3 - 2 = +1$. Both chlorido ligands and both diamine ligands belong inside the coordination brackets. The name specifies no counter-ion, so none should be invented.

Step 4: Conclusion (i) $t_{2g}^3 e_g^1$. (ii) dsp^2 hybridization, square-planar geometry and diamagnetic character. (iii) $[\text{CoCl}_2(\text{en})_2]^+$, where $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.

Quick Tip to Solve: For a named complex, count ligand charges before adding a superscript: two neutral en ligands do not change the charge of Co(III) .

OR

4(b). When a co-ordination compound $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is mixed with AgNO_3 , 2 moles of AgCl are precipitated per mole of the compound. Write

- Structural formula of the complex.
- Secondary valency of 'Ni' in the complex.
- IUPAC name of the complex.

[3 marks]

Solution:

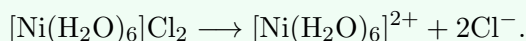
Concept:

- Werner's primary valency corresponds to the metal oxidation state and is satisfied by negative ions. Ionizable counter-ions lie outside the coordination sphere.
- Secondary valency is the coordination number: the number of donor atoms directly bonded to the central metal. Water is a neutral monodentate ligand, named aqua.
- Silver nitrate precipitates free chloride as AgCl . The number of moles precipitated per mole of complex identifies the number of chloride counter-ions.

Step 1: (i) Locate chloride and water in the structural formula The empirical composition is $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, containing two chloride ions per nickel atom. Since one mole of compound gives two moles of AgCl , both chloride ions are ionizable and lie outside the coordination sphere. The six water molecules occupy the coordination sphere around nickel. The structural formula is therefore

Quick Tip to Solve: Compare the AgCl yield with the total chloride count: two precipitated chlorides out of two means both must be outside the brackets.

$[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$, which dissociates in water as



The released ions undergo $2\text{Ag}^+ + 2\text{Cl}^- \longrightarrow 2\text{AgCl} \downarrow$. A chloride ligand inside the brackets would not account for the stated two free chloride ions.

Step 2: (ii) Determine the secondary valency of nickel Each coordinated water molecule donates through one oxygen atom. Six such molecules provide six donor atoms directly bonded to nickel, so its coordination number, and hence its secondary valency, is 6. This differs from the primary valency 2, which follows from the +2 charge on nickel because water is neutral. The coordination entity has an octahedral arrangement of the six aqua ligands.

Step 3: (iii) Construct the IUPAC name Name the coordination cation before the chloride counter-ion. Six water ligands give the prefix hexaaqua. Since the complex is cationic, retain the metal name nickel; indicate its oxidation state by (II). Finally add chloride for the anion outside the coordination brackets. The resulting name is hexaaquanickel(II) chloride. The chloride ions are not named chlorido ligands because they are not directly coordinated to nickel.

Step 4: Conclusion (i) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$. (ii) Secondary valency $\boxed{6}$. (iii) $\boxed{\text{Hexaaquanickel(II) chloride}}$.

Quick Tip to Solve: Compare the AgCl yield with the total chloride count: two precipitated chlorides out of two means both must be outside the brackets.

5. A first order reaction is 50% complete in 40 minutes. Calculate the time required for the completion of 90% of reaction.

[Given: $\log 2 = 0.3010$, $\log 10 = 1$]

[3 marks]

Solution:

Concept:

- For a first order reaction, $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$, where $[A]_0$ is the initial concentration, $[A]_t$ is the concentration remaining after time t , and k is the rate constant.
- Percentage completion refers to the reactant consumed. Thus, 50% completion leaves 50% reactant, whereas 90% completion leaves only 10% reactant. The concentration ratio must use the amount remaining.
- The half-life of a first order reaction is independent of initial concentration. Here the stated time for 50% completion is the half-life, $t_{1/2} = 40$ min.

Step 1: Determine the rate constant from 50% completion Take the initial amount as 100 units. After 40 minutes, 50 units remain, so the initial-to-remaining ratio is $100/50 = 2$. Substituting into the integrated rate equation gives

$$k = \frac{2.303}{40} \log 2 = \frac{2.303 \times 0.3010}{40} = 0.017330075 \text{ min}^{-1}.$$

Using minutes for the time makes the unit of the rate constant min^{-1} . The chosen initial amount

Quick Tip to Solve: For first order percentage problems, use the fraction left: $t_p = t_{1/2} \log[100/(100-p)]/\log 2$. For 90% completion the logarithm is $\log 10$, not $\log 90$.

cancels, so no initial concentration needs to be supplied.

