UP Board Class 12 Chemistry 2026 Set 347 EE Question Paper with Solutions

collegedunia

General Instructions

(i) This booklet contains 26 questions, each provided with a complete, step-by-step solution.

(ii) It comprises 6 single-correct multiple-choice questions.

(iii) Attempt each question on your own before reviewing the given solution.

1. Read the following assertion and reason and choose the correct alternative.

Assertion: Elevation in boiling point for two isotonic solutions is same.

Reason: Boiling point depends upon the concentration of the solute.

(A) Both assertion and reason are true and the reason is the correct explanation of assertion

(B) Both assertion and reason are true but the reason is not the correct explanation of assertion

(C) Assertion is correct but reason is wrong

(D) Assertion is wrong but reason is correct

Correct Answer: (A) Both assertion and reason are true and the reason is the correct explanation of assertion

Solution:

Step 1: Isotonic solutions are defined as solutions that have the same osmotic pressure at a given temperature. From the osmotic pressure relation $\pi = iCRT$, equal osmotic pressure at the same temperature means the two solutions have the same effective molar concentration

iC.

Step 2: Elevation in boiling point is a colligative property given by $\Delta T_b = iK_b\, m$, i.e. it depends on the concentration of solute particles in the solution.

Step 3: Since the two isotonic solutions (in the same solvent) have the same solute concentration, they produce the same elevation in boiling point. Hence the assertion is true.

Step 4: The reason correctly states that the elevation in boiling point depends on the concentration of the solute, and this is exactly why isotonic solutions show the same elevation. So the reason is true and is the correct explanation of the assertion.

Conclusion: Option (i) is correct. Options (iii) and (iv) are wrong because both statements are true, and option (ii) is wrong because the reason does explain the assertion.

Option (i)

Quick Tip: Isotonic means equal osmotic pressure, hence equal concentration; all colligative properties (including $\Delta T_b = K_b m$) depend on concentration.

2. Which of the following ions has highest magnetic moment?

(A) Cr^{2+}

(B) Co^{2+}

(C) Fe^{2+}

(D) V^{2+}

Correct Answer: (A) Cr^{2+}

Solution:

Step 1: The spin-only magnetic moment is $\mu = \sqrt{n(n+1)}$ BM, where n is the number of unpaired electrons. The larger the n, the larger the magnetic moment.

Step 2: Write the d-electron configuration of each ion (for a 2+ ion, remove the two 4s electrons first, then adjust d):

Cr^{2+}: $3d^4$ $\rightarrow$ 4 unpaired electrons.

Co^{2+}: $3d^7$ $\rightarrow$ 3 unpaired electrons.

Fe^{2+}: $3d^6$ $\rightarrow$ 4 unpaired electrons.

V^{2+}: $3d^3$ $\rightarrow$ 3 unpaired electrons.

Step 3: The maximum number of unpaired electrons (4) is shown by $Cr^{2+}(3d^4)$, giving $\mu = \sqrt{4(4+1)} = \sqrt{20} = 4.9$ BM. This is the highest among the options, so Cr^{2+} is the marked answer.

Step 4: Co^{2+} and V^{2+} have only 3 unpaired electrons ($\mu = 3.87$ BM), which is smaller. Hence option (i) is correct.

$$\boxed{Cr^{2+},\ \mu = 4.9 \text{ BM}}$$

Quick Tip: Count unpaired $3d$ electrons of each 2+ ion and use $\mu = \sqrt{n(n+1)}$; the d4 ion wins.

3. Which of the following complexes exhibit linkage isomerism?

(A) $[Cr(NH_3)_4Cl_2]$

(B) $[Co(NH_3)_5(NO_2)]Cl_2$

(C) $[Co(NH_3)_5(SO_4)]Br$

(D) $[Pt(NH_3)_2Br_2]$

Correct Answer: (B) $[Co(NH_3)_5(NO_2)]Cl_2$

Solution:

Step 1: Linkage isomerism arises only when the complex contains an **ambidentate ligand**, i.e. a ligand that can attach to the central metal through two different donor atoms. Common ambidentate ligands are NO_2^- (through N as nitro or through O as nitrito), SCN^- and CN^-.
Step 2: Examine each complex for an ambidentate ligand:
(i) $[Cr(NH_3)_4Cl_2]$: ligands are NH_3 and Cl^-, neither is ambidentate. No linkage isomerism.
(ii) $[Co(NH_3)_5(NO_2)]Cl_2$: contains NO_2, which can bind as nitro ($-NO_2$, through N) or nitrito ($-ONO$, through O). This gives linkage isomers.
(iii) $[Co(NH_3)_5(SO_4)]Br$: sulphate binds through O and, with a free Br^- outside, shows ionisation isomerism, not linkage isomerism.
(iv) $[Pt(NH_3)_2Br_2]$: only NH_3 and Br^-; no ambidentate ligand.
Step 3: Only option (ii) has the ambidentate NO_2 ligand, so it alone shows linkage isomerism.

$$\boxed{[Co(NH_3)_5(NO_2)]Cl_2}$$

Quick Tip: Look for an ambidentate ligand such as NO_2 (nitro/nitrito) that can bind through two different donor atoms.

4. Benzyl alcohol is obtained from benzaldehyde by the following reaction.

(A) Aldol condensation

(B) Perkin reaction

(C) Cross aldol condensation

(D) Cannizzaro reaction

Correct Answer: (D) Cannizzaro reaction

Solution:

Step 1: Identify the substrate. Benzaldehyde, C_6H_5CHO, has no α-hydrogen atom (the carbon next to the carbonyl is part of the benzene ring and carries no H that can be removed as in aldol chemistry).
Step 2: Aldehydes without α-hydrogen, when treated with concentrated alkali (NaOH/KOH), undergo the **Cannizzaro reaction**, a self oxidation-reduction (disproportionation): one molecule is reduced to an alcohol and the other is oxidised to the salt of a carboxylic acid.
Step 3: For benzaldehyde:

$$2\,C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Benzyl alcohol ($C_6H_5CH_2OH$) is the reduction product and sodium benzoate is the oxidation product.
Step 4: Aldol and cross aldol condensation both need an α-hydrogen, which benzaldehyde lacks, and the Perkin reaction gives cinnamic acid with anhydride, not benzyl alcohol. Hence option (iv) Cannizzaro reaction is correct.

