



General Instructions

- (i) **Duration:** The total duration of the examination is 80 minutes.
- (ii) **Total Marks:** The complete paper carries a maximum of 60 marks.
- (iii) **Structure:** The paper has 60 Questions from Physics
- (iv) **Compulsory Questions:** All 60 questions are compulsory.
- (v) Each question has four options. Only **one** option is correct.
- (vi) **Correct Answer:** +1 marks.
- (vii) **Incorrect Answer:** (No Negative marking).
- (viii) **Unanswered/Marked for Review:** 0 marks.

1. $R-CH_2OH$ is converted into $R-CHO$ by reacting with .

- (A) Alkaline $KMnO_4$
- (B) $LiAlH_4$
- (C) Na/C_2H_5OH
- (D) PCC (Pyridinium Chlorochromate)

Correct Answer: (D) PCC (Pyridinium Chlorochromate)

Solution:

Step 1: Understanding the Concept:

Primary alcohols ($R-CH_2OH$) can be oxidized to aldehydes ($R-CHO$) or carboxylic acids ($R-COOH$). To stop the oxidation at the aldehyde stage, a mild oxidizing agent is required.

Step 2: Key Formula or Approach:

Analyze the oxidizing/reducing strength of each given reagent to identify the one that specifically halts oxidation at the aldehyde stage without over-oxidizing the compound.

Step 3: Detailed Explanation:

(A) Alkaline KMnO_4 is a strong oxidizing agent that oxidizes primary alcohols directly to carboxylic acids.

(B) LiAlH_4 is a reducing agent, typically used to convert carbonyl compounds back to alcohols.

(C) $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ is a reducing agent (Bouveault-Blanc reduction).

(D) Pyridinium chlorochromate (PCC) is a specialized mild reagent that selectively oxidizes primary alcohols to aldehydes without further oxidation to carboxylic acids in anhydrous media.

Step 4: Final Answer:

The reagent used for the controlled oxidation of a primary alcohol to an aldehyde is PCC.

Quick Tip: PCC is the "go-to" reagent in competitive exams for the transformation of 1° alcohol $\rightarrow$ aldehyde and 2° alcohol $\rightarrow$ ketone without over-oxidation.

2. Glycerol is a trihydric alcohol. It contains .

- (A) One primary, one secondary and one tertiary alcoholic groups
- (B) Two primary and one secondary alcoholic groups
- (C) Two secondary and one primary alcoholic groups
- (D) One primary and two tertiary alcoholic groups

Correct Answer: (B) Two primary and one secondary alcoholic groups

Solution:**Step 1: Understanding the Concept:**

Glycerol is a polyhydric alcohol with three hydroxyl groups. Identifying the types of alcoholic groups requires examining the degree of the carbon atoms they are attached to.

Step 2: Key Formula or Approach:

Analyze the molecular structure of the compound (Propane-1,2,3-triol) to identify the number

of carbon atoms attached to one (primary) or two (secondary) other carbon atoms, and count the respective attached hydroxyl groups.

Step 3: Detailed Explanation:

The chemical formula of glycerol is $\text{CH}_2\text{OH} - \text{CHOH} - \text{CH}_2\text{OH}$.

1. The two terminal $-\text{OH}$ groups are attached to CH_2 groups. Since these carbons are bonded to only one other carbon atom, they are primary (1°) carbons. Hence, there are two primary alcoholic groups.
2. The middle $-\text{OH}$ group is attached to a CH group. This carbon is bonded to two other carbon atoms, making it a secondary (2°) carbon. Hence, there is one secondary alcoholic group.

Step 4: Final Answer:

Glycerol contains two primary and one secondary alcoholic groups.

Quick Tip: Always draw the structural formula for polyhydric alcohols to avoid confusion. For glycerol, remember "1,2,3-triol" implies the terminal carbons are identical (1°) and the middle one is different (2°).

3. The correct IUPAC name of $\text{CH}_3 - \text{C}(\text{CH}_3)_2 - \text{O} - \text{C}_2\text{H}_5$ is

- (A) Tertiary butoxy ethane
- (B) 1, 1-Dimethyl-1-ethoxyethane
- (C) 2-ethoxy-2-methyl propane
- (D) Ethoxy tertiary butane

Correct Answer: (C) 2-ethoxy-2-methyl propane

Solution:

Step 1: Understanding the Concept:

According to IUPAC nomenclature for ethers, the longer carbon chain is treated as the parent alkane, and the shorter alkoxy group is treated as a substituent.

Step 2: Key Formula or Approach:

Apply IUPAC rules: identify the longest continuous parent carbon chain, treat the $-\text{OR}$ group

as an "alkoxy" substituent, and number the chain to give the substituents the lowest possible locants, arranging them alphabetically.

Step 3: Detailed Explanation:

Structure: $\text{CH}_3 - \text{C}(\text{CH}_3)_2 - \text{O} - \text{CH}_2\text{CH}_3$

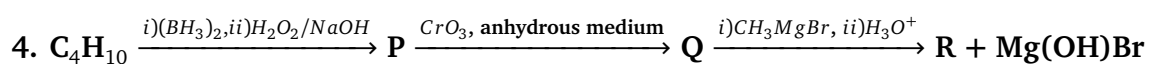
1. Identify the longest chain: The chain bonded to the oxygen on the left side has 3 carbons ($\text{CH}_3 - \text{C} - \text{CH}_3$ with a methyl branch). This is a propane chain.
2. Identify the substituent: The group on the right side of the oxygen is an ethyl group, making the substituent "ethoxy" ($-\text{OCH}_2\text{CH}_3$).
3. Numbering: Number the propane chain to give the ethoxy group the lowest possible number. Starting from either end of the horizontal chain, the central carbon is position 2.
4. Substituents at position 2: There is an ethoxy group and a methyl group.
5. Alphabetical order: "e" in ethoxy comes before "m" in methyl.

Result: 2-ethoxy-2-methylpropane.

Step 4: Final Answer:

The correct IUPAC name is 2-ethoxy-2-methyl propane.

Quick Tip: "Tertiary butoxy ethane" is a common/derived name. In IUPAC, always look for the longest continuous carbon chain and treat the $-\text{OR}$ group as an "alkoxy" substituent.



The organic compounds P, Q and R are

- (A) $\text{P} = \text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{CH}_3$, $\text{Q} = \text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_3$, $\text{R} = \text{CH}_3 - \text{C}(\text{OH})(\text{CH}_3) - \text{CH}_2 - \text{CH}_3$
- (B) $\text{P} = \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$, $\text{Q} = \text{CH}_3 - \text{CH}_2 - \text{CHO}$, $\text{R} = \text{CH}_3 - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_3$
- (C) $\text{P} = \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$, $\text{Q} = \text{CH}_3 - \text{CH}_2 - \text{COOH}$, $\text{R} = \text{CH}_3 - \text{CH}_2 - \text{C}(=\text{O}) - \text{OCH}_3$
- (D) $\text{P} = \text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_3$, $\text{Q} = \text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_3$, $\text{R} = \text{CH}_3 - \text{CH}(\text{OCH}_3) - \text{CH}_3$

Correct Answer: (B) $\text{P} = \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$, $\text{Q} = \text{CH}_3 - \text{CH}_2 - \text{CHO}$, $\text{R} = \text{CH}_3 - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_3$

Solution:

Step 1: Understanding the Concept:

The reaction sequence involves hydroboration-oxidation, controlled oxidation of an alcohol, and Grignard addition to a carbonyl compound.

Step 2: Key Formula or Approach:

Map the reagents to their specific organic transformations: hydroboration-oxidation yields anti-Markovnikov alcohols, CrO_3 in anhydrous media stops at the aldehyde stage, and Grignard addition creates a higher-order alcohol. (Note: The starting material is indicated as C_4H_{10} in OCR, but hydroboration applies to alkenes; we proceed based on the products derived from an implied terminal alkene like propene or butene. Based on the options, the starting alkene is propene C_3H_6 since the products have 3 carbon chains before Grignard.)

Step 3: Detailed Explanation:

Let's analyze the options. The options (B) and (C) suggest the chain "P" has 3 carbons ($CH_3 - CH_2 - CH_2 - OH$). This implies the starting alkene was Propene ($CH_3 - CH = CH_2$), not C_4H_{10} .

1. **Reaction 1 (Hydroboration-Oxidation):** $CH_3 - CH = CH_2$ reacts with $(BH_3)_2$ followed by $H_2O_2/NaOH$. This is an anti-Markovnikov addition of water.

Product P: $CH_3 - CH_2 - CH_2 - OH$ (Propan-1-ol).

2. **Reaction 2 (Mild Oxidation):** P (Propan-1-ol) reacts with CrO_3 in anhydrous medium. Primary alcohols are oxidized to aldehydes.

Product Q: $CH_3 - CH_2 - CHO$ (Propanal).

3. **Reaction 3 (Grignard Reaction):** Q (Propanal) reacts with CH_3MgBr followed by hydrolysis. The nucleophilic CH_3^- attacks the carbonyl carbon of the aldehyde.

Product R: $CH_3 - CH_2 - CH(OH) - CH_3$ (Butan-2-ol).

Step 4: Final Answer:

Matching the derived structures with the options leads to choice (B).

Quick Tip: Hydroboration-Oxidation always gives the anti-Markovnikov alcohol (1° from terminal alkene). Grignard addition to an aldehyde (other than formaldehyde) always yields a 2° alcohol.

5. Match the reagents in List - I with products obtained from their carbonyl compounds in List - II.

List - I

List - II

(a) NH_2OH

(i) Cyanohydrin

- | | |
|--------------------------------|-------------------|
| (b) R-NH_2 | (ii) Oxime |
| (c) R-OH | (iii) Schiff base |
| (d) $\text{H-C}\equiv\text{N}$ | (iv) Acetal |

Codes:

- (A) a – ii, b – iii, c – iv, d – i
 (B) a – i, b – ii, c – iii, d – iv
 (C) a – iii, b – ii, c – i, d – iv
 (D) a – i, b – iii, c – ii, d – iv

Correct Answer: (A) a – ii, b – iii, c – iv, d – i

Solution:

Step 1: Understanding the Concept:

Carbonyl compounds (aldehydes and ketones) undergo nucleophilic addition or nucleophilic addition-elimination reactions with various specific reagents to form characteristic derivatives.

Step 2: Key Formula or Approach:

Recall the standard nucleophilic addition-elimination reactions of aldehydes/ketones with ammonia derivatives ($\text{H}_2\text{N} - \text{Z}$) and straight nucleophilic addition with HCN and alcohols.

Step 3: Detailed Explanation:

(a) NH_2OH (**Hydroxylamine**): Reacts with carbonyl compounds to eliminate water and form $\text{C} = \text{N} - \text{OH}$ compounds called **oximes**. (a $\rightarrow$ ii)

(b) R-NH_2 (**Primary Amine**): Reacts with carbonyl compounds to eliminate water and form substituted imines ($\text{C} = \text{N} - \text{R}$), commonly known as **Schiff bases**. (b $\rightarrow$ iii)

(c) R-OH (**Alcohol**): Two molecules of alcohol react with an aldehyde in the presence of dry HCl gas to undergo nucleophilic addition forming **acetals**. (c $\rightarrow$ iv)

(d) HCN (**Hydrogen Cyanide**): Undergoes simple nucleophilic addition to the carbonyl group to form **cyanohydrins**. (d $\rightarrow$ i)

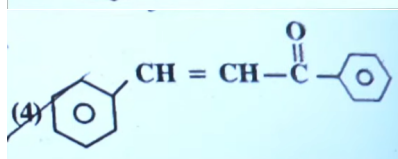
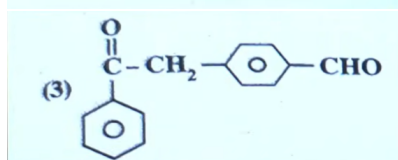
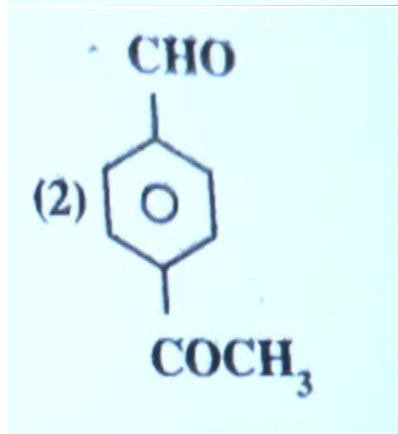
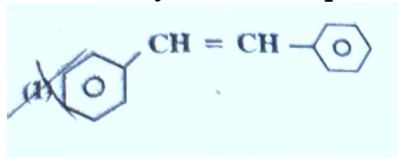
Step 4: Final Answer:

The matching sequence is a-ii, b-iii, c-iv, d-i, which corresponds to option (A).

Quick Tip: A useful mnemonic: Oxygen-containing hydroxylamine gives Oxime. Substituted amine gives Schiff base.

6. The major product 'A' in the given reaction is

Benzaldehyde + Acetophenone $\xrightarrow{OH^-/293K}$ 'A' (Major product)



(A) (1)

(B) (2)

(C) (3)

(D) (4)

Correct Answer: (D) (4)

Solution:

Step 1: Understanding the Concept:

This reaction between an aldehyde with no α -hydrogens and a ketone with α -hydrogens in the presence of a base is a Cross-Aldol condensation, specifically known as the Claisen-Schmidt condensation.

Step 2: Key Formula or Approach:

Identify the acidic α -hydrogens on the ketone, form the enolate ion, and perform a nucleophilic attack on the carbonyl carbon of the aldehyde, followed by dehydration to yield

an α, β -unsaturated ketone.

Step 3: Detailed Explanation:

1. The base (OH^-) abstracts an α -hydrogen from acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) to form a stable enolate ion: $\text{C}_6\text{H}_5\text{COCH}_2^-$.
2. The enolate ion attacks the electrophilic carbonyl carbon of benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$), forming a β -hydroxy ketone intermediate.
3. Protonation and subsequent dehydration (loss of a water molecule) occur easily at 293K (or upon mild heating) due to the extended conjugation of the newly formed double bond with the two benzene rings.

Reaction: $\text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{COC}_6\text{H}_5 \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CO} - \text{C}_6\text{H}_5$ (Chalcone).

Step 4: Final Answer:

Structure (4) representing 1,3-diphenylprop-2-en-1-one (Chalcone) is the correct major product.

Quick Tip: In a cross-aldol condensation between an aldehyde with no α -H and a ketone, the ketone always acts as the nucleophile (forms the enolate) and the aldehyde acts as the electrophile.

7. Carboxylic acids are more acidic than phenols because

- (A) Formation of dimers
- (B) Intermolecular hydrogen bonding
- (C) More covalent nature
- (D) More resonance stabilisation of their conjugate base

Correct Answer: (D) More resonance stabilisation of their conjugate base

Solution:

Step 1: Understanding the Concept:

The acidic strength of an organic compound is directly proportional to the stability of the conjugate base formed after the loss of a proton (H^+).