Step 2: Calculate the time for 90% completion At 90% completion, the unreacted amount is 10 units out of the original 100 units. Therefore $[A]_0/[A]_t = 100/10 = 10$. Denote the elapsed time from the start by t_{90} . Using the same rate constant,

$$t_{90} = \frac{2.303}{k} \log 10.$$

Substitute the expression for k before rounding:

$$t_{90} = \frac{40 \log 10}{\log 2} = \frac{40 \times 1}{0.3010} = 132.89 \text{ min.}$$

This is the total time measured from the beginning of the reaction. It exceeds three half-lives, consistent with the fact that three half-lives leave 12.5% reactant, slightly more than the required 10%.

Step 3: Conclusion The time required for 90% completion is 132.9 min, approximately 133 min.

Quick Tip to Solve: For first order percentage problems, use the fraction left: $t_p = t_{1/2} \log[100/(100-p)]/\log 2$. For 90% completion the logarithm is $\log 10$, not $\log 90$.

6(a). Illustrate the following reactions giving suitable example in each case:

(i) Gabriel phthalimide synthesis.

(ii) Carbylamine reaction.

(iii) Hoffmann bromamide degradation reaction.

[3 marks]

Solution:

Concept:

- Gabriel phthalimide synthesis prepares primary aliphatic amines by alkylation of potassium phthalimide followed by hydrolysis of the substituted imide.
- The carbylamine reaction is a test for primary amines: heating a primary amine with chloroform and alcoholic potassium hydroxide produces an isocyanide with an offensive smell.
- In Hoffmann bromamide degradation, a primary amide reacts with bromine and aqueous alkali to give a primary amine containing one carbon atom fewer than the original amide.

Step 1: Illustrate Gabriel phthalimide synthesis Form potassium phthalimide with alcoholic KOH, then alkylate with bromoethane:



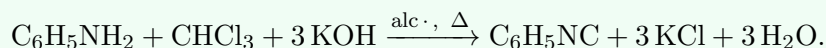
Quick Tip to Solve: Remember the distinguishing change: Gabriel gives a primary alkylamine, carbylamine forms RNC, and Hoffmann degradation removes the amide carbonyl carbon, shortening the carbon chain by one.

Alkaline hydrolysis of N-ethylphthalimide releases ethanamine:



The product is a primary aliphatic amine; the method is unsuitable for preparing aniline from an aryl halide.

Step 2: Illustrate the carbylamine reaction Heat aniline, a primary aromatic amine, with chloroform and alcoholic potassium hydroxide. Phenyl isocyanide is formed:



The offensive smell of phenyl isocyanide provides the positive test. Both primary aliphatic and aromatic amines respond; secondary and tertiary amines do not.

Step 3: Illustrate Hofmann bromamide degradation Warm ethanamide with bromine and aqueous sodium hydroxide to obtain methylamine:



Ethanamide has two carbon atoms and methylamine has one; the removed carbon appears in sodium carbonate.

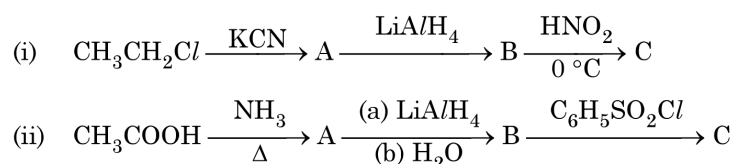
Step 4: Conclusion The examples give ethanamine by Gabriel synthesis, phenyl isocyanide by the carbylamine reaction, and methylamine by Hofmann bromamide degradation.

Quick Tip to Solve: Remember the distinguishing change: Gabriel gives a primary alkylamine, carbylamine forms RNC, and Hofmann degradation removes the amide carbonyl carbon, shortening the carbon chain by one.

OR

6(b). Write the structures of A, B and C in the following reactions:

[3 marks]



Solution:

Concept:

- Cyanide ion substitutes chloride in a primary alkyl halide to give a nitrile, introducing one extra carbon atom into the chain.
- LiAlH_4 reduces nitriles and amides to primary amines. Heating a carboxylic acid with ammonia produces an amide through dehydration of the ammonium salt.
- An aliphatic primary amine reacts with nitrous acid to give an alcohol with evolution of nitrogen; with benzenesulphonyl chloride it forms an *N*-alkylbenzenesulphonamide.

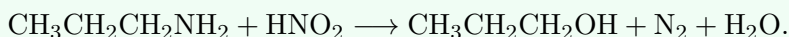
Quick Tip to Solve: Count carbons at each arrow: KCN adds a carbon, while reduction of a nitrile or an amide preserves its carbon skeleton.

Step 1: (i) Identify the nitrile and its reduction product Potassium cyanide supplies the carbon-bonded cyanide nucleophile. Substitution of chlorine in chloroethane gives propanenitrile, so $A = \text{CH}_3\text{CH}_2\text{C} \equiv \text{N}$. Reduction of its nitrile group gives propan-1-amine, so $B = \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$:



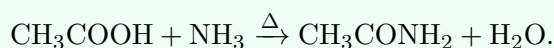
The carbon atom of the cyanide group remains in the product, hence the amine has three carbon atoms.

