UP Board Class 12 Chemistry - 347 (KD) - 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) The amount of Na_2CO_3 to prepare 500 ml 0.2 M solution is –

(A) 1.53 g

(B) 3.06 g

(C) 10.6 g

(D) 5.3 g

Correct Answer: (C) 10.6 g

Solution:

Step 1: Calculate the number of moles of Na_2CO_3 needed.

The number of moles of a solute is given by the product of its molarity and the volume of the solution in liters.

$$\text{Moles} = \text{Molarity (M)} \times \text{Volume (L)}$$

First, convert the volume from ml to L:

$$500\,\text{ml} = 0.5\,\text{L}$$

Now, calculate the moles:

$$\text{Moles} = 0.2\,\text{mol/L} \times 0.5\,\text{L} = 0.1\,\text{mol}$$

Step 2: Calculate the molar mass of Na_2CO_3.

The molar mass is the sum of the atomic masses of the atoms in the formula.

$$\text{Molar Mass of } Na_2CO_3 = (2 \times \text{Na}) + (1 \times \text{C}) + (3 \times \text{O})$$

$$= (2 \times 23.0) + 12.0 + (3 \times 16.0) = 46.0 + 12.0 + 48.0 = 106.0\,\text{g/mol}$$

Step 3: Convert moles to mass in grams.

The mass required is the number of moles multiplied by the molar mass.

$$\text{Mass (g)} = \text{Moles} \times \text{Molar Mass (g/mol)}$$

$$\text{Mass} = 0.1\,\text{mol} \times 106.0\,\text{g/mol} = 10.6\,\text{g}$$

Step 4: Conclusion.

Therefore, 10.6 g of Na_2CO_3 are needed.

$$\boxed{10.6\,g}$$

> **Quick Tip**
>
> Always remember: Moles = Molarity $\times$ Volume (L), and Mass = Moles $\times$ Molar Mass.

(b) Colourless ion in the following is –

(A) Ni^{2+}

(B) Fe^{3+}

(C) Cu^{2+}

(D) Cu^{+1}

Correct Answer: (D) Cu^{+1}

Solution:

Step 1: State the condition for color in transition metal ions.

The color of transition metal ions is generally due to the absorption of visible light, which excites an electron from a lower-energy d-orbital to a higher-energy d-orbital. This phenomenon is called a d-d transition. For a d-d transition to occur, the d-subshell must be partially filled (i.e., contain between 1 and 9 electrons).

Step 2: Determine the electron configuration of each ion.

- **(A) Ni^{2+}:** Neutral Ni is [Ar] $3d^8\ 4s^2$. Removing two 4s electrons gives [Ar] $3d^8$.
- **(B) Fe^{3+}:** Neutral Fe is [Ar] $3d^6\ 4s^2$. Removing two 4s and one 3d electron gives [Ar] $3d^5$.
- **(C) Cu^{2+}:** Neutral Cu is [Ar] $3d^{10}\ 4s^1$. Removing one 4s and one 3d electron gives [Ar] $3d^9$.
- **(D) Cu^{+1}:** Neutral Cu is [Ar] $3d^{10}\ 4s^1$. Removing one 4s electron gives [Ar] $3d^{10}$.

Step 3: Identify the ion incapable of d-d transitions.

- Ni^{2+} ($3d^8$), Fe^{3+} ($3d^5$), and Cu^{2+} ($3d^9$) all have partially filled d-subshells, allowing for d-d transitions. They are therefore colored.
- Cu^{+1} has a $3d^{10}$ configuration. Since the d-subshell is completely full, there are no empty d-orbitals for an electron to be promoted to. No d-d transition is possible, so the ion does not absorb visible light and is colorless.

Step 4: Conclusion.

The Cu^{+1} ion is colorless because its d-subshell is completely filled.

$$\boxed{Cu^{+1}}$$

Quick Tip

Transition metal ions with either completely filled (d^{10}) or completely empty (d^0) d-orbitals are usually colourless.

(c) The value of x in the complex ion $[Ni(CN)_4]^x$ is –

(A) 0

(B) +2

(C) –2

(D) 4

Correct Answer: (C) –2

Solution:

Step 1: Determine the charge of the ligands.

The ligand in this complex is cyanide, CN. The cyanide ion has a charge of -1. Since there are four cyanide ligands, their total contribution to the charge is:

$$4 \times (-1) = -4$$

Step 2: Determine the oxidation state of the central metal.

The central metal is Nickel (Ni). In the tetracyanidonickelate ion, nickel is in its common +2 oxidation state.

$$\text{Oxidation state of Ni} = +2$$

Step 3: Calculate the overall charge of the complex ion.

The overall charge of a complex ion (x) is the sum of the oxidation state of the central metal and the total charge of the ligands.

$$x = (\text{Oxidation state of Ni}) + (\text{Total charge of ligands})$$

$$x = (+2) + (-4)$$

$$x = -2$$

Step 4: Final Answer.

The value of x, which represents the overall charge of the complex ion, is -2.

$$\boxed{-2}$$

> Quick Tip
>
> Always calculate the overall charge on a complex ion by adding the metal oxidation state and the charges of all ligands. CN^- contributes –1 each.

