

# CBSE 12th 2024 Compartment Chemistry Set-2 (56/S/2) Solutions

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## SECTION A

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each.

Q.1. The most stable complex among the following is:

- (A)  $\text{Na}_2[\text{Na}(\text{CN})_5(\text{NO})]$
- (B)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (C)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- (D)  $\text{Na}_2[\text{Ni}(\text{EDTA})]$

Q.2. If amines are arranged in decreasing order of their basic strength in gaseous phase, then the correct order will be:

- (A)  $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$
- (B)  $\text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
- (C)  $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{NH}_3$
- (D)  $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

Q.3 Considering the strength of the ligand, the highest excitation energy will be observed in:

- (A)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- (B)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (C)  $[\text{Co}(\text{CN})_6]^{3-}$
- (D)  $[\text{CoC}_6\text{H}_6]^{3-}$

**Solution.** (C)  $[\text{Co}(\text{CN})_6]^{3-}$ , To determine which complex will have the highest excitation energy, we need to consider the strength of the ligand and its effect on the splitting of the d-orbitals in the metal center. Higher

ligand field strength leads to greater splitting of the d-orbitals and thus higher excitation energy.

Here's a brief overview of the ligand strengths and their corresponding field strengths:

Water ( $\text{H}_2\text{O}$ ): A weak field ligand.

Ammonia ( $\text{NH}_3$ ): A weak to moderate field ligand.

Cyanide ( $\text{CN}^-$ ): A strong field ligand.

Chloride ( $\text{Cl}^-$ ): A weak field ligand.

In the complexes given:

1.  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ : Water is a weak field ligand, leading to a smaller crystal field splitting.

2.  $[\text{Co}(\text{NH}_3)_6]^{3+}$ : Ammonia is a weak to moderate field ligand, leading to moderate crystal field splitting.

3.  $[\text{Co}(\text{CN})_6]^{3-}$ : Cyanide is a strong field ligand, causing significant crystal field splitting.

4.  $[\text{CoCl}_6]^{3-}$ : Chloride is a weak field ligand, leading to minimal crystal field splitting.

Conclusion:

The strongest field ligand among the given options is cyanide ( $\text{CN}^-$ ), which results in the largest crystal field splitting and therefore the highest excitation energy.

So, the correct answer is: (C)  $[\text{Co}(\text{CN})_6]^{3-}$

**Q.4 The standard electrode potential for  $\text{Sn}^{4+}/\text{Sn}^{2+}$  couple is + 0.15 V and for  $\text{Cr}^{3+}/\text{Cr}$  couple is 0.73 V. These two couples are connected to make an electrochemical cell. The redox reaction is spontaneous. The cell potential will be :**

**(A) + 0.88 V**

**(B) + 0.58 V**

**(C) -0.88 V**

**(D) - 0.58 V**

## Solution. (A) + 0.88 V

### 1. Identify the Standard Electrode Potentials:

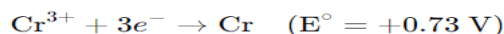
- For  $\text{Sn}^{4+}/\text{Sn}^{2+}$ :  $E^\circ = +0.15 \text{ V}$
- For  $\text{Cr}^{3+}/\text{Cr}$ :  $E^\circ = +0.73 \text{ V}$

### 2. Determine Which Reaction is Oxidation and Which is Reduction:

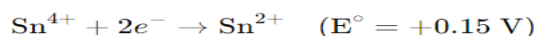
- The couple with the higher standard electrode potential ( $\text{Cr}^{3+}/\text{Cr}$ ) will be the reduction half-reaction because a higher  $E^\circ$  indicates a stronger tendency to gain electrons.
- The couple with the lower standard electrode potential ( $\text{Sn}^{4+}/\text{Sn}^{2+}$ ) will be the oxidation half-reaction because it has a weaker tendency to gain electrons.

### 3. Write the Half-Reactions:

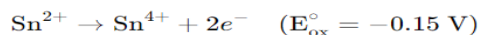
- Reduction Half-Reaction (Higher  $E^\circ$ ):



- Oxidation Half-Reaction (Lower  $E^\circ$ ):



To find the oxidation potential, reverse the reaction and change the sign of the electrode potential:



### 4. Calculate the Cell Potential:

- The cell potential is the difference between the reduction potential of the cathode (where reduction occurs) and the oxidation potential of the anode (where oxidation occurs).

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

Here:

- Cathode (Reduction):  $+0.73 \text{ V}$
- Anode (Oxidation):  $-0.15 \text{ V}$

Therefore:

$$E_{\text{cell}}^\circ = +0.73 \text{ V} - (-0.15 \text{ V}) = +0.73 \text{ V} + 0.15 \text{ V} = +0.88 \text{ V}$$

**Q.5 The chemical test which can be used to distinguish between ethylamine and aniline is:**

- (A) Haloform test
- (B) Tollens' test
- (C) Azo dye test
- (D) Hinsberg test

**Solution.(D) Hinsberg test,** To distinguish between ethylamine and aniline, we need to use a chemical test that differentiates between a

primary aliphatic amine and a primary aromatic amine. Here's a breakdown of the options:

1. Haloform Test:

This test is used to detect methyl ketones or compounds that can be oxidized to methyl ketones. It's not suitable for distinguishing between ethylamine and aniline.

2. Tollens' Test:

Tollens' test is used to detect aldehydes. It's not applicable for differentiating between amines.

3. Azo Dye Test:

The Azo dye test is used for aromatic amines, where the amine is diazotized and then coupled with a suitable coupling component. This test can differentiate between aromatic amines, like aniline, and other types of amines.

4. Hinsberg Test:

The Hinsberg test is specifically used to differentiate between primary, secondary, and tertiary amines. Ethylamine (a primary aliphatic amine) and aniline (a primary aromatic amine) react differently in this test. Ethylamine reacts with benzene sulfonyl chloride to form a sulfonamide that is soluble in alkali, while aniline does not react similarly.

Thus, the chemical test that can be used to distinguish between ethylamine and aniline is (D) Hinsberg test.

**Q.6 The geometry of diamagnetic nickel complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is:**

- (A) Tetrahedral**
- (B) Octahedral**
- (C) Square planar**
- (D) Distorted octahedral**

**Solution. (A) tetrahedral** , To determine the geometry of the paramagnetic nickel complex  $\text{[NiCl}_4\text{]}^{2-}$ , follow these steps:

1. Oxidation State and Electron Configuration:

In  $\text{[NiCl}_4\text{]}^{2-}$ , Nickel (Ni) is in the +2 oxidation state.

The electron configuration of Ni in its +2 state is  $[\text{Ar}] 3d^8$  (after losing 2 electrons from the 4s orbital).

2. Hybridization:

The  $\text{[NiCl}_4\text{]}^{2-}$  complex has four chloride ions as ligands. The geometry of the complex is determined by the hybridization of the central nickel ion.

For four ligands, the hybridization is  $sp^3$ , which typically leads to a tetrahedral geometry.

3. Geometry Determination:

Nickel(II) chloride complex  $\text{[NiCl}_4\text{]}^{2-}$  is a tetrahedral complex. The tetrahedral geometry arises from  $sp^3$  hybridization and is common for such complexes.

4. Paramagnetism:

The presence of unpaired electrons in the d-orbital of  $\text{Ni}^{2+}$  makes the complex paramagnetic. However, this paramagnetism does not affect the tetrahedral geometry resulting from  $sp^3$  hybridization.

Thus, the geometry of the paramagnetic nickel complex  $\text{[NiCl}_4\text{]}^{2-}$  is:  
(A) tetrahedral

**Q.7 Williamson's synthesis of preparing dimethyl ether is a/an:**

- (A) electrophilic substitution
- (B) SN1 reaction
- (C) electrophilic addition
- (D) SN2 reaction

**Solution.(D) SN2 reaction**, Williamson's synthesis involves the preparation of ethers by reacting an alkyl halide with an alkoxide. This reaction is typically characterized as an **\*\*SN2\*\*** (bimolecular nucleophilic substitution) reaction.

1. Reaction Mechanism: Williamson's synthesis involves a nucleophilic attack by an alkoxide ion (the nucleophile) on the carbon of the alkyl halide (the electrophile). This process happens in a single step where the nucleophile displaces the leaving group (halide) from the alkyl halide, leading to the formation of an ether.

2. Characteristics of SN2 Reaction: In SN2 reactions, the nucleophile attacks the electrophile from the opposite side of the leaving group, leading to a simultaneous bond formation and bond breaking process. This is consistent with the mechanism of Williamson's synthesis.

Thus, Williamson's synthesis of dimethyl ether (or any ether) is a classic example of an SN2 reaction.

