

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: Osmotic pressure is a colligative property.

Reason: Osmotic pressure is directly proportional to molarity at a given temperature.

- (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: A colligative property is one that depends only on the number of solute particles present and not on their chemical nature. Osmotic pressure is measured by $\pi = CRT$, where C is the molar concentration

of the solute particles. Since it depends on the number of particles, osmotic pressure is a colligative property, so the assertion is true.

Step 2: From the van't Hoff relation $\pi = CRT = \frac{n}{V}RT$. At a fixed temperature T , the term RT is constant, so π is directly proportional to the molar concentration (molarity). Hence the reason is also true.

Step 3: The reason states exactly the mathematical form that makes osmotic pressure depend on concentration of particles, which is precisely why it behaves as a colligative property. Therefore the reason is the correct explanation of the assertion.

Conclusion: Option (i) is correct.

Why others are wrong: (ii) is wrong because the reason does explain the assertion; (iii) and (iv) are wrong because both statements are individually true.

Quick Tip: Use $\pi = CRT$; at constant T , osmotic pressure tracks molar concentration of particles, which is the very meaning of a colligative property.



2. Which of the following ions forms coloured solution?

- (A) Ti^{4+}
- (B) Fe^{3+}
- (C) Zn^{2+}
- (D) Cu^{+}

Correct Answer: (B) Fe^{3+}

Solution:

Step 1: Colour in transition metal ions arises from d-d electronic transitions. This requires the d-orbitals to be partially filled (some

unpaired d electrons). Ions with empty (d^0) or completely filled (d^{10}) d-orbitals are colourless because no d-d transition is possible.

Step 2: Write the configurations. $Ti^{4+} = [Ar]3d^0$ (no d electron, colourless). $Fe^{3+} = [Ar]3d^5$ (five unpaired d electrons, coloured). $Zn^{2+} = [Ar]3d^{10}$ (filled, colourless). $Cu^+ = [Ar]3d^{10}$ (filled, colourless).

Step 3: Only Fe^{3+} has partially filled d-orbitals, so only its solution is coloured.

Conclusion: Option (ii) Fe^{3+} is correct.

Quick Tip: A transition-metal ion is coloured only if it has partially filled d-orbitals; d^0 and d^{10} ions are colourless.

3. Which type of isomerism exists between the complexes $[CoBr(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]Br$?

- (A) Linkage isomerism
- (B) Solvate isomerism
- (C) Ionisation isomerism
- (D) Coordination isomerism

Correct Answer: (C) Ionisation isomerism

Solution:

Step 1: Ionisation isomers are complexes that have the same molecular formula but exchange an anion between the coordination sphere (bonded to the metal) and the position of the counter ion (outside the sphere). They give different ions when dissolved in water.

Step 2: In $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$, bromide is coordinated to cobalt and sulphate is the free counter ion, so in solution it releases SO_4^{2-} . In $[\text{CoSO}_4(\text{NH}_3)_5]\text{Br}$, sulphate is coordinated and bromide is the free counter ion, so it releases Br^- . The two swap Br^- and SO_4^{2-} between inside and outside the sphere.

Step 3: This exchange of ions between the coordination sphere and the ionisation sphere is the definition of ionisation isomerism (the first gives a white BaSO_4 test negative but AgBr positive difference from the second).

Conclusion: Option (iii) is correct. Linkage isomerism needs an ambidentate ligand, coordination isomerism needs both cation and anion to be complex ions, and solvate isomerism involves water molecules inside or outside the sphere; none of these apply here.

Quick Tip: The anion inside the coordination sphere and the counter ion outside have been swapped; such isomers give different ions in solution.

4. The reagent which does NOT react with both acetone and benzaldehyde is

- (A) Sodium hydrogen sulphite
- (B) Benedict's reagent
- (C) Grignard reagent
- (D) Phenyl hydrazine

Correct Answer: (B) Benedict's reagent

Solution:

Step 1: We must find the reagent that reacts with neither acetone (a ketone) nor benzaldehyde (an aromatic aldehyde).

Step 2: Benedict's reagent (like Fehling's) is a mild oxidising reagent that oxidises only aliphatic aldehydes. It does not oxidise ketones, so it fails with acetone, and it does not oxidise aromatic aldehydes, so it fails with benzaldehyde. Hence Benedict's reagent reacts with neither compound.

Step 3: Check the others. Sodium hydrogen sulphite (NaHSO_3) forms crystalline bisulphite addition compounds with both acetone and benzaldehyde. Grignard reagent adds across the carbonyl ($\text{C}=\text{O}$) of both to give alcohols after hydrolysis. Phenyl hydrazine condenses with the carbonyl of both to form phenylhydrazones. So each of these does react with both.

Conclusion: Option (ii) Benedict's reagent is correct.

Quick Tip: Benedict's and Fehling's reagents oxidise only aliphatic aldehydes, not ketones or aromatic aldehydes.



5. When aniline is heated with CHCl_3 in the presence of KOH , the product formed is

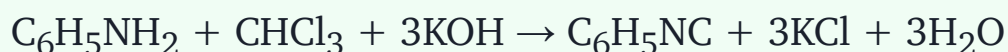
- (A) Phenyl isothiocyanate
- (B) Phenyl isocyanide
- (C) Phenyl cyanide
- (D) Phenol

Correct Answer: (B) Phenyl isocyanide

Solution:

Step 1: This is the carbylamine (isocyanide) test. A primary amine, when heated with chloroform (CHCl_3) and alcoholic KOH, gives a foul-smelling isocyanide (carbylamine).

Step 2: Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) is a primary aromatic amine, so it undergoes this reaction:



Step 3: The organic product is phenyl isocyanide ($\text{C}_6\text{H}_5\text{NC}$), recognised by its extremely unpleasant smell.

Conclusion: Option (ii) Phenyl isocyanide is correct. Phenyl cyanide ($\text{C}_6\text{H}_5\text{CN}$) and phenol are not formed in this reaction, and isothiocyanate needs CS_2 , not CHCl_3 .

Quick Tip: Primary amine + CHCl_3 + alcoholic KOH is the carbylamine reaction, giving a foul-smelling isocyanide.

6. α -D(+)-glucose and β -D(+)-glucose are

- (A) Geometrical isomers
- (B) Epimers
- (C) Enantiomers
- (D) Anomers

Correct Answer: (D) Anomers

Solution:

Step 1: When glucose forms its cyclic (pyranose) structure, the open-chain aldehyde carbon (C1) becomes a new chiral centre called the anomeric carbon. Two ring forms result, differing only in the arrangement of the -OH at this C1.

