UP Board Class 12 Chemistry - 347 (KC) - 2025 Question Paper with Solutions

Time Allowed :3 Hours	**Maximum Marks :**100	**Total questions :**9

General Instructions

1. All questions are compulsory.
2. This question paper has five sections: Section A, Section B, Section C, Section D and Section E.
3. Section A is of multiple choice type and each question carries 1 mark.
4. Section B is of very short answer type and each question carries 1 mark.
5. Section C is of short answer type-I and carries 2 marks each.
6. Section D is of short answer type-II and carries 3 marks each.
7. Section E is of long answer type. Each question carries 5 marks. In all four questions of this section with internal choices have been given. You have to do only one question from the choices given in the question.
8. The symbols used in the question paper have usual meaning.

Section - A

1. (a) 100 ml of 10 M HCl is mixed with 75 ml of 10 M Na_2CO_3. The resulting solution would be –

(A) acidic

(B) basic

(C) neutral

(D) amphoteric

Correct Answer: (B) basic

Solution:

Step 1: Write the balanced chemical equation.

The reaction between hydrochloric acid and sodium carbonate is:

$$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

This shows that 2 moles of HCl react with 1 mole of Na_2CO_3.

Step 2: Calculate the millimoles (mmol) of each reactant.

Millimoles = Molarity (M) $\times$ Volume (ml)

$$\text{mmol of HCl} = 10\,\text{M} \times 100\,\text{ml} = 1000\,\text{mmol}$$

$$\text{mmol of } Na_2CO_3 = 10\,\text{M} \times 75\,\text{ml} = 750\,\text{mmol}$$

Step 3: Determine the limiting reactant.

According to the stoichiometry, 1000 mmol of HCl would require:

$$1000\,\text{mmol HCl} \times \frac{1\,\text{mmol } Na_2CO_3}{2\,\text{mmol HCl}} = 500\,\text{mmol } Na_2CO_3$$

We have 750 mmol of Na_2CO_3, which is more than the 500 mmol needed. Therefore, HCl is the limiting reactant and will be completely consumed.

Step 4: Calculate the amount of excess reactant remaining.

The amount of Na_2CO_3 that will react is 500 mmol.

$$\text{Remaining } Na_2CO_3 = \text{Initial} - \text{Reacted} = 750\,\text{mmol} - 500\,\text{mmol} = 250\,\text{mmol}$$

Step 5: Determine the nature of the resulting solution.

The final solution contains NaCl, water, and 250 mmol of unreacted Na_2CO_3. Sodium carbonate is the salt of a strong base (NaOH) and a weak acid (H_2CO_3). The carbonate ion hydrolyzes in water to produce hydroxide ions (OH^-), making the solution basic.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

Since there is excess Na_2CO_3, the final solution will be basic.

Basic

> Quick Tip
>
> Always check the limiting reagent in acid–base neutralization problems. If base is left unreacted, the solution is basic; if acid is left unreacted, the solution is acidic.

(b) Number of unpaired electrons in Cu^{2+} (Z = 29) is –

(A) 1

(B) 2

(C) 3

(D) 4

Correct Answer: (A) 1

Solution:

Step 1: Determine the ground state electron configuration of Copper (Cu).

The atomic number of Copper (Cu) is 29. Its electron configuration is an exception to the Aufbau principle for enhanced stability. Instead of [Ar] $3d^9 4s^2$, it is:

$$\text{Cu} : [Ar]\, 3d^{10}\, 4s^1$$

This configuration has a completely filled 3d subshell and a half-filled 4s subshell, which is energetically more stable.

Step 2: Determine the electron configuration of the Cu^{2+} ion.

To form a cation, electrons are removed from the outermost shell first (the one with the highest principal quantum number, n).

- The first electron is removed from the n=4 shell (the 4s orbital).
- The second electron must be removed from the next highest shell, which is n=3 (the 3d orbital).

Removing one electron from $4s^1$ and one from $3d^{10}$ gives:

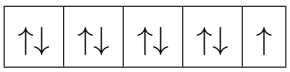
$$\text{Cu}^{2+} : [Ar]\, 3d^9$$

Step 3: Analyze the 3d^9 configuration for unpaired electrons.

The d subshell has 5 orbitals. According to Hund's rule, electrons will occupy orbitals singly before pairing up. For 9 electrons:

- The first 5 electrons will fill each of the 5 orbitals with spin up.
- The next 4 electrons will pair up with 4 of the existing electrons (spin down).

This results in four pairs of electrons and one single, unpaired electron.



Step 4: State the final answer.

The Cu^{2+} ion, with a $3d^9$ configuration, has exactly one unpaired electron.

$$\boxed{1}$$

Quick Tip

Always remember: In transition metals, electrons are lost first from the 4s orbital and then from 3d. For Cu^{2+}, the stable configuration is 3d^9 with one unpaired electron.

(c) Total how many ions are there in [Co(NH$_3$)$_5$Cl]Cl$_2$ solution?

(A) 2

(B) 3

(C) 4

(D) 5

Correct Answer: (B) 3

Solution:

Step 1: Differentiate between the coordination sphere and counter ions.

In the compound $[Co(NH_3)_5Cl]Cl_2$, the part within the square brackets, $[Co(NH_3)_5Cl]$, is the coordination sphere or complex ion. The species outside the brackets, Cl_2, represent the counter ions.

Step 2: Understand the bonding and dissociation.

The ligands (NH_3 and Cl) inside the coordination sphere are held to the central metal (Co) by coordinate covalent bonds and do not dissociate in water. The counter ions (the two Cl^- ions) are held by ionic bonds to the coordination sphere. When the compound dissolves, these ionic bonds break.