Step 2: Key Formula or Approach:

Compare the resonance structures of the carboxylate ion and the phenoxide ion to determine

which effectively disperses the negative charge better.

Step 3: Detailed Explanation:

1. **Carboxylate Ion (RCOO^-):** The negative charge is delocalized equally over two highly electronegative oxygen atoms. The two resonance structures are equivalent, providing a very high degree of stability.

2. **Phenoxide Ion ($\text{C}_6\text{H}_5\text{O}^-$):** The negative charge is delocalized over one oxygen atom and the carbon atoms of the benzene ring. Since carbon is significantly less electronegative than oxygen, the delocalization onto the ring is less effective at stabilizing the charge compared to delocalization between two oxygens. Moreover, the resonance structures are non-equivalent. Because the carboxylate ion is much more stable than the phenoxide ion, carboxylic acids release protons more readily than phenols.

Step 4: Final Answer:

The higher acidity is due to the greater resonance stabilization of the carboxylate conjugate base.

Quick Tip: Equivalency of resonance structures is a powerful stabilizing factor. Two equivalent structures (carboxylate) usually provide greater stability than multiple non-equivalent ones (phenoxide).

8. The compound that does not answer iodoform test is

- (A) Ethanal
- (B) Acetone
- (C) Ethanoic acid
- (D) Acetophenone

Correct Answer: (C) Ethanoic acid

Solution:

Step 1: Understanding the Concept:

The iodoform test (I_2/NaOH) is a specific qualitative test that yields a yellow precipitate of iodoform (CHI_3) for compounds containing the methyl ketone group or secondary alcohols oxidizable to it.

Step 2: Key Formula or Approach:

Examine the structure of each compound to identify the presence or absence of the methyl ketone ($-\text{COCH}_3$) or methyl carbinol ($-\text{CH}(\text{OH})\text{CH}_3$) group.

Step 3: Detailed Explanation:

(A) **Ethanal** (CH_3CHO): Contains the $\text{CH}_3-\text{CO}-$ group. Gives a positive test.

(B) **Acetone** (CH_3COCH_3): Contains the $\text{CH}_3-\text{CO}-$ group. Gives a positive test.

(C) **Ethanoic acid** (CH_3COOH): Although it has a methyl group adjacent to a carbonyl group, it is a carboxylic acid. The acidic $-\text{OH}$ group undergoes rapid acid-base neutralization with the base (NaOH) to form a resonance-stabilized carboxylate ion. The delocalization prevents the enolization and halogenation of the adjacent methyl group. Carboxylic acids do not give the iodoform test.

(D) **Acetophenone** ($\text{C}_6\text{H}_5\text{COCH}_3$): Contains the $\text{CH}_3-\text{CO}-$ group attached to a phenyl ring. Gives a positive test.

Step 4: Final Answer:

Ethanoic acid does not give a positive iodoform test.

Quick Tip: Remember that the "Methyl Ketone" group must be part of an aldehyde or ketone. Esters, amides, and carboxylic acids with a $\text{CH}_3-\text{CO}-$ structural unit generally fail the iodoform test due to resonance involving the heteroatom.

9. Nitration of aniline in strong acidic medium gives significant amount of m-nitroaniline because

- (A) In electrophilic substitution reaction, amino group is meta directing
- (B) In strong acidic medium, aniline is present as anilinium ion
- (C) $-\text{NH}_2$ group always directs to meta position
- (D) m-nitroaniline has higher molar mass than o&p nitroanilines

Correct Answer: (B) In strong acidic medium, aniline is present as anilinium ion

Solution:

Step 1: Understanding the Concept:

The free $-NH_2$ group in aniline is strongly activating and ortho/para directing. However, the nitration reaction conditions vastly alter its directing nature.

Step 2: Key Formula or Approach:

Analyze the effect of a strongly acidic nitrating mixture (conc. HNO_3 and conc. H_2SO_4) on the basic amino group during electrophilic aromatic substitution.

Step 3: Detailed Explanation:

In the presence of the strong acid used for nitration, the highly basic amino group of aniline gets protonated to form the anilinium ion ($C_6H_5NH_3^+$).

The $-NH_3^+$ group is a strongly deactivating group. Because it has a full positive charge directly attached to the benzene ring, it withdraws electron density strongly via the inductive effect ($-I$ effect) and does not possess lone pairs for resonance donation. As a result, it acts as a **meta-directing** group.

Therefore, a significant amount (about 47%) of the meta isomer is formed alongside the expected para (51%) and ortho (2%) products.

Step 4: Final Answer:

The formation of the meta product is due to the presence of the meta-directing anilinium ion in the acidic medium.

Quick Tip: To get purely ortho/para nitroaniline, you must "protect" the amino group first by acetylation (forming acetanilide) before carrying out nitration, and hydrolyze it afterward.

10. Basic strength of alkylamines in aqueous phase is not decided by

- (A) Inductive effect
- (B) Solvation effect
- (C) Steric hindrance
- (D) Hyperconjugation effect

Correct Answer: (D) Hyperconjugation effect

Solution:

Step 1: Understanding the Concept:

The basicity of amines is dependent on the availability of the lone pair on the nitrogen atom and the stability of the substituted ammonium cation formed after accepting a proton in water.

Step 2: Key Formula or Approach:

Evaluate the factors influencing amine basicity in an aqueous solution (Inductive effect, Solvation, Steric hindrance) and identify the unrelated electronic factor.

Step 3: Detailed Explanation:

In the aqueous phase, three main factors compete to determine the order of basicity of alkylamines:

1. **Inductive effect (+I):** Alkyl groups are electron-donating, which pushes electron density toward nitrogen, making the lone pair more available and increasing basicity.
2. **Solvation effect:** Smaller substituted ammonium cations (from primary amines) are more stabilized by hydrogen bonding with water molecules than larger ones (from tertiary amines).
3. **Steric hindrance:** Large alkyl groups physically hinder the approach of protons or the hydration of the resulting cation, decreasing basicity.

Hyperconjugation involves the delocalization of σ electrons of $C-H$ bonds into an adjacent empty p-orbital or π system. It does not play a role in the availability of the non-bonding lone pair on the saturated sp^3 nitrogen of alkylamines.

Step 4: Final Answer:

Hyperconjugation effect does not decide the basic strength of alkylamines.

Quick Tip: Basicity order in water for methyl amines: $2^\circ > 1^\circ > 3^\circ > NH_3$. For ethyl amines: $2^\circ > 3^\circ > 1^\circ > NH_3$. Note the interplay of the three valid factors!

11. The reaction sequence is: Benzene $\xrightarrow{\text{Conc.HNO}_3, \text{Conc.H}_2\text{SO}_4, 323-333\text{K}}$ A $\xrightarrow{\text{Fe/HCl}}$ B $\xrightarrow{\text{NaNO}_2/\text{HCl}, 273\text{K}}$ C
 $\xrightarrow{\text{C}_2\text{H}_5\text{OH}}$ Benzene + D + HCl + N₂. Organic compound 'D' is

(A) Phenol (C₆H₅OH)

(B) Acetic acid (CH₃COOH)

(C) Ethanal (CH_3CHO)

(D) N-ethylaniline ($\text{C}_6\text{H}_5\text{NH}-\text{C}_2\text{H}_5$)

Correct Answer: (C) Ethanal (CH_3CHO)

Solution:

Step 1: Understanding the Concept:

The problem presents a multi-step organic synthesis starting from benzene and passing through a diazonium salt intermediate.

Step 2: Key Formula or Approach:

Trace the multi-step synthesis involving nitration, reduction, diazotization, and the specific redox reaction of diazonium salts with ethanol.

Step 3: Detailed Explanation:

1. **Benzene** $\rightarrow$ **A**: Nitration of benzene with a nitrating mixture gives Nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$).
2. **A** $\rightarrow$ **B**: Reduction of nitrobenzene with a metal/acid combination (Fe/HCl) gives Aniline ($\text{C}_6\text{H}_5\text{NH}_2$).
3. **B** $\rightarrow$ **C**: Diazotization of aniline with NaNO_2/HCl at low temperature ($0-5^\circ\text{C}$ or 273K) yields Benzene diazonium chloride ($\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$).
4. **C** $\rightarrow$ **Benzene** + **D**: Reaction of benzene diazonium chloride with ethanol ($\text{C}_2\text{H}_5\text{OH}$) is a redox reaction. Ethanol acts as a reducing agent, converting the diazonium salt to benzene, and in the process, ethanol is oxidized to ethanal (acetaldehyde).

Reaction: $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}_6\text{H}_6 + \text{CH}_3\text{CHO}$ (Compound D) + $\text{N}_2 + \text{HCl}$.

Step 4: Final Answer:

The compound 'D' produced by the oxidation of ethanol is ethanal.

Quick Tip: Benzene diazonium chloride can be reduced to benzene using either Hypophosphorous acid (H_3PO_2 , which oxidizes to H_3PO_3) or Ethanol ($\text{C}_2\text{H}_5\text{OH}$, which oxidizes to CH_3CHO).

12. Statement I: Staggered conformation of ethane is more stable than the eclipsed conformation.

Statement II: The torsional strain in staggered conformation is more.

Read the above statements and choose the correct answer from the options given below.

- (A) Both Statement I and Statement II are false
(B) Both Statement I and Statement II are true
(C) Statement I is true but Statement II is false
(D) Statement I is false but Statement II is true

Correct Answer: (C) Statement I is true but Statement II is false

Solution:

Step 1: Understanding the Concept:

Conformational isomerism in alkanes involves analyzing the relative stability of different spatial arrangements based on repulsive forces between bonds.

Step 2: Key Formula or Approach:

Define torsional strain (repulsion between electron clouds of eclipsing bonds) and relate it to the dihedral angle and stability of Newman projections.

Step 3: Detailed Explanation:

1. **Statement I:** In the staggered conformation of ethane, the $C-H$ bonds on the two adjacent carbons are as far apart as possible (dihedral angle = 60°). This minimizes electron-electron repulsion. In the eclipsed conformation, they are closest together (dihedral angle = 0°), maximizing repulsion. Thus, the staggered conformation possesses lower potential energy and is more stable. (Statement I is True)

2. **Statement II:** Torsional strain refers to the repulsion between the bonding electrons of adjacent atoms. Since the staggered form has maximum distance between these bonds, it has the **minimum** torsional strain. Conversely, the eclipsed form has maximum torsional strain. (Statement II is False)

Step 4: Final Answer:

Statement I is correct, but Statement II is incorrect.

Quick Tip: Stability is inversely proportional to Torsional Strain. Staggered = Bonds far apart = Low strain = High stability. Eclipsed = Bonds close together = High strain = Low stability.

13. From the given information, select the suitable law of chemical combination:

Cupric Carbonate % of Cu % of C % of O

Natural Sample	51.35	9.74	38.91
Synthetic Sample	51.35	9.74	38.91

- (A) Law of Multiple Proportions
- (B) Gay Lussac's Law of Gaseous Volumes
- (C) Law of Definite Proportions
- (D) Law of Conservation of Mass

Correct Answer: (C) Law of Definite Proportions

Solution:

Step 1: Understanding the Concept:

The fundamental laws of chemical combination describe how elements combine stoichiometrically to form compounds.

Step 2: Key Formula or Approach:

Match the experimental observation (identical mass percentages of elements in a compound obtained from different sources) to the corresponding stoichiometric law.

Step 3: Detailed Explanation:

The **Law of Definite Proportions** (also known as the Law of Constant Composition), proposed by Joseph Proust, states that a given chemical compound always contains its component elements in a fixed ratio by mass, regardless of its source or method of preparation.

The provided data explicitly shows that both the natural sample and the synthetic sample of Cupric Carbonate have exactly the same percentage composition of Copper (51.35%), Carbon (9.74%), and Oxygen (38.91%). This perfectly illustrates and confirms the law.

Step 4: Final Answer:

The information supports the Law of Definite Proportions.

Quick Tip: Look for the keywords "Natural vs Synthetic" or "different sources" in the question; it almost always points directly to the Law of Definite Proportions.

14. Match List - I with List - II and select the correct option (Based on mole concept):

List - I

List - II

(a) 2 moles of ethene

(i) 11.2 L volume at STP

- (b) Molar mass is equal to 66 g (ii) 56 g
 (c) 1 g of H_2 (iii) 12.04×10^{23} molecules
 (d) 2 moles of water vapours (iv) 1.5 mole of CO_2

Codes:

- (A) a – ii, b – iv, c – i, d – iii
 (B) a – iii, b – i, c – iv, d – ii
 (C) a – i, b – iv, c – ii, d – iii
 (D) a – ii, b – iii, c – i, d – iv

Correct Answer: (A) a – ii, b – iv, c – i, d – iii

Solution:

Step 1: Understanding the Concept:

The mole concept allows interconversion between mass, volume at STP, and number of particles using molar mass and Avogadro's number.

Step 2: Key Formula or Approach:

Apply standard mole formulas: $Mass = n \times M_w$, $Volume_{STP} = n \times 22.4 \text{ L}$, and $Molecules = n \times N_A$ ($N_A = 6.022 \times 10^{23}$).

Step 3: Detailed Explanation:

(a) **2 moles of ethene (C_2H_4):** Molar mass = $2(12) + 4(1) = 28 \text{ g/mol}$.

Mass = 2 moles $\times$ 28 g/mol = 56 g. (Matches with ii)

(b) **Molar mass is equal to 66 g:** Let's check the options. For CO_2 , molar mass = $12 + 2(16) = 44 \text{ g/mol}$.

Mass of 1.5 moles of CO_2 = 1.5 moles $\times$ 44 g/mol = 66 g. (Matches with iv)

(c) **1 g of H_2 :** Molar mass of H_2 = 2 g/mol.

Moles = $\frac{1 \text{ g}}{2 \text{ g/mol}} = 0.5 \text{ mol}$.

Volume at STP = 0.5 mol $\times$ 22.4 L/mol = 11.2 L. (Matches with i)

(d) **2 moles of water vapours (H_2O):**

Molecules = $n \times N_A = 2 \times 6.022 \times 10^{23} = 12.044 \times 10^{23}$. (Matches with iii)

Step 4: Final Answer:

The matching sequence is a-ii, b-iv, c-i, d-iii.

Quick Tip: Always start matching with the calculation that seems easiest or most unique (usually mass) to narrow down the given options quickly.

15. Match List – I with List – II:

List - I (Element-Atomic number)

List - II (Position in periodic table)

(a) Ra - 88

(i) 4th period, 13th group

(b) Ga - 31

(ii) 6th period, 6th group

(c) W - 74

(iii) 5th period, 10th group

(d) Pd - 46

(iv) 7th period, 2nd group

Choose the correct answer from the options given below.

(A) a – iv, b – i, c – ii, d – iii

(B) a – i, b – ii, c – iii, d – iv

(C) a – iv, b – ii, c – iii, d – i

(D) a – iii, b – iv, c – i, d – ii

Correct Answer: (A) a – iv, b – i, c – ii, d – iii

Solution:

Step 1: Understanding the Concept:

The position of an element in the periodic table (Group and Period) is determined by its electronic configuration, specifically its valence shell and the number of valence electrons.