**Q.8 Out of Fe<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, the one which shows highest magnetic moment is:**

- (A) Fe<sup>2+</sup>
- (B) Co<sup>2+</sup>
- (C) Cr<sup>3+</sup>
- (D) Ni<sup>2+</sup>

**[Atomic number: Cr=24, Fe = 26, Co=27, Ni = 28]**

**Solution. (D) Ni<sup>2+</sup>** , To determine which ion has the lowest magnetic moment, we need to analyze the electronic configurations and the number of unpaired electrons in each ion. The magnetic moment of a transition metal ion is related to the number of unpaired electrons in its d-orbital. The formula to calculate the magnetic moment is:

$$\mu = \sqrt{n(n + 2)}$$

where n is the number of unpaired electrons.

Let's go through each ion:

1. Fe<sup>2+</sup> (Iron (II)):

Atomic number of Fe = 26

Electron configuration of Fe: [Ar] 3d 4s<sup>2</sup>

Fe<sup>2+</sup> loses 2 electrons: [Ar] 3d<sup>6</sup>

In 3D, the configuration is t<sub>2g</sub><sup>4</sup> e<sub>g</sub><sup>2</sup> (octahedral complex). Number of unpaired electrons = 4

Magnetic moment:  $\mu = \sqrt{4(4 + 2)} = \sqrt{24} \approx 4.89$  BM

2. Fe<sup>3+</sup> (Iron (III)):

Fe<sup>3+</sup> loses 3 electrons: [Ar] 3d<sup>5</sup>

In 3D, the configuration is t<sub>2g</sub><sup>3</sup> e<sub>g</sub><sup>2</sup> (octahedral complex). Number of unpaired electrons = 5

Magnetic moment:  $\mu = 5(5+2) = \sqrt{35} \approx 5.92$  BM

3. Co<sup>2+</sup> (Cobalt (II)):

Atomic number of Co = 27

Electron configuration of Co: [Ar] 3d 4s<sup>2</sup>

Co<sup>2+</sup> loses 2 electrons: [Ar] 3d<sup>7</sup>

In 3d', the configuration is t<sub>2g</sub><sup>5</sup> e<sub>g</sub><sup>2</sup> (octahedral complex). Number of unpaired electrons = 3

Magnetic moment:  $\mu = 3(3+2) = \sqrt{15} \approx 3.87$  BM

4. Cr<sup>3+</sup> (Chromium (III)):

Atomic number of Cr = 24

Electron configuration of Cr: [Ar] 3d 4s<sup>1</sup>

Cr<sup>3+</sup> loses 3 electrons: [Ar] 3d<sup>3</sup>

In 3d<sup>3</sup>, the configuration is t<sub>2g</sub><sup>3</sup> (octahedral complex). Number of unpaired electrons = 3

Magnetic moment:  $\mu = 3(3+2) = \sqrt{15} \approx 3.87$  BM

5. Ni<sup>2+</sup> (Nickel (II)):

Atomic number of Ni = 28

Electron configuration of Ni: [Ar] 3d 4s<sup>2</sup>

Ni<sup>2+</sup> loses 2 electrons: [Ar] 3d<sup>8</sup>

In 3d, the configuration is t<sub>2g</sub><sup>6</sup> e<sub>g</sub><sup>2</sup> (octahedral complex). Number of unpaired electrons = 2

Magnetic moment:  $\mu = 2(2+2) = \sqrt{8} \sim 2.83$  BM

Among the given ions, Ni<sup>2+</sup> has the fewest number of unpaired electrons (2), which results in the lowest magnetic moment.

Thus, the correct answer is:

(D) Ni<sup>2+</sup>

**Q.9 The IUPAC name of the complex [Co(NH<sub>3</sub>)<sub>5</sub>(ONO)]Cl<sub>2</sub> is:**

- (A) Pentaamminenitrito-O-cobalt(III) chloride
- (B) Pentaamminenitrito-N-cobalt(III) chloride
- (C) Pentaamminenitro-cobalt(III) chloride
- (D) Pentaamminenitrito-cobalt(II) chloride

**Solution.** To determine the IUPAC name of the complex [Co(NH<sub>3</sub>)<sub>5</sub>(ONO)]Cl<sub>2</sub>, let's break it down step by step:

1. Identify the Ligands:

NH<sub>3</sub>: This is the ammine ligand.

ONO: This is the nitro ligand. It can be either nitrito-O or nitrito-N depending on how it binds to the metal.

2. Determine the Type of Nitrito Ligand:



Nitrito-O (or O-nitrito): When the oxygen atom of the nitrite group is the donor atom.

Nitrito-N (or N-nitrito): When the nitrogen atom of the nitrite group is the donor atom.

In the complex  $[\text{Co}(\text{NH}_3)_5(\text{ONO})] \text{Cl}_2$ , the nitro group is bonded through the oxygen atom, making it nitrito-O.

### 3. Determine the Oxidation State of the Metal:

The complex is neutral overall, and each chloride ion is -1.

Let's denote the oxidation state of cobalt as  $x$ . Since the ammonia ( $\text{NH}_3$ ) and nitrito-O ( $\text{ONO}$ ) ligands are neutral, the overall charge of the complex must be zero to balance the two chloride ions.

The oxidation state of cobalt is therefore +3 (since the overall charge of the complex must counterbalance the two negative charges from the chloride ions).

### 4. Name the Complex:

The name is constructed in the following order: Ligands (alphabetically), metal with its oxidation state, and counterions.

The ligands are "pentaammine" (since there are five  $\text{NH}_3$  groups) and "nitrito-O" (since the nitrito ligand binds through oxygen).

The metal is cobalt with an oxidation state of +3.

Combining all these parts, the IUPAC name of the complex  $[\text{Co}(\text{NH}_3)_5(\text{ONO})] \text{Cl}_2$  is:

(A) Pentaammine Nitrito-O-cobalt(III) chloride

### Q. 6. Which of the following does not undergo Aldol condensation ?

(A)  $\text{CH}_3\text{CHO}$

(B)  $\text{CH}_3\text{COCH}_3$

(C)  $\text{CH}_3\text{CH}_2\text{CHO}$

(D)  $\text{C}_6\text{H}_5\text{CHO}$

**Solution.**(A)  $\text{HCHO}$ , To determine which compound does not undergo Aldol condensation, let's understand the criteria for Aldol condensation:

### Aldol Condensation Overview:

Aldol condensation is a reaction between two aldehydes or ketones, or one of each, in the presence of a base (or acid), resulting in the formation of  $\beta$ -hydroxyaldehydes or  $\beta$ -hydroxyketones, which can further dehydrate to form  $\alpha,\beta$ -unsaturated carbonyl compounds.

The key requirement is that the molecule must have at least one  $\alpha$ -hydrogen (hydrogen atom on the carbon adjacent to the carbonyl group) for the reaction to occur.

### Analysis of Each Compound:

#### 1. Formaldehyde (HCHO):

Formaldehyde does not have an  $\alpha$ -hydrogen because its carbonyl group is attached directly to two hydrogens (making it a  $\text{CH}_2\text{O}$ ). Therefore, it cannot undergo Aldol condensation.

#### 2. Ethanal ( $\text{CH}_3\text{CHO}$ ):

- Ethanal has one  $\alpha$ -hydrogen (the hydrogen on the carbon adjacent to the carbonyl group). It can undergo Aldol condensation.

#### 3. Acetone ( $\text{CH}_3\text{COCH}_3$ ):

Acetone has two  $\alpha$ -hydrogens (the hydrogens on the two carbons adjacent to the carbonyl group). It can undergo Aldol condensation.

#### 4. Propionaldehyde ( $\text{CH}_3\text{CH}_2\text{CHO}$ ):

Propionaldehyde has two  $\alpha$ -hydrogens (the hydrogens on the carbon adjacent to the carbonyl group). It can undergo Aldol condensation.

### Conclusion:

Based on the requirement of having  $\alpha$ -hydrogens for Aldol condensation, the compound that does not undergo Aldol condensation is:

(A) HCHO (Formaldehyde)

**Q.11** For a chemical reaction,  $A \rightarrow B$ , it was observed that the rate of reaction doubles when the concentration of A is increased four times. The order of the reaction is:

- (A) 2
- (B) 1
- (C)  $1/2$
- (D) Zero

**Solution.** (C)  $1/2$ , To determine the order of the reaction, we can use the relationship between the rate of reaction and the concentration of reactant.

For a reaction where the rate  $r$  depends on the concentration of a single reactant A, the rate law can be written as:  $r = k[A]^n$

where  $k$  is the rate constant and  $n$  is the order of the reaction.

Given the information:

When the concentration of A is increased by a factor of 4, the rate of reaction doubles.

