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.

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

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

(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.

Correct Answer: (B)

Solution:

Assertion (A): Optical activity requires a chiral center. In α-amino acids, the α-carbon is bonded to -H, -NH_2, -COOH, and a side chain -R. If R is different from the other three groups, the α-carbon is chiral. In glycine, R = H, so the α-carbon has two identical H atoms and is achiral (optically inactive). All other common natural α-amino acids have R $\neq$ H, making their α-carbon chiral and hence optically active. Assertion (A) is true.

Reason (R): The vast majority of amino acids found in proteins in nature belong to the L-stereochemical series (relative configuration compared to L-glyceraldehyde). Reason (R) is true.

Explanation: The optical activity (Assertion) is due to the chirality of the α-carbon. The L-configuration (Reason) describes the specific spatial arrangement of the groups around that chiral carbon in most natural amino acids. While both statements are true facts, the reason (L-configuration) doesn't explain the cause of optical activity (chirality). Therefore, Reason (R) is not the correct explanation for Assertion (A).

Quick Tip

Amino Acid Stereochemistry. Optical activity stems from chirality (α-carbon bonded to 4 different groups, except glycine). L/D configuration refers to the spatial arrangement relative to glyceraldehyde. These are distinct concepts.

2.

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

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

(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.

Correct Answer: (C)

Solution:

Assertion (A): Ethanol (CH_3CH_2OH, BP $\approx 78°C$) and methoxymethane (CH_3OCH_3, dimethyl ether, BP $\approx$ -24°C) are isomers (C_2H_6O). Ethanol has a much higher boiling point due to its ability to form strong intermolecular hydrogen bonds via its -OH group. Methoxymethane lacks O-H bonds and experiences only weaker dipole-dipole and van der Waals forces. Assertion (A) is true.

Reason (R): The hydrogen bonding responsible for ethanol's high boiling point is *intermolecular* (between different ethanol molecules). Intramolecular hydrogen bonding occurs within a single molecule (requires specific structures, e.g., o-nitrophenol). Reason (R) incorrectly states intramolecular H-bonding is present. Reason (R) is false.

Since Assertion (A) is true and Reason (R) is false, option (C) is correct.

Quick Tip

Intermolecular Forces and Boiling Point. Hydrogen bonding (especially O-H, N-H) significantly increases boiling points compared to molecules with only dipole-dipole or van der Waals forces. Ethanol exhibits intermolecular H-bonding.

3.

Assertion (A): The boiling points of alkyl halides decrease in the order: R-I > R-Br > R-Cl > R-F..

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

(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.

Correct Answer: (B)

Solution:
Assertion (A): For a given alkyl group R, the size, mass, and number of electrons of the halogen atom increase from F to Cl to Br to I. This leads to stronger intermolecular van der Waals forces (specifically London dispersion forces). Stronger intermolecular forces require more energy to overcome, resulting in higher boiling points. Therefore, the boiling points generally decrease in the order R-I > R-Br > R-Cl > R-F. The assertion states this correct trend. Assertion (A) is true.
Reason (R): Alkyl halides (R-Cl, R-Br, R-I) possess both dipole-dipole interactions (due to the polar C-X bond) and van der Waals forces. Compared to a nonpolar hydrocarbon (alkane) of similar molecular mass (which only has van der Waals forces), the additional dipole-dipole forces and often larger overall van der Waals forces (due to the halogen) lead to significantly higher boiling points for the alkyl halides. Reason (R) is true.
Explanation: While both statements are true, the Reason explains the difference between alkyl halides and alkanes. The Assertion describes the trend *within* the alkyl halide series. This trend (A) is primarily explained by the variation in the strength of van der Waals forces due to the changing size/mass of the halogen, not simply by the comparison to alkanes (R). Therefore, Reason (R) is not the correct explanation for Assertion (A).

Quick Tip

Boiling Point Trends (Alkyl Halides). Trend within series (same R): R-I > R-Br > R-Cl > R-F (due to increasing van der Waals forces). Comparison with alkanes: Alkyl halides > Alkanes (of similar mass) due to polarity and van der Waals forces.

4.

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..

(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.

Correct Answer: (A)

Solution:

Assertion (A): A homoleptic complex has only one type of ligand coordinated to the central metal ion. In $[Cr(H_2O)_6]Cl_2$, the complex ion is $[Cr(H_2O)_6]^{2+}$, where the only ligand is H_2O (aqua). In $[Fe(H_2O)_6]Cl_2$, the complex ion is $[Fe(H_2O)_6]^{2+}$, where the only ligand is also H_2O. Since both complex ions contain only one type of ligand, they are examples of homoleptic complexes. Assertion (A) is true.

Reason (R): This statement provides the correct definition of a homoleptic complex – all attached ligands are of the same type. Reason (R) is true.

Explanation: The definition given in Reason (R) directly justifies why the complexes mentioned in Assertion (A) are classified as homoleptic. Therefore, both are true, and R is the correct explanation of A.

Quick Tip

Homoleptic vs. Heteroleptic. Homoleptic: Only one type of ligand (e.g., $[Co(NH_3)_6]^{3+}$). Heteroleptic: More than one type of ligand (e.g., $[Co(NH_3)_5Cl]^{2+}$).

5.

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 movement of water across a semipermeable membrane from a region of higher water concentration (lower solute concentration) to a region of lower water concentration (higher solute concentration). The cells of the mango contain water with dissolved solutes. The concentrated salt solution outside the mango has a much lower water concentration (higher solute concentration). Therefore, water moves by osmosis out of the mango cells and into the surrounding salt solution. This loss of water causes the mango cells to lose turgor and the mango to shrivel. Reverse osmosis requires external pressure exceeding osmotic pressure and is not relevant here.

Quick Tip

Osmosis & Tonicity. Water moves from hypotonic (lower solute) to hypertonic (higher solute) solution across a semipermeable membrane. Concentrated salt solution is hypertonic to mango cells, causing water loss.

6.