Step 2: Key Formula or Approach:

Determine the group and period by writing the electronic configuration based on the atomic number, usually by finding the preceding noble gas.

Step 3: Detailed Explanation:

(a) **Radium (Ra - 88):** Preceding noble gas is Radon (86). Configuration: $[Rn]7s^2$. Highest principal quantum number is 7 (Period 7). It has 2 valence electrons in the s-orbital (Group 2, Alkaline earth metal). (a → iv)

(b) **Gallium (Ga - 31):** Preceding noble gas is Argon (18). Configuration: $[Ar]3d^{10}4s^24p^1$. Highest $n = 4$ (Period 4). It is a p-block element, Group = 12 + p-electrons = 12 + 1 = 13. (b → i)

(c) **Tungsten (W - 74):** Preceding noble gas is Xenon (54). Configuration: $[Xe]4f^{14}5d^46s^2$.

Highest $n = 6$ (Period 6). It is a d-block element, Group = s-electrons + d-electrons = $2 + 4 = 6$.
(c $\rightarrow$ ii)

(d) **Palladium (Pd - 46)**: Preceding noble gas is Krypton (36). Configuration: Exceptionally $[Kr]4d^{10}5s^0$. It belongs to Period 5. Group = $10 + 0 = 10$. (d $\rightarrow$ iii)

Step 4: Final Answer:

Matching gives: a-iv, b-i, c-ii, d-iii.

Quick Tip: Remember the atomic numbers of noble gases: He(2), Ne(10), Ar(18), Kr(36), Xe(54), Rn(86). Subtracting these from the given atomic number helps you quickly construct the valence shell configuration!

16. The types of hybrid orbitals of nitrogen in NO_2^+ , NO_3^- , and NH_4^+ respectively are

- (A) sp , sp^2 and sp^3
- (B) sp , sp^3 and sp^2
- (C) sp^2 , sp and sp^3
- (D) sp^2 , sp^3 and sp

Correct Answer: (A) sp , sp^2 and sp^3

Solution:

Step 1: Understanding the Concept:

Hybridization of the central atom dictates the molecular geometry and is determined by the number of sigma bonds and lone pairs around the atom.

Step 2: Key Formula or Approach:

Use the Steric Number (SN) formula: $SN = (\text{Number of atoms bonded}) + (\text{Number of lone pairs})$. $SN = 2$ (sp), 3 (sp^2), 4 (sp^3). Adjust valence electrons for ionic charges.

Step 3: Detailed Explanation:

1. **NO_2^+ (Nitryl cation):** Nitrogen group 15 has 5 valence electrons. Subtract 1 for the positive charge = 4 electrons. It forms 2 double bonds with 2 oxygen atoms.

$SN = 2$ (bonded atoms) + 0 (lone pairs) = 2. Hybridization: **sp** . Shape: Linear.

2. NO_3^- (Nitrate ion): Nitrogen has 5 valence electrons. Add 1 for the negative charge = 6 electrons available for bonding. It bonds to 3 oxygen atoms (one double bond, two single coordinate/resonance bonds).

$SN = 3$ (bonded atoms) + 0 (lone pairs) = 3. Hybridization: sp^2 . Shape: Trigonal planar.

3. NH_4^+ (Ammonium ion): Nitrogen has 5 valence electrons. Subtract 1 for positive charge = 4 electrons. It forms 4 single bonds with 4 hydrogen atoms.

$SN = 4$ (bonded atoms) + 0 (lone pairs) = 4. Hybridization: sp^3 . Shape: Tetrahedral.

Step 4: Final Answer:

The order is sp , sp^2 , sp^3 .

Quick Tip: For polyatomic ions, always adjust the valence electron count of the central atom first based on the charge (+ means subtract an electron, – means add one).

17. In which of the following option/options, the order of arrangement does not agree with the variation of property indicated against it?

(a) $\text{BF}_3 > \text{NF}_3 > \text{NH}_3$ (Dipole moment)

(b) $\text{HgCl}_2 > \text{NH}_4^+ > \text{SF}_4$ (Bond angle)

(c) $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ (Strength of intermolecular hydrogen bonding)

(d) $\text{H} - \text{I} > \text{H} - \text{Br} > \text{H} - \text{Cl}$ (Bond length)

(A) a, b and c

(B) a only

(C) c and d only

(D) d only

Correct Answer: (B) a only

Solution:

Step 1: Understanding the Concept:

Evaluate various molecular properties based on molecular symmetry, VSEPR theory, electronegativity, and atomic radii trends across the periodic table.

Step 2: Key Formula or Approach:

Analyze each trend individually: dipole moment relies on vector addition of bond dipoles; bond angle depends on hybridization and lone pair repulsion; H-bonding strength depends on the electronegativity of the donor atom; bond length depends on the atomic radius of the halogen.

Step 3: Detailed Explanation:

(a) **Dipole Moment:** BF_3 is perfectly symmetric (trigonal planar), so its bond dipoles cancel out, making $\mu = 0$. NH_3 and NF_3 are trigonal pyramidal. In NH_3 , the lone pair dipole and $N-H$ bond dipoles reinforce each other. In NF_3 , they oppose each other, lowering the net dipole. The correct order is $NH_3 > NF_3 > BF_3$ (0). The given order is **Incorrect**.

(b) **Bond Angle:** $HgCl_2$ is linear (180°), NH_4^+ is tetrahedral (109.5°), SF_4 has a see-saw shape due to a lone pair, compressing the equatorial angles to $< 120^\circ$ and axial to $< 180^\circ$ (typically referenced by its smallest angles $\approx 90^\circ$). Order: $180^\circ > 109.5^\circ > 90^\circ$ is **Correct**.

(c) **H-bonding Strength:** The strength depends on the electronegativity of the atom bonded to Hydrogen ($F > O > N$). Thus, the single H-bond strength order: $HF > H_2O > NH_3$ is **Correct**.

(d) **Bond Length:** Bond length increases with the size of the atoms involved. Down the halogen group, radius increases ($I > Br > Cl$). Order: $HI > HBr > HCl$ is **Correct**.

Step 4: Final Answer:

Only option (a) provides an incorrect order.

Quick Tip: BF_3 has a zero dipole moment because it is perfectly symmetrical. Always check symmetry first in dipole moment questions! NH_3 vs NF_3 is a classic comparison.

18. With respect to resonance structures of CO_3^{2-} ion, which of the following statements are correct?

- (a) All C-O bonds in CO_3^{2-} are equivalent
- (b) There are three resonance structures possible for CO_3^{2-} ion
- (c) The position of carbon and oxygen should change in every resonance structure
- (d) The formal charge on carbon atom is -2

(A) a, b and c

(B) a and b only

(C) b and d only

(D) a, b and d

Correct Answer: (B) a and b only

Solution:

Step 1: Understanding the Concept:

Resonance is a method of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by one single Lewis structure.

Step 2: Key Formula or Approach:

Apply the rules of resonance: atomic nuclei positions must remain fixed while only electrons (pi bonds and lone pairs) move, creating a hybrid structure.

Step 3: Detailed Explanation:

(a) **Equivalent bonds:** In the resonance hybrid of the carbonate ion, the double bond character is distributed equally among all three C – O bonds. They all have a bond order of 1.33. (Correct)

(b) **Three structures:** The Lewis structure has one double bond and two single bonds. The double bond can be placed on any one of the three oxygen atoms, resulting in three equivalent canonical forms. (Correct)

(c) **Position of atoms:** In resonance, only the arrangement of electrons changes. The spatial positions of the nuclei (atoms) must remain absolutely constant. (Incorrect)

(d) **Formal charge:** In the resonance hybrid, the net charge is -2 . However, the calculated formal charge on the central carbon atom is exactly 0, while each oxygen carries an average formal charge of $-2/3$. (Incorrect)

Step 4: Final Answer:

Statements (a) and (b) are correct.

Quick Tip: Fundamental Rule of Resonance: **Atoms do not move**, only electrons do. If atoms move, it is an isomerisation reaction, not a resonance structure.

19. **Statement I :** In H_2O_2 , each oxygen atom is assigned an oxidation number of -1 , In RbO_2 , each oxygen atom is assigned an oxidation number of $-\frac{1}{2}$.

Statement II : Representation of HAuCl_4 and MnO_2 in stock notation is HAu(III)Cl_4 and Mn(II)O_2 ,

respectively.

Examine the above statements and choose the correct answer.

- (A) Both Statement I and Statement II are correct
- (B) Both Statement I and Statement II are incorrect
- (C) Statement I is correct but Statement II is incorrect
- (D) Statement I is incorrect but Statement II is correct

Correct Answer: (C) Statement I is correct but Statement II is incorrect

Solution:

Step 1: Understanding the Concept:

Oxidation numbers depend on the electronegativity and bonding environment. Stock notation is a method of representing the oxidation state of a metal in a compound using Roman numerals in parentheses.

Step 2: Key Formula or Approach:

Calculate oxidation numbers using standard rules (peroxide = -1, superoxide = -1/2) and apply Roman numerals for the Stock notation based on the calculated oxidation state of the central metal.

Step 3: Detailed Explanation:

1. **Statement I:** H_2O_2 is hydrogen peroxide. In peroxides, the oxidation state of oxygen is strictly -1 . RbO_2 is rubidium superoxide, containing the Rb^+ cation and the O_2^- superoxide anion. The charge of -1 is shared by 2 oxygen atoms, so each O has an average oxidation state of $-1/2$. (Statement I is True)

2. **Statement II:** Let's calculate the oxidation states for the metals:

In $HAuCl_4$: H is +1 and each Cl is -1 . Let Au be x .

$1 + x + 4(-1) = 0 \Rightarrow x - 3 = 0 \Rightarrow x = +3$. So $HAu(III)Cl_4$ is correct.

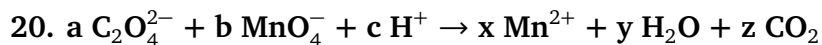
In MnO_2 : oxygen is usually -2 . Let Mn be x .

$x + 2(-2) = 0 \Rightarrow x - 4 = 0 \Rightarrow x = +4$. The stock notation should be $Mn(IV)O_2$, not $Mn(II)O_2$. (Statement II is False)

Step 4: Final Answer:

Statement I is correct but Statement II is incorrect.

Quick Tip: Stock notation always reflects the **actual** calculated oxidation state of the element. Check calculations carefully; MnO_2 is manganese dioxide, a classic example where Mn is in the +4 state.



a and x respectively are

- (A) 5, 2
- (B) 4, 1
- (C) 3, 2
- (D) 4, 2

Correct Answer: (A) 5, 2

Solution:

Step 1: Understanding the Concept:

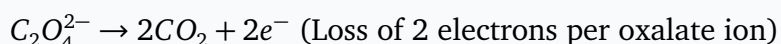
This is a redox reaction happening in an acidic medium involving the oxidation of oxalate ions by permanganate ions.

Step 2: Key Formula or Approach:

Balance the redox equation using the ion-electron (half-reaction) method by separately balancing the oxidation and reduction halves, then equalizing the electrons transferred.

Step 3: Detailed Explanation:

1. **Oxidation half-reaction:** Oxalate ion oxidizes to carbon dioxide.



2. **Reduction half-reaction:** Permanganate ion reduces to Manganese(II) in acidic medium.



3. **Balancing electrons:**

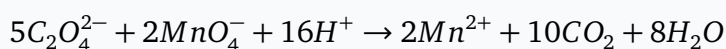
Multiply the oxidation half-reaction by 5:



Multiply the reduction half-reaction by 2:



4. **Summing the reactions:**



Comparing with the given equation: $a = 5$, $b = 2$, $c = 16$, $x = 2$, $y = 8$, $z = 10$.

Step 4: Final Answer:

The values of a and x are 5 and 2 respectively.

Quick Tip: This is the standard permanganate-oxalate titration reaction. Remembering the stoichiometric mole ratio $MnO_4^- : C_2O_4^{2-}$ as 2 : 5 in acidic medium saves a lot of time!

21. Which of the following will not act as an oxidising agent?

- (A) CrO_3
- (B) MoO_3
- (C) CrO_4^{2-}
- (D) $Cr_2O_7^{2-}$

Correct Answer: (B) MoO_3

Solution:**Step 1: Understanding the Concept:**

An oxidizing agent gets reduced during a chemical reaction. A compound tends to act as a strong oxidizing agent when its central metal atom is in a highly unstable maximum oxidation state.

Step 2: Key Formula or Approach:

Determine the oxidation state of each metal and assess its relative stability based on its position in the d-block groups. Heavier transition metals stabilize higher oxidation states better than lighter ones.

Step 3: Detailed Explanation:

1. **Chromium (VI) compounds:** In CrO_3 , CrO_4^{2-} , and $Cr_2O_7^{2-}$, Chromium is in its highest group oxidation state (+6). In the first transition series (3d), this +6 state is quite unstable and eagerly accepts electrons to reduce to the stable Cr^{3+} state, making these species very strong oxidizing agents.

2. **Molybdenum (VI) compound:** Molybdenum is in the same group as Chromium but in the second transition series (4d). A key trend in the d-block is that heavier elements form much more stable higher oxidation states compared to the 3d elements. Therefore, MoO_3 (where

Mo is +6) is thermodynamically very stable and does not readily act as an oxidizing agent.

Step 4: Final Answer:

MoO_3 will not act as a typical oxidizing agent under normal conditions compared to the Cr(VI) species.

Quick Tip: Trend: High oxidation states become more stable as you go **down** a group in the transition metals (e.g., $\text{W(VI)} > \text{Mo(VI)} > \text{Cr(VI)}$). This is opposite to the p-block trend (Inert Pair Effect).

22. The highest oxidation state of manganese in fluoride is +4 (MnF_4), but the highest oxidation state in oxides is +7 (Mn_2O_7), because

- (A) Fluorine is more electronegative than oxygen
- (B) Fluorine possesses d-orbitals
- (C) Fluorine stabilises lower oxidation state
- (D) In covalent compounds, fluorine can form single bond only, while oxygen forms double bond

Correct Answer: (D) In covalent compounds, fluorine can form single bond only, while oxygen forms double bond

Solution:

Step 1: Understanding the Concept:

The ability of an element to exhibit a high oxidation state depends heavily on the bonding characteristics of the electronegative atoms it coordinates with.

Step 2: Key Formula or Approach:

Analyze the valency and bonding capabilities (single vs. multiple bonds) and the resulting steric crowding effects of fluorine compared to oxygen.