We can set up the equation based on the rate law:

1. Initial rate:  $r_1 = k[A]^n$

2. New concentration:  $[A]_{\text{new}} = 4[A]$  New rate:  $r_2 = k(4[A])^n = 4^n k[A]^n$

According to the problem, the new rate  $r_2$  is twice the initial rate  $r_1$ :

$$r_2 = 2r_1$$

$$4^n k[A]^n = 2k[A]^n$$

Divide both sides by  $k[A]^n$ :

$$4^n = 2$$

To solve for  $n$ , take the logarithm base 2:

$$4 = 2^2$$

$$(2^2)^n = 2^1$$

$$2^{2n} = 2^1$$

$$2n = 1$$

$$n = 1/2$$

Therefore, the order of the reaction is (C)  $1/2$

**Q.12. The correct IUPAC name of  $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$  is:**

- (A) 2,2-Methyl-2-bromopropane**
- (B) 1-Bromo-2,2,2-trimethylethane**
- (C) 2-Bromo-1,1,1-trimethylethane**
- (D) 1-Bromo-2,2-dimethylpropane**

**Solution. (D) 1-Bromo-2,2-dimethylpropane,** To determine the correct IUPAC name for the compound  $((\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br})$ , let's break it down:

1. Identify the Longest Carbon Chain:

The longest carbon chain here has 2 carbon atoms, making it part of the propane group. The main chain is a propane chain.

2. Identify the Substituents and Their Positions:

The substituent is a bromine atom attached to a carbon that is connected to a tert-butyl group  $((\text{CH}_3)_3\text{C}-)$ , which is attached to the second carbon of the propane chain.

3. Determine the Correct Naming:

The compound is a 1-bromo derivative of 2,2,2-trimethylpropane. However, the correct structure must be evaluated based on its longest carbon chain and substituent positions.

Putting this together:

The main chain is a propane chain with a bromine attached to the first carbon of this propane chain.

The tert-butyl group is attached to the second carbon of the propane chain.

Thus, the correct IUPAC name is (D) 1-Bromo-2,2-dimethylpropane

**For Questions number 13 to 16, two statements are given one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below.**

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).  
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).  
(C) Assertion (A) is true, but Reason (R) is false.  
(D) Assertion (A) is false, but Reason (R) is true.

**Q.13. Assertion (A):** Rate constant increases with increase in temperature.

**Reason (R):** Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than activation energy.

**Solution.** Assertion (A): Rate constant increases with increase in temperature.

Reason (R): Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than activation energy.

Explanation:

Assertion (A) is true because, according to the Arrhenius equation, the rate constant  $(k)$  of a reaction increases with an increase in temperature.

Reason (R) is also true because raising the temperature increases the number of molecules with energy equal to or greater than the activation energy, which in turn increases the rate constant.

Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

**Q.14 Assertion (A):**  $\text{Cu}^{2+}$  iodide is known.

**Reason (R):**  $\text{Cu}^{2+}$  has a strong tendency to oxidise I to Iodine.

**Solution.** Assertion (A):  $\text{Cu}^{2+}$  iodide is known.

Reason (R):  $\text{Cu}^{2+}$  has a strong tendency to oxidise I to Iodine.

Explanation:

Assertion (A) is false because  $\text{Cu}^{2+}$  iodide ( $\text{CuI}_2$ ) is not a stable or known compound. Copper typically forms  $\text{CuI}$  (copper(I) iodide) rather than  $\text{CuI}_2$ . Reason (R) is true in the context of chemistry;  $\text{Cu}^{2+}$  can indeed oxidise iodide ions to iodine, but this does not validate the existence of  $\text{Cu}^{2+}$  iodide. Answer:(D) Assertion (A) is false, but Reason (R) is true.

**Q.15 Assertion (A): Maltose is a non-reducing sugar.**

**Reason (R): Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit.**

**NHCOCH<sub>3</sub>**

**Solution.** Assertion (A): Maltose is a non-reducing sugar.

Reason (R): Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit.

Explanation:

Assertion (A) is false because maltose is a reducing sugar. It has a free aldehyde group available in the open-chain form, which makes it a reducing sugar.

Reason (R) is true as it accurately describes the linkage in maltose ( $\alpha$ -1,4-glycosidic bond).

Answer:(D) Assertion (A) is false, but Reason (R) is true.

**Q.16. Assertion (A): Acetanilide is more basic than aniline.**

**Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen.**

**Solution.** Assertion (A): Acetanilide is more basic than aniline.

Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen.

Explanation:

Assertion (A) is false. Acetanilide is actually less basic than aniline. The acetylation of aniline decreases the electron density on the nitrogen atom due to the electron-withdrawing effect of the acetyl group.

Reason (R) is true because acetylation does decrease the electron density on the nitrogen atom.

Answer:(D) Assertion (A) is false, but Reason (R) is true.

## SECTION B

**Q.17. Write the reactions of glucose with**

**(a) HCN**

**(b) Conc. HNO<sub>3</sub>**

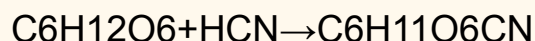
**Solution.**(a) Reaction of Glucose with HCN

Reagent: Hydrocyanic Acid (HCN)

Reaction:

When glucose reacts with HCN, it undergoes a cyanohydrin formation. In this reaction, the carbonyl group (aldehyde group) of glucose reacts with HCN to form a cyanohydrin.

Balanced Chemical Equation:



Explanation:

Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) reacts with HCN to form glucose cyanohydrin.

The reaction involves the addition of the cyanide group (-CN) to the aldehyde group of glucose, resulting in the formation of a cyanohydrin (a molecule with a hydroxyl group and a cyanide group attached to the same carbon atom).

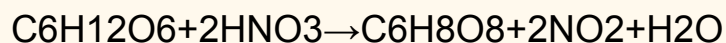
(b) Reaction of Glucose with Concentrated HNO<sub>3</sub>

Reagent: Concentrated Nitric Acid (HNO<sub>3</sub>)

Reaction:

When glucose reacts with concentrated nitric acid, it undergoes oxidation to form a mixture of gluconic acid and gluconic acid. The reaction can also lead to the formation of saccharic acid (or glucaric acid) if the oxidation is more complete.

Balanced Chemical Equations:



Explanation:

Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is oxidised by concentrated nitric acid to form saccharic acid ( $\text{C}_6\text{H}_8\text{O}_8$ ).

Saccharic acid is a dicarboxylic acid where both the aldehyde and alcohol groups are oxidized to carboxyl groups.

The reaction also produces nitrogen dioxide ( $\text{NO}_2$ ) and water as by-products.

**Q.18. (a) Account for the following:**

**(1)  $\text{CH}_3\text{CHO}$  is more reactive than  $\text{CH}_3\text{COCH}_3$  towards reaction with  $\text{HCN}$ .**

**(ii) Carboxylic acids are higher boiling liquids than aldehydes and ketones.**

**Solution.** (i)  $\text{CH}_3\text{CHO}$  is more reactive than  $\text{CH}_3\text{COCH}_3$  towards reaction with  $\text{HCN}$ .

Explanation:

$\text{CH}_3\text{CHO}$  (acetaldehyde) is more reactive than  $\text{CH}_3\text{COCH}_3$  (acetone) towards nucleophilic addition reactions like those with hydrogen cyanide ( $\text{HCN}$ ).

The reason lies in the electronic nature of the carbonyl group. In  $\text{CH}_3\text{CHO}$ , the carbonyl carbon is more electrophilic compared to  $\text{CH}_3\text{COCH}_3$ . This increased electrophilicity is due to the greater electron-donating effect of the two alkyl groups in acetone compared to the one alkyl group in acetaldehyde.

Specifically, acetaldehyde has only one alkyl group (methyl), which provides less electron donation to the carbonyl carbon. In contrast, acetone has two alkyl groups (both methyl groups) that donate electron density through inductive effects. This donation decreases the positive charge on the carbonyl carbon in acetone, making it less electrophilic and less reactive towards nucleophiles like  $\text{HCN}$ .

(ii) Carboxylic acids are higher boiling liquids than aldehydes and ketones.



Explanation:

Carboxylic acids have significantly higher boiling points compared to aldehydes and ketones. This is due to the presence of strong hydrogen bonding in carboxylic acids.

Carboxylic acids can form dimers through hydrogen bonding, which means two molecules of the acid interact with each other through two hydrogen bonds. This dimerization leads to a significant increase in boiling point due to the stronger intermolecular forces.

Aldehydes and ketones, on the other hand, do not have the ability to form such extensive hydrogen bonds. They primarily have dipole-dipole interactions, which are weaker than the hydrogen bonding in carboxylic acids. As a result, carboxylic acids have higher boiling points compared to aldehydes and ketones.

**OR**

**(b) Give chemical tests to distinguish between the following pair of compounds:**

**(i) Propanal and Propanone**

**(ii) Benzaldehyde and Benzoic acid**

**Solution.** To distinguish between the given pairs of compounds, you can use specific chemical tests. Here's how you can differentiate between each pair:

(i) Propanal and Propanone

1. Tollens' Test:

Propanal: It will give a positive result with Tollens' reagent. This is because propanal is an aldehyde, and aldehydes generally reduce Tollens' reagent (a solution of silver nitrate in ammonia) to metallic silver, resulting in a silver mirror on the inner surface of the test tube.