Step 2: (i) React the primary aliphatic amine with nitrous acid At the stated temperature, the unstable aliphatic diazonium intermediate decomposes. Replacement of the amino group by hydroxyl gives propan-1-ol:



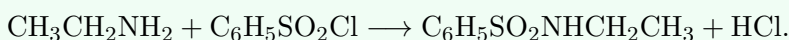
Thus $C = \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$; an isolable diazonium salt is not the final product of this aliphatic amine.

Step 3: (ii) Form ethanamide and reduce it Ethanoic acid first forms ammonium ethanoate with ammonia. On heating, loss of water yields ethanamide, so $A = \text{CH}_3\text{C}(=\text{O})\text{NH}_2$:



Reduction using LiAlH_4 , followed by aqueous work-up, converts the carbonyl group into a methylene group without removing a carbon atom. Hence $B = \text{CH}_3\text{CH}_2\text{NH}_2$, ethanamine.

Step 4: (ii) Identify the sulphonamide Ethanamine reacts with benzenesulphonyl chloride by substituting chloride at the sulphonyl group:



The product retains one hydrogen attached to nitrogen and is *N*-ethylbenzenesulphonamide, with structure $\text{C}_6\text{H}_5\text{S}(=\text{O})_2\text{NHCH}_2\text{CH}_3$.

Step 5: Conclusion (i) $A = \text{CH}_3\text{CH}_2\text{CN}$, $B = \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, $C = \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$.

(ii) $A = \text{CH}_3\text{CONH}_2$, $B = \text{CH}_3\text{CH}_2\text{NH}_2$, $C = \text{C}_6\text{H}_5\text{SO}_2\text{NHCH}_2\text{CH}_3$.

Quick Tip to Solve: Count carbons at each arrow: KCN adds a carbon, while reduction of a nitrile or an amide preserves its carbon skeleton.

7(a). Write any three differences between physisorption and chemisorption.

[3 marks]

Solution:

Concept:

- Adsorption is the accumulation of an adsorbate on the surface of an adsorbent. Physisorption involves weak intermolecular forces, whereas chemisorption involves the formation of chemical bonds.
- The nature and strength of the surface interaction determine the specificity and heat of adsorption. Heat of adsorption is the energy released per mole of adsorbate adsorbed.

Quick Tip to Solve: Link each difference to bond formation: chemical bonds explain the greater strength, greater specificity and higher heat of chemisorption.

Step 1: Difference 1: Nature of the attractive force In physisorption, the adsorbate is held on the adsorbent by weak van der Waals forces. No new chemical bond is formed between the two substances. In chemisorption, the adsorbate is attached to the surface through chemical bonds. These bonds are much stronger than the forces responsible for physical adsorption. For example, physical adsorption of a gas on charcoal depends on intermolecular attraction, while chemical adsorption requires a suitable surface reaction.

Step 2: Difference 2: Specificity Physisorption is not highly specific: many gases can be physically adsorbed on the same solid surface, although the amounts adsorbed differ. Chemisorption is highly specific because chemical bonds form only when the adsorbate and adsorbent have suitable chemical interaction. For instance, hydrogen can be chemisorbed on nickel, whose surface can bond with hydrogen. Thus chemical compatibility is essential for chemisorption but is not the deciding requirement for physisorption.

Step 3: Difference 3: Heat of adsorption Physisorption has a low heat of adsorption, generally about $20\text{--}40\text{ kJ mol}^{-1}$, because only weak intermolecular interactions are established. Chemisorption has a much higher heat of adsorption, generally about $80\text{--}240\text{ kJ mol}^{-1}$, because chemical bonds are formed at the surface. Both processes ordinarily release heat; the difference is the magnitude of the energy released, not a reversal of the sign of the heat change.

Step 4: Conclusion The three differences are: physisorption uses weak van der Waals forces, is non-specific and has a low heat of adsorption; chemisorption forms chemical bonds, is highly specific and has a high heat of adsorption.

Quick Tip to Solve: Link each difference to bond formation: chemical bonds explain the greater strength, greater specificity and higher heat of chemisorption.

OR

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

(i) Lyophilic sol

(ii) Macromolecular colloid

(iii) Coagulation

[3 marks]

Solution:

Concept:

- A sol has a solid dispersed phase and a liquid dispersion medium. The attraction between them determines whether the sol is lyophilic.
- A colloidal particle can be a single large molecule; alternatively, loss of stability can make many particles aggregate and separate.

