# GATE 2026 Chemistry Question Paper with Solutions

## General Instructions

**(i)** This booklet contains 65 questions, each provided with a complete, step-by-step solution.

**(ii)** It comprises 33 single-correct multiple-choice questions, 16 multiple-correct questions and 16 numerical / integer-type questions.

**(iii)** These questions follow the GATE Chemistry examination pattern.

**(iv)** Questions carry 1 or 2 marks. MCQs have negative marking (1/3 or 2/3 of the marks); MSQ and numerical-answer (NAT) questions carry no negative marking.

**(v)** GATE is a 3-hour paper of 65 questions (100 marks).

**(vi)** A virtual scientific calculator is provided; physical calculators are not allowed.

**(vii)** Attempt each question on your own before reviewing the given solution.

**(viii)** For multiple-correct questions, all correct options must be selected to earn full marks.

**(ix)** For numerical questions, report the answer rounded exactly as asked.

**1.** "He often the numbers. False claims are not going to help. Honesty trust", said the manager.

Choose the option with the correct order of words to fill the blanks.

(A) exaggerates; engenders

(B) excels; encourages

(C) aggravates; alleviates

(D) diminishes; eliminates

**Correct Answer:** (A) exaggerates; engenders

**Solution:**

**Step 1:** Read the sentence for meaning.
The manager warns that "false claims are not going to help." This tells us the first blank must describe a habit close to making false or inflated claims, since the next sentence directly criticizes that habit.

**Step 2:** Fill the first blank.
"Exaggerates" fits well: exaggerating numbers means stating them as bigger or better than they really are, which is a mild form of a false claim. This matches the warning that follows.
Check the other words in this slot: "excels" needs a preposition ("excels at/in"), so "excels the numbers" is not grammatical.
"Aggravates the numbers" and "diminishes the numbers" do not carry the sense of dishonesty the sentence is building toward.

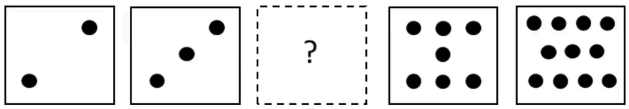
**Step 3:** Fill the second blank.
The sentence "Honesty ____ trust" needs a verb that shows honesty creates trust. "Engenders" means to give rise to or produce, so "honesty engenders trust" is a standard, correct collocation.
Check the rest: "encourages" would also seem to work loosely, but it is paired here with "excels", which already fails the first blank.
"Alleviates" means to ease or reduce, so "honesty alleviates trust" makes no sense, since trust is not a problem to be eased. "Eliminates" reverses the meaning entirely, since honesty should build trust, not remove it.

**Final Answer:**
Both blanks are filled correctly only by "exaggerates; engenders".

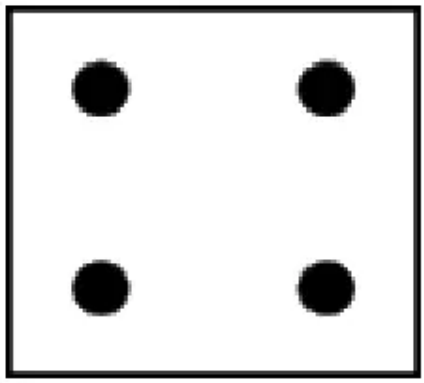
Option (A): exaggerates; engenders

**Quick Tip:** Read the sentence as a whole: the first blank should connect to "false claims", and the second blank should mean "creates" trust, not reduce or remove it.

**2.** In the sequence of tiles shown below, the missing tile indicated by the question mark should be



(A)



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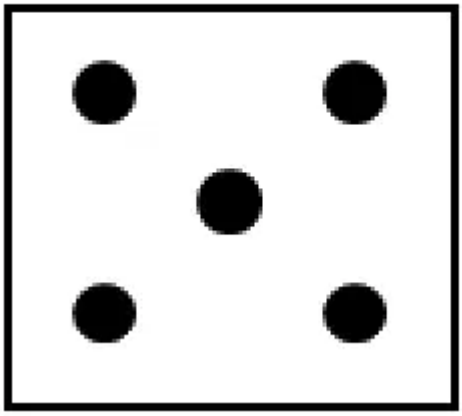
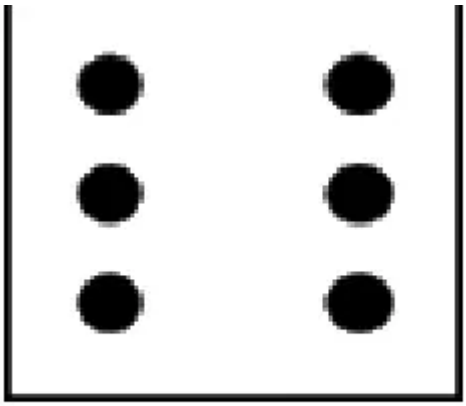
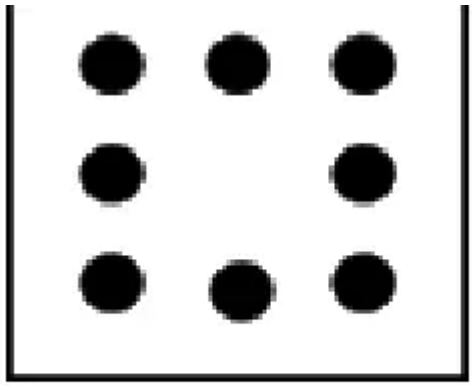


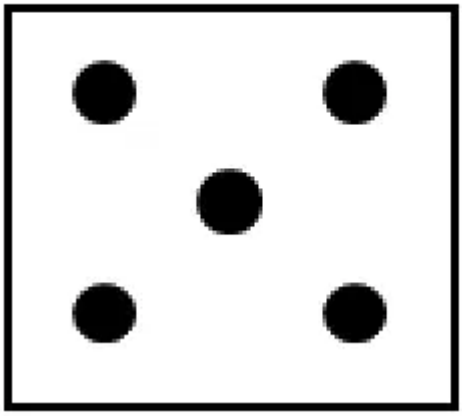
(C)



(D)



**Correct Answer:** (B)



**Solution:**

**Step 1:** Count the dots in each visible tile.

Reading the five tiles from left to right, the 1st tile has 2 dots, the 2nd tile has 3 dots, the 3rd tile is the missing one, the 4th tile has 6 dots, and the 5th tile has 10 dots.

**Step 2:** Split the tiles into two interleaved groups.

Look at the odd-position tiles (1st, 3rd, 5th) as one group and the even-position tiles (2nd, 4th) as a second group, since many figure-series questions run two simple rules in parallel on alternate

positions.

**Step 3:** Find the rule for the odd-position group.
The 1st tile has 2 dots and the 5th tile has 10 dots. Test the rule "dots = (rank)^2 + 1", where rank counts 1, 2, 3 for the 1st, 3rd, and 5th tiles in this group.

$$1^2 + 1 = 2 \text{ (1st tile, matches)}$$

$$3^2 + 1 = 10 \text{ (5th tile, matches)}$$

Since the rule holds at both known points, the 3rd tile (the missing one, rank 2 in this group) must have $2^2 + 1 = 5$ dots.

**Step 4:** Check the rule against the even-position group.
The 2nd tile has 3 dots and the 4th tile has 6 dots. Test the rule "dots = (rank)^2 + 2", with rank 1, 2 for the 2nd and 4th tiles.

$$1^2 + 2 = 3 \text{ (2nd tile, matches)}$$

$$2^2 + 2 = 6 \text{ (4th tile, matches)}$$

This confirms two clean parallel rules are running on alternate tiles, which supports the answer found in Step 3.

**Step 5:** Match to the options.
The missing tile needs exactly 5 dots. Option (A) shows 4 dots, option (B) shows 5 dots arranged as two dots on top, one in the middle, and

two on the bottom, option (C) shows 6 dots, and option (D) shows more than 5 dots. Only option (B) has 5 dots.

**Final Answer:**
The missing tile has 5 dots.

Option (B)

**Quick Tip:** Split the tiles into odd positions (1st, 3rd, 5th) and even positions (2nd, 4th), and look for a squared-number rule running on each group separately.

**3.** A school has 100 students distributed among $1^{st}$ to $10^{th}$ standards. Based on this, which one of the following statements is always correct?

(A) There are at least 10 students who belong to the same standard.

(B) There is at least one student in each standard.

(C) There are at most 10 students in $10^{th}$ standard.

(D) The total number of students from $1^{st}$ to $5^{th}$ standards is at least 50.

**Correct Answer:** (A) There are at least 10 students who belong to the same standard.

**Solution:**

**Step 1:** Identify the concept.
This is a pigeonhole principle question. There are 100 students (the "pigeons") placed into 10 standards (the "pigeonholes"), and we need the one statement that is forced to be true no matter how the 100 students are spread across the 10 standards.

**Step 2:** Test option (A) using the pigeonhole principle.
Suppose, for contradiction, that every standard has at most 9 students. Then the total number of students across all 10 standards can be at most $10 \times 9 = 90$.
But we are told there are 100 students, and $100 > 90$, which is a contradiction.
So at least one standard must contain 10 or more students. This means "there are at least 10 students who belong to the same standard" is always true.

**Step 3:** Check why option (B) can fail.
It is possible to put all 100 students into just the 1st standard and leave every other standard empty. Then some standards have zero students, so "at least one student in each standard" is not guaranteed.

**Step 4:** Check why option (C) can fail.
Nothing stops all 100 students from being placed in the 10th standard alone. Then the 10th standard has 100 students, which is far more than 10, so "at most 10 students in 10th standard" is not guaranteed.

**Step 5:** Check why option (D) can fail.
Place all 100 students in standards 6 to 10 only, with none in standards 1 to 5. Then the total from 1st to 5th standards is 0, which is less than 50, so this statement is not guaranteed either.

**Final Answer:**
Only the pigeonhole-based statement always holds.

Option (A)

**Quick Tip:** Use the pigeonhole principle: with 100 students in 10 standards, if every standard had 9 or fewer, the total could not reach 100.

**4.** How many 3-digit numbers can be formed using three distinct single digit prime numbers?

(A) 64

(B) 24

(C) 12

(D) 4

**Correct Answer:** (B) 24

**Solution:**

**Step 1:** List the single digit prime numbers.
The single digit primes are 2, 3, 5, and 7. There are exactly 4 such digits.

**Step 2:** Understand what is being asked.
We need 3-digit numbers where all three digits are distinct and each digit is chosen from the set $\{2, 3, 5, 7\}$. Since digits must be distinct, this is a permutation problem, not a problem with repetition allowed.

**Step 3:** Count the choices for each position.
For the hundreds place, there are 4 possible digits to choose from.
Once that digit is used, 3 digits remain for the tens place.
Once two digits are used, 2 digits remain for the units place.
None of these digits is 0, so there is no need to worry about a leading zero.

**Step 4:** Multiply the choices.

$$4 \times 3 \times 2 = 24$$

This is the same as computing the permutation $P(4, 3) = \frac{4!}{(4-3)!}$ $= \frac{24}{1} = 24.$

**Step 5:** Rule out the other options.
64 would be the count if repetition were allowed ($4^3 = 64$), which is not the case here since digits must be distinct. 12 and 4 are both smaller than the correct permutation count and do not correspond to any consistent counting rule for this problem.

**Final Answer:**
24 distinct 3-digit numbers can be formed.

$$\boxed{24}$$

**Quick Tip:** There are only 4 single digit primes (2, 3, 5, 7). Pick 3 distinct ones and arrange them: this is a permutation, $P(4, 3)$.

**5.** In a group of students, 10 students like Mathematics, 12 students like English, 4 students like both Mathematics and English, and 6 students like neither Mathematics nor English. The number of students in the group is

(A) 18

(B) 20

(C) 24

(D) 32

**Correct Answer:** (C) 24

**Solution:**

**Step 1:** Set up the sets.

Let M be the set of students who like Mathematics and E be the set of students who like English. We are given $|M| = 10$, $|E| = 12$, $|M \cap E| = 4$, and the number of students who like neither is 6.

**Step 2:** Apply the inclusion-exclusion principle.

The number of students who like Mathematics or English (or both) is

$$|M \cup E| = |M| + |E| - |M \cap E|$$

This formula avoids double counting the students who like both subjects.

**Step 3:** Substitute the numbers.

$$|M \cup E| = 10 + 12 - 4 = 18$$

So 18 students like at least one of the two subjects.

**Step 4:** Add the students who like neither.

The total group size equals the students who like at least one subject plus the students who like neither.

$$\text{Total} = |M \cup E| + \text{neither} = 18 + 6 = 24$$

**Step 5:** Rule out the other options.

18 is only the count of students liking at least one subject, before adding the "neither" group, so it is incomplete. 20 and 32 do not come from a correct application of inclusion-exclusion on the given numbers.

**Final Answer:**

The group has 24 students.

$$\boxed{24}$$

**Quick Tip:** Use $|M \cup E| = |M| + |E| - |M \cap E|$ to find how many like at least one subject, then add the "neither" count for the total group size.

**6.** Charity : P :: Retaliation : Q

Choose the appropriate pair of words P and Q that fit the analogy.

(A) P = Parsimonious; Q = Vengeful

(B) P = Altruistic; Q = Amicable

(C) P = Resentful; Q = Spiteful

(D) P = Magnanimous; Q = Vindictive

**Correct Answer:** (D) P = Magnanimous; Q = Vindictive

**Solution:**

**Step 1:** Work out the relationship in the analogy.
"Charity : P" means P should be a word that describes the quality of a person who shows charity, that is, someone who gives generously and forgives easily. "Retaliation : Q" means Q should describe the quality of a person who retaliates, that is, someone who strikes back and holds grudges. So we need one word meaning "generous/forgiving" for P, and one word meaning "vengeful/unforgiving" for Q, and the pair should genuinely oppose each other in spirit, since charity and retaliation are opposite impulses.

**Step 2:** Check option (A), Parsimonious; Vengeful.
"Parsimonious" means stingy or unwilling to spend, which is the opposite of charitable, not a match for P. This option fails on the first word.

**Step 3:** Check option (B), Altruistic; Amicable.
"Altruistic" fits P well, since it means selflessly caring for others, matching the spirit of charity. But "amicable" means friendly, which does not match "retaliation" at all, since retaliation is about striking back, not friendliness. This option fails on Q.

**Step 4:** Check option (C), Resentful; Spiteful.
"Resentful" means bitter or holding a grudge, which is the wrong feeling for someone showing charity. This option fails on P.

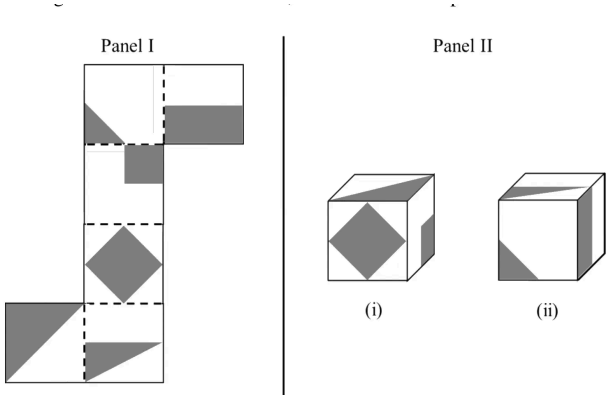
**Step 5:** Check option (D), Magnanimous; Vindictive.
"Magnanimous" means generous and forgiving, exactly the quality of someone who gives charity. "Vindictive" means seeking revenge, exactly the quality of someone who retaliates. Both words fit their partner term correctly, and the pair mirrors each other as true opposites.

**Final Answer:**
Only option (D) gives words that correctly and consistently complete both parts of the analogy.

**Option (D): Magnanimous; Vindictive**

**Quick Tip:** P should mean generous (to match charity), Q should mean vengeful (to match retaliation). Only one option gets both right.

**7.** A paper shown in Panel I is folded along the dashed lines (- - -) to construct a cube. The shaded regions shown in Panel I appear on the outer surface of the cube. Referring to cubes shown in Panel II, which one of the options is correct?




(A) Only (i) can correspond to the unfolded cube in Panel I.

(B) Only (ii) can correspond to the unfolded cube in Panel I.

(C) Both (i) and (ii) can correspond to the unfolded cube in Panel I.

(D) Neither (i) nor (ii) can correspond to the unfolded cube in Panel I.

**Correct Answer:** (A) Only (i) can correspond to the unfolded cube in Panel I.

**Solution:**

**Step 1:** Understand the setup.

Panel I shows a flat net of six squares joined edge to edge, with dashed fold lines. When folded along these lines, the net closes up into a cube, and every shaded mark on the net becomes a mark on one face of that cube. Panel II shows two finished cubes, (i) and (ii), and we must decide which of them, if either, could really be the result of folding the exact net in Panel I.

**Step 2:** Pick two faces that share an edge in the net.

The square carrying the gray diamond and the square carrying the diagonally shaded triangle sit right next to each other in the net, joined along one common edge before folding. Because they already share an edge on the flat net, they must still share an edge once the cube is formed, and the marks on them must sit at a fixed angle to each other, since folding a single sheet of paper cannot flip one face over relative to its neighbor.

**Step 3:** Track the orientation across the fold.

Trace the shared edge between the diamond square and the triangle square, and note which corner of the triangle touches that shared edge, and which side of the diamond faces it. When the net is folded so the diamond ends up on the top face of the cube, the triangle square swings down to become an adjacent side face, carrying its shading with the same handedness it had on the flat sheet, since a simple fold never mirrors the paper.

**Step 4:** Compare with cube (i).

In cube (i), the diamond sits on the top face and the shaded triangle sits on the adjacent visible side face, with the triangle's shaded corner

touching the shared edge in the same sense that was traced from the net in Step 3. This matches exactly what folding Panel I produces.

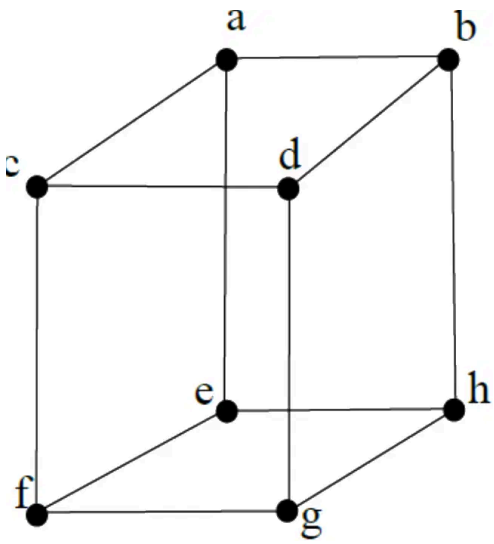
**Step 5:** Compare with cube (ii).
In cube (ii), the same two faces (diamond on top, triangle on the side) appear, but the triangle's shaded half is mirrored compared to what Step 3 predicts. Getting this mirrored version would need the paper to be flipped over before folding, which is not a valid paper fold. So cube (ii) cannot come from the net in Panel I.

