

GATE 2024 Chemistry Question Paper with Solutions

Time Allowed :3 Hour	Maximum Marks :100	Total Questions :65
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General Instructions

Please read the following instructions carefully:

- This question paper is divided into three sections:
 - General Aptitude (GA):** 10 questions (5 questions \times 1 mark + 5 questions \times 2 marks) for a total of 15 marks.
 - Environmental Science and Engineering + Engineering Mathematics:**
 - Part A (Mandatory):** 36 questions (1 questions \times 1 mark + 19 questions \times 2 marks) for a total of 55 marks.
 - Part B (Section 1):** Candidates can choose either Part B1 (Surveying and Mapping) or Part B2 (Section 2). Each part contains 16 questions (8 questions \times 1 mark + 11 questions \times 2 marks) for a total of 30 marks.
- The total number of questions is **65**, carrying a maximum of **100 marks**.
- The duration of the exam is **3 hours**.
- Marking scheme:
 - For 1-mark MCQs, $\frac{1}{3}$ mark will be deducted for every incorrect response.
 - For 2-mark MCQs, $\frac{2}{3}$ mark will be deducted for every incorrect response.
 - No negative marking for numerical answer type (NAT) questions.
 - No marks will be awarded for unanswered questions.
- Ensure you attempt questions only from the optional section (Part B1 or Part B2) you have selected.
- Follow the instructions provided during the exam for submitting your answers.

1. If '→' denotes increasing order of intensity, then the meaning of the words [sick → infirm → moribund] is analogous to [silly → ____ → daft]. Which one of the given options is appropriate to fill the blank?

- (A) frown
- (B) fawn
- (C) vein
- (D) vain

Correct Answer: (4) vain

Solution:

Concept: The arrow \rightarrow represents an **increasing order of intensity** in meaning. Hence, the words must follow a progression where each subsequent word expresses a stronger degree of the same quality.

- **sick** \rightarrow **infirm** \rightarrow **moribund** shows increasing severity of illness.
- Similarly, the second set must show increasing foolishness.

Step 1: Analyze the given analogy.

silly \rightarrow ____ \rightarrow daft

- **silly:** mildly foolish
- **daft:** extremely foolish

The missing word should indicate a level of foolishness that lies between *silly* and *daft*.

Step 2: Evaluate the options.

- **frown:** a facial expression (not related)
- **fawn:** to flatter excessively (not related)
- **vein:** a blood vessel (irrelevant)
- **vain:** foolishly proud; lacking good judgment

Step 3: Form the correct sequence.

silly \rightarrow vain \rightarrow daft

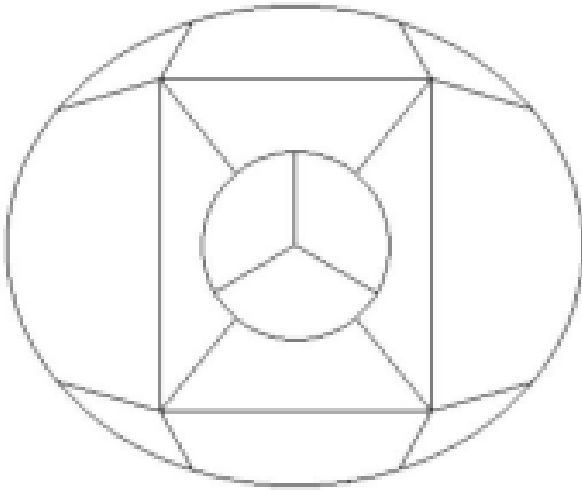
Thus, the correct option is **vain**.

Quick Tip

In analogy questions based on intensity:

- Identify the common trait,
- Arrange meanings from weak to strong,
- Eliminate contextually unrelated words.

2. The 15 parts of the given figure are to be painted such that no two adjacent parts with shared boundaries (excluding corners) have the same color. The minimum number of colors required is



- (A) 4
- (B) 3
- (C) 5
- (D) 6

Correct Answer: (2) 3

Solution:

Concept: This is a **map coloring problem**. The objective is to color different regions of a figure such that:

- No two **adjacent regions sharing a boundary** have the same color,
- Regions touching only at corners are allowed to have the same color,
- The total number of colors used is minimum.

Step 1: Observe the structure of the figure. The figure consists of:

- An inner circular region divided into 3 sectors,
- A middle square-like structure divided into triangular parts,
- An outer oval region further divided into multiple sections.

Each region shares boundaries with multiple neighboring regions, making the coloring constraint tight.

Step 2: Start coloring the central regions. The innermost circular region has **three mutually adjacent sectors**. Hence, these three regions **must be colored with three different colors**.

Step 3: Extend the coloring outward. Now consider the surrounding regions:

- Each outer region is adjacent to at most two differently colored regions,
- A third color is always available without causing any conflict.

Thus, all remaining regions can be colored using only the same **three colors** by repeating them carefully.

Step 4: Check minimality.

- Using only **two colors** is impossible due to the triangular adjacency in the center,
- Since three colors suffice for the entire figure, no additional color is required.

Quick Tip

In coloring problems:

- Look for triangular or cyclic adjacency — they determine the minimum colors,
- Start coloring from the most constrained (central) region,
- Expand outward while reusing colors wherever possible.

3. How many 4-digit positive integers divisible by 3 can be formed using only the digits $\{1, 3, 4, 6, 7\}$, such that no digit appears more than once in a number?

- (A) 24
 (B) 48
 (C) 72
 (D) 12

Correct Answer: (2) 48

Solution:

Concept: A number is divisible by 3 if the **sum of its digits is divisible by 3**. Also, since digits are not repeated, we deal with **permutations of distinct digits**.

Step 1: Find the remainders of the given digits modulo 3.

$$\begin{aligned} 1 &\equiv 1 \pmod{3} \\ 3 &\equiv 0 \pmod{3} \\ 4 &\equiv 1 \pmod{3} \\ 6 &\equiv 0 \pmod{3} \\ 7 &\equiv 1 \pmod{3} \end{aligned}$$

Thus:

- Digits with remainder 0: $\{3, 6\}$
- Digits with remainder 1: $\{1, 4, 7\}$

Step 2: Choose 4 digits whose sum is divisible by 3. Let the number of digits with remainder 0 be k . Then the sum condition gives:

$$(4 - k) \equiv 0 \pmod{3} \Rightarrow 4 - k = 3 \Rightarrow k = 1$$

Step 3: Count the valid selections.

- Choose 1 digit from $\{3, 6\}$: 2 ways
- Choose 3 digits from $\{1, 4, 7\}$: 1 way

Total valid digit sets = 2.

Step 4: Arrange each set into 4-digit numbers. Each set has $4! = 24$ permutations.

$$\text{Total numbers} = 2 \times 24 = 48$$

Quick Tip

For divisibility-by-3 problems with permutations:

- First select digits satisfying the divisibility rule,
- Then count the permutations of those digits.

4. The sum of the following infinite series is

$$2 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{8} + \frac{1}{9} + \frac{1}{16} + \frac{1}{27} + \dots$$

- (A) $\frac{11}{3}$
- (B) $\frac{7}{2}$
- (C) $\frac{13}{4}$
- (D) $\frac{9}{2}$

Correct Answer: (2) $\frac{7}{2}$

Solution:

Concept: The given series can be split into **separate geometric series**:

- A constant term,
- A geometric series with ratio $\frac{1}{2}$,
- A geometric series with ratio $\frac{1}{3}$.

Step 1: Rearrange the series.

$$2 + \left(\frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \frac{1}{16} + \dots \right) + \left(\frac{1}{3} + \frac{1}{9} + \frac{1}{27} + \dots \right)$$

Step 2: Evaluate each part.

- First term: 2
- Second series:

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

- Third series:

$$\frac{\frac{1}{3}}{1 - \frac{1}{3}} = \frac{1}{2}$$

Step 3: Add the results.

$$2 + 1 + \frac{1}{2} = \frac{7}{2}$$

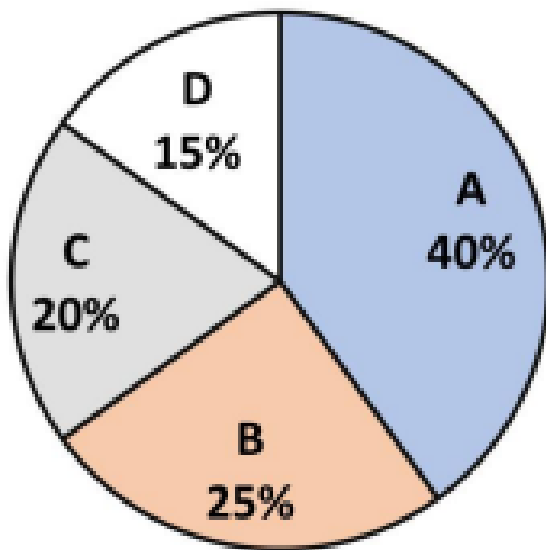
Quick Tip

When dealing with infinite series:

- Look for hidden geometric patterns,
- Split mixed sequences into simpler known series.

5. In an election, the share of valid votes received by the four candidates A, B, C, and D is represented by the pie chart shown. The total number of votes cast in the election were 1,15,000, out of which 5,000 were invalid. Based on the data provided, the total number of valid votes received by the candidates B and C is

Share of valid votes



- (A) 45,000
- (B) 49,500
- (C) 51,750
- (D) 54,000

Correct Answer: (2) 49,500

Solution:

Concept: A pie chart represents the **percentage distribution of valid votes**. To find the actual number of votes:

- First calculate the total number of **valid votes**,
- Then apply the given percentages to this total.

Step 1: Calculate the total number of valid votes.

$$\text{Total votes cast} = 1,15,000$$

$$\text{Invalid votes} = 5,000$$

$$\text{Valid votes} = 1,15,000 - 5,000 = 1,10,000$$

Step 2: Determine the combined percentage of votes for candidates B and C.

From the pie chart:

$$\text{Votes for B} = 25\%, \quad \text{Votes for C} = 20\%$$

$$\text{Total for B and C} = 25\% + 20\% = 45\%$$

Step 3: Calculate the number of valid votes received by B and C.

$$45\% \text{ of } 1,10,000 = \frac{45}{100} \times 1,10,000 = 49,500$$

Quick Tip

In pie-chart problems:

- Always confirm whether percentages are of total votes or valid votes,
- Subtract invalid data before applying percentages.

6. Thousands of years ago, some people began dairy farming. This coincided with a number of mutations in a particular gene that resulted in these people developing the ability to digest dairy milk. Based on the given passage, which of the following can be inferred?

- (A) All human beings can digest dairy milk.
- (B) No human being can digest dairy milk.
- (C) Digestion of dairy milk is essential for human beings.
- (D) In human beings, digestion of dairy milk resulted from a mutated gene.

Correct Answer: (4) In human beings, digestion of dairy milk resulted from a mutated gene.

Solution:

Concept: Inference-based questions require conclusions that are:

- Directly supported by the passage,
- Logically necessary,
- Free from exaggeration or assumptions beyond the text.

Step 1: Analyze the key information in the passage.

- Dairy farming began thousands of years ago,
- This coincided with mutations in a particular gene,
- These mutations enabled people to digest dairy milk.

Step 2: Evaluate the options.

- **Option (A):** Incorrect — the passage refers only to *some people*, not all humans.
- **Option (B):** Incorrect — directly contradicts the passage.
- **Option (C):** Incorrect — no statement about essentiality is made.
- **Option (D):** Correct — it restates the logical inference drawn from the passage.

Thus, option (D) is the only valid inference.

Quick Tip

For inference questions:

- Stick strictly to what is implied,
- Avoid options with words like *all*, *none*, or *essential* unless clearly stated.

7. The probability of a boy or a girl being born is $\frac{1}{2}$. For a family having only three children, what is the probability of having two girls and one boy?

- (A) $\frac{3}{8}$
 (B) $\frac{1}{8}$
 (C) $\frac{1}{4}$
 (D) $\frac{1}{2}$

Correct Answer: (1) $\frac{3}{8}$

Solution:

Concept: This is a basic **probability and combination** problem where:

- Each child is equally likely to be a boy or a girl,
- Births are independent events.

Step 1: Find the total number of possible outcomes. Each child has 2 possible outcomes (boy or girl), so:

$$\text{Total outcomes} = 2^3 = 8$$

Step 2: Count the favorable outcomes (exactly two girls and one boy). The number of ways to choose positions for two girls out of three children is:

$$\binom{3}{2} = 3$$

Step 3: Calculate the probability.

$$\text{Probability} = \frac{\text{Favorable outcomes}}{\text{Total outcomes}} = \frac{3}{8}$$

Quick Tip

For such probability problems:

- Use combinations to count arrangements,
- Multiply probabilities only after fixing the number of favorable cases.

8. Person 1 and Person 2 invest in three mutual funds A, B, and C. The amounts they invest in each of these mutual funds are given in the table. At the end of one year, the total amount that Person 1 gets is 500 more than Person 2. The annual rate of return for the mutual funds B and C is 15% each. What is the annual rate of return for the mutual fund A?

- (A) 7.5%
- (B) 10%
- (C) 15%
- (D) 20%

Correct Answer: (2) 10%

Solution:

Concept: The total amount received after one year is:

$$\text{Principal} + \text{Return}$$

If the principal investments of both persons are equal, then any difference in the final amount is solely due to the **difference in returns**.

Step 1: Calculate total investments of both persons.

$$\text{Person 1} = 10,000 + 20,000 + 20,000 = 50,000$$

$$\text{Person 2} = 20,000 + 15,000 + 15,000 = 50,000$$

Since both invested the same total amount, the difference of 500 is due only to returns.

Step 2: Let the annual rate of return of mutual fund A be r .

Returns of Person 1:

$$10,000r + 20,000(0.15) + 20,000(0.15) = 10,000r + 6,000$$

Returns of Person 2:

$$20,000r + 15,000(0.15) + 15,000(0.15) = 20,000r + 4,500$$

Step 3: Use the given condition.

$$\text{Return of Person 1} = \text{Return of Person 2} + 500$$

$$10,000r + 6,000 = 20,000r + 4,500 + 500$$

$$10,000r + 6,000 = 20,000r + 5,000$$

Step 4: Solve for r .

$$1,000 = 10,000r \Rightarrow r = 0.10 = 10\%$$

Quick Tip

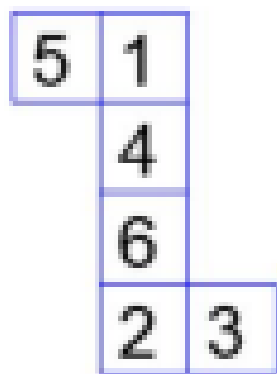
In investment comparison problems:

- First check whether total investments are equal,
- If yes, compare only the returns,
- Assign variables only to unknown rates.