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:

(A) Glucose has an aldehyde group and six carbons. True. (B) Strong reduction with HI/P cleaves all functional groups and yields the parent alkane, n-hexane, confirming the six-carbon straight chain. True. (C) Glucose exists predominantly in cyclic hemiacetal forms. The stable ring size is six-membered (pyranose). While a five-membered furanose ring is possible, it is not the common or stable form for glucose in solution. Fructose typically exists in furanose form (in combination, like sucrose, or as free sugar). False. (D) Despite having an aldehyde group in its small equilibrium concentration of the open-chain form, glucose generally does not give a positive Schiff's test, a characteristic reaction of simple aldehydes. True. Therefore, the statement that is not true is (C).

Quick Tip

Glucose Structure. Aldo-hexose. Straight 6C chain (shown by HI reduction). Predominantly forms 6-membered *pyranose* rings (α and β) in solution. Does not give Schiff's test readily.

7.

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:

The conversion required is $CH_3CH_2CONH_2$ (propanamide) $\rightarrow$ $CH_3CH_2CH_2NH_2$ (propanamine). This involves reducing the amide carbonyl (C=O) to a methylene (CH_2) group while retaining the carbon skeleton. (A) H_2 with catalysts can reduce amides but often requires harsh conditions. (B) Br_2/NaOH causes Hofmann degradation, yielding an amine with one less carbon (ethanamine). (C) I_2/Red P is not a standard reagent for this conversion. (D) $LiAlH_4$ (Lithium Aluminium Hydride) is a powerful reducing agent that specifically

reduces amides to amines with the same number of carbon atoms by converting the C=O group to CH_2. This is the most suitable reagent.

Quick Tip

Amide Reduction vs. Degradation. $LiAlH_4$ reduces $RCONH_2$ to RCH_2NH_2. Hofmann degradation (Br_2/NaOH) converts $RCONH_2$ to RNH_2.

8.

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 $CH_3CH_2CH_2MgBr$. The reaction of a Grignard reagent (RMgX) with carbon dioxide (CO_2) followed by acid hydrolysis is a standard method for synthesizing carboxylic acids (RCOOH). The Grignard reagent adds to CO_2 to form a magnesium carboxylate salt, which is then protonated by acid.

$$CH_3CH_2CH_2MgBr \xrightarrow{1.CO_2} CH_3CH_2CH_2COOMgBr \xrightarrow{2.H_3O^+} CH_3CH_2CH_2COOH$$

The product is butanoic acid, which has the formula C_3H_7COOH (propyl group + COOH group).

Quick Tip

Carboxylic Acid Synthesis. Grignard reagent + CO_2, then H_3O^+ gives RCOOH (adds one carbon).

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:

Comparing acidity: - Phenol (C_6H_5OH): Acidic due to resonance stabilization of the phenoxide conjugate base. - Water (H_2O): Reference point. Conjugate base is OH^-. - Aliphatic Alcohol (ROH): Alkyl groups (R) are electron-donating, destabilizing the alkoxide conjugate base (RO^-) compared to OH^-. The resonance stabilization makes phenoxide much more stable than hydroxide or alkoxide ions. Hydroxide is generally more stable than simple alkoxides. Therefore, the order of acidity is Phenol > Water > Alcohol.

Quick Tip

Acidity of OH groups. Phenols > Water > Alcohols. Acidity depends on the stability of the conjugate base (O^- anion). Resonance stabilizes phenoxide; alkyl groups destabilize alkoxides.

10.

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 (S_N2) proceeds via a one-step mechanism involving backside attack by the nucleophile on the carbon bearing the leaving group. This backside attack forces the configuration of the carbon atom to invert, similar to an umbrella flipping inside out in the wind (Walden inversion). Carbocation formation (D) and subsequent racemization (B) or retention (A, less common) are characteristic of S_N1 reactions.

Quick Tip

S_N2 Stereochemistry. Always proceeds with inversion of configuration at the reaction center due to backside attack by the nucleophile.

11.

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:

These are isomers of C_4H_9Br. Boiling points depend on intermolecular forces (van der Waals and dipole-dipole). For isomers, increased branching leads to a more spherical shape, reduced surface area for contact, weaker van der Waals forces, and thus lower boiling points. - (iii) 2-Bromo-2-methylpropane: Most branched (tertiary halide). Lowest BP. - (i) 1-Bromo-2-methylpropane: Branched (primary halide). Intermediate BP. - (ii)

1-Bromobutane: Straight chain (primary halide). Highest BP. The increasing order is (iii) $<$ (i) $<$ (ii).

Quick Tip

Boiling Point of Isomers. Branching decreases surface area $\rightarrow$ weaker van der Waals forces $\rightarrow$ lower boiling point. Straight chain $>$ Branched chain.

12.

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

(A) Diamminedichloridoplatinum (II)

(B) Diamminedichloridoplatinum (IV)

(C) Diamminedichloridoplatinum (0)

(D) Diamminedichloridoplatinate (IV)

Correct Answer: (B)

Solution:

1. Ligands: NH_3 (ammine), Cl^- (chlorido). Prefix 'di-' for both. Alphabetical order: ammine before chlorido. Name part: Diamminedichlorido. 2. Metal: Platinum (Pt). Complex is cationic (+2), so metal name is used directly: platinum. 3. Oxidation State: Let Pt be x. x + 2(0 for NH_3) + 2(-1 for Cl^-) = +2 (overall charge). x - 2 = +2 $\implies$ x = +4. Oxidation state is (IV). Full name: Diamminedichloridoplatinum(IV).

Quick Tip

Coordination Compound IUPAC Naming. Ligands alphabetically (with prefixes) $\rightarrow$ Metal name (-ate suffix if complex is anion) $\rightarrow$ Metal oxidation state (Roman numerals).

13.

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. MnO_4^- gets reduced to Mn^{2+}. It oxidizes sulphite ions (SO_3^{2-}, S=+4) to sulfate ions (SO_4^{2-}, S=+6).

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

Quick Tip

Oxidation States. $KMnO_4$ (acidic) oxidizes S(+4) in SO_3^{2-} to S(+6) in SO_4^{2-}.

14.

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.

15.

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): $\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}$; $E^\circ_{cathode} = +0.15$ V Anode Reaction (Oxidation): $\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$; $E^\circ_{anode} = -0.74$ 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.

16.

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).