Step 1: (i) Lyophilic sol A lyophilic sol is a colloidal sol in which the dispersed phase has a strong affinity for the dispersion medium. It is readily formed by bringing the two together, is relatively stable, and is usually reversible: the separated dispersed material can form the sol again on adding the medium. For example, starch dispersed in water forms a lyophilic sol; since the medium is water,

Quick Tip to Solve: Link each definition to its distinguishing feature: affinity, one giant molecule, or aggregation and precipitation.

it is also called a hydrophilic sol. The term describes affinity for the liquid, rather than the size of a single molecule.

Step 2: (ii) Macromolecular colloid A macromolecular colloid is a system in which individual molecules of a substance are sufficiently large to have dimensions in the colloidal range. Each dispersed particle is thus a single giant molecule, rather than an aggregate of many small molecules. Such substances form colloidal solutions when dissolved in a suitable dispersion medium. Starch in water is an example; proteins and cellulose are other macromolecular substances. A macromolecular colloid must be distinguished from a multimolecular colloid, whose particles contain aggregates of smaller molecules or atoms.

Step 3: (iii) Coagulation Coagulation is the process in which colloidal particles aggregate into larger particles and consequently separate from the dispersion medium as a precipitate. For a charged lyophobic sol, addition of a suitable electrolyte can neutralise the particle charge, reduce repulsion and allow aggregation. For example, adding sodium chloride solution to a silver sol causes the silver particles to coagulate. Thus, coagulation destroys the stability of the sol; it is not merely the settling of unchanged stable colloidal particles.

Step 4: Conclusion Lyophilic sol: strong affinity between dispersed phase and medium, for example starch in water. Macromolecular colloid: colloidal-sized individual giant molecules, for example starch. Coagulation: aggregation and precipitation of colloidal particles, for example silver sol coagulated by sodium chloride.

Quick Tip to Solve: Link each definition to its distinguishing feature: affinity, one giant molecule, or aggregation and precipitation.

8. Following ions of 3d transition series are given:

V^{3+} , Cr^{2+} , Cu^{+} , Fe^{2+}

(Atomic number: V = 23, Cr = 24, Cu = 29, Fe = 26)

Identify the ion which is

- (a) unstable in aqueous solution.
- (b) a strong reducing agent in aqueous solution.
- (c) colourless in aqueous solution.

Give suitable reason in each.

[3 marks]

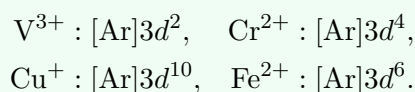
Solution:

Concept:

- Electrons are removed from the 4s orbital before the 3d orbital when forming these transition-metal cations.
- Stability in water depends on the overall energetics, including hydration. A reducing agent readily loses an electron and is itself oxidised.
- In the usual aqueous transition-metal ions, colour arises from electronic transitions between split d orbitals; a filled d^{10} configuration cannot undergo a d-d transition.

Quick Tip to Solve: Write the ionic d-electron counts first; use hydration for Cu(I) instability and the d4-to-d3 change for Cr(II) reduction.

Step 1: Establish the electronic configurations Using the stated atomic numbers and removing 4s electrons first, the configurations of the given ions are



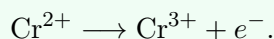
The three questions concern different properties, so the same ion may be the answer to more than one part.

Step 2: (a) Ion unstable in aqueous solution Cu^+ is unstable in aqueous solution and undergoes disproportionation:



One copper(I) ion is oxidised to copper(II), while another is reduced to copper metal. Although Cu^+ has a filled 3d subshell, the much greater hydration enthalpy released by Cu^{2+} makes the overall disproportionation energetically favourable in water. A filled subshell alone therefore does not guarantee aqueous stability.

Step 3: (b) Strong reducing agent Cr^{2+} is a strong reducing agent because it readily loses one electron:



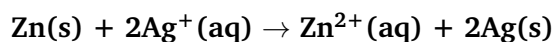
Its $3d^4$ configuration changes to the more stable $3d^3$ configuration of Cr^{3+} . In an octahedral aqueous complex this is t_{2g}^3 , with three singly occupied lower-energy orbitals and appreciable crystal-field stabilisation. This favours oxidation of chromium(II), allowing it to reduce another species.

Step 4: (c) Colourless ion Cu^+ is colourless because its $3d^{10}$ subshell is completely filled. There is no vacant d orbital available for the usual d-d excitation within the split subshell. The other listed ions have partially filled d subshells and their usual aqueous ions are coloured. The electronic reason for colourlessness remains distinct from the hydration argument explaining instability.

Step 5: Conclusion (a) Cu^+ : disproportionates in water because formation of hydrated Cu^{2+} is energetically favourable. (b) Cr^{2+} : readily oxidises to the more stable $3d^3$ chromium(III) ion. (c) Cu^+ : has a filled $3d^{10}$ subshell and no d-d transitions.