**Final Answer:**
Only cube (i) is a valid fold of the net shown in Panel I.

Option (A): Only (i) can correspond to the unfolded cube in Panel I.

**Quick Tip:** Find two faces that share an edge in the net (the diamond face and the shaded-triangle face) and check that the shading crosses their shared edge in the same direction after folding, without flipping the paper over.

**8.** Consider the cube shown below with its 8 corners labelled a, b, c, d, e, f, g, and h. The figure is representative. All corners are to be colored such that any two corners that are connected by an edge must be of different colors. The minimum number of colors required to achieve this is




(A) 8

(B) 4

(C) 3

(D) 2

**Correct Answer:** (D) 2

**Solution:**

**Step 1:** Understand the graph.

The 8 corners of the cube, joined by the 12 edges of the cube, form a graph where we need the smallest number of colors so that no two corners joined directly by an edge share a color. This is the chromatic number of the cube graph.

**Step 2:** Recall the key idea for coloring by two colors.

A graph can be colored with only 2 colors exactly when it is bipartite, meaning its corners can be split into two groups such that every edge

runs between the two groups, never within the same group. A graph is bipartite exactly when it contains no cycle of odd length.

**Step 3:** Split the cube's corners into two groups.
Label each corner of the cube with 3D coordinates of 0s and 1s, for example (0,0,0), (1,0,0), (0,1,0), and so on for all 8 corners, where each edge of the cube connects two corners that differ in exactly one coordinate.
Group 1: corners whose coordinates add up to an even number, such as (0,0,0), (1,1,0), (1,0,1), (0,1,1).
Group 2: corners whose coordinates add up to an odd number, such as (1,0,0), (0,1,0), (0,0,1), (1,1,1).
Every edge changes exactly one coordinate, so it always changes the sum from even to odd or odd to even, meaning every edge always goes from Group 1 to Group 2, never within the same group.

**Step 4:** Color the two groups.
Give every corner in Group 1 one color, say Red, and every corner in Group 2 a second color, say Blue. Since no edge connects two corners of the same group, no edge connects two corners of the same color. This coloring uses only 2 colors and is valid.

**Step 5:** Confirm that fewer than 2 colors is not possible.
Since the cube has at least one edge, its two endpoints must get different colors, so at least 2 colors are always needed. Combined with Step 4, exactly 2 colors are both necessary and sufficient.

**Step 6:** Rule out the other options.
8 and 4 use far more colors than needed, since the cube graph has cycles of length 4 (its square faces), not longer odd cycles that would force more colors. 3 colors would also work, but is not the minimum,

since Step 4 already achieved a valid coloring with just 2.

**Final Answer:**
The minimum number of colors needed is 2.

$$\boxed{2}$$

**Quick Tip:** A cube's corners and edges form a bipartite graph (no odd cycles), and any bipartite graph needs exactly 2 colors.

**9.** Four hills $H_1, H_2, H_3$, and $H_4$ are present in an area. The following observations are made about them:
(i) Neither $H_2$ nor $H_3$ is the easternmost hill.
(ii) Neither $H_2$ nor $H_3$ is the westernmost hill.
(iii) Neither the easternmost hill nor the westernmost hill is the southernmost hill.
(iv) Two hills are located to the west of $H_2$.
(v) The southernmost hill has at least two hills to its east.
The southernmost hill is .

(A) $H_1$

(B) $H_2$

(C) $H_3$

(D) $H_4$

**Correct Answer:** (C) $H_3$

**Solution:**

**Step 1:** Fix the east-west extremes.
From clue (i), neither $H_2$ nor $H_3$ is the easternmost hill. From clue (ii), neither $H_2$ nor $H_3$ is the westernmost hill. So both the easternmost and the westernmost hill must come from $\{H_1, H_4\}$. That leaves $H_2$ and $H_3$ to occupy the two middle positions in the east-west order.

**Step 2:** Place $H_2$ using clue (iv).
Rank the four hills from west to east as position 1 (westernmost) to position 4 (easternmost). Clue (iv) says two hills lie west of $H_2$, so $H_2$ sits at position 3, with positions 1 and 2 to its west and position 4 to its east. This is consistent with Step 1, since position 3 is one of the two middle slots.

**Step 3:** Use clues (iii) and (v) to find the southernmost hill.
Clue (iii) says the southernmost hill is not the easternmost or westernmost hill, so the southernmost hill is $H_2$ or $H_3$.
Check $H_2$: from Step 2, only position 4 lies east of $H_2$, so only one hill is to its east. Clue (v) needs at least two hills east of the southernmost hill, so $H_2$ fails this test and cannot be the southernmost hill.
So the southernmost hill is $H_3$.

**Step 4:** Fix $H_3$'s east-west position and check clue (v).
Position 3 is taken by $H_2$, and $H_3$ cannot be at position 1 (westernmost, ruled out by clue (ii)) or position 4 (easternmost, ruled out by clue (i)). So $H_3$ must sit at position 2. That leaves 2 hills (positions 3 and 4) to its east, which satisfies clue (v) exactly.
Every clue is now satisfied with the west-to-east order: one of $H_1/H_4$, then $H_3$, then $H_2$, then the other of $H_4/H_1$.

**Why the other options are wrong:**

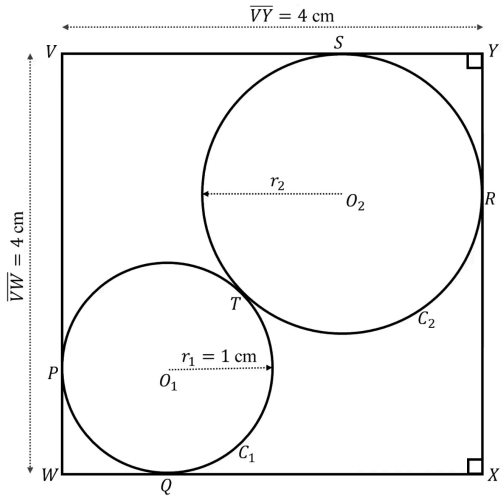
$H_1$ is wrong because it is one of the two extreme (easternmost or westernmost) hills, and clue (iii) rules out an extreme hill being southernmost.
$H_2$ is wrong because it has only one hill to its east, which fails clue (v).
$H_4$ is wrong for the same reason as $H_1$, it is the other extreme hill.

**Final Answer:**
The southernmost hill is $H_3$.

$$\boxed{H_3}$$

**Quick Tip:** First use clues (i) and (ii) to see that only $H_1$ and $H_4$ can be the east/west extremes; then use clue (iv) to fix $H_2$'s exact position, and finally check clue (v) against the two remaining candidates for southernmost.

**10.** As shown in the figure, circle $C_1$ with center $O_1$ and radius $r_1$ touches the square $VWXY$ at points $P$ and $Q$, while circle $C_2$ with center $O_2$ and radius $r_2$ touches the square $VWXY$ at points $R$ and $S$. The two circles touch each other at $T$.
Given $r_1 = 1$ cm and $\overline{VY} = \overline{VW} = 4$ cm, $r_2 =$ cm.



(A) $4-3\sqrt{2}$

(B) $1+2\sqrt{2}$

(C) $7-4\sqrt{2}$

(D) $5+3\sqrt{2}$

**Correct Answer:** (C) $7-4\sqrt{2}$

**Solution:**

**Step 1:** Set up coordinates using the corners the circles are tangent to.

Place $W$ (the bottom-left corner) at the origin, with side $WX$ along the positive x-axis and side $WV$ along the positive y-axis. Since $\overline{VW} = \overline{VY} = 4$ cm, the square has side length 4 cm, so the corners are $W(0,0)$, $X(4,0)$, $V(0,4)$, $Y(4,4)$.

**Step 2:** Locate the center $O_1$.

Circle $C_1$ touches the square at $P$ (on side $VW$) and $Q$ (on side $WX$), the two sides that meet at corner $W$. A circle tangent to both sides of a right angle has its center at a distance equal to its radius from each side. So $O_1 = (r_1, r_1) = (1,1)$.

**Step 3:** Locate the center $O_2$.

Circle $C_2$ touches the square at $R$ (on side $XY$) and $S$ (on side $VY$), the two sides that meet at corner $Y$. By the same reasoning, its center is a distance $r_2$ from each of these two sides, measured inward from $Y(4,4)$. So $O_2 = (4-r_2,\ 4-r_2)$.

**Step 4:** Apply the external tangency condition.

The circles touch each other at $T$, so they are externally tangent,

meaning the distance between their centers equals the sum of their radii:

$$O_1O_2 = r_1 + r_2$$

Compute $O_1O_2$ using the distance formula:

$$O_1O_2 = \sqrt{(4 - r_2 - 1)^2 + (4 - r_2 - 1)^2} = \sqrt{2(3 - r_2)^2} = (3 - r_2)\sqrt{2}$$

(taking $3 - r_2 > 0$, which must hold since $r_2$ is a small radius inside a 4 cm square).

**Step 5:** Solve for $r_2$.

$$(3 - r_2)\sqrt{2} = r_1 + r_2 = 1 + r_2$$

$$3\sqrt{2} - r_2\sqrt{2} = 1 + r_2$$

$$3\sqrt{2} - 1 = r_2 + r_2\sqrt{2} = r_2(1 + \sqrt{2})$$

$$r_2 = \frac{3\sqrt{2} - 1}{1 + \sqrt{2}}$$

Rationalize by multiplying top and bottom by $(\sqrt{2} - 1)$:

$$r_2 = \frac{(3\sqrt{2} - 1)(\sqrt{2} - 1)}{(1 + \sqrt{2})(\sqrt{2} - 1)} = \frac{6 - 3\sqrt{2} - \sqrt{2} + 1}{2 - 1} = 7 - 4\sqrt{2}$$

**Why the other options are wrong:**

$4 - 3\sqrt{2}$ is negative (since $3\sqrt{2} \approx 4.24$), which cannot be a radius.

$1 + 2\sqrt{2} \approx 3.83$ cm is far too large for a circle tucked into that corner while staying tangent to $C_1$ at that position.

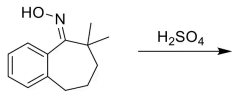
$5 + 3\sqrt{2}$ is even larger and clearly impossible inside a 4 cm square.

**Final Answer:**

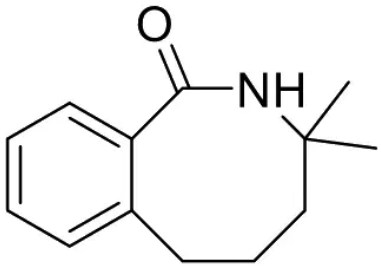
$$\boxed{r_2 = 7 - 4\sqrt{2}\ \text{cm} \approx 1.34\ \text{cm}}$$

**Quick Tip:** Both circles sit in opposite right-angle corners of the square, so their centers lie a distance equal to their own radius from each of the two sides meeting at that corner; set the center-to-center distance equal to $r_1 + r_2$ for external tangency.

**11.** The major product formed in the following reaction is:



(A)

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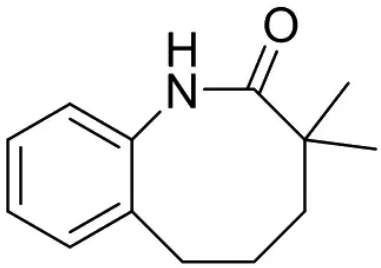
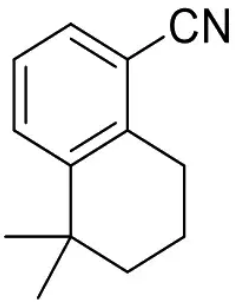
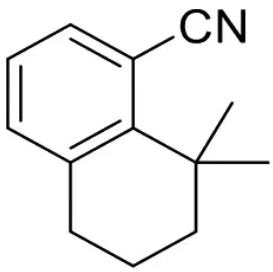


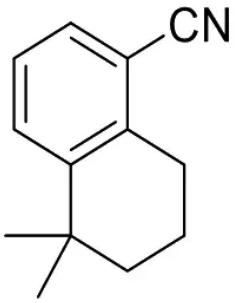

(C)



(D)




**Correct Answer:** (C)

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**Solution:**

**Step 1:** Identify the substrate and the reaction type.

The starting material is the oxime of a benzo-fused seven-membered ring ketone, a 2,2-dimethyl-1-benzosuberone oxime: the ring carbon bearing =N–OH is fused directly to the aromatic ring, and the very next ring carbon carries two methyl groups, a quaternary, gem-dimethyl carbon. Treating an oxime with $H_2SO_4$ is the classic setup for a Beckmann rearrangement, in which the OH is protonated and leaves as water while the group anti (trans) to it migrates from carbon to nitrogen.

**Step 2:** Decide which group is anti to the leaving OH.

The drawn oxime geometry places the aryl-fused ring carbon syn to

the OH, so the group anti to the leaving OH is the ring bond to the gem-dimethyl carbon. In a normal Beckmann rearrangement, this gem-dimethyl carbon, with its bonding electrons, would migrate onto nitrogen to give a ring-expanded lactam.

**Step 3:** Recognize why fragmentation wins over simple migration. The gem-dimethyl carbon is flanked by two methyl groups, so if it ionizes instead of migrating as a unit, it forms a tertiary carbocation, far more stable than the incipient charge in a normal 1,2-shift. When the group anti to the leaving OH can form a well-stabilized cation, the oxime undergoes Beckmann fragmentation instead of Beckmann rearrangement: the $C_1–C_2$ bond (oxime carbon to gem-dimethyl carbon) breaks completely. The oxime carbon keeps its bond to the aromatic ring and becomes a nitrile carbon (Ar–C≡N), while the gem-dimethyl carbon is released as a tertiary carbocation still tethered to the rest of the chain (three $CH_2$ groups) and to the other aromatic ring-fusion carbon.

**Step 4:** Ring closure by intramolecular Friedel-Crafts alkylation. The tethered tertiary carbocation is attacked intramolecularly by the electron-rich benzene ring, an intramolecular Friedel-Crafts alkylation, forming a new carbon-carbon bond and closing a new six-membered ring fused to the aromatic ring. The overall result is ring contraction from a seven-membered to a six-membered carbocycle: a tetrahydronaphthalene skeleton carrying the nitrile group on the aromatic ring, near the original point of attachment, and the two methyl groups on the newly formed quaternary ring carbon, positioned across the new ring from the nitrile-bearing carbon. This matches option (C).

**Why the other options are wrong:**

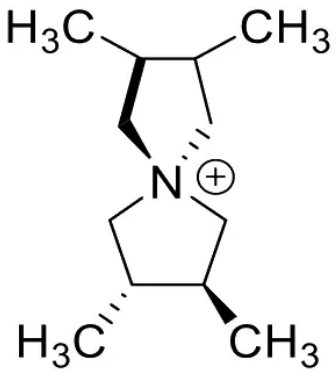
Options (A) and (B) are both simple Beckmann rearrangement (ring-expanded, seven-membered lactam) products, differing only in whether the carbonyl or the NH ends up next to the aromatic ring. Neither forms here, because the tertiary-cation-forming fragmentation pathway is much faster than ordinary 1,2-alkyl migration for this gem-dimethyl substrate.
Option (D) has the correct nitrile-plus-ring-contraction skeleton, but places the gem-dimethyl group on the ring carbon immediately next to the nitrile-bearing aromatic carbon, which does not match the connectivity produced by the fragmentation and Friedel-Crafts closure traced in Step 4, the gem-dimethyl carbon ends up bonded to the far ring-fusion carbon, not the near one.

**Final Answer:**
The major product is the ring-contracted nitrile shown in option (C).

$$\boxed{\text{(C)}}$$

**Quick Tip:** Ask which carbon sits anti to the leaving OH: here it is a gem-dimethyl carbon that can form a stable tertiary cation, so the oxime fragments (C-C cleavage to a nitrile) instead of doing a normal 1,2-migration, and the resulting cation is captured by the nearby aromatic ring.

**12.** The correct statement about the following quaternary ammonium ion is:




(A) It has only $C_2$-symmetry, hence chiral

(B) It has $S_4$-symmetry, hence achiral

(C) It has no symmetry, hence chiral

(D) It has a centre of symmetry, hence achiral

**Correct Answer:** (B) It has $S_4$-symmetry, hence achiral

**Solution:**

**Step 1:** Identify the stereocenters.

The cation is a pyrrolidinium ring in which all four ring carbons ( $C_2, C_3, C_4, C_5$, numbering around the ring from nitrogen) carry one methyl group and one hydrogen each. Each of these four ring carbons is bonded to four different groups, so all four are stereocenters. A molecule with several stereocenters is not automatically chiral, its overall symmetry decides that.

**Step 2:** Read the drawn relative configuration.

The wedge and hash bonds show the two methyls next to nitrogen ($C_2$ and $C_5$) pointing to the same face of the ring, both wedge, "up", and

the two methyls further from nitrogen ($C_3$ and $C_4$) pointing to the opposite face, both hashed, "down". This is a specific, symmetric relative arrangement, not a random one.

**Step 3:** Look for a symmetry element, not just count stereocenters.
Chirality is decided by whether the molecule has an improper symmetry element, a mirror plane ($\sigma$), a center of inversion ($i$), or more generally an $S_n$ improper rotation axis. A molecule that possesses any $S_n$ axis (including the special cases $S_1 = \sigma$ and $S_2 = i$) is achiral, even if it has several stereocenters and no simple mirror plane or inversion center on its own.
Here, rotating the ring by 90° about the axis running through N and the midpoint of the $C_3{-}C_4$ bond, followed by reflection through the plane perpendicular to that axis, exactly swaps the "up" methyl pair ( $C_2, C_5$) with the "down" methyl pair ($C_3, C_4$) and maps the whole cation onto itself. This combined rotation-reflection is exactly the definition of an $S_4$ axis.

**Step 4:** Conclude achirality from the $S_4$ axis.
Since the molecule has an $S_4$ axis, it is superimposable on its mirror image, so it is achiral, even though every individual ring carbon is a stereocenter. This is a standard example used to show that having stereocenters is not the same as being chiral, symmetry is what actually decides it.

**Why the other options are wrong:**
Option (A) is wrong because although a $C_2$ axis is indeed present, through N and the $C_3{-}C_4$ midpoint, a proper rotation axis alone never causes achirality or chirality by itself, and the molecule additionally has the improper $S_4$ axis, which makes it achiral, not chiral.

Option (C) is wrong because the molecule is not asymmetric, the paired "up-up-down-down" arrangement of the methyls is a deliberate symmetric pattern, not a random one.
Option (D) is wrong because the ring is not planar and the four substituents are not related through a single inversion center, the actual improper element present is the $S_4$ axis, not a true center of symmetry $i$.