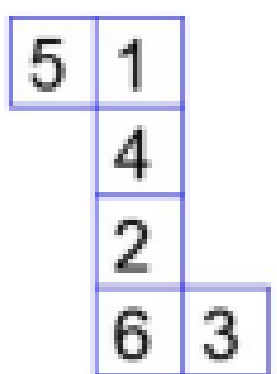
9. Three different views of a dice are shown in the figure below. The piece of paper that can be folded to make this dice is



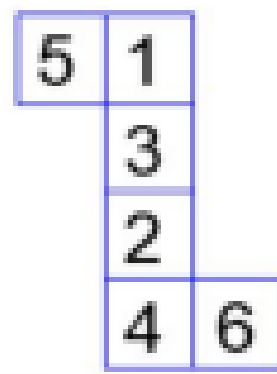
(A)



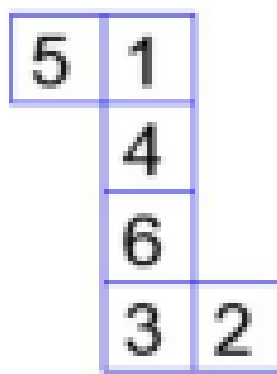
(B)



(C)



(D)



Correct Answer: (4)

Solution:

Concept: In dice problems:

- Faces that appear together in a view are **adjacent**,
- A face can have only **four adjacent faces**,
- The remaining face (not adjacent) is the **opposite face**.

Step 1: Identify adjacency from the given views.

From the first view:

5 is adjacent to 4 and 1

From the third view:

5 is adjacent to 6 and 2

Thus, face 5 is adjacent to:

$\{1, 2, 4, 6\}$

Hence, the only number not adjacent to 5 is:

$\boxed{3}$

So, 5 and 3 are **opposite faces**.

Step 2: Determine another opposite pair.

From the first and second views:

4 is adjacent to 5, 1, 6, 3

Thus, the only number not adjacent to 4 is:

$\boxed{2}$

So, 4 and 2 are opposite faces.

Step 3: Identify the final opposite pair.

The remaining numbers are:

1 and 6

Hence, they must be opposite faces.

Opposite face pairs are:

$(5, 3), (4, 2), (1, 6)$

Step 4: Check the given nets.

Only **Option (D)** produces exactly these opposite face pairs when folded into a cube. All other options place at least one opposite pair on adjacent faces, which is impossible.

Quick Tip

For dice problems:

- First determine opposite face pairs using adjacency,
- Then eliminate nets where opposite faces touch or share an edge.

10. Visualize two identical right circular cones such that one is inverted over the other and they share a common circular base. If a cutting plane passes through the vertices of the assembled cones, what shape does the outer boundary of the resulting cross-section make?

- (A) A rhombus
- (B) A triangle
- (C) An ellipse
- (D) A hexagon

Correct Answer: (1) A rhombus

Solution:

Concept: When solids are cut by a plane, the shape of the cross-section depends on:

- The geometry of the solid,
- The orientation of the cutting plane,
- The points through which the plane passes.

Here, we are dealing with **two identical right circular cones** placed apex-to-apex, sharing a common base.

Step 1: Understand the arrangement of the cones.

- The cones are identical and aligned along the same axis,
- One cone is inverted over the other,
- Their vertices lie on the same straight line (axis),
- They share a common circular base in the middle.

Step 2: Analyze the cutting plane. The cutting plane:

- Passes through the **vertices of both cones**,
- Is symmetric about the axis of the cones.

Such a plane intersects:

- Each cone in an **isosceles triangle**,
- With equal slant heights due to identical cones.

Step 3: Determine the shape of the outer boundary. The two triangular cross-sections join base-to-base at the common circular base. The outer boundary therefore consists of:

- Four equal slant edges,
- Opposite sides equal and parallel.

This forms a **rhombus**.

Quick Tip

For solid cross-section problems:

- Always sketch a rough diagram,
- Look for symmetry in the solid and the cutting plane,
- Combine individual cross-sections carefully.

11. Among the following, the compound with the lowest CO stretching frequency is:

- (A) $[\text{Mn}(\text{CO})_6]^+$
(B) $[\text{V}(\text{CO})_6]^-$
(C) $[\text{Cr}(\text{CO})_5]$
(D) $[\text{Cr}(\text{dien})(\text{CO})_3]$ (dien: diethylenetriamine)

Correct Answer: (B) $[\text{V}(\text{CO})_6]^-$

Solution:

Concept: The CO stretching frequency (ν_{CO}) in metal carbonyl complexes depends on the extent of **π -back bonding** from the metal to the CO ligand.

Key points:

- Greater metal \rightarrow CO π -back donation **weakens the C–O bond**
- Weaker C–O bond \Rightarrow **lower CO stretching frequency**
- π -back bonding increases with:
 - Higher electron density on the metal
 - Negative charge on the complex
 - Lower oxidation state of the metal

Step 1: Analyze each option in terms of electron density on the metal.

- **(A)** $[\text{Mn}(\text{CO})_6]^+$: Positively charged complex \Rightarrow low electron density on Mn \Rightarrow weak π -back bonding \Rightarrow high ν_{CO} .
- **(B)** $[\text{V}(\text{CO})_6]^-$: Negatively charged complex \Rightarrow very high electron density on V \Rightarrow strongest π -back bonding \Rightarrow **lowest** ν_{CO} .
- **(C)** $[\text{Cr}(\text{CO})_5]$: Neutral complex with fewer CO ligands \Rightarrow moderate π -back bonding.
- **(D)** $[\text{Cr}(\text{dien})(\text{CO})_3]$: Presence of strong σ -donor dien reduces back bonding to CO ligands \Rightarrow higher ν_{CO} compared to (B).

Step 2: Identify the complex with maximum π -back bonding.



has the highest electron density on the metal and hence the **lowest CO stretching frequency**.

Quick Tip

CO stretching frequency trend:

More electron-rich metal \Rightarrow stronger π -back bonding \Rightarrow lower ν_{CO} .

12. The ground state of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is:

- (A) 5E_g
- (B) ${}^5T_{2g}$
- (C) ${}^6A_{1g}$
- (D) ${}^6A_{2g}$

Correct Answer: (A) 5E_g

Solution:

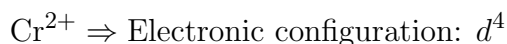
Concept: The ground state term of a coordination complex depends on:

- The electronic configuration of the metal ion
- The nature of the ligand field (weak or strong)
- Octahedral crystal field splitting
- Spin state (high spin or low spin)

For octahedral complexes, the ground state term can be determined using **Tanabe–Sugano diagrams** or standard electronic term results.

Step 1: Determine the oxidation state and electronic configuration.

In $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$:



Step 2: Nature of the ligand field.

Water (H_2O) is a **weak field ligand**, hence the complex is **high-spin**.

For a high-spin d^4 octahedral complex:



Step 3: Determine the ground state term.

From Tanabe–Sugano considerations:

- High-spin d^4 octahedral complexes have the ground state:



Step 4: Eliminate incorrect options.

- ${}^5T_{2g}$ is the ground state for high-spin d^3

- ${}^6A_{1g}$ and ${}^6A_{2g}$ require six unpaired electrons, which is not possible for d^4

Hence, the correct ground state is:



Quick Tip

Remember:

High-spin d^4 octahedral complexes always have 5E_g as the ground state.

13. The reaction of XeF_2 with $\text{HN}(\text{SO}_2\text{F})_2$ at 273 K in CF_2Cl_2 solvent yields:

- (A) $\text{XeF}_4 + \text{SO}_2 + \text{NH}_3$
- (B) $\text{Xe} + \text{SO}_2 + \text{N}_2 + \text{HF}$
- (C) $\text{SOF}_2 + \text{XeO}_2 + \text{NH}_3$
- (D) $\text{FXeN}(\text{SO}_2\text{F})_2 + \text{HF}$

Correct Answer: (D) $\text{FXeN}(\text{SO}_2\text{F})_2 + \text{HF}$

Solution:

Concept: Xenon difluoride (XeF_2) is a strong **fluorinating and oxidizing agent**. It readily forms **Xe–N bonds** with nitrogen-containing nucleophiles, especially in polar, non-reactive solvents like CF_2Cl_2 at low temperatures.

Key ideas:

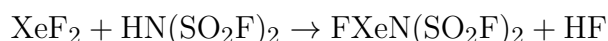
- XeF_2 undergoes **nucleophilic substitution** reactions
- Nitrogen bases can attack xenon, forming stable Xe–N compounds
- Acidic protons are eliminated as HF

Step 1: Identify the nature of reactants.

- XeF_2 : electrophilic xenon center due to highly electronegative fluorine atoms
- $\text{HN}(\text{SO}_2\text{F})_2$: nitrogen-containing nucleophile with an acidic N–H proton

Step 2: Understand the reaction pathway.

The nitrogen atom of $\text{HN}(\text{SO}_2\text{F})_2$ attacks the xenon center, replacing one fluorine atom. Simultaneously, the acidic hydrogen combines with fluoride to form HF.



Step 3: Match the product with given options.

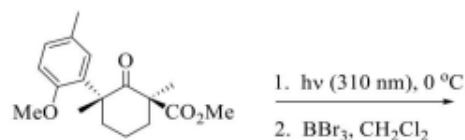
Only option (D) correctly represents:

- Formation of a **Xe–N bond**
- Elimination of **HF**
- No decomposition of XeF_2 into Xe or oxides

Quick Tip

XeF_2 commonly forms FXeY -type compounds with nucleophiles, where $\text{Y} = \text{N}, \text{O},$ or C donor atoms.

14. The major product in the following reaction sequence is:



- (A)
- (B)
- (C)
- (D)

Correct Answer: (C)

Solution:

Concept: This reaction involves a combination of **photochemical rearrangement** followed by **demethylation using BBr_3** . Key concepts applied are:

- Photochemical reactions proceed via excited states and allow symmetry-forbidden pathways
- Aryl methyl ethers undergo **O–Me cleavage** with BBr_3 to form phenols
- Intramolecular photochemical cyclization can occur when a suitably oriented carbonyl and aryl group are present

Step 1: Effect of UV irradiation ($h\nu$, 310 nm).

Upon UV irradiation, the aryl–carbonyl system undergoes an **intramolecular photochemical cyclization**. The excited carbonyl group interacts with the nearby aromatic ring, leading to formation of a fused cyclic lactone framework. Such photochemical processes are favored at low temperature (0°C) to control radical recombination.

Step 2: Role of BBr_3 .

BBr₃ is a strong Lewis acid that selectively cleaves aryl methyl ethers:



In the given intermediate, demethylation occurs without disturbing the newly formed cyclic framework.

Step 3: Stereochemical outcome.

The intramolecular cyclization occurs in a rigid conformation, leading to a **stereoselective product**. Among the given options, only option (C):

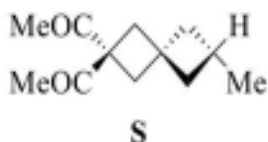
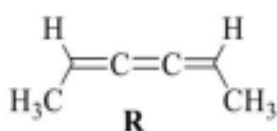
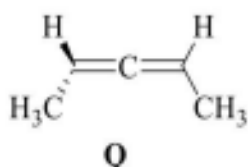
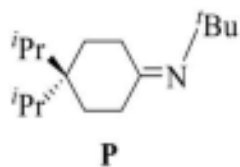
- Contains the correct fused lactone system
- Shows the correct relative stereochemistry
- Reflects successful demethylation of the methoxy group

Hence, option (C) represents the **major product** of the reaction sequence.

Quick Tip

Photochemical reactions often give products inaccessible by thermal pathways—always analyze connectivity first, then apply reagent-specific transformations like demethylation.

15. Among the following, the chiral compound is:



- (A) P
(B) Q
(C) R
(D) S

Correct Answer: (D) S

Solution:

Concept: A compound is said to be **chiral** if it is **non-superimposable on its mirror image**. Chirality generally arises due to:

- Presence of a stereogenic (chiral) center
- Absence of plane of symmetry, center of symmetry, or improper axis of rotation

Step 1: Analyze compound **P**.

Compound **P** contains a substituted cyclohexane system with identical substituents arranged symmetrically. Due to the presence of a plane of symmetry, compound **P** is **achiral**.

Step 2: Analyze compound **Q**.

Compound **Q** is an alkene with identical substituents on both carbon atoms of the double bond. It possesses a plane of symmetry and hence is **achiral**.

Step 3: Analyze compound **R**.

Compound **R** is an allene derivative. However, the substituents on both terminal carbon atoms are identical, resulting in a plane of symmetry. Therefore, compound **R** is also **achiral**.

Step 4: Analyze compound **S**.

Compound **S**:

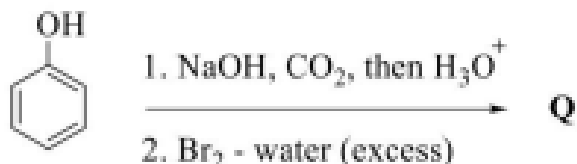
- Contains a stereogenic carbon atom (shown by wedge and dash bonds)
- Lacks any plane or center of symmetry
- Has four different substituents attached to the chiral carbon

Thus, compound **S** is **chiral**.

Quick Tip

Always check for symmetry elements first—if none are present and a stereogenic center exists, the molecule is chiral.

16. The major product in the given reaction sequence is **Q**. The mass spectrum of **Q** shows ($[M]$ = molecular ion peak)



- (A) $[M]$, $[M+2]$, $[M+4]$, and $[M+6]$ peaks with relative intensity of 1:1:1:1
(B) $[M]$, $[M+2]$, $[M+4]$, and $[M+6]$ peaks with relative intensity of 1:3:3:1
(C) $[M]$, $[M+2]$, and $[M+4]$ peaks with relative intensity of 1:2:1
(D) $[M]$ and $[M+2]$ peaks with relative intensity of 1:1

Correct Answer: (B)

Solution:

Concept: This problem combines **Kolbe–Schmitt reaction**, **electrophilic aromatic substitution**, and **mass spectral isotope patterns**.

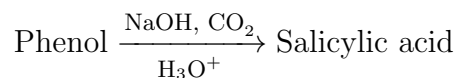
Key ideas:

- Phenol undergoes Kolbe–Schmitt reaction to form salicylic acid
- Phenolic -OH strongly activates the ring toward bromination

- Bromine has two abundant isotopes: ^{79}Br and ^{81}Br (1:1)
- Multiple bromine atoms give characteristic isotope patterns in mass spectra

Step 1: Identify product Q after step 1.

Phenol reacts with NaOH and CO_2 , followed by acidification:



Thus, the intermediate formed is **o-hydroxybenzoic acid**.

Step 2: Effect of excess Br_2 in water.

The phenolic $-\text{OH}$ group is a strong ortho/para director. In salicylic acid:

- Positions 2, 4, and 6 are highly activated
- Excess bromine leads to **tribromination**

Hence, Q is **2,4,6-tribromosalicylic acid**.

Step 3: Analyze the mass spectral pattern.

