Chemistry (Theory) 31st May 2024 Shift 1

Duration :3 hours	**Maximum Marks :**70	**Total Questions :**33.

Important Instructions

Read the following instructions carefully:

1. The test duration is 3 hours, covering Chemistry Theory with 33 questions.
2. Please check that this question paper contains 39 printed pages.
3. The question paper contains 33 questions. Answer them on the provided Answer Sheet.

Section A

Questions No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

Total Marks for Section A: $16 \times 1 = 16$

1.

Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is -0.74 V. The two couples in their standard states are connected to make a cell. The cell potential will be.

(A) +1.19 V

(B) +0.89 V

(C) +0.18 V

(D) +1.83 V

Correct Answer: (B)

Solution:

To construct a voltaic cell, the half-reaction with the higher (more positive) standard reduction potential acts as the cathode (reduction occurs), and the half-reaction with the lower (more negative) standard reduction potential acts as the anode (oxidation occurs). Given reduction potentials: $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = +0.15\,\text{V}$ $E^\circ(\text{Cr}^{3+}/\text{Cr}) = -0.74\,\text{V}$ Since +0.15 V > -0.74 V, the $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple will be the cathode, and the Cr^{3+}/Cr couple will be the anode. Cathode Reaction (Reduction): Sn^{4+} + $2e^-$ → Sn^{2+}; $E^\circ_{cathode} = +0.15$ V Anode Reaction (Oxidation): Cr → Cr^{3+} + $3e^-$; $E^\circ_{anode} = -0.74$ V (This is the reduction potential) The standard cell potential (E°_{cell}) is calculated as:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = (+0.15\,\text{V}) - (-0.74\,\text{V})$$

$$E^\circ_{cell} = +0.15\,\text{V} + 0.74\,\text{V}$$

$$E^\circ_{cell} = +0.89\,\text{V}$$

The cell potential will be +0.89 V.

Quick Tip

Calculating Cell Potential. $E^\circ_{cell} = E^\circ_{reduction,cathode} - E^\circ_{reduction,anode}$. The half-reaction with the more positive $E^\circ_{reduction}$ acts as the cathode. The half-reaction with the less positive (or more negative) $E^\circ_{reduction}$ acts as the anode.

2.

The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion (Atomic no. : Cr = 24) is _____..

(A) 2.87 B.M.

(B) 3.87 B.M.

(C) 3.47 B.M.

(D) 3.57 B.M.

Correct Answer: (B)

Solution:

The spin-only magnetic moment (μ_s) is calculated using the formula:

$$\mu_s = \sqrt{n(n+2)}\,\text{B.M.}$$

where n is the number of unpaired electrons and B.M. stands for Bohr Magneton. First, determine the electronic configuration of Chromium (Cr, Z=24): Cr: [Ar] $3d^5$ $4s^1$ (Note the exception for stability). Next, determine the configuration of the Cr^{3+} ion by removing 3 electrons (first from 4s, then from 3d): Cr $\rightarrow$ Cr^{3+} + $3e^-$ Remove 1 electron from 4s: [Ar] $3d^5$ Remove 2 more electrons from 3d: [Ar] $3d^3$ The electronic configuration of Cr^{3+} is [Ar] $3d^3$. Now, determine the number of unpaired electrons in the 3d subshell. The 3d subshell has 5 orbitals. According to Hund's rule, the 3 electrons will occupy three different orbitals with parallel spins: $\uparrow\uparrow\uparrow$ _ _ Number of unpaired electrons, $n = 3$. Calculate the spin-only magnetic moment:

$$\mu_s = \sqrt{3(3+2)} = \sqrt{3 \times 5} = \sqrt{15}\,\text{B.M.}$$

Calculating the square root: $\sqrt{15} \approx 3.873$ B.M. The closest value is 3.87 B.M.

Quick Tip

Spin-Only Magnetic Moment. Formula: $\mu_s = \sqrt{n(n+2)}$ B.M., where n = number of unpaired electrons. Determine the electronic configuration of the ion, find n using Hund's rule, then calculate μ_s. Remember Cr and Cu electron configuration exceptions.

3.

In case of association, abnormal molar mass of solute will.

(A) increase

(B) decrease

(C) remain same

(D) first increase and then decrease

Correct Answer: (A)

Solution:

Colligative properties (like freezing point depression, boiling point elevation, osmotic pressure) depend on the number of solute particles in a solution, not their identity. Abnormal molar mass arises when the solute undergoes association or dissociation in the solvent, causing the actual number of particles to differ from the number expected based on the formula unit. - **Association:** Solute molecules combine to form larger aggregates (e.g., dimerization: $2A \rightleftharpoons A_2$). This reduces the total number of independent solute particles in the solution compared to the number expected if no association occurred. - **Dissociation:** Solute molecules break apart into smaller ions or molecules (e.g., NaCl $\rightarrow$ Na^+ + Cl^-). This increases the total number of independent solute particles. Experimentally determined molar mass using colligative properties is inversely proportional to the number of particles. The relationship is often expressed using the van't Hoff factor (i):

$$i = \frac{\text{Actual number of particles}}{\text{Expected number of particles}} = \frac{\text{Normal Molar Mass}}{\text{Abnormal Molar Mass}}$$

For association, the actual number of particles is less than expected, so $i < 1$. Rearranging the formula:

$$\text{Abnormal Molar Mass} = \frac{\text{Normal Molar Mass}}{i}$$

Since $i < 1$, the Abnormal Molar Mass will be greater than the Normal Molar Mass. Thus, in case of association, the abnormal molar mass increases.

Quick Tip

Association/Dissociation & Molar Mass. Association $\rightarrow$ Fewer particles $\rightarrow$ van't Hoff factor $i < 1 \rightarrow$ Abnormal Molar Mass $>$ Normal Molar Mass (Increases). Dissociation $\rightarrow$ More particles $\rightarrow i > 1 \rightarrow$ Abnormal Molar Mass ¡ Normal Molar Mass (Decreases).

4.

Alkyl halides undergoing nucleophilic bimolecular substitution reaction involve.

(A) retention of configuration

(B) formation of racemic mixture

(C) inversion of configuration

(D) formation of carbocation

Correct Answer: (C)

Solution:

Nucleophilic bimolecular substitution reaction refers to the S_N2 mechanism. Key features of the S_N2 mechanism: - **Bimolecular:** The rate depends on the concentration of both the alkyl halide and the nucleophile (Rate = k[RX][Nu^-]). - **Mechanism:** It is a single-step process where the nucleophile attacks the substrate from the side opposite to the leaving group (backside attack). Bond formation and bond breaking occur simultaneously through a pentacoordinate transition state. - **Stereochemistry:** Due to the backside attack, the configuration of the chiral center (if present) is inverted during the reaction. This is known as Walden inversion. Retention of configuration (A) or formation of a racemic mixture (B) is characteristic of S_N1 reactions, which proceed via a planar carbocation intermediate (D). Therefore, S_N2 reactions involve inversion of configuration.

Quick Tip

Substitution Mechanisms. S_N2: Bimolecular rate, single step, backside attack, inversion of configuration, favored by $1\circ > 2\circ >> 3\circ$ halides. S_N1: Unimolecular rate, two steps (carbocation intermediate), racemization (or partial inversion), favored by $3\circ > 2\circ$ halides.

5.

Arrange the following compounds in increasing order of their boiling points :.

(i) CH_3-CH(CH_3)-CH_2Br (1-Bromo-2-methylpropane)

(ii) $CH_3CH_2CH_2CH_2Br$ (1-Bromobutane)

(iii) H_3C-C(CH_3)(Br)-CH_3 (2-Bromo-2-methylpropane)

The correct order is.

(A) (ii) ¡ (i) ¡ (iii)

(B) (i) ¡ (ii) ¡ (iii)

(C) (iii) ¡ (i) ¡ (ii)

(D) (iii) ¡ (ii) ¡ (i)

Correct Answer: (C)

Solution:

The compounds are isomers of bromobutane (C_4H_9Br). Boiling points of alkyl halides depend on intermolecular forces (dipole-dipole and van der Waals forces) and molecular shape. For isomers with the same molecular formula: 1. **Branching:** Increased branching leads to a more compact, spherical shape. This reduces the surface area available for intermolecular contact, weakening the van der Waals forces and lowering the boiling point. Comparing the structures: - (ii) 1-Bromobutane: Straight chain (least branched). - (i) 1-Bromo-2-methylpropane: Branched chain (primary halide). - (iii) 2-Bromo-2-methylpropane: Highly branched (tertiary halide, most compact shape). Based on branching, the boiling point should decrease as branching increases. The most branched isomer (iii) will have the lowest boiling point, and the straight-chain isomer (ii) will have the highest boiling point. The order of increasing boiling point is: (iii) ¡ (i) ¡ (ii) This corresponds to option (C).

Quick Tip

Boiling Points of Isomers. For isomers of alkanes or alkyl halides, boiling point generally decreases with increased branching due to reduced surface area contact and weaker van der Waals forces. Straight chain $>$ Branched chain $>$ Highly branched.

6.

The correct IUPAC name of $[Pt(NH_3)_2Cl_2]^{2+}$ is.

(A) Diamminechloridoplatinum (II)

(B) Diamminedichloridoplatinum (IV)

(C) Diamminedichloridoplatinum (0)

(D) Diamminedichloridoplatinate (IV)

Correct Answer: (B)

Solution:

Naming coordination compounds follows specific IUPAC rules: 1. Identify ligands and central metal ion. Ligands: NH_3 (ammine), Cl^- (chlorido). Metal: Pt (platinum). 2. Name ligands alphabetically before the metal. Use prefixes di-, tri-, tetra- for multiple simple ligands. Here: Diammine, Dichlorido. Alphabetically, ammine comes before chlorido. So, Diamminedichlorido. 3. Name the central metal. Since the complex has a positive charge (+2), the metal name is used as is: platinum. 4. Determine the oxidation state of the metal. Let the oxidation state of Pt be x. Ammine (NH_3) is neutral (0). Chlorido (Cl^-) has a -1 charge. The overall charge of the complex is +2. x + 2(0) + 2(-1) = +2 x + 0 - 2 = +2 x = +4 The oxidation state is +4, written in Roman numerals in parentheses: (IV). Putting it together: Diamminedichloridoplatinum(IV). This matches option (B). Option (A) is incorrect ligand name/number and oxidation state. Option (C) has incorrect oxidation state. Option (D) uses the suffix "-ate", which is used for anionic complexes, not cationic ones.