Step 3: Detailed Explanation:

1. Fluorine is a monovalent halogen and can only form a single covalent bond (sigma bond) with the central manganese atom. To reach an oxidation state of +7 solely with fluorine, Mn would theoretically need to be surrounded by 7 bulky fluorine atoms (MnF_7), which creates impossible steric hindrance and repulsion, making such a molecule highly unstable.
2. Oxygen, being divalent, has the ability to form multiple bonds (double bonds utilizing

$p\pi - d\pi$ interactions). This allows oxygen to stabilize the highest oxidation state of Mn (+7 in Mn_2O_7 or MnO_4^-) using significantly fewer coordinating atoms. Only 4 oxygen atoms are needed to reach the valence requirements, vastly reducing steric crowding.

Step 4: Final Answer:

The ability of oxygen to form double bonds is the primary reason it can stabilize higher oxidation states than fluorine.

Quick Tip: While Fluorine is the most electronegative element, Oxygen often "wins" at stabilizing the **highest** oxidation states because its "double bond" capability requires fewer ligands, resolving steric problems.

23. The calculated spin only magnetic moment of Cr^{2+} ion is

- (A) 3.87 BM
- (B) 4.90 BM
- (C) 5.92 BM
- (D) 2.84 BM

Correct Answer: (B) 4.90 BM

Solution:

Step 1: Understanding the Concept:

The magnetic moment of transition metal ions is primarily determined by the number of unpaired electrons in their d-orbitals.

Step 2: Key Formula or Approach:

Write the electronic configuration of the ion, count the number of unpaired electrons (n), and use the spin-only formula: $\mu = \sqrt{n(n+2)}$ BM.

Step 3: Detailed Explanation:

1. The atomic number of Chromium (Cr) is 24. Its neutral electronic configuration is an exception: $[Ar]3d^5 4s^1$.
2. To form the Cr^{2+} cation, 2 electrons are removed. Electrons are removed from the outermost shell first (one from 4s), then from the inner shell (one from 3d).

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

3. In a $3d^4$ configuration, applying Hund's rule, there are 4 unpaired electrons ($n = 4$).

4. Calculation using the formula:

$$\mu = \sqrt{4(4 + 2)}$$

$$\mu = \sqrt{4 \times 6} = \sqrt{24}$$

$$\mu \approx 4.898 \approx 4.90 \text{ BM}$$

Step 4: Final Answer:

The calculated spin-only magnetic moment is 4.90 BM.

Quick Tip: Math Shortcut: If $n = 4$, the magnetic moment will always be 4.something. If $n = 3$, it will be 3.something. This pattern helps identify the answer immediately without calculating square roots!

24. Which of the following is the most stable complex?

- (A) $[Fe(CO)_5]$
- (B) $[Fe(CN)_6]^{4-}$
- (C) $[Fe(C_2O_4)_3]^{3-}$
- (D) $[Fe(H_2O)_6]^{3+}$

Correct Answer: (C) $[Fe(C_2O_4)_3]^{3-}$

Solution:

Step 1: Understanding the Concept:

The stability of a coordination complex depends on various factors including the nature of the

central metal ion, the field strength of the ligands, and prominently, the chelate effect.

Step 2: Key Formula or Approach:

Identify the denticity of the ligands involved. Complexes with chelating ligands (bidentate or polydentate) exhibit exceptional thermodynamic stability.

Step 3: Detailed Explanation:

1. The ligands H_2O and CO are strictly unidentate (monodentate). The CN^- ion is also unidentate.
2. The $C_2O_4^{2-}$ (oxalate) ion is a **bidentate** ligand, meaning it binds to the metal center at two points simultaneously.
3. When a bidentate ligand binds, it forms a ring structure with the central metal. This phenomenon is called the **chelate effect**. The formation of three stable 5-membered rings in $[Fe(C_2O_4)_3]^{3-}$ causes a highly positive entropy change ($\Delta S > 0$), making the formation thermodynamically very favorable and providing immense stability compared to similar complexes with only unidentate ligands.

Step 4: Final Answer:

$[Fe(C_2O_4)_3]^{3-}$ is the most stable complex due to the chelate effect.

Quick Tip: In any comparison of complex stability, look for chelating ligands (like oxalate, en, edta) first. They almost always result in the most stable complex in a multiple-choice setting.

25. How many ions per molecule are produced from the complex $[Co(NH_3)_6]Cl_3$ in solution?

- (A) 6
(B) 4
(C) 3
(D) 2

Correct Answer: (B) 4

Solution:

Step 1: Understanding the Concept:

In coordination chemistry, a complex consists of a coordination sphere (inside the square

brackets) and an ionization sphere (outside the square brackets).

Step 2: Key Formula or Approach:

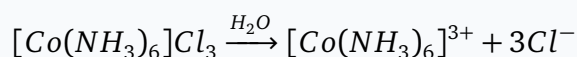
Write the dissociation equation for the complex in water. The coordination sphere does not break apart, acting as a single intact polyatomic ion, while the counter-ions dissociate completely.

Step 3: Detailed Explanation:

The given complex is $[Co(NH_3)_6]Cl_3$.

The entity inside the square brackets, $[Co(NH_3)_6]$, is the complex cation. The three chlorine atoms outside are the ionizable counter-anions.

When dissolved in water, the dissociation reaction is:



Total number of ions produced = 1 (complex cation) + 3 (chloride anions) = 4 ions.

Step 4: Final Answer:

A total of 4 ions are produced per molecule.

Quick Tip: Count the number of species outside the square bracket and add 1 (for the entire bracket).

Here: 3 (Cl) + 1 (complex bracket) = 4.

26. Given below are two statements:

Statement I: The M – C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant d-orbital of the metal

Statement II: The M – C π bond is formed by the donation of a pair of electrons from a filled d-orbital of metal into the vacant antibonding π^* orbital of carbon monoxide.

In the light of the above statements, choose the correct answer from the options given below:

- (A) Both Statement I and Statement II are correct
- (B) Both Statement I and Statement II are incorrect
- (C) Statement I is correct but Statement II is incorrect
- (D) Statement I is incorrect but Statement II is correct

Correct Answer: (A) Both Statement I and Statement II are correct

Solution:

Step 1: Understanding the Concept:

This question deals with the nature of bonding in metal carbonyls, characterized by a unique double-interaction known as **Synergic Bonding**.

Step 2: Key Formula or Approach:

Define the theoretical basis of the synergic mechanism: sigma donation from ligand to metal and pi back-donation from metal to ligand.

Step 3: Detailed Explanation:

1. **Statement I:** The carbon atom of the Carbon Monoxide (CO) ligand acts as a Lewis base. It donates its non-bonding lone pair of electrons into an empty d-orbital (or hybridized orbital) of the transition metal to form a dative σ bond. (Statement I is True)

2. **Statement II:** Simultaneously, the transition metal, which now has increased electron density, acts as a Lewis base. It donates a pair of electrons from a filled, properly aligned d-orbital back into the vacant π^* (antibonding) molecular orbital of the CO ligand. This "back-donation" creates a π bond. (Statement II is True)

This dual interaction creates a self-strengthening cycle (synergism) making the metal-carbon bond exceptionally strong.

Step 4: Final Answer:

Both statements accurately describe the synergic bonding mechanism.

Quick Tip: Synergic bonding explains why CO acts as such a strong field ligand in the spectrochemical series and why metal carbonyls are so highly stable. It's a "two-way street" of electron donation.

27. Match List - I with List - II

List - I (Complex)

List - II (Geometry)

(a) $[Co(NH_3)_6]^{3+}$ (i) Trigonal bipyramidal

(b) $[NiCl_4]^{2-}$ (ii) Octahedral

(c) $[Ni(CN)_4]^{2-}$ (iii) Tetrahedral

(d) $[Fe(CO)_5]$ (iv) Square planar

Choose the correct answer from the options given below.

- (A) a - ii, b - iii, c - iv, d - i
(B) a - ii, b - i, c - iii, d - iv
(C) a - iii, b - ii, c - iv, d - i
(D) a - i, b - iii, c - iv, d - ii

Correct Answer: (A) a - ii, b - iii, c - iv, d - i

Solution:

Step 1: Understanding the Concept:

The geometry of a coordination complex is primarily dictated by its Coordination Number (CN) and the hybridization of the central metal, which is influenced by the field strength of the ligands.

Step 2: Key Formula or Approach:

Determine the coordination number from the formula. For CN=6, the geometry is Octahedral. For CN=5, it's Trigonal Bipyramidal. For CN=4, use Valence Bond Theory (strong vs weak ligands) to distinguish between Tetrahedral (sp^3) and Square Planar (dsp^2).

Step 3: Detailed Explanation:

(a) $[\text{Co}(\text{NH}_3)_6]^{3+}$: CN = 6. With six ligands, the only possible symmetric geometry is **Octahedral**. (a $\rightarrow$ ii)

(b) $[\text{NiCl}_4]^{2-}$: CN = 4. The Cl^- ion is a weak field ligand, so it does not force electron pairing in the Ni^{2+} (d^8) ion. The hybridization utilizes outer orbitals (sp^3), resulting in a **Tetrahedral** geometry. (b $\rightarrow$ iii)

(c) $[\text{Ni}(\text{CN})_4]^{2-}$: CN = 4. The CN^- ion is a very strong field ligand, forcing electron pairing. This frees up an inner d-orbital, leading to dsp^2 hybridization and a **Square planar** geometry. (c $\rightarrow$ iv)

(d) $[\text{Fe}(\text{CO})_5]$: CN = 5. With five ligands, the characteristic geometry is **Trigonal bipyramidal** (dsp^3 hybridization). (d $\rightarrow$ i)

Step 4: Final Answer:

The correct matching sequence is a-ii, b-iii, c-iv, d-i.

Quick Tip: For CN=4, always check the ligand strength. Strong ligands (CN^- , CO) generally lead to dsp^2 (Square Planar), while weak ligands (Cl^- , F^-) lead to sp^3 (Tetrahedral).

28. Match List - I with List – II

List - I (Vitamins)

List - II (Deficiency Diseases)

- | | |
|---------------------|------------------------------------|
| (a) B ₁ | (i) Convulsions |
| (b) B ₂ | (ii) RBC deficiency in haemoglobin |
| (c) B ₆ | (iii) Retarded growth |
| (d) B ₁₂ | (iv) Burning sensation of the skin |

Choose the correct answer from the options given below.

(A) a – ii, b – iv, c – iii, d – i

(B) a – iii, b – iv, c – i, d – ii

(C) a – i, b – ii, c – iii, d – iv

(D) a – iv, b – iii, c – ii, d – i

Correct Answer: (B) a – iii, b – iv, c – i, d – ii

Solution:

Step 1: Understanding the Concept:

Vitamins are essential organic micronutrients. Their chronic deficiency leads to specific, well-documented clinical conditions and diseases.

Step 2: Key Formula or Approach:

Recall the standard biological functions and deficiency diseases associated with the B-complex group of vitamins from memory.

Step 3: Detailed Explanation:

(a) **Vitamin B₁ (Thiamine):** Deficiency typically leads to Beri-beri and presents with symptoms including loss of appetite and **retarded growth**. (a → iii)

(b) **Vitamin B₂ (Riboflavin):** Deficiency causes cheilosis (fissures at the corners of the mouth), digestive disorders, and a **burning sensation of the skin**. (b → iv)

(c) **Vitamin B₆ (Pyridoxine):** Deficiency affects the central nervous system and is uniquely known to cause **convulsions**. (c → i)

(d) **Vitamin B₁₂ (Cyanocobalamin):** Deficiency severely impacts red blood cell production, leading to pernicious anaemia, defined as **RBC deficiency in haemoglobin**. (d → ii)

Step 4: Final Answer:

The matching sequence corresponds to option (B).

Quick Tip: Memorize B_{12} as strictly "Blood related" (Anemia) and B_6 as "Nerve related" (Convulsions) to quickly solve matching questions on B-complex vitamins.

29. Consider the following statements:

Statement I: All monosaccharides are reducing sugars.

Statement II: Sucrose can reduce ammoniacal silver nitrate solution.

Choose the correct answer from the options given below.

- (A) Both Statement I and Statement II are correct
- (B) Both Statement I and Statement II are incorrect
- (C) Statement I is correct but Statement II is incorrect
- (D) Statement I is incorrect but Statement II is correct

Correct Answer: (C) Statement I is correct but Statement II is incorrect

Solution:

Step 1: Understanding the Concept:

Carbohydrates are classified as reducing or non-reducing based on their ability to act as mild reducing agents in basic solutions.

Step 2: Key Formula or Approach:

A sugar is classified as "reducing" if it possesses a free hemiacetal or hemiketal group (a free anomeric carbon) that can equilibrate to form a free aldehyde or ketone group, capable of reducing mild oxidizing agents like Tollen's reagent (ammoniacal silver nitrate).

Step 3: Detailed Explanation:

1. **Statement I:** All monosaccharides (e.g., glucose, fructose, ribose) contain a free anomeric carbon in equilibrium with an open-chain form that contains a carbonyl group. Thus, they are all reducing sugars. (Statement I is True)
2. **Statement II:** Sucrose is a disaccharide formed by the condensation of α -D-glucose and β -D-fructose. The glycosidic linkage involves the anomeric carbons of **both** monomer units (C1 of glucose and C2 of fructose). Since both potential aldehyde and ketone groups are structurally locked in the bond, sucrose has no free hemiacetal/hemiketal groups. Therefore, it is a **non-reducing sugar** and cannot reduce Tollen's reagent. (Statement II is False)

Step 4: Final Answer:

Statement I is correct, and Statement II is incorrect.

Quick Tip: Sucrose is the most common example of a non-reducing sugar tested in exams. Maltose and Lactose, on the other hand, are reducing disaccharides because they have one free anomeric carbon.

30. Incorrect statement about α -amino acids of proteins among the following is

- (A) Methionine is an essential amino acid
- (B) Glycine doesn't exhibit enantiomerism
- (C) Glycylalanylglutamine has three amide linkages
- (D) Zwitterion of valine exhibits amphoteric behaviour

Correct Answer: (C) Glycylalanylglutamine has three amide linkages

Solution:

Step 1: Understanding the Concept:

Analyze the structural characteristics, classification, and bonding properties (peptide bonds) of standard α -amino acids and their polymers.

Step 2: Key Formula or Approach:

Examine the molecular structure for chirality, calculate the peptide bond count using the $(n - 1)$ rule, and recall biological classifications (essential vs non-essential) and zwitterionic properties.

Step 3: Detailed Explanation:

(A) **Methionine:** It is one of the essential amino acids that the human body cannot synthesize and must be obtained through diet. (Correct statement)

(B) **Glycine:** It is the simplest amino acid. Its α -carbon is attached to two identical hydrogen atoms ($H_2N - CH_2 - COOH$). Lacking a chiral center, it is achiral and doesn't show enantiomerism. (Correct statement)

(C) **Glycylalanylglutamine:** The name indicates it is composed of three amino acid residues: Glycine, Alanine, and Glutamine. It is a **tripeptide**. A linear polymer of n amino acids contains $(n - 1)$ peptide (amide) bonds. Therefore, a tripeptide contains exactly **two** peptide linkages, not three. (Incorrect statement)

(D) **Zwitterion:** In aqueous solution, α -amino acids exist as dipolar ions called zwitterions ($H_3N^+ - CHR - COO^-$). They can react with both acids (using the $-COO^-$ group) and bases (using the $-NH_3^+$ group), making them amphoteric. (Correct statement)

Step 4: Final Answer:

Statement (C) is the demonstrably incorrect one.