Quick Tip to Solve: Write the ionic d-electron counts first; use hydration for Cu(I) instability and the d4-to-d3 change for Cr(II) reduction.

9. (a) The standard Gibbs energy ($\Delta_r G^\circ$) for the following cell reaction is -300 kJ mol^{-1} :



Calculate E°_{cell} for the reaction. (Given: $1 \text{ F} = 96500 \text{ C mol}^{-1}$)

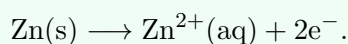
(b) Calculate Λ°_m for MgCl_2 if λ° values for Mg^{2+} ion and Cl^- ion are $106 \text{ S cm}^2 \text{ mol}^{-1}$ and $76.3 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. [3 marks]

Solution:

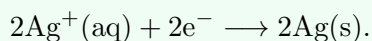
Concept:

- The standard reaction Gibbs energy and standard cell potential obey $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred in the balanced reaction and F is the Faraday constant.
- Kohlrausch's law of independent migration of ions gives the limiting molar conductivity as the sum of ionic contributions, each multiplied by its stoichiometric coefficient.

Step 1: (a) Determine the electron transfer The zinc electrode undergoes oxidation:



Silver ions undergo reduction:



Adding these half-reactions reproduces the given cell reaction. Therefore, two electrons are transferred per reaction as written, so $n = 2$. The coefficient of silver alone is not an independent extra factor in the energy relation.

Step 2: (a) Substitute in the Gibbs energy relation Convert the given energy to joules so that it is compatible with $F = 96500 \text{ C mol}^{-1}$:

$$\Delta_r G^\circ = -300 \times 10^3 \text{ J mol}^{-1}.$$

Rearranging and substituting gives

$$\begin{aligned} E^\circ_{\text{cell}} &= -\frac{\Delta_r G^\circ}{nF} \\ &= -\frac{-300 \times 10^3}{2 \times 96500} \text{ J C}^{-1} \\ &= 1.5544 \text{ V}. \end{aligned}$$

The positive cell potential agrees with the negative standard Gibbs energy, which indicates that the forward reaction is spontaneous under standard conditions.

Step 3: (b) Add the limiting ionic conductivities One mole of magnesium chloride produces one mole of magnesium ions and two moles of chloride ions:



Quick Tip to Solve: Find n from the balanced half-reactions and convert kJ to J before using $\Delta_r G^\circ = -nFE^\circ$; count two chloride contributions for MgCl_2 .

Consequently,

$$\begin{aligned}\Lambda_m^\circ(\text{MgCl}_2) &= \lambda^\circ(\text{Mg}^{2+}) + 2\lambda^\circ(\text{Cl}^-) \\ &= 106 + 2(76.3) \\ &= 258.6 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

The factor of two accounts for the number of chloride ions; ionic charge is already reflected in each supplied ionic conductivity.

Step 4: Conclusion (a) $E_{\text{cell}}^\circ = 1.55 \text{ V}$. (b) $\Lambda_m^\circ(\text{MgCl}_2) = 258.6 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Find n from the balanced half-reactions and convert kJ to J before using $\Delta_r G^\circ = -nFE^\circ$; count two chloride contributions for MgCl_2 .

10. An organic compound 'X' with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$ forms 2,4-DNP derivative, does not reduce Tollens' reagent but gives positive iodoform test on heating with I_2 in the presence of NaOH . Compound 'X' gives ethanoic acid and propanoic acid on vigorous oxidation. Write the

(i) Structure of the compound 'X'.

(ii) Structure of the product obtained when compound 'X' reacts with 2,4-DNP reagent.

(iii) Structures of the products obtained when compound 'X' is heated with I_2 in the presence of NaOH .

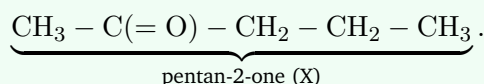
[3 marks]

Solution:

Concept:

- A positive 2,4-DNP test identifies a carbonyl group of an aldehyde or ketone. Failure to reduce Tollens' reagent identifies the present compound as a ketone.
- A methyl ketone RCOCH_3 gives the iodoform reaction, producing CHI_3 and the sodium carboxylate RCOONa in alkaline solution.
- 2,4-Dinitrophenylhydrazine condenses with a carbonyl compound: the carbonyl oxygen is replaced by $\text{N} - \text{NH} - \text{C}_6\text{H}_3(\text{NO}_2)_2$, with elimination of water.