Step 2: In α -D-glucose the C1 -OH points down (opposite side to the C6 CH₂OH reference), while in β -D-glucose the C1 -OH points up.

They differ in configuration only at the anomeric carbon C1.

Step 3: Cyclic sugars that differ in configuration at the anomeric carbon are called anomers.

Conclusion: Option (iv) Anomers is correct. They are not enantiomers (not mirror images at all centres), not epimers (epimers differ at a carbon other than the anomeric one), and not geometrical isomers (no C=C double bond is involved).

Quick Tip: They differ only at the anomeric carbon C1 formed on ring closure; such cyclic sugar isomers are anomers.



7. Aqueous solution of sodium chloride boils at higher temperature than water, but it freezes at lower temperature than water. Explain with reason.

Correct Answer: —

Solution:

Step 1: Sodium chloride is a non-volatile solute. When it is dissolved in water it lowers the vapour pressure of the solution below that of pure water. Elevation of boiling point and depression of freezing point are colligative properties that follow directly from this vapour-pressure lowering.

Step 2 (boils higher): A liquid boils when its vapour pressure equals the external (atmospheric) pressure. Because the salt solution has a lower vapour pressure, it must be heated to a higher temperature to reach atmospheric pressure. Hence the boiling point rises: elevation of boiling point $\Delta T_b = i K_b m$.

Step 3 (freezes lower): Freezing occurs when the vapour pressure of the liquid equals that of the solid solvent (ice). The lowered vapour pressure of the solution meets the ice curve only at a lower temperature, so the solution freezes below 0 degree C: depression of freezing point $\Delta T_f = i K_f m$.

Step 4: NaCl also ionises completely into Na^+ and Cl^- , so the van't Hoff factor $i \approx 2$. This doubles the number of particles and makes both effects even larger. Therefore the NaCl solution boils higher and freezes lower than pure water.

Quick Tip: Non-volatile NaCl lowers the vapour pressure; this raises boiling point ($\Delta T_b = i K_b m$) and lowers freezing point ($\Delta T_f = i K_f m$), with $i \approx 2$.



8. Mention the different steps for the preparation of potassium dichromate from iron chromite ore and draw the structure of dichromate ion.

Correct Answer: —

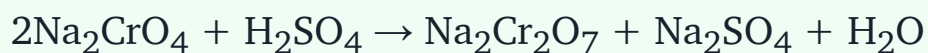
Solution:

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is prepared from chromite ore, FeCr_2O_4 (iron chromite), in three main steps.

Step 1 (Conversion of chromite to sodium chromate): The powdered ore is fused with molten sodium carbonate (or NaOH) in excess air. Chromium is oxidised to the +6 state, giving yellow sodium chromate:

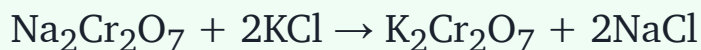


Step 2 (Sodium chromate to sodium dichromate): The chromate solution is acidified with concentrated sulphuric acid, which converts orange-yellow chromate into orange sodium dichromate:



Step 3 (Sodium dichromate to potassium dichromate): The hot sodium dichromate solution is treated with potassium chloride.

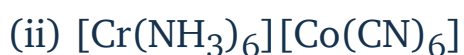
Potassium dichromate, being less soluble, crystallises out on cooling:



Structure of dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$): It consists of two CrO_4 tetrahedra joined by sharing one corner oxygen atom, giving a Cr-O-Cr bridge. Each chromium is in the +6 oxidation state, tetrahedrally surrounded by oxygen; the bridging Cr-O-Cr angle is about 126 degrees.

Quick Tip: Fuse chromite with Na_2CO_3 in air to chromate, acidify to dichromate, then add KCl. The $\text{Cr}_2\text{O}_7^{2-}$ ion is two CrO_4 tetrahedra sharing one oxygen.

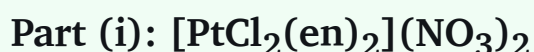
9. Write IUPAC names of the following coordination compounds:



Correct Answer: —

Solution:

Rules used: Ligands are named alphabetically before the metal, anionic ligands take the ending -o (chlorido), the neutral ligand ethane-1,2-diamine (en) is a bis- type so multiplying prefixes bis/tris are used with brackets, and the oxidation state of the metal is written in Roman numerals. In an anionic complex the metal ends in -ate.



Step 1: The two nitrate ions outside carry -2 total charge, so the complex cation is +2.

Step 2: Let the oxidation state of Pt be x. Then $x + 2(-1 \text{ from Cl}) + 2(0 \text{ from en}) = +2$, giving $x = +4$.

Step 3: Naming alphabetically (chlorido before ethanediamine):
dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate.

Part (ii): $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

Step 1: The cation is $[\text{Cr}(\text{NH}_3)_6]^{3+}$ with Cr = +3 (six neutral NH_3).

The anion is $[\text{Co}(\text{CN})_6]^{3-}$ with Co = +3 (six CN^- : $x - 6 = -3$).

Step 2: Cation named first, then anion with -ate ending on cobalt:
hexaamminechromium(III) hexacyanidocobaltate(III).

Quick Tip: Balance charges from the counter ions to get the metal oxidation number, use bis(ethane-1,2-diamine) for en, and end the anionic metal in -ate.

10. Explain the mechanism of bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reaction of alkyl halide.

Correct Answer: —

Solution:

Step 1 (What $\text{S}_{\text{N}}2$ means): $\text{S}_{\text{N}}2$ stands for substitution, nucleophilic, bimolecular. It is a single-step (concerted) reaction in which the nucleophile forms a bond to carbon at the same time as the leaving group (halide) breaks away. Both the alkyl halide and the nucleophile take part in the rate-determining step.

Step 2 (Backside attack): The nucleophile (for example OH^-) approaches the carbon bearing the halogen from the side exactly

opposite to the leaving group. This is because the C-X bond has a region of low electron density on the far side of carbon.

Step 3 (Transition state): At the midpoint a transition state forms in which carbon is partially bonded to both the incoming nucleophile and the outgoing halide. The three other groups on carbon lie in a plane, giving a trigonal bipyramidal (pentacoordinate) arrangement.

Step 4 (Product and inversion): As the nucleophile completes its bond, the halide leaves with the bonding pair, and the three groups flip through to the other side, like an umbrella turning inside out. This gives inversion of configuration (Walden inversion) at the reacting carbon.