Section B

Questions No. 16 to 21

17.

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

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

(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: Chloroethane (CH_3CH_2Cl) reacts with sodium cyanide (NaCN). Cyanide ion (CN^-) is a nucleophile and displaces the chloride ion via an S_N2 reaction to form propanenitrile.

$$\underset{}{CH_3CH_2Cl} + NaCN \rightarrow \underset{(A)}{CH_3CH_2CN} + NaCl$$

Thus, **A is Propanenitrile ($\mathbf{CH_3CH_2CN}$)**. - Step 2: Propanenitrile (A) is reduced by catalytic hydrogenation (H_2/Ni). The triple bond in the nitrile group (-C≡N) is reduced to a single bond, adding hydrogen atoms to both carbon and nitrogen, yielding a primary amine.

$$CH_3CH_2CN + 2H_2 \xrightarrow{\text{Ni catalyst}} \underset{(B)}{CH_3CH_2CH_2NH_2}$$

Thus, **B is Propan-1-amine ($\mathbf{CH_3CH_2CH_2NH_2}$)**.

(b) Sequence starting with Aniline: - Step 1: Aniline ($C_6H_5NH_2$) is treated with sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl) at low temperature (0-5°C). This is the diazotization reaction, converting the primary aromatic amine to a diazonium salt.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5^\circ C} \underset{(A)}{C_6H_5N_2^+Cl^-} + NaCl + 2H_2O$$

Thus, **A is Benzenediazonium chloride ($\mathbf{C_6H_5N_2^+Cl^-}$)**. - Step 2: Benzenediazonium chloride (A) is hydrolyzed by warming with water, typically in the presence of acid (H^+). The diazonium group ($-N_2^+$) is an excellent leaving group and is replaced by a hydroxyl group (-OH), forming phenol and liberating nitrogen gas.

$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{H^+,\Delta\ (\text{Warm})} \underset{(B)}{C_6H_5OH} + N_2(g) + HCl$$

Thus, **B is Phenol ($\mathbf{C_6H_5OH}$)**.

Quick Tip

Reaction Sequences. Recognize key functional group transformations: R-Cl + CN^- → R-CN; R-CN + H_2/Ni → R-CH_2NH_2; Ar-NH_2 + $NaNO_2$/HCl (cold) → Ar-$N_2^+Cl^-$; Ar-$N_2^+Cl^-$ + H_2O/Warm → Ar-OH.

18.

When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured (C). An acidified solution of compound (C) oxidises iodide to (D). Identify (A), (B), (C) and (D)..

Solution:

This sequence describes the extraction of chromium, starting from chromite ore ($FeCr_2O_4$):

1. **Fusion with Na_2CO_3 in air (Oxidation):** Chromite ore is roasted with sodium carbonate in the presence of air (oxygen). Chromium(III) is oxidized to Chromium(VI), forming sodium chromate, which is soluble and gives a yellow solution. Iron(II) is oxidized to Iron(III) oxide.

$$4FeCr_2O_4(s) + 8Na_2CO_3(s) + 7O_2(g) \xrightarrow{\Delta} \underset{\substack{\text{(A) Sodium Chromate}\\ \text{Yellow Solution}}}{8Na_2CrO_4} + 2Fe_2O_3(s) + 8CO_2(g)$$

   So, **A = Na_2CrO_4 (Sodium Chromate)**.

2. **Acidification of (A):** When the yellow solution of sodium chromate (Na_2CrO_4) is acidified (e.g., with H_2SO_4), the chromate ions (CrO_4^{2-}) are converted into dichromate ions ($Cr_2O_7^{2-}$), which form an orange solution. The compound (B) formed in solution is Sodium Dichromate.

$$2Na_2CrO_4 + 2H^+ \rightarrow \underset{\text{(B) Sodium Dichromate}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

   So, **B = $Na_2Cr_2O_7$ (Sodium Dichromate)**.

3. **Reaction of (B) with KCl:** Adding potassium chloride (KCl) to a concentrated solution of sodium dichromate (B) causes the less soluble potassium dichromate to precipitate out due to common ion effect and solubility differences. Potassium dichromate is an orange colored solid.

$$Na_2Cr_2O_7 + 2KCl \rightarrow \underset{\substack{\text{(C) Potassium Dichromate}\\ \text{Orange Solid}}}{K_2Cr_2O_7} + 2NaCl$$

   So, **C = $K_2Cr_2O_7$ (Potassium Dichromate)**.

4. **Oxidation of Iodide by Acidified (C):** An acidified solution of potassium dichromate (C) acts as a strong oxidizing agent. Dichromate ions ($Cr_2O_7^{2-}$, Cr = +6) are reduced to Cr^{3+}. It oxidizes iodide ions (I^-) to iodine (I_2).

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + \underset{\text{(D) Iodine}}{3I_2} + 7H_2O$$

So, **D = I_2 (Iodine)**.

Quick Tip

Chromium Chemistry. Chromite ore ($FeCr_2O_4$) $\xrightarrow{Na_2CO_3/Air}$ Na_2CrO_4 (Chromate, yellow, A) $\xrightarrow{Acid}$ $Na_2Cr_2O_7$ (Dichromate, orange, B) $\xrightarrow{KCl}$ $K_2Cr_2O_7$ (Orange solid, C). Acidified dichromate is a strong oxidizer ($Cr^{6+} \rightarrow Cr^{3+}$), oxidizing I^- to I_2 (D).

19.

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 **less reactive** than propanal (CH_3CH_2CHO) towards nucleophilic addition reactions.

Justification:.

Two main factors contribute to this:

1. **Electronic Effect (Resonance):** The carbonyl group in benzaldehyde is conjugated with the benzene ring. Resonance allows the delocalization of π electrons from the ring into the carbonyl group ($C_6H_5 - CH = O \leftrightarrow C_6H_5^+ = CH - O^-$ contributions, etc.). This resonance effect reduces the partial positive charge (electrophilicity) on the carbonyl carbon atom compared to propanal, making it less attractive to nucleophiles. Propanal lacks such resonance stabilization.