Propanone: It will not react with Tollens' reagent. Propanone is a ketone, and ketones generally do not reduce Tollens' reagent.

2. 2,4-Dinitrophenylhydrazine (2,4-DNPH) Test:

Propanal: When treated with 2,4-DNPH, propanal will form a yellow or orange precipitate of 2,4-dinitrophenylhydrazone. This is because propanal reacts with 2,4-DNPH to form a hydrazone derivative.

Propanone: Similarly, propanone will also form a yellow or orange precipitate with 2,4-DNPH. However, this test is not specific to differentiating aldehydes from ketones but confirms the presence of carbonyl groups.

### 3. Iodoform Test:

Propanal: It does not give a positive iodoform test.

Propanone: It will give a positive iodoform test, which is a characteristic test for ketones with a methyl group adjacent to the carbonyl group. A yellow precipitate of iodoform ( $\text{CHI}_3$ ) will be observed.

## (ii) Benzaldehyde and Benzoic Acid

### 1. Tollens' Test:

Benzaldehyde: It will give a positive Tollens' test. Benzaldehyde, being an aldehyde, reduces Tollens' reagent, producing a silver mirror.

Benzoic Acid: It will not react with Tollens' reagent. Benzoic acid is a carboxylic acid and does not reduce Tollens' reagent.

### 2. Sodium Bicarbonate Test:

Benzaldehyde: It does not react with sodium bicarbonate solution.

Benzoic Acid: It will react with sodium bicarbonate to produce carbon dioxide gas. This reaction occurs because benzoic acid is a carboxylic acid and reacts with the bicarbonate to release  $\text{CO}_2$ .

### 3. 2,4-Dinitrophenylhydrazine (2,4-DNPH) Test:

Benzaldehyde: It will give a positive 2,4-DNPH test, forming a yellow or orange precipitate, similar to propanal.

Benzoic Acid: It will not give a positive result with 2,4-DNPH, as carboxylic acids do not react with this reagent to form a hydrazone.

These tests help to specifically identify and differentiate between the compounds in each pair based on their chemical reactivity.

**Q.19. Write the reaction involved in the following:**

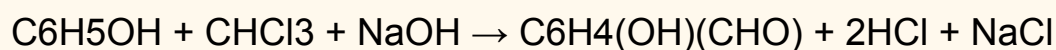
**(a) Reimer-Tiemann reaction**

**(b) Kolbe's reaction**

**Solution.**(a) Reimer-Tiemann Reaction

The Reimer-Tiemann reaction is used to introduce a formyl group (-CHO) into the ortho position of phenols, typically resulting in the formation of ortho-hydroxybenzaldehyde (salicylaldehyde).

Reaction:



In this reaction:

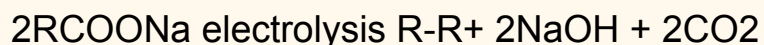
Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) reacts with chloroform ( $\text{CHCl}_3$ ) in the presence of a strong base (sodium hydroxide,  $\text{NaOH}$ ).

The result is ortho-hydroxybenzaldehyde (salicylaldehyde).

**(b) Kolbe's Reaction**

Kolbe's reaction is an electrochemical reaction used to produce alkanes from the corresponding carboxylate salts by decarboxylation.

Reaction:



In this reaction:

Sodium carboxylate salts ( $\text{RCOONa}$ ) are electrolyzed.

The result is the formation of the corresponding alkane ( $\text{R-R}$ ), along with sodium hydroxide ( $\text{NaOH}$ ) and carbon dioxide ( $\text{CO}_2$ ).

In summary:

Reimer-Tiemann Reaction: Phenol + Chloroform +  $\text{NaOH}$  products

Ortho-Hydroxybenzaldehyde + By-

Kolbe's Reaction: Sodium Carboxylate Salts  $\rightarrow$  Alkane +  $\text{NaOH}$  +  $\text{CO}_2$

**Q.20. The thermal decomposition of an acid is a first order reaction with a rate constant of  $2.3 \times 10^{-3} \text{ s}^{-1}$  at a certain temperature. Calculate**

how long it will take for three-fourths of the initial quantity of acid to decompose. (log 40.6021, log 2 = 0.301)

### Solution.

To calculate the time it takes for three-fourths of the initial quantity of an acid to decompose in a first-order reaction, you can use the first-order reaction kinetics formula:

$$t = \frac{\ln\left(\frac{[A_0]}{[A]}\right)}{k}$$

where:

- $t$  is the time required.
- $[A_0]$  is the initial concentration of the reactant.
- $[A]$  is the concentration of the reactant after time  $t$ .
- $k$  is the rate constant.

For a first-order reaction, the formula simplifies to:

$$t = \frac{\ln\left(\frac{[A_0]}{[A]}\right)}{k}$$

We need to find the time when three-fourths of the initial quantity of the acid has decomposed. This means that only one-fourth of the initial quantity remains. So,  $[A]/[A_0] = \frac{1}{4}$ .

Substituting this into the formula:

$$t = \frac{\ln\left(\frac{[A_0]}{\frac{1}{4}[A_0]}\right)}{k}$$

$$t = \frac{\ln(4)}{k}$$

We know that  $\ln(4)$  can be calculated as:

$$\ln(4) = \ln(2^2) = 2 \ln(2)$$

Given that  $\log 2 = 0.301$ , we can use:

$$\ln(2) = 0.301$$

$$\ln(4) = 2 \times 0.301 = 0.602$$

The rate constant  $k$  is given as  $2.3 \times 10^{-3} \text{ s}^{-1}$ .

So, we can calculate the time as:

$$t = \frac{\ln(4)}{k}$$

$$t = \frac{0.602}{2.3 \times 10^{-3}}$$

$$t = 261.74 \text{ s}$$

Therefore, it will take approximately **261.74 seconds** for three-fourths of the initial quantity of the acid to decompose.

## SECTION C

**Q.22. What happens when: (any three)**

**(a) CH<sub>3</sub>MgBr is treated with cyclohexanone followed by hydrolysis**

**(b) Phenol is treated with Br<sub>2</sub> in the presence of CS<sub>2</sub>**

**(c) Benzene diazonium chloride is treated with H<sub>2</sub>O**

**(d) Anisole is treated with HI**

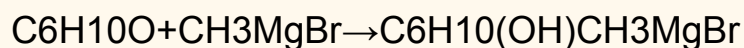
**Solution.** Here's what happens in each of the reactions:

(a) CH<sub>3</sub>MgBr with Cyclohexanone, Followed by Hydrolysis

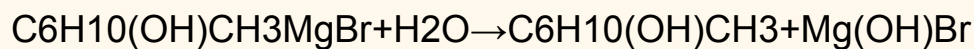
Reagents: Methylmagnesium bromide (CH<sub>3</sub>MgBr), Cyclohexanone, Hydrolysis (water)

Reaction:

First Step (Grignard Reaction): Methylmagnesium bromide (a Grignard reagent) reacts with cyclohexanone. The Grignard reagent adds a methyl group to the carbonyl carbon of cyclohexanone.



Second Step (Hydrolysis): Upon hydrolysis (adding water), the intermediate magnesium alkoxide is converted into a tertiary alcohol.



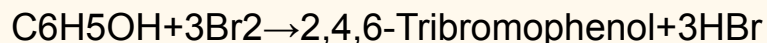
Product: The final product is 1-methyl-1-cyclohexanol.

(b) Phenol with Br<sub>2</sub> in the Presence of CS<sub>2</sub>

Reagents: Bromine (Br<sub>2</sub>), Carbon disulfide (CS<sub>2</sub>)

Reaction:

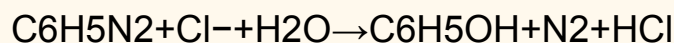
Phenol reacts with bromine in the presence of carbon disulfide to undergo bromination. The phenol's hydroxyl group activates the aromatic ring, leading to multiple bromination.



Product: The main product is 2,4,6-tribromophenol, where bromine atoms are added to the ortho and para positions relative to the hydroxyl group.

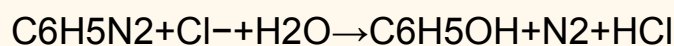
(c) Benzene Diazonium Chloride with H<sub>2</sub>O

Reagents: Benzene diazonium chloride



Reaction:

When benzene diazonium chloride is treated with water, it undergoes hydrolysis to form phenol.



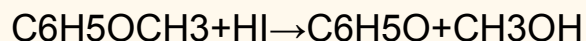
Product: The main product is phenol (C<sub>6</sub>H<sub>5</sub>OH). Nitrogen gas is released, and hydrochloric acid (HCl) is formed.

(d) Anisole with HI

Reagents: Anisole, Hydroiodic Acid (HI)

Reaction:

When anisole is treated with hydroiodic acid, the methoxy group (-OCH<sub>3</sub>) in anisole is replaced by iodine. This is due to the cleavage of the ether bond.



