

CBSE 2024 Compartment Chemistry Set-3 (56/S/3) Solutions

SECTION A

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

Q.1. The standard electrode potential for Ni²⁺/Ni couple is 0.25 V and for Ag⁺/Ag couple is 0.80 V. These two couples are connected to make an electrochemical cell. The redox reaction is spontaneous. The cell potential will be :

- (A) + 1.05 V
- (B) - 1.05 V
- (C) + 0.55 V
- (D) -0.55 V

Solution. (C) + 0.55 V

To determine the cell potential for the given electrochemical cell and confirm its spontaneity, follow these steps:

1. Identify the Electrochemical Couples and Their Standard Electrode Potentials:

- For the Ni²⁺/Ni couple: $E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = 0.25 \text{ V}$
- For the Ag⁺/Ag couple: $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.80 \text{ V}$

2. Determine Which Couple Will Be Oxidized and Which Will Be Reduced:

- The more positive electrode potential will be the cathode (reduction half-cell).
- The less positive electrode potential will be the anode (oxidation half-cell).

In this case:

- Cathode (Reduction): Ag⁺/Ag with $E^{\circ} = 0.80 \text{ V}$
- Anode (Oxidation): Ni²⁺/Ni with $E^{\circ} = 0.25 \text{ V}$

3. Calculate the Cell Potential (E^ocell):

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

$$E_{\text{cell}}^{\circ} = 0.80 \text{ V} - 0.25 \text{ V} = 0.55 \text{ V}$$

4. Determine If the Reaction Is Spontaneous:

- The cell potential E_{cell}° is positive, indicating that the reaction is spontaneous.

Therefore, the cell potential for the electrochemical cell is:

(C) + 0.55 V

Q.2. Out of Fe^{2+} , Co^{2+} , Cr^{3+} , Ni^{2+} , the one which shows lowest magnetic moment is:

- (A) Fe^{2+}
- (B) Co^{2+}
- (C) Cr^{3+}
- (D) Ni^{2+}

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

Solution. (D) Ni^{2+} , To determine which ion has the lowest magnetic moment, we need to analyse 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^{2+} (Iron (II)):

Atomic number of Fe = 26

Electron configuration of Fe: $[\text{Ar}] 3d 4s^2$

Fe^{2+} loses 2 electrons: $[\text{Ar}] 3d^6$

In 3D, the configuration is $t_{2g}^4 e_g^2$ (octahedral complex). Number of unpaired electrons = 4

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

2. Fe^{3+} (Iron (III)):

Fe^{3+} loses 3 electrons: $[\text{Ar}] 3d^5$

In 3D, the configuration is $t_2g^3 e_g^2$ (octahedral complex). Number of unpaired electrons = 5

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

3. Co^{2+} (Cobalt (II)):

Atomic number of Co = 27

Electron configuration of Co: $[\text{Ar}] 3d 4s^2$

Co^{2+} loses 2 electrons: $[\text{Ar}] 3d^2$

In 3d', the configuration is $t_2g e_g^1$ (octahedral complex). Number of unpaired electrons = 3

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

4. Cr^{3+} (Chromium (III)):

Atomic number of Cr = 24

Electron configuration of Cr: $[\text{Ar}] 3d 4s^1$

Cr^{3+} loses 3 electrons: $[\text{Ar}] 3d^3$

In $3d^3$, the configuration is t_2g^3 (octahedral complex). Number of unpaired electrons = 3

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

5. Ni^{2+} (Nickel (II)):

Atomic number of Ni = 28

Electron configuration of Ni: $[\text{Ar}] 3d 4s^2$

Ni^{2+} loses 2 electrons: $[\text{Ar}] 3d^8$

In 3d, the configuration is $t_2g e_g^2$ (octahedral complex). Number of unpaired electrons = 2

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

Among the given ions, Ni^{2+} has the fewest number of unpaired electrons (2), which results in the lowest magnetic moment.