Step 3: Write the dissociation reaction.

The compound will ionize in solution to yield the complex ion and the counter ions separately.

$$[Co(NH_3)_5Cl]Cl_2 \xrightarrow{\text{water}} [Co(NH_3)_5Cl]^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Step 4: Count the total number of individual ions produced.

The dissociation produces:

- One complex cation: $[Co(NH_3)_5Cl]^{2+}$
- Two chloride anions: $2 \times Cl^-$

The total number of ions is $1 + 2 = 3$.

$$\boxed{3}$$

Quick Tip

When calculating total ions in coordination compounds, check which groups are inside the coordination sphere (non-ionizable) and which are outside (ionizable).

(d) Which compound of the following does not reduce Fehling's solution?

(A) CH_3COOH

(B) HCOOH

(C) HCHO

(D) CH_3CHO

Correct Answer: (A) CH_3COOH

Solution:

Step 1: Understand Fehling's Test.

Fehling's test is a chemical test used to identify reducing functional groups, particularly aliphatic aldehydes. A positive test is the formation of a red precipitate of copper(I) oxide (Cu_2O), which results from the reduction of Cu^{2+} ions in the Fehling's solution.

Step 2: Analyze the reactivity of aldehydes.

- **(C) HCHO (Formaldehyde)** and **(D) CH_3CHO (Acetaldehyde)** are both aliphatic aldehydes. The aldehyde functional group (-CHO) is easily oxidized, making these compounds effective reducing agents. They will give a positive Fehling's test.

Step 3: Analyze the reactivity of carboxylic acids.

- **(B) HCOOH (Formic acid)** is a unique carboxylic acid. Its structure, H-C(=O)OH, contains a hydrogen atom directly attached to the carboxyl carbon, similar to an aldehyde. This allows it to be oxidized to carbon dioxide and water, and it is therefore a strong enough reducing agent to give a positive Fehling's test.
- **(A) CH_3COOH (Acetic acid)** is a typical carboxylic acid. The carboxyl carbon is bonded to a methyl group, not a hydrogen atom. This structure is not easily oxidized under the mild conditions of Fehling's test. Therefore, it is a non-reducing agent.

Step 4: Conclusion.

Acetic acid (CH_3COOH) lacks the necessary structure to act as a reducing agent for Fehling's solution. The other three compounds will all yield a positive result.

$\boxed{CH_3COOH}$

Quick Tip

All aliphatic aldehydes reduce Fehling's reagent. Among carboxylic acids, only **formic acid** (HCOOH) reduces it; common acids like acetic acid do not.

(e) How many primary amines are possible for the formula $C_4H_{11}N$?

(A) 1

(B) 2

(C) 3

(D) 4

Correct Answer: (D) 4

Solution:

The general formula for a primary amine is R–NH_2. For molecular formula $C_4H_{11}N$, we must arrange 4 carbons into different alkyl groups attached to –NH_2.

Step 1: Straight chain amines. 1. n-Butylamine: CH_3–CH_2–CH_2–CH_2–NH_2

2. Isobutylamine: $(CH_3)_2CH$–CH_2–NH_2

Step 2: Branched chain amines. 3. sec-Butylamine: CH_3–$CH(NH_2)$–CH_2–CH_3

4. tert-Butylamine: $(CH_3)_3C$–NH_2

Step 3: Count unique structures.

Thus, four distinct primary amines are possible.

$\boxed{4}$

Quick Tip

For counting isomers of amines, remember: n-butyl, sec-butyl, isobutyl, and tert-butyl give four distinct primary amines for $C_4H_{11}N$.

(f) Deficiency of which vitamin causes scurvy?

(A) B

(B) C

(C) D

(D) E

Correct Answer: (B) C

Solution:

Scurvy is a disease characterized by weakness, bleeding gums, loose teeth, and delayed wound healing. It is caused by the deficiency of **Vitamin C** (ascorbic acid).

Explanation of options: - (A) Vitamin B: Deficiency causes beriberi, pellagra, or anemia (depending on type of B vitamin).

- (B) Vitamin C: Deficiency causes scurvy.

- (C) Vitamin D: Deficiency causes rickets in children and osteomalacia in adults.

- (D) Vitamin E: Deficiency causes muscular weakness and neurological problems.

Thus, the correct answer is Vitamin C.

Vitamin C (Ascorbic acid)

Quick Tip

Remember: Vitamin C (ascorbic acid) is essential for collagen synthesis. Its deficiency leads to scurvy, especially seen in sailors who lacked fresh fruits and vegetables in their diet.

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2. (a) What is the relation between elevation in boiling point and molality?

Solution:

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:

- $\Delta T_b = T_b - T_b^\circ$, elevation in boiling point,

- K_b = molal elevation constant (ebullioscopic constant) of the solvent,

- m = molality of the solution (mol solute per kg solvent).

Thus, higher the molality of the solution, greater is the elevation in boiling point.

> Quick Tip
>
> Colligative properties like boiling point elevation depend only on the number of solute particles, not on their nature. Always convert mass of solvent into kilograms while using molality.

(b) Aqueous solutions of $HgCl_2$ and $SnCl_2$ cannot co-exist, why?

Solution:

Aqueous solutions of $HgCl_2$ and $SnCl_2$ cannot co-exist because a redox reaction takes place between them.

- $HgCl_2$ (mercuric chloride) acts as an oxidizing agent.