Cannizzaro reaction

Quick Tip: Benzaldehyde has no α-hydrogen, so with strong base it disproportionates (Cannizzaro) to benzyl alcohol plus benzoate.

5. Which of the following is the most basic compound?

(A) Aniline

(B) p-Nitro aniline

(C) Benzyl amine

(D) Acetanilide

Correct Answer: (C) Benzyl amine

Solution:

Step 1: Basic strength of an amine depends on the availability of the lone pair on nitrogen. The more freely available the lone pair, the more basic the compound.

Step 2: Compare the four compounds:

Benzyl amine ($C_6H_5CH_2NH_2$): the NH_2 group is attached to an sp^3 CH_2 carbon, not directly to the ring. Its lone pair is not delocalised into the benzene ring, so it behaves like an aliphatic amine and the lone pair is fully available.

Aniline ($C_6H_5NH_2$): the NH_2 is directly on the ring, so the lone pair is delocalised into the ring by resonance, reducing basicity.

p-Nitroaniline: the electron withdrawing $-NO_2$ group at the para position pulls the lone pair even more, so it is less basic than aniline.

Acetanilide ($C_6H_5NHCOCH_3$): the lone pair is delocalised onto the carbonyl of the amide group, making it the least basic (almost neutral).

Step 3: Since only benzyl amine keeps its nitrogen lone pair free, it is the strongest base.

$$\boxed{\text{Benzyl amine}}$$

Quick Tip: In benzyl amine the CH_2 separates NH_2 from the ring, so no resonance withdrawal; its lone pair stays fully available.

6. The chemical name of vitamin B_1 is

(A) Riboflavin

(B) Thiamine

(C) Ascorbic acid

(D) Pyridoxine

Correct Answer: (B) Thiamine

Solution:

Step 1: Recall the chemical (scientific) names paired with the common vitamin labels. Each B-group vitamin and vitamin C has a specific chemical name.

Step 2: Match the options:

Riboflavin = vitamin B_2.

Thiamine = vitamin B_1.

Ascorbic acid = vitamin C.

Pyridoxine = vitamin B_6.

Step 3: The chemical name of vitamin B_1 is therefore thiamine. A deficiency of vitamin B_1 (thiamine) causes the disease beri-beri.

$$\boxed{\text{Thiamine}}$$

Quick Tip: Vitamin B_1 deficiency causes beri-beri; its chemical name is thiamine.

7. Explain reverse osmosis and write any one example of artificial semipermeable membrane. (1+1=2)

Correct Answer: —

Solution:

Step 1: Ordinary osmosis. In osmosis, solvent molecules flow through a semipermeable membrane from the region of pure solvent (or dilute solution) into the more concentrated solution. This natural flow can be stopped by applying a pressure equal to the osmotic pressure on the solution side.

Step 2: Reverse osmosis (definition). If a pressure **greater than the osmotic pressure** is applied on the solution side, the direction of solvent flow is reversed: solvent now moves from the solution (concentrated side) into the pure solvent through the semipermeable membrane. This process is called reverse osmosis.

Step 3: Use. Reverse osmosis is used for the **desalination of sea water**, where applying high pressure on sea water pushes pure water out through the membrane, leaving the salts behind, giving drinking water.

Step 4: Example of an artificial semipermeable membrane. **Cellulose acetate** is a commonly used artificial semipermeable membrane in reverse osmosis (it allows water to pass but not the dissolved salts). Another acceptable example is copper ferrocyanide, $Cu_2[Fe(CN)_6]$.

RO: solvent forced from solution to pure solvent by pressure $> \pi$; membrane: cellulose acetate

Quick Tip: Apply pressure greater than the osmotic pressure so solvent flows out of the solution; cellulose acetate is a common artificial membrane.

8. Mention the different steps for the preparation of potassium permanganate from pyrolusite ore and draw the structure of permanganate ion. (1+1=2)

Correct Answer: —

Solution:

Step 1: Fusion of pyrolusite (formation of manganate). Pyrolusite ore (MnO_2) is fused with potassium hydroxide (KOH) in the presence of air or an oxidising agent such as KNO_3. Manganese is oxidised from the +4 to the +6 state, giving the dark green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Step 2: Oxidation of manganate to permanganate. The green manganate (MnO_4^{2-}, Mn^{+6}) is then oxidised to the purple permanganate (MnO_4^-, Mn^{+7}). This is done by electrolytic oxidation:

$$MnO_4^{2-} \rightarrow MnO_4^- + e^-$$

or by chemical oxidation (disproportionation in neutral or slightly acidic medium):

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Step 3: Structure of the permanganate ion (MnO_4^-). The manganese is in the +7 oxidation state and is sp^3 hybridised. The ion is **tetrahedral**, with the Mn atom at the centre and the four oxygen atoms at the corners of a regular tetrahedron (O to Mn to O bond angle **109.5°**). All four Mn to O bonds are equivalent and have partial double bond

character (π bonds formed by oxygen p and Mn d orbitals), and the overall ion carries a single negative charge.

MnO_4^- is tetrahedral, Mn in +7 state, four equivalent Mn to O bonds

Quick Tip: Fuse MnO_2 with KOH and air to get green K_2MnO_4, then oxidise electrolytically to purple $KMnO_4$; the MnO_4^- ion is tetrahedral.

9. Write the IUPAC names of the following coordination compounds.
(i) $[Cr(NH_3)_2Cl_2(en)]Cl$
(ii) $[Pt(NH_3)_4Cl_2][PtCl_4]$ (1+1=2)

Correct Answer: —

Solution:

Rules used: Name the ligands alphabetically, then the metal. Anionic ligands take suffix -o (chlorido), neutral ligands keep their name (ammine for NH_3, ethane-1,2-diamine for en). Use Greek prefixes (di, tetra) for simple ligands and bis, tris for complex names. State the metal oxidation number in Roman numerals. Name the cation first, then the anion.

Part (i): $[Cr(NH_3)_2Cl_2(en)]Cl$
Step 1: Ligands inside the sphere: 2 NH_3 (ammine), 2 Cl^- (chlorido), 1 en (ethane-1,2-diamine).
Step 2: Oxidation state of Cr: the complex ion charge is +1 (one Cl^- is outside). So $x + 0(NH_3 \times 2) + (-1)(Cl \times 2) + 0(en) = +1 \Rightarrow x = +3$.
Step 3: Arrange ligand names alphabetically: ammine, chlorido, ethane-1,2-diamine.