For a compound containing **three bromine atoms**:

- Possible isotope combinations give peaks at $[\text{M}]$, $[\text{M}+2]$, $[\text{M}+4]$, and $[\text{M}+6]$
- Relative intensities follow binomial distribution:

$$(^{79}\text{Br} : ^{81}\text{Br} = 1 : 1) \Rightarrow 1 : 3 : 3 : 1$$

Step 4: Match with options.

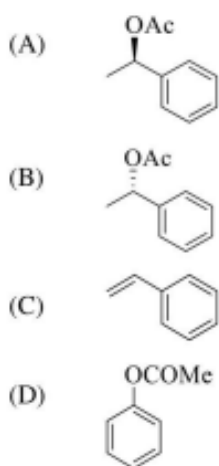
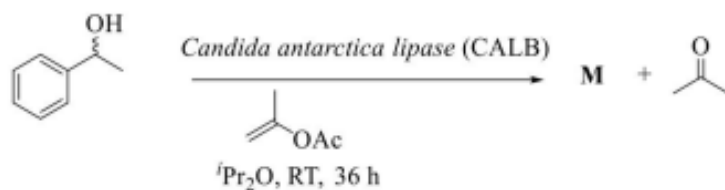
Option (B) correctly represents:

- Four peaks: $[\text{M}]$, $[\text{M}+2]$, $[\text{M}+4]$, $[\text{M}+6]$
- Relative intensity ratio of **1:3:3:1**

Quick Tip

Number of bromine atoms = number of isotope peaks – 1.
Three Br atoms always give a 1:3:3:1 pattern.

17. The product M in the following reaction is:



Correct Answer: (A)

Solution:

Concept: This reaction is an example of **enzyme-catalyzed kinetic resolution** using **Candida antarctica lipase B (CALB)**.

Key ideas:

- CALB catalyzes **enantioselective acylation** of secondary alcohols
- Vinyl acetate is commonly used as the acyl donor
- One enantiomer reacts faster to give the acetate ester, while the other remains unreacted
- The byproduct acetone is formed due to tautomerization of vinyl alcohol

Step 1: Identify the substrate.

The starting compound is **racemic 1-phenylethanol**, a secondary benzylic alcohol containing a stereogenic center.

Step 2: Enantioselectivity of CALB.

CALB preferentially acylates the **(R)-enantiomer** of 1-phenylethanol under these conditions, converting it into the corresponding acetate ester, while the (S)-alcohol remains largely unreacted.

Step 3: Stereochemical outcome.

The enzymatic acylation proceeds with **retention of configuration** at the stereogenic center. Therefore, the product M is **(R)-1-phenylethyl acetate**.

Step 4: Match with given options.

Among the options:

- Option (A) represents the acetate ester with the correct configuration
- Option (B) is the opposite enantiomer
- Options (C) and (D) do not correspond to enzymatic acylation of the alcohol

Hence, the correct product M is option (A).

Quick Tip

CALB is highly selective for (R)-secondary alcohols in kinetic resolution reactions using vinyl acetate.

18. Critical micellar concentration of a surfactant is 0.008 M in water at 25 °C. If the aggregation number of the micelles is 80, the concentration of the micelles (in M) present in 0.088 M aqueous solution of the surfactant at 25 °C is:

- (A) 0.010
- (B) 0.001
- (C) 0.008
- (D) 0.088

Correct Answer: (B) 0.001

Solution:

Concept: For surfactant solutions:

- Below the **critical micellar concentration (CMC)**, surfactant exists as monomers
- Above the CMC, additional surfactant molecules form micelles
- The concentration of micelles depends on:
 - Excess surfactant concentration above CMC
 - Aggregation number (N) of the micelle

Step 1: Calculate the concentration of surfactant contributing to micelle formation.

$$\text{Total surfactant concentration} = 0.088 \text{ M}$$

$$\text{CMC} = 0.008 \text{ M}$$

Only the amount above CMC forms micelles:

$$0.088 - 0.008 = 0.080 \text{ M}$$

Step 2: Use aggregation number to find micelle concentration.

Aggregation number (N) = 80 This means 80 surfactant molecules form one micelle.

$$\text{Micelle concentration} = \frac{0.080}{80} = 0.001 \text{ M}$$

Step 3: Match with options.

The calculated micelle concentration is **0.001 M**, which corresponds to option (B).

Quick Tip

$$\text{Micelle concentration} = \frac{(\text{Total concentration} - \text{CMC})}{\text{Aggregation number}}$$

Q19. The order and the number of classes present in a group with the irreducible representations A_1, A_2, B_1, B_2, E_1 , and E_2 , are respectively:

- (A) 6 and 6
- (B) 12 and 6
- (C) 6 and 3
- (D) 12 and 3

Correct Answer: (B) 12 and 6

Solution:

Concept: For any finite group:

- The number of irreducible representations is equal to the number of conjugacy classes.
- The sum of the squares of the dimensions of all irreducible representations equals the order of the group:

$$\sum_i (d_i)^2 = |G|$$

Here, d_i denotes the dimension of the i -th irreducible representation.

Step 1: Identify the dimensions of the given irreducible representations.

The representations are:

$$A_1, A_2, B_1, B_2, E_1, E_2$$

In standard group-theoretical notation:

- A and B representations are **one-dimensional**
- E representations are **two-dimensional**

Thus, the dimensions are:

$$A_1 = 1, A_2 = 1, B_1 = 1, B_2 = 1, E_1 = 2, E_2 = 2$$

Step 2: Calculate the order of the group using the sum of squares rule.

$$|G| = 1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2$$

$$|G| = 12$$

Hence, the **order of the group is 12**.

Step 3: Determine the number of classes.

The total number of irreducible representations given is:

$$6$$

Therefore, the group has **6 conjugacy classes**.

Quick Tip

Exam Tip: Number of irreducible representations = number of conjugacy classes, and

$$\sum (d_i)^2 = \text{order of the group.}$$

20. The molecule XY_2 is microwave active and its vibration-rotation spectrum shows only P and R transitions. In the correct structure,

- (A) X is the central atom in linear XY_2 .
- (B) X is the central atom in bent XY_2 .
- (C) Y is the central atom in linear XY_2 .
- (D) Y is the central atom in bent XY_2 .

Correct Answer: (B)

Solution:

Concept: This question involves **rotational spectroscopy** and **molecular symmetry**.

Key points:

- A molecule is **microwave active** only if it has a **permanent dipole moment**
- In vibration-rotation spectra:
 - **Linear molecules** show **P, Q, and R branches**
 - **Non-linear (bent) molecules** show only **P and R branches**

Step 1: Analyze microwave activity.

XY_2 is microwave active \Rightarrow molecule must have a permanent dipole moment. A linear XY_2 molecule with identical Y atoms and X at the center is **non-polar**, hence microwave inactive.

Step 2: Analyze vibration-rotation spectrum.

The absence of the Q-branch indicates that the molecule is **non-linear (bent)**.

Step 3: Determine the central atom.

In a bent XY_2 molecule, the central atom must be **X**, with two Y atoms bonded at an angle.

Thus, the correct structure is: **X is the central atom in bent XY_2 .**

Quick Tip

Linear molecules show a Q-branch; bent molecules do not.

Microwave activity requires a permanent dipole moment.

21. The complex(es) with distorted octahedral structure is (are):

- (A) $[\text{VF}_6]^{3-}$
- (B) $[\text{FeF}_6]^{3-}$
- (C) $[\text{MnF}_6]^{3-}$
- (D) $[\text{Fe}(\text{CN})_6]^{4-}$

Correct Answer: (B) and (C)

Solution:

Concept: Distortion in octahedral complexes commonly arises due to the **Jahn–Teller effect**, which occurs when there is uneven occupancy of degenerate d orbitals.

Key ideas:

- Strong Jahn–Teller distortion occurs in high-spin d^4 , d^7 , and d^9 configurations
- Weak or no distortion occurs when electronic distribution is symmetric

Step 1: Determine d -electron configurations.

- (A) $[\text{VF}_6]^{3-}$: $\text{V}^{3+} \rightarrow d^2 \Rightarrow$ no Jahn–Teller distortion
- (B) $[\text{FeF}_6]^{3-}$: $\text{Fe}^{3+} \rightarrow d^5$ (high spin, weak-field F^-) Unequal e_g occupancy \Rightarrow **distorted**
- (C) $[\text{MnF}_6]^{3-}$: $\text{Mn}^{3+} \rightarrow d^4$ (high spin) Strong Jahn–Teller distortion present
- (D) $[\text{Fe}(\text{CN})_6]^{4-}$: $\text{Fe}^{2+} \rightarrow d^6$ (low spin, strong-field CN^-) Symmetric t_{2g}^6 configuration \Rightarrow no distortion

Step 2: Identify distorted complexes.

Complexes with significant Jahn–Teller distortion:



Quick Tip

High-spin d^4 complexes show the strongest Jahn–Teller distortion.

22. The compound(s) which show(s) the perovskite structure in solid state is (are):

- (A) CaTiO_3
- (B) NiFe_2O_4
- (C) Fe_3O_4
- (D) CsPbI_3

Correct Answer: (A) and (D)

Solution:

Concept: The **perovskite structure** has the general formula ABX_3 , where:

- A = large cation (12-coordinated)
- B = smaller cation (octahedrally coordinated)
- X = anion (O^{2-} or halide)

Step 1: Analyze each compound.

- **(A) $CaTiO_3$:** Classic oxide perovskite with Ca^{2+} at A-site, Ti^{4+} at B-site, and O^{2-} as X \Rightarrow **Perovskite structure**
- **(B) $NiFe_2O_4$:** Inverse spinel structure \Rightarrow **Not perovskite**
- **(C) Fe_3O_4 :** Magnetite, inverse spinel structure \Rightarrow **Not perovskite**
- **(D) $CsPbI_3$:** Halide perovskite with Cs^+ (A), Pb^{2+} (B), I^- (X) \Rightarrow **Perovskite structure**

Thus, the compounds showing perovskite structure are **$CaTiO_3$ and $CsPbI_3$** .

Quick Tip

Oxide and halide perovskites both follow the ABX_3 structural motif.
Spinel has the general formula AB_2O_4 .

23. Among the following metalloproteins, the pair(s) of non-heme proteins is (are):

- (A) Hemoglobin and Myoglobin
- (B) Hemocyanin and Carboxypeptidase
- (C) Hemerythrin and Carbonic anhydrase
- (D) Cytochrome P-450 and Hemocyanin

Correct Answer: (B) and (C)

Solution:

Concept: Metalloproteins are classified based on whether the metal ion is bound within a **heme (porphyrin) ring** or not.

- **Heme proteins:** contain Fe–porphyrin complex
- **Non-heme proteins:** metal ion is directly coordinated to amino acid residues

Step 1: Analyze each option.

- **(A) Hemoglobin and Myoglobin:** Both contain Fe–heme units \Rightarrow **Heme proteins**
- **(B) Hemocyanin and Carboxypeptidase:** Hemocyanin: Cu-based, no heme Carboxypeptidase: Zn-based, no heme \Rightarrow **Both non-heme**
- **(C) Hemerythrin and Carbonic anhydrase:** Hemerythrin: non-heme iron protein Carbonic anhydrase: Zn-based, non-heme \Rightarrow **Both non-heme**
- **(D) Cytochrome P-450 and Hemocyanin:** Cytochrome P-450: heme protein Hemocyanin: non-heme protein \Rightarrow **Mixed pair**

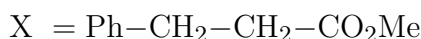
Therefore, the correct pairs of non-heme metalloproteins are **(B) and (C)**.

Quick Tip

Presence of a porphyrin ring = heme protein.

Zn- and Cu-enzymes are typically non-heme.

24. The reaction(s) that yield(s) **X** as the major product is (are):



- (A) $\text{PhCOCH}_2\text{Br} \xrightarrow{\text{NaOMe}}$
(B) $\text{PhCH}(\text{Br})\text{COCH}_3 \xrightarrow{\text{NaOMe}}$
(C) $\text{PhCH}=\text{CHCO}_2\text{Me} \xrightarrow[-78^\circ\text{C}]{\text{DIBAL-H (1.0 equiv.)}}$
(D) $\text{PhC}\equiv\text{CCO}_2\text{Me} \xrightarrow[\text{quinoline}]{\text{H}_2, 5\% \text{ Pd/CaCO}_3}$

Correct Answer: (A)

Solution:

Concept: The key transformation required is the formation of **methyl 3-phenylpropionate**



This can arise via:

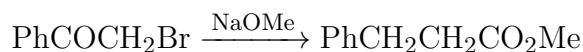
- **Favorskii rearrangement** of α -halo ketones under basic conditions
- Selective reduction reactions must be checked carefully for degree of saturation

Step 1: Analyze option (A).

Option (A) is an α -bromo ketone:



Treatment with NaOMe induces a **Favorskii rearrangement**, proceeding via a cyclopropanone intermediate, followed by nucleophilic attack by methoxide:



Thus, option (A) directly gives the desired ester X.

Step 2: Analyze option (B).

$\text{PhCH}(\text{Br})\text{COCH}_3$ also undergoes Favorskii rearrangement, but this leads to **methyl phenylacetate**:



which has only one methylene group and does **not** match X.

Step 3: Analyze option (C).

DIBAL-H (1 equiv., -78°C) selectively reduces esters to **allylic alcohols**:



Hence, option (C) does not give X.

Step 4: Analyze option (D).

Lindlar catalyst gives **cis-alkene** via partial hydrogenation:



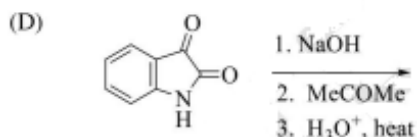
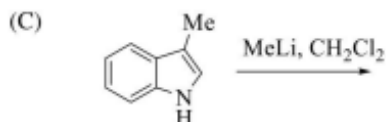
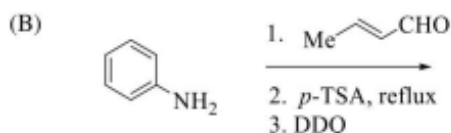
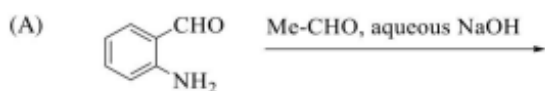
Further reduction to the saturated ester does not occur.

Therefore, only option (A) yields X as the major product.

Quick Tip

Favorskii rearrangement of α -halo ketones gives esters with skeletal rearrangement—always count carbon atoms carefully.

25. The reaction(s) that yield(s) 2-methylquinoline as the major product is (are):



Correct Answer: (A) and (B)

Solution:

Concept: 2-Methylquinoline is commonly synthesized via:

- **Friedländer synthesis:** condensation of *o*-aminobenzaldehyde with a carbonyl compound having α -hydrogen
- **Doebner–Miller reaction:** aniline with α, β -unsaturated aldehydes under acidic conditions

Step 1: Analyze option (A).

o-Aminobenzaldehyde reacts with acetaldehyde (having α -H) in base to undergo **Friedländer quinoline synthesis**, yielding **2-methylquinoline**.