(d) In the reaction $CH_3COCl + H_2 \rightarrow {}^{Pd-BaSO}{}_4$ .....$theproductis–$

(A) Ketone

(B) Aldehyde

(C) Acid

(D) Alcohol

Correct Answer: (B) Aldehyde

Solution:

Step 1: Identify the name and type of the reaction.

This reaction is known as the **Rosenmund reduction**. It is a catalytic hydrogenation process where an acyl chloride is converted into an aldehyde.

Step 2: Analyze the reactants.

The starting material is CH_3COCl, which is acetyl chloride (an acyl chloride). It is being reacted with hydrogen gas (H_2).

Step 3: Understand the role of the specific catalyst.

The catalyst is Palladium on Barium Sulfate ($Pd/BaSO_4$). This is a "poisoned" or deactivated catalyst.

- Palladium (Pd) is a very effective hydrogenation catalyst.
- Barium sulfate ($BaSO_4$) reduces the activity of the palladium. This is crucial because it prevents the reaction from proceeding too far. It stops the reduction at the aldehyde stage and prevents further reduction to a primary alcohol.

Step 4: Predict the product.

The Rosenmund reduction replaces the chlorine atom of the acyl chloride with a hydrogen atom.

$$CH_3 - C(=O) - Cl \xrightarrow{H_2, Pd/BaSO_4} CH_3 - C(=O) - H$$

The starting material is acetyl chloride, and the product is CH_3CHO, which is acetaldehyde. Acetaldehyde is an **aldehyde**.

Aldehyde

Quick Tip

Rosenmund reduction is a selective method for preparing aldehydes from acyl chlorides. Pd–$BaSO_4$ ensures partial reduction only up to aldehyde, not alcohol.

(e) $(CH_3)_3N$ is a –

(A) Primary amine

(B) Secondary amine

(C) Tertiary amine

(D) None of these

Correct Answer: (C) Tertiary amine

Solution:

Step 1: Recall classification of amines.

- A **primary amine (1°)** has one alkyl group attached to nitrogen (R–NH_2).
- A **secondary amine (2°)** has two alkyl groups attached to nitrogen (R_2–NH).
- A **tertiary amine (3°)** has three alkyl groups attached to nitrogen (R_3–N).

Step 2: Apply to given case.

In $(CH_3)_3N$, nitrogen is bonded to three methyl (–CH_3) groups and has no hydrogen directly attached to it.

Step 3: Identify type.

Since three alkyl groups are attached to nitrogen, it is a **tertiary amine**.

Step 4: Final Answer.

Tertiary amine

Quick Tip

To classify amines, just count how many carbon groups (alkyl or aryl) are directly attached to the nitrogen atom: 1 = primary, 2 = secondary, 3 = tertiary.

(f) Ascorbic acid is –

(A) Vitamin

(B) Enzyme

(C) Protein

(D) Hormone

Correct Answer: (A) Vitamin

Solution:

Ascorbic acid is the chemical name of **Vitamin C**. It is a water-soluble vitamin that acts as an antioxidant and is essential for the synthesis of collagen in connective tissues. Its

deficiency leads to **scurvy**, a disease characterized by bleeding gums, loose teeth, and delayed wound healing.

- (A) Vitamin: Correct, because ascorbic acid is Vitamin C.
- (B) Enzyme: Wrong, enzymes are biological catalysts, not vitamins.
- (C) Protein: Wrong, proteins are polymers of amino acids, not vitamins.
- (D) Hormone: Wrong, hormones are chemical messengers secreted by glands, not vitamins.

Vitamin (Vitamin C)

Quick Tip

Remember: Ascorbic acid = Vitamin C, deficiency causes scurvy. It is a water-soluble vitamin, unlike Vitamins A, D, E, and K which are fat-soluble.

2.(a) What is the relation between depression in freezing point and molar mass of the solute?

Solution:

The depression in freezing point (ΔT_f) is directly proportional to the molality of the solution. The relation is:

$$\Delta T_f = K_f \cdot m$$

where K_f is the molal depression constant of the solvent and m is molality.

Since molality $m = \dfrac{w \times 1000}{M \times W}$,

$$\Delta T_f = K_f \cdot \frac{w \times 1000}{M \times W}$$

where: - w = mass of solute (g),

- M = molar mass of solute (g mol^{-1}),

- W = mass of solvent (g).

Thus, molar mass of solute can be calculated as:

$$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

Quick Tip

Freezing point depression is a colligative property, depending only on the number of solute particles. The higher the molar mass, the smaller the depression for a fixed solute mass.

(b) Equivalent mass of $KMnO_4$ is different in acidic and alkaline media. Why?

Solution:

The equivalent mass of a substance depends on the number of electrons gained or lost per mole of substance in a redox reaction. $KMnO_4$ shows different oxidation states of Mn in acidic and alkaline media, hence the number of electrons exchanged is different.