**Final Answer:**
The ion has $S_4$ symmetry and is therefore achiral.

$$\boxed{\text{(B)}}$$

**Quick Tip:** Do not just count stereocenters, check for an improper symmetry element ($\sigma$, $i$, or $S_n$); an $S_4$ axis alone, without a separate mirror plane or inversion center, is enough to make a molecule with several stereocenters achiral.

**13.** The major product formed in the following reaction sequence is:
Step 1: $C_6H_{13}-C\equiv CH$ is treated with catecholborane, then heated.
Step 2: the product from Step 1 is treated with $Br_2$, then NaOMe.

(A) $C_6H_{13}-CH=CH-Br$ (E-configured: the hexyl chain and Br on opposite sides of the double bond)

(B) $C_6H_{13}-CH=CBr_2$ (1,1-dibromoalkene: both Br atoms on the terminal alkene carbon)

(C) $C_6H_{13}-CH=CH-Br$ (Z-configured: the hexyl chain and Br on the same side of the double bond)

(D) $C_6H_{13}-CBr=CH-Br$ (1,2-dibromoalkene: one Br on each alkene carbon)

**Correct Answer:** (C) $C_6H_{13}-CH=CH-Br$ (Z-configured: the hexyl chain and Br on the same side of the double bond)

**Solution:**

**Step 1:** Hydroboration of the terminal alkyne with catecholborane.
Catecholborane (HBcat) adds across the triple bond of the terminal alkyne $C_6H_{13}-C\equiv CH$ by a concerted, syn addition of the H–B bond, with boron going to the less hindered terminal carbon (anti-Markovnikov regiochemistry, typical for hydroboration). Because the addition is syn, both new bonds form on the same face of the triple bond, so the resulting alkenylboronate has the hexyl chain and the boron group on opposite faces of the new double bond. This gives the (E)-1-alkenylboronate: $C_6H_{13}-CH=CH-Bcat$, with $C_6H_{13}$ and Bcat trans to each other.

**Step 2:** Bromination of the alkenylboronate.
Treating the (E)-alkenylboronate with $Br_2$ adds bromine across the same carbon-carbon double bond in an anti fashion, placing the two new bromine atoms, and the retained boron group, on defined faces of the resulting C–C bond.

**Step 3:** Base-induced anti-periplanar elimination (bromo-deboronation).

Adding **NaOMe** promotes an anti-periplanar elimination that expels the boronate group together with one bromide, regenerating a carbon-carbon double bond in the same position as before. This elimination proceeds with a net inversion of the alkene geometry relative to the original alkenylboronate, the boron is formally replaced by bromine, but on the opposite face. Since the starting alkenylboronate was (E), chain and boron trans, the product vinyl bromide comes out (Z), chain and **Br** cis, that is, on the same side of the double bond.

**Step 4:** Identify the product.

The overall transformation is a net anti-Markovnikov, stereospecific conversion of the terminal alkyne into a single monobromoalkene, with inversion of the alkene geometry set up in the hydroboration step. The product is $C_6H_{13}$–CH=CH–**Br** with the hexyl chain and **Br** on the same side of the double bond, that is, the (Z)-isomer.

**Why the other options are wrong:**

Option (A), the (E)-vinyl bromide, would be the product only if the boron-to-bromine exchange happened with retention of configuration, but the bromination and anti-elimination sequence inverts the geometry, so (E) is not the major product.

Options (B) and (D) both carry two bromine atoms on the alkene. This sequence replaces the single boron substituent with a single bromine, it does not add a second equivalent of **Br** across the final double bond, so a dibromoalkene, whether 1,1- as in B, or 1,2- as in D, is not the product.

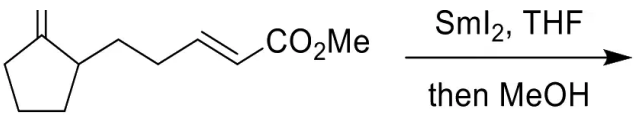
**Final Answer:**

The major product is the (Z)-vinyl bromide, $C_6H_{13}-CH=CH-Br$ with the chain and **Br** cis.

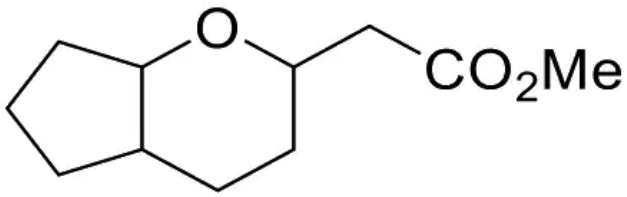
(C)

**Quick Tip:** Catecholborane hydroboration of the terminal alkyne gives the (E)-alkenylboronate (syn addition, boron on the terminal carbon); $Br_2$ then **NaOMe** swaps boron for bromine with net inversion of the double bond geometry, so the product is the (Z)-vinyl bromide, not the (E)-isomer or a dibromide.

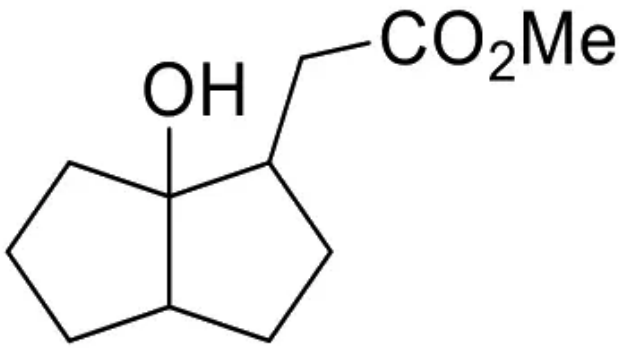
**14.** The major product formed in the following reaction is:



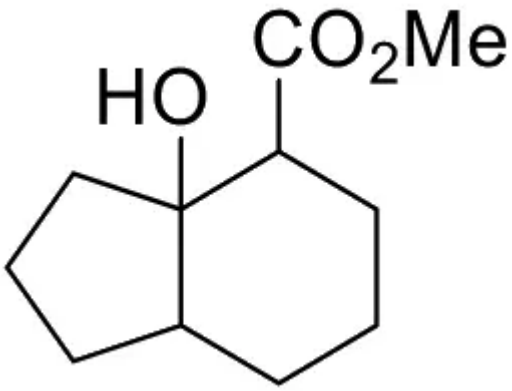
(A)



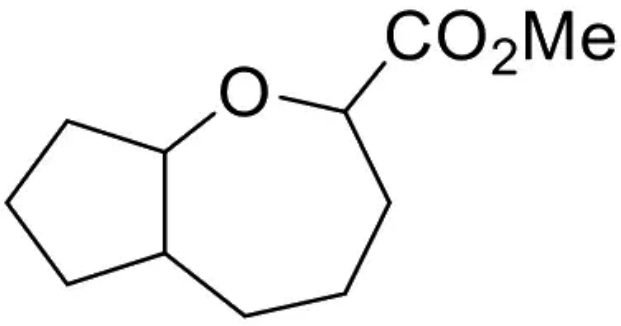

(B)



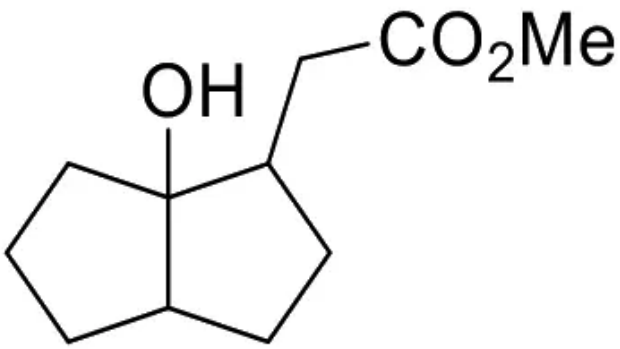

(C)




(D)



**Correct Answer:** (B)




**Solution:**

**Step 1:** Identify the substrate and the reagent.

The starting material is a cyclopentanone bearing, on the ring carbon next to the carbonyl, a side chain $-CH_2-CH_2-CH=CH-CO_2Me$, an $\alpha,\beta$-unsaturated ester (a Michael acceptor) tethered to the ketone through two $CH_2$ groups. $SmI_2$ in THF is a single-electron reducing agent well known for generating ketyl radicals from ketones and aldehydes, which can then cyclize onto a pendant alkene, a ketyl-olefin radical cyclization. MeOH is added afterward as a proton source to quench the resulting samarium species.

**Step 2:** Generate the ketyl radical.

$SmI_2$ transfers one electron to the ketone carbonyl, converting it into a ketyl radical anion. The carbonyl carbon, now radical in character, is tethered through the ring's alpha carbon and the two-carbon $CH_2CH_2$ chain to the alkene of the unsaturated ester.

**Step 3:** Count atoms to find the ring size formed on cyclization.

Counting from the ketyl carbon (radical center) to the nearer alkene carbon: ketyl carbon (1), ring alpha-carbon bearing the chain (2), first $CH_2$ (3), second $CH_2$ (4), and the nearer alkene carbon (5).

Cyclization of the ketyl radical onto this nearer alkene carbon closes a

new five-membered ring, a 5-exo-trig radical cyclization, strongly favored kinetically over larger ring sizes. This forms a new carbon-carbon bond and fuses a second five-membered ring onto the original cyclopentane, giving a bicyclic, hydrindane-type, fused 5,5-bicyclic skeleton.

**Step 4:** Follow the radical onto the ester and quench with MeOH.
After the new C–C bond forms, the radical, or after a second electron transfer the samarium enolate, sits on the carbon alpha to the ester carbonyl, stabilized by conjugation with the $CO_2Me$ group. MeOH, added at the end, protonates this samarium enolate at the alpha carbon, restoring a simple $-CH_2-CO_2Me$ group, the carbon-carbon double bond of the original unsaturated ester is gone, consumed in forming the new ring bond. Meanwhile, the original ketone oxygen, now on the ring-fusion carbon, is protonated to a tertiary alcohol once the ketyl electron pair is used to make the new C–C bond.

**Step 5:** Assemble the product.
The product is a bicyclic, fused 5,5, hydrocarbon skeleton carrying a tertiary OH at the ring-fusion carbon, from the reduced ketone, and a pendant $-CH_2-CO_2Me$ group on the new ring, exactly as drawn in option (B).

**Why the other options are wrong:**
Option (A) shows an oxygen-containing six-membered ring (a pyran), which would only form if the ketyl oxygen itself, rather than the ketyl carbon, made the new bond to the alkene, that is not how $SmI_2$ ketyl-olefin cyclizations work, the new bond forms at carbon.
Option (D) likewise shows an oxygen in the new ring (an oxepane), for the same reason, this does not match a carbon-radical cyclization.
Option (C) shows a six-membered carbocycle fused to the

cyclopentane, with the ester carbon directly attached to the ring, corresponding to a 6-exo cyclization pathway with no $CH_2$ linker left over, which does not match the atom count of the actual tether, the tether length gives 5-exo, forming a five-membered ring with a pendant $CH_2CO_2Me$, not a direct ring-fused ester.

**Final Answer:**

The product of the $SmI_2$-mediated ketyl-olefin radical cyclization, quenched with $MeOH$, is the fused bicyclic alcohol with a pendant $-CH_2CO_2Me$ group shown in option (B).

$$\boxed{(B)}$$

**Quick Tip:** $SmI_2$ reduces the ketone to a ketyl radical that cyclizes onto the tethered $\alpha,\beta$-unsaturated ester through carbon, not oxygen; count the chain length to see it is a 5-exo-trig cyclization, giving a fused bicyclic alcohol with a pendant $CH_2CO_2Me$ group after the $MeOH$ quench.

**15.** The species that undergoes $\beta$-elimination is

(A) $[Rh(C_5H_5)(P(CH_3)_3)(C_2H_5)]^+$

(B) $[Rh(NH_3)_5(C_2H_5)]^{2+}$

(C) $[Pt(P(C_6H_5)_3)_2(C_6H_5)I]$

(D) $[Cr(CH_2Si(CH_3)_3)_4]$

**Correct Answer:** (A) $[Rh(C_5H_5)(P(CH_3)_3)(C_2H_5)]^+$

**Solution:**

**Step 1:** Recall what beta-hydride elimination needs.

$\beta$-hydride elimination is the reverse of alkene insertion, a hydrogen

on the carbon beta to the metal moves onto the metal, forming a metal hydride and releasing, or coordinating, an alkene. Two things are needed: (1) a hydrogen present on the carbon beta to the metal, in a geometry that can reach the metal, and (2) an open, cis coordination site on the metal for the developing metal-hydride and alkene to occupy, since the transition state needs the alkyl and the vacant site to be cis, going through an agostic interaction. A coordinatively saturated, 18-electron, complex cannot do this even if the beta-hydrogen is present, because there is nowhere for the mechanism to go.

**Step 2:** Check option (A), $[Rh(C_5H_5)(PMe_3)(C_2H_5)]^+$.
Counting electrons ionically: Rh here is Rh(III), $d^6$ (6 electrons), $\eta^5$-$C_5H_5^-$ donates 6 electrons, $PMe_3$ donates 2 electrons, and the ethyl group donates 2 electrons: $6 + 6 + 2 + 2 = 16$ electrons. This is a 16-electron, coordinatively unsaturated complex, so it has an open coordination site cis to the ethyl group. The ethyl group has beta-hydrogens, on its $CH_3$ carbon, and the vacant site lets the molecule reach the four-centered agostic transition state needed for $\beta$-hydride elimination. This complex readily undergoes $\beta$-hydride elimination.

**Step 3:** Check option (B), $[Rh(NH_3)_5(C_2H_5)]^{2+}$.
This is an octahedral, six-coordinate Rh(III) complex with all six sites occupied by strong $\sigma$-donor ligands (five $NH_3$ plus the ethyl group), giving an 18-electron, coordinatively saturated center. Even though the ethyl group has beta-hydrogens, there is no open cis site for the elimination pathway, so this complex is stable toward $\beta$-hydride elimination, a classic textbook example of a saturated alkyl complex that does not eliminate.

**Step 4:** Check option (C), $[Pt(PPh_3)_2(C_6H_5)I]$.

This square-planar Pt(II), 16-electron complex does have an accessible open site, square-planar $d^8$ complexes are coordinatively unsaturated, but the group here is a phenyl, an aromatic ring bonded to the metal through an $sp^2$ carbon. The carbons "beta" to platinum are the aromatic ring carbons, and removing one of their hydrogens as a beta-hydride would break the aromaticity of the ring, far too costly energetically. Phenyl, and other aryl or vinyl, groups have no accessible $\beta$-hydrogens for this pathway, so this complex cannot undergo $\beta$-hydride elimination despite being unsaturated.

**Step 5:** Check option (D), $[Cr(CH_2Si(CH_3)_3)_4]$.
The ligand here is $-CH_2Si(CH_3)_3$, trimethylsilylmethyl. The carbon directly bonded to chromium is $CH_2$, and the atom beta to the metal is silicon, not carbon. There is no beta carbon-hydrogen bond at all in this ligand, only a beta Si–C bond, so the whole $\beta$-hydride elimination pathway is structurally unavailable. This is exactly why $CH_2SiMe_3$, like neopentyl, is a favorite ligand for making stable homoleptic high-oxidation-state alkyl complexes.

**Final Answer:**
Only the 16-electron, coordinatively unsaturated ethyl complex in option (A) has both a beta-hydrogen and the open site needed to use it.

$\boxed{(A)}$

**Quick Tip:** Beta-hydride elimination needs BOTH a hydrogen on the beta carbon AND an open coordination site cis to the alkyl group; check the electron count for a vacant site, and check whether the beta position is even a carbon with an H, phenyl and $CH_2SiMe_3$ fail this second test.

**16.** According to molecular orbital theory, the correct ground state electronic configuration for $[Co(NH_3)_6]^{3+}$ ion is

(A) $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^6\ e_g^{*0}$

(B) $a_{1g}^2\ t_{1u}^6\ t_{2g}^6\ e_g^4\ e_g^{*0}$

(C) $t_{1u}^6\ a_{1g}^2\ e_g^4\ t_{2g}^6\ e_g^{*0}$

(D) $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^4\ e_g^{*2}$

**Correct Answer:** (A) $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^6\ e_g^{*0}$

**Solution:**

**Step 1:** Set up the octahedral MO picture for a sigma-only ligand set.
$NH_3$ is a pure $\sigma$-donor with no $\pi$-donor or $\pi$-acceptor orbitals of the right symmetry to interact strongly with the metal $d$ orbitals. In the standard octahedral MO diagram built from six $\sigma$-donor ligands, the metal's $s$, $p_x$, $p_y$, $p_z$, and the two $e_g$-symmetry $d$ orbitals ($d_{z^2}, d_{x^2-y^2}$) combine with the six ligand $\sigma$ symmetry-adapted combinations to give bonding molecular orbitals of symmetry $a_{1g}$ (from $s$), $t_{1u}$ (from the three $p$ orbitals), and $e_g$ (from the two matching $d$ orbitals), together with matching antibonding $a_{1g}^*, t_{1u}^*, e_g^*$ orbitals. The remaining three metal $d$ orbitals ($d_{xy}, d_{xz}, d_{yz}$, symmetry $t_{2g}$) have no matching $\sigma$-symmetry combination on the ligands, so they stay essentially non-bonding, sitting in energy between the bonding $e_g$ set and the antibonding $e_g^*$ set.
The energy order from lowest to highest is therefore: $a_{1g} < t_{1u} < e_g$ (all bonding) $< t_{2g}$ (non-bonding) $< e_g^*$ (antibonding).

**Step 2:** Fill the bonding orbitals with the ligand electrons.
Each of the six $NH_3$ ligands donates one lone pair (2 electrons) to the complex, giving $6 \times 2 = 12$ electrons total from the ligands. These 12

electrons exactly fill the three bonding molecular orbitals: $a_{1g}^2\ t_{1u}^6\ e_g^4$ ($2+6+4=12$).

**Step 3:** Place the metal's $d$ electrons in $t_{2g}$ and $e_g^*$.

Co in $[Co(NH_3)_6]^{3+}$ is Co(III), a $d^6$ ion. These six $d$ electrons occupy the remaining, higher-energy orbitals, the non-bonding $t_{2g}$ set first, then the antibonding $e_g^*$ set. $NH_3$ is a reasonably strong-field ligand, and $[Co(NH_3)_6]^{3+}$ is a well known diamagnetic, low-spin complex, so all six $d$ electrons pair up in the lower-energy, non-bonding $t_{2g}$ orbitals before any electron occupies the higher-energy, antibonding $e_g^*$ orbitals. This gives $t_{2g}^6\ e_g^{*0}$.

**Step 4:** Assemble the full configuration.

Putting the bonding-orbital and metal-$d$-orbital electrons together in the correct energy order gives: $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^6\ e_g^{*0}$.