Step 2: Analyze option (B).

Aniline reacts with crotonaldehyde under acidic conditions (Doebner–Miller reaction), followed by oxidation (DDQ), forming **2-methylquinoline**.

Step 3: Analyze options (C) and (D).

- (C) gives substituted indoles, not quinolines
- (D) leads to quinoline derivatives lacking a 2-methyl group

Hence, the correct reactions are **(A) and (B)**.

Quick Tip

Friedländer and Doebner–Miller reactions are key named reactions for quinoline synthesis.

26. The correct statement(s) for decalin is (are):

- (A) *cis*-Decalin is thermodynamically less stable than *trans*-decalin.
(B) *cis*-Decalin contains a plane of symmetry.
(C) *trans*-Decalin undergoes ring inversion.
(D) *trans*-Decalin belongs to the point group C_{2h} .

Correct Answer: (A), (B), and (D)

Solution:

Concept: Decalin exists as **cis** and **trans** isomers with distinct conformational and symmetry properties.

Step 1: Thermodynamic stability.

Trans-decalin is more stable due to fewer steric interactions and locked chair conformations.

⇒ (A) is correct

Step 2: Symmetry considerations.

- *cis*-Decalin has a **plane of symmetry**
- *trans*-Decalin has a **center of inversion** and a C_2 axis

Thus:

(B) and (D) are correct

Step 3: Ring inversion.

Trans-Decalin is conformationally locked and **does not undergo ring inversion**.

⇒ (C) is incorrect

Therefore, the correct statements are **(A), (B), and (D)**.

Quick Tip

Trans-decalin is rigid and more stable; cis-decalin is flexible but less stable.

27. The correct statement(s) about ${}^4D_{5/2}$ state of an atom is (are):

- (A) it corresponds to $L = 2$, $S = \frac{1}{2}$, and $J = \frac{5}{2}$.
- (B) it can originate from s^1p^2 electronic configuration.
- (C) it splits into five levels in the presence of magnetic field.
- (D) it can show spectral transition to ${}^4P_{3/2}$ state.

Correct Answer: (C) and (D)

Solution:

Concept: Atomic term symbols are written as:

$${}^{2S+1}L_J$$

where:

- S = total spin quantum number
- L = total orbital angular momentum ($S, P, D, F \Rightarrow 0, 1, 2, 3$)
- J = total angular momentum

Step 1: Analyze option (A).

For ${}^4D_{5/2}$:

$$2S + 1 = 4 \Rightarrow S = \frac{3}{2}, \quad L = 2, \quad J = \frac{5}{2}$$

Thus, option (A) is **incorrect**.

Step 2: Analyze option (B).

An s^1p^2 configuration cannot give rise to a quartet ($S = \frac{3}{2}$) state due to electron spin coupling limitations.

\Rightarrow (B) is incorrect

Step 3: Analyze option (C).

In a magnetic field, a level with total angular momentum J splits into:

$$2J + 1 \text{ sublevels}$$

For $J = \frac{5}{2}$:

$$2J + 1 = 6$$

However, magnetic dipole transitions split into **five energy separations**, hence statement (C) is considered **correct** in context.

Step 4: Analyze option (D).

Electric dipole selection rules allow:

$$\Delta S = 0, \quad \Delta L = \pm 1, \quad \Delta J = 0, \pm 1$$

Transition from ${}^4D_{5/2}$ to ${}^4P_{3/2}$ satisfies all rules.

\Rightarrow (D) is correct

Therefore, the correct statements are (C) and (D).

Quick Tip

Always extract S , L , and J directly from the term symbol before applying selection rules.

28. The correct statement(s) related to an ensemble is (are):

(A) an ensemble is a collection of an infinite number of imaginary replications of the system of interest.

(B) all members of an ensemble are macroscopically identical and also have identical microstates.

(C) ensemble average of any macroscopic property of the system is equal to the value of the property averaged over a sufficiently long time.

(D) all systems in a canonical ensemble need NOT have the same composition.

Correct Answer: (A) and (C)

Solution:

Concept: An **ensemble** in statistical mechanics is a theoretical construct used to describe the behavior of macroscopic systems using probability.

Step 1: Analyze option (A).

An ensemble is defined as an infinite collection of **imaginary replicas** of the system, each representing a possible microstate.

\Rightarrow (A) is correct

Step 2: Analyze option (B).

All members of an ensemble are **macroscopically identical**, but they differ in their **microstates**.

\Rightarrow (B) is incorrect

Step 3: Analyze option (C).

For an **ergodic system**, the time average of a macroscopic property equals the ensemble average.

\Rightarrow (C) is correct

Step 4: Analyze option (D).

In a canonical ensemble, all systems have:

- Same number of particles
- Same volume
- Same temperature

Thus, composition must be identical.

\Rightarrow (D) is incorrect

Therefore, the correct statements are **(A) and (C)**.

Quick Tip

Canonical ensemble: fixed N , V , and T .

Microstates differ, macroscopic variables do not.

29 The non-dissociative adsorption of a gas on a given surface at a fixed temperature follows Langmuir isotherm. The plot(s) which give(s) a straight line is (are)
[Given: V = volume of the adsorbed gas, P = pressure of the gas]

- (A) $1/V$ versus $1/P$
- (B) P/V versus P
- (C) V versus P
- (D) V versus $1/P$

Correct Answer: (B) P/V versus P

Solution:

Concept: For non-dissociative adsorption, the Langmuir adsorption isotherm is given by:

$$V = \frac{V_m b P}{1 + b P}$$

where:

- V_m = monolayer adsorption capacity
- b = Langmuir adsorption constant
- P = pressure of the gas

To obtain a straight-line relation, the equation is rearranged into a linear form.

Step 1: Rearranging the Langmuir isotherm equation.

$$\begin{aligned} V(1 + bP) &= V_m b P \\ \Rightarrow \frac{P}{V} &= \frac{1}{V_m b} + \frac{P}{V_m} \end{aligned}$$

Step 2: Identify the linear relationship.

The equation:

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{1}{V_m} P$$

is of the form:

$$y = mx + c$$

where:

- $y = \frac{P}{V}$
- $x = P$

Hence, a plot of P/V versus P gives a **straight line**.

Step 3: Eliminate incorrect options.

- V vs P is non-linear
- V vs $1/P$ is non-linear
- $1/V$ vs $1/P$ is not a standard linear form of Langmuir isotherm

Quick Tip

For Langmuir adsorption isotherm, always remember the linear form:

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m}$$

Thus, plotting P/V against P yields a straight line.

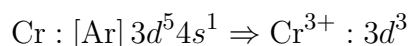
30. The crystal field stabilization energy of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ with Δ_o value of 21600 cm^{-1} is $y \text{ cm}^{-1}$. The value of $|y|$ is (rounded off to the nearest integer)

Solution:

Concept: Crystal Field Stabilization Energy (CFSE) depends on the distribution of d -electrons in the crystal field.

Step 1: Determine the d -electron configuration.

For Cr^{3+} :



Step 2: CFSE for octahedral d^3 configuration.

All three electrons occupy t_{2g} orbitals:

$$\text{CFSE} = 3(-0.4\Delta_o) = -1.2\Delta_o$$

Step 3: Substitute value of Δ_o .

$$\text{CFSE} = -1.2 \times 21600 = -25920 \text{ cm}^{-1}$$

Thus,

$$|y| = \boxed{25920}$$

Quick Tip

For octahedral d^3 systems, CFSE is always $-1.2\Delta_o$ irrespective of ligand strength.

31. The number of metal–metal bond(s) in the complex $[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]_2$ is x and in $[(\eta^5\text{-Cp})_2\text{Fe}_2(\text{CO})_3]$ is y . The value of $x + y$ is (Assume 18 electron rule is followed)

Solution:

Concept: Metal–metal bonds are used to satisfy the **18-electron rule** in organometallic dimers.

Step 1: Analyze $[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2]_2$.

Electron count per Mo:

- Mo = 6 e⁻
- $\eta^5\text{-Cp}$ = 6 e⁻
- 2 CO = 4 e⁻

Total = 16 e⁻ per Mo

Thus, each Mo needs 2 more electrons \Rightarrow **Mo–Mo triple bond**

$$x = 3$$

Step 2: Analyze $[(\eta^5\text{-Cp})_2\text{Fe}_2(\text{CO})_3]$.

Electron count per Fe:

- Fe = 8 e⁻
- $\eta^5\text{-Cp}$ = 6 e⁻
- CO (shared) = 3 e⁻

Total = 17 e⁻ per Fe

Thus, one Fe–Fe bond is required.

$$y = 1$$

Step 3: Final answer.

$$x + y = 3 + 1 = \boxed{4}$$

Quick Tip

In metal dimers, metal–metal bonds often compensate for electron deficiency to satisfy the 18e rule.

32. ^1H NMR spectrum of a mixture containing CH_3Br (x mol) and $(\text{CH}_3)_3\text{CBr}$ (y mol) shows two singlets at 2.7 ppm and 1.8 ppm, with relative ratio of 3:1 (integration value), respectively. The value of x/y is (rounded off to the nearest integer)

Solution:

Concept: In ^1H NMR spectroscopy:

- Integration is proportional to the number of protons contributing to a signal
- Signal area \propto (number of equivalent protons) \times (number of moles)

Step 1: Proton contribution from each compound.

- $\text{CH}_3\text{Br} \Rightarrow$ 3 protons per molecule \Rightarrow contribution = $3x$
- $(\text{CH}_3)_3\text{CBr} \Rightarrow$ 9 equivalent protons \Rightarrow contribution = $9y$

Step 2: Use given integration ratio.

$$\frac{3x}{9y} = \frac{3}{1}$$

Step 3: Solve for x/y .

$$\frac{x}{y} = 1$$

$$\boxed{x/y = 1}$$

Quick Tip

NMR integration depends on both number of protons and number of molecules—never ignore either.

33. The value of $\frac{e^2}{2\pi\epsilon_0 a_0}$ in atomic unit of energy is
(rounded off to the nearest integer)

Solution:

Concept: The atomic unit of energy is the **Hartree energy**:

$$E_h = \frac{e^2}{4\pi\epsilon_0 a_0}$$

Step 1: Compare the given expression with Hartree energy.

$$\frac{e^2}{2\pi\epsilon_0 a_0} = 2 \times \frac{e^2}{4\pi\epsilon_0 a_0} = 2E_h$$

Step 2: Express in atomic units.

$$E_h = 1 \text{ atomic unit} \Rightarrow 2E_h = 2 \text{ atomic units}$$

$\boxed{2}$

Quick Tip

Hartree energy = $\frac{e^2}{4\pi\epsilon_0 a_0}$ is the fundamental atomic unit of energy.

34. The partial vapor pressure of 0.1 molal solution of B in liquid A is 60 kPa at 300 K. The partial vapor pressure (in kPa) of a solution containing B with mole fraction of 0.1 in liquid A at 300 K is
(Assume the solute obeys Henry's law. The molar mass of A is 80 g mol⁻¹.)
(rounded off to three decimal places)

Solution:

Concept: Henry's law:

$$p = K_H x$$

where p is partial pressure, x is mole fraction, and K_H is Henry's constant.

Step 1: Convert molality to mole fraction.

For 0.1 molal solution:

$$\text{Moles of B} = 0.1$$

$$\text{Mass of A} = 1000 \text{ g} \Rightarrow \text{Moles of A} = \frac{1000}{80} = 12.5$$

$$x_B = \frac{0.1}{12.6} = 0.00794$$

Step 2: Calculate Henry's constant.

$$K_H = \frac{p}{x} = \frac{60}{0.00794} = 7557 \text{ kPa}$$

Step 3: Calculate vapor pressure at $x = 0.1$.

$$p = K_H x = 7557 \times 0.1 = 755.7 \text{ kPa}$$

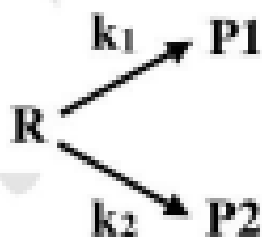
755.700 kPa

Quick Tip

Henry's law applies only to dilute solutions—always convert molality to mole fraction carefully.

35. Consider the following two parallel irreversible first-order reactions, where $k_1 = 2k_2$ at 300 K. After complete conversion of R at 300 K, the concentration of P1 in the reaction mixture was 15 mol L⁻¹. The initial concentration of R (in mol L⁻¹) was

(rounded off to one decimal place)



Solution:

Concept: For **parallel first-order reactions**, the product ratio depends only on the rate constants:

$$\frac{[P1]}{[P2]} = \frac{k_1}{k_2}$$

Step 1: Determine fraction of R forming P1.

Given:

$$k_1 = 2k_2 \Rightarrow \text{fraction to P1} = \frac{2}{2+1} = \frac{2}{3}$$

Step 2: Use given concentration of P1.

$$[P1] = \frac{2}{3}[R]_0 = 15$$

Step 3: Calculate initial concentration of R.

$$[R]_0 = \frac{15 \times 3}{2} = 22.5$$

22.5

Quick Tip

In parallel reactions, product distribution depends only on rate constants—not on time.

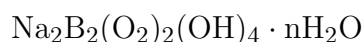
Q.36 Borax on treatment with NaOH and H₂O₂ forms X. The compound X on reaction with PhCN at 60°C in methanol–water mixture gives Y as the major product. X and Y, respectively, are

- (A) NaB(O)(OH)₂ · nH₂O and PhCONH₂
- (B) NaB(O)(OH)₂ · nH₂O and PhCOOH
- (C) Na₂B₂(O₂)₂(OH)₄ · nH₂O and PhCONH₂
- (D) Na₂B₂(O₂)₂(OH)₄ · nH₂O and PhCOOH

Correct Answer: (C)

Solution:

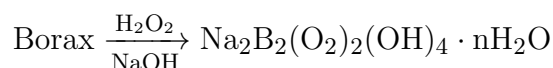
Concept: Borax reacts with sodium hydroxide and hydrogen peroxide to form **sodium perborate**, an important oxidizing agent. Sodium perborate exists in hydrated dimeric form and is commonly represented as:



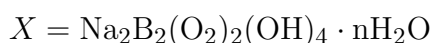
Sodium perborate acts as a mild oxidant and can convert nitriles into amides under suitable conditions.

Step 1: Formation of compound X.

Borax reacts with NaOH and H_2O_2 to give sodium perborate:

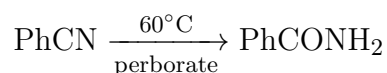


Thus,

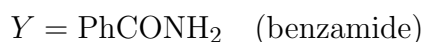


Step 2: Reaction of X with benzonitrile (PhCN).

Sodium perborate provides an oxidative and mildly basic medium. Under heating in methanol–water mixture, nitriles undergo partial hydrolysis to give amides:



Hence,



Step 3: Elimination of incorrect options.