Step 1: (i) Identify the structure of X The molecular formula is $\text{C}_5\text{H}_{10}\text{O}$. The 2,4-DNP test establishes the presence of a carbonyl group, while the negative Tollens' test rules out an aldehyde. The positive iodoform test requires a $\text{CH}_3\text{CO}-$ group. Thus the remaining three carbon atoms form the group attached to this methyl ketone. The oxidation products are ethanoic acid and propanoic acid, which select the straight-chain ketone:

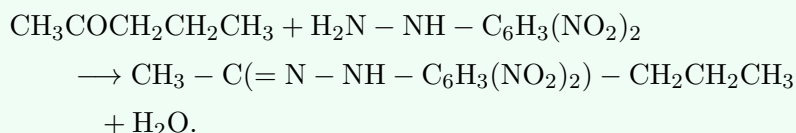


Cleavage between the carbonyl carbon and the adjacent methylene carbon gives the stated two-carbon and three-carbon acids. The branched methyl ketone would not give this same pair.

Step 2: (ii) Form the 2,4-DNP derivative The terminal amino group of 2,4-dinitrophenylhydrazine

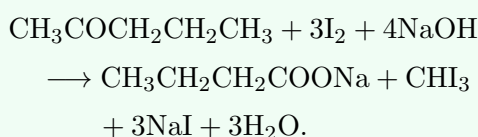
Quick Tip to Solve: In the iodoform reaction, split RCOCH_3 into RCOONa and CHI_3 ; keep the carbonyl carbon in the carboxylate.

reacts with the carbonyl group. Condensation removes one molecule of water and forms a hydrazone:



The product is pentan-2-one 2,4-dinitrophenylhydrazone. In the displayed aryl group, the two NO_2 substituents occupy positions 2 and 4 relative to the carbon bonded to $-\text{NH}-$. Both original alkyl groups stay attached to the carbon of the new $\text{C} = \text{N}$ bond.

Step 3: (iii) Obtain the iodoform reaction products For RCOCH_3 , take $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_3$. Successive iodination of the methyl group followed by alkaline cleavage gives the balanced equation



The requested organic products are sodium butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{O}^-\text{Na}^+$, and iodoform, $\text{H} - \text{C}(\text{I})_3$, a yellow precipitate. The carboxylate retains the original carbonyl carbon, hence it contains four carbon atoms. Because the medium is alkaline, the product is the sodium salt rather than free butanoic acid.

Step 4: Conclusion (i) X is pentan-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$.

(ii) The product is its 2,4-dinitrophenylhydrazone, shown in step 2.

(iii) The organic products are iodoform, CHI_3 , and sodium butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$.

Quick Tip to Solve: In the iodoform reaction, split RCOCH_3 into RCOONa and CHI_3 ; keep the carbonyl carbon in the carboxylate.

11(a). Account for the following:

(i) Transition metals and their compounds act as good catalysts.

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

(iii) Chromium is hard whereas Zinc is soft metal.

[3 marks]

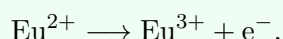
Solution:

Concept:

- Catalysts offer an alternative reaction pathway of lower activation energy; variable oxidation states and adsorption help transition metals do this.
- A reducing agent loses electrons and is oxidised. Metallic hardness depends on the strength of metallic bonding.

Step 1: (i) Catalytic action Transition metals possess variable oxidation states because their outer ns and $(n-1)d$ electrons have comparable energies. Their compounds can therefore form intermediate species with reactants and then regenerate the catalyst, providing a pathway with lower activation energy. Finely divided metals also adsorb reactants on their surfaces, bringing them together and weakening reactant bonds. Both effects account for their good catalytic activity.

Step 2: (ii) Reducing character of europium(II) Eu^{2+} readily donates an electron and changes to the more usual trivalent lanthanoid state:



Thus it reduces another species while itself undergoing oxidation. Although Eu^{2+} has a half-filled $4f^7$ configuration, this does not prevent its strong reducing behaviour in aqueous solution, where formation and hydration of the trivalent ion favour oxidation.

Step 3: (iii) Hardness of chromium and softness of zinc Chromium has the configuration $[\text{Ar}] 3d^5 4s^1$, with several unpaired electrons available for strong metallic bonding. Zinc has $[\text{Ar}] 3d^{10} 4s^2$, with a completely filled d subshell and no unpaired electrons. Its filled d electrons contribute much less effectively to metallic bonding. Consequently the metallic bonds are stronger in chromium, making it hard, whereas zinc is comparatively soft.

Step 4: Conclusion Transition metals catalyse through variable oxidation states and adsorption; Eu^{2+} reduces by oxidation to Eu^{3+} ; chromium is harder than zinc because its metallic bonding is stronger.

Quick Tip to Solve: Link catalysis to intermediates, reducing power to electron loss, and hardness to metallic bond strength.

11(b). What is Lanthanoid contraction? Write two consequences of Lanthanoid contraction. [3 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series, especially for ions in the same +3 oxidation state.
- The 4f electrons shield the increasing nuclear charge poorly, so the effective attraction experienced by the outer electrons increases.