Quick Tip

Coordination Compound Naming. 1. Name ligands alphabetically (use prefixes di-, tri- if needed). 2. Name central metal (use base name for cations/neutral, add -ate for anions). 3. Indicate metal oxidation state with Roman numerals in parentheses. Cation named before anion if ionic compound.

7.

The acid formed when propyl magnesium bromide is treated with CO_2 followed by acid hydrolysis is :.

(A) C_3H_7COOH

(B) C_2H_5COOH

(C) CH_3COOH

(D) C_3H_7OH

Correct Answer: (A)

Solution:

Propyl magnesium bromide is a Grignard reagent with the formula $CH_3CH_2CH_2MgBr$ (often written as C_3H_7MgBr). Grignard reagents react with carbon dioxide (CO_2) via nucleophilic addition to form the magnesium salt of a carboxylic acid. The propyl group acts as a nucleophile attacking the electrophilic carbon of CO_2. Step 1: Reaction with CO_2 (usually dry ice)

$$CH_3CH_2CH_2MgBr + O{=}C{=}O \rightarrow CH_3CH_2CH_2\text{-}COO^-MgBr^+$$

Step 2: Acid hydrolysis (e.g., with H_3O^+) protonates the carboxylate salt to yield the carboxylic acid.

$$CH_3CH_2CH_2\text{-}COO^-MgBr^+ \xrightarrow{H_3O^+} CH_3CH_2CH_2\text{-}COOH + Mg^{2+} + Br^- + H_2O$$

The product is butanoic acid ($CH_3CH_2CH_2COOH$ or C_3H_7COOH). This reaction adds one carbon atom (from CO_2) to the original alkyl group of the Grignard reagent. Option (A) represents butanoic acid. Option (B) is propanoic acid. Option (C) is acetic acid. Option (D) is propanol (formed if Grignard reacts with formaldehyde).

Quick Tip

Grignard Reagent + CO_2. Reaction sequence RMgX + CO_2 $\rightarrow$ RCOOMgX $\xrightarrow{H_3O^+}$ RCOOH. Forms a carboxylic acid with one more carbon atom than the original alkyl/aryl group (R) of the Grignard reagent.

8.

Acidified $KMnO_4$ oxidises sulphite to.

(A) $S_2O_3^{2-}$

(B) $S_2O_8^{2-}$

(C) $SO_2(g)$

(D) SO_4^{2-}

Correct Answer: (D)

Solution:

Acidified potassium permanganate ($KMnO_4$) is a strong oxidizing agent. The permanganate ion (MnO_4^-) is reduced, typically to Mn^{2+} in acidic solution. Sulphite ion (SO_3^{2-}) contains sulfur in the +4 oxidation state. Strong oxidizing agents like acidified $KMnO_4$ will oxidize sulphite to the highest common oxidation state of sulfur, which is +6, found in the sulfate ion (SO_4^{2-}). The balanced redox reaction (simplified ionic) is:

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

The sulphite ion (SO_3^{2-}) is oxidized to the sulfate ion (SO_4^{2-}). Thiosulfate ($S_2O_3^{2-}$) and peroxodisulfate ($S_2O_8^{2-}$) are different ions. SO_2 contains sulfur in the +4 state, same as sulphite.

Quick Tip

Redox Reactions. Acidified $KMnO_4$ is a strong oxidizing agent ($MnO_4^- \rightarrow Mn^{2+}$). It oxidizes lower oxidation state sulfur compounds (like S^{2-}, SO_3^{2-}) to sulfate (SO_4^{2-}, S=+6 oxidation state).

9.

Which is the correct order of acid strength from the following ?.

(A) $C_6H_5OH > H_2O > ROH$

(B) $C_6H_5OH > ROH > H_2O$

(C) $ROH > C_6H_5OH > H_2O$

(D) $H_2O > C_6H_5OH > ROH$

Correct Answer: (A)

Solution:

We need to compare the acidic strength of phenol (C_6H_5OH), water (H_2O), and a typical aliphatic alcohol (ROH, where R is an alkyl group like methyl, ethyl, etc.). Acid strength relates to the ease of donating a proton (H^+) and the stability of the resulting conjugate base. - **Phenol (C_6H_5OH):** The conjugate base is the phenoxide ion ($C_6H_5O^-$). The negative charge on oxygen can be delocalized into the benzene ring through resonance, stabilizing the

anion. This makes phenol significantly more acidic than aliphatic alcohols and water. (pKa $\approx$ 10). - **Water (H_2O):** The conjugate base is hydroxide ion (OH^-). Water acts as a reference. (pKa $\approx$ 15.7 at 25°C, often approximated as 14 in contexts relative to Kw). - **Aliphatic Alcohols (ROH):** The conjugate base is the alkoxide ion (RO^-). Alkyl groups (R) are generally electron-donating (inductive effect), which tends to destabilize the negative charge on oxygen compared to OH^-. This makes simple aliphatic alcohols typically weaker acids than water. (pKa $\approx$ 16-18). Therefore, the general order of increasing acid strength is ROH ¡ H_2O ¡ C_6H_5OH. Or, decreasing acid strength: $C_6H_5OH > H_2O >$ ROH. This matches option (A).

Quick Tip

Acidity Order. Factors affecting acidity: stability of conjugate base. Phenols are more acidic than water, which is generally more acidic than simple aliphatic alcohols. Phenoxide stabilized by resonance $>$ OH^- $>$ Alkoxide (destabilized by alkyl inductive effect).

10.

An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because _____..

(A) it gains water due to osmosis

(B) it loses water due to reverse osmosis

(C) it gains water due to reverse osmosis

(D) it loses water due to osmosis

Correct Answer: (D)

Solution:

Osmosis is the net movement of water molecules across a selectively permeable membrane from a region of higher water potential (lower solute concentration) to a region of lower water potential (higher solute concentration). - An unripe mango contains cells with cell sap, which has a certain solute concentration (lower water potential than pure water). - A

concentrated salt solution has a very high solute concentration and therefore a very low water potential. When the mango is placed in the concentrated salt solution, the water potential inside the mango cells is higher than the water potential of the surrounding salt solution. Consequently, water moves *out* of the mango cells into the salt solution via osmosis, across the cell membranes. This loss of water causes the cells, and thus the mango, to shrivel. Reverse osmosis involves applying pressure to force water against its osmotic gradient, which is not occurring here.

Quick Tip

Osmosis. Net movement of water across a semipermeable membrane from high water potential (low solute conc.) to low water potential (high solute conc.). Placing cells in a hypertonic solution (like concentrated salt solution) causes them to lose water and shrivel.

11.

The best reagent for converting propanamide into propanamine is.

(A) excess H_2

(B) Br_2 in aqueous NaOH

(C) iodine in the presence of red phosphorus

(D) $LiAlH_4$ in ether

Correct Answer: (D)

Solution:

We want to convert propanamide ($CH_3CH_2CONH_2$) into propanamine ($CH_3CH_2CH_2NH_2$). This transformation involves the reduction of the amide carbonyl group (C=O) to a methylene group (CH_2) without changing the number of carbon atoms. Let's examine the reagents: (A) Excess H_2 (catalytic hydrogenation): Can reduce some functional groups, but typically requires harsh conditions or specific catalysts for amide reduction, often not as effective as hydrides. (B) Br_2 in aqueous NaOH: These are reagents for the Hofmann bromamide degradation, which converts an amide to an amine with *one less* carbon atom

($CH_3CH_2CONH_2 \rightarrow CH_3CH_2NH_2$, ethanamine). Incorrect product. (C) Iodine in presence of red phosphorus: Used often in conjunction with HI for reductions, particularly of alcohols, but not the standard reagent for amide reduction to amine. (D) $LiAlH_4$ (Lithium Aluminium Hydride) in ether: $LiAlH_4$ is a powerful reducing agent that effectively reduces amides (as well as carboxylic acids, esters, nitriles) to the corresponding amines. It reduces the C=O group of the amide to a CH_2 group. $CH_3CH_2CONH_2 \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$. Correct product. Therefore, $LiAlH_4$ in ether is the best reagent for this conversion.

Quick Tip

Amide Reduction. $LiAlH_4$ reduces amides $RCONH_2$, RCONHR', RCONR'R" to the corresponding amines RCH_2NH_2, RCH_2NHR', $RCH_2NR'R"$. Hofmann degradation (Br_2/NaOH) converts $RCONH_2$ to RNH_2 (one carbon less).

12.

Which of the following statements is not true about glucose ?.

(A) It is an aldohexose.

(B) On heating with HI it forms n-hexane.

(C) It exists in furanose form.

(D) It does not give Schiff's test.

Correct Answer: (C)

Solution:

Let's evaluate the statements about glucose ($C_6H_{12}O_6$): (A) Glucose contains an aldehyde group (-CHO) at C1 and a total of six carbon atoms, with hydroxyl groups on the others. It is classified as an aldohexose. True. (B) Strong reduction of glucose with concentrated hydroiodic acid (HI) and red phosphorus reduces all the hydroxyl groups and the aldehyde group completely, forming n-hexane ($CH_3(CH_2)_4CH_3$). This indicates a straight chain of six carbon atoms. True. (C) Glucose predominantly exists in cyclic hemiacetal forms. The stable ring structure is a six-membered ring, called the pyranose form (α-glucopyranose and β-glucopyranose). While five-membered furanose rings can be formed theoretically, the

pyranose form is overwhelmingly favored and is the common representation in solution and polysaccharides like starch/cellulose. Stating it exists in furanose form as a typical characteristic is generally considered not true in the context of its dominant structures. False. (D) Although glucose has an aldehyde group in its open-chain form, it exists primarily in the cyclic hemiacetal forms in solution. These cyclic forms are in equilibrium with a small amount of the open-chain form. However, glucose does not readily give some typical aldehyde tests like Schiff's test or react with $NaHSO_3$, likely due to the low concentration of the open-chain form and the stability of the cyclic forms. True. Therefore, the statement that is not true is (C).