2. **Steric Hindrance:** The large, bulky phenyl group (C_6H_5-) in benzaldehyde hinders the approach of the nucleophile to the carbonyl carbon more effectively than the smaller ethyl group (CH_3CH_2-) in propanal.

Both the reduced electrophilicity and increased steric hindrance make benzaldehyde less reactive towards nucleophilic addition compared to aliphatic aldehydes like propanal.

Quick Tip

Nucleophilic Addition Reactivity (Aldehydes). Factors: (1) Electrophilicity of carbonyl carbon ($\delta+$). (2) Steric hindrance around carbonyl carbon. Aromatic aldehydes (like benzaldehyde) are less reactive than aliphatic aldehydes (like propanal) due to resonance decreasing electrophilicity and the bulky aryl group increasing steric hindrance.

20.

(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: A pressure cooker works by trapping steam generated from boiling water inside a sealed pot. This buildup of steam increases the internal pressure significantly above atmospheric pressure. Since the boiling point of a liquid increases with increasing external pressure, the water inside the cooker boils at a temperature higher than 100°C (typically 110-120°C). Cooking food at these elevated temperatures accelerates the chemical reactions involved (like denaturation of proteins, softening of cellulose), leading to much faster cooking times compared to an open pan where water boils at 100°C (at sea level).

(b) Mixing Liquids X and Y:

- **Volume Decrease ($\Delta V_{mix} < 0$):** When the volume of the solution is less than the sum of

the volumes of the pure components, it indicates that the intermolecular attractive forces between the molecules of X and Y in the solution (X-Y interactions) are stronger than the average intermolecular forces in the pure liquids (X-X and Y-Y interactions). This stronger attraction pulls the molecules closer together, resulting in a volume contraction upon mixing.

- **Deviation from Raoult's Law:** Stronger X-Y interactions mean that molecules have a lower tendency to escape from the liquid phase into the vapor phase compared to an ideal solution. This results in the actual vapor pressure of the solution being lower than that predicted by Raoult's law. This is known as a **negative deviation** from Raoult's law.
- **Temperature Change (ΔH_{mix}):** The formation of stronger intermolecular bonds between X and Y releases energy. Therefore, the mixing process is **exothermic** ($\Delta H_{mix} < 0$). If the mixing is done adiabatically (no heat exchange with surroundings), the temperature of the solution will **increase**.

OR.

(B) Azeotrope Definition and Example:.

- **Definition:** An azeotrope, or constant boiling mixture, is a liquid mixture of two or more components which boils at a constant temperature and whose vapor has the same composition as the liquid phase at a given pressure. Because the liquid and vapor compositions are identical, an azeotrope cannot be separated into its pure components by simple fractional distillation.
- **Type formed by Negative Deviation:** Mixtures exhibiting negative deviation from Raoult's law have stronger intermolecular forces in the mixture than in pure components, leading to lower vapor pressures than ideal. Such mixtures exhibit a maximum boiling point at the azeotropic composition. This is called a **maximum boiling azeotrope**.
- **Example:** A mixture of nitric acid ($\approx 68\%$ by mass) and water boils at a constant maximum temperature of ≈ 120.5°C, higher than the boiling points of both pure water (100°C) and pure nitric acid (≈ 83°C). Another example is acetone and chloroform.

Quick Tip

Concepts Summary. Pressure Cooker: High P $\rightarrow$ High BP $\rightarrow$ Fast cooking. Mixing: $\Delta V_{mix} < 0 \implies$ Stronger A-B forces $\implies$ Negative deviation $\implies$ Exothermic ($\Delta H_{mix} < 0$). Azeotrope: Constant boiling mixture (liquid comp = vapor comp). Negative deviation $\rightarrow$ Max boiling azeotrope. Positive deviation $\rightarrow$ Min boiling azeotrope.

21.

Give reasons for the following :.

(a) The melting points of α-amino acids are generally higher than that of the corresponding carboxylic acids..

(b) Amino acids show amphoteric behaviour..

Solution:

(a) High Melting Points of Amino Acids: α-Amino acids exist predominantly as zwitterions (dipolar ions) in the solid state and in neutral aqueous solution. In the zwitterionic form, the amino group is protonated (-NH_3^+) and the carboxyl group is deprotonated (-COO^-). These charged groups lead to strong electrostatic attractions (ionic interactions) and hydrogen bonding between different amino acid molecules in the crystal lattice. These intermolecular forces are much stronger than the typical hydrogen bonding found between molecules of the corresponding carboxylic acids (which lack the positively charged amino group). Overcoming these strong ionic and hydrogen bonding forces requires a large amount of energy, resulting in high melting points (often decomposing before melting) for amino acids compared to carboxylic acids of similar size.

(b) Amphoteric Behaviour of Amino Acids: Amphoteric substances can act as both acids and bases. Amino acids exhibit this behaviour due to the presence of both an acidic carboxyl group (-COOH) and a basic amino group (-NH_2) attached to the α-carbon.

- The carboxyl group can donate a proton ($-COOH \rightarrow -COO^- + H^+$), acting as an acid.
- The amino group can accept a proton ($-NH_2 + H^+ \rightarrow -NH_3^+$), acting as a base.

In aqueous solution, they predominantly exist as zwitterions, which can react with added

acids (protonating the -COO^- group) or added bases (deprotonating the -NH_3^+ group), demonstrating their ability to act as both acid and base.

Quick Tip

Amino Acid Properties. High Melting Point: Due to strong intermolecular forces (ionic attraction, H-bonding) in the zwitterionic form. Amphoteric: Possess both acidic (-COOH) and basic (-NH_2) groups, can react with both acids and bases.

Section C

Questions No. 22 to 27

22.

A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution..

Solution:

Isotonic solutions are solutions that have the same osmotic pressure at the same temperature. According to the formula for osmotic pressure ($\Pi = CRT$, where C is molar concentration), isotonic solutions must have the same molar concentration, assuming they are non-electrolytes or have the same van't Hoff factor (which is the case for urea and glucose, both non-electrolytes, $i = 1$).