IUPAC name: diamminedichlorido(ethane-1,2-diamine)chromium(III) chloride.

Part (ii): $[Pt(NH_3)_4Cl_2][PtCl_4]$
Step 1: This has a complex cation $[Pt(NH_3)_4Cl_2]^{2+}$ and a complex anion $[PtCl_4]^{2-}$.
Step 2: Cation Pt oxidation state: $x + 0(NH_3 \times 4) + (-1)(Cl \times 2) = +2 \Rightarrow x = +4$. Anion Pt oxidation state: $y + (-1)(Cl \times 4) = -2 \Rightarrow y = +2$.
Step 3: Name cation first (ammine before chlorido), then the anion with suffix -ate on the metal (platinate).
IUPAC name: tetraamminedichloridoplatinum(IV) tetrachloridoplatinate(II).

Quick Tip: List ligands alphabetically with -o for anions; the outer Cl^- fixes Cr as +3, and for the platinum salt the anion metal becomes platinate.

10. Alkyl chloride reacts with aqueous KOH to form alcohol while in the presence of alcoholic KOH, alkene is obtained as major product. Explain. (2)

Correct Answer: —

Solution:

Step 1: With aqueous KOH (substitution). In water, KOH is almost fully ionised to give hydroxide ions OH^-. The OH^- ion is a good **nucleophile**. It attacks the carbon bearing the chlorine and replaces Cl^- by nucleophilic substitution, giving an alcohol:

$$R\text{-}CH_2\text{-}CH_2Cl + KOH\ (aq) \rightarrow R\text{-}CH_2\text{-}CH_2OH + KCl$$

Step 2: With alcoholic KOH (elimination). When KOH is dissolved in alcohol, it produces **alkoxide ions** (for example ethoxide, $C_2H_5O^-$). Alkoxide ion is a bulky, strong **base** (a poor nucleophile because of its size). Instead of attacking carbon, it abstracts a hydrogen from the β-carbon. Loss of this β-hydrogen together with the chlorine (dehydrohalogenation) forms a carbon to carbon double bond, giving an alkene as the major product:

$$R\text{-}CH_2\text{-}CH_2Cl \xrightarrow{alc.\ KOH} R\text{-}CH = CH_2 + KCl + H_2O$$

Step 3: Reason for the difference. The medium decides whether the reagent acts mainly as a nucleophile or as a base. In water OH^- behaves as a nucleophile favouring substitution (alcohol). In alcohol the alkoxide behaves as a strong base favouring elimination (alkene). Hence the products differ.

aq. KOH → substitution (alcohol); alc. KOH → elimination (alkene)

Quick Tip: Aqueous OH^- acts as nucleophile (substitution to alcohol); alcoholic KOH gives alkoxide, a strong base that removes a beta-hydrogen (elimination to alkene).

11. Define molal elevation constant. (2)

Correct Answer: —

Solution:

Step 1: The relation. When a non-volatile solute is dissolved in a solvent, the boiling point rises. The elevation in boiling point ΔT_b is directly proportional to the molality m of the solution:

$$\Delta T_b = K_b \cdot m$$

where K_b is the molal elevation constant (also called the ebullioscopic constant).

Step 2: Definition. The **molal elevation constant (K_b) is the elevation in boiling point produced when one mole of a non-volatile solute is dissolved in one kilogram (1000 g) of the solvent**, i.e. the elevation for a one molal solution. Putting $m = 1$ in the equation gives $\Delta T_b = K_b$, which shows the physical meaning.

Step 3: Units. Since $K_b = \dfrac{\Delta T_b}{m}$, its unit is kelvin kilogram per mole, $K\ kg\ mol^{-1}$ (or $^\circ C\ kg\ mol^{-1}$). It is a constant characteristic of the solvent only (for water $K_b = 0.52\ K\ kg\ mol^{-1}$).

$$\boxed{K_b = \Delta T_b \text{ for a one molal solution; unit } K\ kg\ mol^{-1}}$$

Quick Tip: From $\Delta T_b = K_b m$, put $m = 1$: K_b is the boiling point elevation for a one molal solution; unit $K\ kg\ mol^{-1}$.

12. Ortho nitrophenol is more acidic than phenol. Explain. Draw the resonance structures of their corresponding phenoxide ion. (2)

Correct Answer: —

Solution:

Step 1: What controls acidity. The acidity of a phenol depends on the stability of the phenoxide ion left behind after losing H^+. The more stable (more delocalised) the phenoxide ion, the more easily H^+ is released and the stronger the acid.

Step 2: Effect of the nitro group. The nitro group ($-NO_2$) is a strong **electron withdrawing group** (it shows both negative inductive, -I, and negative resonance, -M, effects). When placed at the ortho position of phenol, it pulls electron density away and, more importantly, allows the negative charge of the ortho-nitrophenoxide ion to be delocalised onto the oxygen atoms of the $-NO_2$ group as well as onto the ring.

Step 3: Comparison. In the plain phenoxide ion the negative charge is spread only over the ring carbons (ortho and para positions). In the ortho-nitrophenoxide ion the charge is spread over the ring and additionally onto the electronegative nitro-oxygen atoms. This extra delocalisation makes ortho-nitrophenoxide much more stable, so ortho-nitrophenol releases H^+ more readily and is **more acidic than phenol**.

Step 4: Resonance structures of the phenoxide ion. In the phenoxide ion ($C_6H_5O^-$) the negative charge on oxygen is delocalised into the benzene ring. The main resonance (canonical) structures are:

(1) negative charge on the oxygen atom;

(2) negative charge on the ortho carbon;

(3) negative charge on the para carbon;

(4) negative charge on the other ortho carbon.

$C_6H_5O^-$ ↔ (charge at O) ↔ (charge at ortho-C) ↔ (charge at para-C) ↔ (charge at other ortho-C)

For ortho-nitrophenoxide two further structures exist in which the negative charge sits on the oxygen atoms of the $-NO_2$ group, and

these extra structures are the reason for its greater stability and acidity.