- $SnCl_2$ (stannous chloride) acts as a reducing agent.

$$HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 \downarrow + SnCl_4$$

Here, Hg^{2+} in $HgCl_2$ is reduced to Hg^+ (in Hg_2Cl_2), $while Sn^{2+}$ in $SnCl_2$ is oxidized to Sn^{4+}. Hence, they cannot remain together in the same solution.

> Quick Tip
>
> Whenever an oxidizing salt ($HgCl_2$) and a reducing salt ($SnCl_2$) are mixed in aqueous medium, a redox reaction occurs, preventing their coexistence.

(c) Prove with example that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

Solution:

Idea of ionisation isomerism:

Two coordination compounds having the same overall composition but differing in the *counter-ion outside* the coordination sphere (which can be interchanged with a ligand inside) are called **ionisation isomers**.

Given pair:

$[\,\mathrm{Co(NH_3)_5Cl}\,]\mathrm{SO_4} \;\leftrightarrow\; [\,\mathrm{Co(NH_3)_5SO_4}\,]\mathrm{Cl}$

In the first salt, $\mathrm{SO_4^{2-}}$ is the counter-ion and $\mathrm{Cl^-}$ is bound to Co(III) inside the sphere.

In the second, $\mathrm{Cl^-}$ is the counter-ion and $\mathrm{SO_4^{2-}}$ is coordinated to Co(III).

Experimental proof by precipitation tests:

Test for free sulphate ($\mathrm{BaCl_2}$ test):

$$[\,\mathrm{Co(NH_3)_5Cl}\,]\mathrm{SO_4(aq)} + \mathrm{Ba^{2+}(aq)} \longrightarrow \mathrm{BaSO_4(s)}\downarrow + [\,\mathrm{Co(NH_3)_5Cl}\,]^{2+}$$

White precipitate of $\mathrm{BaSO_4}$ confirms free $\mathrm{SO_4^{2-}}$.

Test for free chloride ($\mathrm{AgNO_3}$ test):

$$[\,\mathrm{Co(NH_3)_5SO_4}\,]\mathrm{Cl(aq)} + \mathrm{Ag^{+}(aq)} \longrightarrow \mathrm{AgCl(s)}\downarrow + [\,\mathrm{Co(NH_3)_5SO_4}\,]^{+}$$

Curdy white precipitate of AgCl confirms free $\mathrm{Cl^-}$.

Hence the pair are ionisation isomers since the counter-ion and a coordinated ligand exchange positions

> **Quick Tip**
>
> Ionisation isomers differ in which ion is inside the coordination sphere and which is outside. They can be identified easily by simple precipitation tests like $\mathrm{AgNO_3}$ (for $\mathrm{Cl^-}$) or $\mathrm{BaCl_2}$ (for $\mathrm{SO_4^{2-}}$).

(d) Complete the following chemical equation: $\mathrm{C_2H_5Br} \xrightarrow{\mathrm{KOH(aq)}} (A) \xrightarrow[\Delta]{\mathrm{K_2Cr_2O_7,\ H_2SO_4}} (B)$**.**

Solution:

Step 1 (Nucleophilic substitution with aqueous KOH):

$$C_2H_5Br + OH^- \longrightarrow C_2H_5OH + Br^-$$

Therefore, $\boxed{A = C_2H_5OH \text{ (ethanol)}}$.

Step 2 (Oxidation with acidified $K_2Cr_2O_7$ under heat):

Under reflux/heat, primary alcohols are oxidised to carboxylic acids.

$$C_2H_5OH \ + \ [O] \ \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4} \ CH_3COOH \ + \ H_2O$$

Hence, $\boxed{B = CH_3COOH \text{ (ethanoic acid)}}$.

Quick Tip

Aqueous KOH leads to substitution ($R{-}X \rightarrow R{-}OH$), while alcoholic KOH favours elimination ($R{-}X \rightarrow R{=}Alkene$). Acidified $K_2Cr_2O_7$ oxidises primary alcohols to aldehydes under mild conditions and to acids under strong reflux.

3.(a) 6 g urea is dissolved in 200 g water. Calculate the elevation in boiling point. Molal elevation constant for water is 0.52 K kg mol^{-1}.

Solution:

Elevation of boiling point is given by $\Delta T_b = K_b \times m$.

Here $K_b = 0.52\,\text{K kg mol}^{-1}$ and m is molality.

Step 1: Moles of urea (solute).

Molar mass of urea $= 60\,\text{g mol}^{-1}$.

$n = \dfrac{6}{60} = 0.10\,\text{mol}.$

Step 2: Mass of solvent (water) in kg.

$200\,\text{g} = 0.200\,\text{kg}.$

Step 3: Molality.

$m = \dfrac{0.10}{0.200} = 0.50\,\text{mol kg}^{-1}.$

Step 4: Elevation in boiling point.

$\Delta T_b = K_b \times m = 0.52 \times 0.50 = 0.26\,\text{K}.$

$$\boxed{\Delta T_b = 0.26\,\text{K}}$$

Quick Tip

For colligative properties, always convert solvent mass to kilograms and use moles of solute. Urea is non-electrolyte (van't Hoff factor $i = 1$).

(b) Write the names of the reagents used in the following reactions:

i) Conversion of benzyl alcohol into benzoic acid

ii) Formation of butan-2-ol from butan-2-one

Solution:

i) Benzyl alcohol $\rightarrow$ Benzoic acid (oxidation):

Use a strong oxidizing agent such as **acidified potassium dichromate** $(\mathrm{K_2Cr_2O_7/H_2SO_4})$ *or* **alkaline/acidified potassium permanganate** $(\mathrm{KMnO_4})$.

ii) Butan-2-one $\rightarrow$ Butan-2-ol (reduction):

Use a reducing agent such as **sodium borohydride** $(\mathrm{NaBH_4})$ *or* **lithium aluminium hydride** $(\mathrm{LiAlH_4})$ (followed by hydrolysis), *or* catalytic hydrogenation $(\mathrm{H_2/Ni})$.