Quick Tip

Glucose Properties. Aldo-hexose (aldehyde + 6C). Reduces to n-hexane with HI/P. Exists mainly as cyclic hemiacetal, predominantly the six-membered *pyranose* ring form (α β). Does not give Schiff's test despite having an aldehyde group in open-chain form. Fructose exists in furanose form.

13.

Assertion (A) : All naturally occurring α-amino acids except glycine are optically active..

Reason (R) : Most naturally occurring amino acids have L-configuration..

Correct Answer: (B)

Solution:

Assertion (A): Amino acids have a central carbon (α-carbon) bonded to an amino group ($-NH_2$), a carboxyl group (-COOH), a hydrogen atom (-H), and a side chain (-R). For an amino acid to be optically active, the α-carbon must be chiral (asymmetric), meaning it must be bonded to four different groups. In glycine, the side chain R is simply -H. Therefore, the α-carbon in glycine is bonded to two hydrogen atoms, making it achiral and optically inactive. All other common naturally occurring α-amino acids have R groups different from

-H, -NH_2, and -COOH, making their α-carbon chiral and thus optically active. Assertion (A) is true.

Reason (R): Naturally occurring amino acids (found in proteins) predominantly have the L-configuration relative to L-glyceraldehyde (based on the arrangement around the α-carbon, not necessarily optical rotation direction). This statement is also true.

Explanation: While both statements are true facts about amino acids, the fact that most have L-configuration (Reason) does not explain *why* they are optically active (Assertion). The reason for optical activity is the presence of a chiral α-carbon (except in glycine). Therefore, Reason (R) is not the correct explanation of Assertion (A).

Quick Tip

Amino Acid Chirality. Optically active if α-carbon is chiral (bonded to 4 different groups). Glycine (R=H) is achiral. Most natural amino acids are L-isomers. L/D configuration doesn't directly determine optical activity (chirality does).

14.

Assertion (A) : The boiling point of ethanol is higher than that of methoxymethane..

Reason (R) : There is intramolecular hydrogen bonding in ethanol..

Correct Answer: (C)

Solution:

Assertion (A): Ethanol (CH_3CH_2OH) and methoxymethane (dimethyl ether, CH_3OCH_3) are isomers with the same molecular formula (C_2H_6O) and similar molecular weights. Ethanol is a liquid with a boiling point of 78.4°C, while methoxymethane is a gas with a boiling point of -24°C. Ethanol's boiling point is significantly higher. Assertion (A) is true.

Reason (R): Ethanol molecules possess an -OH group, allowing them to form *intermolecular* hydrogen bonds (between different ethanol molecules). These strong intermolecular forces require significant energy to overcome, leading to a high boiling point. Methoxymethane, an ether, lacks an O-H bond and cannot form hydrogen bonds between its own molecules; it only has weaker dipole-dipole and van der Waals forces. The reason

incorrectly states *intramolecular* hydrogen bonding (bonding within the same molecule), which doesn't occur significantly in simple ethanol and isn't the cause of its high boiling point relative to the ether. Reason (R) is false.
Since Assertion (A) is true and Reason (R) is false, option (C) is correct.

Quick Tip

Boiling Points H-Bonding. Alcohols have high boiling points compared to ethers or alkanes of similar molecular weight due to strong *intermolecular* hydrogen bonding between -OH groups. Intramolecular H-bonding occurs within a single molecule (e.g., ortho-nitrophenol).

15.

Assertion (A) : The boiling points of alkyl halides decrease in the order RI $>$ RBr $>$ RCl $>$ RF..

Reason (R) : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass..

Correct Answer: (B)

Solution:

Assertion (A): For a given alkyl group (R), the boiling point of alkyl halides generally increases with the size and mass of the halogen atom. This is because larger halogen atoms have more electrons, leading to stronger van der Waals (London dispersion) forces between molecules. The order of halogen atomic mass is I $>$ Br $>$ Cl $>$ F. Therefore, the boiling point order is typically RI $>$ RBr $>$ RCl $>$ RF. Assertion (A) states the order of decrease is RI $>$ RBr $>$ RCl $>$ RF, which means boiling point decreases from RI to RF. This statement is true.
Reason (R): Alkyl halides are polar molecules (due to the C-X bond dipole) and have larger molecular masses than corresponding alkanes. Both factors lead to stronger intermolecular forces (dipole-dipole and van der Waals) compared to alkanes of similar mass.
Consequently, alkyl chlorides, bromides, and iodides generally have significantly higher boiling points than hydrocarbons of comparable molecular mass. This statement is true.

Explanation: While both Assertion and Reason are true statements about alkyl halide boiling points, the reason (comparison to hydrocarbons) does not directly explain the specific order of boiling points among different alkyl halides (Assertion). The explanation for the Assertion lies in the increasing strength of van der Waals forces with increasing halogen size/mass. Therefore, Reason (R) is not the correct explanation of Assertion (A).

Quick Tip

Alkyl Halide Boiling Points. For same R: BP increases with halogen size/mass (RI $>$ RBr $>$ RCl $>$ RF) due to stronger van der Waals forces. Alkyl halides have higher BPs than alkanes of similar mass due to polarity and mass.

16.

Assertion (A) : $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are examples of homoleptic complexes..

Reason (R) : All the ligands attached to the metal are the same..

Correct Answer: (A)

Solution:

Assertion (A): A homoleptic complex is one where the central metal ion is coordinated to only one type of ligand. In $[Cr(H_2O)_6]Cl_2$, the complex ion is $[Cr(H_2O)_6]^{2+}$. The ligands attached to the central Cr^{2+} ion are six water (aqua) molecules. Since only one type of ligand (H_2O) is present, this is a homoleptic complex. Similarly, in $[Fe(H_2O)_6]Cl_2$, the complex ion is $[Fe(H_2O)_6]^{2+}$, and the only ligand is H_2O, making it homoleptic. Assertion (A) is true.
Reason (R): The reason given is the definition of a homoleptic complex: all ligands attached to the metal are the same type. Reason (R) is true.
Explanation: The reason provides the correct definition that justifies why the complexes in the assertion are classified as homoleptic. Therefore, both are true, and R is the correct explanation of A.

Quick Tip

Homoleptic Complexes. Contain only one type of ligand bonded to the central metal ion (e.g., $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Cr(H_2O)_6]^{2+}$). Heteroleptic complexes have multiple types of ligands.

Section B

Questions No. 16 to 21

17.

Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal ? Justify your answer..

Solution:

Benzaldehyde (C_6H_5CHO) is expected to be **less reactive** than propanal (CH_3CH_2CHO) towards nucleophilic addition reactions.

Justification:.

There are two main reasons: 1. **Steric Hindrance:** The bulky phenyl group (C_6H_5-) attached to the carbonyl carbon in benzaldehyde offers more steric hindrance to the approaching nucleophile compared to the smaller ethyl group (CH_3CH_2-) in propanal. This makes the attack by the nucleophile on the carbonyl carbon more difficult in benzaldehyde. 2. **Electronic Effects (Resonance):** The carbonyl group in benzaldehyde is directly attached to the benzene ring. The electrophilicity (positive character) of the carbonyl carbon is reduced due to resonance involving the benzene ring. The π electrons of the ring can delocalize with the carbonyl group, decreasing the partial positive charge on the carbonyl carbon. Propanal lacks this resonance stabilization and the carbonyl carbon is relatively more electrophilic due to the inductive effect of the alkyl group (though alkyl groups are mildly electron-donating, the resonance effect in benzaldehyde is more significant in reducing reactivity towards nucleophiles). Therefore, due to greater steric hindrance and reduced electrophilicity of the

carbonyl carbon caused by resonance, benzaldehyde is less reactive than propanal towards nucleophilic addition.

Quick Tip

Aldehyde Reactivity (Nucleophilic Addition). Reactivity depends on: (1) Steric hindrance around carbonyl carbon (less hindrance = more reactive). (2) Electrophilicity of carbonyl carbon (more positive charge = more reactive). Alkyl groups (propanal) offer less hindrance than aryl groups (benzaldehyde). Resonance with aryl ring reduces electrophilicity of carbonyl carbon in benzaldehyde. Generally, aliphatic aldehydes > aromatic aldehydes.

18.

Complete and balance the following chemical equations :.

(a) MnO_4^- + $3S_2O_3^{2-}$ + H_2O →.

(b) $Cr_2O_7^{2-}$ + $3Sn^{2+}$ + $14H^+$ →.

Solution:

(a) Reaction of Permanganate with Thiosulfate (Neutral/Alkaline Medium assumed due to H_2O):.

In neutral or faintly alkaline solution, MnO_4^- (Mn=+7) is typically reduced to MnO_2 (Mn=+4), and thiosulfate ($S_2O_3^{2-}$, avg S=+2) is oxidized to sulfate (SO_4^{2-}, S=+6). Reduction half-reaction: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ Oxidation half-reaction: $S_2O_3^{2-} + 10OH^- \rightarrow 2SO_4^{2-} + 5H_2O + 8e^-$ To balance electrons, multiply reduction by 8 and oxidation by 3: $8MnO_4^- + 16H_2O + 24e^- \rightarrow 8MnO_2 + 32OH^-$ $3S_2O_3^{2-} + 30OH^- \rightarrow 6SO_4^{2-} + 15H_2O + 24e^-$ Add them: $8MnO_4^- + 3S_2O_3^{2-} + 16H_2O + 30OH^- \rightarrow 8MnO_2 + 6SO_4^{2-} + 15H_2O + 32OH^-$ Simplify: $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$ *(Note: The stoichiometry '3' given for $S_2O_3^{2-}$ in the question stem perfectly matches this balanced equation)* **Completed Equation (a): $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2(s) + 6SO_4^{2-} + 2OH^-$.**

(b) Reaction of Dichromate with Tin(II) (Acidic Medium):.

In acidic solution, dichromate ($Cr_2O_7^{2-}$, Cr=+6) is reduced to Cr^{3+}, and Tin(II) (Sn^{2+}) is oxidized to Tin(IV) (Sn^{4+}). Reduction half-reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ Oxidation half-reaction: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ To balance electrons, multiply the oxidation half-reaction by 3: $3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$ Add the half-reactions: $Cr_2O_7^{2-} + 14H^+ + 6e^- + 3Sn^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+} + 6e^-$ Cancel electrons: $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$ *(Note: The stoichiometry given in the question stem matches this balanced equation exactly)* **Completed Equation (b): $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$.**

Quick Tip

Balancing Redox Reactions. Identify oxidation and reduction half-reactions. Balance atoms (except O, H). Balance O with H_2O. Balance H with H^+ (acidic) or OH^-/H_2O (basic). Balance charge with e^-. Equalize e^- count and add half-reactions. Simplify. $MnO_4^- \rightarrow MnO_2$ (neutral/basic); $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (acidic).