Product: The products are iodobenzene (C<sub>6</sub>H<sub>5</sub>I) and methanol (CH<sub>3</sub>OH).

**Q.23. Hydrolysis of sucrose takes place by the chemical reaction: H<sup>+</sup> C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> + H<sub>2</sub>O (excess) Based on the above reaction, write :  
C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> + C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>**

**(a) Rate law equation**

**(b) Molecularity and order of reaction**

**(c) What do you call such reactions?**

**Q.23. Hydrolysis of ethyl ethanoate takes place by the chemical reaction :  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$  (excess)  $\text{H}^+$  Based on the above reaction, write :  $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$**

**(a) What do you call such reactions?**

**(b) Rate law equation**

**(c) What do you call such reactions?**

**Solution.** The hydrolysis of ethyl ethanoate (ethyl acetate) in the presence of an acid catalyst is known as acid-catalysed hydrolysis or more specifically, ester hydrolysis. This type of reaction is also referred to as saponification when it is done under basic conditions, but in the given scenario with an acid catalyst, it's simply ester hydrolysis.

**(b) Rate Law Equation**

The rate law for the acid-catalysed hydrolysis of ethyl ethanoate can be expressed as follows:

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

In this reaction:

$k$  is the rate constant.

$[\text{CH}_3\text{COOC}_2\text{H}_5]$  is the concentration of ethyl ethanoate (ester).

$[\text{H}_2\text{O}]$  is the concentration of water.

For ester hydrolysis in an acid-catalysed reaction, the rate typically depends on the concentration of the ester and the acid catalyst. However, since water is in excess, its concentration is essentially constant and does not affect the rate of reaction significantly, thus making the rate law primarily depend on the concentrations of the ester and the acid.

**Q.24. Account for the following:**

**(a) n-butyl bromide has a higher boiling point than t-butyl bromide.**

**(b) Alkyl halides are insoluble in water.**

**(c) Cyclohexyl chloride possesses a higher dipole moment than chlorobenzene.**

**Solution.** (a) n-Butyl Bromide Has a Higher Boiling Point Than t-Butyl Bromide

Explanation:

n-Butyl Bromide: This is a straight-chain alkyl bromide.

t-Butyl Bromide: This is a branched alkyl bromide with a tert-butyl group.

Reason for Higher Boiling Point:

n-Butyl Bromide has a higher boiling point than t-Butyl Bromide because it has a longer, straight-chain structure that allows for more surface contact between molecules. This results in stronger van der Waals forces (London dispersion forces) between the molecules.

t-Butyl Bromide is more branched, which reduces the surface area for intermolecular interactions, leading to weaker van der Waals forces and thus a lower boiling point.

(b) Alkyl Halides Are Insoluble in Water

Explanation:

Alkyl Halides are compounds with a carbon-hydrogen chain attached to a halogen (like Cl, Br, I).

Reason for Insolubility:

Water Solubility depends on the ability of a substance to form hydrogen bonds or interact favourably with water molecules.

Alkyl Halides are generally non-polar or only slightly polar. They do not form strong hydrogen bonds with water molecules.

Water is a highly polar solvent and favours interactions with other polar substances or those capable of hydrogen bonding. Since alkyl halides cannot form hydrogen bonds with water, they are generally insoluble in water.

(c) Cyclohexyl Chloride Has a Higher Dipole Moment Than Chlorobenzene

Explanation:

Cyclohexyl Chloride is a cyclohexane ring with a chlorine atom attached.

Chlorobenzene is a benzene ring with a chlorine atom attached.

Reason for Higher Dipole Moment:

Cyclohexyl Chloride has a higher dipole moment because the chlorine atom is attached to a cyclohexane ring which has a more flexible, non-planar structure compared to the benzene ring. This non-planarity allows for better alignment of the dipole moment of the C-Cl bond in the direction of the molecule's overall dipole. Chlorobenzene, on the other



hand, is planar, and the resonance in the benzene ring distributes the electron density, which partially offsets the dipole moment of the C-Cl bond. As a result, the overall dipole moment is less compared to cyclohexyl chloride.

Summary:

(a)n-Butyl Bromide has a higher boiling point than t-Butyl Bromide due to stronger intermolecular forces in the straight-chain structure.

(b)Alkyl Halides are insoluble in water because they cannot form hydrogen bonds with water and are generally non-polar.

(c)Cyclohexyl Chloride has a higher dipole moment than Chlorobenzene due to the non-planar nature of the cyclohexane ring enhancing the dipole alignment.

**Q.25. Give plausible explanation for the following:**

**(a) Diazonium salts of aromatic amines are stable.**

**(b) Aniline does not undergo Friedel-Crafts reaction.**

**(c) Aniline on nitration gives a substantial amount of meta product.**

**Solution.** (a) Diazonium Salts of Aromatic Amines Are Stable

Explanation:

Diazonium Salts: These are compounds with the general formula  $\text{Ar-N}_2^+\text{Cl}^-$ , where Ar is an aromatic ring.

Stability Factors:

Aromatic System: The diazonium group ( $-\text{N}_2^+$ ) is stabilised by the aromatic ring through resonance. The positive charge on the nitrogen can delocalize into the aromatic system, which provides stability.

Resonance Effect: The aromatic ring helps to delocalize the positive charge on the diazonium group, making it less reactive and more stable.

Temperature and Conditions: Diazonium salts are usually stable at low temperatures and under specific conditions. They decompose easily at higher temperatures or when exposed to moisture.

(b) Aniline Does Not Undergo Friedel-Crafts Reaction

Explanation:

Friedel-Crafts Reaction: This is a type of electrophilic aromatic substitution reaction that involves the alkylation or acylation of an aromatic ring.

Reason for Non-Reactivity:

Electron-Donating Effect of Amino Group: Aniline ( $C_6H_5NH_2$ ) has an amino group ( $-NH_2$ ) that is a strong electron-donating group through its lone pair of electrons. This increases the electron density of the aromatic ring.

Reaction Conditions: The Friedel-Crafts reaction typically requires a strong electrophile and a Lewis acid catalyst (like  $AlCl_3$ ). The amino group in aniline is very basic and can form a complex with the Lewis acid catalyst, which prevents the formation of the necessary electrophile for the reaction.

(c) Aniline on Nitration Gives a Substantial Amount of Meta Product

Explanation:

Nitration Reaction: Nitration of aniline typically involves the introduction of nitro groups ( $-NO_2$ ) onto the benzene ring.

Directing Effects:

Amino Group: The amino group ( $-NH_2$ ) is an electron-donating group and generally directs electrophilic substitution to the ortho and para positions on the ring.

Reaction Conditions: Under strong nitrating conditions (concentrated nitric acid and sulfuric acid), the amino group of aniline can be protonated, which reduces its electron-donating effect and makes the ring less reactive towards electrophiles. This can lead to the formation of a significant amount of meta-nitroaniline as well.

Formation of Nitro Compounds: In strong acidic conditions, the aniline can form nitrosyl cations that may lead to the meta position being favoured due to the deactivation of ortho and para positions.

© Aniline on Nitration gives substantial meta product due to the protonation of the amino group under strong acidic conditions, which affects the directing influence of the group.

**Q.26. Calculate elevation of the boiling point of solution when 2 g of MgSO<sub>4</sub> (molar mass 120 g/mol) was dissolved in 100 g of water, assuming MgSO<sub>4</sub> undergoes complete dissociation. [K for water = 0.52 K kg mol<sup>-1</sup>]**

**Solution.**

**1. Calculate the number of moles of MgSO<sub>4</sub>**

- Molar Mass of MgSO<sub>4</sub>: 120 g/mol
- Mass of MgSO<sub>4</sub>: 2 g

The number of moles  $n$  is given by:

$$n = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{2 \text{ g}}{120 \text{ g/mol}} = 0.0167 \text{ mol}$$

**2. Determine the van't Hoff factor (i)**

Magnesium sulfate (MgSO<sub>4</sub>) dissociates completely into ions in water:



This dissociation yields 2 ions (Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>) per formula unit of MgSO<sub>4</sub>. Thus, the van't Hoff factor  $i$  is:

$$i = 2$$

**3. Calculate the molality of the solution**

Molality  $m$  is given by:

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (kg)}}$$

- Mass of water (solvent): 100 g = 0.1 kg

So:

$$m = \frac{0.0167 \text{ mol}}{0.1 \text{ kg}} = 0.167 \text{ mol/kg}$$

#### 4. Calculate the elevation in boiling point

The elevation in boiling point  $\Delta T_b$  is given by:

$$\Delta T_b = i \times K_b \times m$$

where:

- $i = 2$  (van't Hoff factor)
- $K_b = 0.52 \text{ K kg/mol}$  (boiling point elevation constant for water)
- $m = 0.167 \text{ mol/kg}$  (molality)