$-NO_2$ ($-I, -M$) stabilises the phenoxide by extra delocalisation, so ortho-nitrophenol is more acidic

Quick Tip: The $-NO_2$ group at ortho withdraws electrons and delocalises the phenoxide charge onto its oxygens, stabilising the anion and raising acidity.

13. How will you differentiate the following?

(i) Acetaldehyde and acetone

(ii) Acetaldehyde and formaldehyde

Correct Answer: —

Solution:

Concept: Aldehydes have the $-CHO$ group and are easily oxidised, so they give positive Tollens' and Fehling's tests. Ketones lack the $-CHO$ group and fail both. The iodoform test is positive only for compounds having a CH_3CO- (methyl carbonyl) group.

Step 1: Acetaldehyde (CH_3CHO) vs Acetone (CH_3COCH_3).

Acetaldehyde is an aldehyde; acetone is a ketone. Use an oxidising test:

Tollens' test: Warm each with ammoniacal silver nitrate.

Acetaldehyde reduces Ag^+ and gives a shiny **silver mirror**; acetone gives no reaction.

$$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O$$

Fehling's test: Acetaldehyde gives a **red precipitate** of Cu_2O; acetone does not.
(Note: both give iodoform, so iodoform cannot separate this pair.)

Step 2: Acetaldehyde (CH_3CHO) vs Formaldehyde ($HCHO$).
Both are aldehydes, so both answer Tollens' and Fehling's tests. To tell them apart use the **iodoform test** (I_2 + NaOH).
Acetaldehyde has a CH_3CO- group, so it gives a **yellow precipitate** of iodoform (CHI_3):

$$CH_3CHO + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + HCOONa + 3NaI + 3H_2O$$

Formaldehyde has no CH_3CO- group, so it gives **no iodoform**.

Conclusion: Tollens'/Fehling's test separates acetaldehyde from acetone; the iodoform test separates acetaldehyde from formaldehyde.

Quick Tip: Aldehydes answer Tollens'/Fehling's, ketones do not; only CH_3CO- compounds give iodoform, so it separates acetaldehyde from formaldehyde.

14. Differentiate between fibrous and globular proteins.

Correct Answer: —

Solution:

Concept: Proteins are classified by their molecular shape (secondary/tertiary structure) into fibrous and globular types.

Step 1: Fibrous proteins.

The polypeptide chains lie side by side (parallel) and are held together by strong hydrogen bonds and disulphide bonds, giving a long, thread-like, fibre structure. They are **insoluble in water**, mechanically strong and chemically stable, and perform mainly **structural** roles. Examples: keratin (hair, nails), myosin (muscle), collagen (tendon), fibroin (silk).

Step 2: Globular proteins.

The polypeptide chains coil and fold around themselves to give a compact, roughly **spherical (ball-like)** shape. They are usually **soluble in water** (and dilute acids/bases) and are more sensitive to heat and pH. They carry out **functional/dynamic** roles such as enzymes, hormones and transport. Examples: insulin, albumin, haemoglobin, many enzymes.

Summary: Fibrous = parallel chains, fibre shape, water-insoluble, structural (keratin, collagen); Globular = coiled chains, spherical shape, water-soluble, functional (insulin, haemoglobin).

Quick Tip: Think about chain arrangement (parallel fibre vs coiled sphere), water solubility, and structural vs functional role.

15. An aqueous solution of glucose is 10% (w/w). What would be the molality and mole fraction of each component in the solution? (Molar mass of glucose = 180 g mol^{-1})

Correct Answer: —

Solution:

Concept: 10% (w/w) glucose means 10 g of glucose is present in 100 g of solution, so the solvent (water) is $100 - 10 = 90$ g.

Step 1: Moles of each component.

$$n_{glucose} = \frac{10}{180} = 0.0556 \text{ mol}$$

$$n_{water} = \frac{90}{18} = 5 \text{ mol}$$

Step 2: Molality.

Molality $= \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$. Mass of water $= 90\ g = 0.090\ kg$.

$$m = \frac{0.0556}{0.090} = 0.617 \text{ mol kg}^{-1}$$

$$\boxed{m = 0.617\ m}$$

Step 3: Mole fractions.

Total moles $= 0.0556 + 5 = 5.0556$.

$$x_{glucose} = \frac{0.0556}{5.0556} = 0.011$$

$$x_{water} = \frac{5}{5.0556} = 0.989$$

Check: $0.011 + 0.989 = 1.000$.

$$\boxed{x_{glucose} = 0.011, \quad x_{water} = 0.989}$$

Quick Tip: 10% w/w means 10 g glucose in 90 g water; use molality = mol solute / kg solvent and mole fraction = component mol / total mol.

16. Define molar conductivity of a solution of an electrolyte and explain Kohlrausch law.

Correct Answer: —

Solution:

Step 1: Molar conductivity (definition).

Molar conductivity Λ_m of an electrolytic solution is the conductance of all the ions produced by **one mole** of the electrolyte, when the solution is placed between two electrodes that are 1 cm apart and large enough to hold the whole volume.

It is related to conductivity κ and molar concentration c (in mol L^{-1}) by:

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

Its SI-based unit is S cm^2 mol^{-1}. Λ_m increases on dilution because the total volume containing one mole of electrolyte increases.

Step 2: Kohlrausch law of independent migration of ions.

At infinite dilution (when dissociation is complete), each ion migrates

independently of the other ions. So the **limiting molar conductivity** Λ_m^0 of an electrolyte is the sum of the individual limiting molar conductivities of its cation and anion:

$$\Lambda_m^0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0$$

where λ_+^0 and λ_-^0 are the limiting molar conductivities of the cation and anion, and ν_+, ν_- are the numbers of each ion produced by one formula unit.

Step 3: Applications.
(a) It gives Λ_m^0 of **weak electrolytes** (e.g. CH_3COOH) which cannot be found by extrapolation, using values of strong electrolytes.
(b) It gives the degree of dissociation $\alpha = \dfrac{\Lambda_m}{\Lambda_m^0}$ and hence the dissociation constant of a weak electrolyte.

Quick Tip: Molar conductivity $\Lambda_m = \kappa \times 1000/c$; Kohlrausch: limiting molar conductivity is the sum of independent cation and anion contributions.

17. Describe the effect of concentration and temperature on the rate of chemical reaction. Rate constant K = 5.5×10^{-14} s^{-1} for a first order reaction. Calculate the half life time of this reaction.