19.

(A) Give reasons :.

(a) Cooking is faster in pressure cooker than in an open pan..

(b) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution ? What change in temperature would you observe after mixing liquids X and Y ?.

OR.

(B) Define Azeotrope. What type of Azeotrope is formed by negative deviation from Raoult's law ? Give an example..

Solution:

(A) Reasons:.

(a) Pressure Cooker: In a pressure cooker, the lid seals the pot, preventing steam from escaping easily. As the water inside boils, the trapped steam builds up pressure. According to the relationship between pressure and boiling point, increasing the pressure above

atmospheric pressure raises the boiling point of water (e.g., to 110-120°C instead of 100°C). Cooking food at this higher temperature significantly speeds up the chemical and physical changes involved in cooking, making the process faster than in an open pan where water boils at approx 100°C (at sea level).

(b) Mixing Liquids X and Y: When mixing two liquids X and Y results in a decrease in the total volume ($V_{\text{mix}} < V_X + V_Y$, i.e., $\Delta V_{\text{mixing}} < 0$), it indicates that the intermolecular forces of attraction between X and Y molecules in the solution (X-Y attractions) are stronger than the average forces between molecules in the pure liquids (X-X and Y-Y attractions). This leads to the molecules packing more closely together.

- **Deviation from Raoult's Law:** Stronger X-Y attractions mean molecules escape into the vapor phase less readily than predicted by Raoult's law (which assumes ideal interactions). This results in a lower total vapor pressure than expected for an ideal solution, which is characteristic of a **negative deviation** from Raoult's law.
- **Temperature Change:** The formation of stronger intermolecular bonds (X-Y) upon mixing releases energy. This makes the mixing process **exothermic**, and an **increase in temperature** ($\Delta H_{\text{mixing}} < 0$) would be observed if the mixing occurs adiabatically, or heat would need to be removed to maintain constant temperature.

OR.

(B) Azeotrope Definition and Example:.

- **Definition:** An azeotrope (or constant boiling mixture) is a liquid mixture of two or more components that has a constant boiling point and whose vapor has the same composition as the liquid. Because the liquid and vapor have the same composition, the components of an azeotrope cannot be separated by simple fractional distillation. - **Type formed by Negative Deviation:** Mixtures exhibiting a negative deviation from Raoult's law (due to stronger intermolecular forces between components than within pure components) have vapor pressures lower than expected. Consequently, they exhibit a maximum boiling point azeotrope. At the azeotropic composition, the mixture boils at a higher temperature than either pure component. - **Example:** A common example of a maximum boiling azeotrope (formed by negative deviation) is a mixture of nitric acid (HNO_3, BP $\approx$ 83°C) and water (H_2O, BP = 100°C). The azeotrope forms at about 68% HNO_3 by mass and boils at

approximately 120.5°C. Another example is acetone-chloroform.

Quick Tip

Concepts. Pressure Cooker: Increased pressure → Increased boiling point → Faster cooking. Solution Deviations: Negative deviation → Stronger A-B forces, $\Delta V_{mix} < 0$, $\Delta H_{mix} < 0$ (Exothermic), P_{total} ¡ P_{ideal}, forms Max Boiling Azeotrope. Positive deviation → Weaker A-B forces, $\Delta V_{mix} > 0$, $\Delta H_{mix} > 0$ (Endothermic), $P_{total} > P_{ideal}$, forms Min Boiling Azeotrope. Azeotrope: Constant boiling mixture with same liquid/vapor composition.

20.

Identify A and B in each of the following reaction sequence :.

(a) $\mathbf{CH_3CH_2Cl} \xrightarrow{\mathbf{NaCN}} \mathbf{A} \xrightarrow{\mathbf{H_2/Ni}} \mathbf{B.}$

(b) $\mathbf{C_6H_5NH_2} \xrightarrow{\mathbf{NaNO_2/HCl},\, 0-5^\circ C} \mathbf{A} \xrightarrow{\mathbf{H^+/H_2O},\Delta} \mathbf{B.}$

Solution:

(a) Sequence starting with Chloroethane: Step 1: CH_3CH_2Cl (Chloroethane) reacts with NaCN. This is a nucleophilic substitution (S_N2) where cyanide ion (CN^-) displaces chloride ion (Cl^-). CH_3CH_2Cl + NaCN → CH_3CH_2CN + NaCl Product [A] is Propanenitrile (CH_3CH_2CN). Step 2: Propanenitrile [A] is treated with H_2/Ni. This is catalytic hydrogenation, which reduces the nitrile group (-C≡N) to a primary amine group ($-CH_2NH_2$). $CH_3CH_2CN + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_2NH_2$ Product [B] is Propan-1-amine (or n-propylamine). **A = CH_3CH_2CN (Propanenitrile), B = $CH_3CH_2CH_2NH_2$ (Propan-1-amine).**

(b) Sequence starting with Aniline: Step 1: $C_6H_5NH_2$ (Aniline) reacts with $NaNO_2$/HCl at low temperature (0-5°C). This is the diazotization reaction, which converts the primary aromatic amine group ($-NH_2$) into a diazonium salt group ($-N_2^+Cl^-$). $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5^\circ C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$ Product [A] is Benzenediazonium chloride ($C_6H_5N_2^+Cl^-$). Step 2: Benzenediazonium chloride [A] is treated with H^+/H_2O and warmed (or boiled). This reaction causes the diazonium group to be replaced by a hydroxyl group

(-OH), releasing nitrogen gas. $C_6H_5N_2^+Cl^-$ + $H_2O \xrightarrow{H^+,\Delta} C_6H_5OH$ + N_2 + HCl Product [B] is Phenol (C_6H_5OH). **A = $C_6H_5N_2^+Cl^-$ (Benzenediazonium chloride), B = C_6H_5OH (Phenol).**

Quick Tip

Organic Reactions. (a) Alkyl Halide + CN^- $\rightarrow$ Nitrile (S_N2). Nitrile + H_2/Ni $\rightarrow$ Primary Amine. (b) Aromatic Amine + $NaNO_2$/HCl (cold) $\rightarrow$ Diazonium Salt. Diazonium Salt + H_2O/Warm $\rightarrow$ Phenol.

21.

What are the hydrolysis products of :.

(a) Sucrose.

(b) Lactose.

Solution:

Hydrolysis involves breaking a bond (in this case, a glycosidic bond) by adding water, usually catalyzed by acid or enzymes. **(a) Sucrose:** Sucrose (common table sugar) is a disaccharide composed of one unit of α-glucose and one unit of β-fructose linked by an α, β-1,2-glycosidic bond. Hydrolysis of sucrose yields one molecule of glucose and one molecule of fructose.

$$\text{Sucrose} + H_2O \xrightarrow{H^+ \text{ or Sucrase}} \text{Glucose} + \text{Fructose}$$

Hydrolysis Products of Sucrose: Glucose and Fructose..

(b) Lactose: Lactose (milk sugar) is a disaccharide composed of one unit of β-galactose and one unit of glucose (either α or β) linked by a β-1,4-glycosidic bond. Hydrolysis of lactose yields one molecule of galactose and one molecule of glucose.

$$\text{Lactose} + H_2O \xrightarrow{H^+ \text{ or Lactase}} \text{Galactose} + \text{Glucose}$$

Hydrolysis Products of Lactose: Galactose and Glucose..

Quick Tip

Disaccharide Hydrolysis. Sucrose $\rightarrow$ Glucose + Fructose. Lactose $\rightarrow$ Galactose + Glucose. Maltose $\rightarrow$ Glucose + Glucose. Hydrolysis breaks the glycosidic bond.

Section C

Questions No. 22 to 27

22.

Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the number of moles of CO_2 in 500 ml of soda water when packed under 2.53×10^5 Pa at the same temperature..

Solution:

According to Henry's Law, the partial pressure (p) of a gas above a liquid is directly proportional to the mole fraction (x) of the gas dissolved in the liquid:

$$p = K_H x$$

where K_H is Henry's law constant. Given: Henry's law constant for CO_2, $K_H = 1.67 \times 10^8$ Pa. Partial pressure of CO_2 under which the soda water is packed, $p_{CO_2} = 2.53 \times 10^5$ Pa. Volume of water = 500 ml. Temperature T = 298 K (though not directly needed for this calculation if K_H is given at this T).

First, calculate the mole fraction (x_{CO_2}) of CO_2 dissolved in water:

$$x_{CO_2} = \frac{p_{CO_2}}{K_H} = \frac{2.53 \times 10^5 \,\text{Pa}}{1.67 \times 10^8 \,\text{Pa}}$$

$$x_{CO_2} \approx 1.515 \times 10^{-3}$$

Mole fraction is defined as:

$$x_{CO_2} = \frac{\text{moles of } CO_2}{\text{moles of } CO_2 + \text{moles of } H_2O}$$

Let n_{CO_2} be the moles of CO_2 and n_{H_2O} be the moles of water. Since the solubility of CO_2 is low (mole fraction is small), we can approximate $n_{CO_2} + n_{H_2O} \approx n_{H_2O}$.

$$x_{CO_2} \approx \frac{n_{CO_2}}{n_{H_2O}}$$

Now, calculate the moles of water in 500 ml. Assume the density of water is approximately 1 g/ml. Mass of water = Volume $\times$ Density = 500 ml $\times$ 1 g/ml = 500 g. Molar mass of water (H_2O) = 2(1.01) + 16.00 = 18.02 g/mol $\approx$ 18 g/mol. Moles of water $n_{H_2O} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{500\,\text{g}}{18\,\text{g/mol}} \approx 27.78\,\text{mol}$. Now, calculate the moles of CO_2:

$$n_{CO_2} \approx x_{CO_2} \times n_{H_2O}$$

$$n_{CO_2} \approx (1.515 \times 10^{-3}) \times (27.78\,\text{mol})$$

$$n_{CO_2} \approx 0.04209\,\text{mol}$$

The number of moles of CO_2 dissolved is approximately 0.0421 mol.