Thus, the correct answer is:

(D) Ni^{2+}

Q.3. The geometry of paramagnetic nickel complex $[\text{NiCl}_4]^{2-}$ is:

(A) tetrahedral

(B) octahedral

(C) square planar

(D) distorted octahedral

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

1. Oxidation State and Electron Configuration:

In $[\text{NiCl}_4]^{2-}$, 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 $[\text{NiCl}_4]^{2-}$ 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 $[\text{NiCl}_4]^{2-}$ 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 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.4. Which of the following does not undergo Aldol condensation?

(A) HCHO

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

(C) CH_3COCH_3

(D) CH_3CHO

Solution.(A) 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 β -hydroxyaldehydes or β -hydroxyketones, which can further dehydrate to form α,β -unsaturated carbonyl compounds.

The key requirement is that the molecule must have at least one α -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 α -hydrogen because its carbonyl group is attached directly to two hydrogens (making it a CH_2O). Therefore, it cannot undergo Aldol condensation.

2. Ethanal (CH_3CHO):

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

3. Acetone (CH_3COCH_3):

Acetone has two α -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 α -hydrogens (the hydrogens on the carbon adjacent to the carbonyl group). It can undergo Aldol condensation.

Conclusion:

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

(A) HCHO (Formaldehyde)

Q.5 The IUPAC name of the complex $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ 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 $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$, let's break it down step by step:

1. Identify the Ligands:

NH_3 : 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 (NH_3) and nitrito-O (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 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. The most stable complex among the following is:

(A) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(B) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

(C) $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$

(D) $\text{K}_4[\text{Fe}(\text{CN})_6]$

Solution. (D) $\text{K}_4[\text{Fe}(\text{CN})_6]$, To determine which complex among the given options is the most stable, let's analyse each one based on its stability:

1. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$:

Type: Square planar complex.

Ligands: Two ammonia (NH_3) and two chloride (Cl^-) ligands.

Stability: While square planar complexes of platinum (II) are generally stable, this particular complex is not as stable as some other options due to less steric and electronic stabilisation compared to others.

2. $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$:

Type: Linear complex (diamine silver(I)).

Ligands: Two ammonia (NH_3) ligands and one chloride (Cl^-) as a counterion.

Stability: This complex is relatively stable due to the involvement of silver (I) in a linear geometry, which is quite stable in aqueous solution.

3. $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$:

Type: Octahedral complex.

Ligands: Two ethylenediamine (en) ligands and two chloride (Cl^-) ligands.

Stability: The ethylenediamine (en) ligands are bidentate and form chelate rings, which increase the stability of the complex. This complex is generally more stable due to chelation effects.

4. $\text{K}_4[\text{Fe}(\text{CN})_6]$:

Type: Octahedral complex.

Ligands: Six cyanide (CN^-) ligands.

Stability: This complex is known for its high stability. The cyanide ligands are strong field ligands and form very stable complexes with iron.

Additionally, the iron in this complex is in the +2 oxidation state (ferrous), which further contributes to its stability.

Given the above analysis, the most stable complex among the options is:
(D) $\text{K}_4[\text{Fe}(\text{CN})_6]$

The high stability of this complex is due to the strong field effect of the cyanide ligands and the overall stability of the iron (II) centre in the octahedral arrangement.

Q.8. 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 oxidised 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.9. 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 3 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

Q.10. 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) $[\text{CoC}_6]^{3-}$

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 (H_2O): A weak field ligand.

Ammonia (NH_3): A weak to moderate field ligand.

Cyanide (CN^-): A strong field ligand.

Chloride (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 (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.11. For a chemical reaction, A 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) $\frac{1}{2}$, 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:

$$4 = 2^2$$

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

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

$$2n = 1$$

$$n = \frac{1}{2}$$

Therefore, the order of the reaction is:

(C) $\frac{1}{2}$

Q.12. 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 characterised 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.

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): Cu^{2+} iodide is known.

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

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

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

Explanation:

Assertion (A) is false because Cu^{2+} iodide (CuI_2) is not a stable or known compound. Copper typically forms CuI (copper(I) iodide) rather than CuI_2 .