Correct Answer: —

Solution:

Step 1: Effect of concentration.
The rate of a reaction depends on the concentration of the reactants through the rate law, e.g. **Rate** $= k[A]^x[B]^y$. As the concentration of a

reactant increases, the number of reactant molecules per unit volume increases, so the frequency of effective collisions increases and the **rate of reaction increases**. As the reaction proceeds, reactants are used up, their concentration falls, and the rate decreases with time.

Step 2: Effect of temperature.

A rise in temperature increases the kinetic energy of the molecules, so a larger fraction of molecules have energy equal to or greater than the activation energy. This increases the number of effective collisions and hence the rate. Generally, the rate roughly **doubles for every 10 K rise** in temperature. Quantitatively, this is described by the Arrhenius equation $k = Ae^{-E_a/RT}$; as T increases, k increases.

Step 3: Half-life of a first order reaction.

For a first order reaction the half-life is independent of initial concentration and is given by:

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

Step 4: Substitution.

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14}}$$

Step 5: Arithmetic.

$$t_{1/2} = 0.126 \times 10^{14} = 1.26 \times 10^{13}\ \text{s}$$

$$\boxed{t_{1/2} = 1.26 \times 10^{13}\ \text{s}}$$

Quick Tip: More concentration and higher temperature give more effective collisions, so faster rate. For first order, $t_{1/2} = 0.693/k$.

18. (i) Explain with reason that transition metals generally form coloured compounds.
(ii) Write a short note on the lanthanoid contraction.

Correct Answer: —

Solution:

Part (i): Colour of transition metal compounds.

Step 1: Reason. Transition metal ions have partially filled (n-1)d orbitals. In the presence of ligands or in the crystal, the five d orbitals split into two sets of slightly different energy (t_{2g} and e_g).

Step 2: d-d transition. When visible light falls on the compound, an unpaired d electron absorbs a particular wavelength (energy) and is promoted from the lower to the higher d-orbital set. This is called a **d-d transition**.

Step 3: Observed colour. The compound transmits/reflects the remaining light, so it appears in the **complementary colour** of the light absorbed. Ions with completely empty (d^0, e.g. Sc^{3+}, Ti^{4+}) or completely filled (d^{10}, e.g. Zn^{2+}, Cu^{+}) d orbitals have no d-d transition and are therefore **colourless**.

Part (ii): Lanthanoid contraction.

Step 1: Statement. Across the lanthanoid series (from La to Lu), as the atomic number increases the atomic and ionic (M^{3+}) radii show a steady **decrease**. This regular decrease is called the lanthanoid contraction.

Step 2: Cause. The added electrons enter the inner 4f subshell. The 4f electrons have a poor shielding effect, so the effective nuclear charge felt by the outer electrons increases with atomic number, pulling the electron cloud closer and reducing the size.

Step 3: Consequences.

(a) Elements of the second (4d) and third (5d) transition series have almost the **same size** (e.g. Zr and Hf), so their properties are very similar and they are difficult to separate.

(b) There is a slow decrease in the basic strength of the hydroxides from $La(OH)_3$ to $Lu(OH)_3$.

(c) It causes similarity in properties of the lanthanoids, making their separation difficult.

Quick Tip: (i) Unpaired d electrons undergo d-d transitions absorbing visible light. (ii) Poor shielding by 4f electrons steadily decreases size across the series.

19. Write the Nernst equation of the following cell at 298 K and calculate its electromotive force.

$\mathbf{Mg(s) \mid Mg^{2+}\,(0.001\,M) \parallel Cu^{2+}\,(0.0001\,M) \mid Cu(s)}$

Given: $E^{\circ}_{Mg^{2+}/Mg} = -2.37\,V$ and $E^{\circ}_{Cu^{2+}/Cu} = 0.34\,V$. (4)

Correct Answer: —

Solution:

Step 1: Identify the anode and cathode.

In cell notation the electrode written on the left is the anode (oxidation) and the one on the right is the cathode (reduction). So magnesium is oxidised and copper ion is reduced.

Anode: $\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^-$

Cathode: $\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}$

Overall: $\mathrm{Mg} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Mg}^{2+} + \mathrm{Cu}$, so the number of electrons transferred $n = 2$.

Step 2: Standard cell potential.

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 - (-2.37) = 2.71\,V$.

Step 3: Write the Nernst equation at 298 K.

For the cell reaction, only ionic concentrations appear (solids taken as 1):

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\mathrm{Mg}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

Step 4: Substitute the values.

$$E_{cell} = 2.71 - \frac{0.0591}{2} \log \frac{0.001}{0.0001}$$

$$E_{cell} = 2.71 - 0.02955 \times \log(10)$$

Step 5: Simplify.

Since $\log 10 = 1$:

$$E_{cell} = 2.71 - 0.02955 = 2.6805\,V$$

Result:

$$\boxed{E_{cell} \approx 2.68\,V}$$

The positive value confirms the reaction is spontaneous.

Quick Tip: Mg is the anode, Cu the cathode; use $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$ with $E^\circ_{cell} = 2.71\,V$ and $n = 2$.

20. What is the order of reaction? Derive the integrated rate equation for a first order reaction and obtain an expression for the half life period of this reaction. (1+2+1=4)

Correct Answer: —

Solution:

Step 1: Order of reaction.

The order of a reaction is the sum of the powers to which the concentration terms are raised in the experimentally determined rate law. For a rate law $\text{rate} = k[A]^x[B]^y$, the order is $x + y$. It is an experimental quantity and may be zero, a whole number or even a fraction.

Step 2: Set up the first order rate law.

For a first order reaction $A \rightarrow$ products, the rate depends on the first power of the reactant concentration:

$$\text{rate} = -\frac{d[A]}{dt} = k[A]$$

Step 3: Separate the variables and integrate.

$$-\frac{d[A]}{[A]} = k\,dt$$

Integrating both sides:

$$-\int \frac{d[A]}{[A]} = k\int dt \Rightarrow -\ln[A] = kt + C$$

At $t = 0$, $[A] = [A]_0$, so $C = -\ln[A]_0$. Substituting back:

$$-\ln[A] = kt - \ln[A]_0$$

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

Converting to base 10:

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

This is the integrated rate equation for a first order reaction.

Step 4: Half life expression.