Quick Tip

Henry's Law. $p = K_H x$. Relates partial pressure of gas (p) to its mole fraction (x) in solution via Henry's constant (K_H). For dilute solutions, $x_{gas} \approx n_{gas}/n_{solvent}$.

23.

Calculate $\Delta_r G^\circ$ and log K_C of the reaction..

2Cr(s) + 3Cd^{2+}(aq) $\rightarrow$ 2Cr^{3+}(aq) + 3Cd(s).

Given $E^\circ_{Cr^{3+}/Cr}$ = -0.74 V.

$E^\circ_{Cd^{2+}/Cd}$ = -0.40 V.

[R = 8.314 J K^{-1} mol^{-1}, F = 96500 C mol^{-1}].

Solution:

First, identify the half-reactions and calculate the standard cell potential (E°_{cell}). The reaction shows Cr(s) being oxidized to Cr^{3+} and Cd^{2+} being reduced to Cd(s). Anode (Oxidation): Cr(s) $\rightarrow$ Cr^{3+}(aq) + 3e$^-$. $E^\circ_{anode} = E^\circ_{Cr^{3+}/Cr} = -0.74$ V. Cathode (Reduction): Cd^{2+}(aq) + 2e$^-$ $\rightarrow$ Cd(s). $E^\circ_{cathode} = E^\circ_{Cd^{2+}/Cd} = -0.40$ V. Calculate standard cell potential:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = (-0.40\,\text{V}) - (-0.74\,\text{V})$$

$$E^\circ_{cell} = -0.40 + 0.74 = +0.34\,\text{V}$$

Next, determine the number of moles of electrons (n) transferred in the balanced overall reaction. Oxidation: $2Cr \rightarrow 2Cr^{3+} + 6e^-$ Reduction: $3Cd^{2+} + 6e^- \rightarrow 3Cd$ The number of electrons transferred is $n = 6$. Now calculate the standard Gibbs free energy change ($\Delta_r G^\circ$):

$$\Delta_r G^\circ = -nFE^\circ_{cell}$$

$$\Delta_r G^\circ = -(6\,\text{mol}) \times (96500\,\text{C mol}^{-1}) \times (0.34\,\text{V})$$

Note: 1 C × 1 V = 1 J.

$$\Delta_r G^\circ = -(6 \times 96500 \times 0.34)\,\text{J}$$

$$\Delta_r G^\circ = -196860\,\text{J} = -196.86\,\text{kJ}$$

Finally, calculate the logarithm of the equilibrium constant (log K_C). The relationship is:

$$\Delta_r G^\circ = -RT \ln K_c = -RT(2.303 \log_{10} K_c)$$

$$\log_{10} K_c = -\frac{\Delta_r G^\circ}{2.303RT}$$

Assuming standard temperature T = 298 K:

$$\log_{10} K_c = -\frac{-196860\,\text{J mol}^{-1}}{2.303 \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}$$

$$\log_{10} K_c = \frac{196860}{2.303 \times 8.314 \times 298} \approx \frac{196860}{5705.8} \approx 34.50$$

Alternatively, using the Nernst equation relationship at standard conditions:

$$E^\circ_{cell} = \frac{RT}{nF} \ln K_c = \frac{2.303RT}{nF} \log_{10} K_c$$

At T=298 K, $\frac{2.303RT}{F} \approx 0.0591$ V.

$$E^\circ_{cell} = \frac{0.0591}{n} \log_{10} K_c$$

$$0.34 = \frac{0.0591}{6} \log_{10} K_c$$

$$\log_{10} K_c = \frac{0.34 \times 6}{0.0591} = \frac{2.04}{0.0591} \approx 34.517$$

Results:

$$\Delta_r G^\circ \approx -196.9\,\text{kJ/mol}$$

$$\log_{10} K_c \approx 34.5$$

Quick Tip

Electrochemistry Relations. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$. $\Delta G^\circ = -nFE^\circ_{cell}$. $\Delta G^\circ = -RT\ln K_c$ or $E^\circ_{cell} = (RT/nF)\ln K_c$. Determine n from balanced half-reactions.

24.

The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature..

[Given : log 4 = 0.602, log 2 = 0.301, R = 8.314 J K^{-1} mol^{-1}].

Solution:

We use the Arrhenius equation, which relates the rate constant (k) to temperature (T) and activation energy (E_a):

$$k = Ae^{-E_a/RT}$$

where A is the pre-exponential factor. Consider the rates at two different temperatures, $T_1 = 293$ K and $T_2 = 313$ K. Let the corresponding rate constants be k_1 and k_2.

$$k_1 = Ae^{-E_a/RT_1}$$

$$k_2 = Ae^{-E_a/RT_2}$$

Since the rate quadruples (Rate $\propto$ k, assuming concentrations are constant), we have $k_2 = 4k_1$. Taking the ratio k_2/k_1:

$$\frac{k_2}{k_1} = \frac{Ae^{-E_a/RT_2}}{Ae^{-E_a/RT_1}} = e^{-\frac{E_a}{RT_2}+\frac{E_a}{RT_1}} = e^{\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

We have $k_2/k_1 = 4$. Taking the natural logarithm of both sides:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\ln(4) = \frac{E_a}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

Converting natural log to base 10 log ($\ln x = 2.303\log_{10} x$):

$$2.303\log_{10}(4) = \frac{E_a}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

Substitute the given values: $\log_{10}(4) = 0.602$ (Note:

$log4 = log(2^2) = 2log2 = 2 \times 0.301 = 0.602$) $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ $T_1 = 293\ \text{K}$ $T_2 = 313\ \text{K}$

$T_2 - T_1 = 313 - 293 = 20\ \text{K}$ $T_1T_2 = 293 \times 313 = 91709\ \text{K}^2$

$$2.303 \times 0.602 = \frac{E_a}{8.314}\left(\frac{20}{91709}\right)$$

$$1.3864 \approx \frac{E_a}{8.314}\left(2.181 \times 10^{-4}\right)$$

$$E_a \approx \frac{1.3864 \times 8.314}{2.181 \times 10^{-4}}$$

$$E_a \approx \frac{11.526}{2.181 \times 10^{-4}} \approx 52847\,\text{J/mol}$$

$$E_a \approx 52.85\,\text{kJ/mol}$$

The energy of activation is approximately 52.85 kJ/mol.

Quick Tip

Arrhenius Equation (Two Temperatures). $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Use absolute temperatures (K). Remember $\ln x = 2.303 \log_{10} x$. k_2/k_1 is the factor by which the rate increases.

25.

(A) Draw the structure of the major monohalo product for each of the following reaction :.

(a) Ethylbenzene + Br_2/Heat.

(b) Methylcyclohexane + HBr.

(c) p-Cresol + HCl/Heat.

OR.

(B) How do you convert :.

(a) Chlorobenzene to biphenyl.

(b) Propene to 1-Iodopropane.

(c) 2-bromobutane to but-2-ene..

Solution:

(A) Major Monohalo Products:.

(a) Ethylbenzene + Br_2/Heat (or UV light): This condition favors free radical halogenation at the benzylic position because the benzylic radical intermediate is resonance stabilized. Bromination occurs preferentially at the secondary benzylic carbon. Product: **1-Bromo-1-phenylethane** (C_6H_5-CH(Br)-CH_3).

(b) Methylcyclohexane + HBr: This is electrophilic addition of HBr to an alkene, but methylcyclohexane is an alkane. Alkanes do not readily react with HBr under normal conditions (unless free radical conditions are specified, which are not). Assuming the starting material was methylcyclohexene (e.g., 1-methylcyclohexene), HBr adds according to Markovnikov's rule. The H^+ adds to the double bond carbon with more hydrogens, forming the more stable carbocation (tertiary in this case). Br^- then attacks the carbocation. Product (assuming 1-methylcyclohexene): **1-Bromo-1-methylcyclohexane**.

(c) p-Cresol + HCl/Heat: p-Cresol is 4-methylphenol. Phenols are generally unreactive towards nucleophilic substitution at the OH group under these conditions. Reaction with HCl primarily involves the aromatic ring undergoing electrophilic substitution if conditions are harsh (e.g., with Lewis acid), but HCl is a weak electrophile source. Direct substitution of OH by Cl with HCl/Heat is usually ineffective for phenols. However, if considering electrophilic substitution on the ring, the OH group is strongly activating and ortho/para directing. The methyl group is also activating (ortho/para). The ortho positions to OH are most activated. Possible Product (Electrophilic Substitution): **2-Chloro-4-methylphenol**. (Reaction may be slow or require a catalyst). If forcing conditions replace OH, product might be p-chlorotoluene, but this is less likely.

OR.

(B) Conversions:.

(a) Chlorobenzene to biphenyl: Wurtz-Fittig reaction or Fittig reaction. React chlorobenzene with sodium metal in dry ether. Two molecules of chlorobenzene couple.

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

(b) Propene to 1-Iodopropane: This requires anti-Markovnikov addition of HI. This is typically achieved by adding HBr in the presence of peroxides (free radical mechanism gives anti-Markovnikov product 1-bromopropane), followed by substitution of Br with I using NaI in acetone (Finkelstein reaction). Direct anti-Markovnikov addition of HI is not standard.

Step 1: CH_3-CH=CH_2 + HBr $\xrightarrow{\text{Peroxides}}$ $CH_3CH_2CH_2Br$

Step 2: $CH_3CH_2CH_2Br$ + NaI $\xrightarrow{\text{Acetone}}$ $CH_3CH_2CH_2I$ + NaBr

(c) 2-bromobutane to but-2-ene: This is an elimination reaction (dehydrohalogenation). Treat 2-bromobutane with a strong base in alcohol, typically alcoholic KOH, and heat. Elimination follows Saytzeff's (Zaitsev's) rule, favoring the formation of the more substituted alkene. CH_3-CH(Br)-CH_2-CH_3 $\xrightarrow{\text{Alc. KOH},\Delta}$ CH_3-CH=CH-CH_3 (But-2-ene, major product) + CH_2=CH-CH_2-CH_3 (But-1-ene, minor product) + KBr + H_2O

Quick Tip

Reactions. Free radical halogenation (alkanes/benzylic). Electrophilic addition (alkenes, Markovnikov). Phenol reactivity (ring activation, difficult OH substitution). Fittig/Wurtz-Fittig (aryl/alkyl halide coupling with Na). Anti-Markovnikov addition (HBr/peroxide). Elimination (Alkyl halide + Alc. Base $\rightarrow$ Alkene, Saytzeff's rule).