Step 5 (Kinetics and reactivity): Because both species appear in the slow step, the rate law is $\text{rate} = k[\text{alkyl halide}][\text{nucleophile}]$, i.e. second order. Less hindered carbons react faster, so the order of reactivity is primary > secondary > tertiary alkyl halide.

Example: $\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$.

Quick Tip: Concerted one-step backside attack by the nucleophile, a pentacoordinate transition state, inversion of configuration, and second-order $\text{rate} = k[\text{RX}][\text{Nu}]$.

11. Define molality and molarity.

Correct Answer: —

Solution:

Step 1 (Molality): Molality (m) is the number of moles of solute dissolved per kilogram of solvent. It is expressed in mol kg^{-1} :

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

Because it is based on mass, molality does not change with temperature.

Step 2 (Molarity): Molarity (M) is the number of moles of solute dissolved per litre of solution. It is expressed in mol L^{-1} :

$$M = \frac{\text{moles of solute}}{\text{volume of solution in litres}}$$

Since volume expands or contracts with temperature, molarity changes slightly with temperature.

Step 3 (Note): Molality uses mass of the solvent, whereas molarity uses the volume of the whole solution, which is the key difference between the two.

Quick Tip: Molality = moles solute per kg of solvent (temperature independent); molarity = moles solute per litre of solution (temperature dependent).

12. Explain why phenol is more acidic than ethyl alcohol.

Correct Answer: —

Solution:

Step 1 (Acidity depends on anion stability): An -OH compound is more acidic when the anion left after losing H^+ is more stable. So we compare the phenoxide ion (from phenol) with the ethoxide ion (from ethanol).

Step 2 (Phenoxide is resonance stabilised): In the phenoxide ion the oxygen lone pair and its negative charge are delocalised into the benzene ring through resonance, spreading the charge over the ortho and para carbons. This delocalisation strongly stabilises the phenoxide ion.

Step 3 (Ethoxide is not stabilised): In the ethoxide ion the negative charge stays localised on the single oxygen atom, with no ring to disperse it. Moreover the ethyl group is electron releasing (+I effect), which pushes electron density towards oxygen and destabilises the anion.

Step 4 (Bond polarity): In phenol the oxygen is attached to an sp^2 carbon of the ring, which is more electronegative and pulls electron density, making the O-H bond more polar and easier to break.

Conclusion: Because the phenoxide ion is much more stable (resonance) than the ethoxide ion, phenol releases H^+ more readily and is therefore more acidic than ethyl alcohol.

Quick Tip: The phenoxide ion is resonance stabilised over the ring, while ethoxide keeps the charge on one oxygen and is destabilised by the +I ethyl group.

13. Write the chemical equations when an aldehyde reacts with the following: (i) Tollen's reagent (ii) Fehling's reagent. (1 + 1 = 2)

Correct Answer: —

Solution:

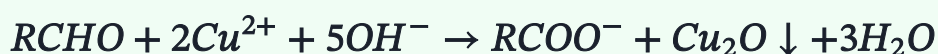
Concept: Aldehydes are readily oxidised by mild oxidising agents. Tollen's reagent and Fehling's solution are gentle oxidisers used to

detect the aldehyde group; they oxidise the aldehyde to the corresponding carboxylate ion while they themselves get reduced. Ketones do not respond to these tests.

Step 1: Reaction with Tollen's reagent. Tollen's reagent is an ammoniacal solution of silver nitrate, i.e. it contains the diammine silver(I) ion $[Ag(NH_3)_2]^+$. On warming with an aldehyde, silver ion is reduced to metallic silver, which deposits as a shiny silver mirror on the inside of the tube. The aldehyde is oxidised to a carboxylate ion.



Step 2: Reaction with Fehling's reagent. Fehling's solution is a deep blue alkaline solution of a copper(II) complex (Fehling A = copper sulphate, Fehling B = sodium potassium tartrate in NaOH). On heating with an aliphatic aldehyde the blue Cu^{2+} is reduced to a red-brown precipitate of cuprous oxide Cu_2O , while the aldehyde is oxidised to the carboxylate.



Result: A silver mirror confirms Tollen's test and a red-brown Cu_2O precipitate confirms Fehling's test; both prove the presence of the aldehyde group.

Quick Tip: Both are mild oxidisers of the aldehyde group: Tollen's gives a silver mirror (Ag) and Fehling's gives a red precipitate of Cu_2O , while the aldehyde becomes a carboxylate.

14. Write a short note on the structure of nucleic acid. (2)

Correct Answer: —

Solution:

Concept: Nucleic acids (DNA and RNA) are long-chain biomolecules (polynucleotides) that store and transfer genetic information. Their structure is best understood at two levels: the building block (nucleotide) and the way these blocks join into a chain.

Step 1: The building unit. The repeating unit of a nucleic acid is a nucleotide, made of three parts joined together:

(a) a nitrogen-containing base, (b) a pentose sugar, and (c) a phosphate group.

A base joined to only the sugar is a nucleoside; adding the phosphate makes it a nucleotide.

Step 2: The components.

Sugar: β -D-2-deoxyribose in DNA and β -D-ribose in RNA.

Bases: purines adenine (A) and guanine (G); pyrimidines cytosine (C), thymine (T, only in DNA) and uracil (U, only in RNA).

Step 3: How the chain is built (primary structure). The nucleotides are linked through phosphodiester bonds: the phosphate connects the 3'-carbon of one sugar to the 5'-carbon of the next sugar, giving a sugar-phosphate backbone with the bases sticking out sideways.

Step 4: The double helix (secondary structure of DNA). In DNA two such strands coil around a common axis to form a right-handed double helix (Watson and Crick model). The two strands run in opposite directions (antiparallel) and are held together by hydrogen

bonds between complementary bases: adenine pairs with thymine ($A = T$, two H-bonds) and guanine pairs with cytosine ($G \equiv C$, three H-bonds). RNA is normally single-stranded.

Result: A nucleic acid is a polynucleotide whose sugar-phosphate backbone carries a definite base sequence; in DNA two complementary, antiparallel strands twist into a double helix held by base-pair hydrogen bonds.

Quick Tip: Nucleic acids are polynucleotides; each nucleotide = base + pentose sugar + phosphate, joined by 3',5'-phosphodiester bonds, and DNA forms a double helix with A-T and G-C base pairing.