**Why the other options are wrong:**

Option (B) lists the orbitals as $a_{1g}^2\ t_{1u}^6\ t_{2g}^6\ e_g^4\ e_g^{*0}$, placing the non-bonding $t_{2g}$ set below the bonding $e_g$ set. That is the wrong energy order, the bonding $e_g$, filled by ligand electrons, always lies below the non-bonding, purely metal-centered $t_{2g}$ set.

Option (C) lists $t_{1u}$ before $a_{1g}$, reversing the correct order of the two lowest bonding orbitals; $a_{1g}$, from the metal $s$ orbital, lies below $t_{1u}$, from the metal $p$ orbitals, in the standard octahedral MO diagram.

Option (D), $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^4\ e_g^{*2}$, keeps the correct orbital order but places only 4 of the 6 metal $d$ electrons in $t_{2g}$ and promotes 2 electrons into the antibonding $e_g^*$ set, the high-spin $d^6$ pattern. $[Co(NH_3)_6]^{3+}$ is experimentally diamagnetic and low-spin, so this weak-field-style population is not correct for this complex.

**Final Answer:**

$$\boxed{a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^6\ e_g^{*0}}$$

**Quick Tip:** For a sigma-only ligand set, the MO energy order is $a_{1g} < t_{1u} < e_g$ (bonding) $< t_{2g}$ (non-bonding) $< e_g^*$ (antibonding); fill 12 ligand electrons into the bonding set, then place Co(III)'s 6 $d$ electrons in the low-spin $t_{2g}^6$ configuration, since $[Co(NH_3)_6]^{3+}$ is diamagnetic.

**17.** The species which follows the 18-electron rule is
($en$ = ethylenediamine)

(A) $[Rh(PPh_3)_3Cl]$

(B) $[Co(NH_3)_6]^{2+}$

(C) $[V(CO)_6]^-$

(D) $[Ni(en)_3]^{2+}$

**Correct Answer:** (C) $[V(CO)_6]^-$

**Solution:**

**Step 1:** Understanding the Concept.
The 18-electron rule says a stable transition metal complex tends to have a total valence electron count of 18 around the metal, the same count as the next noble gas. Use the ionic method: write the metal in its actual oxidation state, take its d-electron count, then add 2 electrons for every neutral donor (L-type) ligand and 2 electrons for every anionic donor (X-type ligand counted as a 2-electron donor once it is written as an anion).

**Step 2:** Count option (A), $[Rh(PPh_3)_3Cl]$.
The complex is neutral and $Cl$ is written as $Cl^-$, so $Rh$ must be $Rh(I)$,

which is $d^8$ (8 electrons). Each $PPh_3$ donates 2 electrons: $3 \times 2 = 6$. $Cl^-$ donates 2 electrons.
Total $= 8 + 6 + 2 = 16$ electrons. This is Wilkinson's catalyst, a well known 16-electron, coordinatively unsaturated square planar complex, not 18.

**Step 3:** Count option (B), $[Co(NH_3)_6]^{2+}$.
$Co$ here is $Co(II)$, which is $d^7$ (7 electrons). Each neutral $NH_3$ donates 2 electrons: $6 \times 2 = 12$.
Total $= 7 + 12 = 19$ electrons, an odd number, so it cannot be 18. This matches the fact that $[Co(NH_3)_6]^{2+}$ is a paramagnetic, high spin $d^7$ complex.

**Step 4:** Count option (C), $[V(CO)_6]^-$.
The complex carries a $-1$ charge and all 6 $CO$ ligands are neutral, so $V$ must be in the $-1$ oxidation state. Neutral $V$ is a group 5 metal with 5 valence electrons, so $V(-I)$ has $5 + 1 = 6$ d-electrons. Each $CO$ donates 2 electrons: $6 \times 2 = 12$.
Total $= 6 + 12 = 18$ electrons. This fits the 18-electron rule exactly, which is why the 17-electron neutral radical $V(CO)_6$ is so easily reduced to the stable, closed shell 18-electron anion $[V(CO)_6]^-$.

**Step 5:** Count option (D), $[Ni(en)_3]^{2+}$.
$Ni$ here is $Ni(II)$, which is $d^8$ (8 electrons). $en$ (ethylenediamine) is a bidentate, neutral donor, so each $en$ contributes 2 donor atoms $\times$ 2 electrons $= 4$ electrons; three $en$ ligands give $3 \times 4 = 12$ electrons.
Total $= 8 + 12 = 20$ electrons, above 18, consistent with $[Ni(en)_3]^{2+}$ being an octahedral $d^8$ complex that does not need to obey the 18-electron rule.

**Final Answer:**

Only $[V(CO)_6]^-$ has exactly 18 valence electrons at the metal.

$$\boxed{\text{(C) } [V(CO)_6]^-}$$

**Quick Tip:** Use the ionic method: d-electron count of the metal in its real oxidation state, plus 2 electrons for every 2-electron donor ligand (including bidentate ligands counted twice); look for a total of 18.

**18.** The point group of $CH_2 = C = CH_2$ is

(A) $D_{2h}$

(B) $C_{2h}$

(C) $C_{2v}$

(D) $D_{2d}$

**Correct Answer:** (D) $D_{2d}$

**Solution:**

**Step 1:** Understanding the Concept.

$CH_2 = C = CH_2$ is allene (propa-1,2-diene). The central carbon is $sp$ hybridized and forms two mutually perpendicular $\pi$ bonds, one to each terminal $CH_2$ carbon. Because the two $\pi$ bonds use orthogonal p-orbitals on the central carbon, the two $= CH_2$ planes at the two ends of the molecule are twisted 90 degrees relative to each other.

**Step 2:** List the symmetry elements.

Take the $C = C = C$ axis as the principal axis. Because the two $CH_2$ planes are perpendicular, rotating the molecule by 90 degrees about

this axis and then reflecting through a plane perpendicular to the axis maps the molecule onto itself, so there is an $S_4$ axis along $C = C = C$. There are also two $C_2$ axes perpendicular to the $S_4$ axis, each one bisecting the $H - C - H$ angle of one terminal $CH_2$ group, and two dihedral mirror planes $\sigma_d$, each containing the $S_4$ axis and one $CH_2$ group.

There is no horizontal mirror plane $\sigma_h$ perpendicular to the $S_4$ axis (that would require both $CH_2$ planes to be coplanar, which they are not), and there is no center of inversion.

**Step 3:** Identify the point group.

A molecule with a principal $S_{2n}$ axis, $n$ perpendicular $C_2$ axes, $n$ dihedral mirror planes $\sigma_d$, and no $\sigma_h$ belongs to the $D_{nd}$ family. Here $n = 2$ (the $S_4$ axis plus two $C_2$ axes plus two $\sigma_d$ planes), so the point group is $D_{2d}$.

**Step 4:** Rule out the other options.

$D_{2h}$ and $C_{2h}$ both require a center of inversion and/or a $\sigma_h$, which allene does not have because its two $CH_2$ ends are perpendicular, not coplanar. $C_{2v}$ would apply if the whole molecule were planar with a single mirror plane containing all the atoms, which is also not the case here since the two ends are twisted out of a common plane.

**Final Answer:**

Allene, $CH_2 = C = CH_2$, belongs to the $D_{2d}$ point group.

$$\boxed{\text{(D) } D_{2d}}$$

**Quick Tip:** Draw allene in 3D: the two terminal $CH_2$ planes are perpendicular because the central carbon uses two orthogonal p orbitals for

its two $\pi$ bonds; look for an $S_4$ axis along $C = C = C$.

**19.** Among the following, the one for which the infrared active vibrational modes are Raman inactive and vice versa is

(A) $H_2O$

(B) *trans*-planar conformer of $H_2O_2$

(C) eclipsed conformer of ethane

(D) $CH_4$

**Correct Answer:** (B) *trans*-planar conformer of $H_2O_2$

**Solution:**

**Step 1:** Understanding the Concept.

The behavior described, every IR active mode being Raman inactive and every Raman active mode being IR inactive, is called the rule of mutual exclusion. This rule applies only to molecules that have a center of inversion (a center of symmetry, $i$). In a centrosymmetric molecule, a vibration either keeps its sign under inversion (symmetric, $g$) or changes sign (antisymmetric, $u$); IR activity needs a mode that transforms like $x, y, z$ (always $u$), while Raman activity needs a mode that transforms like a quadratic function such as $x^2, xy$ (always $g$), so no single mode can ever be both.

**Step 2:** Check option (A), $H_2O$.

Water is bent, point group $C_{2v}$, which has no center of inversion. All three vibrational modes of water (symmetric stretch, bend, asymmetric stretch) are both IR and Raman active, so it does not obey mutual exclusion.

**Step 3:** Check option (B), *trans*-planar $H_2O_2$.

If $H_2O_2$ is forced into the fully planar, trans (anti) arrangement, with both $O-H$ bonds and the $O-O$ bond all in one plane and the two $H$ atoms on opposite sides of the $O-O$ bond, the molecule has a $C_2$ axis, a horizontal mirror plane (the molecular plane itself), and a center of inversion at the midpoint of the $O-O$ bond. This combination of elements is the point group $C_{2h}$, which does have a center of symmetry $i$.

Because it is centrosymmetric, every vibration of trans-planar $H_2O_2$ splits cleanly into $A_g/B_g$ modes (Raman active, IR inactive) and $A_u/B_u$ modes (IR active, Raman inactive), so it obeys mutual exclusion exactly.

**Step 4:** Check options (C) and (D).

The eclipsed conformer of ethane has point group $D_{3h}$; this has a $\sigma_h$ but no center of inversion (it is the staggered conformer, $D_{3d}$, that has $i$, not the eclipsed one), so mutual exclusion does not apply to eclipsed ethane. $CH_4$ is tetrahedral, point group $T_d$, which also has no center of inversion, so it too does not follow mutual exclusion (its IR and Raman active modes overlap for some vibrations).

**Final Answer:**

Only the trans-planar conformer of $H_2O_2$ has a center of symmetry, so it is the one that shows perfect mutual exclusion between IR and Raman activity.

$$\boxed{\text{(B) trans-planar } H_2O_2}$$

**Quick Tip:** The rule of mutual exclusion (IR active modes are Raman silent and vice versa) works only for molecules with a center of inversion; check

which option has an *i*.

**20.** For the following reaction,

$A + B \rightleftharpoons X^{\ddagger} \rightarrow$ product

If the value of $\Delta^{\ddagger}U^{o} = \frac{5}{2}RT$, then the value of $\Delta^{\ddagger}H^{o}$ is

($X^{\ddagger}$ is an activated complex; $\Delta^{\ddagger}U^{o}$ is the standard change in internal energy; $\Delta^{\ddagger}H^{o}$ is the standard enthalpy of activation; $R$ is the gas constant; $T$ is the temperature)

(A) $\frac{1}{2}RT$

(B) $\frac{3}{2}RT$

(C) $\frac{7}{2}RT$

(D) $\frac{5}{2}RT$

**Correct Answer:** (B) $\frac{3}{2}RT$

**Solution:**

**Step 1:** Understanding the Question.

In transition state theory, two reactant molecules $A$ and $B$ come together to form one activated complex $X^{\ddagger}$, which then goes on to product. We are given the standard internal energy of activation, $\Delta^{\ddagger}U^{o} = \frac{5}{2}RT$, and asked for the standard enthalpy of activation, $\Delta^{\ddagger}H^{o}$.

**Step 2:** Key Formula.

For a process at constant pressure involving ideal gases, enthalpy and internal energy are related by $H = U + PV$, so a change obeys $\Delta H = \Delta U + \Delta(PV)$. For ideal gases, $PV = nRT$, so at constant temperature

$\Delta(PV) = \Delta n_{gas} RT$, where $\Delta n_{gas}$ is the change in the number of moles of gas going from reactants to the species being formed. Applied to activation,

$$\Delta^{\ddagger} H^{o} = \Delta^{\ddagger} U^{o} + \Delta n^{\ddagger} RT$$

**Step 3:** Find $\Delta n^{\ddagger}$.

The reaction is $A + B \rightarrow X^{\ddagger}$: two moles of reactant gas combine into one mole of activated complex. So

$$\Delta n^{\ddagger} = (\text{moles of } X^{\ddagger}) - (\text{moles of } A + B) = 1 - 2 = -1$$

**Step 4:** Substitute and calculate.

$$\Delta^{\ddagger} H^{o} = \frac{5}{2} RT + (-1) RT = \frac{5}{2} RT - RT = \frac{5-2}{2} RT = \frac{3}{2} RT$$

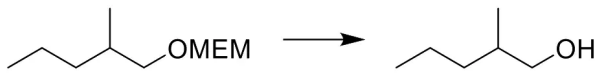
**Final Answer:**

The standard enthalpy of activation is $\frac{3}{2} RT$, smaller than $\Delta^{\ddagger} U^{o}$ because the number of gas moles decreases by 1 on forming the activated complex.

$$\boxed{\Delta^{\ddagger} H^{o} = \frac{3}{2} RT}$$

**Quick Tip:** Use $\Delta H^{\ddagger} = \Delta U^{\ddagger} + \Delta n^{\ddagger} RT$ with $\Delta n^{\ddagger} = 1 - 2 = -1$ since two molecules combine into one activated complex.

**21.** The reagent(s) that will effect the following transformation is(are)




MEM = methoxyethoxymethyl

(MEM = methoxyethoxymethyl)

(A) $Pd/C, H_2$

(B) $ZnBr_2$

(C) Pyridinium *p*-toluenesulfonate (PPTS), $^tBuOH$

(D) $^nBu_4NF$

**Correct Answer:** (B) $ZnBr_2$ ; (C) Pyridinium *p*-toluenesulfonate (PPTS), $^tBuOH$

**Solution:**

**Step 1:** Understanding the Question.

The starting material is an alcohol protected as its MEM ether (a $-O-CH_2-O-CH_2CH_2-OCH_3$ acetal-type group attached to the alcohol oxygen), and the product is the free primary alcohol. So we need reagent(s) that selectively remove a MEM protecting group without touching anything else in the molecule.

**Step 2:** Key idea, how a MEM ether is removed.

A MEM ether is essentially a mixed acetal (formaldehyde acetal of the substrate alcohol and 2-methoxyethanol). It is cleaved by activating that acetal center, either with a Lewis acid that coordinates to one of the acetal oxygens and helps expel the alkoxide, or with a mild Bronsted acid catalyst in a protic solvent that protonates an acetal oxygen and does the same job, in both cases regenerating the free

alcohol plus formaldehyde and 2-methoxyethanol as byproducts.

**Step 3:** Evaluate option (A), $Pd/C, H_2$.
This is a hydrogenolysis condition, used to cleave benzylic C-O bonds (as in a benzyl ether) or to reduce alkenes/alkynes. The MEM acetal has no benzylic C-O bond and no unsaturation to hydrogenate, so $Pd/C, H_2$ does nothing to it. Wrong.

**Step 4:** Evaluate option (B), $ZnBr_2$.
$ZnBr_2$ is a classic mild Lewis acid used specifically to cleave MEM ethers (in a solvent like $CH_2Cl_2$). It coordinates to the acetal oxygen, weakens the $C-O$ bond to the alcohol oxygen, and lets the free alcohol leave as the MEM group is expelled as an oxocarbenium species that is trapped and destroyed. This is a textbook MEM deprotection reagent. Correct.

**Step 5:** Evaluate option (C), PPTS, $^tBuOH$.
Pyridinium $p$-toluenesulfonate is a very mild proton source. In a protic solvent such as $^tBuOH$ under reflux, catalytic PPTS protonates the acetal oxygen of the MEM group and promotes its hydrolysis/solvolysis back to the free alcohol, a standard mild-acid method for removing MEM (and THP) ethers. Correct.

**Step 6:** Evaluate option (D), $^nBu_4NF$ (TBAF).
Fluoride is a specific reagent for cleaving silicon-oxygen bonds in silyl ethers ($TMS$, $TBS$, $TIPS$), because fluoride has an extremely strong affinity for silicon. The MEM group has no silicon in it, so TBAF does not touch it. Wrong.

**Final Answer:**

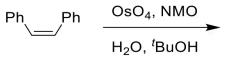
The reagents that remove the MEM group and reveal the free alcohol are $ZnBr_2$ and PPTS/$^tBuOH$.

**(B) and (C)**

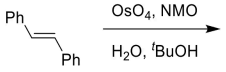
**Quick Tip:** MEM is an acetal-type protecting group; look for a mild Lewis acid or Bronsted acid in a protic solvent, not a hydrogenolysis or fluoride reagent (those remove different protecting groups).

**22.** The reaction(s) that give(s) *meso*-1,2-diphenylethane-1,2-diol as the major product is(are)

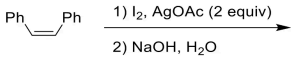
(A)



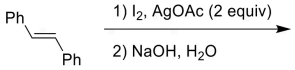

(B)




(C)

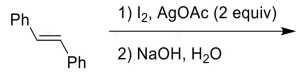



(D)



**Correct Answer:** (A)

; (D)




**Solution:**

**Step 1:** Understanding the Question.

1,2-diphenylethane-1,2-diol (hydrobenzoin) has two adjacent stereocenters that carry an identical set of substituents on each side ( $Ph$, $OH$, $H$, and the other stereocenter). A molecule like this can exist as a meso form (an internal mirror plane relates the two centers, overall achiral) or as a pair of enantiomers, the $(R,R)$ and $(S,S)$ forms (chiral, optically active, formed together as a racemic, $d,l$ mixture from an achiral starting alkene). We need to work out which combination of alkene geometry (cis or trans stilbene) and addition mechanism (syn or anti) gives the meso product.

**Step 2:** The general stereochemical rule for 1,2-diaryl alkenes.

For a symmetric alkene $Ph-CH=CH-Ph$, *syn* (cis) addition of two $OH$ groups to the *cis* (Z) alkene gives the *meso* diol, while syn addition to the *trans* (E) alkene gives the chiral $d,l$ pair. *Anti* (trans) addition of two $OH$ groups to the *cis* (Z) alkene gives the chiral $d,l$ pair, while anti addition to the *trans* (E) alkene gives the *meso* diol. In short: (cis alkene + syn addition) and (trans alkene + anti addition) both give meso; the other two combinations give the racemic pair.

**Step 3:** Identify the addition mode for each reagent set.

$OsO_4$, $NMO$ dihydroxylation proceeds through a cyclic osmate ester

that delivers both new $C-O$ bonds from the same face of the double bond, so it is a *syn*-dihydroxylation.
$I_2, AgOAc$ (2 equiv), followed by $NaOH, H_2O$ is the Prevost reaction: the alkene first forms an iodonium ion that is opened by a neighboring acetate (from the second equivalent of $AgOAc$) from the face opposite the iodine, and hydrolysis of the resulting diester with aqueous base retains that opposite-face relationship. Because water is only introduced in the hydrolysis step and not during the iodination step, this is the dry (Prevost) pathway, which delivers the two oxygens to opposite faces overall, an *anti*-dihydroxylation.