Let C_{urea} be the molar concentration of the urea solution and C_{glucose} be the molar concentration of the glucose solution. Since they are isotonic:

$$C_{\text{urea}} = C_{\text{glucose}}$$

Calculate the molar concentration of the urea solution: Mass of urea = 15 g

Molar mass of urea = 60 g mol^{-1}

Volume of solution = 1 litre

$$C_{\text{urea}} = \frac{\text{moles of urea}}{\text{Volume of solution (L)}} = \frac{\text{Mass of urea / Molar mass of urea}}{\text{Volume}}$$

$$C_{\text{urea}} = \frac{15\,\text{g}/60\,\text{g mol}^{-1}}{1\,\text{L}} = \frac{0.25\,\text{mol}}{1\,\text{L}} = 0.25\,\text{mol L}^{-1}$$

Since the solutions are isotonic, the molar concentration of the glucose solution is also 0.25 mol L^{-1}:

$$C_{\text{glucose}} = 0.25\,\text{mol L}^{-1}$$

Now, calculate the mass of glucose required to make 1 litre of this solution: Molar mass of glucose = 180 g mol^{-1}

Volume of solution = 1 litre

$$C_{\text{glucose}} = \frac{\text{moles of glucose}}{\text{Volume of solution (L)}} = \frac{\text{Mass of glucose / Molar mass of glucose}}{\text{Volume}}$$

$$0.25\,\text{mol L}^{-1} = \frac{\text{Mass of glucose}/180\,\text{g mol}^{-1}}{1\,\text{L}}$$

$$\text{Mass of glucose} = 0.25\,\text{mol} \times 180\,\text{g mol}^{-1}$$

$$\text{Mass of glucose} = 45\,\text{g}$$

The mass of glucose present in one litre of its solution is 45 g.

Quick Tip

Isotonic Solutions. Have the same osmotic pressure (Π). For non-electrolytes, this means they have the same molar concentration (C) at the same temperature ($\Pi = CRT$). Molar concentration $C = \frac{\text{mass}}{\text{Molar mass} \times \text{Volume}}$.

23.

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

Fe^{2+}(aq) + Ag^{+}(aq) $\rightarrow$ Fe^{3+}(aq) + Ag(s).

Given $E^{\circ}_{Ag^{+}/Ag}$ = 0.80 V, $E^{\circ}_{Fe^{3+}/Fe^{2+}}$ = 0.77 V.

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

Solution:

The overall reaction shows Ag^{+} being reduced to Ag(s) and Fe^{2+} being oxidized to Fe^{3+}. Identify the half-reactions and their standard potentials:

- Cathode (Reduction): Ag^{+}(aq) + e^{-} $\rightarrow$ Ag(s); $E^{\circ}_{\text{cathode}} = E^{\circ}_{Ag^{+}/Ag} = +0.80$ V
- Anode (Oxidation): Fe^{2+}(aq) $\rightarrow$ Fe^{3+}(aq) + e^{-}. The standard potential for this oxidation is the negative of the reduction potential for Fe^{3+}/Fe^{2+}. However, we use the reduction potentials directly in the E°_{cell} formula. $E^{\circ}_{\text{anode}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} = +0.77$ V.

Calculate the standard cell potential (E°_{cell}):

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

$$E^{\circ}_{\text{cell}} = (+0.80\,\text{V}) - (+0.77\,\text{V})$$

$$E^{\circ}_{\text{cell}} = +0.03\,\text{V}$$

The number of electrons transferred (n) in the balanced reaction is 1 (since one electron is lost by Fe^{2+} and one electron is gained by Ag^{+}). So, $n = 1$.

Calculate the standard Gibbs free energy change ($\Delta_r G^{\circ}$):

$$\Delta_r G^{\circ} = -nF E^{\circ}_{\text{cell}}$$

$$\Delta_r G^{\circ} = -(1\,\text{mol}) \times (96500\,\text{C mol}^{-1}) \times (0.03\,\text{V})$$

$$\Delta_r G^{\circ} = -(96500 \times 0.03)\,\text{J}$$

$$\Delta_r G^{\circ} = -2895\,\text{J/mol} = -2.895\,\text{kJ/mol}$$

Calculate the logarithm of the equilibrium constant ($\log_{10} K_C$): Using the relationship $E^\circ_{\text{cell}} = \frac{0.0591}{n} \log_{10} K_c$ at 298 K (assuming standard temperature):

$$0.03\,\text{V} = \frac{0.0591\,\text{V}}{1} \log_{10} K_c$$

$$\log_{10} K_c = \frac{0.03}{0.0591} \approx 0.5076$$

Alternatively, using $\Delta_r G^\circ = -2.303RT \log_{10} K_c$:

$$\log_{10} K_c = -\frac{\Delta_r G^\circ}{2.303RT} = -\frac{-2895\,\text{J mol}^{-1}}{2.303 \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}$$

$$\log_{10} K_c = \frac{2895}{5705.8} \approx 0.5074$$

Results:

$$\Delta_r G^\circ \approx -2.90\,\text{kJ/mol}$$

$$\log_{10} K_c \approx 0.507$$

Quick Tip

Electrochemical Calculations. Identify cathode (higher E°_{red}) and anode (lower E°_{red}). Calculate $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. Find n (electrons transferred in balanced reaction). Use $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ and $E^\circ_{\text{cell}} = (0.0591/n) \log_{10} K_c$ (at 298K).

24.

(a) Arrange the following in decreasing order of pK$_b$:.

Aniline, p-nitroaniline, p-methylaniline.

(b) Account for the following :.

(i) Diazonium salts of aromatic amines are more stable than those of aliphatic amines..

(ii) Methylamine in water reacts with FeCl$_3$ to precipitate hydrated ferric oxide..

Solution:

(a) Decreasing Order of pK_b:.

pK_b is inversely related to basic strength (K_b). A higher pK_b means a weaker base. We need to arrange the amines in order of decreasing pK_b, which means arranging them in order of increasing basic strength. Basicity depends on the availability of the lone pair on the nitrogen atom. - Aniline ($C_6H_5NH_2$): Lone pair is delocalized into the benzene ring via resonance, reducing availability. Weak base. - p-Nitroaniline (p-NO_2-C_6H_4-NH_2): The nitro group (-NO_2) is a strong electron-withdrawing group (by resonance and induction), further delocalizing the lone pair and drastically reducing its availability. Very weak base. - p-Methylaniline (p-CH_3-C_6H_4-NH_2, p-toluidine): The methyl group (-CH_3) is an electron-donating group (by hyperconjugation and weak induction), which slightly increases the electron density on the ring and makes the lone pair slightly more available compared to aniline. Stronger base than aniline. Order of increasing basic strength: p-Nitroaniline $<$ Aniline $<$ p-Methylaniline. Order of decreasing pK_b: **p-Nitroaniline** $>$ **Aniline** $>$ **p-Methylaniline**.