15. (i) Explain Henry's law. (ii) 200 ml of an aqueous solution of a protein contains 1.26 g of protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein. (1+2=3)

Correct Answer: —

Solution:

Part (i): Henry's law.

Henry's law describes how much of a gas dissolves in a liquid. It states that, at a constant temperature, the solubility of a gas in a liquid (or the mole fraction of the gas in solution) is directly proportional to the partial pressure of that gas over the liquid.

$$p = K_H \cdot x$$

where p = partial pressure of the gas above the solution, x = mole fraction of the gas in the solution, and K_H = Henry's law constant (a value that depends on the nature of the gas and the temperature). A higher K_H means the gas is less soluble. This law explains, for example, why soda bottles are sealed under high pressure and why fizzing occurs when the cap is opened.

Part (ii): Molar mass from osmotic pressure.

Step 1: Formula. Osmotic pressure π is related to concentration by $\pi = CRT$, where $C = \frac{n}{V} = \frac{w}{MV}$. Rearranging for molar mass:

$$M = \frac{wRT}{\pi V}$$

Step 2: List the data (in consistent units).

$w = 1.26 \text{ g}$; $R = 0.083 \text{ L bar K}^{-1}\text{mol}^{-1}$; $T = 300 \text{ K}$; $\pi = 2.57 \times 10^{-3} \text{ bar}$;
 $V = 200 \text{ mL} = 0.200 \text{ L}$.

Step 3: Substitute.

$$M = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 0.200}$$

Step 4: Arithmetic. Numerator = $1.26 \times 0.083 \times 300 = 31.374$.

Denominator = $2.57 \times 10^{-3} \times 0.200 = 5.14 \times 10^{-4}$.

$$M = \frac{31.374}{5.14 \times 10^{-4}} \approx 61039 \text{ g mol}^{-1}$$

$$M \approx 6.10 \times 10^4 \text{ g mol}^{-1}$$

Quick Tip: Henry's law: $p = K_H x$. For part (ii) use the osmotic pressure relation $M = wRT/(\pi V)$ with $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$ and V in litres.



16. Describe the charging and discharging mechanism of lead storage battery with the help of chemical reactions. (1+1=2)

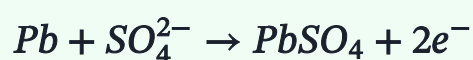
Correct Answer: —

Solution:

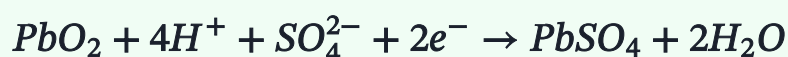
Concept: A lead storage battery (car battery) is a secondary (rechargeable) cell. It has a lead (Pb) anode and a grid of lead packed with lead dioxide (PbO₂) as the cathode, both dipped in about 38% sulphuric acid (H₂SO₄) as the electrolyte.

Step 1: Discharging (working as a cell). While supplying current, oxidation occurs at the Pb anode and reduction at the PbO₂ cathode.

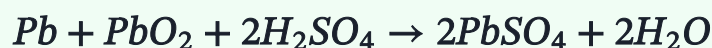
At anode (oxidation):



At cathode (reduction):



Overall discharge reaction:



Both electrodes get coated with insoluble white lead sulphate (PbSO_4) and sulphuric acid is used up, so the density of the acid falls.

Step 2: Charging (recharging). When an external current is passed in the opposite direction, the electrode reactions reverse; the cell now acts as an electrolytic cell and the PbSO_4 is converted back to Pb and PbO_2 .



The sulphuric acid is regenerated, so its density rises again, restoring the battery.

Result: On discharge, Pb and PbO_2 both turn into PbSO_4 and acid is consumed; on charging this is exactly reversed, regenerating Pb, PbO_2 and H_2SO_4 .

Quick Tip: Anode Pb, cathode PbO_2 , electrolyte H_2SO_4 . Overall discharge: $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$; charging is the reverse.



17. Derive the integrated rate equation for first order reaction. Show that half life period for this reaction does not depend on initial concentration of the reactants. (2+1=3)

Correct Answer: —

Solution:

Concept: A first order reaction is one whose rate depends on the first power of the concentration of a single reactant, i.e. $R \rightarrow \text{products}$ with rate $= k[R]$.

Step 1: Write the rate law as a differential equation. The rate of disappearance of R is

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

Step 2: Separate the variables.

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

Step 3: Integrate. Let the concentration be $[R]_0$ at $t = 0$ and $[R]$ at time t .

$$\int_{[R]_0}^{[R]} \frac{d[R]}{[R]} = -k \int_0^t dt$$

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

Step 4: Rearrange into the integrated rate law.

$$\ln \frac{[R]_0}{[R]} = kt \Rightarrow k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

This is the integrated first order rate equation. A plot of $\log[R]$ against t is a straight line of slope $-k/2.303$.

Step 5: Half-life. Half life $t_{1/2}$ is the time when half the reactant is left, i.e. $[R] = \frac{[R]_0}{2}$. Substituting:

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

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

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

Conclusion: The expression for $t_{1/2}$ contains only the rate constant k ; the initial concentration $[R]_0$ has cancelled out. Hence for a first order reaction the half-life is independent of the initial concentration of the reactant.

Quick Tip: Start from $-d[R]/dt = k[R]$, separate and integrate to get $k = (2.303/t) \log([R]_0/[R])$; put $[R] = [R]_0/2$ to get $t_{1/2} = 0.693/k$, which has no $[R]_0$ term.

18. Compare the lanthanoid and actinoid elements with reference to the following: (i) Atomic and ionic sizes (ii) Oxidation state.
($\frac{1}{2}; +\frac{1}{2}; =3$)

Correct Answer: —

Solution:

Concept: Lanthanoids are the 4f-series (Ce to Lu) and actinoids are the 5f-series (Th to Lr). Both are inner-transition (f-block) elements, but they differ because 5f electrons are more diffuse and shield the nucleus less effectively than 4f electrons.

Step 1: (i) Atomic and ionic sizes.

In both series the atomic and ionic radii decrease steadily as we move across, because each added f-electron shields the nuclear charge poorly, so the effective nuclear charge felt by the outer electrons rises and pulls them in.

- In lanthanoids this gradual decrease is called the **lanthanoid contraction**.
- In actinoids the same type of decrease is called the **actinoid contraction**. Because 5f electrons shield even more poorly than 4f electrons, the contraction from element to element is slightly greater in the actinoids.

Step 2: (ii) Oxidation state.