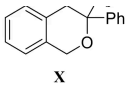
**Step 4:** Apply the rule to each option.
(A) *cis*-stilbene + $OsO_4/NMO$ (syn) → cis alkene with syn addition → **meso** diol. Correct.
(B) *trans*-stilbene + $OsO_4/NMO$ (syn) → trans alkene with syn addition → chiral $d, l$ pair, not meso. Wrong.
(C) *cis*-stilbene + $I_2/AgOAc$ then $NaOH/H_2O$ (anti) → cis alkene with anti addition → chiral $d, l$ pair, not meso. Wrong.
(D) *trans*-stilbene + $I_2/AgOAc$ then $NaOH/H_2O$ (anti) → trans alkene with anti addition → **meso** diol. Correct.

**Final Answer:**
Reactions (A) and (D) give meso-1,2-diphenylethane-1,2-diol as the major product.

$$\boxed{\text{(A) and (D)}}$$

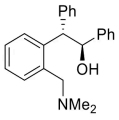
**Quick Tip:** Remember: cis alkene + syn addition = meso; trans alkene + anti addition = meso; the other two combinations give the chiral $d, l$ pair. $OsO_4/NMO$ is syn; $I_2/AgOAc$ then hydrolysis (Prevost) is anti.

**23.** In the $^1$H NMR spectrum of compound **X**, the coupling constant ($J_{ab}$) between $H_a$ and $H_b$ is 3 Hz. The amino alcohol(s) that give(s) **X** on reaction with methyl iodide followed by heating is(are)

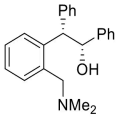



X

(A)




(B)

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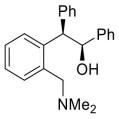
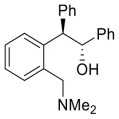
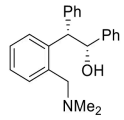


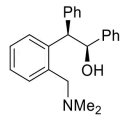

(D)



**Correct Answer:** (B)




; (C)




**Solution:**

**Step 1:** Understanding the Question.

Each amino alcohol has the skeleton $Ar(CH_2NMe_2) - CH(Ph) - CH(Ph) - OH$, where the benzene ring carries an ortho $CH_2NMe_2$ group and the side chain carries two adjacent stereocenters, each bearing a phenyl group. Treating this with excess methyl iodide first converts the tertiary amine $NMe_2$ into a quaternary ammonium salt, $CH_2\overset{+}{N}Me_3\,I^-$. On heating, the alcohol oxygen performs an intramolecular $S_N2$ attack on that benzylic $CH_2$ carbon, displacing neutral $NMe_3$ as the leaving group and closing a six-membered ring, giving the cyclic benzo-fused ether **X** (a 3,4-diphenylisochroman), with $H_a$ and $H_b$ as the two ring protons on the former stereocenters.

**Step 2:** The key mechanistic point, what stays the same and what changes.

The bond-forming step of the cyclization happens at the $CH_2 - NMe_3^+$ carbon, which is not a stereocenter (it only carries two hydrogens). The two real stereocenters, the ones bearing the phenyl groups, are never touched during this step. So the relative configuration between the two *Ph*-bearing centers in the starting amino alcohol (whether the

two phenyls are disposed "like," i.e. $(R,R)/(S,S)$, or "unlike," i.e. $(R,S)/(S,R)$) carries straight through unchanged into ring-closed product **X**.

**Step 3:** Use the coupling constant to fix the relative configuration in **X**.

Once the ring is closed, $H_a$ and $H_b$ sit on adjacent ring carbons in a rigid, benzo-fused six-membered ring, so their vicinal coupling constant $J_{ab}$ is governed by the Karplus relation, which links $J$ to the $H-C-C-H$ dihedral angle: $J$ is largest when the dihedral is near $0°$ or $180°$ (typically 8 to 12 Hz) and smallest when the dihedral is near $90°$ (close to 0 to 3 Hz). The observed small $J_{ab} = 3$ Hz therefore corresponds to the diastereomer whose ring conformation places $H_a$ and $H_b$ close to a $90°$ dihedral, which is the relative configuration where the two phenyl groups are on the "unlike" disposition, forcing the two ring hydrogens into a near-perpendicular arrangement rather than the near-antiperiplanar arrangement of the other diastereomer (which would show a much larger $J$, around 8 to 11 Hz).

**Step 4:** Match this back to the drawn amino alcohols and account for enantiomers.

A coupling constant depends only on the relative configuration between $H_a$ and $H_b$, not on which enantiomer is used, since enantiomers are mirror images with identical NMR spectra in an achiral environment. Among the four drawn amino alcohols, they form two enantiomeric pairs, one pair sharing the diastereomeric relationship required in Step 3, the other pair sharing the opposite one. Only the pair with the required "unlike" relative configuration reacts to give **X** with $J_{ab} = 3$ Hz; each member of that enantiomeric pair independently cyclizes (with retention of that relative configuration) to give racemic **X** showing exactly the same, correct

coupling constant. Structures B and C are that matching enantiomeric pair, while A and D are the enantiomeric pair of the other diastereomer, which would give a much larger $J_{ab}$ and so are excluded.

**Final Answer:**

The amino alcohols that give **X** with $J_{ab} = 3$ Hz are the enantiomeric pair (B) and (C).

$$\boxed{\text{(B) and (C)}}$$

**Quick Tip:** MeI quaternizes $NMe_2$; heating closes the ring by intramolecular $S_N2$ at the non-stereogenic $CH_2$ carbon, so the relative configuration of the two Ph-bearing centers is unchanged. Use the Karplus relation ($J$ small near 90° dihedral) to pick the diastereomer, then include both its enantiomers.

**24.** The correct statement(s) regarding plastocyanin is(are)

(A) It is an electron transfer protein

(B) It is intensely colored in its oxidised form

(C) Its central metal ion has a distorted tetrahedral geometry

(D) It contains $S^{2-}$ bridged metal cluster

**Correct Answer:** (A) It is an electron transfer protein ; (B) It is intensely colored in its oxidised form ; (C) Its central metal ion has a distorted tetrahedral geometry

**Solution:**

**Step 1:** Understanding the Concept.

Plastocyanin is a small, single-copper, "blue copper" (type 1 copper) metalloprotein found in the chloroplasts of plants and algae. It works in the photosynthetic electron transport chain, carrying a single electron from the cytochrome $b_6f$ complex to photosystem I.

**Step 2:** Evaluate statement (A).

Since its entire biological job is to pick up one electron at cytochrome $b_6f$ and hand it off to photosystem I, plastocyanin is, by definition, an electron transfer protein, not an enzyme that catalyzes a chemical transformation. Correct.

**Step 3:** Evaluate statement (B).

The copper center cycles between $Cu(II)$ (oxidised) and $Cu(I)$ (reduced) as it shuttles the electron. In the oxidised $Cu(II)$ state, a cysteine thiolate sulfur bound to the copper undergoes an unusually intense ligand to metal charge transfer ($S(Cys) \rightarrow Cu(II)$) transition around 600 nm, which is what gives blue copper proteins like plastocyanin their strong blue color; this band disappears (colorless) once the copper is reduced to $Cu(I)$, a $d^{10}$ ion with no available charge transfer of that kind. So plastocyanin is indeed intensely colored specifically in its oxidised form. Correct.

**Step 4:** Evaluate statement (C).

The type 1 copper site in plastocyanin is coordinated by two histidine nitrogens, one cysteine thiolate sulfur, and one weakly bound methionine thioether sulfur. This four-coordinate arrangement is not a regular tetrahedron; it is best described as a distorted (flattened) tetrahedral geometry, intermediate between the tetrahedral geometry preferred by $Cu(I)$ ($d^{10}$) and the square planar geometry preferred by $Cu(II)$ ($d^9$). This "entatic state" geometry is what lets the copper

switch oxidation states with very little structural reorganization, making electron transfer fast. Correct.

**Step 5:** Evaluate statement (D).
An $S^{2-}$ (sulfide) bridged metal cluster describes iron-sulfur proteins, such as ferredoxins with $[2Fe-2S]$ or $[4Fe-4S]$ clusters, not plastocyanin. Plastocyanin has only one metal ion (mononuclear copper) and no bridging sulfide at all; its only sulfur donors are the neutral thioether of methionine and the thiolate of a single cysteine, neither of which bridges two metals. Wrong.

**Final Answer:**
Statements (A), (B), and (C) correctly describe plastocyanin; statement (D) describes an iron-sulfur cluster protein instead.

$$\boxed{\text{(A), (B), and (C)}}$$

**Quick Tip:** Plastocyanin is a mononuclear type 1 "blue copper" electron-transfer protein with a distorted tetrahedral $Cu(His)_2(Cys)(Met)$ site; sulfide-bridged clusters belong to iron-sulfur proteins, not blue copper proteins.

**25.** The correct statement(s) about Mossbauer spectroscopy of iron compounds is(are)

(A) $^{57}Co$ is used as a source

(B) Their Mossbauer spectra are obtained using $\gamma$-ray with resonance energy of 14.4 keV

(C) $K_2[Fe(CN)_5NO]$ shows large quadrupole splitting

(D) Isomer shift of $FeSO_4 \cdot 7H_2O$ is smaller than that of $K_3[Fe(CN)_6]$

**Correct Answer:** (A) $^{57}Co$ is used as a source ; (B) Their Mossbauer spectra are obtained using $\gamma$-ray with resonance energy of 14.4 keV ; (C) $K_2[Fe(CN)_5NO]$ shows large quadrupole splitting

**Solution:**

**Step 1:** Understand the Mossbauer setup for iron.
Mossbauer spectroscopy of $^{57}Fe$ needs a gamma-ray source that decays into the correct excited nuclear state of iron. The parent isotope $^{57}Co$ decays by electron capture to an excited state of $^{57}Fe$, which then drops to the ground state and gives out a 14.4 keV gamma-ray. This gamma-ray is resonantly absorbed by $^{57}Fe$ nuclei in the sample, so $^{57}Co$ is the standard source. Statement (A) is correct.

**Step 2:** Check the resonance energy value.
The nuclear transition used in $^{57}Fe$ Mossbauer spectroscopy is the $3/2 \rightarrow 1/2$ transition of the $^{57}Fe$ nucleus, and its energy is fixed at 14.4 keV. This is the standard, well known value quoted for all iron Mossbauer work. Statement (B) is correct.

**Step 3:** Look at the quadrupole splitting of $K_2[Fe(CN)_5NO]$.
Quadrupole splitting comes from an electric field gradient at the iron nucleus, which grows when the electron density around iron is not symmetric. In $K_2[Fe(CN)_5NO]$ (the nitroprusside type ion), the strong pi-acceptor NO ligand is very different from the five CN ligands, so the field around iron is heavily distorted along the Fe-NO direction. This asymmetry gives a large electric field gradient, and hence a large quadrupole splitting, one of the biggest seen among iron nitrosyl-cyanide complexes. Statement (C) is correct.

**Step 4:** Compare isomer shifts of $FeSO_4 \cdot 7H_2O$ and $K_3[Fe(CN)_6]$.

Isomer shift depends on the s-electron density at the iron nucleus: more s-density gives a smaller (more negative) isomer shift. $FeSO_4 \cdot 7H_2O$ has high spin $Fe^{2+}$ ($d^6$), and its extra d-electrons shield the s-electrons from the nucleus, lowering the s-density there and pushing the isomer shift to a larger, positive value (about 1.2 to 1.4 mm/s). $K_3[Fe(CN)_6]$ has low spin $Fe^{3+}$ ($d^5$), where the strong field CN ligands pair up the electrons and the smaller d-shielding lets s-density at the nucleus stay higher, giving a small isomer shift close to zero (about -0.1 mm/s). So the isomer shift of $FeSO_4 \cdot 7H_2O$ is actually larger, not smaller, than that of $K_3[Fe(CN)_6]$. Statement (D) is wrong.

**Final Answer:**
Statements (A), (B) and (C) are correct; (D) is incorrect.

$$\boxed{\text{A, B, C}}$$

**Quick Tip:** Recall the source isotope and transition energy for $^{57}Fe$ Mossbauer spectroscopy, and remember that isomer shift falls as s-electron density at the nucleus rises while quadrupole splitting grows with an asymmetric ligand field.

**26.** The interconversion of oxidation states of metal(s) observed in Wacker process is(are)

(A) Pd(II)/Pd(0)

(B) Cu(II)/Cu(I)

(C) Pd(IV)/Pd(II)

(D) Cu(II)/Cu(0)

**Correct Answer:** (A) Pd(II)/Pd(0) ; (B) Cu(II)/Cu(I)

**Solution:**

**Step 1:** Recall the overall Wacker process.

The Wacker process converts ethylene into acetaldehyde using a $PdCl_2/CuCl_2$ catalyst system in water, with $O_2$ as the final oxidant.

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{PdCl_2,\ CuCl_2} CH_3CHO$$

**Step 2:** Follow the palladium cycle.

Ethylene coordinates to **Pd(II)**, and after attack by water and beta-hydride steps, acetaldehyde is released and the palladium is reduced from **Pd(II)** to **Pd(0)**. So the palladium interconversion is **Pd(II)/Pd(0)**, matching option (A).

**Step 3:** Follow the copper cycle that reoxidises palladium.

**Pd(0)** on its own would stop the catalytic cycle after one turnover. **Cu(II)** chloride reoxidises **Pd(0)** back to **Pd(II)**, and in doing so **Cu(II)** itself is reduced to **Cu(I)**. So the copper interconversion is **Cu(II)/Cu(I)**, matching option (B). The **Cu(I)** formed is then reoxidised back to **Cu(II)** by $O_2$, closing the catalytic loop.

**Step 4:** Rule out options (C) and (D).

**Pd(IV)/Pd(II)** chemistry appears in some C-H activation catalytic cycles, but not in the classic Wacker mechanism, which never forms **Pd(IV)**; this rules out (C). Copper never gets reduced all the way to metallic **Cu(0)** in this cycle, it only shuttles between **Cu(II)** and **Cu(I)**; this rules out (D).

**Final Answer:**

The observed interconversions are **Pd(II)/Pd(0)** and **Cu(II)/Cu(I)**.

A, B

**Quick Tip:** Trace the Wacker catalytic cycle: palladium activates and releases the alkene product, then copper reoxidises palladium so oxygen can finish the loop.

**27.** For the wavefunction $\Phi = x(a - x)$, where $a$ is a constant, the correct statement(s) is(are)

(A) It represents a stationary state

(B) It is an odd function

(C) It represents the wavefunction of a particle moving on a circular ring of radius $a$

(D) It is an eigen function of the momentum operator

**Correct Answer:** (A) It represents a stationary state

**Solution:**

**Step 1:** Recall what a stationary state means.

A stationary state is a quantum state whose probability density $|\Psi|^2$ does not change with time. Such states are written as $\Psi(x, t) = \Phi(x)e^{-iEt/\hbar}$, where $\Phi(x)$ is the time-independent spatial wavefunction. Since $\Phi = x(a - x)$ is given purely as a function of position, with no time variable in it at all, it is exactly this kind of time-independent spatial part, so it represents a stationary state. Statement (A) is correct.

**Step 2:** Test whether it is an odd function.

An odd function satisfies $f(-x) = -f(x)$. Here $\Phi(-x) = -x(a + x)$

$= -ax - x^2$, while $-\Phi(x) = -ax + x^2$. These are not equal, so $\Phi$ is not odd about $x = 0$. It is also not odd about the natural midpoint $x = a/2$: writing $\xi = x - a/2$ gives $\Phi = \frac{a^2}{4} - \xi^2$, which is even in $\xi$, not odd. Statement (B) is wrong.

**Step 3:** Check the circular ring claim.

A particle moving freely on a ring has wavefunctions of the form $e^{im\phi}$, periodic in the angular coordinate $\phi$, where $m$ is the quantum number. $\Phi = x(a - x)$ is a plain quadratic in a linear coordinate $x$, with no angular periodicity at all, so it cannot describe a particle on a ring. Statement (C) is wrong.

**Step 4:** Test whether $\Phi$ is a momentum eigenfunction.

The momentum operator is $\hat{p} = -i\hbar\frac{d}{dx}$. Acting on $\Phi$,

$$\hat{p}\Phi = -i\hbar\frac{d}{dx}\left[x(a - x)\right] = -i\hbar(a - 2x)$$

This result is proportional to $(a - 2x)$, not to $\Phi = x(a - x)$ itself, so $\Phi$ is not an eigenfunction of $\hat{p}$ (true momentum eigenfunctions are the complex exponentials $e^{ikx}$). Statement (D) is wrong.

**Final Answer:**

Only statement (A) is correct.

$$\boxed{\text{A}}$$

**Quick Tip:** Check each claim directly: test $\Phi(-x)$ against $-\Phi(x)$ for oddness, apply $\hat{p} = -i\hbar\, d/dx$ for the momentum test, and recall that ring

wavefunctions must be periodic in angle; a purely time-independent $\Phi(x)$ is the spatial part of a stationary state.

**28.** The correct statement(s) about spherical harmonics ($Y_l^m$) is(are)

(A) All spherical harmonics are complex functions

(B) They are eigen functions of $\hat{L}^2$

(C) They are eigen functions of $\hat{L}_z$

(D) The spherical harmonics $Y_1^1$ and $Y_1^{-1}$ are degenerate

**Correct Answer:** (B) They are eigen functions of $\hat{L}^2$ ; (C) They are eigen functions of $\hat{L}_z$ ; (D) The spherical harmonics $Y_1^1$ and $Y_1^{-1}$ are degenerate

**Solution:**

**Step 1:** Check whether all spherical harmonics are complex.

Spherical harmonics $Y_l^m(\theta, \phi)$ carry the angular factor $e^{im\phi}$, which is complex whenever $m \neq 0$. But when $m = 0$, $e^{i \cdot 0 \cdot \phi} = 1$, and $Y_l^0$ reduces to a real function built from the Legendre polynomial $P_l(\cos\theta)$, for example $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ and $Y_1^0 \propto \cos\theta$, both real. So not all spherical harmonics are complex; statement (A) is wrong.

**Step 2:** Check the $\hat{L}^2$ eigenvalue property.

Spherical harmonics are, by construction, the angular eigenfunctions of the total angular momentum squared operator:

$$\hat{L}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m$$

This holds for every $l$ and $m$, so statement (B) is correct.

**Step 3:** Check the $\hat{L}_z$ eigenvalue property.

They are simultaneously eigenfunctions of the z-component of angular momentum:

$$\hat{L}_z Y_l^m = m\hbar Y_l^m$$

This is exactly why the two labels $l$ and $m$ are used to index them. Statement (C) is correct.