Quick Tip: Always remember the $(n - 1)$ rule for linear peptides: Dipeptides have 1 bond, Tripeptides have 2 bonds, Polypeptides with n residues have $n - 1$ bonds.

31. Match List I with List II and select the correct options

List - I (Functional group)

List - II (Functional group reagent)

- | | |
|------------------------------|-----------------------------------|
| (a) Secondary Alcohol | (i) Neutral ferric chloride test |
| (b) $C_6H_5NH_2$ (Aniline) | (ii) Azo dye test |
| (c) CH_3CH_2CHO (Propanal) | (iii) Ceric ammonium nitrate test |
| (d) Phenol | (iv) Tollen's reagent test |

Codes:

- (A) a - iv, b - i, c - ii, d - iii
(B) a - iii, b - ii, c - iv, d - i
(C) a - iii, b - ii, c - i, d - iv
(D) a - ii, b - iii, c - iv, d - i

Correct Answer: (B) a - iii, b - ii, c - iv, d - i

Solution:

Step 1: Understanding the Concept:

Different functional groups in organic chemistry are identified using specific qualitative chemical tests that produce observable changes like color or precipitates.

Step 2: Key Formula or Approach:

Match the standard qualitative reagents to their corresponding functional groups: Ceric ammonium nitrate for alcohols, Diazotization (Azo dye) for primary aromatic amines, Tollen's for aldehydes, and Neutral $FeCl_3$ for phenols.

Step 3: Detailed Explanation:

(a) **Secondary Alcohol:** Alcohols react with ceric ammonium nitrate solution to produce a characteristic red or pink color. (a $\rightarrow$ iii)

(b) **C₆H₅NH₂ (Aniline):** As a primary aromatic amine, aniline undergoes diazotization at low temperatures, followed by coupling with a phenol (like β -naphthol) to form a brightly colored Azo dye. (b $\rightarrow$ ii)

(c) **CH₃CH₂CHO (Propanal):** Aliphatic and aromatic aldehydes reduce Tollen's reagent (ammoniacal silver nitrate) to form a silver mirror. (c $\rightarrow$ iv)

(d) **Phenol:** Phenols react with neutral ferric chloride (FeCl₃) solution to give characteristic violet, green, or blue colored complexes. (d $\rightarrow$ i)

Step 4: Final Answer:

Matching gives: a-iii, b-ii, c-iv, d-i, which corresponds to option (B).

Quick Tip: Phenol + FeCl₃ $\rightarrow$ Violet color. Aldehyde + Tollen's $\rightarrow$ Silver mirror. These two are the most frequently asked qualitative tests, knowing them instantly eliminates most wrong options!

32. When salt BA is treated with Conc. H₂SO₄, reddish brown gas is liberated. The aqueous solution of BA gives pale yellow precipitate with AgNO₃ solution. Which of the following anion(A) is present in the salt BA?

- (A) Cl⁻
- (B) CO₃²⁻
- (C) SO₄²⁻
- (D) Br⁻

Correct Answer: (D) Br⁻

Solution:**Step 1: Understanding the Concept:**

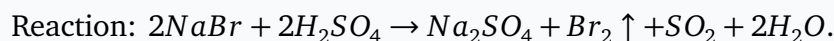
This problem pertains to the systematic qualitative analysis of inorganic salts, specifically identifying anions based on their reaction with concentrated acid and silver nitrate.

Step 2: Key Formula or Approach:

Correlate the physical observations (reddish-brown gas with Conc. H_2SO_4 and pale yellow precipitate with $AgNO_3$) to the standard confirmatory tests for halide ions.

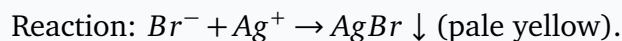
Step 3: Detailed Explanation:

1. **Reaction with Conc. H_2SO_4 :** Bromide salts react with concentrated sulphuric acid to liberate hydrogen bromide (HBr), which is subsequently oxidized by the acid to bromine gas (Br_2). Bromine is a **reddish-brown** gas.



(Note: Nitrates also give brown gas NO_2 , but the next test differentiates it).

2. **Reaction with $AgNO_3$:** Aqueous solution of bromide ions reacts with silver nitrate to form Silver Bromide ($AgBr$), which is a **pale yellow** precipitate. This precipitate is partially soluble in dilute aqueous ammonia but soluble in concentrated ammonia.



In contrast, Cl^- gives a white ppt ($AgCl$), and I^- gives a bright yellow ppt (AgI).

Step 4: Final Answer:

The observations perfectly correspond to the Bromide ion (Br^-).

Quick Tip: Color coded precipitates with $AgNO_3$ are vital to memorize: Cl^- (White), Br^- (Pale Yellow), I^- (Bright Yellow).

33. Which of the following represents de Broglie equation?

(A) $\lambda = \frac{h}{\sqrt{mv}}$

(B) $\lambda = \frac{h}{mv}$

(C) $\lambda = \frac{h}{mp}$

(D) $\lambda = \frac{\mu}{p}$

Correct Answer: (B) $\lambda = \frac{h}{mv}$

Solution:

Step 1: Understanding the Concept:

The de Broglie hypothesis relates the wave nature of matter to its particle nature, establishing the dual nature of matter.

Step 2: Key Formula or Approach:

The fundamental de Broglie relationship states that the wavelength (λ) of a moving particle is inversely proportional to its momentum (p). Use the definition of momentum ($p = m \times v$) to find the expanded form.

Step 3: Detailed Explanation:

The de Broglie equation is given by:

$$\lambda = \frac{h}{p}$$

Where:

λ = de Broglie wavelength

h = Planck's constant (6.626×10^{-34} J s)

p = momentum of the particle

Since momentum (p) is the product of mass (m) and velocity (v), we can substitute $p = mv$:

$$\lambda = \frac{h}{mv}$$

Step 4: Final Answer:

The correct representation of the de Broglie equation is $\lambda = \frac{h}{mv}$.

Quick Tip: The de Broglie equation is also frequently tested in terms of kinetic energy (K): $\lambda = \frac{h}{\sqrt{2mK}}$.
Be prepared to recognize both forms!

34. Which of the following is the CORRECT statement about Ψ^2 ?

- (A) Ψ^2 represents atomic orbit
- (B) Probability density of the electron at that point
- (C) $\Psi^2 \neq 0$ for nodes
- (D) Ψ^2 has no physical meaning

Correct Answer: (B) Probability density of the electron at that point

Solution:

Step 1: Understanding the Concept:

In the quantum mechanical model of the atom, Ψ represents the wave function (amplitude of the electron wave), while its square, Ψ^2 , has a strict statistical interpretation.

Step 2: Key Formula or Approach:

Recall the Born Interpretation of quantum mechanics, which links the mathematical wave function to the physical probability of locating a particle.

Step 3: Detailed Explanation:

(A) **Atomic orbit:** An orbit is a classical 2D circular path (Bohr model). Ψ^2 defines an "orbital" (a 3D region of space), not an orbit. (Incorrect)

(B) **Probability density:** According to Max Born, the value of Ψ^2 at any given point in space around the nucleus gives the **probability density** of finding an electron at that exact point. (Correct)

(C) **Nodes:** A node is specifically defined as a region where the probability of finding an electron is exactly zero. Therefore, at nodes, $\Psi^2 = 0$. (Incorrect)

(D) **Physical meaning:** While the wave function Ψ itself has no direct physical meaning (it can be positive, negative, or complex), Ψ^2 is always positive and has a very profound physical meaning: probability density. (Incorrect)

Step 4: Final Answer:

Ψ^2 represents the probability density of the electron.

Quick Tip: Ψ can be positive or negative and has no physical meaning on its own. Ψ^2 is always positive and represents the probability density.

35. A: Entropy of a perfect crystalline solid at absolute zero approaches zero.

B: For spontaneity of a reaction, $T\Delta S > \Delta H$.

Among the two statements given above, identify the correct answer from the options given below.

(A) Both 'A' and 'B' are true

(B) 'A' is true but 'B' is false

(C) Both 'A' and 'B' are false

(D) 'A' is false but 'B' is true

Correct Answer: (A) Both 'A' and 'B' are true

Solution:

Step 1: Understanding the Concept:

Evaluate statement A using the Third Law of Thermodynamics and statement B using the Gibbs Free Energy criterion for spontaneity.

Step 2: Key Formula or Approach:

Third Law of Thermodynamics: $S \rightarrow 0$ as $T \rightarrow 0$ K.

Gibbs Free Energy Equation: $\Delta G = \Delta H - T \Delta S$. Spontaneity strictly requires $\Delta G < 0$.

Step 3: Detailed Explanation:

1. **Statement A:** This is the formal definition of the **Third Law of Thermodynamics**. At absolute zero (0 K), there is no thermal motion, and perfectly ordered crystalline solids have zero disorder. Hence, their entropy is exactly zero. (Statement A is True)

2. **Statement B:** For a reaction to be spontaneous at constant temperature and pressure, the change in Gibbs free energy (ΔG) must be negative ($\Delta G < 0$).

Using the equation: $\Delta H - T \Delta S < 0$.

Rearranging this inequality gives:

$$\Delta H < T \Delta S$$

Which is exactly the same as: $T \Delta S > \Delta H$.

This mathematical condition ensures that the negative entropy term overcomes any positive enthalpy term, leading to a spontaneous process. (Statement B is True)

Step 4: Final Answer:

Both statements 'A' and 'B' are true.

Quick Tip: Always remember the master equation: $\Delta G = \Delta H - T \Delta S$. A process is spontaneous if the total entropy of the universe increases, which mathematically translates to $\Delta G < 0$.

36. Which of the following is a correct statement for a thermodynamic system?

(A) The internal energy changes in all processes

- (B) Internal energy and entropy are state functions
(C) Work is a state function
(D) The work done in an adiabatic process is always zero

Correct Answer: (B) Internal energy and entropy are state functions

Solution:

Step 1: Understanding the Concept:

Thermodynamic properties are strictly classified as either state functions (independent of the path taken) or path functions (dependent on the specific sequence of steps).

Step 2: Key Formula or Approach:

Analyze each statement against fundamental thermodynamic definitions, such as conditions for isothermal/adiabatic processes, and identify state vs. path variables.

Step 3: Detailed Explanation:

(A) In an **isothermal process** involving an ideal gas, temperature remains constant. Since the internal energy (U) of an ideal gas depends solely on temperature, internal energy does *not* change ($\Delta U = 0$). Therefore, it doesn't change in all processes. (Incorrect)

(B) **Internal energy (U)** and **Entropy (S)** depend exclusively on the current equilibrium state of the system (characterized by P, V, T), not on how that state was reached. They are **state functions**. (Correct)

(C) **Work (w)** and **Heat (q)** are heavily dependent on the specific path (e.g., reversible vs. irreversible expansion). They are **path functions**, not state functions. (Incorrect)

(D) In an adiabatic process, heat exchange is zero ($q = 0$). According to the First Law ($\Delta U = q + w$), the change in internal energy equals the work done ($\Delta U = w_{ad}$). Work is not zero unless it's free expansion. (Incorrect)

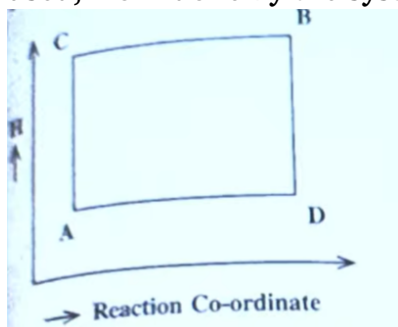
Step 4: Final Answer:

Statement (B) is the correct statement.

Quick Tip: Mnemonic for state functions: **P, V, T, H, U, S, G**. (Pressure, Volume, Temp, Enthalpy, Internal Energy, Entropy, Gibbs). Heat (q) and Work (w) are the main path functions.

37. A gas can be taken from A to B via two different paths ACB and ADB. When path ACB is used, 60J of heat flows into the system and 30J of work is done by the system. If path ADB is

used, work done by the system is 10J. The heat flow into the system in path ADB is



- (A) 80J
- (B) 20J
- (C) 100J
- (D) 40J

Correct Answer: (D) 40J

Solution:

Step 1: Understanding the Concept:

The change in internal energy (ΔU) of a system is a **state function**. This means ΔU is identical for any path taken between the same initial state (A) and final state (B).

Step 2: Key Formula or Approach:

Apply the First Law of Thermodynamics: $\Delta U = q + w$.

(Using IUPAC sign convention: q is positive if heat flows *into* the system; w is negative if work is done *by* the system).

Step 3: Detailed Explanation:

1. Analyze Path ACB:

Heat added to system, $q_{ACB} = +60 \text{ J}$.

Work done by the system, $w_{ACB} = -30 \text{ J}$.

Calculate internal energy change:

$$\Delta U = q_{ACB} + w_{ACB} = 60 + (-30) = 30 \text{ J}.$$

Because ΔU is a state function, $\Delta U_{A \rightarrow B}$ is 30 J regardless of the path.

2. Analyze Path ADB:

We know $\Delta U = 30 \text{ J}$.

Work done by the system, $w_{ADB} = -10 \text{ J}$.

Use the First Law to find the unknown heat flow (q_{ADB}):

$$\Delta U = q_{ADB} + w_{ADB}$$

$$30 = q_{ADB} + (-10)$$

$$q_{ADB} = 30 + 10 = 40 \text{ J.}$$

Since q_{ADB} is positive, 40 J of heat flows into the system.

Step 4: Final Answer:

The heat flow into the system via path ADB is 40J.

Quick Tip: Always identify state functions (ΔU) and path functions (q, w) first. Calculate ΔU from the fully defined path and directly apply it to the partially defined path. Watch your signs!

38. For the reversible reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. When the partial pressure is measured in atmosphere, the value of K_p at 500°C is 1.44×10^{-5} . The value of K_c when the concentration is expressed in mol L^{-1} is:

- (A) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$
 (B) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
 (C) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$
 (D) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

Correct Answer: (D) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

Solution:

Step 1: Understanding the Concept:

The equilibrium constants expressed in terms of partial pressure (K_p) and concentration (K_c) are related through the ideal gas law.

Step 2: Key Formula or Approach:

Use the relationship formula: $K_p = K_c(RT)^{\Delta n_g}$, rearranging it to solve for K_c : $K_c = K_p(RT)^{-\Delta n_g}$. Calculate $\Delta n_g = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants})$, and convert temperature to Kelvin.

Step 3: Detailed Explanation:

1. **Reaction:** $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$.

2. **Calculate Δn_g :**

$$\Delta n_g = 2 (\text{products}) - (1 + 3) (\text{reactants}) = 2 - 4 = -2.$$

3. **Convert Temperature:**

$$T = 500^{\circ}\text{C} + 273 = 773 \text{ K.}$$

4. Gas Constant:

Since pressure is in atmosphere, use $R = 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}$.