In acidic medium:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Manganese changes from +7 to +2 oxidation state ($\Delta = 5e^-$).

$$\text{Equivalent mass} = \frac{\text{Molar mass of } KMnO_4}{5}$$

In neutral/alkaline medium:

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

Manganese changes from +7 to +4 oxidation state ($\Delta = 3e^-$).

$$\text{Equivalent mass} = \frac{\text{Molar mass of } KMnO_4}{3}$$

Therefore, the equivalent mass of $KMnO_4$ differs because the change in oxidation number of Mn (and hence electrons transferred) is different in acidic and alkaline medium.

Quick Tip

Always calculate equivalent mass using:

$$\text{Eq. mass} = \frac{\text{Molar mass}}{\text{Number of electrons gained or lost}}$$

For $KMnO_4$: 5 electrons in acidic medium, 3 electrons in alkaline medium.

(c) $Cu(OH)_2$ is soluble in NH_4OH solution but not in NaOH solution. Why?

Solution:

$Cu(OH)_2$ dissolves in aqueous ammonia due to **complex formation**.

In excess NH_3, Cu^{2+} forms the deep-blue ammine complex:

$$\mathrm{Cu(OH)_2 \; + \; 4\,NH_3 \; + \; 2\,H_2O \; \longrightarrow \; [Cu(NH_3)_4(H_2O)_2]^{2+} \; + \; 2\,OH^-}$$

This complex is soluble, so the precipitate dissolves.

In NaOH, no such soluble cuprate complex is formed ($Cu(OH)_2$ is not appreciably amphoteric),

hence $Cu(OH)_2$ remains as an insoluble blue precipitate.

Quick Tip

Transition-metal hydroxides often dissolve in *ligand* bases like NH_3 by forming soluble complexes, but not necessarily in strong bases like NaOH unless they are amphoteric (e.g., $Al(OH)_3$).

(d) Complete the following chemical equation:

$\mathrm{CH_3CHBrCH_3} \xrightarrow[\Delta]{\mathrm{KOH(alc)}} (A) \xrightarrow[\mathrm{ROOR}]{\mathrm{HBr}} (B)$**.**

Solution:

Step 1 (Dehydrohalogenation, alcoholic KOH, heat):

$$\mathrm{CH_3{-}CHBr{-}CH_3} \xrightarrow[\Delta]{\mathrm{KOH(alc)}} \mathrm{CH_3{-}CH{=}CH_2 \; + \; KBr \; + \; H_2O}$$

Thus, $\boxed{A = \mathrm{CH_3{-}CH{=}CH_2}\ \text{(propene)}}$.

Step 2 (Anti-Markovnikov addition of HBr in presence of peroxides):

$$\mathrm{CH_3{-}CH{=}CH_2} \xrightarrow[\mathrm{ROOR}]{\mathrm{HBr}} \mathrm{CH_3{-}CH_2{-}CH_2Br}$$

Thus, $\boxed{B = \mathrm{CH_3{-}CH_2{-}CH_2Br}\ \text{(1-bromopropane)}}$.

> **Quick Tip**
>
> Alcoholic KOH promotes **elimination (E2)** to an alkene, whereas HBr with peroxides adds **anti-Markovnikov** via a radical chain to give the *primary* bromoalkane.

3.(a) 54% (w/w) water is present in the mixture of ethyl alcohol and water. Calculate the mole fraction of ethyl alcohol and water in the mixture.

Solution:

Let us consider 100 g of solution.

Mass of water = 54 g, Mass of ethanol = 46 g.

Step 1: Calculate moles of water.

Molar mass of water = 18 g $\mathrm{mol^{-1}}$.

Moles of water = $\dfrac{54}{18} = 3.00$ mol.

Step 2: Calculate moles of ethanol.

Molar mass of ethanol = 46 g $\mathrm{mol^{-1}}$.

Moles of ethanol = $\dfrac{46}{46} = 1.00$ mol.

Step 3: Total moles.

Total moles = $3.00 + 1.00 = 4.00$ mol.

Step 4: Mole fractions.

Mole fraction of water = $\dfrac{3.00}{4.00} = 0.75$.

Mole fraction of ethanol = $\dfrac{1.00}{4.00} = 0.25$.

$$\boxed{X_{\text{water}} = 0.75, \quad X_{\text{ethanol}} = 0.25}$$

Quick Tip

Always take a 100 g basis for w/w problems. Then convert given masses into moles and divide by total moles to find mole fraction.

(b) Write the chemical equations of the following reactions:

i) Reaction of dilute HNO_3 with phenol

ii) Reaction of phenol with chloroform in the presence of NaOH (aq.)

Solution:

i) Reaction of dilute HNO_3 with phenol:

Phenol undergoes nitration with dilute HNO_3 to form ortho- and para-nitrophenol.

$$C_6H_5OH + HNO_3 \rightarrow o\text{-}C_6H_4(OH)(NO_2) + p\text{-}C_6H_4(OH)(NO_2) + H_2O$$

ii) Reaction of phenol with chloroform in the presence of NaOH (aq.):

This is the Reimer-Tiemann reaction. Phenol reacts with chloroform and NaOH to give salicylaldehyde (o-hydroxybenzaldehyde).

$$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow o\text{-}OH\text{-}C_6H_4CHO + 3NaCl + 2H_2O$$

Quick Tip

Dilute nitration of phenol mainly gives ortho and para products. Reimer-Tiemann reaction (phenol + $CHCl_3$/NaOH) is a key method to introduce a $-CHO$ group at the ortho-position of phenol.