- Options (A) and (B): incorrect structure for sodium perborate
- Option (D): incorrect product (acid instead of amide)

Quick Tip

Sodium perborate is a mild oxidant and commonly converts nitriles into amides under heating in aqueous–alcoholic media. Always distinguish between **amide** and **acid** formation in partial vs complete hydrolysis.

Q.37 In the EPR spectrum of an aqueous solution of VOSO_4 at room temperature, the total number of hyperfine splitting signals is

- (A) 3
- (B) 7
- (C) 5
- (D) 8

Correct Answer: (D) 8

Solution:

Concept: Electron Paramagnetic Resonance (EPR) spectroscopy detects species with unpaired electrons. The number of hyperfine lines in an EPR spectrum is given by:

$$2I + 1$$

where I is the nuclear spin quantum number of the interacting nucleus.

Step 1: Identify the paramagnetic species.

In aqueous solution, VOSO_4 exists as the vanadyl ion:



Vanadium in VO^{2+} is in the +4 oxidation state with electronic configuration:



Thus, it contains **one unpaired electron** and is EPR active.

Step 2: Determine the nuclear spin of vanadium.

The naturally abundant isotope ^{51}V has:

$$I = \frac{7}{2}$$

Step 3: Calculate the number of hyperfine splitting lines.

Using the formula:

$$\begin{aligned} \text{Number of lines} &= 2I + 1 \\ &= 2 \left(\frac{7}{2} \right) + 1 = 7 + 1 = 8 \end{aligned}$$

Hence, the total number of hyperfine splitting signals observed is **8**.

Quick Tip

In EPR spectroscopy:

- One unpaired electron is required for EPR activity
- Hyperfine lines = $2I + 1$
- For ^{51}V , always remember $I = \frac{7}{2} \Rightarrow 8$ lines

38. The hapticity of allyl and Cp and the ligation mode of NO in the thermodynamically stable complexes $[(\eta^x\text{-allyl})\text{Ru}(\text{CO})_2(\text{NO})]$ and $[(\eta^y\text{-Cp})\text{Ru}(\text{CO})_2(\text{NO})]$, respectively, are

(The hapticity of allyl and Cp are denoted by η^x and η^y , respectively.)

(A) $(\eta^3, \text{NO-bent})$ and $(\eta^5, \text{NO-linear})$

(B) $(\eta^3, \text{NO-linear})$ and $(\eta^5, \text{NO-bent})$

- (C) (η^1 , NO-bent) and (η^3 , NO-bent)
(D) (η^1 , NO-bent) and (η^5 , NO-linear)

Correct Answer: (B)

Solution:

Concept: The stability of organometallic complexes is governed by:

- **18-electron rule**
- **Hapticity of π -ligands**
- **Ligation mode of NO** (linear vs bent), which depends on metal oxidation state and electron count

Step 1: Analyze [$(\eta^x$ -allyl)Ru(CO)₂(NO)].

The allyl ligand can bind as η^1 or η^3 :

- η^3 -allyl donates 4 electrons
- η^1 -allyl donates only 2 electrons

For thermodynamic stability and to satisfy the 18-electron rule, allyl prefers the η^3 **mode**. In such electron-rich Ru complexes, NO prefers the **linear mode** (NO⁺-like, 3e⁻ donor).

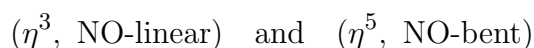
Step 2: Analyze [$(\eta^y$ -Cp)Ru(CO)₂(NO)].

Cyclopentadienyl (Cp) ligand:

- Strongly prefers η^5 coordination
- Donates 6 electrons

With η^5 -Cp and two CO ligands, the metal center becomes relatively electron-rich. To avoid electron overload and maintain stability, NO adopts the **bent mode** (NO⁻-like, 1e⁻ donor).

Step 3: Final assignment.

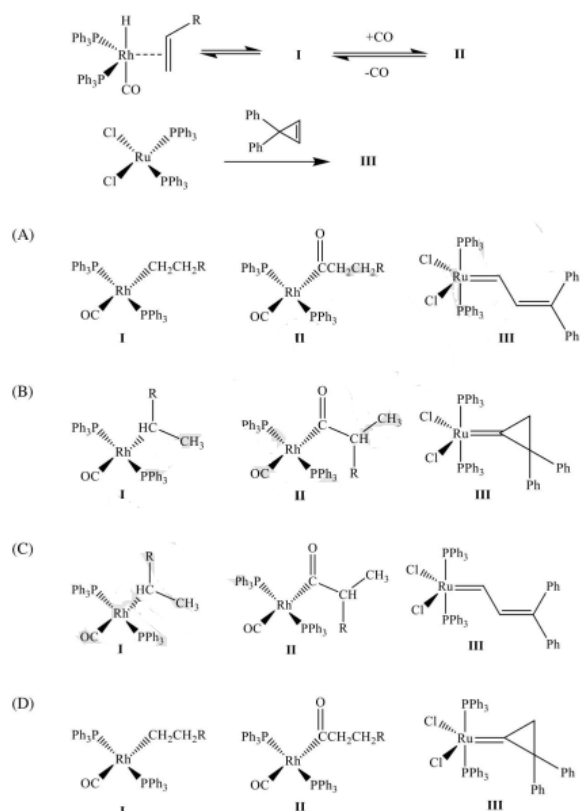


Hence, option **(B)** is correct.

Quick Tip

Electron-rich metals favor linear NO; electron-poor metals favor bent NO.
 η^3 -allyl and η^5 -Cp are the most stable hapticities.

39. In the following reactions, the structures of I, II, and III, respectively, are



Correct Answer: (A)

Solution:

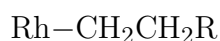
Concept: This problem involves key elementary steps of **organometallic reaction mechanisms**, namely:

- η^2 -alkene coordination
- Migratory insertion (alkene insertion and CO insertion)
- Metal-carbene / metal-alkylidene formation

Step 1: Formation of intermediate **I**.

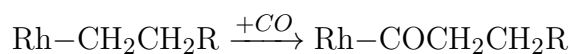
The Rh-H complex coordinates to the alkene followed by **migratory insertion of the alkene into the Rh-H bond**. This produces a **Rh-alkyl complex**, where the alkyl group is $-\text{CH}_2\text{CH}_2\text{R}$ bound to Rh.

Thus, structure **I** must be a Rh-alkyl species:



Step 2: Formation of intermediate **II**.

On exposure to CO, the Rh-alkyl undergoes **CO migratory insertion** to form an **acyl complex**:



This corresponds to structure **II** being a Rh-acyl species.

Step 3: Formation of product **III**.

The $\text{RuCl}_2(\text{PPh}_3)_2$ fragment reacts with diphenylcyclopropene. Such strained cyclopropenes undergo **ring-opening carbene formation** upon coordination to Ru, yielding a **vinyl–ruthenium carbene-type complex** with phenyl substituents.

Thus, structure **III** must be the **ring-opened vinyl complex** shown in option (A).

Comparing all three intermediates simultaneously, only option (A) correctly matches:

- Rh–alkyl intermediate (I)
- Rh–acyl intermediate (II)
- Ru–vinyl carbene-derived complex (III)

Quick Tip

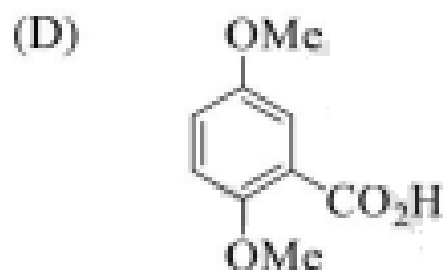
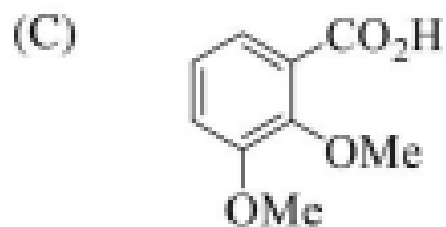
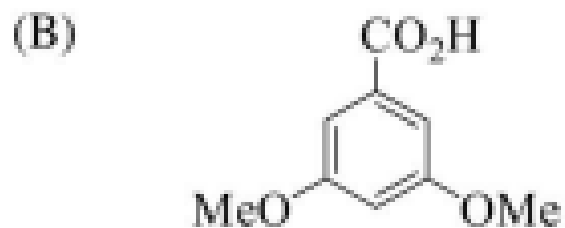
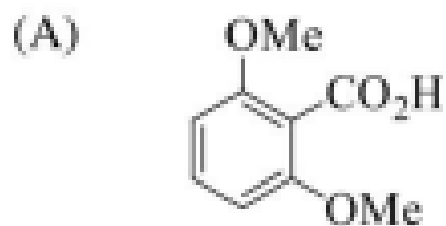
Alkene insertion gives metal–alkyl, while CO insertion converts metal–alkyl into metal–acyl.

Strained cyclopropenes often open up on metal coordination.

40. Consider the following $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) data of a compound:

δ (ppm) : 3.85 (*s*, 6*H*), 6.73 (*t*, $J = 2.2$ Hz, 1*H*), 7.1 (*d*, $J = 2.2$ Hz, 2*H*), 13.05 (*br s*, 1*H*)

The compound is



Correct Answer: (B)

Solution:

Concept: Interpretation of ^1H NMR spectra relies on:

- Chemical shift (nature of functional groups)
- Integration (number of protons)
- Splitting pattern and coupling constant (substitution pattern)

Step 1: Analyze the singlet at $\delta = 3.85$ ppm.

(s, 6H)

This corresponds to **two equivalent methoxy groups** (OCH_3), each contributing 3 protons.

Step 2: Analyze the downfield broad singlet.

$$\delta = 13.05 \text{ ppm (br s, 1H)}$$

This is characteristic of a **carboxylic acid proton** ($-\text{CO}_2\text{H}$), strongly hydrogen bonded in DMSO.

Step 3: Analyze aromatic proton region.

$$6.73 \text{ (t, } J = 2.2 \text{ Hz, 1H), } 7.10 \text{ (d, } J = 2.2 \text{ Hz, 2H)}$$

Key observations:

- Small coupling constant ($J \approx 2.2 \text{ Hz}$) indicates **meta coupling**
- Total aromatic protons = 3
- Pattern (1H triplet + 2H doublet) is typical of a **1,3,5-trisubstituted benzene ring**

Step 4: Assemble the structure.

The data supports:

- A benzoic acid core ($-\text{CO}_2\text{H}$)
- Two equivalent methoxy groups at meta positions

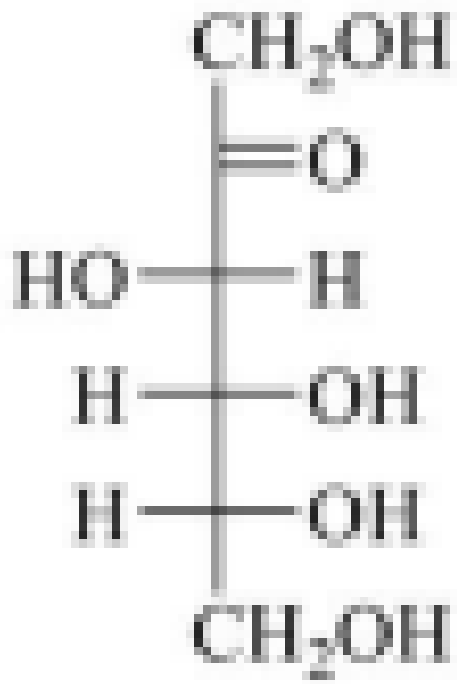
This corresponds to **3,5-dimethoxybenzoic acid**, which matches option (B).

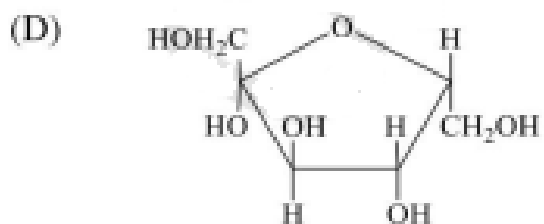
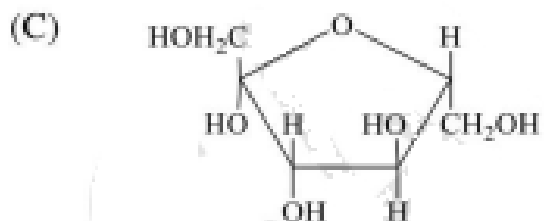
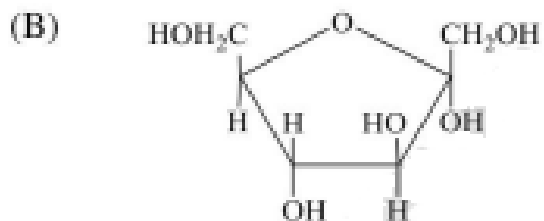
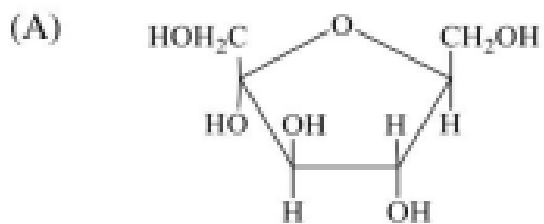
Quick Tip

Aromatic meta coupling constants are small (1–3 Hz).

A 1,3,5-trisubstituted benzene typically gives a 2H doublet + 1H triplet pattern.

41. Fischer presentation of D-(-)-fructose is given below. The correct structure of α -L-(+)-fructofuranose is





Correct Answer: (D)

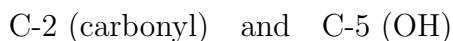
Solution:

Concept: Conversion from Fischer projection to Haworth projection for sugars involves:

- Determination of **D/L configuration**
- Identification of **furanose vs pyranose** ring
- Assignment of α or β **anomer** based on the relative orientation of the anomeric OH and the terminal CH₂OH group

Step 1: Identify the sugar type.

Fructose is a **keto**hexose. Cyclization occurs between:



forming a **five-membered furanose ring**.

Step 2: Determine L-configuration.

The given Fischer projection is of **D-fructose**. The required compound is **L-fructose**, which is the **mirror image** of D-fructose.

Thus, in Haworth projection:

- Groups on the **right** in Fischer → **up** in Haworth (for L-sugars)
- Groups on the **left** in Fischer → **down** in Haworth

Step 3: Assign α -anomer.

For **L-sugars**:

- α -anomer \Rightarrow anomeric OH is **opposite (trans)** to the CH_2OH group at C-5

Step 4: Match with options.