26.

The elements of 3d transition series are given as : Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn. Answer the following :.

(a) Copper has exceptionally positive $E^{\circ}_{M^{2+}/M}$ value, why ?.

(b) Which element is a strong reducing agent in +2 oxidation state and why ?.

(c) Zn^{2+} salts are colourless. Why ?.

Solution:

(a) Positive $E^{\circ}_{Cu^{2+}/Cu}$ Value: The standard electrode potential involves the enthalpy changes for atomization ($\Delta_{\text{at}}H$), ionization ($IE_1 + IE_2$), and hydration ($\Delta_{\text{hyd}}H$). M(s) $\xrightarrow{\Delta_{\text{at}}H}$ M(g) $\xrightarrow{IE_1+IE_2}$ M^{2+}(g) $\xrightarrow{\Delta_{\text{hyd}}H}$ M^{2+}(aq).

Copper has a high enthalpy of atomization and relatively high sum of first and second ionization enthalpies (especially IE_2 due to removing an electron from the stable d^{10} configuration of Cu^+). Although the hydration enthalpy of Cu^{2+} is high (negative), it does not fully compensate for the high energy required to form Cu^{2+}(g) from Cu(s). This results in a positive overall energy change for the process relative to the standard hydrogen

electrode, leading to a positive standard reduction potential $E^{\circ}_{Cu^{2+}/Cu}$ (+0.34 V). This means copper is less readily oxidized than hydrogen.

(b) Strong Reducing Agent in +2 State: A strong reducing agent readily loses electrons (gets oxidized). We need an element whose M^{2+} ion can be easily oxidized further, or whose M^{2+} ion is less stable relative to a higher oxidation state or the metal itself. Considering the M^{3+}/M^{2+} potentials, Cr^{2+} is a strong reducing agent because its configuration changes from d^4 to the more stable half-filled $t_{2g}{}^3$ configuration of Cr^{3+} ($E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.41$ V, meaning Cr^{2+} is easily oxidized). Similarly, Fe^{2+} (d^6) can be oxidized to Fe^{3+} (d^5, half-filled). Comparing standard potentials, Cr^{2+} is generally considered the strongest reducing agent among the common +2 ions of the first transition series in aqueous solution.

Answer: Chromium (Cr). **Reason:** Cr^{2+} (d^4) is readily oxidized to Cr^{3+} (d^3) because Cr^{3+} achieves a stable half-filled t_{2g} level in an octahedral field ($t^3_{2g}e^0_g$).

(c) Zn^{2+} Salts are Colourless: The color of transition metal compounds often arises from d-d electronic transitions, where an electron absorbs visible light energy to move from a lower energy d-orbital to a higher energy d-orbital (split by the ligand field). This requires the presence of partially filled d-orbitals. Zinc (Zn) has atomic number 30, with electronic configuration [Ar] $3d^{10}$ $4s^2$. The Zn^{2+} ion is formed by losing the two 4s electrons, resulting in the configuration [Ar] $3d^{10}$. Since the 3d subshell is completely filled (d^{10}), there are no available d-orbitals for electrons to transition into upon absorbing visible light energy. Therefore, d-d transitions cannot occur, and Zn^{2+} salts are typically colorless (or white).

Quick Tip

Transition Metal Properties. Electrode potentials depend on $\Delta_{at}H, IE, \Delta_{hyd}H$. Reducing strength relates to ease of oxidation (check electrode potentials, electronic configuration stability). Color arises from d-d transitions, requiring partially filled d-orbitals. d^0 and d^{10} ions are colorless.

27.

(a) Arrange the following compounds in increasing order of their boiling point :. $(CH_3)_2NH$, $CH_3CH_2NH_2$, CH_3CH_2OH..

(b) Give plausible explanation for each of the following :.

(i) Aromatic primary amines cannot be prepared by Gabriel Phthalimide synthesis..

(ii) Amides are less basic than amines..

Solution:

(a) Boiling Point Order: Boiling points depend on intermolecular forces. All three compounds have similar molecular weights (Ethanol=46, Ethylamine=45, Dimethylamine=45). - CH_3CH_2OH (Ethanol): A primary alcohol. Oxygen is highly electronegative. Ethanol exhibits strong intermolecular hydrogen bonding due to the O-H group. - $CH_3CH_2NH_2$ (Ethylamine): A primary amine. Nitrogen is less electronegative than oxygen. Ethylamine exhibits intermolecular hydrogen bonding due to the N-H bonds, but these are weaker than O-H hydrogen bonds. - $(CH_3)_2NH$ (Dimethylamine): A secondary amine. It has one N-H bond and can participate in hydrogen bonding, but the steric hindrance from the two methyl groups might slightly reduce the effectiveness compared to the primary amine. Also, the N-H bond polarity is similar to ethylamine. Generally, $1\circ$ amines have slightly higher BPs than isomeric $2\circ$ amines due to better H-bonding potential. Comparing strengths of intermolecular forces: O-H bonds $>$ N-H bonds. Therefore, ethanol will have the highest boiling point. Comparing the amines, the primary amine (ethylamine) can form more extensive hydrogen bonds than the secondary amine (dimethylamine), leading to a slightly higher boiling point. Increasing order of boiling point: **$(CH_3)_2NH$ ¡ $CH_3CH_2NH_2$ ¡ CH_3CH_2OH**.

(b) Plausible Explanations:.

(i) Gabriel Synthesis Limitation: The Gabriel synthesis involves the nucleophilic attack of the phthalimide anion on an alkyl halide (S_N2 reaction), followed by hydrolysis to yield a primary amine. For preparing aromatic primary amines (like aniline), the required starting material would be an aryl halide (e.g., chlorobenzene). Aryl halides are generally unreactive towards nucleophilic substitution (S_N2) reactions because the C-X bond has partial double bond character due to resonance with the ring, and backside attack required for S_N2 is sterically hindered by the ring. Therefore, the phthalimide anion cannot effectively displace the halide from an aryl halide, making Gabriel synthesis unsuitable for preparing aromatic primary amines.

(ii) Amides vs Amines Basicity: Basicity relates to the availability of the lone pair of electrons on the nitrogen atom to accept a proton.

- In amines (like RNH_2), the lone pair on nitrogen is localized and readily available for protonation.
- In amides ($RCONH_2$), the lone pair on the nitrogen atom is adjacent to the electron-withdrawing carbonyl group (C=O). This lone pair can participate in resonance with the carbonyl group ($-C(=O)-NH_2 \leftrightarrow -C(O^-)=N^+H_2$). This delocalization makes the lone pair on nitrogen less available for accepting a proton compared to amines. Consequently, amides are much weaker bases (essentially neutral in water) than amines.

Quick Tip

Concepts. Boiling Points: H-bonding strength O-H $>$ N-H. Primary amines often have slightly higher BP than isomeric secondary amines. Gabriel Synthesis: S_N2 reaction, works for alkyl halides, fails for unreactive aryl halides. Basicity: Availability of N lone pair. Resonance delocalization (amides) decreases basicity compared to localized lone pair (amines).

28.

Define the following terms :.

(a) Native Protein.

(b) Nucleotide.

(c) Essential amino acid.

Solution:

(a) Native Protein:.

The term ”native protein” refers to a protein in its functional, fully folded three-dimensional conformation, as it exists naturally within a biological system. This specific spatial arrangement (including secondary, tertiary, and potentially quaternary structure) is crucial for

the protein's biological activity. When a protein loses this specific structure (e.g., due to heat, pH changes, chemicals), it undergoes denaturation and loses its function; the denatured state is non-native.

(b) Nucleotide:.

A nucleotide is the basic structural unit (monomer) of nucleic acids like DNA and RNA. It consists of three components covalently linked together: 1. A nitrogenous base (either a purine: Adenine (A), Guanine (G); or a pyrimidine: Cytosine (C), Thymine (T) in DNA, Uracil (U) in RNA). 2. A pentose sugar (Deoxyribose in DNA, Ribose in RNA). 3. One or more phosphate groups (typically attached to the 5' carbon of the sugar). Nucleotides also serve as energy carriers (e.g., ATP, GTP) and signaling molecules (e.g., cAMP).

(c) Essential Amino Acid:.

Essential amino acids are amino acids that cannot be synthesized by an organism (specifically, humans in this context) in sufficient quantities to meet its physiological needs and must therefore be obtained from the diet. There are typically considered 9 essential amino acids for adult humans: histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine. Lack of any essential amino acid in the diet can lead to protein deficiency and health problems.

Quick Tip

Biomolecule Definitions. Native Protein: Functional, folded 3D structure. Nucleotide: Base + Sugar + Phosphate (monomer of nucleic acids). Essential Amino Acid: Cannot be synthesized by the body, must be obtained from diet.

Section D

Questions No. 29 to 30

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

29.

Phenols undergo electrophilic substitution reactions readily due to the strong activating effect of the OH group attached to the benzene ring. Since, the OH group increases the electron density more to the ortho- and para- positions, therefore OH group is ortho, para-directing. Reimer-Tiemann reaction is one of the examples of aldehyde group being introduced on the aromatic ring of phenol, ortho to the hydroxyl group. This is a general method used for the ortho-formylation of phenols..

Answer the following questions:.

(a) What happens when phenol reacts with:.

(i) Br_2/CS_2

(ii) Conc. HNO_3

(b) Why phenol does not undergo protonation readily?.

(c) Which is a stronger acid – phenol or cresol? Give reason..

OR.

(d) Write the IUPAC name of the product formed in the Reimer-Tiemann reaction..

Solution:

(a) What happens when phenol reacts with:.

(i) **Br_2/CS_2:**

Phenol reacts with bromine in carbon disulfide (CS_2) to form 2,4,6-Tribromophenol. The hydroxyl group (-OH) is an electron-donating group and increases the electron density on the benzene ring, especially at the ortho- and para-positions, leading to the substitution of bromine at these positions. The major product is 2,4,6-tribromophenol.

$$C_6H_5OH + 3Br_2 \xrightarrow{CS_2} C_6H_2(Br)_3OH$$

(ii) **Conc. HNO_3:**

Phenol reacts with concentrated nitric acid (HNO_3) to form picric acid (2,4,6-Trinitrophenol). The reaction involves nitration where the -OH group makes the phenol more reactive towards the electrophilic nitronium ion (NO_2^+) formed in the reaction.