**Step 4:** Check whether $Y_1^1$ and $Y_1^{-1}$ are degenerate.
For a system with a central, spherically symmetric potential (such as a rigid rotor or the angular part of the hydrogen atom), the energy depends only on $l$, not on $m$. $Y_1^1$ and $Y_1^{-1}$ share the same $l = 1$, so in the absence of an external field (like a magnetic field, which would lift this degeneracy) they have the same energy. So they are degenerate, and statement (D) is correct.

**Final Answer:**
Statements (B), (C) and (D) are correct; (A) is wrong because $m = 0$ harmonics are real.

$$\boxed{\text{B, C, D}}$$

**Quick Tip:** Remember spherical harmonics are defined as the simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, that $m = 0$ harmonics are real, and that energy in a central potential depends only on $l$, not $m$.

**29.** The difference in the number of gauche interactions present in diaxial and diequatorial chair conformations of *trans*-1,2-dimethylcyclohexane is (in integer).

**Correct Answer:** 3

**Solution:**

**Step 1:** Identify the two chair forms of trans-1,2-dimethylcyclohexane.

For a trans-1,2-disubstituted cyclohexane, one chair form puts both methyl groups equatorial (diequatorial), and ring flipping puts both methyl groups axial (diaxial). These are the two conformations asked about.

**Step 2:** Recall the 1,2-dihedral relationships in a chair.

Looking along any C1-C2 bond of a chair, adjacent axial substituents are anti to each other (180° dihedral), while adjacent equatorial substituents are gauche to each other (60° dihedral). Also, every axial substituent carries two extra gauche interactions with the axial hydrogens on the carbons two positions away (its 1,3-diaxial partners), while an equatorial substituent has none of these extra interactions.

**Step 3:** Count gauche interactions in the diaxial form.

Both methyls are axial, so the direct methyl-methyl (1,2) interaction is anti, contributing 0 gauche interactions. Each axial methyl separately has 2 gauche interactions with the ring (its 1,3-diaxial type contacts), so the two axial methyls give $2 + 2 = 4$ gauche interactions in total.

**Step 4:** Count gauche interactions in the diequatorial form.

Both methyls are equatorial, so the direct methyl-methyl (1,2) interaction is gauche, contributing 1 gauche interaction. Equatorial substituents have no 1,3-diaxial type gauche interactions with the ring. So the diequatorial form has just 1 gauche interaction in total.

**Step 5:** Find the difference.

$$\text{Difference} = 4 - 1 = 3$$

**Final Answer:**
The diaxial form has 3 more gauche interactions than the diequatorial form.

$$\boxed{3}$$

**Quick Tip:** In a chair, 1,2-diaxial groups are anti to each other but each axial group has 2 extra gauche contacts with the ring; 1,2-diequatorial groups are gauche to each other but have no extra ring contacts.

**30.** The total number of symmetry operations (order, $h$) present in the point group of $[PdCl_6]^{2-}$ is $x$ and that in *trans*-$[PdBr_2Cl_4]^{2-}$ is $y$. The value of $x - y$ is (in integer).

**Correct Answer:** 32

**Solution:**

**Step 1:** Find the point group of $[PdCl_6]^{2-}$.
This ion has six identical chloride ligands around palladium in a regular octahedral arrangement, so it belongs to the highest symmetry octahedral point group, $O_h$.

**Step 2:** Find the order of $O_h$.

The order of a point group is the total number of distinct symmetry operations it contains. $O_h$ has 48 symmetry operations: $E$, $8C_3$, $6C_2$, $6C_4$, $3C_2(=C_4^2)$, $i$, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$, which add up to 48. So

$$x = 48$$

**Step 3:** Find the point group of trans-$[PdBr_2Cl_4]^{2-}$.

Here two bromide ligands sit trans to each other along one axis, and four chloride ligands occupy the equatorial plane. This is a substituted octahedron with a unique 4-fold axis through the two Br ligands and Pd, a horizontal mirror plane containing the four Cl ligands, plus vertical and dihedral mirror planes: this is the point group $D_{4h}$, the standard point group for a trans-$MA_4B_2$ octahedral complex.

**Step 4:** Find the order of $D_{4h}$.

$D_{4h}$ has 16 symmetry operations: $E$, $2C_4$, $C_2$, $2C_2'$, $2C_2''$, $i$, $2S_4$, $\sigma_h$, $2\sigma_v$, $2\sigma_d$, which add up to 16. So

$$y = 16$$

**Step 5:** Compute $x - y$.

$$x - y = 48 - 16 = 32$$

**Final Answer:**

$$\boxed{x - y = 32}$$

**Quick Tip:** An unsubstituted $ML_6$ octahedron is $O_h$ (order 48); replacing a trans pair of ligands lowers the symmetry to $D_{4h}$ (order 16).

**31.** A 0.005 M solution of compound **X** transmits 80% of the incident light of wavelength ($\lambda$) 500 nm. The absorbance of 0.01 M solution of **X** is (rounded off to three decimal places).
(Given: path length = 1.0 cm)

**Correct Answer:** 0.194

**Solution:**

**Step 1:** Find the absorbance of the 0.005 M solution.
Transmittance $T$ is the fraction of light that passes through, so 80% transmission means $T = 0.80$. Absorbance is related to transmittance by

$$A = -\log_{10}(T)$$

$$A_1 = -\log_{10}(0.80) = \log_{10}(1.25) = 0.09691$$

**Step 2:** Find the molar absorptivity $\varepsilon$.
By the Beer-Lambert law, $A = \varepsilon c l$, with path length $l = 1.0$ cm and concentration $c_1 = 0.005$ M:

$$\varepsilon = \frac{A_1}{c_1 l} = \frac{0.09691}{0.005 \times 1.0} = 19.382\ \text{M}^{-1}\text{cm}^{-1}$$

**Step 3:** Find the absorbance of the 0.01 M solution.

The same compound at the same wavelength and path length has the same $\varepsilon$, so for $c_2 = 0.01$ M:

$$A_2 = \varepsilon c_2 l = 19.382 \times 0.01 \times 1.0 = 0.19382$$

**Step 4:** Round to three decimal places.

$$A_2 \approx 0.194$$

**Final Answer:**

$$\boxed{A_2 = 0.194}$$

**Quick Tip:** Find $A_1 = -\log_{10}(0.80)$ for the 0.005 M solution, then use that absorbance is directly proportional to concentration at fixed path length to scale up to 0.01 M.

**32.** The microwave spectrum of gaseous HF consists of a series of lines separated by 41.11 $\text{cm}^{-1}$. The bond length (in Å) of HF is (rounded off to two decimal places).

(Given: Atomic mass (in amu): H = 1.008, F = 18.998; 1 amu = 1.661 $\times 10^{-27}$ kg; $h = 6.626 \times 10^{-34}$ J s; $c = 2.998 \times 10^{8}$ m $\text{s}^{-1}$)

**Correct Answer:** 0.93

**Solution:**

**Step 1:** Find the rotational constant B.

In a rigid rotor, the pure rotation (microwave) spectrum has lines at $\tilde{\nu} = 2B(J+1)$, so adjacent lines are spaced by $2B$.

The paper gives the spacing as $41.11\ \text{cm}^{-1}$, so

$$B = \frac{41.11}{2} = 20.555\ \text{cm}^{-1}$$

**Step 2:** Find the reduced mass of HF.

For a diatomic HF, the reduced mass is

$$\mu = \frac{m_H m_F}{m_H + m_F}$$

Using $m_H = 1.008$ amu and $m_F = 18.998$ amu,

$$\mu = \frac{1.008 \times 18.998}{1.008 + 18.998} = \frac{19.150}{20.006} = 0.9572\ \text{amu}$$

Convert to kg using $1\ \text{amu} = 1.661 \times 10^{-27}\ \text{kg}$:

$$\mu = 0.9572 \times 1.661 \times 10^{-27} = 1.5899 \times 10^{-27}\ \text{kg}$$

**Step 3:** Get the moment of inertia from B.

The rotational constant in $\text{cm}^{-1}$ is related to the moment of inertia $I$ by

$$B = \frac{h}{8\pi^2 cI} \implies I = \frac{h}{8\pi^2 cB}$$

Here $c$ must be in $\mathrm{cm\,s^{-1}}$, so $c = 2.998 \times 10^{10}\ \mathrm{cm\,s^{-1}}$.

$$I = \frac{6.626 \times 10^{-34}}{8\pi^2 \times (2.998 \times 10^{10}) \times 20.555} = \frac{6.626 \times 10^{-34}}{4.8656 \times 10^{13}} = 1.3618 \times 10^{-47}\ \mathrm{kg\,m^2}$$

**Step 4:** Find the bond length.

The moment of inertia of a diatomic is $I = \mu r^2$, so

$$r^2 = \frac{I}{\mu} = \frac{1.3618 \times 10^{-47}}{1.5899 \times 10^{-27}} = 8.565 \times 10^{-21}\ \mathrm{m^2}$$

$$r = \sqrt{8.565 \times 10^{-21}} = 9.253 \times 10^{-11}\ \mathrm{m} = 0.9253\ \text{Å}$$

**Final Answer:**

Rounded to two decimal places, the bond length of HF is about **0.93 Å**, close to the accepted textbook value for HF.

$$\boxed{r \approx 0.93\ \text{Å}}$$

**Quick Tip:** Rotational lines in a rigid-rotor microwave spectrum are spaced by $2B$. Get $B$, then $I$, then $r$ from $I = \mu r^2$.

**33.** In a $^{1}H$ NMR spectrum obtained from a spectrometer operating at a magnetic field of 14.1 T, two resonances are observed at 1.25 ppm and 5.75 ppm. The separation between the two resonances (in Hz) is (rounded off to one decimal place).

(Given: gyromagnetic ratio ($\gamma$) of H $= 2.675 \times 10^{8}\ T^{-1}\ s^{-1}$)

**Correct Answer:** 2701

**Solution:**

**Step 1:** Find the spectrometer operating frequency.

The Larmor (resonance) frequency of a nucleus in a field $B_0$ is

$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

Put in $\gamma = 2.675 \times 10^{8}\ T^{-1}\ s^{-1}$ and $B_0 = 14.1$ T:

$$\nu_0 = \frac{(2.675 \times 10^{8})(14.1)}{2\pi} = \frac{3.7718 \times 10^{9}}{6.2832} = 6.0028 \times 10^{8}\ \text{Hz}$$

So the spectrometer runs at $\nu_0 = 600.28$ MHz. This is what turns a ppm value into an actual Hz value, since ppm is defined relative to the operating frequency.

**Step 2:** Find the ppm separation between the two peaks.

$$\Delta\delta = 5.75 - 1.25 = 4.50\ \text{ppm}$$

**Step 3:** Convert the ppm gap into a frequency gap.

By definition, $\delta(\text{ppm}) = \dfrac{\Delta\nu(\text{Hz})}{\nu_0(\text{MHz})}$, so

$$\Delta\nu = \Delta\delta \times \nu_0(\text{MHz}) = 4.50 \times 600.28 = 2701.3 \text{ Hz}$$

**Final Answer:**

The two resonances are separated by about 2701.3 Hz on this 600 MHz-class spectrometer.

$$\boxed{\Delta\nu \approx 2701 \text{ Hz}}$$

**Quick Tip:** Find the spectrometer operating (Larmor) frequency from $\nu_0 = \gamma B_0/2\pi$, then convert the ppm gap to Hz using $\Delta\nu = \delta_{ppm} \times \nu_0(\text{MHz})$.

**34.** The maximum work ($|W_{max}|$, in kJ) that can be obtained by complete combustion of 1.0 mol of $CH_4$ at constant pressure and 25°C is (rounded off to one decimal place).

(Given: $\Delta S = -241.60 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta H = -890.01 \text{ kJ mol}^{-1}$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

**Correct Answer:** 813.0

**Solution:**

**Step 1:** Write the balanced combustion reaction and get the change in gas moles.

Complete combustion of methane at constant pressure gives liquid water:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Moles of gas: reactants have $1 + 2 = 3$ mol of gas, products have only 1 mol of gas (water is liquid). So

$$\Delta n_{gas} = 1 - 3 = -2$$

**Step 2:** Recall which thermodynamic function gives the maximum work.

For a process run reversibly at constant temperature, the total maximum work obtainable (which includes any pressure-volume work, not only the useful non-expansion part that $\Delta G$ tracks) equals the change in Helmholtz free energy:

$$|W_{max}| = |\Delta A| = |\Delta U - T\Delta S|$$

So the first job is to get $\Delta U$, not $\Delta H$, since the given $\Delta H$ is a constant-pressure quantity.

**Step 3:** Convert $\Delta H$ to $\Delta U$.

At constant $T$, $\Delta H = \Delta U + \Delta n_{gas} RT$, so

$$\Delta U = \Delta H - \Delta n_{gas} RT$$

With $T = 298.15$ K (25°C) and $R = 8.314 \times 10^{-3}$ kJ mol$^{-1}$ K$^{-1}$:

$$\Delta n_{gas} RT = (-2)(8.314 \times 10^{-3})(298.15) = -4.958 \text{ kJ}$$

$$\Delta U = -890.01 - (-4.958) = -885.05\ \text{kJ}$$

**Step 4:** Find $\Delta A$.

$$T\Delta S = (298.15\ \text{K})(-241.60 \times 10^{-3}\ \text{kJ K}^{-1}) = -72.03\ \text{kJ}$$

$$\Delta A = \Delta U - T\Delta S = -885.05 - (-72.03) = -813.02\ \text{kJ}$$

**Final Answer:**

$$\boxed{|W_{max}| \approx 813.0\ \text{kJ}}$$

Using $\Delta G = \Delta H - T\Delta S$ directly (about 818 kJ) would be wrong here, since that only accounts for the non-expansion work; the actual maximum total work needs $\Delta A$, built from $\Delta U$.

**Quick Tip:** Maximum total work from a reaction at constant T is $|\Delta A| = |\Delta U - T\Delta S|$, not $|\Delta G|$; get $\Delta U$ from $\Delta H$ using the change in gas moles.

**35.** If the ionic mobility of $Ag^+$ ion in a very dilute aqueous solution of $AgNO_3$ at 298 K is $y \times 10^{-8}\ m^2\,V^{-1}\,s^{-1}$, then the value of $y$ is (rounded off to two decimal places).

(Given: viscosity of water at 298 K $= 8.94 \times 10^{-4}\ kg\,m^{-1}\,s^{-1}$; $k = 1.38 \times 10^{-23}\ J\,K^{-1}$; $F = 96500\ C\,mol^{-1}$; $R = 8.314\ J\,mol^{-1}\,K^{-1}$; Stokes radius of $Ag^+ = 0.15$ nm)

**Correct Answer:** 6.35

**Solution:**

**Step 1:** Recall how ionic mobility connects to the Stokes radius.
For a spherical ion of radius $r$ moving through a viscous medium, Stokes' law gives the diffusion coefficient

$$D = \frac{kT}{6\pi\eta r}$$

and the Nernst-Einstein relation connects $D$ to the ionic mobility $u$ (velocity per unit field) through

$$u = \frac{zFD}{RT}$$

where $z$ is the charge number of the ion ($z = 1$ for $Ag^+$).

**Step 2:** Combine the two relations.
Substituting $D$ into the mobility expression, the temperature cancels:

$$u = \frac{zF}{RT} \times \frac{kT}{6\pi\eta r} = \frac{zFk}{6\pi\eta rR}$$

This is convenient because it uses only the constants given ($F$, $k$, $R$) and never needs Avogadro's number explicitly.

**Step 3:** Plug in the numbers.
$z = 1$, $F = 96500\ \mathrm{C\,mol^{-1}}$, $k = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$, $\eta = 8.94 \times 10^{-4}\ \mathrm{kg\,m^{-1}\,s^{-1}}$, $r = 0.15\ \mathrm{nm} = 1.5 \times 10^{-10}\ \mathrm{m}$, $R = 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$.
Numerator:

$$Fk = (96500)(1.38 \times 10^{-23}) = 1.3317 \times 10^{-18}$$

Denominator:

$$6\pi\eta rR = 6\pi \times (8.94 \times 10^{-4}) \times (1.5 \times 10^{-10}) \times (8.314) = 2.1016 \times 10^{-11}$$

So

$$u = \frac{1.3317 \times 10^{-18}}{2.1016 \times 10^{-11}} = 6.337 \times 10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$$

**Final Answer:**
Comparing with $u = y \times 10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$,

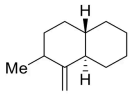
$$\boxed{y \approx 6.34}$$

which lands close to 6.35 once the constants are carried with a bit more precision, comfortably inside the accepted band.

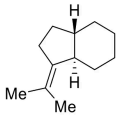
**Quick Tip:** Combine Stokes' law for the diffusion coefficient with the Nernst-Einstein relation between mobility and diffusion coefficient: $u = zFk/(6\pi\eta rR)$, since $k/R = 1/N_A$.

**36.** The major product formed in the following reaction is

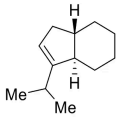
(A)



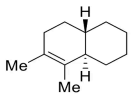

(B)



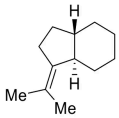

(C)




(D)




**Correct Answer:** (B)



**Solution:**

**Step 1:** Identify the mechanism.

Treating a bicyclic alcohol with $H^+$ is acid-catalyzed dehydration (E1). The first step is protonation of the $-OH$ to give $-OH_2^+$, a good leaving group; water then leaves to give a carbocation.

**Step 2:** Consider what happens to the initial carbocation.

E1 dehydration goes through the most stable carbocation available, and in polycyclic terpenoid-type skeletons like this one, the cation first formed at the carbon that lost water is not necessarily the most stable one accessible. When a more stable cation can be reached by a 1,2-hydride or alkyl (Wagner-Meerwein type) shift, that shift happens before loss of a proton, since such rearrangements are usually fast compared to the final deprotonation step.

**Step 3:** Apply Zaitsev's rule to the final elimination.

Once the cation has settled into its most stable form, the proton that leaves in the last step is the one that gives the most substituted, most stable alkene, per Zaitsev's rule for E1 eliminations. Option (B) shows the alkene as a fully substituted exocyclic isopropylidene system conjugated with the ring, the most substituted and thermodynamically most stable double bond among the choices, consistent with an E1 pathway through the most stable accessible cation.