(c) Write IUPAC names of the following compounds:

(i) $CH_3CO(CH_2)_4CH_3$

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

Solution:

(i) Longest chain contains 7 carbons including the carbonyl carbon; the C=O is at C-2.

Heptan-2-one

(ii) Parent chain includes the $-\mathrm{CHO}$ group $\Rightarrow$ hexanal; substituents: bromo at C-4 and methyl at C-2.

4-Bromo-2-methylhexanal

> Quick Tip
>
> For aldehydes, number from the $-$CHO carbon as C-1; for ketones, give the carbonyl the lowest possible locant.

(d) How are vitamins classified? Name the vitamin responsible for coagulation of blood.

Solution:

Classification:

• **Fat-soluble:** A, D, E, K.

• **Water-soluble:** B-complex (B_1, B_2, B_3, B_5, B_6, B_7, B_9, B_{12}) and C.

Vitamin for blood coagulation: Vitamin K (e.g., phylloquinone).

> Quick Tip
>
> Remember "**ADEK**" as the fat-soluble group; all others (B-complex and C) are water-soluble.

4.(a) Write the definition of molality. 1/10 mole of a solute is dissolved in 100 g solvent. Calculate the molality of the solution.

Solution:

Definition:

Molality (m) is defined as the number of moles of solute present in 1 kilogram of solvent.

$$m = \frac{n_{\text{solute}}}{w_{\text{solvent}}(\text{in kg})}$$

Given:

Moles of solute = $\frac{1}{10} = 0.1$ mol.

Mass of solvent = 100 g $= 0.100$ kg.

Step 1: Calculate molality.

$$m = \frac{0.1}{0.100} = 1.0 \text{ mol kg}^{-1}$$

$$\boxed{\text{Molality of the solution } = 1.0 \text{ m}}$$

> **Quick Tip**
>
> Molality depends only on mass of solvent (kg), not on volume. Hence, unlike molarity, it is independent of temperature.

(b) What is Kohlrausch law? Write its two applications.

Solution:

Statement of Kohlrausch's Law:

At infinite dilution, the molar conductivity of an electrolyte is equal to the sum of the contributions of its individual ions.

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

where λ_+^0 and λ_-^0 are the limiting molar conductivities of cations and anions respectively.

Applications:

1. To calculate the molar conductivity of weak electrolytes at infinite dilution (since they cannot be measured directly).

2. To determine the degree of dissociation (α) and dissociation constant (K_a, K_b) of weak electrolytes.

Quick Tip

Kohlrausch's law is very useful for weak electrolytes like acetic acid. By knowing the Λ_m^∞ values of strong electrolytes, we can indirectly calculate Λ_m^∞ of weak electrolytes.

(c) The rate constant for a first–order reaction is $60\ \mathrm{s}^{-1}$. How much time will it take to reduce the initial concentration of the reactant to $\frac{1}{16}$th?

Solution:

For a first–order reaction, $\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$.

Here $\frac{[A]_0}{[A]_t} = 16 \Rightarrow \ln 16 = 4\ln 2 = 4 \times 0.693 = 2.772$.

Given $k = 60\ \mathrm{s}^{-1}$.

$$t = \frac{\ln 16}{k} = \frac{2.772}{60} = 4.62 \times 10^{-2}\ \mathrm{s} \approx 0.046\ \mathrm{s}.$$

$$\boxed{t \approx 4.6 \times 10^{-2}\ \mathrm{s}}$$

Quick Tip

For "reduce to a fraction" questions in first–order kinetics, use $t = \frac{1}{k}\ln\left(\frac{1}{\text{fraction remaining}}\right)$; powers of 2 are quick via $\ln 2 \approx 0.693$.

(d) When a brown coloured salt (A) of Mn reacts with HCl, a gas (B) is obtained. This gas in excess reacts with NH_3 to form an explosive salt (C). Identify (A), (B) and (C) and write the chemical equations.

Solution:

Identification: (A) = MnO_2 (brown–black solid); (B) = Cl_2; (C) = NCl_3 (explosive).

Equations:

Generation of chlorine from manganese dioxide and HCl:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Action of Cl_2 (excess) on ammonia giving explosive nitrogen trichloride:

$$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$$

Quick Tip

Chlorine with *excess NH_3* can form explosive NCl_3; with *excess NH_3* consumed and limited Cl_2, the main products are N_2 and NH_4Cl. Always note which reagent is in excess.

5.(a) What is Nernst equation? Write the relation between standard electrode potential and electrode potential.

Solution:

The Nernst equation gives the relation between electrode potential and the concentrations (activities) of the ions involved in the electrode reaction.