Quick Tip

Primary alcohol $\rightarrow$ carboxylic acid needs strong oxidants ($\mathrm{K_2Cr_2O_7/H^+}$ or $\mathrm{KMnO_4}$). Ketone $\rightarrow$ secondary alcohol is efficiently done with $\mathrm{NaBH_4}$ (mild) or $\mathrm{LiAlH_4}$ (strong).

(c) How will you convert ethanol into the following compounds? Write chemical equation only.

(i) 3-Hydroxybutanol (ii) But-2-enal

Solution:

(i) 3-Hydroxybutanol (3-hydroxybutan-1-ol $\equiv$ 1,3-butanediol) from ethanol

$$\mathrm{CH_3CH_2OH} \xrightarrow{[O]} \mathrm{CH_3CHO} \Rightarrow 2\,\mathrm{CH_3CHO} \xrightarrow[\text{aldol}]{\text{dil. NaOH}} \mathrm{CH_3-CH(OH)-CH_2-CHO} \xrightarrow{\mathrm{NaBH_4\ (or)\ H_2/Ni}} \boxed{\mathrm{HO-C}}$$

(ii) But-2-enal (crotonaldehyde) from ethanol

$$\mathrm{CH_3CH_2OH} \xrightarrow{[O]} \mathrm{CH_3CHO} \Rightarrow 2\,\mathrm{CH_3CHO} \xrightarrow[\text{aldol}]{\text{dil. NaOH}} \mathrm{CH_3-CH(OH)-CH_2-CHO} \xrightarrow[-\mathrm{H_2O}]{\Delta} \boxed{\mathrm{CH_3-CH{=}CH-}}$$

Quick Tip

From ethanol, go via acetaldehyde: aldol addition gives 3-hydroxybutanal; $-\mathrm{H_2O}$ $\Rightarrow$ crotonaldehyde, while reduction of the aldehyde group $\Rightarrow$ 1,3-butanediol (3-hydroxybutanol).

(d) Ketones do not reduce Fehling's solution and Tollen's reagent while fructose containing ketonic group does. Why?

Solution:

Ordinary ketones are not readily oxidised by Fehling's or Tollen's reagents, hence they are non-reducing.

Fructose (a ketohexose), however, in alkaline medium undergoes *enediol* formation and the Lobry de Bruyn–van Ekenstein rearrangement to give the corresponding aldoses (glucose/mannose), which *are* reducing and therefore reduce $[\mathrm{Ag(NH_3)_2}]^+$ (Tollen's) and Cu^{2+} (Fehling's).

$$\text{Fructose (keto)} \xrightarrow{[\mathrm{OH^-}]} \text{enediol} \longrightarrow \text{Glucose/Mannose (aldehydo)} \Rightarrow \text{reduces Fehling's \& Tollen's}$$

Quick Tip

Remember: "Ketose becomes aldose in base." The transient enediol tautomer lets fructose behave like a reducing sugar.

4.(a) Write the definition of osmotic pressure. Calculate the osmotic pressure of 2% aqueous solution of urea at 27°C. Solution constant $R = 0.082$ L atm $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.

Solution:

Definition:

Osmotic pressure (π) is the excess pressure that must be applied to a solution *separated from its pure solvent by a semipermeable membrane* to prevent the net flow of solvent into the solution.

Formula (for a non-electrolyte):

$$\pi = iMRT \quad (i = 1 \text{ for urea})$$

Given/Assumption:

2% (w/v) solution $\Rightarrow$ 2 g urea in 100 mL solution.

Molar mass of urea $= 60$ g mol^{-1}. Temperature $T = 27°\text{C} = 300$ K.

Step 1: Molarity M.

Mass per litre $= 20$ g L^{-1} $\Rightarrow M = \dfrac{20}{60} = 0.333$ mol L^{-1}.

Step 2: Osmotic pressure.

$$\pi = (0.333) \times (0.082) \times (300) = 8.19 \text{ atm} \approx 8.2 \text{ atm}$$

$$\boxed{\pi \approx 8.2 \text{ atm (at } 27°\text{C)}}$$

> Quick Tip
>
> For dilute, non-electrolyte solutions use $\pi = MRT$.
>
> "2% (w/v)" means 2 g solute per 100 mL solution; convert to mol L^{-1} before using RT.

(b) Explain Faraday's laws of electrolysis.

Solution:

First Law (Mass–Charge law):

The mass m of a substance liberated (or deposited) at an electrode is directly proportional to the quantity of electricity Q passed through the electrolyte.

$$m \propto Q = It \quad \Rightarrow \quad m = ZIt$$

where I is current in ampere, t is time in seconds, and Z is the electrochemical equivalent (g C^{-1}).

Second Law (Equivalent–Weight law):

When the same quantity of electricity passes through different electrolytes, the masses of substances liberated are proportional to their chemical (equivalent) weights.

$$\frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{M_1/z_1}{M_2/z_2}$$

where M is molar mass and z is the electrons transferred per ion (valency).

Equivalently, for a given substance:

$$m = \frac{Q}{F}\frac{M}{z} = \frac{It}{F}\frac{M}{z}$$

with $F = 96485$ C mol^{-1} (Faraday constant).