Reason (R) is true in the context of chemistry; Cu^{2+} can indeed oxidise iodide ions to iodine, but this does not validate the existence of 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_3

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 (α -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. (a) Account for the following:

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN .

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

OR

Solution. (a) Account for the following:

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN .

Explanation:

CH_3CHO (acetaldehyde) is more reactive than CH_3COCH_3 (acetone) towards nucleophilic addition reactions like those with hydrogen cyanide (HCN).

The reason lies in the electronic nature of the carbonyl group. In CH_3CHO , the carbonyl carbon is more electrophilic compared to CH_3COCH_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 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.

(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 (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 CO₂.

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.18. Write the reaction involved in the following:

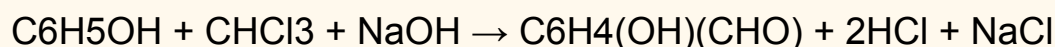
(a) Reimer-Tiemann reaction

(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 (C₆H₅OH) reacts with chloroform (CHCl₃) in the presence of a strong base (sodium hydroxide, 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 (RCOONa) are electrolyzed.

The result is the formation of the corresponding alkane (R-R), along with sodium hydroxide (NaOH) and carbon dioxide (CO₂).

In summary:

Reimer-Tiemann Reaction: Phenol + Chloroform + NaOH products

Ortho-Hydroxybenzaldehyde + By-

Kolbe's Reaction: Sodium Carboxylate Salts → Alkane + NaOH + CO₂

Q.19. Write the reaction of glucose with:

(a) HI

(b) Br₂ water

Solution. (a) Glucose with HI

When glucose reacts with hydriodic acid (HI), it undergoes a cleavage reaction where the sugar is broken down into simpler compounds.

Specifically, glucose is converted into n-hexane (an alkane) and iodoform.

Reaction:



In this reaction:

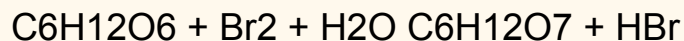
Glucose (C₆H₁₂O₆) reacts with hydriodic acid (HI).

The result is n-hexane (C₆H₁₄), iodine (I₂), and water (H₂O).

(b) Glucose with Br₂ Water

When glucose reacts with bromine water (Br₂ water), it undergoes an oxidation reaction, where the aldehyde group of glucose is oxidized to a carboxyl group, converting glucose to gluconic acid.

Reaction:



In this reaction:

Glucose (C₆H₁₂O₆) reacts with bromine water (Br₂) and water (H₂O).

The result is gluconic acid (C₆H₁₂O₇) and hydrobromic acid (HBr).

To summarise:

Glucose + HI: Converts to n-hexane and iodine.

Glucose + Br₂ water: Oxidises to gluconic acid.

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. 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 of aromatic amines are generally stable due to the following reasons:

1. Resonance Stabilisation: The diazonium ion ($R-N_2$) can delocalize its positive charge through resonance with the aromatic ring. This resonance stabilisation of the diazonium ion contributes to its stability.
2. Strong ionic Bonding: In the diazonium salt, the diazonium ion is stabilised by ionic interactions with the counterion (usually a halide or sulphate). This ionic bonding helps in stabilising the diazonium salt.
3. Substitution Effects: The stability of the diazonium salt can be enhanced by substituents on the aromatic ring that stabilise the positive charge through inductive or resonance effects.

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

Explanation:

Aniline does not undergo Friedel-Crafts reactions (either acylation or alkylation) because:

1. Strongly Activating Amino Group: The amino group ($-NH_2$) is a strongly activating group for electrophilic aromatic substitution, making the ring highly reactive. However, in Friedel-Crafts reactions, the electrophiles (such as alkyl or acyl cations) are often too reactive and can lead to side reactions or rearrangements.
2. Formation of Complexes: The amino group can coordinate with the Lewis acid catalysts used in Friedel-Crafts reactions (like $AlCl_3$), forming complexes that deactivate the catalyst or prevent it from effectively reacting with the aromatic ring. This complex formation reduces the effectiveness of the Friedel-Crafts catalyst.
3. Formation of by-products: The Friedel-Crafts reaction involves the generation of carbocation intermediates, which can lead to polymerization or side reactions when interacting with the highly nucleophilic amino group.