5. Apply Formula:

$$K_p = K_c(RT)^{\Delta n_g}$$

$$K_c = K_p(RT)^{-\Delta n_g}$$

Substitute the values:

$$K_c = 1.44 \times 10^{-5} \times (0.082 \times 773)^{-(-2)}$$

$$K_c = 1.44 \times 10^{-5} \times (0.082 \times 773)^2$$

To match the specific format of the options, note that mathematically, $x^2 = \frac{1}{x^{-2}}$. Therefore:

$$K_c = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$$

Step 4: Final Answer:

Matching this result with the given choices, (D) is the correct expression.

Quick Tip: A frequent trap is failing to convert Celsius to Kelvin. Always ensure Temperature is in Kelvin! Another trap is algebraic manipulation of exponents ($x^y = 1/x^{-y}$).

39. For the following gaseous reversible reaction: $3\text{A}_{(g)} + \text{B}_{(g)} \rightleftharpoons \text{A}_3\text{B}_{(g)}$ ($\Delta H = -q \text{ kJ}$), The amount of product $\text{A}_3\text{B}_{(g)}$ is affected by

- (A) Temperature alone
- (B) Pressure alone
- (C) Both temperature and pressure
- (D) Temperature, pressure and catalyst

Correct Answer: (C) Both temperature and pressure

Solution:

Step 1: Understanding the Concept:

Le Chatelier's Principle dictates how an equilibrium system responds to external changes in temperature, pressure, or the addition of a catalyst to minimize that change.

Step 2: Key Formula or Approach:

Assess the effect of Temperature (based on ΔH) and Pressure (based on Δn_g) on the equilibrium position. A catalyst affects the rate of approaching equilibrium, not the final equilibrium amount.

Step 3: Detailed Explanation:

1. **Temperature Effect:** The reaction is specified as exothermic ($\Delta H = -q$ kJ). According to Le Chatelier's Principle, increasing the temperature shifts an exothermic equilibrium backward (to the reactants side), while decreasing it shifts it forward (to the products side). Thus, temperature significantly affects the amount of A_3B formed.
2. **Pressure Effect:** On the reactant side, there are 4 moles of gas ($3 + 1$). On the product side, there is 1 mole of gas. An increase in pressure will shift the equilibrium toward the side with fewer moles of gas to reduce pressure. A decrease shifts it toward more moles. Thus, pressure affects the yield of A_3B .
3. **Catalyst Effect:** A catalyst lowers the activation energy for both forward and reverse reactions equally. It only speeds up the time taken to reach equilibrium but does *not* alter the final equilibrium concentration or amounts.

Step 4: Final Answer:

Both temperature and pressure affect the equilibrium concentration of the product.

Quick Tip: Equilibrium **amounts** or **yield** are changed by Temperature, Pressure, and Concentration. The equilibrium **constant** (K) is changed **only** by Temperature. Catalysts change neither.

40. A 0.15 mole of pyridinium chloride has been added to 500 cm³ of 0.2M pyridine solution (a base). Assuming there is no change in volume upon mixing, the pH of the resulting solution is (Note: K_b for pyridine is 1.5×10^{-9})

- (A) 5
- (B) 6
- (C) 7
- (D) 8

Correct Answer: (A) 5

Solution:

Step 1: Understanding the Concept:

The mixture of a weak base (pyridine) and its conjugate acid salt (pyridinium chloride) forms a basic buffer solution. We need to calculate its pH.

Step 2: Key Formula or Approach:

Use the Henderson-Hasselbalch equation for basic buffers:

$$pOH = pK_b + \log\left(\frac{[\text{Salt}]}{[\text{Base}]}\right)$$

Followed by the relation at 25°C: $pH = 14 - pOH$.

Step 3: Detailed Explanation:

1. Determine Concentrations:

Volume of solution = 500 cm³ = 0.5 L.

Concentration of Base (Pyridine) = 0.2 M.

Concentration of Salt (Pyridinium chloride) = $\frac{\text{Moles}}{\text{Volume}} = \frac{0.15 \text{ mol}}{0.5 \text{ L}} = 0.3 \text{ M}$.

2. Calculate pK_b :

$$K_b = 1.5 \times 10^{-9}.$$

$$pK_b = -\log(1.5 \times 10^{-9}) = 9 - \log(1.5).$$

We leave $\log(1.5)$ as it will cancel out perfectly in the next step.

3. Calculate pOH:

$$pOH = pK_b + \log\left(\frac{[\text{Salt}]}{[\text{Base}]}\right)$$

$$pOH = [9 - \log(1.5)] + \log\left(\frac{0.3}{0.2}\right)$$

$$pOH = 9 - \log(1.5) + \log(1.5)$$

The $\log(1.5)$ terms completely cancel out.

$$pOH = 9$$

4. Calculate pH:

$$pH = 14 - pOH = 14 - 9 = 5.$$

Step 4: Final Answer:

The pH of the resulting buffer solution is 5.

Quick Tip: Always ensure your salt and base concentrations are in the same unit (Molarity). Here, recognizing that $0.3/0.2 = 1.5$ immediately tells you that the log terms will perfectly cancel the mantissa of the K_b , saving you from doing complex logarithm math!

41. Which of the following is CORRECT with respect to the property mentioned against it?

- (A) Osmotic pressure at 298K : 0.1M NaCl solution < 0.1M Urea solution
- (B) Concentration of NaCl in the solution : 2ppm > 2M
- (C) ΔT_b : 0.02M Urea solution > 0.02M NaCl solution
- (D) Vapour pressure at 298K : Salt water < Pure water

Correct Answer: (D) Vapour pressure at 298K : Salt water < Pure water

Solution:

Step 1: Understanding the Concept:

Evaluate various colligative properties (Osmotic pressure, elevation of boiling point, relative lowering of vapor pressure) and concentration units. Colligative properties rely strictly on the total number of solute particles (ions/molecules) in the solution, governed by the Van't Hoff factor (i).

Step 2: Key Formula or Approach:

For colligative properties, apply the formulas: $\pi = iCRT$ and $\Delta T_b = iK_b m$. Compare i values: $NaCl$ ($i \approx 2$) vs. Urea ($i = 1$). Compare concentration magnitudes for ppm vs. Molarity.

Step 3: Detailed Explanation:

(A) **Osmotic Pressure (π):** For the same molarity (C), π depends on i . $NaCl$ dissociates into 2 ions ($i = 2$), while Urea is a non-electrolyte ($i = 1$). Thus, $\pi_{NaCl} > \pi_{Urea}$. The given statement is reversed. (Incorrect)

(B) **Concentration:** Parts per million (ppm) is for highly dilute traces. 2 M of $NaCl$ is roughly 117 g per Liter (117,000 mg/L or ppm). Clearly, 2 ppm is exponentially smaller than 2 M. (Incorrect)

(C) **Elevation in Boiling Point (ΔT_b):** Similar to osmotic pressure, for equal concentrations, $NaCl$ ($i = 2$) creates a higher elevation in boiling point than Urea ($i = 1$). Thus, $\Delta T_{b(NaCl)} > \Delta T_{b(Urea)}$. (Incorrect)

(D) **Vapour Pressure:** Raoult's Law states that the addition of a non-volatile solute (like salt) to a pure solvent (water) physically blocks solvent molecules from escaping, which continuously lowers the vapour pressure. Thus, salt water has a strictly lower Vapour Pressure than pure water. (Correct)

Step 4: Final Answer:

Option (D) is the correct statement.

Quick Tip: Colligative property magnitudes: ΔT_b , ΔT_f (depression magnitude), and π **increase** with higher i . Conversely, the actual Vapour Pressure and Freezing Point **decrease** with higher i .

42. Match List - I (Laws) with the List - II (Mathematical expressions):

List - I

(a) Henry's law

List - II

(i) $P_1 = x_1 P_1^0$

- (b) Raoult's law (ii) $p = K_H \cdot x$
 (c) First law of thermodynamics (iii) $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$
 (d) Kohlrausch's law (iv) $\Delta U = q + w$

Codes:

- (A) a - i, b - ii, c - iii, d - iv
 (B) a - ii, b - i, c - iii, d - iv
 (C) a - ii, b - i, c - iv, d - iii
 (D) a - i, b - ii, c - iv, d - iii

Correct Answer: (C) a - ii, b - i, c - iv, d - iii

Solution:

Step 1: Understanding the Concept:

Match fundamental chemical and physical laws from different chapters (Solutions, Thermodynamics, Electrochemistry) to their standard governing mathematical formulas.

Step 2: Key Formula or Approach:

Recall the specific equations. Henry's relates gas pressure to solubility (K_H), Raoult's relates solution vapor pressure to pure solvent (P^0), First law represents energy conservation, and Kohlrausch's law sums limiting molar conductivities.

Step 3: Detailed Explanation:

(a) **Henry's Law:** States that the partial pressure of a gas in the vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution. Formula: $p = K_H \cdot x$. (a $\rightarrow$ ii)

(b) **Raoult's Law:** For a solution containing volatile liquids, the partial vapour pressure of a component (P_1) is proportional to its mole fraction in the liquid phase (x_1) multiplied by its pure vapour pressure (P_1^0). Formula: $P_1 = x_1 P_1^0$. (b $\rightarrow$ i)

(c) **First Law of Thermodynamics:** The law of conservation of energy expressed mathematically as the change in internal energy (ΔU) equals heat added (q) plus work done (w). Formula: $\Delta U = q + w$. (c $\rightarrow$ iv)

(d) **Kohlrausch's Law of Independent Migration of Ions:** The limiting molar conductivity of a strong electrolyte (Λ_m^0) is the sum of the individual ionic contributions (λ_+^0, λ_-^0) scaled by their stoichiometric coefficients (ν_+, ν_-). Formula: $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$. (d $\rightarrow$ iii)

Step 4: Final Answer:

Matching sequence is a-ii, b-i, c-iv, d-iii.

Quick Tip: Don't confuse Henry's Law ($p \propto x$ for gas dissolved in liquid) with Raoult's Law ($p \propto x$ for liquid-liquid mixtures). One uses the Henry's constant K_H , the other uses the pure vapor pressure P^0 .

43. When 0.0106 mole of acetic acid was dissolved in 1 kg of water, the freezing point depression for this strength of acid was 0.0205 K. If the calculated freezing point depression is 0.0197 K, Van't Hoff factor (i) and degree of dissociation of acetic acid respectively are

- (A) 0.041 and 1.041
- (B) 1.041 and 0.1041
- (C) 0.041 and 0.041
- (D) 1.041 and 0.041

Correct Answer: (D) 1.041 and 0.041

Solution:

Step 1: Understanding the Concept:

The Van't Hoff factor (i) corrects colligative property equations for solutes that dissociate or associate. The degree of dissociation (α) relates directly to i for weak electrolytes.

Step 2: Key Formula or Approach:

1. Calculate i : $i = \frac{\Delta T_f(\text{observed})}{\Delta T_f(\text{calculated})}$
2. Relate i to α : For acetic acid dissociating into 2 ions ($\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$), $n = 2$. The formula is $i = 1 + \alpha(n - 1)$, which simplifies to $i = 1 + \alpha$.

Step 3: Detailed Explanation:

1. Calculate Van't Hoff factor (i):

Given observed depression = 0.0205 K.

Given calculated (theoretical) depression = 0.0197 K.

$$i = \frac{0.0205}{0.0197} \approx 1.0406 \approx 1.041.$$

2. Calculate degree of dissociation (α):

Using the relation $i = 1 + \alpha$:

$$1.041 = 1 + \alpha$$

$$\alpha = 1.041 - 1 = 0.041.$$

Step 4: Final Answer:

The Van't Hoff factor is 1.041 and the degree of dissociation is 0.041.

Quick Tip: The observed property is always "greater" for dissociation ($i > 1$) and "smaller" for association ($i < 1$). Since acetic acid is an acid (an electrolyte undergoing ionization), its i factor must logically be > 1 .

44. The relative lowering of vapour pressure produced by dissolving 18 g of urea (Molar mass = 60 g mol^{-1}) in 100 g of water is

- (A) 0.025
- (B) 0.5
- (C) 0.05
- (D) 0.25

Correct Answer: (C) 0.05

Solution:

Step 1: Understanding the Concept:

According to Raoult's Law, the Relative Lowering of Vapour Pressure (RLVP) of a solution containing a non-volatile solute is equal to the mole fraction of the solute.

Step 2: Key Formula or Approach:

Use the formula: $RLVP = \frac{p^0 - p}{p^0} = X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$.

Calculate moles of urea and moles of water first.

Step 3: Detailed Explanation:

1. **Calculate Moles of Urea (n_{urea}):**

Mass given = 18 g, Molar Mass = 60 g/mol .

$$n_{\text{urea}} = \frac{18 \text{ g}}{60 \text{ g/mol}} = 0.3 \text{ mol.}$$

2. Calculate Moles of Water (n_{water}):

Mass given = 100 g, Molar Mass = 18 g/mol.

$$n_{\text{water}} = \frac{100 \text{ g}}{18 \text{ g/mol}} \approx 5.55 \text{ mol.}$$

3. Calculate Mole fraction of Urea (X_{urea}):

$$X_{\text{urea}} = \frac{n_{\text{urea}}}{n_{\text{urea}} + n_{\text{water}}}$$

$$X_{\text{urea}} = \frac{0.3}{0.3 + 5.55} = \frac{0.3}{5.85}$$

$$X_{\text{urea}} \approx 0.051 \approx 0.05.$$

Step 4: Final Answer:

The relative lowering of vapour pressure is approximately 0.05.

Quick Tip: For very dilute solutions where $n_{\text{solute}} \ll n_{\text{solvent}}$, you can approximate $X_{\text{solute}} \approx \frac{n_{\text{solute}}}{n_{\text{solvent}}}$. In this specific case, $0.3/5.55 \approx 0.054$, which still confidently points to option C (0.05) in a multiple-choice format.

45. During the electrolysis of acidified water, 16 g of O_2 gas is formed at anode. The volume of H_2 gas liberated at cathode under STP conditions is

- (A) 22.4 L
- (B) 11.2 L

(C) 2.24 L

(D) 1.12 L

Correct Answer: (A) 22.4 L

Solution:

Step 1: Understanding the Concept:

The overall reaction for the electrolysis of water dictates the stoichiometric ratio of Hydrogen gas produced to Oxygen gas produced.

Step 2: Key Formula or Approach:

Write the balanced chemical equation for the electrolysis of water ($2H_2O \rightarrow 2H_2 + O_2$). Convert the given mass of O_2 to moles, use the stoichiometric ratio to find moles of H_2 , and then convert it to volume at STP using $V = n \times 22.4$ L.

Step 3: Detailed Explanation:

1. Balanced Equation:

The electrolysis of water is given by: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$.

This shows that 2 moles of H_2 are produced for every 1 mole of O_2 . The molar ratio is $n(H_2) : n(O_2) = 2 : 1$.