For a general half-cell reaction:

$$M^{n+} + ne^- \rightleftharpoons M$$

The Nernst equation is:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

or equivalently,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[Ox]}{[Red]}$$

Relation:

- E° = standard electrode potential (when ion concentration is 1 M).
- E = electrode potential under given conditions.

Thus, electrode potential depends on concentration, number of electrons transferred, and temperature.

$$\boxed{E = E^\circ - \frac{0.0591}{n} \log Q}$$

where Q = reaction quotient.

> Quick Tip
>
> The Nernst equation corrects the electrode potential for non-standard conditions (other than 1 M, 1 atm, 298 K).

(b) Explain the rate of reaction. Describe the order of reaction with example.

Solution:

Rate of reaction:

The rate of reaction is defined as the change in concentration of a reactant or product per unit time.

$$\text{Rate} = -\frac{d[\text{Reactant}]}{dt} = \frac{d[\text{Product}]}{dt}$$

Order of reaction:

The order of a reaction is the sum of the powers of the concentration terms of reactants in the experimentally determined rate law.

For a reaction:

$$aA + bB \ \rightarrow \ Products$$

Rate law is:

$$r = k[A]^x[B]^y$$

Here, order of reaction = $x + y$.

Examples:

1. **First-order reaction:** Decomposition of H_2O_2

$$2H_2O_2 \ \rightarrow \ 2H_2O + O_2$$

Rate = $k[H_2O_2]$, order = 1.

2. **Second-order reaction:** Saponification of ester with NaOH Rate = k[Ester][NaOH], order = 2.

Order is always determined experimentally and can be 0, fractional, or whole.

Quick Tip

Molecularity is theoretical and whole number, while order is experimental and may be fractional or zero. Always check experimental data to find order of reaction.

(c) Write IUPAC names of the following:

(i) $K_2[HgI_4]$

(ii) $[Cu(NH_3)_4]SO_4$

(iii) $K_3[Al(C_2O_4)_3]$

(iv) $[Cr(CO)_6]$

Solution:

(i) Potassium tetraiodidomercurate(II)

(ii) Tetraamminecopper(II) sulfate

(iii) Potassium tris(oxalato)aluminate(III)

(iv) Hexacarbonylchromium(0)

Quick Tip

For anionic complexes, use metal name ending in "-ate" (mercurate, aluminate). Neutral ligands: NH_3 = ammine, CO = carbonyl; give oxidation state in Roman numerals.

(d) What is Tollen's reagent? Write the chemical equation for the reactions of this reagent with glucose and fructose.

Solution:

Tollen's reagent: Freshly prepared ammoniacal silver nitrate containing the complex ion $[Ag(NH_3)_2]^+$ (often written as $[Ag(NH_3)_2]OH$). It oxidises aldehydes to carboxylates giving a silver mirror.

With glucose (an aldose):

$$C_6H_{12}O_6 + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow C_6H_{11}O_6^- + 2\,Ag(s) + 4\,NH_3 + 2\,H_2O$$

(*on acidification* $C_6H_{11}O_6^- \rightarrow C_6H_{12}O_7$, gluconic acid).

With fructose (a ketose):

In alkaline medium fructose $\rightleftharpoons$ enediol $\rightleftharpoons$ glucose/mannose, hence it also reduces Tollen's reagent:

$$C_6H_{12}O_6\ (\text{fructose}) + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow C_6H_{11}O_6^- + 2\,Ag(s) + 4\,NH_3 + 2\,H_2O$$

> Quick Tip
>
> Remember: Tollen's tests for $-CHO$. Ketoses like fructose still give a positive test because base-induced enediol formation converts them to aldoses first.

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

i) Phenol reacts with Br_2 water?

ii) Acetylation of phenol happens in the presence of pyridine?

iii) Phenol is heated with PCl_5?

iv) Phenol reacts with NaOH?

v) Vapour of the mixture of phenol and methyl alcohol is passed through hot thoria (ThO_2)?

Solution:

i) Phenol + Br_2(aq):

$$C_6H_5OH + 3\,Br_2 \rightarrow 2,4,6\text{-}C_6H_2Br_3OH \downarrow + 3\,HBr$$

(Product: 2,4,6-tribromophenol, white ppt.)

ii) Acetylation (pyridine as base):

$$C_6H_5OH + CH_3COCl \xrightarrow{\text{pyridine}} C_6H_5OCOCH_3 + HCl$$

(Product: phenyl acetate)

iii) Phenol + PCl_5 (on heating):

No reaction (aryl–OH is not replaced by Cl by PCl_5).

iv) Phenol + NaOH:

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

(Product: sodium phenoxide)

v) Vapours over hot ThO_2 (vapour-phase alkylation):

$$C_6H_5OH + CH_3OH \xrightarrow{ThO_2,\ \Delta} C_6H_5OCH_3 + H_2O$$

(Product: anisole)

> **Quick Tip**
>
> Phenol is strongly activated: Br_2(aq) gives 2,4,6-tribromophenol instantly.
>
> Aryl–OH is not converted to aryl chloride by PCl_5; use diazonium route for Ar–Cl.
>
> Hot thoria catalyzes vapour-phase O-alkylation to anisole.