> Quick Tip
>
> Use $m = ZIt$ for direct calculations with given Z; otherwise use $m = \frac{It}{F}\frac{M}{z}$.
> Always match z to the electrode reaction (e.g., $Cu^{2+} + 2e^- \rightarrow$ Cu, so $z = 2$).

(c) Decomposition of NH_3 on the surface of platinum is a zero–order reaction. What will be the rate of formation of N_2 and H_2? (Given: $k = 2.5 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}$)

Solution:

Overall reaction on Pt: $2\,NH_3 \rightarrow N_2 + 3\,H_2$.

For a reaction $2\,NH_3 \rightarrow N_2 + 3\,H_2$: $-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = r$.

Zero order in NH_3 on Pt means the rate of *disappearance* of NH_3 is $-\frac{d[NH_3]}{dt} = k$.

Hence $r = \dfrac{k}{2}$.

$\Rightarrow$ Rate of formation of nitrogen: $\dfrac{d[N_2]}{dt} = r = \dfrac{k}{2} = \dfrac{2.5 \times 10^{-4}}{2} = 1.25 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}$.

$\Rightarrow$ Rate of formation of hydrogen: $\dfrac{d[H_2]}{dt} = 3r = \dfrac{3k}{2} = 3.75 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}$.

$$\boxed{\frac{d[\mathrm{N_2}]}{dt} = 1.25 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}, \quad \frac{d[\mathrm{H_2}]}{dt} = 3.75 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}$$

Quick Tip

For any reaction $aA \rightarrow$ products, the common rate is $-\frac{1}{a}\frac{d[A]}{dt}$.
If $-\frac{d[A]}{dt} = k$ (zero order), multiply the common rate by each stoichiometric coefficient to get individual product formation rates.

(d) Write the colour of the following ions in aqueous solution: (i) Zn^{2+} (ii) Cu^{2+} (iii) Fe^{2+}.

Solution:

(i) Zn^{2+} : **colourless**.

(ii) Cu^{2+} : **blue** (azure/light blue).

(iii) Fe^{2+} : **pale green**.

Quick Tip

Colour in aqueous transition-metal ions arises from $d \rightarrow d$ transitions; d^{10} ions like Zn^{2+} are colourless, while Cu^{2+} (d^9) is blue and Fe^{2+} (d^6) appears pale green.

5.(a) What is electrode potential? Mention the factors affecting it.

Solution:

Definition:

Electrode potential is the potential difference developed between a metal electrode and its electrolyte solution when the electrode is in equilibrium with its ions.

It represents the tendency of the electrode to lose or gain electrons.

Factors affecting electrode potential:

1. **Nature of metal:** Different metals have different tendencies to lose or gain electrons, hence different electrode potentials.

2. **Concentration of ions:** The concentration of metal ions in solution affects electrode potential according to the Nernst equation.
3. **Temperature:** Electrode potential varies with temperature as it affects the movement of ions.
4. **Pressure of gas (if involved):** For electrodes involving gases (like hydrogen electrode), the gas pressure influences the electrode potential.
Thus, electrode potential is not fixed, but depends on these experimental conditions.

> Quick Tip
>
> Remember the Nernst equation: $E = E^\circ - \frac{0.0591}{n} \log \frac{[Red]}{[Ox]}$. This shows how concentration and temperature affect electrode potential.

(b) Explain with example the difference between molecularity and order of reaction.

Solution:

Molecularity:

- Molecularity of a reaction is the number of reactant species (atoms, ions or molecules) that collide simultaneously in a single step to bring about the reaction.
- It is always a whole number (1, 2, or 3).
- It is a theoretical concept based on reaction mechanism.

Example:

Unimolecular reaction: Decomposition of N_2O_5 in a single step has molecularity = 1.

Order of reaction:

- The order of a reaction is the sum of the powers of the concentrations of reactants in the experimentally determined rate law expression.
- It can be zero, fractional, or whole number.
- Order is determined experimentally.

Example:

For decomposition of H_2O_2: Rate = k[H_2O_2], order = 1.

Key Differences:

1. Molecularity is theoretical and cannot be zero or fractional, while order can be zero or fractional.
2. Molecularity refers to a single step, whereas order is obtained from the overall rate law.

Molecularity is mechanism-based, order is experiment-based.

Quick Tip

A simple way to remember: Molecularity = "how many molecules collide" in a step, Order = "how rate depends on concentration" in experiment.

(c) Write IUPAC names of the following:

(i) $K_3[AlF_6]$

(ii) $[Fe(H_2O)_6]Cl_2$

(iii) $[Co(NH_3)_5Cl]SO_4$

(iv) $K_3[Fe(CN)_6]$

Solution:

(i) Potassium hexafluoridoaluminate(III)

(ii) Hexaaquairon(II) chloride

(iii) Pentaamminechloridocobalt(III) sulfate

(iv) Potassium hexacyanidoferrate(III)

Quick Tip

Use *fluorido, chlorido, cyanido, aqu(a)* for ligand names; for complex anions, end the metal name with "-ate" (aluminate, ferrate) and give oxidation state in Roman numerals.

(d) Write chemical equations of the reactions of formation of n-hexane, pentaacetyl glucose, glucose cyanohydrin and gluconic acid from glucose.

Solution:

(i) n-Hexane from glucose

$$\mathrm{C_6H_{12}O_6} \xrightarrow[\text{Red P}]{\mathrm{HI},\,\Delta} \mathrm{n-C_6H_{14}}$$

(*Often shown via sorbitol:* $\mathrm{C_6H_{12}O_6 + H_2} \xrightarrow{\mathrm{Ni}} \mathrm{C_6H_{14}O_6} \xrightarrow[\text{Red P}]{12\,\mathrm{HI},\,\Delta} \mathrm{n-C_6H_{14} + 6H_2O + 12I_2}$).