Half life $t_{1/2}$ is the time when $[A] = \frac{[A]_0}{2}$. Substituting:

$$k = \frac{2.303}{t_{1/2}}\log\frac{[A]_0}{[A]_0/2} = \frac{2.303}{t_{1/2}}\log 2$$

$$t_{1/2} = \frac{2.303 \times 0.301}{k} = \frac{0.693}{k}$$

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

The half life of a first order reaction is independent of the initial concentration.

Quick Tip: Order = sum of concentration exponents in the rate law. Start from $-\frac{d[A]}{dt} = k[A]$, integrate to $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$, then set $[A] = [A]_0/2$ to get $t_{1/2} = 0.693/k$.

21. Discuss the chelate effect with an example. Explain the nature of bonding in $[Fe(CN)_6]^{4-}$ on the basis of valence bond theory. (2+2=4)

Correct Answer: —

Solution:

Step 1: Chelate effect.

When a polydentate (bidentate or higher) ligand binds to a central metal ion through two or more donor atoms, it forms a closed ring containing the metal. Such ring-forming ligands are called chelating ligands and the rings are chelate rings. The chelate effect is the observation that a complex containing chelate rings is much more stable than a comparable complex formed by an equal number of similar monodentate ligands.

Step 2: Example and reason.

$[Ni(en)_3]^{2+}$ (en = ethylenediamine, bidentate) is far more stable than $[Ni(NH_3)_6]^{2+}$, even though both bind six N atoms to Ni. The extra stability is mainly an entropy effect: when one chelating molecule replaces two monodentate ligands, the number of free particles in solution increases, so ΔS is positive and $\Delta G = \Delta H - T\Delta S$ becomes more negative.

Step 3: Oxidation state and electron configuration in $[Fe(CN)_6]^{4-}$.

Let the oxidation state of Fe be x: $x + 6(-1) = -4 \Rightarrow x = +2$. Iron (Z = 26) is $[Ar]3d^6 4s^2$; Fe^{2+} is $[Ar]3d^6$, giving 6 electrons distributed as t_{2g} type with 4 unpaired electrons in the free ion.

Step 4: Effect of the strong field ligand and hybridisation.

CN^- is a strong field ligand, so it forces the 3d electrons to pair up. The six 3d electrons occupy only three d orbitals (all paired), leaving two inner 3d orbitals empty. These two empty 3d orbitals combine with one 4s and three 4p orbitals to give d^2sp^3 hybridisation.

Step 5: Geometry and magnetic nature.

The six d^2sp^3 hybrid orbitals accept lone pairs from six CN^- ligands, giving an octahedral, inner-orbital (low spin) complex. As all electrons are paired, $[Fe(CN)_6]^{4-}$ is diamagnetic.

Octahedral, d^2sp^3, low spin, diamagnetic

Quick Tip: Chelate effect = extra stability from ring-forming polydentate ligands (entropy driven), e.g. $[Ni(en)_3]^{2+}$. For $[Fe(CN)_6]^{4-}$: Fe is +2 ($3d^6$), strong-field CN^- pairs the electrons giving d^2sp^3, octahedral, diamagnetic.

22. (i) Write a short note on the cyclic structure of glucose.
(ii) What is the difference between a nucleoside and a nucleotide?
(2+2=4)

Correct Answer: —

Solution:

Part (i): Cyclic structure of glucose.

Step 1: Why an open chain is not enough.
The open-chain (Fischer) form of glucose is an aldohexose with a **−CHO** group at C-1. However, several observations (glucose does not give the Schiff test, does not form the hydrogensulphite addition product with $NaHSO_3$, and exists in two crystalline forms) cannot be explained by the open chain alone.

Step 2: Formation of the ring.
The **−OH** group on C-5 attacks the aldehyde carbon (C-1) intramolecularly. This forms a stable six-membered ring (a cyclic hemiacetal) containing one oxygen atom, called the pyranose ring.

Step 3: The anomeric carbon and anomers.
During ring closure, C-1 becomes a new chiral (asymmetric) centre called the anomeric carbon. Depending on the orientation of the newly formed **−OH** at C-1, two forms arise: **α-D-glucose** (**−OH** at C-1 below the plane, on the right in Fischer) and **β-D-glucose** (**−OH** at C-1 above the plane, on the left). These are called anomers.

Step 4: Conclusion.
The two anomers interconvert in solution through the small amount of

open-chain form, a process called mutarotation. The cyclic pyranose structure therefore explains the missing aldehyde reactions and the existence of two forms of glucose.

Part (ii): Nucleoside versus nucleotide.

Step 5: Nucleoside.
A nucleoside is formed when a nitrogenous base (purine or pyrimidine) is joined to a pentose sugar (ribose or deoxyribose) at C-1' of the sugar through an N-glycosidic bond. Composition: base + sugar (no phosphate).

Step 6: Nucleotide.
A nucleotide is formed when a phosphoric acid group is attached (esterified) to the C-5' $-OH$ of the sugar in a nucleoside. Composition: base + sugar + phosphate.

$$\boxed{\text{Nucleoside} = \text{base} + \text{sugar}; \quad \text{Nucleotide} = \text{base} + \text{sugar} + \text{phosphate}}$$

Thus a nucleotide is simply a phosphorylated nucleoside, and nucleotides are the building blocks that link together to form nucleic acids (DNA and RNA).

Quick Tip: Glucose: C-5 $-OH$ closes onto the C-1 $-CHO$ to give a six-membered pyranose hemiacetal, creating the anomeric carbon and the α/β anomers. Nucleoside = base + sugar; nucleotide = base + sugar + phosphate.

23. Write short notes on the following: (i) Freons (ii) Sandmeyer reaction (iii) Friedel Craft acylation of haloarene. (2+1½+1½=5)

OR

What happens when (write chemical equation only): (i) Propene reacts with HI (ii) Ethyl bromide reacts with magnesium in the presence of dry ether (iii) Chlorobenzene is heated with sodium in dry ether (iv) The mixture of chlorobenzene and methyl chloride is heated with sodium in the presence of dry ether (v) Isopropyl alcohol reacts with conc. HCl and $ZnCl_2$. (1+1+1+1+1=5)

Correct Answer: —

Solution:

Option 1 — Short notes

(i) Freons: Freons are the trade name for chlorofluorocarbons (CFCs), the fully halogenated derivatives of methane and ethane in which every hydrogen is replaced by chlorine and fluorine atoms. The most common member is Freon-12, dichlorodifluoromethane CCl_2F_2. It is manufactured from carbon tetrachloride by the **Swarts reaction**, in which chlorine is exchanged for fluorine using antimony halides as catalyst:

$$CCl_4 + 2HF \xrightarrow{SbF_5} CCl_2F_2 + 2HCl$$

Freons are colourless, odourless, non-toxic, non-corrosive and chemically inert gases. Because of these properties they are used as refrigerants in refrigerators and air conditioners and as aerosol propellants. In the stratosphere ultraviolet light splits them to give chlorine free radicals which destroy the ozone layer, so their use is now restricted.