2. Calculate moles of O_2 :

Mass of $O_2 = 16$ g. Molar mass of $O_2 = 32$ g/mol.

Moles of $O_2 = \frac{16}{32} = 0.5$ mol.

3. Calculate moles of H_2 :

From the 2 : 1 ratio, moles of $H_2 = 2 \times 0.5 = 1.0$ mol.

4. Calculate volume at STP:

Volume of 1 mole of an ideal gas at standard temperature and pressure (STP) is 22.4 L.

Volume of $H_2 = 1.0 \text{ mol} \times 22.4 \text{ L/mol} = 22.4$ L.

Step 4: Final Answer:

The volume of hydrogen gas liberated is 22.4 L.

Quick Tip: Shortcut: In water electrolysis, the molar (and therefore volume) ratio of hydrogen to oxygen is **always exactly double** (2 : 1). 0.5 mol O_2 occupies 11.2 L, so H_2 must occupy precisely $2 \times 11.2 = 22.4$ L.

46. $\Lambda_m^\circ(\text{NH}_4\text{OH})$ is equal to

- (A) $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{HCl})$
(B) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$
(C) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NaOH})$
(D) $\Lambda_m^\circ(\text{NaOH}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$

Correct Answer: (B) $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$

Solution:

Step 1: Understanding the Concept:

According to Kohlrausch's law of independent migration of ions, the limiting molar conductivity of an electrolyte is the algebraic sum of the limiting molar conductivities of its constituent ions. This allows the calculation of Λ_m° for weak electrolytes using values from strong electrolytes.

Step 2: Key Formula or Approach:

We want to find $\Lambda_m^\circ(\text{NH}_4\text{OH}) = \lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{OH}^-)$. We must algebraically combine the conductivities of strong electrolytes to isolate these two specific ions.

Step 3: Detailed Explanation:

Let's evaluate the correct algebraic manipulation. We need NH_4^+ and OH^- .

Consider Option (B):

$$\text{Expression: } \Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$$

Expand each term into its constituent ions based on Kohlrausch's law:

$$= [\lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{Cl}^-)] + [\lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{OH}^-)] - [\lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-)]$$

Group the terms:

$$= \lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{OH}^-) + \lambda^\circ(\text{Cl}^-) + \lambda^\circ(\text{Na}^+) - \lambda^\circ(\text{Na}^+) - \lambda^\circ(\text{Cl}^-)$$

The Na^+ and Cl^- ion conductivities perfectly cancel out:

$$= \lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{OH}^-)$$

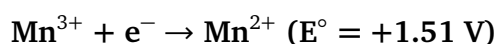
This exact sum represents $\Lambda_m^\circ(\text{NH}_4\text{OH})$.

Step 4: Final Answer:

Option (B) correctly represents the relationship.

Quick Tip: Algebra of Ions shortcut: To find a weak electrolyte, ADD the strong electrolyte containing the desired cation (NH_4Cl), ADD the strong electrolyte containing the desired anion ($NaOH$), and SUBTRACT the "spectator" salt formed by the remaining ions ($NaCl$).

47. Given below are the half-cell reactions:



The E°_{cell} for $3 Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be _____

- (A) - 2.69 V, the reaction will not occur (Non-Spontaneous)
(B) 2.69 V, the reaction will occur (Spontaneous)
(C) - 0.33 V, the reaction will not occur (Non-Spontaneous)
(D) - 0.33 V, the reaction will occur (Spontaneous)

Correct Answer: (A) - 2.69 V, the reaction will not occur (Non-Spontaneous)

Solution:

Step 1: Understanding the Concept:

To evaluate the feasibility of a reaction, calculate the standard cell potential (E°_{cell}). A positive value indicates a spontaneous reaction, while a negative value indicates non-spontaneity.

Step 2: Key Formula or Approach:

1. Identify the oxidation (anode) and reduction (cathode) half-reactions from the overall target equation.
2. Calculate $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ (using standard reduction potentials).
3. Determine spontaneity based on the sign of E°_{cell} .

Step 3: Detailed Explanation:

The target overall reaction is a disproportionation variant: $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$.

Let's break it down into halves:

1. **Reduction (Cathode):** $Mn^{2+} + 2e^- \rightarrow Mn$.

The standard reduction potential is directly given: $E^\circ_{cathode} = -1.18 \text{ V}$.

2. **Oxidation (Anode):** $2Mn^{2+} \rightarrow 2Mn^{3+} + 2e^-$.

The species being oxidized is Mn^{2+} converting to Mn^{3+} . The given reduction potential for the reverse process ($Mn^{3+} + e^- \rightarrow Mn^{2+}$) is +1.51 V.

Therefore, E_{anode}° (the standard reduction potential of the species undergoing oxidation) is +1.51 V.

3. Calculate E_{cell}° :

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

$$E_{cell}^{\circ} = (-1.18 \text{ V}) - (+1.51 \text{ V}) = -2.69 \text{ V}.$$

Since E_{cell}° is heavily negative, the reaction is thermodynamically non-spontaneous under standard conditions.

Step 4: Final Answer:

The potential is -2.69 V and the reaction will not occur (Non-Spontaneous).

Quick Tip: This reaction represents the reverse of a disproportionation. Mn^{2+} is exceptionally stable because it has a exactly half-filled d^5 configuration. Forcing it to become both Mn^0 and Mn^{3+} is energetically highly unfavorable, hence the large negative voltage.

48. The conductivity of centimolar solution of KCl at 298 K is $0.021 \text{ Ohm}^{-1} \text{ cm}^{-1}$ and the resistance of the cell containing the solution at 298 K is 60Ω . The value of cell constant (G^*) is

- (A) 3.28 cm^{-1}
- (B) 1.26 cm^{-1}
- (C) 3.34 cm^{-1}
- (D) 1.34 cm^{-1}

Correct Answer: (B) 1.26 cm^{-1}

Solution:

Step 1: Understanding the Concept:

The cell constant (G^*) is a geometric property of a specific conductivity cell, defined as the

ratio of the distance between electrodes (l) to their area of cross-section (A). It linearly relates electrical resistance to the conductivity of the solution.

Step 2: Key Formula or Approach:

Use the relationship: Conductivity (κ) = Conductance (G) $\times$ Cell Constant (G^*).

Since Conductance (G) is the reciprocal of Resistance ($1/R$), the formula becomes:

$$\kappa = \left(\frac{1}{R}\right) \times G^* \implies G^* = \kappa \times R.$$

Step 3: Detailed Explanation:

1. Identify the given values:

Conductivity (κ) = $0.021 \text{ Ohm}^{-1} \text{ cm}^{-1}$

Resistance (R) = $60 \text{ } \Omega$ (which is 60 Ohm)

2. Perform the calculation:

$$G^* = \kappa \times R$$

$$G^* = 0.021 \text{ Ohm}^{-1} \text{ cm}^{-1} \times 60 \text{ Ohm}$$

The Ohm^{-1} and Ohm units cancel out.

$$G^* = 1.26 \text{ cm}^{-1}$$

Step 4: Final Answer:

The cell constant is 1.26 cm^{-1} .

Quick Tip: Dimensional analysis (Unit check) is a lifesaver here: $[\text{Ohm}^{-1} \text{ cm}^{-1}] \times [\text{Ohm}] = \text{cm}^{-1}$. The units themselves tell you whether you should multiply or divide the numbers!

49. Which one of the following graph is not applicable for a 1st order reaction ($R \rightarrow P$)?

(A) A graph of $[R]$ vs t with a downward sloping curve.

- (B) A graph of $\ln[R]$ vs t with a downward sloping straight line.
- (C) A graph of $\log_{10}[R]$ vs t with an upward sloping straight line.
- (D) A graph of $\log_{10}([R]_0/[R])$ vs t with an upward sloping straight line through the origin.

Correct Answer: (C) A graph of $\log_{10}[R]$ vs t with an upward sloping straight line.

Solution:

Step 1: Understanding the Concept:

Graphical analysis of reaction kinetics relies on plotting the integrated rate equation in various linear and exponential formats.

Step 2: Key Formula or Approach:

Evaluate the standard integrated rate equation for a first-order reaction: $[R] = [R]_0 e^{-kt}$. Take natural and base-10 logarithms to check the straight-line dependencies $y = mx + c$.

Step 3: Detailed Explanation:

- Option (A):** From $[R] = [R]_0 e^{-kt}$, concentration shows an exponential decay over time. A plot of $[R]$ vs t is indeed a downward sloping curve. (Applicable)
- Option (B):** Taking the natural log gives $\ln[R] = \ln[R]_0 - kt$. This is a straight line equation ($y = c + mx$) with a negative slope ($m = -k$). It forms a downward sloping straight line. (Applicable)
- Option (C):** Converting to base-10 log gives $\log_{10}[R] = \log_{10}[R]_0 - \frac{kt}{2.303}$. This is a straight line with a **negative** slope ($-\frac{k}{2.303}$). An "upward sloping" line implies that the concentration of the reactant increases over time, which is physically impossible. (Not Applicable)
- Option (D):** Rearranging the log equation gives $\log_{10}\left(\frac{[R]_0}{[R]}\right) = \frac{k}{2.303}t$. This fits $y = mx$, which is a straight line passing through the origin with a positive (upward) slope. (Applicable)

Step 4: Final Answer:

Graph (C) is the one that is not applicable.

Quick Tip: Reactant concentrations **always** decrease with time as they are consumed. Any graph describing an increase in reactant concentration (positive/upward slope for $[R]$, $\ln[R]$, or $\log[R]$) is immediately false.

50. For a reaction having three steps, the overall rate constant is $K = \frac{k_1 k_3}{k_2}$. The values of E_{a1} , E_{a2} , and E_{a3} (activation energies stepwise) are 40, 50 and 60 kJ mol^{-1} respectively. Then the

overall E_a (activation energy) of the reaction is

- (A) 30 kJ mol^{-1}
- (B) 40 kJ mol^{-1}
- (C) 50 kJ mol^{-1}
- (D) 60 kJ mol^{-1}

Correct Answer: (C) 50 kJ mol^{-1}

Solution:

Step 1: Understanding the Concept:

For complex reactions, the overall rate constant is often a composite of rate constants from multiple elementary steps. The overall activation energy is derived from the Arrhenius equation.

Step 2: Key Formula or Approach:

If an overall rate constant is given as a product or quotient of elementary rate constants ($K = \frac{k_1^n k_3^m}{k_2^p}$), the overall activation energy relates algebraically: $E_a = nE_{a1} + mE_{a3} - pE_{a2}$.

Step 3: Detailed Explanation:

Given the composite rate constant expression: $K = \frac{k_1 k_3}{k_2}$.

Taking the natural logarithm ($\ln$) on both sides:

$$\ln K = \ln k_1 + \ln k_3 - \ln k_2$$

According to the Arrhenius equation, differentiating $\ln k$ with respect to temperature (T) yields: $\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2}$.

Applying this derivative to our equation:

$$\frac{E_{a(\text{overall})}}{RT^2} = \frac{E_{a1}}{RT^2} + \frac{E_{a3}}{RT^2} - \frac{E_{a2}}{RT^2}$$

Multiplying entirely by RT^2 :

$$E_a = E_{a1} + E_{a3} - E_{a2}$$

Plugging in the provided numerical values:

$$E_a = 40 + 60 - 50 = 100 - 50 = 50 \text{ kJ mol}^{-1}.$$

Step 4: Final Answer:

The overall activation energy is 50 kJ mol^{-1} .

Quick Tip: Rules of thumb for E_a : Multiplied rate constants in the numerator mean you Add their E_a s; Divided rate constants in the denominator mean you Subtract their E_a s.

51. For a 1st order change $R \rightarrow P$, the concentration of Reactant R changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of R is 0.01 M is

- (A) $1.73 \times 10^{-5} \text{ M min}^{-1}$
- (B) $3.47 \times 10^{-4} \text{ M min}^{-1}$
- (C) $3.47 \times 10^{-5} \text{ M min}^{-1}$
- (D) $1.73 \times 10^{-4} \text{ M min}^{-1}$

Correct Answer: (B) $3.47 \times 10^{-4} \text{ M min}^{-1}$

Solution:

Step 1: Understanding the Concept:

To find the rate at a specific concentration, we first need to determine the first-order rate constant (k) from the provided concentration-time data.

Step 2: Key Formula or Approach:

1. Recognize half-life intervals to quickly find $t_{1/2}$, or use $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$.
2. Then calculate $k = \frac{0.693}{t_{1/2}}$.
3. Finally, calculate the specific rate using the differential rate law: $\text{Rate} = k[R]$.

Step 3: Detailed Explanation:

1. Calculate the Rate Constant (k):

Initial concentration, $[R]_0 = 0.1 \text{ M}$.

Final concentration, $[R]_t = 0.025 \text{ M}$.

Total time, $t = 40 \text{ min}$.

Notice the simple ratio: $0.1 \xrightarrow{t_{1/2}} 0.05 \xrightarrow{t_{1/2}} 0.025$.

The concentration dropped to one-fourth, meaning exactly two half-lives have passed.

$$2 \times t_{1/2} = 40 \text{ min} \implies t_{1/2} = 20 \text{ min}.$$

Now, calculate k :

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20} = 0.03465 \text{ min}^{-1}.$$

2. Calculate the Rate at $[R] = 0.01 \text{ M}$:

$$\text{Rate} = k \times [R]$$

$$\text{Rate} = 0.03465 \text{ min}^{-1} \times 0.01 \text{ M}$$

$$\text{Rate} = 3.465 \times 10^{-4} \text{ M min}^{-1} \approx 3.47 \times 10^{-4} \text{ M min}^{-1}.$$

Step 4: Final Answer:

The reaction rate at 0.01 M is $3.47 \times 10^{-4} \text{ M min}^{-1}$.

Quick Tip: Spot the "shortcuts" in concentration drops: 0.1 to 0.05 is one half-life; 0.05 to 0.025 is the second. Since total time is 40 , $t_{1/2}$ must be 20 . This conceptual trick entirely bypasses the need for long logarithm calculations!

52. The activation energy for the reaction $X \rightarrow Y$ is 150 kJ mol^{-1} . The change in enthalpy for the above reaction is -135 kJ mol^{-1} . Then the activation energy for $Y \rightarrow X$ is

(A) 280 kJ mol^{-1}

- (B) 285 kJ mol^{-1}
(C) 270 kJ mol^{-1}
(D) 15 kJ mol^{-1}

Correct Answer: (B) 285 kJ mol^{-1}

Solution:

Step 1: Understanding the Concept:

The enthalpy change of a reaction (ΔH) represents the overall energy difference between the products and reactants. It mathematically bridges the activation energy of the forward reaction and the backward reaction.

Step 2: Key Formula or Approach:

Use the fundamental thermodynamic-kinetic relationship: $\Delta H = E_{a(\text{forward})} - E_{a(\text{backward})}$.

Step 3: Detailed Explanation:

Given parameters:

Forward activation energy, $E_{af} = 150 \text{ kJ mol}^{-1}$.