(b) Explanations:.

(i) Stability of Diazonium Salts: Aromatic diazonium salts (Ar-$N_2^+X^-$) are relatively stable at low temperatures (0-5°C) because the positive charge on the diazonium group can be dispersed over the aromatic ring through resonance. The diazonium ion forms resonance structures where the positive charge is delocalized onto the ortho and para positions of the ring. Aliphatic diazonium salts (R-$N_2^+X^-$) lack this resonance stabilization. The aliphatic diazonium ion is highly unstable and readily decomposes, even at low temperatures, by losing nitrogen gas (N_2) to form a carbocation (R^+), which then reacts further.

(ii) Methylamine + $FeCl_3$ Reaction: Methylamine (CH_3NH_2) is an amine and acts as a weak base in water, producing hydroxide ions:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

Ferric chloride ($FeCl_3$) is a salt of a weak base ($Fe(OH)_3$) and a strong acid (HCl). In water, Fe^{3+} ions partially hydrolyze. When methylamine solution (which contains OH^-) is added to $FeCl_3$ solution, the hydroxide ions react with the Fe^{3+} ions to precipitate insoluble ferric hydroxide, $Fe(OH)_3$, which dehydrates to form hydrated ferric oxide ($Fe_2O_3.xH_2O$), often

seen as a reddish-brown precipitate.

$$Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s) \downarrow \quad (\text{or } Fe_2O_3 \cdot xH_2O)$$

The basic nature of methylamine provides the necessary hydroxide ions to cause the precipitation.

Quick Tip

Concepts. Basicity Order (Anilines): Electron-donating groups (like -CH_3) increase basicity (decrease pK_b). Electron-withdrawing groups (like -NO_2) decrease basicity (increase pK_b). Aromatic Diazonium Salts: Stabilized by resonance. Aliphatic Diazonium Salts: Unstable, decompose readily. Amine Basicity: Amines are weak bases in water, producing OH^-. Fe^{3+} precipitates as $Fe(OH)_3$ / hydrated oxide in basic solution.

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): Free radical bromination occurs preferentially at the benzylic position (stabilized radical). Product: **1-Bromo-1-phenylethane** (C_6H_5-CH(Br)-CH_3).

(b) Methylcyclohexane + HBr: Alkanes are generally unreactive to HBr. If the reactant was 1-methylcyclohexene, Markovnikov addition occurs: H^+ adds to the less substituted end of C=C, forming a tertiary carbocation, which Br^- attacks. Product (from 1-methylcyclohexene): **1-Bromo-1-methylcyclohexane**. If no reaction assumed for alkane, state "No reaction".

(c) p-Cresol + HCl/Heat: p-Cresol (4-methylphenol). The OH group activates the ring towards electrophilic substitution (o/p directing). The methyl group is also o/p directing. Reaction with HCl/Heat is unlikely to substitute the OH group directly. Electrophilic chlorination might occur ortho to the OH group (position 2 or 6 relative to OH). Product: **2-Chloro-4-methylphenol**.

OR.

(B) Conversions:.

(a) Chlorobenzene to biphenyl: Use the Fittig reaction. React chlorobenzene with sodium metal in dry ether.

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

(b) Propene to 1-Iodopropane: Anti-Markovnikov addition is needed. Use HBr with peroxides for anti-Markovnikov addition of Br, then use NaI/acetone (Finkelstein reaction) to substitute Br with I. Step 1: CH_3-CH=CH_2 + HBr $\xrightarrow{\text{Peroxide}}$ $CH_3CH_2CH_2Br$

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

(c) 2-bromobutane to but-2-ene: Dehydrohalogenation using a strong base in alcohol (e.g., alcoholic KOH) and heat. Favors Saytzeff product (more substituted alkene).

$$CH_3\text{-}CH(Br)\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{Alc. KOH},\Delta} CH_3\text{-}CH{=}CH\text{-}CH_3 \quad \text{(But-2-ene)}$$

Quick Tip

Key Reactions. Benzylic Halogenation (Free radical). Markovnikov Addition (Alkene+HX). Electrophilic Aromatic Substitution (Phenols). Fittig Reaction (ArX+Na). Anti-Markovnikov Addition (Alkene+HBr/Peroxide). Finkelstein (RBr+NaI). Dehydrohalogenation (Alkyl halide + Alc. Base, Saytzeff 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 $E^{\circ}_{Cu^{2+}/Cu}$: This positive value (+0.34 V) indicates copper is less easily oxidized than hydrogen. It arises from a balance of energy terms. Copper has a high enthalpy of atomization ($\Delta_{at}H$) and a high sum of first and second ionization enthalpies ($IE_1 + IE_2$). While the hydration enthalpy ($\Delta_{hyd}H$) of Cu^{2+} is large and negative (favorable), it is not sufficient to overcome the high energy required to convert Cu(s) to Cu^{2+}(g). The overall energy change for Cu(s) $\rightarrow$ Cu^{2+}(aq) + $2e^-$ is less favorable (more positive ΔG) compared to hydrogen, resulting in a positive standard electrode potential.

(b) Strong Reducing Agent (M^{2+}): A strong reducing agent in the +2 state is easily oxidized to a higher state, typically +3. Chromium (Cr) fits this description well. Cr^{2+} has a d^4 configuration. In an octahedral field, Cr^{3+} has a d^3 configuration, which corresponds to a stable, half-filled t_{2g} subshell ($t_{2g}^3 e_g^0$). This stability drives the oxidation of Cr^{2+} to Cr^{3+}, making Cr^{2+} a strong reducing agent ($E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.41$ V).