(ii) Pentaacetyl glucose

$$\text{Glucose} \xrightarrow[\text{pyridine}]{(\mathrm{CH_3CO})_2\mathrm{O}} \text{Glucose penta-acetate} + 5\,\mathrm{CH_3COOH}$$

(iii) Glucose cyanohydrin

$$\text{Glucose (open-chain)} \xrightarrow[\text{trace KCN}]{\mathrm{HCN}} \text{Glucose cyanohydrin}$$

(iv) Gluconic acid

$$\text{Glucose} \xrightarrow{\mathrm{Br_2/H_2O}} \text{Gluconic acid}$$

> **Quick Tip**
>
> From glucose, remember: (a) strong $\mathrm{HI/Red\ P}$ reduces to hydrocarbon; (b) $\mathrm{Ac_2O}$/pyridine protects all OH groups $\Rightarrow$ pentaacetate; (c) HCN adds to the aldehyde carbonyl $\Rightarrow$ cyanohydrin; (d) mild oxidation with $\mathrm{Br_2/H_2O}$ converts the $-\mathrm{CHO}$ to $-\mathrm{COOH}$ $\Rightarrow$ gluconic acid.

6.(a) What happens when (Write chemical equation only):

(i) Silver propionate reacts with Br_2 in CCl_4:

(ii) Bromobenzene reacts with Mg in the presence of dry ether:

(iii) Methyl bromide reacts with KCN (alc.):

(iv) Ethyl bromide is heated with sodium ethoxide:

(v) Ethyl bromide reacts with silver acetate:

Solution:

(i) Silver propionate reacts with Br_2 in CCl_4:

(Hunsdiecker reaction)

$$C_2H_5COOAg + Br_2 \xrightarrow{CCl_4,\ \Delta} C_2H_5Br + CO_2 + AgBr$$

(ii) Bromobenzene reacts with Mg in the presence of dry ether:

(Grignard reagent formation)

$$C_6H_5Br + Mg \xrightarrow{dry\ ether} C_6H_5MgBr$$

(iii) Methyl bromide reacts with KCN (alc.):

$$CH_3Br + KCN \longrightarrow CH_3CN + KBr$$

(iv) Ethyl bromide is heated with sodium ethoxide:

(Dehydrohalogenation – elimination, gives ethene)

$$CH_3CH_2Br + C_2H_5ONa \xrightarrow{\Delta} CH_2 = CH_2 + NaBr + C_2H_5OH$$

(v) Ethyl bromide reacts with silver acetate:

$$CH_3CH_2Br + CH_3COOAg \longrightarrow CH_3CH_2OCOCH_3 + AgBr$$

(Product: ethyl acetate)

Quick Tip

- Hunsdiecker reaction: silver salt of acid + halogen $\rightarrow$ alkyl halide + CO_2.
- Grignard reagent: ArX + Mg (dry ether) $\rightarrow$ ArMgX.
- KCN gives alkyl cyanides; $AgCN$ would give isocyanides.
- $NaOEt$ (alc.) promotes β-elimination to form alkenes.
- Silver acetate replaces halogen with $-OCOCH_3$ group.

(b) Write short notes on the following:

(i) Williamson's synthesis

(ii) Gattermann reaction

(iii) Kolbe's reaction

Solution:

(i) Williamson's Synthesis:

- This is an important laboratory method for the preparation of ethers.

- It involves the reaction of an alkoxide ion with a primary alkyl halide via nucleophilic substitution (SN2).

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

Example:

$$C_2H_5ONa + CH_3I \longrightarrow C_2H_5{-}O{-}CH_3 + NaI$$

(Product: methyl ethyl ether).

(ii) Gattermann Reaction:

- Used for formylation of aromatic compounds (introduction of –CHO group).

- Benzene or substituted aromatic compound reacts with HCN and HCl in the presence of a Lewis acid catalyst ($AlCl_3$ or $ZnCl_2$).

$$C_6H_6 \xrightarrow[ZnCl_2]{HCN/HCl} C_6H_5{-}CHO$$

(Product: benzaldehyde).

- Sometimes CO and HCl are used with $AlCl_3$/CuCl catalyst for the same transformation.

(iii) Kolbe's Reaction:

- Phenol on treatment with CO_2 under high pressure (4–7 atm) and 400 K in the presence of NaOH gives salicylic acid (o-hydroxybenzoic acid).

$$C_6H_5ONa + CO_2 \xrightarrow[400K,\ 4-7atm]{} o\text{-HO–C}_6H_4{-}COONa$$

On acidification:

$$o\text{-HO–C}_6H_4{-}COONa + HCl \longrightarrow o\text{-HO–C}_6H_4{-}COOH + NaCl$$

(Product: salicylic acid).

> Quick Tip
>
> - Williamson's synthesis is best with primary halides (secondary/tertiary may lead to elimination).
> - Gattermann reaction is useful for preparing aromatic aldehydes.
> - Kolbe's reaction is industrially important for the synthesis of salicylic acid (precursor of aspirin).