- Lanthanoids show mainly the **+3** oxidation state as their common and stable state; a few also show +2 or +4 (for example Eu^{2+} , Ce^{4+}) but these are less common.
- Actinoids show a much **wider range of oxidation states** (from +3 up to +7, for example U shows +3, +4, +5 and +6). This is because in actinoids the 5f, 6d and 7s orbitals lie close in energy, so more electrons can take part in bonding.

Result: Both series show a steady contraction in size (a little larger in actinoids), but lanthanoids are dominated by the +3 state whereas actinoids display many oxidation states owing to the comparable energies of their 5f, 6d and 7s orbitals.

Quick Tip: Both show a steady f-contraction (lanthanoid vs actinoid contraction, larger for actinoids). Lanthanoids are mostly +3; actinoids show many oxidation states because 5f, 6d and 7s are close in energy.

19. (i) Define molar conductance of the solution of an electrolyte and discuss its change with the concentration.

(ii) Calculate the electromotive force (EMF) of the following cell:



(Given: $E_{\text{cell}}^{\circ} = 1.05 \text{ V}$, $\log_{10} 2 = 0.3010$)

Correct Answer: —

Solution:

Part (i): Molar conductance

Step 1 (Definition): Molar conductance (Λ_m) is the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. It is related to conductivity (κ) by

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

where c is the molar concentration (mol L^{-1}) and κ is the conductivity (S cm^{-1}). Its unit is $\text{S cm}^2 \text{ mol}^{-1}$.

Step 2 (Variation with concentration): Molar conductance increases as concentration decreases (i.e. on dilution), because the total volume containing one mole of electrolyte increases and more ions conduct freely.

- For a **strong electrolyte** the increase is small and Λ_m follows Debye-Huckel-Onsager equation $\Lambda_m = \Lambda_m^{\circ} - A\sqrt{c}$; Λ_m° is obtained by extrapolating the straight line to zero concentration.

- For a **weak electrolyte** the increase is very sharp near infinite dilution because the degree of dissociation rises steeply, so Λ_m° cannot be found by extrapolation (it is found using Kohlrausch's law).

Part (ii): EMF of the cell

Step 1 (Electrode reactions): Anode (oxidation): $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$.

Cathode (reduction): $\text{Ag}^+ + e^- \rightarrow \text{Ag}$ (multiply by 2). Net reaction: $\text{Ni} + 2\text{Ag}^+ \rightarrow \text{Ni}^{2+} + 2\text{Ag}$, so number of electrons $n = 2$.

Step 2 (Reaction quotient):

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.16}{(0.002)^2} = \frac{0.16}{4 \times 10^{-6}} = 4 \times 10^4$$

Step 3 (Nernst equation):

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$$

Step 4 (Evaluate log): $\log(4 \times 10^4) = 2 \log 2 + 4 = 2(0.3010) + 4 = 4.6020$.

Step 5 (Substitute):

$$E_{\text{cell}} = 1.05 - \frac{0.0591}{2}(4.6020) = 1.05 - (0.02955)(4.6020)$$

$$E_{\text{cell}} = 1.05 - 0.136 = 0.914 \text{ V}$$

$$\boxed{E_{\text{cell}} \approx 0.914 \text{ V}}$$

Quick Tip: Molar conductance $\Lambda_m = 1000\kappa/c$, rises on dilution. For EMF use Nernst $E = E^\circ - (0.0591/n) \log([\text{Ni}^{2+}]/[\text{Ag}^+]^2)$ with $n = 2$.



20. A first order reaction takes 10 min for 20% decomposition. Calculate the time taken for the reaction to go to 80% decomposition. (Given, $\log_{10} 2 = 0.3010$)

Correct Answer: —

Solution:

Step 1 (First order formula): For a first order reaction the rate constant is

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

where $[A]_0$ is the initial concentration and $[A]$ is the concentration left after time t .

Step 2 (Find k from the 20% data): Let $[A]_0 = 100$. After 20% decomposition, $[A] = 80$, so $[A]_0/[A] = 100/80 = 1.25$.

$$k = \frac{2.303}{10} \log 1.25$$

$$\log 1.25 = \log \frac{5}{4} = 1 - 3 \log 2 = 1 - 3(0.3010) = 1 - 0.9030 = 0.0970.$$

$$k = \frac{2.303}{10} (0.0970) = 0.02234 \text{ min}^{-1}$$

Step 3 (Time for 80% decomposition): Now $[A] = 20$, so $[A]_0/[A] = 100/20 = 5$.

$$t = \frac{2.303}{k} \log 5$$

$$\log 5 = 1 - \log 2 = 1 - 0.3010 = 0.6990.$$

Step 4 (Substitute):

$$t = \frac{2.303}{0.02234} (0.6990) = (103.09)(0.6990) = 72.06 \text{ min}$$

$$t \approx 72.1 \text{ minutes}$$

Quick Tip: Use $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$. Find k from 20% (remaining 80%), then use it to find t for 80% decomposition (remaining 20%).



21. (i) Discuss the violet colour of the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ on the basis of crystal field theory.

(ii) Explain with reason that $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.

Correct Answer: —

Solution:

Part (i): Violet colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

Step 1 (Oxidation state and configuration): In this complex titanium is in the +3 state. Ti (Z = 22) is $[\text{Ar}]3d^24s^2$; removing 3 electrons gives $\text{Ti}^{3+} = 3d^1$, i.e. one d-electron.

Step 2 (Crystal field splitting): The six H_2O ligands form an octahedral field which splits the five d-orbitals into a lower set t_{2g} (three orbitals) and a higher set e_g (two orbitals), separated by the

crystal field splitting energy Δ_o . In the ground state the single electron sits in a t_{2g} orbital.

Step 3 (d-d transition): When visible (white) light passes through the solution, this electron absorbs a photon of energy equal to Δ_o and is promoted from t_{2g} to e_g (a d-d transition). The energy absorbed corresponds to yellow-green light (around 500 nm, $\approx 20300 \text{ cm}^{-1}$).

Step 4 (Complementary colour): Since yellow-green light is absorbed, the transmitted light is its complementary colour, violet (purple). Hence the solution looks violet.

Part (ii): Magnetic behaviour of Ni complexes

Step 1 (Oxidation state): In both complexes nickel is Ni^{2+} , which is $3d^8$ (two unpaired electrons in the free ion).

Step 2 ($[\text{NiCl}_4]^{2-}$): Cl^- is a **weak field** ligand, so it cannot pair up the d-electrons. The ion uses sp^3 hybridisation giving a **tetrahedral** shape; the two unpaired electrons remain, so the complex is **paramagnetic**.