(c) Colourless Zn^{2+} Salts: Zinc has the electronic configuration [Ar] $3d^{10}$ $4s^2$. The Zn^{2+} ion has the configuration [Ar] $3d^{10}$. Color in transition metal ions typically arises from d-d electronic transitions, where an electron absorbs visible light to move between d-orbitals split by the ligand field. For this to occur, the d-subshell must be partially filled. Since Zn^{2+} has a completely filled d-subshell (d^{10}), d-d transitions are not possible. Therefore, Zn^{2+} salts are typically white or colorless.

Quick Tip

Transition Metal Ion Properties. E° values depend on $\Delta_{at}H, IE, \Delta_{hyd}H$. Reducing agents are easily oxidized (look for stable higher oxidation states, e.g., $Cr^{2+} \rightarrow Cr^{3+}$). Color depends on d-d transitions, requiring partially filled d orbitals (d^0 and d^{10} ions like Sc^{3+}, Ti^{4+}, Zn^{2+} are colorless).

27.

A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction. **[R = 8.314 J K^{-1} mol^{-1}; log 4 = 0.602].**

Solution:

For a first order reaction, the rate constant k is related to the time taken for the reaction to reach 50% completion, as given by the equation:

$$k = \frac{0.693}{t_{1/2}}$$

where $t_{1/2}$ is the half-life of the reaction. At 300 K, the reaction is 50% complete in 20 minutes, so:

$$k_1 = \frac{0.693}{20\,\text{min}} = \frac{0.693}{20 \times 60\,\text{s}} = 5.775 \times 10^{-4}\,\text{s}^{-1}$$

At 350 K, the reaction is 50% complete in 5 minutes, so:

$$k_2 = \frac{0.693}{5\,\text{min}} = \frac{0.693}{5 \times 60\,\text{s}} = 2.31 \times 10^{-3}\,\text{s}^{-1}$$

Now, using the Arrhenius equation to calculate the activation energy (E_a):

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

where: - k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively. - R is the gas constant, $8.314\,\text{J mol}^{-1}\text{K}^{-1}$. - $T_1 = 300\,\text{K}$, $T_2 = 350\,\text{K}$.

Substitute the values:

$$\ln \frac{2.31 \times 10^{-3}}{5.775 \times 10^{-4}} = \frac{E_a}{8.314}\left(\frac{1}{300} - \frac{1}{350}\right)$$

First, calculate the left-hand side:

$$\ln\left(\frac{2.31 \times 10^{-3}}{5.775 \times 10^{-4}}\right) = \ln 4 = 0.602$$

Now, calculate the right-hand side:

$$\left(\frac{1}{300} - \frac{1}{350}\right) = \frac{350 - 300}{300 \times 350} = \frac{50}{105000} = 4.76 \times 10^{-4}\,\text{K}^{-1}$$

Now, solve for E_a:

$$0.602 = \frac{E_a}{8.314} \times 4.76 \times 10^{-4}$$

$$E_a = \frac{0.602 \times 8.314}{4.76 \times 10^{-4}} = 105.8\,\text{kJ/mol}$$

Therefore, the activation energy E_a is $\boxed{105.8\,\text{kJ/mol}}$.

Quick Tip

Activation Energy and Arrhenius Equation. The activation energy can be calculated using the Arrhenius equation by comparing the rate constants at different temperatures. The equation is:

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

where T_1 and T_2 are the temperatures and k_1 and k_2 are the rate constants.

28.

(a) Write the reaction when D-glucose reacts with the following:.

(i) NH_2OH

(ii) Acetic anhydride

(b) Why vitamin C cannot be stored in our body?.

Solution:

(a) D-Glucose Reacts with:.

(i) **NH_2OH** (Hydroxylamine): The reaction of glucose with hydroxylamine results in the formation of glucosamine, a type of amine sugar.

$$C_6H_{12}O_6 + NH_2OH \rightarrow C_6H_{11}NO_5 + H_2O$$

This is the formation of glucosamine from glucose and hydroxylamine.

(ii) **Acetic Anhydride:** The reaction of glucose with acetic anhydride results in the formation of glucose pentaacetate, where the hydroxyl groups of glucose are esterified with acetic acid.

$$C_6H_{12}O_6 + (CH_3CO)_2O \rightarrow C_6H_9O_6(C_3H_3O_2)_5 + CH_3COOH$$

(b) Why vitamin C cannot be stored in our body?.

Vitamin C (ascorbic acid) is a water-soluble vitamin, and our body does not have the capability to store water-soluble vitamins. Once absorbed, the body uses what it needs and excretes the excess through urine. Unlike fat-soluble vitamins, which are stored in the liver and fat tissues, water-soluble vitamins like vitamin C are not retained for long periods. Therefore, vitamin C must be replenished regularly through diet.

Quick Tip

Vitamin C Storage. Vitamin C is water-soluble and cannot be stored in the body. It must be consumed regularly through dietary sources such as fruits and vegetables.

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.

Read the passage about chemical kinetics and answer the following questions:.

(a) (i) What is a rate determining step ?.

(ii) Define complex reaction..

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

OR.

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

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

Solution:

(a) (i) Rate Determining Step: In a multi-step reaction mechanism (a complex reaction), the overall rate of the reaction is governed by the slowest step in the sequence. This slowest step, which acts as a bottleneck, is called the rate-determining step (RDS). The rate law for the overall reaction often reflects the molecularity and reactants involved in the rate-determining step.

(a) (ii) Complex Reaction: A complex reaction is a chemical reaction that proceeds through a sequence of two or more elementary steps. The overall stoichiometry of the reaction does not necessarily reflect the actual mechanism, which involves intermediate species that are formed and consumed during the sequence. The rate law for a complex reaction cannot generally be predicted from the overall stoichiometry and must be determined experimentally or derived from the proposed mechanism (often using approximations like the steady-state approximation).

(b) Effect of Temperature on Rate Constant: Generally, the rate constant (k) of a chemical reaction increases significantly with an increase in temperature. This relationship is quantitatively described by the Arrhenius equation:

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

where A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature. As T increases, the term $-E_a/RT$ becomes less negative (or more positive), causing the exponential term $e^{-E_a/RT}$ to increase, which in turn increases the rate constant k. A common rule of thumb is that the rate constant approximately doubles for every 10°C (or 10 K) rise in temperature near room temperature, although this depends on the activation energy.