OR

(a) Write short notes on the following:

i) Wurtz reaction

ii) Wurtz-Fittig reaction

iii) Fittig reaction

Solution:

i) Wurtz Reaction:

- The Wurtz reaction is used for the synthesis of higher alkanes from alkyl halides.
- In this reaction, two molecules of alkyl halide react with sodium metal in dry ether to give a higher alkane.

$$2R{-}X + 2Na \xrightarrow[\text{dry ether}]{} R{-}R + 2NaX$$

Example:

$$2CH_3Cl + 2Na \xrightarrow[\text{dry ether}]{} C_2H_6 + 2NaCl$$

ii) Wurtz-Fittig Reaction:

- This reaction is used to prepare alkyl-substituted aromatic hydrocarbons.
- An alkyl halide reacts with an aryl halide in the presence of sodium metal and dry ether to form an alkyl-substituted benzene.

$$Ar{-}X + R{-}X + 2Na \xrightarrow[\text{dry ether}]{} Ar{-}R + 2NaX$$

Example:

$$C_6H_5Br + CH_3Cl + 2Na \xrightarrow[\text{dry ether}]{} C_6H_5CH_3 + 2NaCl$$

iii) Fittig Reaction:

- The Fittig reaction is used for the synthesis of biaryl compounds (diphenyl and its derivatives).
- In this reaction, two aryl halide molecules react with sodium metal in dry ether to form a biaryl.

$$2Ar{-}X + 2Na \xrightarrow[\text{dry ether}]{} Ar{-}Ar + 2NaX$$

Example:

$$2C_6H_5Cl + 2Na \xrightarrow[\text{dry ether}]{} C_6H_5{-}C_6H_5 + 2NaCl$$

Thus, these three reactions (Wurtz, Wurtz-Fittig, and Fittig) are important methods for carbon-carbon bond formation in organic chemistry.

> Quick Tip
>
> Wurtz → alkane synthesis, Wurtz-Fittig → alkylbenzene synthesis, Fittig → biaryl synthesis. All involve sodium metal in dry ether as the reagent.

(b) How will you convert (Write chemical equation only):

(i) Propene into propan-2-ol (ii) Benzyl chloride into benzyl alcohol (iii) Phenol into 2,4,6-tribromophenol (iv) Phenol into picric acid (v) Salicylic acid into phenol

Solution:

(i) Propene → propan-2-ol

$$CH_3CH{=}CH_2 + H_2O$$

(ii) Benzyl chloride → benzyl alcohol

$$\mathrm{C_6H_5CH_2Cl + KOH_{(aq)} \rightarrow C_6H_5CH_2OH + KCl}$$

(iii) Phenol → 2,4,6-tribromophenol

$$\mathrm{C_6H_5OH + 3\,Br_2\ (aq) \rightarrow 2,4,6{-}C_6H_2Br_3OH + 3\,HBr}$$

(iv) Phenol → picric acid (2,4,6-trinitrophenol)

$$\mathrm{C_6H_5OH + 3\,HNO_3 \xrightarrow{\text{conc. } HNO_3/H_2SO_4} 2,4,6{-}(NO_2)_3C_6H_2OH + 3\,H_2O}$$

(v) Salicylic acid → phenol

$$\mathrm{o{-}HO{-}C_6H_4{-}COOH \xrightarrow{\Delta} C_6H_5OH + CO_2}$$

> Quick Tip
>
> Use electrophilic additions/substitutions guided by directing effects: alkene hydration (Markovnikov) gives 2° alcohol; benzyl halide hydrolyses with aqueous base; phenol is strongly activating so Br_2(aq) gives 2,4,6-tribromo; mixed-acid nitration gives picric acid; salicylic acid decarboxylates on heating to phenol.

7.(a) Complete the following equations:

(i) $\mathrm{CH_3CHO} \xrightarrow{CH_3MgBr} (A) \xrightarrow{(B)} CH_3{-}CHOH{-}CH_3 \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4} (C) \xrightarrow[\Delta]{NH_2OH} (D)$

(ii) $\mathrm{C_6H_5CN + H_2O \xrightarrow{dil.\ H_2SO_4}}$ (E)

Solution:

(i) Sequence from ethanal via Grignard, oxidation and oxime formation:

$\mathrm{CH_3CHO + CH_3MgBr \rightarrow CH_3{-}CH(OMgBr){-}CH_3} \Rightarrow \boxed{(A) = \mathrm{CH_3{-}CH(OMgBr){-}CH_3}}$ (magnesium alkoxide).

(B) = acidic hydrolysis $(H_2O/H^+) \Rightarrow \mathrm{CH_3{-}CHOH{-}CH_3}$ (isopropyl alcohol).

Oxidation: $\mathrm{CH_3{-}CHOH{-}CH_3} \xrightarrow{\mathrm{K_2Cr_2O_7/H_2SO_4,\ \Delta}} \mathrm{CH_3{-}CO{-}CH_3} \Rightarrow \boxed{(C) = (\mathrm{CH_3})_2CO}$ (acetone).

Oxime formation: $(CH_3)_2CO + NH_2OH \xrightarrow{\Delta} (CH_3)_2C{=}NOH + H_2O \Rightarrow \boxed{(D) = \text{acetoxime}}$.

(ii) Hydrolysis of benzonitrile:

$C_6H_5CN + 2H_2O \xrightarrow{\text{dil. } H_2SO_4} C_6H_5COOH + NH_3 \Rightarrow \boxed{(E) = \text{benzoic acid}}$.

> **Quick Tip**
>
> Grignard addition to aldehydes gives alkoxides → on hydrolysis secondary alcohols.
> Secondary alcohols oxidize to ketones with $K_2Cr_2O_7/H_2SO_4$, and ketones give oximes with NH_2OH.
> Nitriles hydrolyze (acidic) to carboxylic acids.

(b) Write short notes on the following:

(i) Carbylamine reaction

(ii) Hofmann's bromamide reaction

(iii) Schmidt reaction

Solution:

(i) Carbylamine Reaction:

- This is a test for primary amines (both aliphatic and aromatic).
- When a primary amine is heated with chloroform and alcoholic KOH, it gives an isocyanide (carbylamine) with a very offensive odour.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R{-}NC + 3KCl + 3H_2O$$

- Secondary and tertiary amines do not respond to this test.