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

Explanation:

Aniline on nitration typically yields a substantial amount of meta product due to the following reasons:

1. **Strong Activating Effect of the Amino Group:** The amino group (-NH₂) is a strong electron-donating group through resonance. This increases the electron density of the ring, making the ring more reactive towards electrophiles such as the nitronium ion (NO₂⁺).
2. **Formation of a Nitrosonium Intermediate:** The nitronium ion (NO₂⁺) is a strong electrophile in the nitration reaction. The amino group can form a nitrosylated intermediate that results in the formation of the meta product as well as the ortho and para products.
3. **Deactivating Effects:** Despite being strongly activating, the amino group can also exert a deactivating effect under certain conditions, leading to a preference for meta substitution. This is due to steric hindrance or the formation of resonance structures that may favor meta positions over ortho and para positions.

In summary, the amino group in aniline, while being strongly activating, can influence the distribution of products due to its electronic effects and interactions with the electrophile in the nitration reaction.

Q.23. Account for the following:

- (a) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- (b) Alkyl halides are immiscible in water.
- (c) t-butyl bromide has lower boiling point than n-butyl bromide.

Solution.(a) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

Explanation:

1. **Electron Withdrawing Effects:** In chlorobenzene, the chlorine atom is attached to a benzene ring. The chlorine atom is highly electronegative and withdraws electron density through the sigma bond. However, the benzene

ring also has resonance structures that can delocalize some of the electron density, which reduces the overall dipole moment.

2. Resonance Stabilisation: The delocalization of the electron density in the aromatic ring of chlorobenzene leads to a partial offset of the dipole moment. This resonance effect causes the dipole moment of chlorobenzene to be less than that of cyclohexyl chloride.

3. Cyclohexyl Chloride Characteristics: Cyclohexyl chloride, where the chlorine is attached to a cyclohexane ring, lacks such delocalization. Therefore, the dipole moment of cyclohexyl chloride is higher because the entire dipole due to the chlorine is preserved without resonance effects counteracting it.

**Q.24. (a) Draw the geometrical isomers of the complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.
(b) Give the electronic configuration of d^4 ion when $A_0 > P$.
(c) Solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green in colour whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Give a reason. [Atomic number: Ni = 28]**

Solution. (a) Geometrical Isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

The complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ can exhibit geometrical isomerism due to the different spatial arrangements of the ligands around the platinum ion.

Platinum (II) complexes typically adopt a square planar geometry. For $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, the geometrical isomers are:

1. Cis-Isomer:

In the cis-isomer, the two ammonia (NH_3) groups are adjacent to each other, and the two chloride (Cl) ions are also adjacent.

2. Trans-Isomer:

In the trans-isomer, the two ammonia (NH_3) groups are opposite each other, and the two chloride (Cl) ions are also opposite each other.

(b) Electronic Configuration of d^2 Ion when $A_0 > P$

In the context of octahedral complexes, the electronic configuration of a d ion depends on the magnitude of the crystal field splitting energy (A_0) compared to the pairing energy (P).

When $A > P$: The crystal field splitting energy is large compared to the pairing energy. This leads to the low-spin configuration where electrons pair up in the lower energy t_{2g} orbitals.

For a d^1 configuration in an octahedral field with $A_0 > P$:

Electronic Configuration: The d-orbitals will be arranged as follows:

t_{2g} : 1111 (paired)

e_g : (empty)

Thus, the electronic configuration will be:

t_{2g} : 4 electrons (all paired)

e_g : 0 electrons

(c) Colour Differences between $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$

1. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$:

The complex $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is typically green in color. This is due to the relatively weak field strength of water as a ligand, which causes partial splitting of the d-orbitals in the octahedral field. This partial splitting allows for the absorption of light in the visible region, particularly in the red to orange part of the spectrum, while the green color is transmitted.