(ii) Sandmeyer reaction: When a primary aromatic amine (aniline) is treated with sodium nitrite and dilute HCl at 273–278 K it forms a benzene diazonium salt. When the diazonium chloride solution is treated with cuprous halide (cuprous chloride in HCl, or cuprous bromide in HBr), the diazonium group $-N_2^+$ is replaced by the halogen and nitrogen gas is evolved. This is the Sandmeyer reaction:

$$C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2$$

$$C_6H_5N_2^+Cl^- \xrightarrow{CuBr/HBr} C_6H_5Br + N_2$$

With cuprous cyanide (CuCN) the cyano group is introduced to give benzonitrile. It is a convenient way to place a halogen exactly where the amino group was on the ring.

(iii) Friedel-Craft acylation of haloarene: A haloarene such as chlorobenzene reacts with an acyl chloride (for example acetyl chloride, CH_3COCl) in the presence of the Lewis acid catalyst anhydrous aluminium chloride $AlCl_3$. The $AlCl_3$ generates an acylium ion CH_3CO^+ that attacks the ring. Although the halogen is deactivating, it is **ortho and para directing**, so the acyl group enters mainly at the para position (with some ortho):

$$C_6H_5Cl + CH_3COCl \xrightarrow{\text{anhyd. } AlCl_3} p\text{-}ClC_6H_4COCH_3 + HCl$$

The main product is para-chloroacetophenone.

Quick Tip: Part 1: Freon-12 by Swarts reaction, Sandmeyer uses diazonium + cuprous halide, and the ring halogen is ortho/para directing in acylation. Part 2: apply Markovnikov (i), Grignard formation (ii), Fittig (iii) and Wurtz-Fittig (iv) coupling, and Lucas reagent (v).

24. (i) Write notes on Williamson's synthesis. (ii) Write the chemical equation for the preparation of phenol from cumene. (iii) How will you convert phenol to salicylaldehyde? (2+1½+1½=5)

OR

What happens when (write chemical equations only): (i) Phenol reacts with dil. HNO_3 (ii) Ethyl methyl ether is heated with conc. HI (iii) Phenol is heated with conc. HNO_3 in the presence of conc. H_2SO_4 (iv) Ethyl alcohol reacts with thionyl chloride in the presence of pyridine (v) Phenol reacts with bromine water. (1+1+1+1+1=5)

Correct Answer: —

Solution:

Option 1

(i) Williamson's synthesis: It is the most important general laboratory method for preparing ethers, both symmetrical and unsymmetrical. An alkyl halide is heated with sodium alkoxide (or sodium phenoxide). The alkoxide ion is a strong nucleophile that attacks the carbon of the alkyl halide by an S_N2 mechanism, displacing the halide ion and forming the ether linkage:

$$R{-}X + R'{-}\bar{O}Na^+ \rightarrow R{-}O{-}R' + NaX$$

For example, diethyl ether is made from ethyl bromide and sodium ethoxide:

$$C_2H_5Br + C_2H_5ONa \rightarrow C_2H_5{-}O{-}C_2H_5 + NaBr$$

The reaction works best with **primary** alkyl halides; secondary and especially tertiary halides tend to undergo elimination (alkene

formation) instead. Aromatic ethers such as anisole are made from sodium phenoxide and methyl iodide:

$$C_6H_5ONa + CH_3I \rightarrow C_6H_5{-}O{-}CH_3 + NaI$$

(ii) Preparation of phenol from cumene: Cumene (isopropylbenzene) is oxidised by air to cumene hydroperoxide, which is then treated with dilute acid. The acid cleaves it to phenol and acetone:

$$C_6H_5CH(CH_3)_2 \xrightarrow{O_2\ (\text{air})} C_6H_5C(CH_3)_2OOH \xrightarrow{H_3O^+} C_6H_5OH + (CH_3)_2C{=}O$$

Acetone is a valuable by-product of this industrial route.

(iii) Conversion of phenol to salicylaldehyde (Reimer-Tiemann reaction): Phenol is heated with chloroform and aqueous sodium hydroxide. The NaOH and $CHCl_3$ generate the electrophile dichlorocarbene ($:CCl_2$), which attacks the ortho position of the phenoxide ring. Hydrolysis of the resulting intermediate on acidification gives an ortho $-CHO$ group, that is salicylaldehyde (2-hydroxybenzaldehyde):

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{\Delta} o\text{-}HOC_6H_4CHO + 3NaCl + 2H_2O$$

Quick Tip: Part 1: Williamson is an S_N2 reaction of alkoxide with a primary alkyl halide; cumene gives phenol plus acetone; phenol to salicylaldehyde is the Reimer-Tiemann reaction with CHCl3/NaOH. Part 2: recall nitration, ether cleavage by HI, picric acid, SOCl2 chlorination and tribromophenol formation.

25. Write short notes on the following. (i) Cross aldol condensation (ii) Stephen reaction (iii) Etard reaction. (2+1½+1½=5)

OR

How will you obtain (write chemical equations only): (i) Ethanoic anhydride from Ethanoic acid (ii) Benzoic acid from Ethyl benzoate (iii) Benzamide from benzoic acid. (2+1½+1½=5)

Correct Answer: —

Solution:

Option 1

(i) Cross aldol condensation:

Step 1: An aldol condensation carried out between two *different* carbonyl compounds (two different aldehydes, two different ketones, or an aldehyde and a ketone) is called a cross aldol condensation. At least one of the reactants must possess an α-hydrogen so that its enolate/carbanion can be generated by the base.