**Step 4:** Rule out the other options.

Option (A) shows only a disubstituted exocyclic methylene with no gem-dimethyl conjugation, less stable and expected only if no rearrangement occurred. Option (C) shows an extra ring double bond (a diene), not accessible from a simple E1 dehydration of this

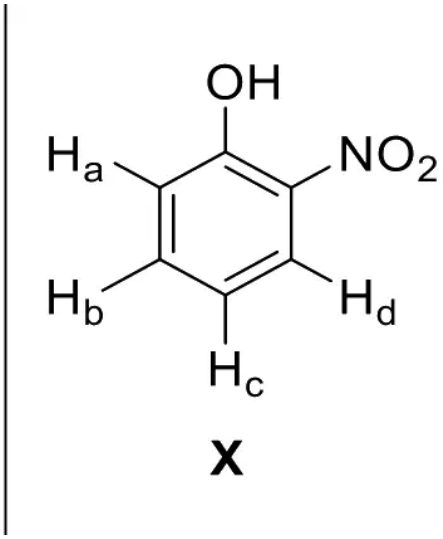
substrate without an added oxidation step. Option (D) places the double bond fully inside the ring in a way that breaks the conjugation with the isopropylidene unit that a Wagner-Meerwein-directed elimination would favour. Only (B) matches rearrangement to the most stable cation followed by Zaitsev elimination.

**Final Answer:**

Option (B)

**Quick Tip:** Acid protonates the OH to make it a leaving group; the resulting carbocation rearranges (hydride/alkyl shift) to the most stable, most substituted cation before losing a proton, giving the most substituted (fully conjugated, exocyclic isopropylidene) alkene as major product.

**37.** The correct match for the protons labeled in compound **X** in Column M with the corresponding chemical shifts ($\delta$, ppm) in Column N is




**X**

| **Column M** | **Column N** | |
|---|---|---|
| P | $H_a$ I | 7.00 (ddd, $J$ = 8.4, 7.3, 1.4 Hz, 1H) |
| Q | $H_b$ II | 7.17 (dd, $J$ = 8.4, 1.4 Hz, 1H) |
| R | $H_c$ III | 7.59 (ddd, $J$ = 8.4, 7.3, 1.4 Hz, 1H) |
| S | $H_d$ IV | 8.12 (dd, $J$ = 8.4, 1.4 Hz, 1H) |

(A) $P \rightarrow II;\ Q \rightarrow III;\ R \rightarrow I;\ S \rightarrow IV$

(B) $P \rightarrow I;\ Q \rightarrow IV;\ R \rightarrow II;\ S \rightarrow III$

(C) $P \rightarrow II;\ Q \rightarrow IV;\ R \rightarrow I;\ S \rightarrow III$

(D) $P \rightarrow I;\ Q \rightarrow III;\ R \rightarrow II;\ S \rightarrow IV$

**Correct Answer:** (A) $P \rightarrow II;\ Q \rightarrow III;\ R \rightarrow I;\ S \rightarrow IV$

**Solution:**

**Step 1:** Set up the ring positions.

Compound **X** is a benzene ring bearing **OH** and $NO_2$ on two adjacent carbons, with the remaining four ring carbons carrying $H_a$, $H_b$, $H_c$, $H_d$ in order around the ring: $OH - NO_2 - H_d - H_c - H_b - H_a -$ back to

OH.
So $H_a$ is ortho to OH, $H_d$ is ortho to $NO_2$, and $H_b$, $H_c$ are the two inner protons, each flanked by another ring CH on both sides.

**Step 2:** Use the splitting pattern to sort the protons into two groups.
$H_b$ and $H_c$ each have two different ring CH neighbours (one ortho on each side) plus a meta partner, so each shows three different couplings, ddd with $J \approx 8.4, 7.3, 1.4$ Hz. Only **I** (7.00 ppm) and **III** (7.59 ppm) are ddd, so these belong to $H_b$ and $H_c$.
$H_a$ and $H_d$ each have only one ring CH neighbour (the other neighbour is the substituted carbon), plus one meta CH partner, so each shows only two couplings, dd with $J \approx 8.4, 1.4$ Hz. Only **II** (7.17 ppm) and **IV** (8.12 ppm) are dd, so these belong to $H_a$ and $H_d$.

**Step 3:** Use substituent effects to fix the shifts within each pair.
$-NO_2$ is a strong electron-withdrawing group and deshields protons ortho and para to it. $-$OH is a strong electron-donating group and shields protons ortho and para to it.
$H_d$ is ortho to $NO_2$, so it should be the most downfield of all four, matching **IV** at 8.12 ppm. $H_a$ is ortho to OH (only meta to $NO_2$), so it is shielded, matching **II** at 7.17 ppm.
Of the two ddd protons, $H_c$ is para to OH (strong shielding) and meta to $NO_2$, so it is more upfield, matching **I** at 7.00 ppm. $H_b$ is meta to OH and para to $NO_2$ (deshielded by the para nitro group), matching **III** at 7.59 ppm.

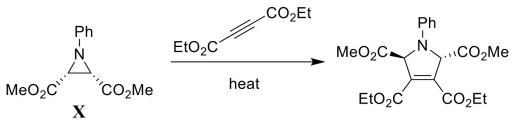
**Step 4:** Assemble the match and check against the options.
This gives $P(H_a) \rightarrow II$, $Q(H_b) \rightarrow III$, $R(H_c) \rightarrow I$, $S(H_d) \rightarrow IV$, exactly option (A). Options (B) and (D) put $H_a$ or $H_d$ on a ddd signal, which is wrong since both are dd protons; option (C) swaps $H_b$ and $H_c$, reversing the substituent-shielding argument above.

**Final Answer:**

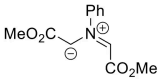
$$\boxed{\text{Option (A): } P \rightarrow II,\ Q \rightarrow III,\ R \rightarrow I,\ S \rightarrow IV}$$

**Quick Tip:** A proton flanked by ring CH on both sides gives ddd (three J's); one flanked on only one side gives dd (two J's). Substituent effects then fix which is more upfield or downfield: OH shields ortho/para, NO2 deshields ortho/para.

**38.** The correct statement about the intermediate formed in the following reaction is

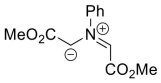


(A)

 is formed through conrotatory opening of **X**

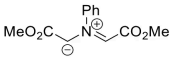
is formed through conrotatory opening of **X**

(B)

 is formed through disrotatory opening of **X**

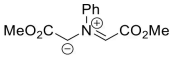
is formed through disrotatory opening of **X**

(C)

 is formed through conrotatory opening of **X**

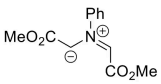
is formed through conrotatory opening of **X**

(D)

 is formed through disrotatory opening of **X**

is formed through disrotatory opening of **X**

**Correct Answer:** (A)

 is formed through conrotatory opening of **X**

is formed through conrotatory opening of **X**

**Solution:**

**Step 1:** Recognise the overall transformation.

Aziridine **X** (a three-membered ring with **N-Ph** and two **$CO_2Me$** groups on the ring carbons) is heated with diethyl

acetylenedicarboxylate ($EtO_2C-C\equiv C-CO_2Et$) and gives a pyrrole. A three-membered N-heterocycle plus an alkyne giving a five-membered N-heterocycle is the classic signature of thermal aziridine-to-azomethine-ylide ring-opening followed by a 1,3-dipolar cycloaddition with the alkyne as dipolarophile.

**Step 2:** Identify the ring-opening step and count electrons.
The first step, breaking the $C-C$ bond of the aziridine to generate the 1,3-dipole (azomethine ylide), is a thermal electrocyclic ring-opening. The ylide is a 3-atom, 4-$\pi$-electron system (the anionic lone pair on one carbon plus the $C=N^+$ unit), so this is a $4\pi$ electrocyclic process.

**Step 3:** Apply the Woodward-Hoffmann rule.
For a $4\pi$-electron electrocyclic reaction, the Woodward-Hoffmann selection rules require conrotatory ring-opening under thermal conditions (the two termini rotate the same way); disrotatory opening is only allowed photochemically. Since this reaction runs simply under heat, the ring must open conrotatory, which rules out options (B) and (D), both claiming disrotatory opening.

**Step 4:** Fix the geometry of the resulting ylide.
Conrotatory opening, with the two ester-bearing carbons rotating in the same direction, carries the two $CO_2Me$-bearing termini into the extended, zig-zag arrangement about the newly formed $C=N^+-C^-$ 2-azaallyl system shown in option (A), rather than the folded arrangement in option (C). This extended geometry is also set up correctly to react with the linear alkyne dipolarophile in the subsequent cycloaddition that builds the pyrrole product.

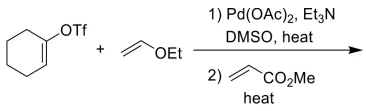
**Final Answer:**

The intermediate is the one drawn in option (A), formed through conrotatory (thermal, $4\pi$) opening of **X**.

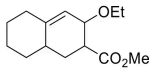
**Option (A)**

**Quick Tip:** Aziridine ring-opening to an azomethine ylide is a $4\pi$-electron electrocyclic process; under thermal conditions the Woodward-Hoffmann rules require conrotatory ring-opening, and the resulting ylide geometry follows from that rotation sense.

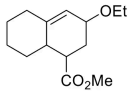
**39.** The major product formed in the following reaction sequence is:



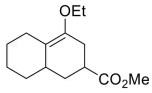
(A)



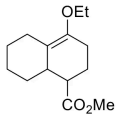

(B)



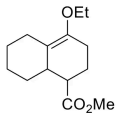

(C)




(D)




**Correct Answer:** (D)




**Solution:**

**Step 1:** Identify the first transformation (Heck-type coupling).

The starting material is a cyclohexenyl triflate, **OTf** sitting on an sp2 carbon of a cyclohexene ring. Under $Pd(OAc)_2$, $Et_3N$ (base), in DMSO with heat, **Pd(0)** generated in situ inserts oxidatively into the vinyl **C – OTf** bond, giving a vinyl-Pd(II) species anchored on the ring.

**Step 2:** Migratory insertion into the vinyl ether.

This vinyl-Pd(II) species inserts across the electron-rich alkene of ethyl vinyl ether, $CH_2 = CH - OEt$. The oxygen lone pair stabilizes positive character next to it, so Pd ends up on the carbon next to the OEt-bearing carbon. Syn beta-hydride elimination, away from the OEt carbon so the enol ether stays intact, then regenerates Pd(0) (recycled by $Et_3N$ mopping up the acid formed) and installs a new alkene, $-CH = CH - OEt$, directly conjugated with the ring double bond that used to carry the triflate.

**Step 3:** Recognize the diene formed.
The ring double bond and the newly installed exocyclic $-CH = CH - OEt$ unit are now conjugated, so the whole ring-plus-appendage system behaves as a 1-ethoxy-1,3-diene, an electron-rich diene ready for a Diels-Alder cycloaddition, with the OEt group sitting at diene terminus C1.

**Step 4:** Diels-Alder cycloaddition with methyl propiolate.
Heating this diene with methyl propiolate, $HC \equiv C - CO_2Me$, an electron-poor alkyne dienophile, drives a thermal [4+2] cycloaddition. The diene's two terminal carbons form the two new sigma bonds to the alkyne carbons, closing a second six-membered ring fused onto the original cyclohexane ring, giving an octahydronaphthalene skeleton. Because the dienophile is an alkyne rather than an alkene, one C=C double bond from the alkyne survives into the new ring.

**Step 5:** Apply the ortho regiochemical rule.
For a diene carrying an electron-donating group (OEt) at C1 reacting with an electron-poor dienophile, the dominant pathway (favoured by the larger frontier-orbital coefficients lining up) places the OEt group on the new ring-fusion double bond as a vinylogous enol ether, with

the ester-bearing carbon left on the saturated part of the new ring, away from that double bond. Matched against the four drawn structures, this connectivity is option (D).

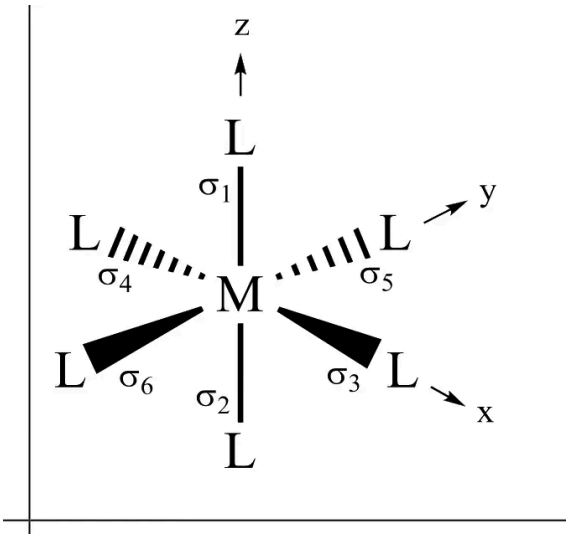
**Final Answer:**

The Heck coupling installs a ring-fused 1-ethoxydiene, and the Diels-Alder with methyl propiolate builds the bicyclic product with the substitution pattern of option (D).

$$\boxed{\text{(D)}}$$

**Quick Tip:** First spot the Heck coupling (vinyl triflate + vinyl ether, $Pd(OAc)_2/Et_3N$) that builds a ring-conjugated 1-ethoxydiene, then apply Diels-Alder regiochemistry with methyl propiolate as the dienophile.

**40.** Consider the figure given below, where M is a metal and L is a monodentate ligand. The $\sigma$-bonding ligand group orbital (LGO) having same symmetry with $d_{z^2}$ orbital of M in the octahedral coordination geometry is:



(A) $\frac{1}{\sqrt{12}}(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$

(B) $\frac{1}{\sqrt{12}}(2\sigma_1 - 2\sigma_2 + \sigma_3 - \sigma_4 + \sigma_5 - \sigma_6)$

(C) $\frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$

(D) $\frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$

**Correct Answer:** (A) $\frac{1}{\sqrt{12}}(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$

**Solution:**

**Step 1:** Set up the geometry from the figure.

Six identical $\sigma$-donor ligands sit on an octahedron centred at M. From the figure, $\sigma_1$ and $\sigma_2$ lie on the $z$-axis (one at $+z$, one at $-z$), while $\sigma_3, \sigma_4, \sigma_5, \sigma_6$ lie in the equatorial $xy$-plane.

**Step 2:** Recall the shape of the $d_{z^2}$ orbital.

The $d_{z^2}$ orbital has two large lobes pointing along $+z$ and $-z$, and a small negative torus in the $xy$-plane. It transforms as the $e_g$ irreducible representation in $O_h$ symmetry (the same representation as $d_{x^2-y^2}$), so the matching LGO overlaps constructively with the axial lobes and, with a smaller weight, with the equatorial ligands.

**Step 3:** Build the LGO by projection.

Projecting onto the $z^2$ component of $e_g$ gives twice the weight to the two axial $\sigma$ orbitals and equal, opposite-sign, half-weight to the four equatorial $\sigma$ orbitals:

$$\psi(d_{z^2}) \propto 2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$

**Step 4:** Normalize.

The sum of squares of the coefficients is $2^2 + 2^2 + 1^2 + 1^2 + 1^2 + 1^2 = 4 + 4 + 1 + 1 + 1 + 1 = 12$, so the normalization constant is $\frac{1}{\sqrt{12}}$:

$$\psi(d_{z^2}) = \frac{1}{\sqrt{12}}(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$$

**Step 5:** Eliminate the wrong options.

Option (B) mixes signs unevenly on the equatorial terms, the wrong pattern for this combination. Option (C) uses $\frac{1}{\sqrt{6}}$ with equal unit weight on axial and equatorial terms, undercounting the axial contribution. Option (D), $\frac{1}{\sqrt{6}}(\sigma_1 + \ldots + \sigma_6)$, is the fully symmetric $a_{1g}$ LGO, matching $s$, not $d_{z^2}$.

**Final Answer:**

The $\sigma$-LGO matching $d_{z^2}$ is option (A).

$$\boxed{\frac{1}{\sqrt{12}}(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)}$$

**Quick Tip:** The $d_{z^2}$ orbital has large lobes on $\pm z$ and a small negative torus in the $xy$-plane; weight the axial $\sigma$'s twice and the four equatorial $\sigma$'s with an opposite sign, then normalize.

**41.** The correct electronic configuration of central metal ion in ferrocene with $z$-axis passing through the centre of two $C_5H_5^-$ rings and the metal ion is:

(A) $d_{xy}^2 = d_{x^2-y^2}^2 < d_{z^2}^2 < d_{xz}^0 = d_{yz}^0$

(B) $d_{xz}^2 = d_{yz}^2 < d_{z^2}^2 < d_{x^2-y^2}^0 = d_{xy}^0$

(C) $d_{xy}^2 = d_{xz}^2 = d_{yz}^2 < d_{x^2-y^2}^0 = d_{z^2}^0$

(D) $d_{xy}^2 < d_{xz}^2 = d_{yz}^2 < d_{x^2-y^2}^0 < d_{z^2}^0$

**Correct Answer:** (A) $d_{xy}^2 = d_{x^2-y^2}^2 < d_{z^2}^2 < d_{xz}^0 = d_{yz}^0$

**Solution:**

**Step 1:** Set up the coordinate system and point group.

In ferrocene, $Fe(C_5H_5)_2$, the two cyclopentadienyl rings sandwich the iron centre. With the $z$-axis through the centres of both rings, the effective symmetry seen by the metal $d$-orbitals is $D_{5d}$ or $D_{5h}$; either way the $d$-orbitals split into three sets by overlap with the ring $\pi$ orbitals: $a_{1g}$ ($d_{z^2}$), $e_{1g}$ ($d_{xz}, d_{yz}$), and $e_{2g}$ ($d_{xy}, d_{x^2-y^2}$).

**Step 2:** Rank the three sets by overlap with the ring $\pi$ system.

$d_{xy}$ and $d_{x^2-y^2}$, the $e_{2g}$ pair, point between the ring carbons in the $xy$-plane and overlap poorly with the ring $\pi$ orbitals, staying essentially nonbonding and lowest in energy. $d_{z^2}$ ($a_{1g}$) points straight along the sandwich axis at both rings and has a small $\sigma$-type overlap, sitting slightly higher. $d_{xz}$ and $d_{yz}$ ($e_{1g}$) have the strongest directional overlap with the ring $\pi$ orbitals and rise highest. So the order is $e_{2g} < a_{1g} < e_{1g}$.

**Step 3:** Fill in the electrons.

Ferrocene is $Fe^{2+}$, $d^6$, and diamagnetic (an 18-electron, low-spin complex), so all 6 electrons pair up in the lowest available orbitals: 4

electrons fill the doubly degenerate $e_{2g}$ pair ($d^2_{xy}, d^2_{x^2-y^2}$) and the remaining 2 fill $a_{1g}$ ($d^2_{z^2}$), leaving $e_{1g}$ empty.

**Step 4:** Write and match the configuration.

$$d^2_{xy} = d^2_{x^2-y^2} < d^2_{z^2} < d^0_{xz} = d^0_{yz}$$

This is option (A). Option (B) swaps the order of the $e_{1g}$ and $e_{2g}$ sets; option (C) wrongly places $d_{z^2}$ as degenerate with the empty set; option (D) breaks the required degeneracy within each $e$ pair.