2. $[\text{Ni}(\text{CN})_4]^{2-}$:

The complex $[\text{Ni}(\text{CN})_4]^{2-}$ is colorless. Cyanide (CN) is a strong field ligand and causes a large splitting of the d-orbitals in a square planar field (or tetrahedral for some complexes). This large splitting results in a large energy gap between the split d-orbitals, and thus, no visible light is absorbed. The absorption occurs in the ultraviolet region, and the complex appears colorless to the visible eye.

Summary:

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green due to weak field ligands causing partial d-orbital splitting and visible light absorption.

[Ni(CN)₄]²⁻ is colorless due to strong field ligands causing large d-orbital splitting, absorbing UV light instead of visible light.

Q.25. The electrical resistance of a column of 0.05 M NaOH solution of cell constant 50 cm⁻¹ is 4.5×10³ ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution.

To calculate the resistivity, conductivity, and molar conductivity of the NaOH solution, follow these steps:

Given Data:

- Molarity of NaOH solution (C) = 0.05 M
- Cell constant (k) = 50 cm⁻¹
- Resistance (R) = 4.5 × 10³ Ω

(1) Resistivity (ρ)

Resistivity is given by the formula:

$$\rho = R \times A/L$$

where A/L is the cell constant k .

Since resistivity ρ can also be calculated directly from:

$$\rho = R \times \text{cell constant}$$

So,

$$\rho = R \times k$$

$$\rho = 4.5 \times 10^3 \Omega \times 50 \text{ cm}^{-1}$$

$$\rho = 2.25 \times 10^5 \Omega \cdot \text{cm}$$

(2) Conductivity (κ)

Conductivity is the reciprocal of resistivity:

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

Thus:

$$\kappa = \frac{1}{2.25 \times 10^5} \text{ S/cm}$$

$$\kappa \approx 4.44 \times 10^{-6} \text{ S/cm}$$

(3) Molar Conductivity (Λ_m)

Molar conductivity is given by:

$$\Lambda_m = \kappa \times C$$

where C is the molarity of the solution.

So:

$$\Lambda_m = 4.44 \times 10^{-6} \text{ S/cm} \times 0.05 \text{ mol/L}$$

$$\Lambda_m = 2.22 \times 10^{-7} \text{ S} \cdot \text{cm}^2/\text{mol}$$

Summary

1. Resistivity (ρ): $2.25 \times 10^5 \Omega \cdot \text{cm}$
2. Conductivity (κ): $4.44 \times 10^{-6} \text{ S/cm}$
3. Molar Conductivity (Λ_m): $2.22 \times 10^{-7} \text{ S} \cdot \text{cm}^2/\text{mol}$

These calculations give you the resistivity, conductivity, and molar conductivity of the 0.05 M NaOH solution based on the provided cell constant and resistance.

Q.26. Calculate elevation of the boiling point of the solution when 4 g of MgSO_4 (molar mass = 120 g/mol) was dissolved in 100 g of water, assuming MgSO_4 undergoes complete ionisation. (K_b for water = 0.52 K kg mol⁻¹)

Solution.

To calculate the elevation in boiling point of the solution, we use the formula for boiling point elevation:

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

where:

- ΔT_b is the boiling point elevation.
- i is the van't Hoff factor, which represents the number of particles the solute dissociates into.
- K_b is the ebullioscopic constant (boiling point elevation constant) of the solvent (water in this case).
- m is the molality of the solution.

Given Data:

- Mass of MgSO₄ = 4 g
- Molar mass of MgSO₄ = 120 g/mol
- K_b for water = 0.52 K kg/mol
- Mass of water = 100 g = 0.1 kg
- MgSO₄ completely ionizes into Mg²⁺ and SO₄²⁻, so $i = 3$

Steps to Calculate:

1. Calculate the number of moles of MgSO₄:

$$\begin{aligned}\text{Moles of MgSO}_4 &= \frac{\text{Mass}}{\text{Molar mass}} \\ \text{Moles of MgSO}_4 &= \frac{4 \text{ g}}{120 \text{ g/mol}} \\ \text{Moles of MgSO}_4 &= \frac{1}{30} \text{ mol} \\ \text{Moles of MgSO}_4 &= 0.0333 \text{ mol}\end{aligned}$$