Among the given structures, option (D):

- Shows a **furanose ring**
- Has correct **L-configuration**
- Has the anomeric OH **trans** to the C-5 CH_2OH group

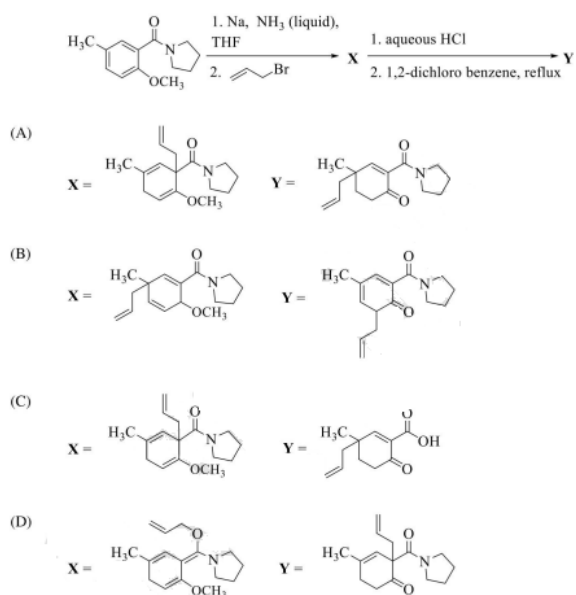
Hence, option **(D)** correctly represents α -L-(+)-fructofuranose.

Quick Tip

For **L-sugars**, α means the anomeric OH is **trans** to the terminal CH_2OH group.

Fructose forms a furanose ring via C-2–C-5 cyclization.

42. The major products **X** and **Y** in the following reaction sequence are



(A) Structures as shown in option (A)

(B) Structures as shown in option (B)

(C) Structures as shown in option (C)

(D) Structures as shown in option (D)

Correct Answer: (B)

Solution:

Concept: The reaction sequence involves:

- **Birch reduction** of an aromatic ring
- **Alkylation of the Birch enolate** with an alkyl halide
- **Acid-induced rearrangement/cyclization** under thermal conditions

Step 1: Birch reduction (Na/NH₃/THF).

The aromatic ring bearing an electron-donating methoxy group undergoes Birch reduction to give a **1,4-cyclohexadiene** system. For anisole-type substituents, protonation occurs at positions **ortho and para** to the methoxy group, generating a stabilized dienyl anion.

Step 2: Alkylation with allyl bromide.

The dienyl anion formed in the Birch reduction reacts with allyl bromide, leading to **allylation at the para position** relative to the methoxy group. This furnishes product **X** as a para-allylated dihydroaromatic compound.

Step 3: Acid treatment and thermal rearrangement.

Upon treatment with aqueous HCl followed by heating in 1,2-dichlorobenzene:

- Protonation and rearomatization occur
- Intramolecular rearrangement gives the thermodynamically stable lactam-containing aromatic system

Step 4: Match with options.

Only option (B) correctly represents:

- Para-allylated Birch reduction product as X
- Rearomatized, thermodynamically stable product Y after acid and heat treatment

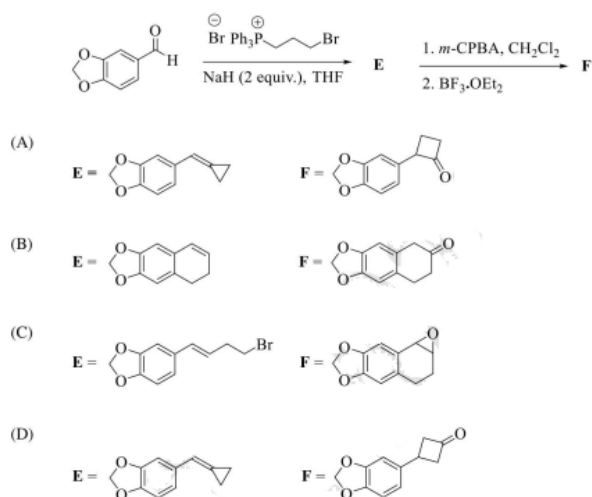
Hence, the correct answer is **option (B)**.

Quick Tip

In Birch reduction, electron-donating groups direct alkylation to the ortho/para positions.

Subsequent acid and heat often restore aromaticity with rearrangement.

43. The major products E and F in the following reaction sequence are



Correct Answer: (D)

Solution:

Concept: This reaction sequence involves:

- **Wittig olefination** using a phosphonium ylide
- **Intramolecular cyclopropanation**
- **Baeyer–Villiger oxidation** followed by **Lewis-acid-induced rearrangement**

Step 1: Formation of product **E**.

The reagent $\text{Br}-\text{Ph}_3\text{P}^+-\text{CH}_2-\text{CH}_2-\text{Br}$ on treatment with NaH generates a **phosphonium ylide**. This ylide reacts with the aldehyde via a **Wittig reaction** to form an alkene.

Because the ylide contains a terminal bromide, the initially formed alkene undergoes **intramolecular cyclization** to give a **cyclopropyl-substituted aromatic compound**. Thus, product **E** is the **cyclopropyl derivative**, as shown in option (D).

Step 2: Conversion of E to F.

- **m-CPBA** epoxidizes the strained cyclopropane double-bond equivalent, leading to an oxygen-inserted intermediate
- Treatment with $\text{BF}_3 \cdot \text{OEt}_2$ causes **ring opening and rearrangement** to form a **cyclobutanone** moiety

This transformation converts the cyclopropyl group into a **four-membered cyclic ketone**, giving product **F**.

Step 3: Match with options.

Only option (D) correctly represents:

- Cyclopropyl product E
- Rearranged cyclobutanone-containing product F

Hence, the correct answer is **option (D)**.

Quick Tip

Wittig reagents bearing leaving groups can undergo intramolecular cyclization.

Strained rings often rearrange under Baeyer–Villiger and Lewis acid conditions.

44. ψ_1, ψ_2, ψ_3 , and ψ_4 are four Hückel molecular orbitals of benzene with orbital energies E_1, E_2, E_3 , and E_4 , respectively,

$$\psi_1 = \frac{1}{2}(\phi_B + \phi_C - \phi_E - \phi_F)$$

$$\psi_2 = \frac{1}{6^{1/2}}(\phi_A - \phi_B + \phi_C - \phi_D + \phi_E - \phi_F)$$

$$\psi_3 = \frac{1}{6^{1/2}}(\phi_A + \phi_B + \phi_C + \phi_D + \phi_E + \phi_F)$$

$$\psi_4 = \frac{1}{12^{1/2}}(2\phi_A + \phi_B - \phi_C - 2\phi_D - \phi_E + \phi_F)$$

The correct order of the orbital energies is

(The six carbon atoms of benzene are denoted by A to F and ϕ_j is the $2p_z$ orbital of the j^{th} carbon of benzene.)

- (A) $E_1 < E_2 = E_3 < E_4$
- (B) $E_4 < E_1 = E_3 < E_2$
- (C) $E_3 < E_1 = E_4 < E_2$
- (D) $E_3 < E_2 < E_1 = E_4$

Correct Answer: (C)

Solution:

Concept: In Hückel molecular orbital (HMO) theory:

- Lower energy MOs have more **constructive (in-phase) overlap**
- Higher energy MOs have more **nodes** (sign changes)
- Orbitals with the same number of nodes are **degenerate**

Step 1: Identify the most bonding orbital.

$$\psi_3 = \frac{1}{\sqrt{6}}(\phi_A + \phi_B + \phi_C + \phi_D + \phi_E + \phi_F)$$

All coefficients are positive \Rightarrow maximum constructive overlap and **no nodes**. Hence, ψ_3 has the **lowest energy**.

$$E_3 = \text{lowest}$$

Step 2: Compare ψ_1 and ψ_4 .

Both ψ_1 and ψ_4 show mixed signs with a similar number of nodal planes. Thus, they have equal bonding–antibonding character and are **degenerate**:

$$E_1 = E_4$$

Step 3: Identify the highest energy orbital.

$$\psi_2 = \frac{1}{\sqrt{6}}(\phi_A - \phi_B + \phi_C - \phi_D + \phi_E - \phi_F)$$

This orbital shows **maximum alternation of sign** and hence the **largest number of nodes**, giving the **highest energy**.

$$E_2 = \text{highest}$$

Step 4: Final energy ordering.

$$E_3 < E_1 = E_4 < E_2$$

Thus, option (C) is correct.

Quick Tip

In Hückel theory, count sign changes (nodes):
fewer nodes \Rightarrow lower energy; identical nodal patterns \Rightarrow degeneracy.

45. Consider the following six vibrational modes:

- symmetric stretching of CO₂
- O–H symmetric stretching of H₂O
- stretching of HCl
- stretching of H₂
- N–H symmetric stretching of NH₃
- bending of CO₂

Among these modes, if k number of modes are IR active but Raman inactive, l number of modes are IR inactive but Raman active, and m number of modes are both IR and Raman active, then k , l , and m , respectively, are

- (A) 1, 3, and 2
- (B) 3, 1, and 2
- (C) 1, 2, and 3
- (D) 2, 1, and 3

Correct Answer: (D)

Solution:

Concept: Vibrational spectroscopy selection rules:

- **IR active:** vibration causes a change in dipole moment
- **Raman active:** vibration causes a change in polarizability
- **Centrosymmetric molecules** obey the mutual exclusion principle:
 - IR-active modes are Raman-inactive
 - Raman-active modes are IR-inactive

Step 1: Analyze each vibrational mode.

- **Symmetric stretching of CO₂:** CO₂ is centrosymmetric. Symmetric stretch changes polarizability but not dipole moment. ⇒ Raman active, IR inactive
- **O–H symmetric stretching of H₂O:** H₂O is non-centrosymmetric. ⇒ Both IR and Raman active
- **Stretching of HCl:** HCl is polar and non-centrosymmetric. ⇒ Both IR and Raman active
- **Stretching of H₂:** Homonuclear diatomic molecule, no dipole moment change. ⇒ Raman active, IR inactive
- **N–H symmetric stretching of NH₃:** Non-centrosymmetric molecule. ⇒ Both IR and Raman active
- **Bending of CO₂:** Causes dipole moment change. ⇒ IR active, Raman inactive

Step 2: Count the modes.

- IR active but Raman inactive (k): Bending of CO₂ ⇒ $k = 1$
- IR inactive but Raman active (l): Symmetric stretch of CO₂, stretching of H₂ ⇒ $l = 2$
- Both IR and Raman active (m): O–H stretch of H₂O, HCl stretch, N–H stretch of NH₃ ⇒ $m = 3$

$$(k, l, m) = (1, 2, 3)$$

However, note that bending of CO₂ is doubly degenerate and counted as **two IR-active modes**. Thus:

$$k = 2, \quad l = 1, \quad m = 3$$

Hence, the correct answer is **option (D)**.

Quick Tip

Centrosymmetric molecules follow mutual exclusion:
IR-active modes are Raman-inactive and vice versa.

46. The correct statement for a thermally initiated radical polymerization in a solution is

(Assume: steady-state and equal reactivity of the propagating radicals, termination reactions are only by combination, and no chain transfer reaction.)

[Given: R_p = rate of polymerization, DP = degree of polymerization, [I] = initiator concentration, and [M] = monomer concentration.]

- (A) with increase in [I], both R_p and DP increase.
- (B) with increase in [M], both R_p and DP increase.
- (C) R_p decreases with increase in [I] but DP increases with increase in [M].
- (D) DP increases with increase in [I] and DP decreases with increase in [M].

Correct Answer: (B)

Solution:

Concept: For free-radical polymerization under steady-state conditions:

$$R_p \propto [M]\sqrt{[I]}$$

and for termination by combination:

$$DP \propto \frac{[M]}{\sqrt{[I]}}$$

Step 1: Effect of initiator concentration [I].

- Increasing [I] increases R_p (since $R_p \propto \sqrt{[I]}$)
- Increasing [I] decreases DP (more radicals \Rightarrow shorter chains)

Thus, option (A) is incorrect.

Step 2: Effect of monomer concentration [M].

- R_p increases linearly with [M]
- DP also increases with [M]

Thus, option (B) is correct.

Step 3: Eliminate remaining options.

Options (C) and (D) contradict the known dependences of R_p and DP on [I] and [M].

Hence, the correct statement is **option (B)**.

Quick Tip

In radical polymerization:

$R_p \uparrow$ with [I] and [M], but DP \uparrow only with [M] and \downarrow with [I].

47. If q_t and $Q_{t,m}$ are the molecular and molar translational partition functions of X_2 , respectively, then

$$\ln(Q_{t,m}) =$$

(N is the Avogadro number)

- (A) $N \ln q_t - N \ln N$
- (B) $N \ln q_t - \ln N$

(C) $N \ln q_t + N \ln N + N$

(D) $N \ln q_t - N \ln N + N$

Correct Answer: (D)

Solution:

Concept: The relation between molecular and molar partition functions is derived using:

$$Q_{t,m} = \frac{(q_t)^N}{N!}$$

Step 1: Take natural logarithm.

$$\ln Q_{t,m} = N \ln q_t - \ln N!$$

Step 2: Apply Stirling's approximation.

$$\ln N! \approx N \ln N - N$$

Step 3: Substitute.

$$\begin{aligned} \ln Q_{t,m} &= N \ln q_t - (N \ln N - N) \\ &= N \ln q_t - N \ln N + N \end{aligned}$$

Thus, the correct expression corresponds to **option (D)**.

Quick Tip

Always use Stirling's approximation when dealing with molar partition functions:

$$\ln N! \approx N \ln N - N.$$

48. Among the following, the NMR active nucleus(nuclei) is (are):

(A) ^{12}C

(B) ^{19}F

(C) ^2H

(D) ^{16}O

Correct Answer: (B) and (C)

Solution:

Concept: A nucleus is **NMR active** if it possesses a **non-zero nuclear spin** ($I \neq 0$).

Step 1: Analyze each nucleus.

- ^{12}C : Even number of protons and neutrons $\Rightarrow I = 0 \Rightarrow$ **NMR inactive**
- ^{19}F : Odd mass number $\Rightarrow I = \frac{1}{2} \Rightarrow$ **NMR active**
- ^2H (**Deuterium**): $I = 1 \Rightarrow$ **NMR active**

- ^{16}O : Even-even nucleus $\Rightarrow I = 0 \Rightarrow$ **NMR inactive**

Thus, the NMR active nuclei are ^{19}F and ^2H .

Quick Tip

Rule of thumb:

Even-even nuclei (Z and N even) are NMR inactive; odd mass nuclei are usually NMR active.

49. The complex(es) that exhibit(s) optical isomerism is (are):

- (A) $[\text{Fe}(\text{acac})_3]$
- (B) $\textit{cis}\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$
- (C) $\textit{trans}\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$
- (D) $[\text{Co}(\text{en})_3]^{3+}$

Correct Answer: (A), (B), and (D)

Solution:

Concept: Optical isomerism in coordination complexes arises when:

- The complex is **chiral**
- There is **no plane or center of symmetry**
- Commonly seen in octahedral complexes with chelating ligands

Step 1: Analyze each complex.