Plugging in the values:

$$\Delta T_b = 2 \times 0.52 \text{ K kg/mol} \times 0.167 \text{ mol/kg}$$

$$\Delta T_b = 0.173 \text{ K}$$

**Q.27. The electrical resistance of a column of 0.05 M KOH solution of cell constant 60 cm<sup>-1</sup> is 5.4 x 10<sup>3</sup> ohm. Calculate its resistivity, conductivity and molar conductivity.**

**Solution.**

##### 1. Calculate the Conductivity ( $\kappa$ )

Conductivity is the reciprocal of resistance multiplied by the cell constant.

$$\kappa = \frac{1}{R} \times \text{Cell Constant}$$

Plugging in the values:

$$\kappa = \frac{1}{5.4 \times 10^3} \times 60$$

$$\kappa = \frac{60}{5.4 \times 10^3}$$

$$\kappa \approx 0.0111 \text{ S/cm}$$

##### 2. Calculate the Resistivity ( $\rho$ )

Resistivity is the reciprocal of conductivity.

$$\rho = \frac{1}{\kappa}$$

Plugging in the conductivity:

$$\rho = \frac{1}{0.0111}$$

$$\rho \approx 90.1 \Omega \cdot \text{cm}$$

### 3. Calculate the Molar Conductivity ( $\Lambda_m$ )

Molar conductivity is given by:

$$\Lambda_m = \kappa \times \text{Molarity}$$

Plugging in the values:

$$\Lambda_m = 0.01111 \text{ S/cm} \times 0.05 \text{ mol/L}$$

$$\Lambda_m = 0.0005555 \text{ S} \cdot \text{cm}^2/\text{mol}$$

#### Summary

- Conductivity ( $\kappa$ ): 0.01111 S/cm
- Resistivity ( $\rho$ ): 90.1  $\Omega \cdot \text{cm}$
- Molar Conductivity ( $\Lambda_m$ ): 0.0005555 S  $\cdot \text{cm}^2/\text{mol}$

**Q.28. (a) Draw the geometrical isomers of the complex  $[\text{Mn}(\text{Br})_2(\text{Cl})_2]^{2-}$ .**

**(b) Give the electronic configuration of d4 ion when A < P.**

**(c) Solution of  $[\text{CoF}_6]^{3-}$  is coloured whereas  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless. Explain. [Atomic number: Co = 27, Ni = 28]**

**Solution.** (a) Geometrical Isomers of  $[\text{Mn}(\text{Br})_2(\text{Cl})_2]^{2-}$

The complex ion  $[\text{Mn}(\text{Br})_2(\text{Cl})_2]^{2-}$  is an octahedral complex with manganese (Mn) at the center, surrounded by two bromide ( $\text{Br}^-$ ) and two chloride ( $\text{Cl}^-$ ) ligands.

Geometrical Isomers:

1. Cis-Isomer: In this isomer, the two bromide ligands are adjacent to each other, and similarly, the two chloride ligands are adjacent to each other.

Trans-Isomer: In this isomer, the two bromide ligands are opposite each other, and similarly, the two chloride ligands are opposite each other.

(b) Electronic Configuration of d<sup>4</sup> Ion When A < P

Here, we need to determine the electronic configuration of a d4 ion for a metal with atomic number less than phosphorus (P, atomic number 15). Let's consider an example of a metal ion with d4 configuration, such as a d4 ion in the 3d series.

For a d4 ion, such as  $\text{Cr}^{2+}$  (Chromium in its +2 oxidation state):

- Chromium (Cr) Atomic Number: 24
- Ground-State Configuration of Cr:  $[\text{Ar}] 4s^2 3d^4$

In the +2 oxidation state, 2 electrons are removed from the 4s orbital first:

- Configuration of  $\text{Cr}^{2+}$ :  $[\text{Ar}] 3d^4$

So the electronic configuration for a d4 ion in a metal with atomic number less than 15 is similar. For simplicity:

- d<sup>4</sup> Ion:  $[\text{Ar}] 3d^4$

(c) Color Differences in  $[\text{CoF}_6]^{3-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$

Explanation:

- $[\text{CoF}_6]^{3-}$ : This complex contains cobalt in the +3 oxidation state, which has a  $d^6$  configuration. In an octahedral field, the d-orbitals split into two sets (e.g.,  $e_g$  and  $t_{2g}$ ). The fluorides are weak field ligands, and the complex shows some splitting of the d-orbitals, which allows for electron transitions within the d-orbitals. This absorption of light results in the appearance of colour. The complex is coloured due to these electronic transitions.
- $[\text{Ni}(\text{CN})_4]^{2-}$ : This complex has nickel in the +2 oxidation state, with a  $d^8$  configuration. The cyanide ions are strong field ligands and cause a large splitting of the d-orbitals in the octahedral field. For such strong field ligands, the splitting energy can be large enough to result in the pairing of electrons, which means there are no available d-d transitions in the visible range. Thus, the complex appears colorless because it does not absorb visible light.

Summary:

- (a) Geometrical isomers of  $[\text{Mn}(\text{Br})_2(\text{Cl})_2]^{2-}$  are the cis and trans forms.
- (b) The electronic configuration of a  $d^4d^4d^4$  ion (like  $\text{Cr}^{2+}$ ) is  $[\text{Ar}] 3d^4$ .
- (c)  $[\text{CoF}_6]^{3-}$  is colored due to electronic transitions in weak field ligand complexes, while  $[\text{Ni}(\text{CN})_4]^{2-}$  is colorless due to strong field ligand-induced electron pairing and lack of d-d transitions.

## SECTION D

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

**Q.29.** The cause for deviation from Raoult's law in the colligative properties of non-ideal solutions lie in the nature of interactions at the molecular level. These properties show deviations from Raoult's law due to differences in interactions between solute solvent, solute solute and solvent solvent. Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope.

Based on the above passage, answer the following questions :

(a) Pure ethanol cannot be prepared by fractional distillation of ethanol - water mixture. Comment.

(b) Why does a mixture of chloroform and acetone show deviation from ideal behaviour?

(c) (i) The vapour pressure of pure benzene at a certain temperature is 1.25 atm. When 1.2 g of non-volatile, non-electrolyte solute is added to 60 g of benzene ( $M = 78 \text{ g mol}^{-1}$ ), the vapour pressure of the

**solution becomes 1.237 atm. Calculate the molar mass of the non-volatile solute.**

**OR**

**© (ii) The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute is dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute.  $K_b$  for benzene is 2.53 K kg mol<sup>-1</sup>.**

**Solution.** (a) Pure Ethanol and Fractional Distillation

Pure ethanol cannot be prepared by fractional distillation of an ethanol-water mixture because ethanol and water form an azeotrope. An azeotrope is a mixture that has a constant boiling point and composition in both the liquid and vapour phases. For ethanol-water, this azeotrope boils at a lower temperature than the boiling points of pure ethanol or pure water. Therefore, fractional distillation will not completely separate ethanol from water, as the azeotrope limits the purity of the separated ethanol.

(b) A mixture of chloroform and acetone shows deviation from ideal behaviour due to strong specific interactions between the molecules of the two substances. These interactions are different from the interactions in pure chloroform or pure acetone. In this case, chloroform and acetone form hydrogen bonds or have other interactions that can alter the vapour pressure of the mixture compared to what Raoult's law would predict. These deviations result in non-ideal behaviour, either as positive or negative deviations depending on the nature of these interactions.



### (c) Molar Mass Calculations

#### (i) Molar Mass of the Non-Volatile Solute:

Given:

- Vapour pressure of pure benzene  $P_{\text{benzene}}^0 = 1.25$  atm
- Vapour pressure of the solution  $P_{\text{solution}} = 1.237$  atm
- Mass of solute = 1.2 g
- Mass of benzene = 60 g
- Molar mass of benzene = 78 g/mol

1. Calculate the change in vapor pressure ( $\Delta P$ ):

$$\Delta P = P_{\text{benzene}}^0 - P_{\text{solution}} = 1.25 - 1.237 = 0.013 \text{ atm}$$

2. Calculate the mole fraction of the solute ( $X_{\text{solute}}$ ):

$$\frac{\Delta P}{P_{\text{benzene}}^0} = X_{\text{solute}}$$

$$X_{\text{solute}} = \frac{0.013}{1.25} = 0.0104$$

3. Calculate the moles of benzene:

$$\text{Moles of benzene} = \frac{60 \text{ g}}{78 \text{ g/mol}} = 0.769 \text{ mol}$$

4. Calculate the moles of solute using mole fraction:

$$X_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of benzene}}$$

$$0.0104 = \frac{\text{Moles of solute}}{\text{Moles of solute} + 0.769}$$

$$\text{Moles of solute} = 0.0104 \times (\text{Moles of solute} + 0.769)$$

$$\text{Moles of solute} = 0.0104 \times \text{Moles of solute} + 0.008$$

$$0.992 \times \text{Moles of solute} = 0.008$$

$$\text{Moles of solute} = 0.008/0.992 = 0.00806 \text{ mol}$$

5. Calculate the molar mass of the solute:

$$\text{Molar mass} = \frac{\text{Mass of solute}}{\text{Moles of solute}} = \frac{1.2 \text{ g}}{0.00806 \text{ mol}} = 148.5 \text{ g/mol}$$