Given Data:

- Mass of MgSO₄ = 4 g
- Molar mass of MgSO₄ = 120 g/mol
- K_b for water = 0.52 K kg/mol
- Mass of water = 100 g = 0.1 kg
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Steps to Calculate:

1. Calculate the number of moles of MgSO₄:

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Q.27. Hydrolysis of ethyl ethanoate takes place by the chemical reaction : CH₃COOC₂H₅ + H₂O (excess) H⁺ Based on the above reaction, write : CH₃COOH + C₂H₅OH

(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.28. What happens when: (any three)

MgBr (a) is treated with CH_3CHO followed by hydrolysis.

(b) Phenol is treated with conc. ($\text{HNO}_3 + \text{H}_2\text{SO}_4$).

(c) Anisole is treated with CH_3COCl in the presence of anhydrous AlCl_3 .

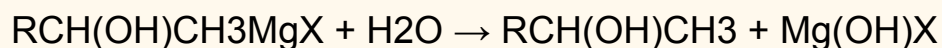
(d) Propan-2-ol is heated with Cu at 573 K.

Solution. (a) MgBr_2 is treated with CH_3CHO followed by hydrolysis
Reaction: This is a Grignard reaction followed by hydrolysis.

Step 1: The Grignard reagent (MgBr_2 , although this is typically denoted as RMgX) reacts with the aldehyde (CH_3CHO , which is acetaldehyde) to form a tertiary alcohol.



Step 2: Hydrolysis of the reaction mixture produces the corresponding alcohol.



Result: If $\text{R} = \text{CH}_3$, the product is 1-Phenylethanol.

(b) Phenol is treated with concentrated HNO_3 and H_2SO_4

Reaction: Phenol reacts with concentrated nitric acid (HNO_3) in the presence of sulfuric acid (H_2SO_4) to give nitrophenols.

Product Formation: The reaction typically results in the formation of a mixture of ortho- and para-nitrophenol due to the activating effect of the hydroxyl group in phenol.



Result: The main products are 2-nitrophenol and 4-nitrophenol.

(c) Anisole is treated with CH_3COCl in the presence of anhydrous AlCl_3

Reaction: This is a Friedel-Crafts acylation reaction.

Reaction: Anisole (methoxybenzene) reacts with acetyl chloride (CH_3COCl) in the presence of anhydrous aluminum chloride (AlCl_3), resulting in the formation of acetophenone.



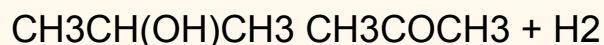
Result: The product is acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$).

(d) Propan-2-ol is heated with Cu at 573 K

Reaction: This is a dehydrogenation reaction.

Reaction: Propan-2-ol (isopropanol) is heated with copper at high temperature (573 K), leading to the removal of hydrogen and the formation of acetone.

Cu, 573 K



Result: The product is acetone (propan-2-one).

Feel free to ask if you need further details or explanations on these reactions.

SECTION D

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

Q.29. 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) Why Are the Two Strands of DNA Complementary?*

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.

Q.30 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 $2.53 \text{ K kg mol}^{-1}$.

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 (ΔP):

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

2. Calculate the mole fraction of the solute (X_{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 (ΔT_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.

SECTION E

Q.31.(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 is passed through the solution of AgNO₃.

[Molar mass of Ag = 108 g mol⁻¹, 1 F = 96500 C mol⁻¹]

OR

(b) (i) State Kohlrausch's law of independent migration of ions. Molar conductivity at infinite dilution for NH₄Cl, NaOH and NaCl solution at 298 K are 110, 100 and 105 S cm² mol⁻¹ respectively. Calculate the molar conductivity of NH₄OH solution.

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



Given: E²⁺ Zn/Zn = -0.76 V

E²⁺ Cu/Cu = + 0.34 V

1 F = 96500 C mol⁻¹

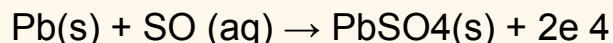
Solution. (i) Lead Storage Battery

Type of Battery:

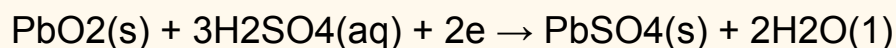
The lead storage battery is a type of secondary (rechargeable) battery.