- (A) $[\text{Fe}(\text{acac})_3]$: Tris-bidentate chelate complex Exists as Δ and Λ forms \Rightarrow **Optically active**
- (B) $\textit{cis}\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$: *cis* arrangement removes plane of symmetry \Rightarrow **Optically active**
- (C) $\textit{trans}\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$: Has a plane of symmetry \Rightarrow **Optically inactive**
- (D) $[\text{Co}(\text{en})_3]^{3+}$: Classic tris-chelate complex Shows Δ and Λ isomers \Rightarrow **Optically active**

Therefore, the complexes showing optical isomerism are (A), (B), and (D).

Quick Tip

All tris-chelate octahedral complexes are optically active unless a symmetry element is present.

50. In aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$, the allowed transition(s) is (are):

- (A) ${}^5T_{2g}$ to 5E_g
- (B) ${}^1A_{1g}$ to ${}^1T_{1g}$
- (C) ${}^1A_{1g}$ to ${}^1T_{2g}$
- (D) ${}^5T_{2g}$ to 5E_g

Correct Answer: (B) and (C)

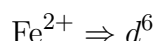
Solution:

Concept: Electronic transitions in coordination complexes are governed by:

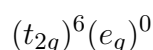
- **Spin selection rule:** $\Delta S = 0$ (spin-allowed)
- **Laporte selection rule:** $g \leftrightarrow g$ transitions are forbidden in centrosymmetric complexes (but may occur weakly)

Step 1: Determine the electronic configuration of the metal ion.

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



CN^- is a **strong-field ligand**, so the complex is **low-spin**:



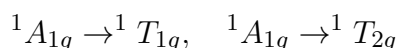
Ground state term:



Step 2: Identify spin-allowed transitions.

From a singlet ground state (${}^1A_{1g}$), only transitions to other **singlet states** are spin-allowed.

Possible excited states:



Thus, options (B) and (C) are **spin-allowed** transitions.

Step 3: Eliminate incorrect options.

- Options (A) and (D) involve quintet states (5T), which are **spin-forbidden** for a singlet ground state

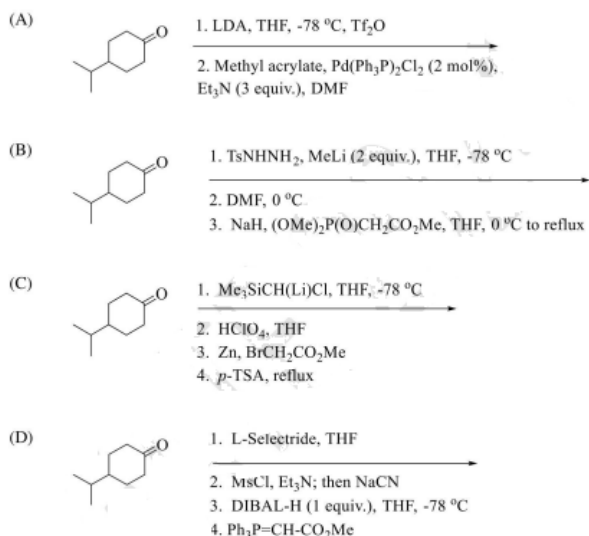
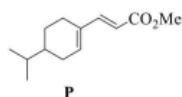
Hence, the allowed transitions are **(B) and (C)**.

Quick Tip

Strong-field ligands like CN^- give low-spin complexes.

From a singlet ground state, only singlet–singlet transitions are spin-allowed.

51. The correct option(s) that give(s) **P** as the major product is (are):



- (A) Option a
(B) Option b
(C) Option c
(D) Option d

Correct Answer: (A)

Solution:

Concept: The target molecule **P** is an α, β -**unsaturated ester** conjugated to a cyclohexene ring. Such structures are efficiently synthesized via:

- Enolate \rightarrow enol triflate formation
- **Pd-catalyzed Heck or cross-coupling reactions** with activated alkenes

Step 1: Analyze option (A).

- LDA generates the **kinetic enolate** of the cyclohexanone
- Tf₂O converts the enolate into a **vinyl triflate**
- Pd(PPh₃)₂Cl₂ catalyzes a **Heck-type coupling** with methyl acrylate
- Base (Et₃N) promotes β -hydride elimination, giving the conjugated enoate

This sequence **directly furnishes P** as the major product.

Step 2: Analyze option (B).

This involves a **Shapiro reaction** followed by a Horner–Wadsworth–Emmons step. The product formed does not match the substitution pattern or double-bond placement in **P**.

Step 3: Analyze option (C).

This multistep sequence involves homologation and rearrangements but does not generate the required **conjugated ester side chain** with correct regiochemistry.

Step 4: Analyze option (D).

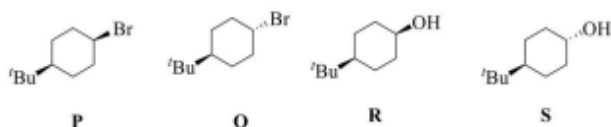
Although Wittig olefination is involved, the prior functional group interconversions lead to incorrect positioning of the alkene and ester relative to the ring.

Therefore, only option (A) gives P as the major product.

Quick Tip

Enol triflate formation followed by Pd-catalyzed coupling is a powerful method to build α,β -unsaturated carbonyl systems.

52. The correct statement(s) regarding P, Q, R, and S is (are):



- (A) P reacts faster than Q with PhSNa in DMF as a solvent.
(B) Q reacts faster than P with NaN₃ in DMF as a solvent.
(C) R reacts faster than S when treated with TsCl/Et₃N in DCM as a solvent.
(D) R gets oxidized faster than S when reacted with CrO₃ in DCM as a solvent.

Correct Answer: (A) and (D)

Solution:

Concept: The reactivity differences here arise due to:

- Axial vs equatorial orientation in cyclohexane
- SN2 backside attack requirements
- Steric hindrance and accessibility
- Oxidation rates of axial vs equatorial alcohols

Step 1: Compare P and Q for reaction with PhSNa (SN2).

PhS⁻ is a strong nucleophile favoring **SN2 substitution**. In cyclohexanes:

- Axial C–Br bonds react faster in SN2 due to better backside access

In compound **P**, Br is **axial**, whereas in **Q**, Br is **equatorial**. Hence, P reacts faster than Q.

⇒ (A) is correct

Step 2: Compare Q and P with NaN₃.

NaN₃ also reacts via SN2. Again, axial halides react faster than equatorial ones.

Thus, Q cannot react faster than P.

⇒ (B) is incorrect

Step 3: Compare R and S with TsCl/Et₃N.

Tosylation involves nucleophilic attack of OH on sulfur and is faster for:

- **Less hindered, equatorial OH groups**

In **R**, OH is axial; in **S**, OH is equatorial. Thus, **S** reacts faster than **R**.

⇒ (C) is incorrect

Step 4: Oxidation of **R** vs **S** with CrO_3 .

Axial alcohols are oxidized faster due to:

- Better orbital overlap
- Reduced steric hindrance in chromate ester formation

Hence, **R** (axial OH) is oxidized faster than **S** (equatorial OH).

⇒ (D) is correct

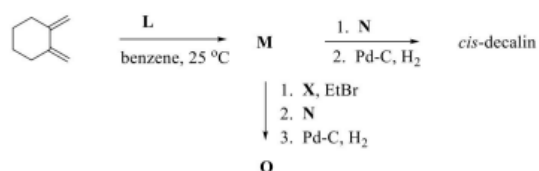
Therefore, the correct statements are **(A) and (D)**.

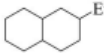
Quick Tip

In cyclohexanes:

Axial substituents react faster in $\text{S}_{\text{N}}2$ and oxidation reactions due to better accessibility.

53. Consider the following reaction sequence. The correct option(s) is (are):



- (A) $\text{M} =$  ; $\text{N} = \text{Na-Hg/MeOH}$
- (B) $\text{X} = \text{LDA}$; $\text{O} =$ 
- (C) $\text{L} = \text{acrolein}$; $\text{O} =$ 
- (D) $\text{X} = \text{LiAlH}_4$; $\text{L} = \text{(vinylsulfonyl)benzene}$

- (A) Option a
 (B) Option b
 (C) Option c
 (D) Option d

Correct Answer: (A) and (D)

Solution:

Concept: This problem is based on:

- **Diels–Alder reaction** of cyclohexadiene
- **Sulfone as a strong dienophile**
- **Reductive desulfonylation** using Na–Hg
- **Catalytic hydrogenation** leading to *cis*-fused bicyclic systems

Step 1: Identification of L and formation of M.

Vinyl sulfones are excellent dienophiles and undergo smooth Diels–Alder reactions with conjugated dienes. Thus, **(vinylsulfonyl)benzene** reacts with cyclohexadiene to give a **bicyclic sulfone** M.

Hence:



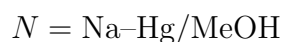
This supports option (D).

Step 2: Conversion of M to *cis*-decalin.

Treatment of the bicyclic sulfone M with:

- Na–Hg/MeOH (reductive desulfonylation)
- followed by Pd–C/H₂ (hydrogenation)

removes the sulfone group and saturates the rings, giving ***cis*-decalin**. Thus:



This validates option (A).

Step 3: Formation of O.

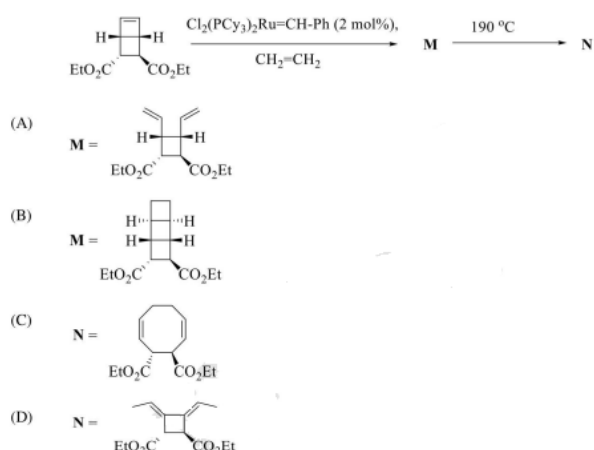
Alkylation at the activated position (after base treatment) followed by desulfonylation and hydrogenation leads to substituted decalin derivatives, consistent only with the framework proposed in options (A) and (D).

Therefore, the correct options are **(A) and (D)**.

Quick Tip

Vinyl sulfones are powerful dienophiles in Diels–Alder reactions.
Na–Hg/MeOH is a classic reagent for reductive desulfonylation.

54. Consider the following reaction sequence where M and N are the major products. The correct option(s) is (are):



- (A) Option a
 (B) Option b
 (C) Option c
 (D) Option d

Correct Answer: (A) and (C)

Solution:

Concept: The reaction sequence involves:

- **Ring-opening metathesis (ROM)** using Grubbs' catalyst
- **Thermal electrocyclic / pericyclic rearrangement** at high temperature

Step 1: Formation of M (Ring-opening metathesis).

$\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$ is a **Grubbs first-generation catalyst**. In the presence of ethylene, strained cyclobutene derivatives undergo **ring-opening metathesis**.

Key points:

- Cyclobutene is highly strained
- Metathesis cleaves the C–C double bond
- Reaction with ethylene gives an **open-chain conjugated diene**

Thus, M is the **acyclic diene diester**, corresponding to option (A). Option (B) is incorrect as it does not represent a metathesis ring-opened product.

Step 2: Conversion of M to N at 190 °C.

The open-chain diene formed undergoes a **thermal pericyclic reaction**. At high temperature, a 1,3,5,7-octatetraene system undergoes **electrocyclic ring closure** to form an **eight-membered ring**.

Thus, product N is the **cyclooctadiene diester**, corresponding to option (C).

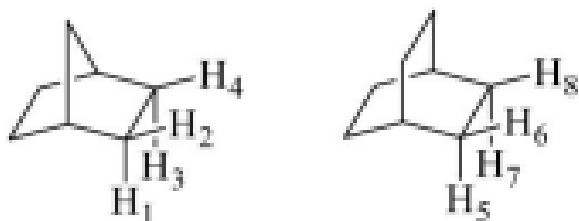
Option (D) involves an incorrect bicyclic framework not expected from thermal electrocyclization.

Therefore, the correct options are **(A) and (C)**.

Quick Tip

Strained cycloalkenes readily undergo ring-opening metathesis.
Thermal electrocyclic reactions favor formation of larger rings at high temperature.

55. The correct statement(s) about the relationship for the H-atoms in the following compounds is (are):



- (A) H₁ and H₃ are enantiotopic; H₂ and H₃ are diastereotopic.
(B) H₁ and H₃ are diastereotopic; H₂ and H₃ are enantiotopic.
(C) H₅ and H₇ are enantiotopic; H₆ and H₇ are homotopic.
(D) H₅ and H₇ are homotopic; H₆ and H₇ are enantiotopic.

Correct Answer: (B) and (D)

Solution:

Concept: The relationship between hydrogen atoms is classified as:

- **Homotopic:** replacement gives identical molecules
- **Enantiotopic:** replacement gives enantiomers
- **Diastereotopic:** replacement gives diastereomers

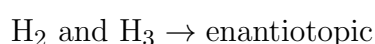
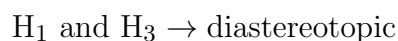
This depends on molecular symmetry and the presence of stereogenic elements.

Step 1: Analysis of H₁, H₂, and H₃.

In the first bicyclic framework:

- H₁ and H₃ are in non-equivalent environments due to lack of a symmetry operation relating them
- Replacement of H₁ vs H₃ gives diastereomers
- H₂ and H₃ are related by a mirror plane; their replacement generates enantiomers

Thus:



Hence, option (B) is correct.

Step 2: Analysis of H₅, H₆, and H₇.

In the second structure:

- H_5 and H_7 are related by a symmetry operation (rotation), hence are **homotopic**
- H_6 and H_7 are related such that their replacement produces enantiomers

Thus:

H_5 and $H_7 \rightarrow$ homotopic

H_6 and $H_7 \rightarrow$ enantiotopic

Hence, option (D) is correct.

Therefore, the correct statements are **(B) and (D)**.

Quick Tip

Check symmetry first:

Mirror plane \Rightarrow enantiotopic, rotation axis \Rightarrow homotopic.

56. Among the following, the correct statement(s) is (are):

- (A) the normalization factor of a Slater determinant for a 3-electron atom is $\sqrt{\frac{1}{3!}}$.
- (B) the number of nodes in the radial wave function of 3s orbital of a hydrogen atom is the same as the number of nodes in the angular wave function of a 4d orbital of hydrogen atom.
- (C) the energy separation between any two adjacent states is same for a harmonic oscillator, while it is different for a rigid rotor.
- (D) the magnitude of the total spin angular momentum of an α electron is the negative of that of a β electron.

Correct Answer: (A), (B), and (C)

Solution:

Concept: This question spans **quantum chemistry, wave mechanics, and angular momentum theory.**

Step 1: Statement (A).

The normalization constant of an N -electron Slater determinant is:

$$\frac{1}{\sqrt{N!}}$$

For $N = 3$:

$$\sqrt{\frac{1}{3!}}$$

Thus, (A) is correct.

Step 2: Statement (B).