Enthalpy change, $\Delta H = -135 \text{ kJ mol}^{-1}$ (The negative sign indicates an exothermic reaction where products are lower in energy than reactants).

We need to find the backward activation energy, E_{ab} for the reverse reaction $Y \rightarrow X$.

Rearranging the formula:

$$\Delta H = E_{af} - E_{ab}$$

$$E_{ab} = E_{af} - \Delta H$$

Substitute the values carefully observing the signs:

$$E_{ab} = 150 - (-135)$$

$$E_{ab} = 150 + 135 = 285 \text{ kJ mol}^{-1}.$$

Step 4: Final Answer:

The activation energy for the backward reaction is 285 kJ mol^{-1} .

Quick Tip: Mental check: For an exothermic reaction ($\Delta H < 0$), you are going "downhill." Consequently, climbing back "uphill" for the reverse reaction means E_{ab} MUST be strictly larger than E_{af} .

53. The intermediates in heteropolar reactions are

- (A) Free radicals only
- (B) Cations only
- (C) Anions only
- (D) Both anions and cations

Correct Answer: (D) Both anions and cations

Solution:**Step 1: Understanding the Concept:**

Chemical reactions generally fall into two broad categories based on how covalent bonds break: homopolar (non-polar) or heteropolar (polar/ionic) mechanisms.

Step 2: Key Formula or Approach:

Analyze the products of heterolytic bond cleavage. When a bond breaks unevenly, electrical charges form.

Step 3: Detailed Explanation:

1. **Heteropolar (or Heterolytic) fission:** During the reaction, the shared covalent bond breaks asymmetrically such that both electrons of the shared pair remain entirely with one of the fragments (usually the more electronegative atom). This results in the formation of charged species: an **anion** (negatively charged fragment that kept the electrons) and a **cation** (positively charged fragment that lost the electrons).
2. Standard examples in organic chemistry include the formation of carbocations and carbanions during S_N1 or Electrophilic Addition reactions.
3. In direct contrast, homopolar (homolytic) fission breaks bonds symmetrically, producing neutral free radicals.

Step 4: Final Answer:

Heteropolar reactions inherently involve both anions and cations as intermediates.

Quick Tip: Vocabulary mapping: Heteropolar = Heterolytic = Uneven break = Different charges (Ions).

Homopolar = Homolytic = Even break = Neutral species (Radicals).

54. Statement I: Nitrogen in pyridine cannot be estimated by Kjeldahl's method

Statement II: Nitrogen in pyridine changes to ammonium sulphate when heated with conc. H_2SO_4 in Kjeldahl's method.

Read the above given statements and choose the correct answer from the given options.

- (A) Statement I is true but Statement II is false
- (B) Both Statement I and Statement II are false
- (C) Both Statement I and Statement II are true
- (D) Statement I is false but Statement II is true

Correct Answer: (A) Statement I is true but Statement II is false

Solution:**Step 1: Understanding the Concept:**

Kjeldahl's method is the standard quantitative analytical technique used to estimate nitrogen in organic compounds, but it has specific chemical limitations based on the structural environment of the nitrogen atom.

Step 2: Key Formula or Approach:

Evaluate the core principle of Kjeldahl digestion: the organic nitrogen **MUST** be capable of converting quantitatively into ammonium sulfate. Assess if pyridine meets this condition.

Step 3: Detailed Explanation:

1. **Statement I:** Kjeldahl's method fails for compounds containing nitrogen situated in a stable aromatic ring (like pyridine, quinoline), nitrogen present in nitro groups ($-\text{NO}_2$), or nitrogen in azo groups ($-\text{N}=\text{N}-$). (Statement I is True)
2. **Statement II:** The fundamental reason Kjeldahl's method fails for pyridine is precisely because its ring nitrogen is exceptionally stable and tightly bound. When heated with conc.

H_2SO_4 , it **does not** quantitatively undergo decomposition and thus does not change to ammonium sulphate under standard digestion conditions. (Statement II is False)

Step 4: Final Answer:

Statement I is correct, and Statement II is incorrect.

Quick Tip: Remember the "Exclusions" for Kjeldahl: Pyridine/Quinoline (rings), Nitro, and Azo. For these resilient compounds, chemists rely on the **Dumas method** instead, which converts all nitrogen to N_2 gas.

55. The number of chain isomers possible for the hydrocarbon with molecular formula C_5H_{12} is

- (A) 4
- (B) 3
- (C) 2
- (D) 1

Correct Answer: (B) 3

Solution:

Step 1: Understanding the Concept:

Isomers are distinct chemical compounds that share the exact same molecular formula but have different structural arrangements. Chain isomers specifically differ in the branching arrangement of their carbon skeleton.

Step 2: Key Formula or Approach:

Systematically draw and name the alkane skeletons for 5 carbons, starting from a straight chain and systematically shortening it to add branches.

Step 3: Detailed Explanation:

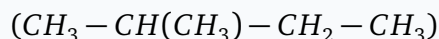
For the alkane pentane (C_5H_{12}), the following unique carbon skeletons can be constructed:

1. **n-Pentane:** A completely unbranched straight chain of 5 carbons.



2. **Isopentane (IUPAC: 2-methylbutane):** A 4-carbon main chain with a single methyl

branch attached to the second carbon.



3. **Neopentane (IUPAC: 2,2-dimethylpropane):** A 3-carbon main chain with two methyl branches attached to the central carbon.



Any other attempt to branch (like 3-methylbutane) is just a reverse numbering of an already listed structure.

Step 4: Final Answer:

There are 3 unique chain isomers for pentane.

Quick Tip: Memorize the isomer counts for small alkanes to save time on exams: Butane (2), Pentane (3), Hexane (5), Heptane (9).

56. The compound with molecular formula $C_{20}H_{42}$ is

- (A) Decane
- (B) Dodecane
- (C) Eicosane
- (D) Hicosane

Correct Answer: (C) Eicosane

Solution:

Step 1: Understanding the Concept:

Acyclic alkanes follow the general mathematical formula C_nH_{2n+2} . The IUPAC nomenclature system utilizes specific Greek/Latin numerical prefixes to denote the exact number of carbon atoms in the main chain.

Step 2: Key Formula or Approach:

Verify it is an alkane, then match the carbon count ($n = 20$) to the internationally recognized IUPAC prefix list for higher alkanes.

Step 3: Detailed Explanation:

1. **Formula check:** For $n = 20$, the number of hydrogens is $H = 2(20) + 2 = 42$. This matches

the given formula $C_{20}H_{42}$, confirming it is an alkane.

2. Nomenclature prefixes:

(A) **Dec-** is the prefix for 10 carbons. Decane is $C_{10}H_{22}$.

(B) **Dodec-** is the prefix for 12 carbons. Dodecane is $C_{12}H_{26}$.

(C) **Eicos-** is the universally accepted prefix for 20 carbons. Therefore, Eicosane is $C_{20}H_{42}$.

(D) Hicosane is a misspelling and not a standard IUPAC term; Eicosane is the correct Greek-derived root.

Step 4: Final Answer:

The compound containing 20 carbons is Eicosane.

Quick Tip: Common higher alkane prefixes you should recognize: 11 (Undec-), 12 (Dodec-), 20 (Eicos-), 30 (Triacont-).

57. C-Cl bond in methyl chloride compared to C-Cl bond in chlorobenzene is

- (A) Longer and stronger
- (B) Shorter and stronger
- (C) Shorter and weaker
- (D) Longer and weaker

Correct Answer: (D) Longer and weaker

Solution:

Step 1: Understanding the Concept:

Bond length and bond strength are primarily dictated by the state of hybridization of the bonded carbon atom and the presence or absence of electron delocalization (resonance).

Step 2: Key Formula or Approach:

Compare the hybridization (sp^3 vs sp^2) of the carbon atoms attached to chlorine in both molecules and analyze the partial double bond character arising from resonance in aromatic systems.

Step 3: Detailed Explanation:

1. **In Methyl Chloride (CH_3Cl):** The carbon atom is sp^3 hybridized. The $C-Cl$ bond is a

pure, localized single sigma bond.

2. In Chlorobenzene (C_6H_5Cl):

- The carbon atom attached to the chlorine is sp^2 hybridized. sp^2 hybridized carbons have more s-character, making them smaller and more electronegative, which inherently pulls the chlorine atom closer.
- More importantly, **Resonance**: The lone pairs of electrons on the Chlorine atom are delocalized into the π system of the benzene ring. This imparts a **partial double bond character** to the $C - Cl$ bond.

Because double bonds are shorter and stronger than single bonds, the $C - Cl$ bond in chlorobenzene is **shorter and stronger**.

Therefore, by relative comparison, the pure single bond in methyl chloride is **longer and weaker**.

Step 4: Final Answer:

The C-Cl bond in methyl chloride is longer and weaker.

Quick Tip: Sequence of bond properties: Partial double bond character $\rightarrow$ Shorter bond length $\rightarrow$ Higher bond dissociation energy (strength). This explains why aryl halides are notoriously unreactive towards nucleophilic substitution!

58. The compound from which chlorobenzene cannot be prepared easily is

- (A) Aniline
- (B) Benzene
- (C) Phenol
- (D) Benzene diazonium chloride

Correct Answer: (C) Phenol

Solution:

Step 1: Understanding the Concept:

Aryl halides (like chlorobenzene) require specific synthetic pathways due to the unreactivity of aromatic rings toward standard nucleophilic substitution. We must evaluate standard

industrial and laboratory syntheses.

Step 2: Key Formula or Approach:

Review the reactivity of the functional groups in each option towards halogenation or substitution reactions to yield chlorobenzene.

Step 3: Detailed Explanation:

(A) **Aniline:** Can be easily converted via diazotization (NaNO_2/HCl) to benzene diazonium chloride, which then yields chlorobenzene via the Sandmeyer reaction.

(B) **Benzene:** Direct electrophilic aromatic halogenation with Cl_2 in the presence of an anhydrous Lewis acid catalyst (like FeCl_3 or AlCl_3) easily produces chlorobenzene.

(C) **Phenol:** Replacing the strong $-\text{OH}$ group on an aromatic ring directly with a halogen is exceedingly difficult. While alcohols easily react with PCl_5 or SOCl_2 to give alkyl halides, phenols do not. The $\text{C}-\text{O}$ bond has strong partial double bond character due to resonance. Reactions with PCl_5 give very poor yields and mostly result in triphenyl phosphate esters.

(D) **Benzene diazonium chloride:** Reacts flawlessly with CuCl/HCl (Sandmeyer reaction) or Cu powder/ HCl (Gattermann reaction) to give high yields of chlorobenzene.

Step 4: Final Answer:

Phenol is the compound from which chlorobenzene cannot be prepared easily.

Quick Tip: In aromatic chemistry, directly substituting the strongly bound $-\text{OH}$ of Phenol to get an Aryl Halide is a synthetic dead end. It is almost always better to detour through the versatile diazonium salt route!

59. In $\text{S}_{\text{N}}1$ reaction, the alkyl halide that on hydrolysis produces racemic mixture is

- (A) Tertiary butyl bromide
- (B) 2-bromobutane
- (C) Isopropyl bromide
- (D) Methyl bromide

Correct Answer: (B) 2-bromobutane

Solution:

Step 1: Understanding the Concept:

S_N1 reactions proceed via a two-step mechanism involving a planar, sp^2 hybridized carbocation intermediate. If the starting alkyl halide has a chiral center, the planar intermediate loses the original stereochemistry, allowing nucleophilic attack from both faces, yielding a racemic mixture.

Step 2: Key Formula or Approach:

Identify which of the given alkyl halides possesses a chiral carbon (an asymmetric carbon atom bonded to four different groups). Only optically active substrates can yield a noticeably racemic mixture upon S_N1 hydrolysis.

Step 3: Detailed Explanation:

1. **Tertiary butyl bromide:** The central carbon is attached to three identical methyl groups and one bromine. It is achiral. The product (tert-butanol) is also achiral. It cannot form a racemic mixture.
2. **2-bromobutane:** The C2 carbon is attached to four distinct groups: a Hydrogen atom, a Methyl group (CH_3), an Ethyl group (C_2H_5), and a Bromine atom. It is a **chiral center**. Upon ionizing to form the planar carbocation ($CH_3 - CH^+ - C_2H_5$), water can attack equally from the top or bottom face, leading to equal amounts of the (*R*) and (*S*) enantiomers of 2-butanol (a racemic mixture). (Correct)
3. **Isopropyl bromide:** The central carbon is attached to two identical methyl groups. Achiral.
4. **Methyl bromide:** Achiral (and it typically undergoes S_N2 exclusively anyway).

Step 4: Final Answer:

2-bromobutane is the optically active halide that produces a racemic mixture.

Quick Tip: To "see" a racemic mixture produced in S_N1 , search the options for a **chiral secondary** or specifically tailored tertiary alkyl halide. Primary halides don't do S_N1 , and simple tertiary ones are usually symmetrical and achiral.

60. Match the compounds of List-I with their effects in List-II

List-I

(a) Chloramphenicol

(b) Thyroxine

List-II

(i) Malaria

(ii) Anesthetic

- (c) Chloroquine (iii) Goiter
(d) Chloroform (iv) Typhoid fever

Codes:

- (A) a – i, b – ii, c – iii, d – iv
(B) a – iv, b – iii, c – i, d – ii
(C) a – i, b – iii, c – iv, d – ii
(D) a – iv, b – iii, c – ii, d – i

Correct Answer: (B) a – iv, b – iii, c – i, d – ii

Solution:

Step 1: Understanding the Concept:

This requires factual knowledge linking common medicinal chemistry compounds and biochemical hormones with the specific diseases or physiological conditions they are intended to treat or affect.

Step 2: Key Formula or Approach:

Rely on standard memory recall of drug classifications from the "Chemistry in Everyday Life" curriculum. Match the drug to its therapeutic action.

Step 3: Detailed Explanation:

(a) **Chloramphenicol**: This is a potent, broad-spectrum antibiotic historically famous for its high effectiveness in the specific treatment of severe **typhoid fever**. (a → iv)

(b) **Thyroxine**: This is the main iodine-containing hormone produced by the thyroid gland. A dietary deficiency of iodine reduces its production, leading to the enlargement of the thyroid, a condition known as **goiter**. (b → iii)

(c) **Chloroquine**: An essential synthetic antimalarial medication widely utilized for the treatment and prophylaxis of **malaria**. (c → i)

(d) **Chloroform** (CHCl_3): Historically, its vapors were widely utilized as a general **anesthetic** in surgery, though its high toxicity has led to its replacement by safer alternatives today. (d → ii)

Step 4: Final Answer:

The matching sequence is a-iv, b-iii, c-i, d-ii, which aligns with option (B).

Quick Tip: Medicinal chemistry matches are straightforward "easy marks." Always lock in the easiest associations first—Chloroquine with Malaria, and Chloramphenicol with Typhoid—they are standard staple examples in chemistry textbooks.