Reactions in the Lead Storage Battery:

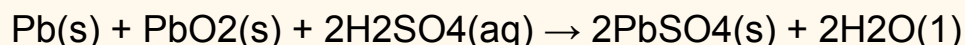
Anode Reaction (during discharge):



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:

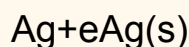
Calculate the moles of silver deposited:

Moles of Ag = Mass/molar mass = 1.5 g / 107.8682 g/mol

Moles of Ag = 0.01389 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 mol \times 96500 C/mol

3. Calculate the time using the current:

Time = Charge / Current = 1340 C / 1.5 A = 893.33 s \approx 14.89 minutes

OR

(b) (i) Kohlrausch's Law and Molar Conductivity of NH_4OH

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 NH_4OH :

Given:

Molar conductivity of NH_4Cl = 110 $\text{S cm}^2 \text{mol}^{-1}$

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

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

For NH_4OH :

Molar conductivity of NH_4OH = Molar conductivity of NH_4Cl + Molar conductivity of NaOH - Molar conductivity of NaCl

Molar conductivity of OH = Molar conductivity of NaOH - Molar conductivity of Na
Since Na does not contribute to OH's molar conductivity, we directly use:

Molar conductivity of OH = Molar conductivity of NaOH - 100

Molar conductivity of NH₄OH = 110 + 100 - 100 = 105 S cm² mol⁻¹

(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_{cell} :

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

2. Calculate AG:

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

For the cell reaction:

$\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$

$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu(s)}$

Number of electrons $n = 2$:

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

Q.32. (a) (i) Explain with the help of chemical reaction when :

(1) 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:

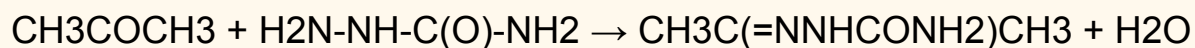
(I) CH₃CH₂CH₂COOH, BrCH₂CH₂CH₂COOH, CH₃CHBrCH₂COOH, CH₃CH₂CHBrCOOH

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

Solution. (a) (i) Chemical Reactions

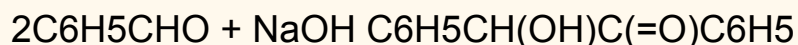
(1) Acetone with Semicarbazide:

When acetone reacts with semicarbazide, it forms a semicarbazone. This is a typical reaction used to detect and identify ketones and aldehydes. The reaction is:



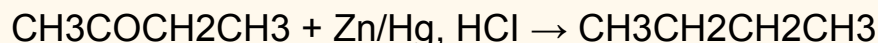
(II) Benzaldehyde with Conc. NaOH:

When two molecules of benzaldehyde react with concentrated sodium hydroxide (NaOH), they undergo benzoin condensation. This reaction forms benzoin:



(III) Butan-2-one with Zn/Hg and Conc. HCl:

When butan-2-one is treated with zinc amalgam (Zn/Hg) and concentrated hydrochloric acid (HCl), it undergoes Clemmensen reduction to yield butane:



(ii) Acidic Strength

(1) Arrange in Increasing Order of Acidity:

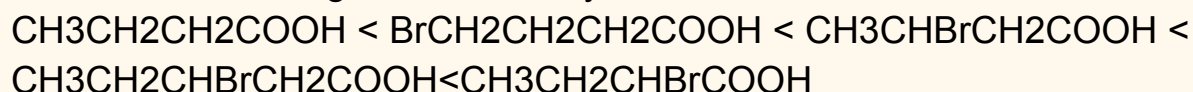
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (Butanoic acid) - Base case.

$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ (3-Bromobutanoic acid) - The bromine atom is at the end of the chain, causing a slight electron-withdrawing effect.