The nitration occurs predominantly at the ortho- and para-positions relative to the hydroxyl group.

$$C_6H_5OH + 3HNO_3 \rightarrow C_6H_2(NO_2)_3OH$$

(b) Why phenol does not undergo protonation readily?.

Phenol does not undergo protonation readily because the lone pair of electrons on the oxygen atom of the -OH group is involved in resonance with the benzene ring, making the electron density on the oxygen atom lower. This delocalization of the lone pair makes phenol less basic compared to alcohols, and hence, it is less likely to accept a proton under normal conditions.

(c) Which is a stronger acid – phenol or cresol? Give reason..

Cresol (methylphenol) is a stronger acid than phenol. The methyl group (-CH_3) is an electron-donating group, which increases the electron density on the benzene ring. This makes the phenoxide ion (the conjugate base) less stabilized and thus increases the acidity of phenol compared to cresol. Therefore, cresol is a stronger acid than phenol.

OR.

(d) Write the IUPAC name of the product formed in the Reimer-Tiemann reaction..

The Reimer-Tiemann reaction involves the formylation of phenol with chloroform ($CHCl_3$) in the presence of a base (such as NaOH) to form an ortho-hydroxybenzaldehyde (salicylaldehyde). The IUPAC name of the product is **2-Hydroxybenzaldehyde**. The formyl group (-CHO) is introduced at the ortho position to the hydroxyl group on the benzene ring.

Quick Tip

Electrophilic Substitution in Phenols. The hydroxyl group ($-OH$) in phenols is an electron-donating group and makes the benzene ring more reactive towards electrophiles, especially at the ortho- and para- positions. This is why phenol undergoes electrophilic substitution reactions like halogenation and nitration more readily than benzene itself.

30.

The rate of a chemical reaction is expressed either in terms of decrease in the concentration of reactants or increase in the concentration of a product per unit time. Rate of the reaction depends upon the nature of reactants, concentration of reactants, temperature, presence of catalyst, surface area of the reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the Rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction..

Answer the following questions:.

(i) What is a rate determining step?.

(ii) Define complex reaction..

(iii) What is the effect of temperature on the rate constant of a reaction?.

OR.

(a) Why is molecularity applicable only for elementary reactions whereas order is applicable for elementary as well as complex reactions?.

(b) The conversion of molecule X to Y follows second-order kinetics. If the concentration of X is increased 3 times, how will it affect the rate of formation of Y?.

Solution:

(i) What is a rate determining step?.

The rate-determining step (RDS) is the slowest step in a multi-step reaction mechanism. It limits the overall rate of the reaction and dictates the reaction rate, as the rest of the steps occur faster. The rate law of the overall reaction is often determined by the rate-determining step.

(ii) Define complex reaction..

A complex reaction is a chemical reaction that occurs via a sequence of two or more elementary steps. Unlike a simple reaction that proceeds in one step, a complex reaction involves intermediates that are formed and consumed during the process. The overall

reaction does not necessarily reflect the stoichiometry of the elementary steps.

(iii) What is the effect of temperature on the rate constant of a reaction?.

According to the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature in Kelvin. As the temperature increases, the rate constant k increases, because the exponential factor $e^{-E_a/RT}$ becomes larger, meaning the reaction is more likely to occur at higher temperatures.

OR.

(a) Why is molecularity applicable only for elementary reactions whereas order is applicable for elementary as well as complex reactions?.

Molecularity refers to the number of reacting species involved in an elementary reaction, and it is always a small integer (1, 2, or 3). It cannot be determined for complex reactions, which occur in multiple steps. In complex reactions, the overall reaction order is determined experimentally from the rate law, not from molecularity. The order of reaction can be fractional, zero, or even negative, making it applicable to both elementary and complex reactions.

(b) The conversion of molecule X to Y follows second-order kinetics. If the concentration of X is increased 3 times, how will it affect the rate of formation of Y?.

For second-order reactions, the rate law is:

$$\text{Rate} = k[\text{X}]^2$$

If the concentration of X is increased 3 times, the new rate will be:

$$\text{New Rate} = k(3[\text{X}])^2 = 9 \times k[\text{X}]^2$$

Thus, the rate will increase by a factor of $3^2 = 9$.

Quick Tip

Rate Law and Molecularity. The rate-determining step is the slowest step in a reaction mechanism that limits the overall reaction rate. Molecularity applies only to elementary reactions and represents the number of molecules involved in that step, while order applies to both elementary and complex reactions and is determined experimentally.

Section E

Questions No. 31 to 33

31.

(A).

(a) Carry out the following conversions :.

(i) Ethanal to But-2-enal.

(ii) Propanoic acid to ethane.

(b) An alkene A with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds B and C. Compound B gives positive Fehling test and also reacts with iodine and NaOH solution. Compound C does not give Fehling solution test but forms iodoform. Identify the compounds A, B and C..

OR.

(B) An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolyzed with dilute sulphuric acid to get a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives But-1-ene. Identify (A), (B) and (C) and write chemical equations for the reactions involved..

Solution:

(A).

(a) Conversions:.

(i) Ethanal to But-2-enal: This is an Aldol condensation followed by dehydration.

1. Aldol Addition: Two molecules of ethanal condense in the presence of dilute base.

$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{CH_3CH(OH)CH_2CHO}$$

2. Dehydration: Heating the aldol product eliminates water.

$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} \underset{\text{But-2-enal}}{CH_3CH{=}CHCHO} + H_2O$$

(ii) Propanoic acid to ethane: Soda lime decarboxylation of the sodium salt.

1. Salt formation:

$$CH_3CH_2COOH + NaOH \rightarrow \underset{\text{Sodium propanoate}}{CH_3CH_2COONa} + H_2O$$

2. Decarboxylation: Heating the salt with soda lime.

$$CH_3CH_2COONa + NaOH \xrightarrow{CaO,\Delta} \underset{\text{Ethane}}{CH_3CH_3} + Na_2CO_3$$

(b) Identification of A, B, and C:.

Alkene A (C_5H_{10}) $\xrightarrow{\text{Ozonolysis}}$ B + C. - B gives positive Fehling test $\implies$ B is an aldehyde. - B gives positive Iodoform test $\implies$ B has CH_3CO- group or is ethanal. Since B is an aldehyde, **B must be Ethanal (CH_3CHO)**. - C does not give Fehling test $\implies$ C is a ketone. - C gives positive Iodoform test $\implies$ C has CH_3CO- group (is a methyl ketone). - Total carbons in A = 5. Carbons in B = 2. Carbons in C = 5 - 2 = 3. - A 3-carbon methyl ketone is **Propanone (Acetone, CH_3COCH_3)** = C. - To find A, join the carbonyl carbons of B and C with a double bond:

$$CH_3CH{=}O + O{=}C(CH_3)_2 \rightarrow CH_3CH{=}C(CH_3)_2$$

- Alkene **A is 2-Methylbut-2-ene**. (Formula C_5H_{10}, consistent).

OR.

(B) Identification of A, B, and C:.

1. Compound A ($C_8H_{16}O_2$) is hydrolyzed by dilute acid to give carboxylic acid B and alcohol C. This indicates A is an ester.

$$\underset{\text{(A)}}{RCOOR'} + H_2O \xrightarrow{H^+} \underset{\text{(B)}}{RCOOH} + \underset{\text{(C)}}{R'OH}$$

2. Alcohol C on dehydration gives But-1-ene ($CH_3CH_2CH{=}CH_2$). Dehydration removes -OH and an adjacent -H. Since But-1-ene is formed, the alcohol C must have 4 carbons and the -OH group must be on C1 or C2. The structure must be $CH_3CH_2CH_2CH_2OH$ (Butan-1-ol) or $CH_3CH_2CH(OH)CH_3$ (Butan-2-ol). Dehydration of Butan-1-ol mainly gives But-1-ene. Dehydration of Butan-2-ol mainly gives But-2-ene (Saytzeff). Since But-1-ene is formed, **C is Butan-1-ol ($\mathbf{CH_3CH_2CH_2CH_2OH}$)**.

3. Oxidation of alcohol C (Butan-1-ol) with chromic acid (a strong oxidizing agent) produced carboxylic acid B. Oxidation of a primary alcohol (Butan-1-ol) gives the corresponding carboxylic acid with the same number of carbons.

$$CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Chromic Acid}} CH_3CH_2CH_2COOH$$

So, **B is Butanoic acid ($\mathbf{CH_3CH_2CH_2COOH}$)**.

4. Ester A is formed from acid B and alcohol C. A = RCOOR'. Here RCOOH is Butanoic acid (R = $CH_3CH_2CH_2$-) and R'OH is Butan-1-ol (R' = $CH_3CH_2CH_2CH_3$). So, A is Butyl butanoate. **A = Butyl butanoate ($\mathbf{CH_3CH_2CH_2COO\text{-}CH_2CH_2CH_2CH_3}$)**. Check formula for A: $C_8H_{16}O_2$. (4C in acid part + 4C in alcohol part = 8C; 7H in acid alkyl + 9H in alcohol alkyl = 16H; 2O). Formula matches.

Chemical Equations: - Hydrolysis of A:

$$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH$$

- Oxidation of C:

$$CH_3CH_2CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CH_2COOH$$

(Using Chromic acid, e.g., $K_2Cr_2O_7/H_2SO_4$) - Dehydration of C:

$$CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Conc. } H_2SO_4, \Delta} CH_3CH_2CH{=}CH_2 + H_2O$$

Quick Tip

Organic Reactions Structure Determination. Use characteristic reactions: Aldol (2 Aldehydes $\rightarrow$ α,β-Unsaturated Aldehyde), Soda Lime (RCOONa $\rightarrow$ RH), Ozonolysis (C=C $\rightarrow$ C=O), Fehling's (+Aldehyde), Iodoform (+CH_3CO- or $CH_3CH(OH)$-), Ester Hydrolysis ($\rightarrow$ Acid + Alcohol), Alcohol Oxidation ($1^\circ \rightarrow$ Acid (strong ox.)), Alcohol Dehydration ($\rightarrow$ Alkene).

32.