(b) Complete the following equations:

(i) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow ?$

(ii) $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow ?$

(iii) $(CH_3)_3CBr + KOH \longrightarrow ?$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{Ethanol (aq.)}} ?$

(v) $CH_3CH_2Br + AgNO_2 \xrightarrow{\text{alc.}} ?$

Solution:

(i) Reaction with thionyl chloride ($SOCl_2$):

$$\mathrm{CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl}$$

(Product: 1-chloropropane).

(ii) Addition of HBr to alkene (Markovnikov's rule):

$$\mathrm{CH_3CH_2CH{=}CH_2 + HBr \longrightarrow CH_3CH_2CHBrCH_3}$$

(Product: 2-bromobutane).

(iii) Tertiary alkyl halide with KOH (alc., elimination):

$$\mathrm{(CH_3)_3CBr + KOH \longrightarrow (CH_3)_2C{=}CH_2 + KBr + H_2O}$$

(Product: isobutene, via elimination E2).

(iv) Substitution with KCN (nucleophilic substitution):

$$\mathrm{CH_3CH_2Br + KCN \xrightarrow{Ethanol} CH_3CH_2CN + KBr}$$

(Product: propionitrile).

(v) Reaction with $AgNO_2$ (alc.):

$$\mathrm{CH_3CH_2Br + AgNO_2 \longrightarrow CH_3CH_2{-}ONO + AgBr}$$

(Product: ethyl nitrite, an isomeric nitro–oxy compound).

Quick Tip

- Alcohol + $SOCl_2$ $\Rightarrow$ alkyl chloride (best method as byproducts are gases).
- Alkene + HX $\Rightarrow$ halogen addition (Markovnikov unless peroxides present).
- Tertiary halides with KOH (alc.) favour elimination $\Rightarrow$ alkene.
- KCN $\Rightarrow$ cyanides (C–C bond formation).
- $AgNO_2$ gives alkyl nitrites ($R{-}ONO$), while KNO_2 gives nitroalkanes ($R{-}NO_2$).

OR

(a) How will you obtain (Write chemical equation only):

i) Ethyl alcohol from Grignard's reagent

ii) Tertiary alcohol from Grignard's reagent

iii) Ethyl alcohol from Methyl alcohol

iv) Diethyl ether from Ethyl alcohol

v) Ethyl acetate from Ethyl alcohol

Solution:

i) Ethyl alcohol from Grignard's reagent:

$$C_2H_5MgBr + HCHO \xrightarrow{ether} C_2H_5CH_2OMgBr \xrightarrow{H_2O} C_2H_5CH_2OH$$

ii) Tertiary alcohol from Grignard's reagent:

$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{ether} (CH_3)_2C(OMgBr)C_2H_5 \xrightarrow{H_2O} (CH_3)_2C(OH)C_2H_5$$

iii) Ethyl alcohol from Methyl alcohol:

$$CH_3OH \xrightarrow{P/I_2} CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow{H_2/Ni} CH_3CH_2NH_2 \xrightarrow{NaNO_2/HCl} C_2H_5OH$$

iv) Diethyl ether from Ethyl alcohol:

$$2C_2H_5OH \xrightarrow{conc.\,H_2SO_4,\,413\,K} C_2H_5OC_2H_5 + H_2O$$

v) Ethyl acetate from Ethyl alcohol:

$$C_2H_5OH + CH_3COOH \xrightarrow{conc.\,H_2SO_4} CH_3COOC_2H_5 + H_2O$$

Quick Tip

Grignard's reagent with formaldehyde gives primary alcohol, with aldehydes/ketones gives secondary or tertiary alcohols. Dehydration of ethanol gives ether, while esterification with acetic acid gives ethyl acetate.

(b) Write short notes on the following:

(i) Hunsdiecker reaction

(ii) Frankland's reaction

(iii) Dehydrohalogenation

Solution:

(i) Hunsdiecker (Hunsdiecker–Borodin) reaction:

Decarboxylative halogenation of the *silver salt* of a carboxylic acid with halogen ($\mathrm{Br_2}$ or $\mathrm{Cl_2}$) in $\mathrm{CCl_4}$ under light/heat to give an alkyl halide with 1 carbon less. Radical mechanism.

$$\mathrm{RCOOAg + X_2 \xrightarrow[h\nu \text{ or } \Delta]{CCl_4} R{-}X + CO_2 + AgX}$$

Example: $\mathrm{C_2H_5COOAg + Br_2 \rightarrow C_2H_5Br + CO_2 + AgBr}$.

(ii) Frankland's reaction (zinc coupling):

Two alkyl halides couple in presence of zinc to form a higher alkane (symmetrical), with zinc halide as by-product.

$$\mathrm{2\,R{-}X + Zn \longrightarrow R{-}R + ZnX_2}$$

Example: $\mathrm{2\,CH_3I + Zn \rightarrow C_2H_6 + ZnI_2}$.