Step 1: Define and explain the contraction The regular decrease in the size of lanthanoid atoms and, particularly, Ln^{3+} ions with increasing atomic number from lanthanum to lutetium is called lanthanoid contraction. Across the series, nuclear charge increases while additional electrons enter the 4f subshell. Because these electrons have poor shielding ability, they do not fully offset the increased nuclear charge. The electron cloud is therefore drawn progressively closer to the nucleus.

Step 2: First consequence: similarity of zirconium and hafnium The contraction nearly compensates for the size increase expected on adding another electron shell. Consequently corresponding elements of the second and third transition series have nearly equal radii. For example, zirconium and hafnium have almost identical atomic and ionic sizes, and hence very similar chemical properties. Their chemical separation is therefore difficult.

Step 3: Second consequence: decreasing basicity of hydroxides As the size of Ln^{3+} decreases, its polarising power increases. The metal–oxygen bond acquires greater covalent character and the hydroxide becomes less basic. Thus basicity decreases along the series:



Lanthanum hydroxide is consequently more basic than lutetium hydroxide.

Step 4: Conclusion Lanthanoid contraction is the gradual decrease in lanthanoid radii with increasing atomic number. Two consequences are the close similarity of zirconium and hafnium and the decrease in basicity of lanthanoid hydroxides from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$.

Quick Tip to Solve: Remember poor shielding by the 4f electrons, then connect smaller ions with greater polarising power and lower hydroxide basicity.

Section C (5 marks)

12(a). Case Study (read the passage): Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules due to higher electro-negativity of oxygen relative to carbon in the carbonyl group. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled reduction of acyl halides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group but carboxylic acid does not undergo nucleophilic addition reaction. The alpha (α) hydrogens of aldehydes and ketones are acidic. Therefore aldehydes and ketones having at least one α -hydrogen undergo Aldol condensation. Aldehydes are easily oxidised by mild oxidising agents such as Tollens' reagent and Fehling's reagent. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and by hydrolysis of nitriles. Aromatic carboxylic acids are prepared by side-chain oxidation of alkyl benzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

(a) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction:

CH_3COCH_3 , CH_3CHO , HCHO , $\text{C}_6\text{H}_5\text{COCH}_3$

[1 mark]

Solution:

Concept:

- Nucleophilic addition is favoured by greater positive character on the carbonyl carbon and less steric hindrance around it.
- Alkyl groups donate electron density; conjugation with a phenyl group also reduces the electrophilicity of the carbonyl carbon.

Step 1: Compare aldehydes with ketones Formaldehyde has no electron-donating alkyl group and the least steric hindrance, so it is the most reactive. Ethanal has one methyl group and is less reactive than formaldehyde. Propanone has two methyl groups, whose electron donation and steric hindrance reduce its reactivity below that of ethanal.

Step 2: Place acetophenone In acetophenone, the carbonyl group is conjugated with the phenyl ring. Resonance reduces the positive character of the carbonyl carbon, and the bulky phenyl group also hinders nucleophilic approach. It is therefore less reactive than propanone.

Step 3: Conclusion The increasing order of reactivity is



Quick Tip to Solve: Put formaldehyde last in an increasing order; then compare electron donation, steric hindrance and phenyl conjugation.

12(b). Give a simple chemical test to distinguish between Ethanal and Propanone.

[1 mark]

Solution:

Concept:

- Tollens' reagent, ammoniacal silver nitrate, oxidises aldehydes but does not oxidise ordinary ketones.

Step 1: Apply Tollens' test Warm separate samples gently with freshly prepared Tollens' reagent. Ethanal, CH_3CHO , reduces silver(I) ions to metallic silver, producing a silver mirror on the inner wall of the test tube.

Step 2: Compare the observations Propanone, CH_3COCH_3 , gives no silver mirror under these conditions. Ethanal is oxidised to ethanoate while propanone remains unchanged. Iodoform is unsuitable for distinguishing this pair because both compounds give that test.

Step 3: Conclusion Ethanal gives a silver mirror with Tollens' reagent; propanone does not.

Quick Tip to Solve: Use Tollens' test here: both ethanal and propanone give the iodoform test.

12(c). Why carboxylic acid does not give nucleophilic addition reactions like aldehydes and ketones?

[1 mark]

Solution:

Concept:

- Nucleophilic addition requires an electrophilic carbonyl carbon; greater positive character favours attack.
- In a carboxyl group, the hydroxyl oxygen donates a lone pair into the carbonyl system by resonance.

Step 1: Account for resonance The lone pair on the $-\text{OH}$ oxygen is conjugated with the $\text{C}=\text{O}$ group. Its donation reduces the positive character of the carbonyl carbon compared with that in aldehydes and ketones.