OR.

(b) Molecularity vs Order Applicability:

- **Molecularity:** Molecularity is defined only for an elementary reaction (a single step in a reaction mechanism). It represents the number of reactant molecules, atoms, or ions that must collide simultaneously to bring about the chemical reaction in that single step. It is a theoretical concept derived from the stoichiometry of the elementary step and must be a small positive integer (usually 1, 2, or rarely 3). It cannot be zero, fractional, or negative. Since complex reactions involve multiple steps, the concept of a single molecularity for the overall reaction is meaningless.
- **Order:** The order of a reaction is determined experimentally from the rate law expression (Rate = k[A]^x[B]^y...). It represents the sum of the exponents ($x + y + \ldots$) to which the concentration terms are raised in the experimentally determined rate law. The order reflects how the rate actually depends on reactant concentrations and can be applied to both elementary and complex reactions. It can be an integer, zero, fractional, or even negative, and it is not necessarily related to the stoichiometric coefficients of the overall reaction, especially for complex reactions.

(c) Effect of Concentration on Second Order Rate: The reaction X $\rightarrow$ Y follows second-order kinetics. This means the rate law is:

$$\text{Rate of formation of Y} = \text{Rate of reaction} = k[\text{X}]^2$$

Let the initial rate be $R_1 = k[\text{X}]^2$. If the concentration of X is increased 3 times, the new concentration is $[\text{X}]_{new} = 3[\text{X}]$. The new rate ($R_2$) will be:

$$R_2 = k([\text{X}]_{new})^2 = k(3[\text{X}])^2 = k(9[\text{X}]^2) = 9(k[\text{X}]^2)$$

$$R_2 = 9R_1$$

Therefore, if the concentration of X is tripled, the rate of formation of Y will increase by a factor of $3^2 = 9$.

Quick Tip

Kinetics Concepts. Rate Determining Step (RDS): Slowest step in mechanism. Complex Reaction: Multi-step reaction. Rate Constant (k): Increases with temperature (Arrhenius Eq). Molecularity: Theoretical, for elementary steps only, integer (1, 2, 3). Order: Experimental, from rate law, can be integer/zero/fractional, applies to overall reaction. Rate $\propto$ [Reactant]$^{\text{order}}$.

30.

Read the passage about phenol chemistry and 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.

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

Solution:

(a) Reactions of Phenol:.

(i) Phenol + Br_2/CS_2: Bromination of phenol is very facile due to the highly activating -OH group. Using bromine in a non-polar solvent like carbon disulfide (CS_2) (or CCl_4) at low temperature moderates the reaction, leading primarily to monobromination. Since -OH is ortho/para directing, a mixture of ortho-bromophenol and para-bromophenol is formed, with the para isomer often being the major product due to less steric hindrance. **Products: o-Bromophenol and p-Bromophenol (Major).**

(ii) Phenol + Conc. HNO_3: Nitration of phenol with concentrated nitric acid (often in the presence of concentrated sulfuric acid, though conc. HNO_3 alone can work due to phenol's high reactivity) is a vigorous reaction. It leads to polysubstitution at the ortho and para positions. The major product formed under these strong nitrating conditions is 2,4,6-trinitrophenol, commonly known as picric acid. **Product: 2,4,6-Trinitrophenol**

(Picric Acid)..

(b) Protonation of Phenol: Phenols are weak acids, meaning they tend to donate the proton from the -OH group rather than accept one. Protonation would occur on the oxygen atom's lone pair. However, the lone pairs on the oxygen atom in phenol are involved in resonance with the benzene ring, delocalizing them and making them less available to accept a proton compared to the lone pairs on oxygen in aliphatic alcohols. Furthermore, protonation would disrupt the aromaticity of the ring, which is energetically unfavorable. Therefore, phenol does not undergo protonation readily.

(c) Acidity of Phenol vs Cresol: Cresols are methylphenols (e.g., o-cresol, m-cresol, p-cresol). The methyl group (-CH_3) is an electron-donating group (due to hyperconjugation and weak inductive effect). Electron-donating groups attached to the benzene ring tend to destabilize the phenoxide anion (the conjugate base formed after proton donation) by intensifying the negative charge. Destabilization of the conjugate base makes the parent acid weaker. Therefore, cresols are generally weaker acids than phenol itself. **Stronger Acid: Phenol. Reason:** The electron-donating methyl group in cresol destabilizes the conjugate base (cresoxide ion) relative to the phenoxide ion, making cresol a weaker acid than phenol.

OR.

(c) IUPAC Name of Reimer-Tiemann Product: The Reimer-Tiemann reaction involves treating phenol with chloroform ($CHCl_3$) and aqueous alkali (e.g., NaOH or KOH) followed by acidification. It introduces an aldehyde group (-CHO) primarily at the ortho position to the hydroxyl group. The major product is ortho-hydroxybenzaldehyde, also known by its common name salicylaldehyde. Its IUPAC name is **2-Hydroxybenzaldehyde**.

Quick Tip

Phenol Reactions Properties. Electrophilic Substitution: Highly activated ring, o,p-directing. Bromination: $Br_2/CS_2 \rightarrow$ mono (o/p); $Br_2/H_2O \rightarrow$ tribromo. Nitration: Dil $HNO_3 \rightarrow$ mono (o/p); Conc $HNO_3 \rightarrow$ Picric acid (2,4,6-trinitro). Acidity: Phenol $>$ Water $>$ Alcohol. Electron-donating groups decrease phenol acidity (Cresol $<$ Phenol). Reimer-Tiemann: Phenol $\xrightarrow{CHCl_3/OH^-}$ Salicylaldehyde (2-Hydroxybenzaldehyde).

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:

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

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 ($CH_3CH_2CH_2CH_2OH$)**.

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 ($CH_3CH_2CH_2COOH$)**.

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 ($CH_3CH_2CH_2COO$-$CH_2CH_2CH_2CH_3$)**. 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$^\circ$ 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$^\circ$ = 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.