(A).

For the complex $[Fe(en)_2Cl_2]^+$, identify:

(a) The oxidation number of iron.

(b) The hybridization and the shape of the complex.

(c) The magnetic behaviour of the complex.

(d) Whether there is an optical isomer of the complex? If so, draw its structure.

(e) IUPAC name of the complex.

(At. no. of Fe = 26)

Solution:

(a) Oxidation number of iron:.

In the complex $[Fe(en)_2Cl_2]^+$, en (ethylenediamine) is a neutral ligand, and Cl is a monodentate anionic ligand. Let the oxidation number of Fe be x. For two chloride ions, each with a charge of -1, the charge balance equation is:

$$x + 2(-1) + 0 = +1 \quad \text{(since the overall charge of the complex is +1)}$$

Thus, $x = +3$. Therefore, the oxidation number of iron is +3.

(b) Hybridization and Shape of the Complex:.

Since the complex involves 2 bidentate ethylenediamine ligands and 2 chloride ions, the coordination number of iron is 6. In this case, iron will be in an octahedral arrangement with respect to the ligands. Hence, the hybridization of Fe is d^2sp^3, and the shape of the complex is octahedral.

(c) Magnetic Behaviour of the Complex:.

The electronic configuration of Fe^{3+} is $3d^5$. Since there are 5 unpaired electrons in the d-orbitals, the complex will be paramagnetic.

(d) Optical Isomerism:.

Since the complex contains two bidentate ligands (ethylenediamine), it may exhibit optical isomerism. This is because the complex does not have a plane of symmetry, making it capable of existing as non-superimposable mirror images. Therefore, the complex exhibits optical isomerism.

(e) IUPAC Name of the Complex:.

The IUPAC name of the complex is **bis(ethylenediamine)chloridoiron(III) chloride**.

OR.

(B) (a) Using IUPAC norms, write the names of the following:

(i) $[Co(NH_3)_4Cl(NO_3)]Cl$

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

(iii) $[Cr(C_2O_4)_3]^{3-}$

Solution:

(i) IUPAC Name:.

For $[Co(NH_3)_4Cl(NO_3)]Cl$, the central metal is cobalt, and the ligands are four ammine (NH_3), one chloride (Cl), and one nitrate (NO_3). The IUPAC name is **tetraamminechloridonitratocobalt(III) chloride**.

(ii) IUPAC Name:.

For $K_3[Fe(CN)_6]$, the central metal is iron, and the ligand is cyanide (CN). The complex is in the +3 oxidation state of iron. The IUPAC name is **potassium hexacyanoferrate(III)**.

(iii) IUPAC Name:.

For $[Cr(C_2O_4)_3]^{3-}$, the central metal is chromium, and the ligand is oxalate ($C_2O_4^{2-}$). The IUPAC name is **tris(oxalato)chromium(III)**.

(b) What is crystal field splitting energy? Why low spin tetrahedral complexes are not formed?.

Solution:

Crystal Field Splitting Energy (CFSE):.

Crystal Field Splitting Energy is the energy difference between two sets of degenerate orbitals in a metal complex, caused by the interaction between the central metal ion and the ligands. In octahedral complexes, the d-orbitals split into two sets, e_g (higher energy) and t_{2g} (lower energy), and the difference between these energy levels is called the crystal field splitting energy (Δ). The value of Δ determines the stability and magnetic properties of the complex.

Low Spin Tetrahedral Complexes:.

Tetrahedral complexes are generally high spin because the crystal field splitting energy (Δ_t) in tetrahedral geometry is much smaller than in octahedral geometry. In tetrahedral complexes, the splitting energy between the e and t_2 orbitals is relatively small, and it does not favor the pairing of electrons. Hence, low spin tetrahedral complexes are rare. The low spin state is usually favored in octahedral complexes with strong field ligands.

Quick Tip

Magnetic Properties and Field Strength. In octahedral complexes, stronger field ligands lead to larger crystal field splitting energy (Δ), which may favor the low spin state (fewer unpaired electrons). In tetrahedral complexes, the splitting energy is smaller, making them typically high spin with more unpaired electrons.

33.

(A).

(a) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K:.

Sn(s) — Sn^{2+} (0.004 M) —— H^+ (0.02 M) — H_2(g) (1 Bar) — Pt(s).

(Given: $E^\circ_{Sn^{2+}/Sn}$ = -0.14 V, $E^\circ_{H^+/H_2(g),Pt}$ = 0.00V).

(b) Account for the following ; (i) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl..

(ii) Conductivity of CH_3COOH decreases on dilution..

OR.

(B).

(a) Write the anode and cathode reactions and the overall cell reaction occurring in a lead storage battery during its use..

(b) Calculate the potential for half-cell containing 0.01 M $K_2Cr_2O_7$(aq), 0.01M Cr^{3+} (aq) and 1.0 x 10^{-4} M H^+(aq)..

The half cell reaction is.

$Cr_2O_7^{2-}$(aq) + 14H^+(aq) + 6e^- $\rightarrow$ 2Cr^{3+}(aq) + 7H_2O(l).

and the standard electrode potential is given as E° = 1.33 V..

[Given : log 10 = 1].

Solution:

(A).

(a) Cell Reaction and EMF Calculation:.

Half-reactions based on standard potentials ($E^\circ_{H^+/H_2} = 0.00V > E^\circ_{Sn^{2+}/Sn} = -0.14V$): Anode (Oxidation): Sn(s) $\rightarrow$ Sn^{2+}(aq, 0.004 M) + $2e^-$

Cathode (Reduction): $2H^+$(aq, 0.02 M) + $2e^- \rightarrow$ H_2(g, 1 Bar)

Overall Cell Reaction: **Sn(s) + $2H^+$(aq, 0.02 M) $\rightarrow$ Sn^{2+}(aq, 0.004 M) + H_2(g, 1 Bar).**

Standard Cell EMF: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.00 - (-0.14) = +0.14$ V.

Nernst Equation at 298 K: $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log_{10} Q$

Number of electrons transferred $n = 2$.

Reaction Quotient $Q = \frac{[Sn^{2+}]P_{H_2}}{[H^+]^2} = \frac{(0.004)(1)}{(0.02)^2} = \frac{0.004}{0.0004} = 10$.

$$E_{cell} = 0.14 - \frac{0.0591}{2} \log_{10}(10)$$

$$E_{cell} = 0.14 - \frac{0.0591}{2} \times 1$$

$$E_{cell} = 0.14 - 0.02955$$

$$E_{cell} \approx 0.110\,\text{V}$$

Cell EMF at 298 K is approximately 0.110 V..

(b) Account for the following:.

(i) Electrolysis of Aqueous NaCl: At the anode (oxidation), possible reactions are: 1. $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad E^\circ_{ox} = -1.36$ V (Note: Oxidation potential = - Reduction Potential) 2. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^\circ_{ox} = -1.23$ V Based solely on standard potentials, the oxidation of water to O_2 ($E^\circ_{ox} = -1.23$ V) is thermodynamically more favorable (less negative oxidation potential) than the oxidation of chloride to Cl_2 ($E^\circ_{ox} = -1.36$ V). However, the formation of oxygen gas from water often requires a significant overpotential (extra voltage) on many electrode surfaces (like platinum or graphite). This overpotential makes the actual voltage required for O_2 liberation higher than the theoretical value. Consequently, under typical electrolysis conditions (especially with

concentrated NaCl), the oxidation of chloride ions to Cl_2 becomes kinetically favored and occurs preferentially, despite the standard potential values suggesting otherwise.

(ii) Conductivity of CH_3COOH on Dilution: Acetic acid (CH_3COOH) is a weak electrolyte. Its conductivity depends on both the concentration of ions and their mobility. $CH_3COOH \rightleftharpoons CH_3COO^-$ + H^+ Upon dilution, the degree of dissociation (α) of a weak electrolyte increases according to Ostwald's dilution law. This leads to an increase in the *total number* of ions in the solution relative to the undissociated molecules. However, the *concentration* (number of ions per unit volume) decreases because the volume increases more rapidly than the number of ions increases (as α doesn't increase proportionally to volume). Conductivity (κ) is directly proportional to the concentration of ions and their mobilities. Since the concentration of ions per unit volume decreases significantly upon dilution, the specific conductivity (κ) decreases, even though the degree of dissociation increases. (Note: Molar conductivity $\Lambda_m = \kappa/C$ increases on dilution for weak electrolytes).

OR.

(B).

(a) Lead Storage Battery (Discharge Reactions):.

Anode (Negative Plate - Lead):

$$\text{Pb}(s) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + 2e^-$$

Cathode (Positive Plate - Lead Dioxide):

$$\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$

Overall Cell Reaction:

$$\text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$

(b) Half-Cell Potential Calculation:.

Reaction: $Cr_2O_7^{2-}$(aq) + 14H^+(aq) + 6e^- $\rightarrow$ 2Cr^{3+}(aq) + 7H_2O(l) $E^\circ = 1.33$ V, n = 6.

Concentrations: [$Cr_2O_7^{2-}$] = 0.01 M, [Cr^{3+}] = 0.01 M, [H^+] = 1.0 x 10^{-4} M. Reaction Quotient $Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$

$$Q = \frac{(0.01)^2}{(0.01)(10^{-4})^{14}} = \frac{(10^{-2})^2}{(10^{-2})(10^{-56})} = \frac{10^{-4}}{10^{-58}} = 10^{54}$$

Nernst Equation at 298 K:

$$E = E^\circ - \frac{0.0591}{n} \log_{10} Q$$

$$E = 1.33 - \frac{0.0591}{6} \log_{10}(10^{54})$$

$$E = 1.33 - \frac{0.0591}{6} \times 54$$

$$E = 1.33 - (0.0591 \times 9)$$

$$E = 1.33 - 0.5319$$

$$E = 0.7981\,\text{V}$$

The potential for the half-cell is approximately 0.798 V..

Quick Tip

Electrochemistry Concepts. Nernst Eq: $E = E^\circ - (RT/nF) \ln Q$. Overpotential: Extra voltage needed for some electrode reactions (like O_2 evolution) makes them kinetically slower. Weak Electrolyte Conductivity (κ): Decreases on dilution due to lower ion concentration per unit volume, despite increased dissociation (α). Lead Storage Battery: Know anode, cathode, overall discharge reactions.