Step 3 ($[\text{Ni}(\text{CN})_4]^{2-}$): CN^- is a **strong field** ligand, so it forces the two unpaired 3d electrons to pair up, freeing one 3d orbital. The ion then uses dsp^2 hybridisation giving a **square planar** shape with no unpaired electrons, so the complex is **diamagnetic**.

Quick Tip: Ti^{3+} is d^1 ; the single electron makes a d-d transition ($t_{2g} \rightarrow e_g$) absorbing yellow-green light so violet is seen. For Ni: Cl^- weak field (tetrahedral, unpaired) vs CN^- strong field (square planar, paired).

22. Explain the following in relation to proteins:

- (i) Peptide bond
- (ii) Denaturation

Correct Answer: —

Solution:

Part (i): Peptide bond

Step 1 (What it is): A peptide bond is the amide linkage ($-\text{CO} - \text{NH} -$) that joins two amino acids in a protein.

Step 2 (How it forms): It is formed by a condensation reaction between the carboxyl group ($-\text{COOH}$) of one amino acid and the amino group ($-\text{NH}_2$) of the next amino acid, with the elimination of one water molecule.



Step 3 (Significance): The product of two amino acids is a dipeptide; many such peptide bonds link amino acids into long polypeptide chains that make up proteins.

Part (ii): Denaturation

Step 1 (Definition): Denaturation is the process in which a protein loses its biological activity when it is subjected to a physical change (such as heating) or a chemical change (such as adding acid, alkali, or heavy metal salts).

Step 2 (What changes): During denaturation the hydrogen bonds and other weak forces that maintain the secondary and tertiary structures are broken, so the protein uncoils. The native three-dimensional shape is destroyed, but the primary structure (the sequence of amino acids linked by peptide bonds) remains intact.

Step 3 (Examples): Coagulation of egg white (soluble globular protein) into a solid on boiling, and the curdling of milk, are common examples. Denaturation is generally irreversible.

Quick Tip: Peptide bond = amide ($-\text{CO} - \text{NH}-$) linkage formed by loss of water between $-\text{COOH}$ and $-\text{NH}_2$. Denaturation = loss of biological activity by breaking $2^\circ/3^\circ$ structure while primary structure stays intact.

23. Write short notes on the following: (i) Coupling reaction (ii) Sandmeyer reaction (iii) Friedel-Craft reaction. ($2 + 1\frac{1}{2} + 1\frac{1}{2} = 5$)

OR

Write chemical equations for obtaining the following from benzene diazonium chloride: (i) Phenyl cyanide (ii) Bromobenzene (iii) Nitrobenzene (iv) p-hydroxyazobenzene (v) p-Aminoazobenzene. ($1 + 1 + 1 + 1 + 1 = 5$)

Correct Answer: —

Solution:

Option 1: Short notes

Step 1: Coupling reaction. Benzene diazonium chloride $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ contains a diazonium cation that behaves as a weak electrophile. It attacks electron-rich aromatic rings such as phenol or aniline at the para position (electrophilic aromatic substitution) to give brightly coloured azo dyes carrying the $-\text{N} = \text{N}-$ linkage.

With phenol (mildly alkaline medium): $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{OH} \rightarrow p\text{-HOC}_6\text{H}_4\text{N} = \text{NC}_6\text{H}_5 + \text{HCl}$ (p-hydroxyazobenzene, orange).

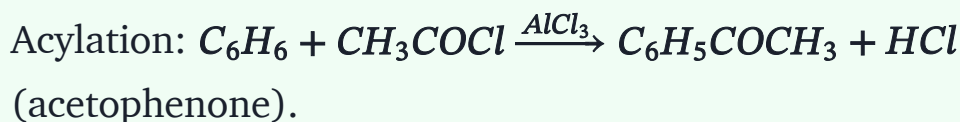
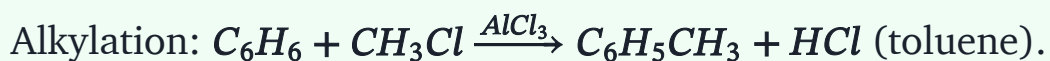
With aniline (mildly acidic medium): $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow p\text{-H}_2\text{NC}_6\text{H}_4\text{N} = \text{NC}_6\text{H}_5 + \text{HCl}$ (p-aminoazobenzene, yellow).

Step 2: Sandmeyer reaction. The diazonium group $-\text{N}_2^+$ is replaced by $-\text{Cl}$, $-\text{Br}$ or $-\text{CN}$ when the diazonium salt is warmed with the

corresponding cuprous halide or cuprous cyanide; nitrogen gas is evolved.



Step 3: Friedel-Crafts reaction. Aromatic hydrocarbons undergo alkylation or acylation in the presence of anhydrous $AlCl_3$ (a Lewis acid), which generates the attacking electrophile (R^+ or acylium RCO^+).



Option 2: Equations from benzene diazonium chloride

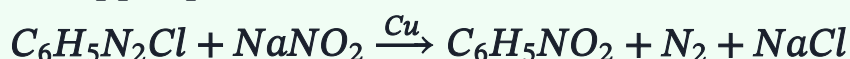
Step 1: (i) Phenyl cyanide (benzonitrile) by Sandmeyer reaction using cuprous cyanide:



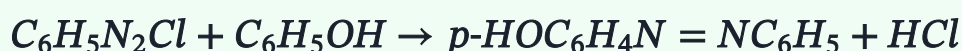
Step 2: (ii) Bromobenzene by Sandmeyer reaction using cuprous bromide:



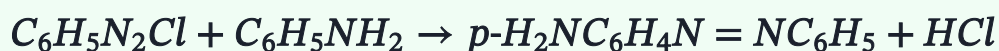
Step 3: (iii) Nitrobenzene by warming with sodium nitrite in presence of copper powder (via the fluoroborate):



Step 4: (iv) p-hydroxyazobenzene by coupling with phenol in mildly alkaline medium:



Step 5: (v) **p-Aminoazobenzene** by coupling with aniline in mildly acidic medium:



Both alternatives use the reactions of benzene diazonium chloride.

Quick Tip: Diazonium chemistry: with cuprous salts the $-N_2^+$ group leaves as N_2 (Sandmeyer), while with phenol or aniline it stays and couples to form a coloured azo dye. Friedel-Crafts needs anhydrous $AlCl_3$.