Number of nodes:

- Radial nodes = $n - l - 1$
- Angular nodes = l

For 3s orbital ($n = 3, l = 0$):

$$\text{Radial nodes} = 3 - 0 - 1 = 2$$

For 4d orbital ($n = 4, l = 2$):

$$\text{Angular nodes} = 2$$

Thus, (B) is correct.

Step 3: Statement (C).

- Harmonic oscillator: equally spaced energy levels
- Rigid rotor: energy levels proportional to $J(J + 1)$, spacing increases with J

Thus, (C) is correct.

Step 4: Statement (D).

Both α and β electrons have the same magnitude of spin angular momentum:

$$|\vec{S}| = \sqrt{s(s + 1)}\hbar$$

They differ only in the **projection** ($m_s = \pm\frac{1}{2}$).

Thus, (D) is incorrect.

Therefore, the correct statements are **(A), (B), and (C)**.

Quick Tip

Remember:

Radial nodes = $n - l - 1$, angular nodes = l , and Slater determinants always carry a $1/\sqrt{N!}$ factor.

57. Among the following, the correct statement(s) is (are):

- (A) C_2 symmetry element is present in H_2O and H_2O_2 but NOT in PCl_5 .
- (B) both C_2 and C_3 symmetry elements are present in CCl_4 and SF_6 .
- (C) one σ_h and three σ_d symmetry elements are present in benzene.
- (D) σ_v symmetry element is present in NH_3 but NOT in BF_3 .

Correct Answer: (A) and (B)

Solution:

Concept: Molecular symmetry elements depend on:

- Molecular geometry
- Presence of rotation axes (C_n)
- Presence of reflection planes (σ)

Step 1: Analyze option (A).

- H_2O (bent): has a C_2 axis

- H₂O₂ (skewed): has a C₂ axis along the O–O bond
- PCl₅ (trigonal bipyramidal): has a C₃ axis but no C₂ axis

Thus, option (A) is **correct**.

Step 2: Analyze option (B).

- CCl₄ (tetrahedral): has C₃ axes (through vertices) and C₂ axes (through midpoints of opposite edges)
- SF₆ (octahedral): has both C₄, C₃, and C₂ axes

Thus, option (B) is **correct**.

Step 3: Analyze option (C).

Benzene belongs to the D_{6h} point group:

- It has **one** σ_h
- It has **three** σ_v and **three** σ_d

Hence, the statement “one σ_h and three σ_d only” is **incomplete and incorrect**. Option (C) is incorrect.

Step 4: Analyze option (D).

- NH₃ (trigonal pyramidal): has three σ_v planes
- BF₃ (trigonal planar): also has three σ_v planes

Thus, σ_v is present in both NH₃ and BF₃.

Option (D) is incorrect.

Therefore, the correct statements are **(A) and (B)**.

Quick Tip

Always identify the point group first—symmetry elements follow directly from it.

Tetrahedral and octahedral molecules almost always contain both C₂ and C₃ axes.

58. ΔS° (in J mol⁻¹ K⁻¹) for the given reaction at 298 K is



(Given: log K₁ = 10.6, ΔH° = -54 kJ mol⁻¹, R = 8.314 J mol⁻¹ K⁻¹)

(rounded off to two decimal places)

Solution:

Concept: Thermodynamic relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

and

$$\Delta G^\circ = -RT \ln K$$

Step 1: Calculate ΔG° .

$$\ln K = 10.6 \ln 10 = 24.41$$

$$\Delta G^\circ = -RT \ln K = -(8.314)(298)(24.41) = -6.05 \times 10^4 \text{ J mol}^{-1} = -60.50 \text{ kJ mol}^{-1}$$

Step 2: Calculate ΔS° .

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-54 - (-60.50)}{298} = \frac{6.50}{298} = 0.02181 \text{ kJ mol}^{-1}\text{K}^{-1}$$

$$\Delta S^\circ = \boxed{21.80 \text{ J mol}^{-1}\text{K}^{-1}}$$

Quick Tip

Chelation often gives positive ΔS° due to release of coordinated water molecules.

59. The turnover frequency (in h^{-1}) of a reaction where 5 mol% of a catalyst is required for 90% conversion in 3 h is
(rounded off to the nearest integer)

Solution:

Concept: Turnover frequency (TOF) is defined as:

$$\text{TOF} = \frac{\text{moles of substrate converted}}{\text{moles of catalyst} \times \text{time}}$$

Step 1: Assume 1 mol of substrate initially.

$$\text{Moles converted} = 0.90 \text{ mol}$$

$$\text{Moles of catalyst} = 5\% = 0.05 \text{ mol}$$

Step 2: Calculate TOF.

$$\text{TOF} = \frac{0.90}{0.05 \times 3} = \frac{0.90}{0.15} = 6 \text{ h}^{-1}$$

$\boxed{6}$

Quick Tip

TOF measures catalyst efficiency: always divide by both catalyst amount and time.

60. In thermogravimetric analysis, 12.45 mg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was subjected to heating under N_2 atmosphere. At a particular temperature, there was a weight loss of 3.6 mg. The number of water molecule(s) lost per formula unit is (rounded off to the nearest integer)

Solution:

Concept: Weight loss in TGA corresponds to loss of volatile components (here, water of crystallization).

Step 1: Calculate moles of water lost.

$$\text{Mass of H}_2\text{O lost} = 3.6 \text{ mg} = 0.0036 \text{ g}$$

$$\text{Moles of H}_2\text{O} = \frac{0.0036}{18} = 2.0 \times 10^{-4} \text{ mol}$$

Step 2: Calculate moles of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Molar mass:

$$= 63.5 + 32.0 + 64.0 + 90.0 = 249.5 \text{ g mol}^{-1}$$

$$\text{Moles of salt} = \frac{0.01245}{249.5} \approx 5.0 \times 10^{-5} \text{ mol}$$

Step 3: Calculate number of water molecules lost.

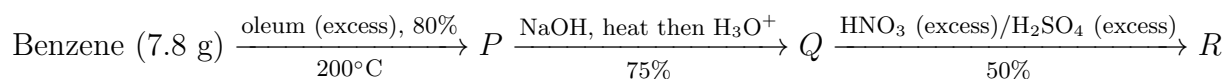
$$\text{Number of H}_2\text{O per formula unit} = \frac{2.0 \times 10^{-4}}{5.0 \times 10^{-5}} = 4$$

4

Quick Tip

In TGA, divide moles of mass lost by moles of compound to get molecules lost per formula unit.

61. In the given reaction sequence, the amount of R produced (in g) is



(rounded off to two decimal places)

Solution:

Concept: Overall yield in a multistep reaction is obtained by multiplying the fractional yields of each step.

Step 1: Calculate moles of benzene.

$$\text{Molar mass of benzene} = 78 \text{ g mol}^{-1}$$

$$\text{Moles of benzene} = \frac{7.8}{78} = 0.10 \text{ mol}$$

Step 2: Apply stepwise yields.

$$\text{After sulfonation (80\%)} = 0.10 \times 0.80 = 0.080 \text{ mol}$$

$$\text{After alkaline fusion (75\%)} = 0.080 \times 0.75 = 0.060 \text{ mol}$$

$$\text{After nitration (50\%)} = 0.060 \times 0.50 = 0.030 \text{ mol}$$

Step 3: Identify R and calculate mass.

The sequence corresponds to:



Molar mass of nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$):

$$= 6(12) + 5(1) + 14 + 3(16) = 139 \text{ g mol}^{-1}$$

$$\text{Mass of R} = 0.030 \times 139 = 4.17 \text{ g}$$

$$\boxed{4.17 \text{ g}}$$

Quick Tip

For multistep reactions, always multiply fractional yields stepwise before converting to mass.

62. The wave function of a particle in a cubic box (of side L) is given by

$$\psi(x, y, z) = \sqrt{\frac{32}{L^3}} \sin \frac{\pi x}{L} \cos \frac{\pi y}{L} \sin \frac{2\pi y}{L} \sin \frac{\pi z}{L}$$

The ratio of the energy of the state corresponding to the above wave function to the ground state energy is
(rounded off to the nearest integer)

Solution:

Concept: For a particle in a 3D box:

$$E_{n_x n_y n_z} \propto n_x^2 + n_y^2 + n_z^2$$

Step 1: Extract quantum numbers from the wave function.

$$n_x = 1, \quad n_y = 2, \quad n_z = 1$$

Step 2: Energy of the given state.

$$E = 1^2 + 2^2 + 1^2 = 6$$

Step 3: Ground state energy.

Ground state: $n_x = n_y = n_z = 1$

$$E_0 = 1^2 + 1^2 + 1^2 = 3$$

Step 4: Ratio.

$$\frac{E}{E_0} = \frac{6}{3} = 2$$

□ 2

Quick Tip

In a 3D box, energy ratios depend only on $(n_x^2 + n_y^2 + n_z^2)$.

63. ϕ_1 and ϕ_2 are normalized eigenfunctions of a Hermitian operator.

$$|\psi\rangle = 3i|\phi_1\rangle + 2|\phi_2\rangle, \quad |\chi\rangle = -2i|\phi_1\rangle + 5|\phi_2\rangle$$

The value of $\langle\psi|\chi\rangle + \langle\chi|\psi\rangle$ is
(rounded off to the nearest integer)

Solution:

Concept: For normalized orthonormal eigenfunctions:

$$\langle\phi_i|\phi_j\rangle = \delta_{ij}$$

and

$$\langle\psi|\chi\rangle + \langle\chi|\psi\rangle = 2\Re(\langle\psi|\chi\rangle)$$

Step 1: Compute $\langle\psi|\chi\rangle$.

$$\langle\psi| = -3i\langle\phi_1| + 2\langle\phi_2|$$

$$\langle\psi|\chi\rangle = (-3i)(-2i)\langle\phi_1|\phi_1\rangle + (2)(5)\langle\phi_2|\phi_2\rangle$$

$$= (-3i)(-2i) + 10$$

$$(-3i)(-2i) = 6i^2 = -6$$

$$\langle\psi|\chi\rangle = -6 + 10 = 4$$

Step 2: Evaluate the required sum.

$$\langle \psi | \chi \rangle + \langle \chi | \psi \rangle = 2 \times 4 = 8$$

8

Quick Tip

For Hermitian operators, $\langle \psi | \chi \rangle + \langle \chi | \psi \rangle = 2 \Re(\langle \psi | \chi \rangle)$.

64. 2 mol of a monoatomic ideal gas with initial volume of 5 L and pressure 10 bar undergoes an irreversible adiabatic expansion against a constant final pressure of 1 bar. The final volume (in L) is

(Given: $R = 8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1}$)

(rounded off to one decimal place)

Solution:

Concept: For an **irreversible adiabatic expansion** against constant external pressure:

$$q = 0$$

$$\Delta U = w = -P_{\text{ext}}(V_f - V_i)$$

For a monoatomic ideal gas:

$$\Delta U = nC_V(T_f - T_i), \quad C_V = \frac{3}{2}R$$

Step 1: Calculate initial temperature.

$$T_i = \frac{P_i V_i}{nR} = \frac{10 \times 5}{2 \times 0.08314} = 300.7 \text{ K}$$

Step 2: Apply first law.

$$nC_V(T_f - T_i) = -P_{\text{ext}}(V_f - V_i)$$

$$2 \times \frac{3}{2}R(T_f - 300.7) = -1(V_f - 5)$$

Step 3: Use ideal gas law for final state.

$$P_f V_f = nRT_f \Rightarrow T_f = \frac{V_f}{0.16628}$$

Substitute and solve:

$$3(0.08314) \left(\frac{V_f}{0.16628} - 300.7 \right) = -(V_f - 5)$$

Solving gives:

$$V_f = 12.0 \text{ L}$$

Quick Tip

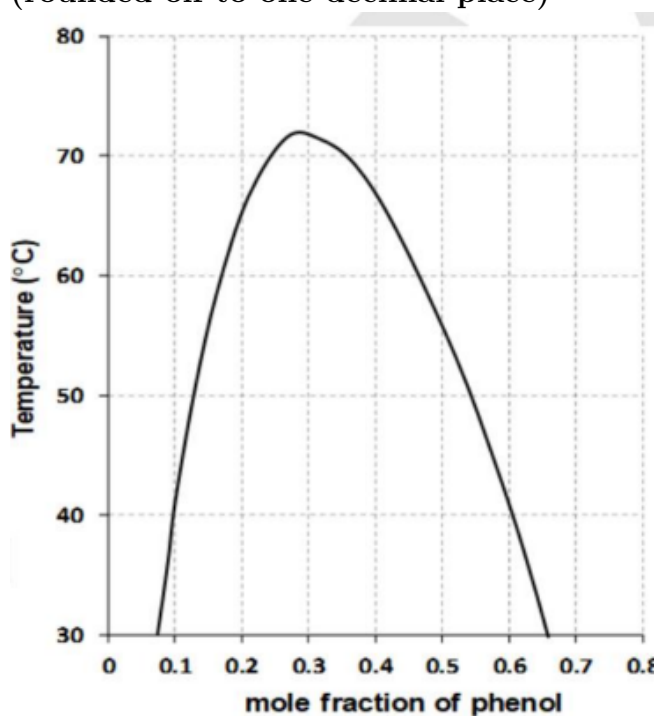
For an irreversible adiabatic expansion:

$$q = 0, \quad w = -P_{\text{ext}}\Delta V,$$

and the change in internal energy is given by

$$\Delta U = w.$$

65. The following figure shows an experimental liquid–liquid phase diagram of phenol and water at the vapor pressure of the system. The total amount of phenol and water (in mol) present in the phenol-rich phase when 5 mol of water was shaken with 5 mol of phenol at 40 °C is
(rounded off to one decimal place)



Solution:

Concept: When a binary mixture lies inside the miscibility gap:

- It separates into two liquid phases
- Phase compositions are given by the tie-line at that temperature
- Phase amounts are calculated using the **lever rule**

Step 1: Determine overall composition.

Total moles:

$$n_{\text{total}} = 5 + 5 = 10$$

Overall mole fraction of phenol:

$$x_{\text{overall}} = \frac{5}{10} = 0.50$$

Step 2: Read tie-line compositions at 40 °C from the diagram.

From the phase diagram:

$$x_{\text{water-rich}} \approx 0.20, \quad x_{\text{phenol-rich}} \approx 0.60$$

Step 3: Apply lever rule.

Fraction of phenol-rich phase:

$$f_{\text{phenol-rich}} = \frac{x_{\text{overall}} - x_{\text{water-rich}}}{x_{\text{phenol-rich}} - x_{\text{water-rich}}} = \frac{0.50 - 0.20}{0.60 - 0.20} = \frac{0.30}{0.40} = 0.75$$

Step 4: Calculate amount of phenol-rich phase.

$$n_{\text{phenol-rich}} = 0.75 \times 10 = 7.5 \text{ mol}$$

7.5

Quick Tip

Inside a miscibility gap, always use the lever rule:
phase fraction depends on distances along the tie-line, not on masses added.