(iii) Dehydrohalogenation:

Base-induced elimination of HX from an alkyl halide to form an alkene; carried out with alcoholic KOH/NaOEt and heat; follows Zaitsev's rule (more substituted alkene major, via E2).

$$\mathrm{RCH_2CHXCH_3 \xrightarrow[\Delta]{\text{alc. KOH}} RCH{=}CHCH_3 + KX + H_2O}$$

Example: $\mathrm{CH_3CH_2CH_2Br \xrightarrow[\Delta]{\text{alc. KOH}} CH_3CH{=}CH_2 + KBr + H_2O}$.

Quick Tip

Remember: Hunsdiecker = silver carboxylate $\rightarrow$ halide $-\mathrm{CO_2}$ (chain shortens by 1 C); Frankland = Zn couples two R–X to R–R; Dehydrohalogenation = β-elimination with alcoholic base giving the more substituted alkene (Zaitsev).

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7. (a) Write short notes on the following:

i) Tischenko reaction

ii) Cannizzaro's reaction

iii) Clemmensen reduction

Solution:

i) Tischenko Reaction:

- It is the disproportionation of aldehydes (without α-hydrogen) in the presence of an alkoxide catalyst to give esters.

$$2R{-}CHO \xrightarrow{Al(OR)_3} RCH_2O{-}COR$$

Example:

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3CH_2OCOCH_3$$

(Product: ethyl acetate)

ii) Cannizzaro's Reaction:

- This is the base-induced disproportionation of aldehydes without α-hydrogen into alcohol and carboxylate salt.

$$2R{-}CHO \xrightarrow{conc.\ NaOH} RCH_2OH + RCOONa$$

Example:

$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$

iii) Clemmensen Reduction:

- It is the reduction of carbonyl compounds (aldehydes and ketones) to hydrocarbons using zinc amalgam and concentrated HCl.

$$R{-}CO{-}R' \xrightarrow[\Delta]{Zn(Hg)/conc.\ HCl} R{-}CH_2{-}R'$$

Example:

$$C_6H_5COCH_3 \xrightarrow{Zn(Hg)/HCl} C_6H_5CH_3$$

(Product: toluene)

Thus, these three reactions are important methods: Tischenko (ester formation), Cannizzaro (disproportionation), and Clemmensen (reduction).

> **Quick Tip**
>
> - Tischenko: aldehyde $\rightarrow$ ester (via $Al(OR)_3$ catalyst).
> - Cannizzaro: aldehyde (no α-H) $\rightarrow$ alcohol + carboxylate (via base).
> - Clemmensen: carbonyl $\rightarrow$ hydrocarbon (Zn(Hg)/HCl).

(b) Complete the following equations:

(i) $\mathrm{C_6H_5NH_2 + CHCl_3 + KOH(alc)} \longrightarrow$

(ii) $\mathrm{C_6H_5NH_2 + Br_2(aq)} \longrightarrow$

(iii) $\mathrm{C_6H_5NH_2 + (CH_3CO)_2O} \longrightarrow$

(iv) $\mathrm{C_6H_5NH_2 + H_2SO_4(conc.)} \longrightarrow$

(v) $\mathrm{C_6H_5NH_2 + CH_3COCl} \xrightarrow{\text{base}} \longrightarrow$

Solution:

(i) Carbylamine reaction (isocyanide test):

$$\mathrm{C_6H_5NH_2 + CHCl_3 + 3KOH} \longrightarrow \mathrm{C_6H_5NC + 3KCl + 3H_2O}\,.$$

(ii) Bromination in water (tribromination):

$$\mathrm{C_6H_5NH_2 + 3Br_2(aq)} \longrightarrow 2,4,6{-}\mathrm{C_6H_2Br_3NH_2\,(s) + 3HBr}\,.$$

(iii) Acetylation with acetic anhydride:

$$\mathrm{C_6H_5NH_2} + (\mathrm{CH_3CO})_2\mathrm{O} \longrightarrow \mathrm{C_6H_5NHCOCH_3}\ (\text{acetanilide}) + \mathrm{CH_3COOH}\,.$$

(iv) Protonation by conc. sulfuric acid:

$$\mathrm{C_6H_5NH_2} + \mathrm{H_2SO_4} \longrightarrow \mathrm{C_6H_5NH_3^+\ HSO_4^-}\ (\text{anilinium hydrogensulfate})\,.$$

(v) Acetylation with acetyl chloride (base present):

$$\mathrm{C_6H_5NH_2} + \mathrm{CH_3COCl} \xrightarrow{\text{base}} \mathrm{C_6H_5NHCOCH_3}\ (\text{acetanilide}) + \mathrm{HCl}\,,$$

(the base neutralises HCl as $\mathrm{base}\cdot\mathrm{HCl}$).

> **Quick Tip**
>
> Aniline is strongly activating and ortho/para–directing; in aqueous bromine it gives 2,4,6-tribromoaniline instantly. Protecting the $-NH_2$ group by acetylation (acetanilide) moderates its reactivity for controlled EAS. Carbylamine forms foul-smelling isocyanides only from *primary* amines.