OR

(ii) Molar Mass Calculation using Boiling Point Elevation:

Given:

- Boiling point of pure benzene = 353.23 K
- Boiling point of solution = 354.11 K
- Mass of solute = 1.80 g
- Mass of benzene = 90 g
- $K_b$  for benzene = 2.53 K kg/mol

1. Calculate the boiling point elevation ( $\Delta T_b$ ):

$$\Delta T_b = 354.11 - 353.23 = 0.88 \text{ K}$$

2. Use the formula for boiling point elevation:

$$\Delta T_b = K_b \times m$$

$$m = \frac{\Delta T_b}{K_b} = \frac{0.88}{2.53} = 0.348 \text{ mol/kg}$$

3. Calculate moles of solute:

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

$$\text{Mass of benzene in kg} = \frac{90}{1000} = 0.09 \text{ kg}$$

$$\text{Moles of solute} = m \times \text{Mass of solvent} = 0.348 \times 0.09 = 0.03132 \text{ mol}$$

4. Calculate the molar mass of the solute:

$$\text{Molar mass} = \frac{\text{Mass of solute}}{\text{Moles of solute}} = \frac{1.80 \text{ g}}{0.03132 \text{ mol}} = 57.5 \text{ g/mol}$$

These calculations show how to determine the molar mass of the solute using both the vapor pressure lowering and boiling point elevation methods.

**Q.30. The particles in the nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids. These are mainly of two**

types, DNA and RNA. Nucleic acids on hydrolysis yield a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds. Nucleic acids have a very diverse set of functions, such as cell creation, the storage and processing of genetic information, protein synthesis and the generation of energy cells. Although their functions may differ, the structure of DNA and RNA are very similar, with only a few fundamental differences in their molecular make-up. Based on the above passage, answer the following questions:

(a) Write three types of RNA molecules.

(b) What products will be formed when a nucleotide from DNA containing thymine is hydrolysed?

(c) (i) Give two differences between DNA and RNA.

**OR**

(ii) (1) Why are the two strands of DNA complementary ?

(ii) What type of linkage joins two nucleotides?

**Solution.** Certainly! Let's tackle the questions based on the provided passage about nucleic acids:

(a) Three Types of RNA Molecules

The three main types of RNA molecules are:

1. mRNA (messenger RNA) - Carries genetic information from DNA to the ribosome, where proteins are synthesized.
2. tRNA (transfer RNA) - Brings amino acids to the ribosome during protein synthesis, matching the amino acids to the appropriate codons on the mRNA.
3. rRNA (ribosomal RNA) - Combines with proteins to form ribosomes, which are the sites of protein synthesis.

(b) Products Formed When a Nucleotide from DNA Containing Thymine is Hydrolysed

When a nucleotide from DNA containing thymine is hydrolyzed, the following products are formed:

1. Pentose Sugar- Deoxyribose (in DNA).
2. Phosphoric Acid - Phosphate group.
3. Nitrogen-Containing Heterocyclic Compound\*\* - Thymine (one of the four nitrogenous bases in DNA).

(c) Differences Between DNA and RNA

(i) Two Differences Between DNA and RNA:\*\*

1. Sugar Component:

DNA: Contains deoxyribose sugar.

RNA: Contains ribose sugar.

2. Nitrogenous Bases:

DNA: Contains adenine (A), cytosine (C), guanine (G), and thymine (T).

RNA: Contains adenine (A), cytosine (C), guanine (G), and uracil (U) instead of thymine.

OR

(ii) The two strands of DNA are complementary because of the specific base pairing rules:

Adenine (A) pairs with Thymine (T) via two hydrogen bonds.

Cytosine (C) pairs with Guanine (G) via three hydrogen bonds.

This complementary base pairing ensures that the genetic information is accurately replicated and transcribed.

Nucleotides are joined together by \*\*phosphodiester bonds\*\*. These bonds connect the phosphate group of one nucleotide to the hydroxyl group of the sugar in the next nucleotide, forming the backbone of the nucleic acid strand.

## SECTION E

**Q.31.(a) (i) Explain with the help of chemical reaction when :**

**(I) Acetone is treated with semicarbazide.**

**(II) Two molecules of benzaldehyde are treated with conc. NaOH.**

**(III) Butan-2-one is treated with Zn/Hg and conc. HCl.**

**(ii) Arrange the following in the increasing order of their acidic strength:**

**(I) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH, BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH, CH<sub>3</sub>CHBrCH<sub>2</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>CHBrCOOH**

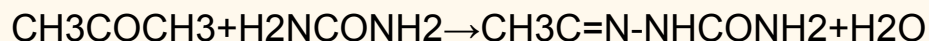
**(II) Benzoic acid, 4-Methoxybenzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid**

**OR**

**Solution.**(I) Acetone is treated with semicarbazide:\*\*

Reaction:

Acetone reacts with semicarbazide to form a \*\*semicarbazone\*\*.



Explanation:

Acetone (CH<sub>3</sub>COCH<sub>3</sub>) is a ketone.

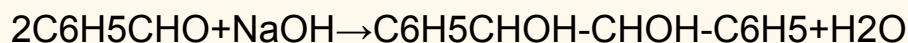
Semicarbazide (H<sub>2</sub>NCONH<sub>2</sub>) reacts with the carbonyl group of acetone to form a semicarbazone.

This reaction is used for the identification and characterization of ketones and aldehydes.

**(II) Two molecules of benzaldehyde are treated with conc. NaOH:**

Reaction:

This reaction is known as the benzoin condensation.

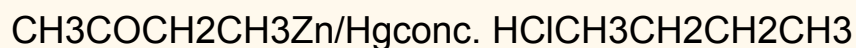


Explanation:

Benzaldehyde ( $C_6H_5CHO$ ) reacts with sodium hydroxide to form benzoin. This is a typical condensation reaction where two molecules of benzaldehyde combine in the presence of a base to form benzoin.

(III) Butan-2-one is treated with Zn/Hg and conc. HCl:  
Reaction:

This is the Clemmensen reduction.



Explanation:

Butan-2-one ( $CH_3COCH_2CH_3$ ) is a ketone.

The Clemmensen reduction reduces the ketone to the corresponding alkane.

The reaction uses zinc amalgam and concentrated hydrochloric acid to remove the carbonyl group and convert the ketone into butane.

(a)(ii) Arrange in Increasing Order of Acidity:

(I) Acidity of Carboxylic Acids:

Given Acids:

1.  $CH_3CH_2CH_2COOH$  (Butyric acid)
2.  $BrCH_2CH_2CH_2COOH$  (3-Bromobutyric acid)
3.  $CH_3CHBrCH_2COOH$  (2-Bromobutyric acid)
4.  $CH_3CH_2CHBrCOOH$  (4-Bromobutyric acid)

Order of Increasing Acidity:

1.  $CH_3CH_2CH_2COOH$  (Butyric acid)
2.  $CH_3CH_2CHBrCOOH$  (4-Bromobutyric acid)
3.  $CH_3CHBrCH_2COOH$  (2-Bromobutyric acid)
4.  $BrCH_2CH_2CH_2COOH$  (3-Bromobutyric acid)

Explanation: The presence of a bromine atom (a strong electron-withdrawing group) increases the acidity of the carboxylic acid.

The position of the bromine atom is crucial; it is most effective at increasing acidity when it is closer to the carboxyl group.

Hence, **3-Bromobutyric acid** is the most acidic due to the proximity of the bromine atom to the carboxyl group.

(II) Acidity of Benzoic Acids:

Given Acids:

1. Benzoic acid
2. 4-Methoxybenzoic acid (4-Methoxybenzoic acid)
3. 4-Nitrobenzoic acid (4-Nitrobenzoic acid)
4. 3,4-Dinitrobenzoic acid (3,4-Dinitrobenzoic acid)

Order of Increasing Acidity:

1. 4-Methoxybenzoic acid (least acidic)
2. Benzoic acid
3. 4-Nitrobenzoic acid
4. 3,4-Dinitrobenzoic acid (most acidic)

Explanation:

Electron-withdrawing groups (like  $-\text{NO}_2$ ) increase acidity by stabilizing the negative charge on the conjugate base of the carboxylate ion.

Electron-donating groups (like  $-\text{OCH}_3$ ) decrease acidity by destabilizing the negative charge on the conjugate base.

4-Nitrobenzoic acid and 3,4-Dinitrobenzoic acid are more acidic due to the electron-withdrawing effects of the nitro groups, with the dinitro compound being the most acidic due to the additional electron-withdrawing effect.