24. (i) Explain the mechanism of the formation of ethanol by acid catalyzed hydration of ethene. (ii) Explain hydroboration-oxidation reaction with an example. ($2\frac{1}{2} + 2\frac{1}{2} = 5$)

OR

What happens when? (Write chemical equations only) (i) Ethyl bromide reacts with sodium ethoxide. (ii) Phenol is heated with conc. HNO_3 in the presence of conc. H_2SO_4 . (iii) Methoxybenzene is heated with acetyl chloride in the presence of anhydrous $AlCl_3$. (iv) Phenol reacts with chloroform in the presence of aqueous $NaOH$. (v) Ethyl methyl ether is heated with conc. HI . ($1 + 1 + 1 + 1 + 1 = 5$)

Correct Answer: —

Solution:

Option 1

(i) Acid catalyzed hydration of ethene to ethanol. Overall: CH_2

$= \text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}$. It follows Markovnikov addition through three steps.

Step 1: Protonation. The π electrons of ethene attack a proton supplied by the acid (H_3O^+ from H_2SO_4), forming a carbocation: $\text{CH}_2 = \text{CH}_2 + \text{H}^+ \rightarrow \text{CH}_3\overset{+}{\text{C}}\text{H}_2$ (ethyl carbocation).

Step 2: Nucleophilic attack of water. A water molecule uses its lone pair to attack the positively charged carbon, giving a protonated alcohol (oxonium ion): $\text{CH}_3\overset{+}{\text{C}}\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\overset{+}{\text{O}}\text{H}_2$.

Step 3: Deprotonation. Another water molecule removes the extra proton, regenerating the catalyst and giving ethanol: $\text{CH}_3\text{CH}_2\overset{+}{\text{O}}\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_3\text{O}^+$.

(ii) Hydroboration-oxidation. An alkene adds diborane $(\text{BH}_3)_2$; the boron atom adds to the less substituted (terminal) carbon and hydrogen to the more substituted carbon, so the addition is anti-Markovnikov and syn. The resulting trialkylborane is then oxidised by alkaline hydrogen peroxide to the alcohol.

Step 1: Addition of borane. $3\text{CH}_3\text{CH}=\text{CH}_2 + (\text{BH}_3)_2 \rightarrow 2(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B}$ (tripropylborane; boron on terminal carbon).

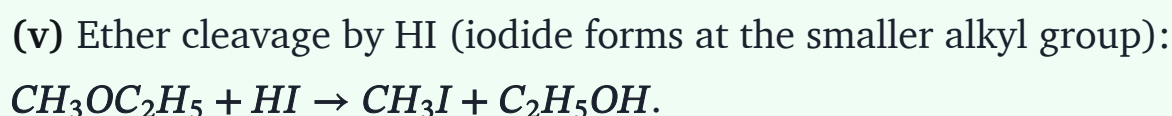
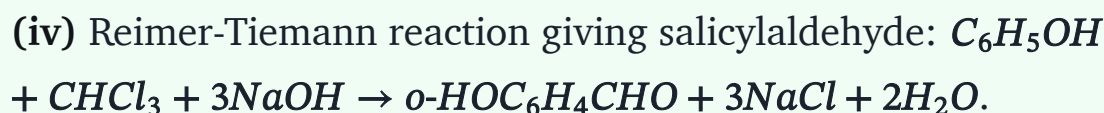
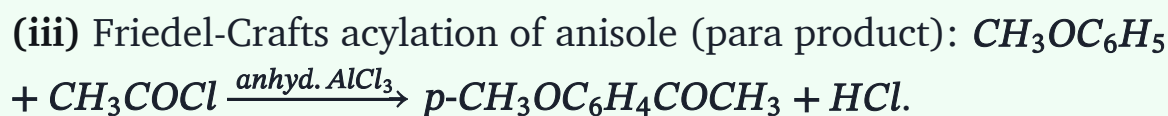
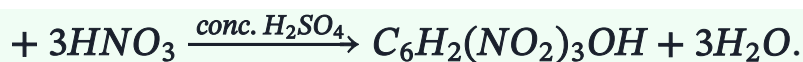
Step 2: Oxidation. $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B} + 3\text{H}_2\text{O}_2 \xrightarrow{\text{OH}^-} 3\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H}_3\text{BO}_3$.

Net result: propene gives propan-1-ol, the anti-Markovnikov (primary) alcohol.

Option 2: Equations only

(i) Williamson ether synthesis: $\text{C}_2\text{H}_5\text{Br} + \text{NaOC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{NaBr}$ (diethyl ether).

(ii) Nitration of phenol to picric acid (2,4,6-trinitrophenol): $\text{C}_6\text{H}_5\text{OH}$



Hydration gives Markovnikov ethanol; hydroboration gives anti-Markovnikov alcohol.

Quick Tip: Acid hydration is a three-step Markovnikov addition through a carbocation; hydroboration-oxidation is anti-Markovnikov giving the primary alcohol. For the equations, recall Williamson, nitration to picric acid, Friedel-Crafts acylation, Reimer-Tiemann, and ether cleavage by HI.

25. (a) Write short notes on the following: (i) Cannizzaro's reaction (ii) Aldol condensation (iii) Gattermann-Koch reaction.

(2 + 1 + 1 = 5)

OR

How will you obtain (write chemical equations only): (i) Benzaldehyde from Toluene (ii) Benzamide from Benzoic acid (iii) Phthalimide from Phthalic acid (iv) m-nitrobenzaldehyde from Benzaldehyde (v)

Benzaldehyde from Benzene. (1 + 1 + 1 + 1 + 1 = 5)

Correct Answer: —

Solution:

Option 1: Short notes

(i) Cannizzaro's reaction: Aldehydes that have **no α -hydrogen** undergo self oxidation and reduction (disproportionation) when warmed with concentrated alkali. One molecule is oxidised to a carboxylate salt while the other is reduced to a primary alcohol.

Example (benzaldehyde): $2 \text{C}_6\text{H}_5\text{CHO} + \text{NaOH}(\text{conc.}) \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COONa}$

Here benzaldehyde gives benzyl alcohol (reduction) and sodium benzoate (oxidation). Formaldehyde behaves similarly: $2 \text{HCHO} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOONa}$.

(ii) Aldol condensation: Aldehydes or ketones having at least one **α -hydrogen** react in the presence of dilute alkali (dil. NaOH) to give a β -hydroxy aldehyde (aldol) or β -hydroxy ketone (ketol).