OR

(a) Complete the following equations and identify A, B, C, D and E.

i) $\mathrm{CH_3COCH_3} \xrightarrow[\text{distillation}]{\text{conc. } H_2SO_4} (A)$

ii) $\mathrm{CH_3COCH_3} \xrightarrow[\text{Heat}]{I_2+NaOH} (B)$

iii) $\mathrm{CH_3CHO} \xrightarrow{\text{dil. } NaOH} (C) \xrightarrow{\text{Heat}} (D)$

iv) $\mathrm{HCHO} \xrightarrow{Ca(OH)_2} (E)$

Solution:

i) Acetone + conc. H_2SO_4 (distillation):

Self-condensation and aromatization give mesitylene.

$$3\,\mathrm{CH_3COCH_3} \xrightarrow[\text{distill.}]{\text{conc. } H_2SO_4} \mathrm{C_6H_3(CH_3)_3}\ (A)\ +\ 3\,\mathrm{H_2O}$$

$A =$ **Mesitylene (1,3,5-trimethylbenzene)**, formula $\mathrm{C_9H_{12}}$.

ii) Iodoform reaction of acetone (NaOH, I_2, heat):

$$\mathrm{CH_3COCH_3} + 3\,I_2 + 4\,NaOH \rightarrow \underbrace{\mathrm{CHI_3}}_{(B)} + \mathrm{CH_3COONa} + 3\,\mathrm{NaI} + 3\,\mathrm{H_2O}$$

$B =$ **Iodoform**, formula $\mathrm{CHI_3}$ (yellow ppt.).

iii) Aldol reaction of acetaldehyde then dehydration:

$$2\,\mathrm{CH_3CHO} \xrightarrow{\text{dil. } NaOH} \mathrm{CH_3CH(OH)CH_2CHO}\ (C)$$

$$\mathrm{CH_3CH(OH)CH_2CHO} \xrightarrow{\text{Heat}} \mathrm{CH_3CH{=}CHCHO}\ (D) + \mathrm{H_2O}$$

$C =$ **3-Hydroxybutanal (aldol)**, formula $\mathrm{C_4H_8O_2}$.

$D =$ **Crotonaldehyde (but-2-enal)**, formula $\mathrm{C_4H_6O}$.

iv) Formaldehyde with $Ca(OH)_2$ (Cannizzaro):

$$2\,\mathrm{HCHO} + Ca(OH)_2 \rightarrow \underbrace{(HCOO)_2Ca}_{(E)} + \mathrm{CH_3OH}$$

$E =$ **Calcium formate**, formula $\mathrm{(HCOO)_2Ca}$.

> Quick Tip
>
> Acetone shows iodoform test $\rightarrow \mathrm{CHI_3}$. Acetaldehyde gives aldol $\rightarrow$ dehydration to α,β-unsaturated aldehyde. Formaldehyde undergoes Cannizzaro with bases to give formate salt + methanol.

(b) Write short notes on the following:

(i) Carbylamine reaction

(ii) Hofmann–bromamide reaction

(iii) Diazotisation

Solution:

(i) Carbylamine (Isocyanide) reaction:

Primary amines (aliphatic or aromatic) on heating with chloroform and alcoholic KOH give foul-smelling isocyanides (carbylamines). Secondary and tertiary amines do not respond, so this is a *specific test for 1° amines*.

$$\mathrm{R{-}NH_2 + CHCl_3 + 3\,KOH \xrightarrow[\Delta]{\text{alc.}} R{-}NC + 3\,KCl + 3\,H_2O}$$

Example: $\mathrm{C_6H_5NH_2} \xrightarrow[\mathrm{CHCl_3}]{\text{alc. KOH, }\Delta} \mathrm{C_6H_5NC}$ (phenyl isocyanide).

(ii) Hofmann–bromamide reaction (Hofmann rearrangement):

An amide reacts with bromine in aqueous/alkaline medium to give a primary amine with **one carbon less**; proceeds via N-bromamide $\rightarrow$ rearrangement to isocyanate $\rightarrow$ hydrolysis. Stereochemistry at the migrating carbon is retained.

$$\mathrm{RCONH_2 + Br_2 + 4\,NaOH \rightarrow RNH_2 + 2\,NaBr + Na_2CO_3 + 2\,H_2O}$$

Key use: chain shortening in synthesis.

(iii) Diazotisation:

Primary *aromatic* amines react with nitrous acid (from $\mathrm{NaNO_2/HCl}$) at $0{-}5^\circ\mathrm{C}$ to form stable diazonium salts (at low temperature). These are versatile intermediates (Sandmeyer, Gattermann, Schiemann, azo-coupling).

$$\mathrm{ArNH_2 + NaNO_2 + 2\,HCl \xrightarrow{0{-}5^\circ C} ArN_2^+Cl^- + NaCl + 2\,H_2O}$$

Aliphatic diazonium salts are unstable and decompose.

> **Quick Tip**
>
> Carbylamine test $\Rightarrow$ identifies 1° amines by isocyanide odour; Hofmann rearrangement $\Rightarrow$ amide $\rightarrow$ amine with -1 carbon; Diazotisation must be done at $0{-}5^\circ\mathrm{C}$ and opens many substitution routes via diazonium salts.