(ii) Hofmann's Bromamide Reaction:

- This reaction converts amides into amines with one carbon atom less than the parent amide.
- The reaction involves treatment of amide with bromine and alkali (KOH/NaOH).

$$RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- This is a useful method for descending homologation of amides to amines.

(iii) Schmidt Reaction:

- This reaction involves treatment of carboxylic acids with hydrazoic acid (HN_3) in the presence of concentrated H_2SO_4 to form amines.

$$RCOOH + HN_3 \xrightarrow{conc.\ H_2SO_4} RNH_2 + CO_2$$

- It is used for the conversion of acids into amines (with loss of one carbon atom).

> Quick Tip
>
> - Carbylamine test ⇒ identification of primary amines by foul-smelling isocyanides.
> - Hofmann's bromamide ⇒ converts amides to amines with one C less (useful in organic synthesis).
> - Schmidt reaction ⇒ converts carboxylic acids to amines, also reducing chain length by one C.

OR

(a) Complete the following reactions and write the names and formulae of A, B, C, D and E.

i) $(\mathrm{HCOO})_2\mathrm{Ca} \xrightarrow[\text{Dry distillation}]{} (A) \xrightarrow[\text{NaOH}]{} (B) + \mathrm{CH_3OH}$

ii) $(\mathrm{CH_3COO})_2\mathrm{Ca} + (\mathrm{HCOO})_2\mathrm{Ca} \xrightarrow[\text{Dry distillation}]{} (C) \xrightarrow[\text{HCN}]{} (D) \xrightarrow[\mathrm{H_2O}]{} (E)$

Solution:

(i) Identification and equations:

Dry distillation of calcium formate gives **formaldehyde**.

$(\mathrm{HCOO})_2\mathrm{Ca} \xrightarrow[\Delta]{\text{dry dist.}} \mathrm{HCHO}\ (A)\ +\ \mathrm{CaCO_3}$

Formaldehyde undergoes Cannizzaro reaction with NaOH to give **sodium formate** and methanol.

$2\,\mathrm{HCHO}\ (A) + \mathrm{NaOH} \rightarrow \mathrm{HCOONa}\ (B) + \mathrm{CH_3OH}$

Therefore:

$A =$ **Formaldehyde**, formula HCHO.

$B =$ **Sodium formate**, formula HCOONa.

(ii) Identification and equations:

Dry distillation of mixed calcium acetate and calcium formate gives **acetaldehyde**.

$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow[\Delta]{\text{dry dist.}} CH_3CHO\ (C) + \text{(by-product(s) } CaCO_3)$$

Addition of HCN to acetaldehyde gives its cyanohydrin (**lactonitrile**).

$$CH_3CHO\ (C) + HCN \rightarrow CH_3CH(OH)CN\ (D)$$

Hydrolysis of the nitrile yields **lactic acid** (2-hydroxypropanoic acid).

$$CH_3CH(OH)CN\ (D) \xrightarrow{H_2O/\text{hydrolysis}} CH_3CH(OH)COOH\ (E)$$

Therefore:

$C =$ **Acetaldehyde**, formula CH_3CHO.

$D =$ **Acetaldehyde cyanohydrin (lactonitrile)**, formula $CH_3CH(OH)CN$.

$E =$ **Lactic acid (2-hydroxypropanoic acid)**, formula $CH_3CH(OH)COOH$.

> Quick Tip
>
> Dry distillation of calcium salts: acetate $\rightarrow$ ketone; formate + acetate (mixed) $\rightarrow$ corresponding aldehyde. Carbonyl + HCN gives cyanohydrin, which on hydrolysis $\rightarrow$ α-hydroxy acid.

(b) How will you obtain Ethylamine from the following? Write chemical equation only:

(i) Methyl cyanide

(ii) Propanamide

(iii) Acetamide

(iv) Nitroethane

(v) Ethyl isocyanate

Solution:

(i) From methyl cyanide (acetonitrile)

$$CH_3CN + 2\,H_2 \xrightarrow[\Delta]{\text{Ni}} CH_3CH_2NH_2 \quad \text{(reduction of nitrile)}$$

(ii) From propanamide (Hofmann bromamide)

$$CH_3CH_2CONH_2 + Br_2 + 4\,NaOH \rightarrow CH_3CH_2NH_2 + 2\,NaBr + Na_2CO_3 + 2\,H_2O$$

(iii) From acetamide (LAH reduction)

$$\mathrm{CH_3CONH_2} \xrightarrow[\mathrm{H_3O^+}]{\mathrm{LiAlH_4/ether}} \mathrm{CH_3CH_2NH_2}$$

(iv) From nitroethane

$$\mathrm{CH_3CH_2NO_2 + 3\,H_2} \xrightarrow{\mathrm{Ni}} \mathrm{CH_3CH_2NH_2 + 2\,H_2O} \quad (\text{or } \mathrm{Fe/HCl})$$

(v) From ethyl isocyanate (hydrolysis)

$$\mathrm{CH_3CH_2NCO + H_2O} \xrightarrow{\Delta} \mathrm{CH_3CH_2NH_2 + CO_2}$$

Quick Tip

Nitrile reduction and amide (LAH) reduction preserve the carbon count; Hofmann bromamide shortens the chain by one carbon; nitro $\Rightarrow$ amine by reduction; isocyanate $\Rightarrow$ amine by hydrolysis with loss of CO_2.