$2 \text{CH}_3\text{CHO} \xrightarrow{(\text{dil. NaOH})} \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ (3-hydroxybutanal, the 'aldol').

On heating, the aldol loses water to give an α,β -unsaturated carbonyl compound: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} \xrightarrow{(\Delta)} \text{CH}_3\text{CH}=\text{CHCHO}$ (but-2-enal) + H_2O .

(iii) Gattermann-Koch reaction: When benzene (or a benzene derivative) is treated with **carbon monoxide and hydrogen chloride** in the presence of anhydrous AlCl_3 (with a little CuCl), it gives benzaldehyde. It is a formylation that puts a $-\text{CHO}$ group on the ring.

$$\text{C}_6\text{H}_6 + \text{CO} + \text{HCl} \xrightarrow{(\text{anhyd. AlCl}_3/\text{CuCl})} \text{C}_6\text{H}_5\text{CHO}$$

Option 2: Preparations (equations)

(i) Benzaldehyde from Toluene (Etard reaction): $\text{C}_6\text{H}_5\text{CH}_3 + \text{CrO}_2\text{Cl}_2 \rightarrow (\text{CS}_2) \text{ chromium complex} \rightarrow (\text{H}_3\text{O}^+) \text{C}_6\text{H}_5\text{CHO}$.

(ii) Benzamide from Benzoic acid: $\text{C}_6\text{H}_5\text{COOH} \rightarrow (\text{SOCl}_2) \text{C}_6\text{H}_5\text{COCl} \rightarrow (\text{NH}_3) \text{C}_6\text{H}_5\text{CONH}_2$.

(iii) Phthalimide from Phthalic acid: Phthalic acid $\rightarrow (\Delta, -\text{H}_2\text{O})$ phthalic anhydride $\rightarrow (\text{NH}_3, \Delta)$ phthalimide (the cyclic imide).

(iv) m-Nitrobenzaldehyde from Benzaldehyde: $\text{C}_6\text{H}_5\text{CHO} + \text{conc. HNO}_3 \rightarrow (\text{conc. H}_2\text{SO}_4) \text{m-O}_2\text{N-C}_6\text{H}_4\text{-CHO}$. The -CHO group is a deactivating, meta-directing group, so nitration occurs at the meta position.

(v) Benzaldehyde from Benzene (Gattermann-Koch): $\text{C}_6\text{H}_6 + \text{CO} + \text{HCl} \rightarrow (\text{anhyd. AlCl}_3/\text{CuCl}) \text{C}_6\text{H}_5\text{CHO}$.

Quick Tip: For Option 1 recall three named aldehyde reactions: disproportionation of aldehydes with no $\alpha\text{-H}$ (Cannizzaro), $\alpha\text{-H}$ self-addition then dehydration (aldol), and $\text{CO} + \text{HCl}$ with AlCl_3 ring formylation (Gattermann-Koch). For Option 2 think Etard, acid to acid chloride to amide, cyclic imide, meta-directing -CHO, and Gattermann-Koch.

26. (b) (i) Describe any one method for the identification of primary, secondary and tertiary amines. Also write the chemical reactions. (ii) Write a short note on Gabriel Phthalimide Synthesis. (3+2=5)

OR

How will you obtain (write chemical equations only): (i) Benzene diazonium chloride from Aniline (ii) Methylamine from Acetamide (iii) Aniline from Nitrobenzene. (2+1+1=4)

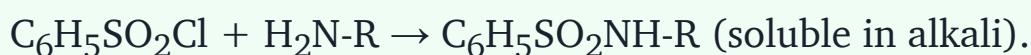
Solution:

Option 1

(i) Identification of 1°, 2° and 3° amines – Hinsberg's test:

The reagent is **benzenesulphonyl chloride** ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, 'Hinsberg's reagent'). The amine is shaken with it and the mixture is then treated with aqueous KOH.

Primary amine: gives an N-alkylbenzenesulphonamide. The H left on nitrogen is acidic (activated by the $-\text{SO}_2-$ group), so the product **dissolves in KOH**.



Secondary amine: gives an N,N-dialkylbenzenesulphonamide. No N-H is left, so it is **insoluble in KOH** (a solid separates).



Tertiary amine: has no replaceable N-H, so it **does not react** and stays as an insoluble layer.

So: soluble product means 1°, insoluble product means 2°, no reaction means 3°.

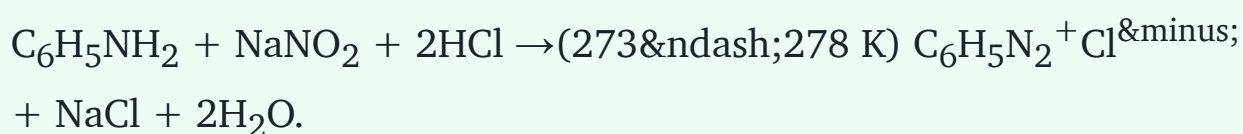
(ii) Gabriel phthalimide synthesis: a route to pure **primary aliphatic amines**. Steps: (1) Phthalimide is treated with KOH to give potassium phthalimide. (2) This is heated with an alkyl halide (R-X) to give N-alkylphthalimide. (3) Alkaline or acidic hydrolysis (or hydrazinolysis) then sets the primary amine free together with phthalic acid.

Phthalimide $\rightarrow$ (KOH) potassium phthalimide $\rightarrow$ (R-X) N-alkylphthalimide $\rightarrow$ (hydrolysis) R-NH₂ + phthalic acid.

Aromatic primary amines cannot be made this way because aryl halides do not undergo the needed nucleophilic substitution with potassium phthalimide.

Option 2: Preparations (equations)

(i) Benzene diazonium chloride from Aniline (diazotisation):



(ii) Methylamine from Acetamide (Hoffmann bromamide degradation): $\text{CH}_3\text{CONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{CH}_3\text{NH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$. The amine has one carbon fewer than the amide.

(iii) Aniline from Nitrobenzene (reduction): $\text{C}_6\text{H}_5\text{NO}_2 + 3\text{H}_2 \rightarrow (\text{Ni/Pt/Pd}) \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$. Sn + HCl or Fe + HCl also reduces nitrobenzene to aniline.

Quick Tip: For Option 1 use Hinsberg's reagent (C₆H₅SO₂Cl) and judge solubility in KOH; recall Gabriel synthesis gives only primary aliphatic amines. For Option 2 think diazotisation, Hoffmann bromamide degradation, and reduction of nitrobenzene.