Step 2: Relate this to nucleophilic attack The carboxyl carbon is therefore less electrophilic and does not undergo the usual nucleophilic addition reactions of aldehydes and ketones. Carboxylic acids may instead undergo nucleophilic acyl substitution under suitable conditions.

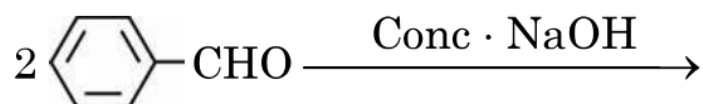
Step 3: Conclusion Resonance donation from the hydroxyl oxygen reduces the electrophilicity of the carbonyl carbon, preventing the usual nucleophilic addition.

Quick Tip to Solve: For carboxylic acids, focus on lone-pair donation from the hydroxyl oxygen.

12(d). (i) Why α -hydrogen of aldehydes and ketones are acidic in nature?

(ii) Write the products in the following:

[2 marks]

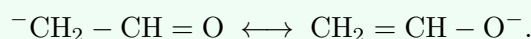


Solution:

Concept:

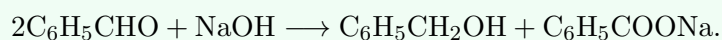
- An α -hydrogen is attached to the carbon adjacent to a carbonyl group; its removal gives a resonance-stabilised enolate ion.
- An aldehyde without an α -hydrogen undergoes Cannizzaro disproportionation with concentrated alkali.

Step 1: (i) Explain alpha-hydrogen acidity The electron-withdrawing carbonyl group helps the removal of an adjacent hydrogen as H^+ . More importantly, the conjugate base is stabilised because its negative charge is delocalised between the alpha carbon and oxygen. For ethanal the enolate resonance forms are



This stabilisation makes alpha-hydrogens more acidic than ordinary alkane hydrogens.

Step 2: (ii) Identify the reaction and products Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has no alpha-hydrogen and undergoes the Cannizzaro reaction with concentrated NaOH . One molecule is reduced to benzyl alcohol while the other is oxidised to sodium benzoate:



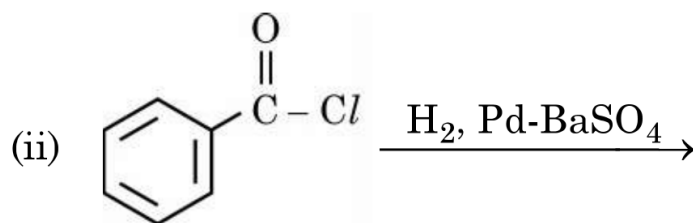
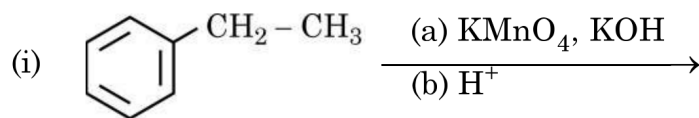
The reaction mixture is alkaline, so the oxidation product is the sodium salt, rather than free benzoic acid.

Step 3: Conclusion (i) Alpha-hydrogens are acidic because their removal forms a resonance-stabilised enolate. (ii) The products are benzyl alcohol and sodium benzoate.

Quick Tip to Solve: Check for alpha-hydrogens first; benzaldehyde with concentrated alkali gives Cannizzaro products.

12(d). Write the major products of the following reactions:

[2 marks]

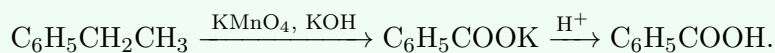


Solution:

Concept:

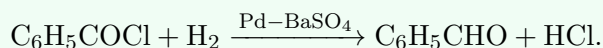
- Alkaline potassium permanganate oxidises an alkylbenzene side chain with a benzylic hydrogen to a carboxylate; acidification gives the carboxylic acid.
- Rosenmund reduction converts an acyl chloride to an aldehyde using H_2 and palladium supported on BaSO_4 .

Step 1: (i) Oxidise ethylbenzene The reactant is ethylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$. Its benzylic carbon bears hydrogen, so KMnO_4/KOH oxidises the side chain to potassium benzoate. Subsequent acidification with H^+ yields benzoic acid:



The extra side-chain carbon is removed during the vigorous oxidation; the product is not phenylacetic acid.

Step 2: (ii) Reduce benzoyl chloride The second reactant is benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$. With $\text{H}_2/\text{Pd} - \text{BaSO}_4$, controlled Rosenmund reduction replaces the chlorine of the acyl chloride by hydrogen:



The catalyst system limits further reduction, so the major organic product is the aldehyde rather than benzyl alcohol.

Step 3: Conclusion (i) Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. (ii) Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

Quick Tip to Solve: Follow acidification after side-chain oxidation; identify Pd-BaSO_4 as the Rosenmund catalyst.