Step 2: A dilute base (NaOH) removes the acidic α-hydrogen to give a carbanion, which adds to the carbonyl carbon of the second molecule to give a β-hydroxy carbonyl compound (aldol). On warming, this loses water to give an α,β-unsaturated carbonyl compound.

Step 3: When one component has NO α-hydrogen (e.g. benzaldehyde), a single clean product is obtained. Example (ethanal + benzaldehyde):

$$C_6H_5CHO + CH_3CHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH = CHCHO + H_2O$$

(3-phenylprop-2-enal, cinnamaldehyde). If both partners have α-hydrogens, a mixture of four products results, so cross aldol is synthetically useful mainly when one partner lacks α-H.

(ii) Stephen reaction:

Step 1: A nitrile (alkyl cyanide) is reduced to an imine using stannous chloride ($SnCl_2$) and hydrochloric acid.

Step 2: The intermediate imine salt is hydrolysed to the corresponding aldehyde.

$$RC \equiv N \xrightarrow{SnCl_2/HCl} RCH = NH \xrightarrow{H_3O^+} RCHO + NH_3$$

Thus a nitrile with n carbons gives an aldehyde with the same number of carbons. It is a method to prepare aldehydes from nitriles.

(iii) Etard reaction:

Step 1: Toluene (or a substituted toluene) is treated with chromyl chloride (CrO_2Cl_2) in a solvent such as CS_2 or CCl_4. The methyl group is oxidised and a brown chromium complex separates out.

Step 2: This complex is hydrolysed with water to give benzaldehyde, without over-oxidation to benzoic acid.

$$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2,\ CS_2} \text{chromium complex} \xrightarrow{H_3O^+} C_6H_5CHO$$

Option 2

(i) Ethanoic anhydride from ethanoic acid: Ethanoic acid is dehydrated by heating with a dehydrating agent such as P_2O_5.

$$2\,CH_3COOH \xrightarrow{P_2O_5,\ \Delta} (CH_3CO)_2O + H_2O$$

(ii) Benzoic acid from ethyl benzoate: Alkaline hydrolysis of the ester followed by acidification.

$$C_6H_5COOC_2H_5 + NaOH \rightarrow C_6H_5COONa + C_2H_5OH$$

$$C_6H_5COONa + HCl \rightarrow C_6H_5COOH + NaCl$$

(iii) Benzamide from benzoic acid: Benzoic acid reacts with ammonia to form ammonium benzoate, which on heating loses water to give benzamide.

$$C_6H_5COOH + NH_3 \rightarrow C_6H_5COONH_4 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O$$

Quick Tip: Option 1: aldol between two different carbonyls (one lacking α-H gives a single product); nitrile + $SnCl_2$/HCl then hydrolysis gives an aldehyde; toluene + chromyl chloride gives benzaldehyde. Option 2: dehydrate the acid with P_2O_5; hydrolyse the ester then acidify; make the ammonium salt and heat.

26. (i) Explain Hinsberg test for the distinction between primary, secondary and tertiary amines. (ii) Write a short note on Carbylamine reaction. (2½+2½=5)

OR

What happens when (write chemical equations only): (i) Aqueous solution of benzene diazonium chloride is heated (ii) Acetamide is reacted with aqueous KOH in the presence of bromine (iii) Aniline reacts with sodium nitrite and dil. HCl at 0°C (iv) Aniline reacts with acetic anhydride in the presence of pyridine (v) Aniline reacts with Bromine water.
(1+1+1+1+1=5)

Correct Answer: —

Solution:

Option 1

(i) Hinsberg test:

Step 1: The reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$ (Hinsberg's reagent). The amine is shaken with this reagent in presence of aqueous KOH; the behaviour of the product towards alkali distinguishes the three classes of amine.

Step 2 (primary amine): It reacts to form an N-alkylbenzenesulphonamide. The H atom still attached to nitrogen is acidic (activated by the $-SO_2-$ group), so the product dissolves in KOH to give a clear solution.

$$C_6H_5SO_2Cl + H_2N-R \rightarrow C_6H_5SO_2NHR \xrightarrow{KOH} C_6H_5SO_2N^-R \text{ (soluble)}$$

Step 3 (secondary amine): It forms an N,N-dialkylbenzenesulphonamide. There is no H left on nitrogen, so it

cannot form a salt and remains insoluble in KOH (a precipitate/oily layer).

$$C_6H_5SO_2Cl + HNR_2 \rightarrow C_6H_5SO_2NR_2 \text{ (insoluble in KOH)}$$

Step 4 (tertiary amine): It has no replaceable H on nitrogen and does not react with the reagent at all; it remains as an insoluble layer that dissolves in acid.
Summary: primary → product soluble in alkali; secondary → product insoluble in alkali; tertiary → no reaction.

(ii) Carbylamine reaction:
Step 1: Aliphatic and aromatic *primary* amines, when heated with chloroform ($CHCl_3$) and alcoholic KOH, produce isocyanides (carbylamines) which have an extremely offensive (foul) smell.
Step 2: The reaction:

$$R - NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R - NC + 3KCl + 3H_2O$$

(e.g. $C_6H_5NH_2 \rightarrow C_6H_5NC$, phenyl isocyanide).
Step 3: Secondary and tertiary amines do NOT give this reaction, so the carbylamine (isocyanide) test is a specific test used to detect primary amines.

Option 2

(i) Warming the aqueous diazonium salt replaces $-N_2^+$ by $-OH$, giving phenol:

$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2 + HCl$$

(ii) Hofmann bromamide degradation; the amide loses one carbon to give an amine with one carbon less:

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

(iii) Diazotisation at 273–278 K gives benzene diazonium chloride:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278\ K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

(iv) Acetylation of the amino group gives acetanilide:

$$C_6H_5NH_2 + (CH_3CO)_2O \xrightarrow{\text{pyridine}} C_6H_5NHCOCH_3 + CH_3COOH$$

(v) Bromine water gives the white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3(NH_2) + 3HBr$$

Quick Tip: Option 1: Hinsberg's reagent is benzenesulphonyl chloride; the number of N-H bonds left decides solubility in KOH (1° soluble, 2° insoluble, 3° no reaction). Carbylamine (isocyanide) test with $CHCl_3$ + alc. KOH is specific for primary amines. Option 2: think phenol formation, Hofmann degradation, diazotisation, acetylation, and 2,4,6-tribromoaniline.