**32. Attempt any five of the following:**

**(a) Cut is not stable in aqueous solution. Comment.**

**(b) Out of  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$ , which one is a stronger reducing agent and why ?**

**(c) Actinoid contraction is greater from element to element than lanthanoid contraction. Why?**

**(d)  $\text{KMnO}_4$  acts as an oxidising agent in acidic medium. Write the ionic equation to support this.**

- (e) Name the metal in the first transition series which exhibits +1 oxidation state most frequently.
- (f) Transition metals and their compounds are good catalysts. Justify.
- (g) Scandium forms no coloured ions, yet it is regarded as a transition element. Why?

**Solution.** Copper(1) ions ( $\text{Cu}^+$ ) are not stable in aqueous solutions due to their tendency to disproportionate into  $\text{Cu}^{2+}$  and  $\text{Cu}$ . This disproportionation reaction occurs because  $\text{Cu}^+$  is thermodynamically unstable:



The  $\text{Cu}^+$  ion is prone to oxidation because the  $\text{Cu}^+$  ion has a relatively high free energy compared to  $\text{Cu}^{2+}$ , and water or oxygen in the environment can facilitate this oxidation.

$\text{Cr}^{2+}$  is a stronger reducing agent than  $\text{Fe}^{2+}$ . This is because  $\text{Cr}^{2+}$  can be readily oxidised to  $\text{Cr}^{3+}$ , and  $\text{Cr}^{2+}$  has a higher tendency to lose electrons compared to  $\text{Fe}^{2+}$ , which is oxidised to  $\text{Fe}^{3+}$ . The standard reduction potential ( $E^\circ$ ) for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  is more negative than for  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , indicating that  $\text{Cr}^{2+}$  has a greater tendency to lose electrons (be oxidised) compared to  $\text{Fe}^{2+}$ .

Actinoid contraction is greater than lanthanoid contraction due to the less effective shielding of the nuclear charge by the 5f electrons compared to the 4f electrons. In the lanthanides (lanthanide series), the 4f electrons shield the nuclear charge fairly effectively, leading to a more gradual increase in nuclear charge and size reduction. However, in the actinides (actinide series), the 5f electrons are less effective at shielding, leading to a greater increase in the effective nuclear charge felt by the electrons. This results in a more significant contraction in size from element to element in the actinide series.

In acidic medium, potassium permanganate ( $\text{KMnO}_4$ ) acts as a strong oxidising agent and gets reduced to manganese(II) ion ( $\text{Mn}^{2+}$ ). The balanced ionic equation for this reaction is:





In this reaction,  $\text{MnO}_4^-$  (permanganate ion) is reduced to  $\text{Mn}^{2+}$ , and in the process, it oxidises 4 other substances.

The metal in the first transition series that exhibits the +1 oxidation state most frequently is Copper (Cu). Copper commonly shows two oxidation states: +1 and +2. The +1 oxidation state is particularly notable in compounds like copper(I) chloride ( $\text{CuCl}$ ) and copper(I) oxide ( $\text{Cu}_2\text{O}$ ).

Transition metals and their compounds are excellent catalysts due to several reasons:

1. **Variable Oxidation States:** Transition metals can exist in multiple oxidation states, which allows them to participate in various redox reactions during catalysis.
2. **Formation of Complexes:** Transition metals can form coordination complexes with substrates, providing an environment where the reaction can proceed more efficiently.
3. **Ability to Provide Empty d-Orbitals:** Transition metals have empty d-orbitals that can accept electrons from reactants, facilitating the formation of reaction intermediates.
4. **High Surface Area:** In heterogeneous catalysis, transition metals often form solid catalysts with high surface areas, allowing for more effective interactions with reactants.

Scandium is regarded as a transition element because it has partially filled d-orbitals in its compounds, which is a characteristic feature of transition metals. However, Scandium forms only  $\text{Sc}^{3+}$  ions in its compounds, which have no d-electrons (since the 3d orbitals are empty after losing three electrons). The lack of colour in its ions is due to the absence of d-d electron transitions in  $\text{Sc}^{3+}$ . Despite this, Scandium is included in the transition series because it occupies a position in the periodic table where transition metals are found and exhibits similar properties, such as variable oxidation states in its compounds.

**Q.33.(a) (i) What type of battery is the lead storage battery ? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it.**

**(ii) Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 A was passed through the solution of AgNO<sub>3</sub>. [Molar mass of Ag = 108 g mol<sup>-1</sup>, 1 F = 96500 C mol<sup>-1</sup>]**

**OR**

**(b) (i) State Kohlrausch's law of independent migration of ions. Molar conductivity at infinite dilution for NH<sub>4</sub>Cl, NaOH and NaCl solution at 298 K are 110, 100 and 105 S cm<sup>2</sup> mol<sup>-1</sup> respectively. Calculate the molar conductivity of NH<sub>4</sub>OH solution.**

**3**

**(ii) Calculate AG° of the following cell at 25°C:**

**2**

**Zn (s) | Zn<sup>2+</sup>(aq) || Cu<sup>2+</sup> || Cu<sup>2+</sup> (aq) | Cu (s)**

**Given: E<sup>2+</sup> = -0.76 V Zn/Zn E<sup>2+</sup> Cu/Cu = + 0.34 V 1 F = 96500 C mol<sup>-1</sup>**

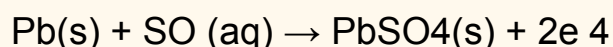
**Solution. (i) Lead Storage Battery**

Type of Battery:

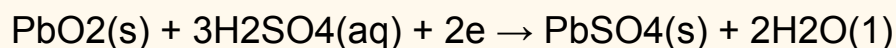
The lead storage battery is a type of secondary (rechargeable) battery.

Reactions in the Lead Storage Battery:

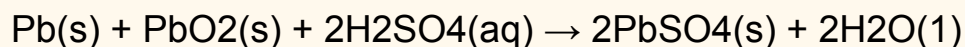
Anode Reaction (during discharge):



Cathode Reaction (during discharge):



Overall Reaction (during discharge):



(a) (ii) Calculating Time to Deposit Silver

To deposit 1.5 g of silver, we use the following steps:

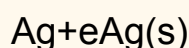
Calculate the moles of silver deposited:

Moles of Ag-Mass/molar mass =  $1.5 \text{ g} / 107.8682 \text{ g/mol}$

Moles of Ag Molar Mass =  $0.01389 \text{ mol}$

2. Calculate the total charge required:

The reaction for silver deposition is:



For 1 mole of silver, 1 mole of electrons (1 Faraday) is needed. Therefore:

Charge required = Moles of Ag  $\times$  Faraday Constant =  $0.01389 \text{ mol} \times 96500 \text{ C/mol}$

3. Calculate the time using the current:

Time/ Charge =  $1340 \text{ C} / 1.5 \text{ A} = 893.33 \approx 14.89 \text{ minutes}$

OR

(b) (i) Kohlrausch's Law and Molar Conductivity of  $\text{NH}_4\text{OH}$

Kohlrausch's Law:

Kohlrausch's Law states that the molar conductivity at infinite dilution of an electrolyte is equal to the sum of the molar conductivities of its ions, each extrapolated to infinite dilution.

Calculate the Molar Conductivity of  $\text{NH}_4\text{OH}$ :

Given:

Molar conductivity of  $\text{NH}_4\text{Cl}$  =  $110 \text{ S cm}^2 \text{ mol}^{-1}$

Molar conductivity of  $\text{NaOH}$  =  $100 \text{ S cm}^2 \text{ mol}^{-1}$

Molar conductivity of  $\text{NaCl}$  =  $105 \text{ S cm}^2 \text{ mol}^{-1}$

For  $\text{NH}_4\text{OH}$ :

Molar conductivity of  $\text{NH}_4\text{OH}$  = Molar conductivity of  $\text{NH}_4\text{Cl}$  + Molar conductivity

Molar conductivity of  $\text{OH}^-$  = Molar conductivity of  $\text{NaOH}$  - Molar conductivity of  $\text{Na}^+$  Since  $\text{Na}^+$  does not contribute to  $\text{OH}^-$ 's molar conductivity, we directly use:

Molar conductivity of OH Molar conductivity of NaOH 100  
Molar conductivity of NH<sub>4</sub>OH = 110+100 = 210 S cm<sup>2</sup> mol<sup>-1</sup>

(ii) Calculating AG for the Cell Reaction

Given:

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

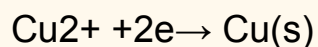
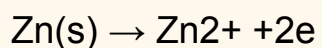
1. Calculate the cell potential E<sub>cell</sub>:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.34 - (-0.76) = 1.10 \text{ V}$$

2. Calculate AG:

$$\Delta G^{\circ} = -nFE_{\text{cell}}$$

For the cell reaction:



Number of electrons n = 2:

$$\Delta G = 2 \times 96500 \text{ C/mol} \times 1.10 \text{ V} = -212300 \text{ J/mol} = -212.3 \text{ kJ/mol}$$