$\text{CH}_3\text{CHBrCH}_2\text{COOH}$ (2-Bromo-butanoic acid) - The bromine atom is attached to the middle carbon of the chain, causing a stronger electron-withdrawing effect.

$\text{CH}_3\text{CH}_2\text{CHBrCOOH}$ (3-Bromo-butanoic acid) - Bromine at the beta position shows stronger electron-withdrawing effect compared to others.

Thus, the increasing order of acidity is:



(II) Arrange in Increasing Order of Acidity:

- Benzoic acid – Basic carboxyl group with no additional substituents.
- 4-Methoxybenzoic acid – The Methoxy group is an electron-donating group, which decreases the acidity.
- 4-Nitrobenzoic acid – Nitro group is a strong electron-withdrawing group, which increases the acidity.
- 3,4-Dinitrobenzoic acid – Two nitro groups strongly withdraw electron density, making it very acidic.

Thus, the increasing order of acidity is:

Benzoic acid < 4-Methoxybenzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

OR

(ii) How will you bring about the following conversions?

(I) Propanone to Propene

(II) Benzoic acid to Benzaldehyde

(III) Ethanal to But-2-enal

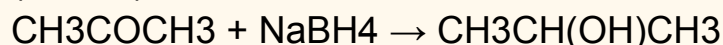
Solution. (ii) Conversions

(1) Propanone to Propene:

To convert propanone (a ketone) to propene (an alkene), you can use a reduction reaction followed by dehydrogenation. Specifically:

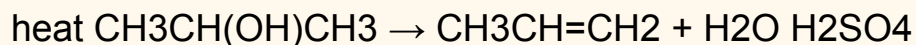
1. Reduction to Propan-2-ol:

Reduce propanone to propan-2-ol (a secondary alcohol) using a reducing agent like sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4):



2. Dehydration to Propene:

Dehydrate propan-2-ol to propene using an acid catalyst like sulfuric acid (H_2SO_4):



(II) Benzoic Acid to Benzaldehyde:

To convert benzoic acid to benzaldehyde, you can use the reduction reaction known as the "reduction of carboxylic acids to aldehydes":

1. Reduction with Lithium Aluminium Hydride (LiAlH_4):

First, reduce benzoic acid to benzyl alcohol:



2. Oxidation with Pyridinium Chlorochromate (PCC):

Oxidize benzyl alcohol to benzaldehyde using PCC:

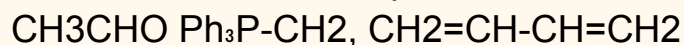


(III) Ethanal to But-2-enal:

To convert ethanal (acetaldehyde) to but-2-enal (an aldehyde with a double bond in the middle), you can follow these steps:

1. Formation of 1,3-Butadiene:

Perform a Wittig reaction using ethanal and a phosphonium ylide to form 1,3-butadiene. This step is indirect but involves:



2. Oxidation to But-2-enal:

React 1,3-butadiene with an oxidising agent to introduce an aldehyde group at the 2-position: $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}-\text{CHO}$

This reaction requires specific conditions and reagents to introduce the aldehyde group at the desired position.

Q.33. Attempt any five of the following:

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

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

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

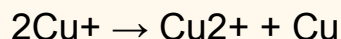
(d) KMnO_4 acts as an oxidising agent in acidic medium. Write the ionic equation to support this.

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



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

Cr^{2+} is a stronger reducing agent than Fe^{2+} . This is because Cr^{2+} can be readily oxidised to Cr^{3+} , and Cr^{2+} has a higher tendency to lose electrons compared to Fe^{2+} , which is oxidised to Fe^{3+} . The standard reduction potential (E°) for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is more negative than for $\text{Fe}^{3+}/\text{Fe}^{2+}$, indicating that Cr^{2+} has a greater tendency to lose electrons (be oxidised) compared to 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 (KMnO_4) acts as a strong oxidising agent and gets reduced to manganese(II) ion (Mn^{2+}). The balanced ionic equation for this reaction is:



In this reaction, MnO_4^- (permanganate ion) is reduced to 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 (CuCl) and copper(I) oxide (Cu_2O).

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 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 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.