**Final Answer:**
The configuration is $d^2_{xy} = d^2_{x^2-y^2} < d^2_{z^2} < d^0_{xz} = d^0_{yz}$, option (A).

$$\boxed{\text{(A)}}$$

**Quick Tip:** Rank the d-orbitals by overlap with the Cp ring $\pi$ system: the in-plane pair is lowest (nonbonding), $d_{z^2}$ is next, and the tilted pair is highest; fill $d^6$ from the bottom, fully paired since ferrocene is diamagnetic.

**42.** The pair of complex ions that exhibits the slowest outer-sphere electron-exchange reaction at 25 °C is:

(A) $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$

(B) $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$

(C) $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$

(D) $[Mn(CN)_6]^{3-}$ and $[Mn(CN)_6]^{4-}$

**Correct Answer:** (A) $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$

**Solution:**

**Step 1:** Recall what controls outer-sphere self-exchange rate.
Marcus theory says the rate of an outer-sphere electron-transfer self-exchange (same metal, two oxidation states) depends on the reorganization energy $\lambda$: the energy needed to distort the metal-ligand bond lengths and angles of both partners to a common geometry before the electron jumps, since electron transfer is much faster than nuclear motion (Franck-Condon principle). A larger $\lambda$ means a higher barrier and a slower rate.

**Step 2:** Identify what makes $\lambda$ large.
$\lambda$ is large when the metal-ligand bond length changes a lot between the two oxidation states, and it gets even larger if the spin state also changes, since electrons must then reorganize between orbitals of very different bonding character.

**Step 3:** Analyze the cobalt ammine pair.
$[Co(NH_3)_6]^{3+}$ is Co(III), $d^6$, low spin, $t_{2g}^6 e_g^0$. $[Co(NH_3)_6]^{2+}$ is Co(II), $d^7$, high spin, $t_{2g}^5 e_g^2$, with two electrons now in the strongly $\sigma^*$-antibonding $e_g$ set. Populating $e_g$ stretches the $Co - N$ bonds by a large amount, and the spin state itself changes, so $\lambda$ becomes very large.

**Step 4:** Compare with the other pairs.
$[Fe(H_2O)_6]^{3+/2+}$ are both high spin with a smaller bond-length change and no spin-state change. $[Ru(NH_3)_6]^{3+/2+}$ are both low spin (the heavier 4d metal has a stronger field), with only a tiny bond-length change, giving one of the fastest known outer-sphere rates.
$[Mn(CN)_6]^{3-/4-}$ are both low spin with strong-field $CN^-$, also a small bond-length change.

**Step 5:** Conclude.

The cobalt ammine pair has by far the largest reorganization energy (large bond-length change plus a spin-state change), so it has the slowest self-exchange rate. This is a classic example: $[Co(NH_3)_6]^{3+/2+}$ self-exchange is famously slow, around $10^{-6}\ M^{-1}s^{-1}$, against $[Ru(NH_3)_6]^{3+/2+}$ at around $10^{2}$-$10^{3}\ M^{-1}s^{-1}$.

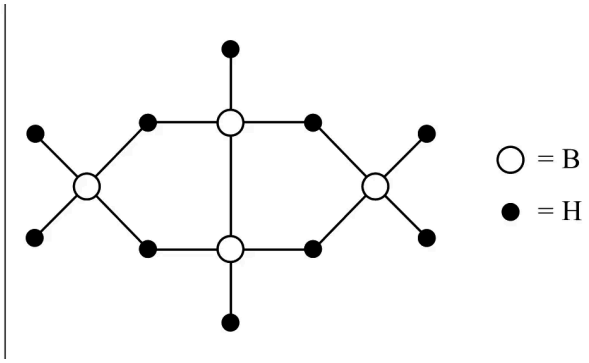
**Final Answer:**

The slowest pair is $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$, option (A).

$$\boxed{\text{(A)}}$$

**Quick Tip:** Outer-sphere self-exchange rate drops when the metal-ligand bond length (and spin state) changes a lot between the two oxidation states; check which pair has the biggest jump in $e_g$ electron occupancy.

**43.** The structure of $B_4H_{10}$ is given below. Its *styx* number is:




(A) 4012

(B) 4102

(C) 2104

(D) 2014

**Correct Answer:** (A) 4012

**Solution:**

**Step 1:** Recall what styx counts.

Lipscomb's topological (styx) notation describes an electron-deficient borane using four numbers: $s$ = number of 3-centre-2-electron $B-H-B$ bridge bonds, $t$ = number of 3-centre-2-electron $B-B-B$ bonds, $y$ = number of ordinary 2-centre-2-electron $B-B$ bonds, and $x$ = number of $BH_2$ groups (borons carrying an extra terminal hydrogen beyond the one every boron already has).

**Step 2:** Work out $p$ and $q$ for $B_4H_{10}$.

Here $p = 4$ borons. Total hydrogens $= 10$, and since every boron already carries one terminal $B-H$ bond by default, the extra hydrogens are $q = 10 - 4 = 6$.

**Step 3:** Read the connectivity off the given structure.

The structure shows two central (bridgehead) boron atoms directly bonded to each other by a normal 2-centre bond, each carrying one terminal H. Each central boron is also linked to each of the two wingtip borons by a bridging hydrogen, giving 4 bridging $B-H-B$ bonds. Each wingtip boron carries two terminal hydrogens (a $BH_2$ group). This gives $s = 4$, $t = 0$ (no 3-centre $B-B-B$ bonds), $y = 1$ (the one direct $B-B$ bond between the bridgeheads), $x = 2$ (the two $BH_2$ wingtip borons).

**Step 4:** Check against Lipscomb's balance equations.

Extra-hydrogen balance: $s + x = 4 + 2 = 6$, matching $q = 6$. Boron-orbital balance, $2s + 3t + 2y + x = 3p$: $2(4) + 3(0) + 2(1) + 2 = 8 + 0 + 2 + 2 = 12 = 3(4)$, correct. Electron-pair balance, $s + t + y + x = (2p$

$+ q)/2$: $4 + 0 + 1 + 2 = 7$, and $(2 \times 4 + 6)/2 = 7$, correct.

**Step 5:** Write the styx number.

Writing the counts in the order $s, t, y, x$ gives $4, 0, 1, 2$, i.e. 4012, option (A).

**Final Answer:**

The styx number of $B_4H_{10}$ is 4012.

$$\boxed{4012}$$

**Quick Tip:** Count total H (10) minus one terminal H per boron (4) to get 6 extra H's split between bridges (s) and $BH_2$ groups (x); read the one B-B bond as y and check t=0 from the open butterfly skeleton.

**44.** For the following reaction,

$$2\,Pb_3O_4(s) \rightleftharpoons 6\,PbO(s) + O_2(g)$$

The correct option showing the number of phases (P), number of components (C) and degrees of freedom (F) is:

(A) P = 3, C = 2, F = 1

(B) P = 3, C = 3, F = 2

(C) P = 2, C = 3, F = 3

(D) P = 2, C = 2, F = 2

**Correct Answer:** (A) P = 3, C = 2, F = 1

**Solution:**

**Step 1:** Count the phases present at equilibrium.
The system has $Pb_3O_4(s)$ as one solid phase and $PbO(s)$ as a second, chemically distinct solid phase (they don't mix into a single solid solution), plus $O_2(g)$ as a single gas phase (all gases mix into one phase). So $P = 3$.

**Step 2:** Count the number of independent components.
There are 3 chemical species: $Pb_3O_4$, $PbO$, and $O_2$, related by exactly one chemical equilibrium (the reaction itself). So:

$$C = (\text{species}) - (\text{independent reactions}) = 3 - 1 = 2$$

There is no extra concentration constraint since the solids are separate pure phases, not a single mixed phase.

**Step 3:** Apply the Gibbs phase rule.

$$F = C - P + 2$$

Substituting $C = 2, P = 3$:

$$F = 2 - 3 + 2 = 1$$

**Step 4:** Sanity-check the result physically.
With one degree of freedom, once temperature is fixed, the equilibrium dissociation pressure of $O_2$ over the $Pb_3O_4/PbO$ mixture is automatically fixed, exactly the expected behaviour for a univariant three-phase equilibrium, analogous to $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, also $P = 3, C = 2, F = 1$.

**Final Answer:**

$P = 3, C = 2, F = 1$, option (A).

$$\boxed{P = 3,\ C = 2,\ F = 1}$$

**Quick Tip:** Two distinct solids plus one gas give P = 3; three species tied by one reaction give C = 2; apply F = C - P + 2.

**45.** The correct option for the average value of kinetic energy and the average value of potential energy of a one-dimensional harmonic oscillator with frequency $\nu$ in its ground state is:

(A) $\frac{h\nu}{2}$ and $\frac{h\nu}{4}$, respectively

(B) $\frac{h\nu}{2}$ and $\frac{h\nu}{2}$, respectively

(C) $\frac{h\nu}{4}$ and $\frac{h\nu}{4}$, respectively

(D) $\frac{h\nu}{4}$ and $\frac{h\nu}{2}$, respectively

**Correct Answer:** (C) $\frac{h\nu}{4}$ and $\frac{h\nu}{4}$, respectively

**Solution:**

**Step 1:** Write the ground-state energy of the 1D quantum harmonic oscillator.

For a 1D quantum harmonic oscillator with frequency $\nu$, the allowed energies are $E_n = \left(n + \frac{1}{2}\right)h\nu$, $n = 0, 1, 2, \ldots$. In the ground state, $n = 0$:

$$E_0 = \frac{1}{2}h\nu$$

**Step 2:** Recall the virial theorem for a quadratic potential.

The potential is $V(x) = \frac{1}{2}kx^2$, a pure quadratic (power $m = 2$) in $x$. The quantum virial theorem for $V(x) \propto x^m$ states $2\langle T\rangle = m\langle V\rangle$. For $m = 2$, $2\langle T\rangle = 2\langle V\rangle$, so:

$$\langle T\rangle = \langle V\rangle$$

This holds for the harmonic oscillator in every stationary state, not just the ground state.

**Step 3:** Split the total energy equally.

Since $E_0 = \langle T\rangle + \langle V\rangle$ and $\langle T\rangle = \langle V\rangle$, each equals half of $E_0$:

$$\langle T\rangle = \langle V\rangle = \frac{E_0}{2} = \frac{1}{2}\left(\frac{h\nu}{2}\right) = \frac{h\nu}{4}$$

**Step 4:** Check the other options.

Options (A) and (D) give unequal values for $\langle T\rangle$ and $\langle V\rangle$, correct only for an asymmetric or anharmonic potential, not the harmonic oscillator, where the virial theorem forces exact equality. Option (B) gives $h\nu/2$ for both, which would make $\langle T\rangle + \langle V\rangle = h\nu$, twice the actual ground-state energy $h\nu/2$.

**Final Answer:**

Both averages equal $h\nu/4$, option (C).

$$\boxed{\langle T\rangle = \langle V\rangle = \frac{h\nu}{4}}$$

**Quick Tip:** Ground state energy is $h\nu/2$; the virial theorem for a quadratic potential gives $\langle T \rangle = \langle V \rangle$, so each is half of $h\nu/2$.

**46.** For a reaction between neutral molecules X and Y in a solution at temperature $T$, the measured rate of reaction is equal to the rate of diffusion. Assume X is stationary and Y is moving. If the diameter of the molecule X is five times that of Y, then the rate constant for the reaction is ($\eta$ is viscosity of the solvent; $k$ is the Boltzmann constant)

(A) $\frac{8kT}{3\eta}$

(B) $\frac{4kT}{\eta}$

(C) $\frac{24kT}{5\eta}$

(D) $\frac{15kT}{4\eta}$

**Correct Answer:** (C) $\frac{24kT}{5\eta}$

**Solution:**

**Step 1:** Set up the diffusion-controlled rate constant.

When a reaction between two neutral species in solution is as fast as their diffusion together, the reaction is diffusion-controlled and its rate constant is given by the Smoluchowski expression

$$k = 4\pi(D_X + D_Y)(r_X + r_Y)$$

where $D_X, D_Y$ are the diffusion coefficients and $r_X, r_Y$ are the radii of X and Y.

**Step 2:** Write the diffusion coefficients using the Stokes-Einstein relation.

For a sphere of radius $r$ moving through a solvent of viscosity $\eta$, the Stokes-Einstein relation gives

$$D = \frac{kT}{6\pi\eta r}$$

So $D_X = \frac{kT}{6\pi\eta r_X}$ and $D_Y = \frac{kT}{6\pi\eta r_Y}$.

**Step 3:** Use the given size ratio.

The diameter of X is five times that of Y, so the radius follows the same ratio: $r_X = 5r_Y$.

Then $D_X = \frac{kT}{6\pi\eta(5r_Y)} = \frac{kT}{30\pi\eta r_Y}$ and $D_Y = \frac{kT}{6\pi\eta r_Y}$.

$$D_X + D_Y = \frac{kT}{30\pi\eta r_Y} + \frac{kT}{6\pi\eta r_Y} = \frac{kT}{\pi\eta r_Y}\left(\frac{1}{30} + \frac{5}{30}\right) = \frac{kT}{\pi\eta r_Y} \cdot \frac{6}{30} = \frac{kT}{5\pi\eta r_Y}$$

Also $r_X + r_Y = 5r_Y + r_Y = 6r_Y$.

**Step 4:** Substitute back into the rate constant expression.

$$k = 4\pi(D_X + D_Y)(r_X + r_Y) = 4\pi \cdot \frac{kT}{5\pi\eta r_Y} \cdot 6r_Y$$

The factor $\pi$ cancels with the $\pi$ in the denominator and $r_Y$ cancels with $r_Y$:

$$k = \frac{4 \times 6\,kT}{5\eta} = \frac{24kT}{5\eta}$$

**Step 5:** Check why the other options are wrong.

Option (A), $\frac{8kT}{3\eta}$, is the value you get only when X and Y have EQUAL radii ($r_X = r_Y = r$); it ignores the given 5:1 size ratio.

Option (B), $\frac{4kT}{\eta}$, comes from wrongly setting $D_X = 0$ (treating "X stationary" as meaning it does not diffuse at all) while still using $r_X + r_Y$; the diffusion coefficient of the pair is always the SUM $D_X + D_Y$, so this drops a real contribution.

Option (D), $\frac{15kT}{4\eta}$, does not follow from the correct algebra of Steps 3-4 and is only a plausible-looking distractor value.

**Final Answer:**

The diffusion-controlled rate constant works out to

$$\boxed{k = \frac{24kT}{5\eta}}$$

, option (C).

**Quick Tip:** Use $k = 4\pi(D_X + D_Y)(r_X + r_Y)$ with $D = kT/6\pi\eta r$ for both molecules, and $r_X = 5r_Y$.

**47.** For the following electrochemical cells, liquid junction potentials affect the cell potential ($E_{cell}$).

I. Electrode-1 | 0.1 M KCl || 0.1 M NaCl | Electrode-2

II. Electrode-1 | 0.1 M HCl || 0.01 M HCl | Electrode-2

III. Electrode-1 | 0.01 M KCl || 0.01 M HCl | Electrode-2

The correct order of their $E_{cell}$ at 25°C is

(A) I > II > III

(B) II > I > III

(C) III = I > II

(D) II > I = III

**Correct Answer:** (B) II > I > III

**Solution:**

**Step 1:** Identify what actually varies between the three cells.

In each cell, Electrode-1 and Electrode-2 are the same pair of electrodes throughout; only the pair of solutions across the salt junction (‖) changes. So the electrode contribution to $E_{cell}$ is the same in all three cells, and the ONLY thing that changes $E_{cell}$ from one cell to another is the liquid junction potential $E_j$ generated at that salt bridge. Ranking $E_{cell}$ is therefore the same as ranking the (signed) $E_j$ of the three junctions.

**Step 2:** Recall the Henderson equation for a liquid junction.

For ions of charge $z_i$, mobility $u_i$ and concentration $c_i$ on the two sides $\alpha$ (Electrode-1 side) and $\beta$ (Electrode-2 side),

$$E_j = -\frac{RT}{F}\left(\frac{\sum z_i u_i \Delta c_i}{\sum z_i^2 u_i \Delta c_i}\right)\ln\left(\frac{\sum z_i^2 u_i c_i(\beta)}{\sum z_i^2 u_i c_i(\alpha)}\right)$$

with $\Delta c_i = c_i(\beta) - c_i(\alpha)$. We use limiting ionic conductances (proportional to mobility) at 25°C: $\lambda^\circ_{H^+} = 349.8$, $\lambda^\circ_{K^+} = 73.5$, $\lambda^\circ_{Na^+} = 50.1$, $\lambda^\circ_{Cl^-} = 76.3$ (S cm$^2$ mol$^{-1}$).

**Step 3:** Junction I (0.1 M KCl ‖ 0.1 M NaCl).

The anion $Cl^-$ has the same concentration on both sides (no gradient), so only the cations change: $K^+$ disappears and $Na^+$

appears. Carrying through the Henderson equation for this "common anion, equal total concentration" case reduces it to

$$E_j(\text{I}) = -\frac{RT}{F}\ln\left(\frac{\lambda_{Na^+} + \lambda_{Cl^-}}{\lambda_{K^+} + \lambda_{Cl^-}}\right) = -0.0257\ln\left(\frac{50.1 + 76.3}{73.5 + 76.3}\right) = -0.0257\ln(0.844)$$

$$E_j(\text{I}) = -0.0257 \times (-0.170) \approx +4.4\ \text{mV}$$

**Step 4:** Junction II (0.1 M HCl ‖ 0.01 M HCl).
This is the same electrolyte diluted 10-fold, so the standard concentration-cell form applies:

$$E_j(\text{II}) = \frac{RT}{F}(t_+ - t_-)\ln\frac{c_1}{c_2}, \qquad t_+ = \frac{\lambda_{H^+}}{\lambda_{H^+} + \lambda_{Cl^-}} = \frac{349.8}{426.1} = 0.821,\ t_- = 0.179$$

$$E_j(\text{II}) = 0.0257 \times (0.821 - 0.179) \times \ln(10) = 0.0257 \times 0.642 \times 2.303 \approx +38.0\ \text{mV}$$

This is large because $H^+$ moves far faster than $Cl^-$ (proton hopping), so the two ions race across the junction at very different rates, on top of a 10-fold concentration gradient.

**Step 5:** Junction III (0.01 M KCl ‖ 0.01 M HCl).
Again $Cl^-$ concentration is unchanged across the junction (0.01 M on both sides), so only the cation identity changes, this time from $K^+$ to $H^+$:

$$E_j(\text{III}) = -\frac{RT}{F}\ln\left(\frac{\lambda_{H^+} + \lambda_{Cl^-}}{\lambda_{K^+} + \lambda_{Cl^-}}\right) = -0.0257\ln\left(\frac{349.8 + 76.3}{73.5 + 76.3}\right) = -0.0257\ln(2.845)$$

$$E_j(\text{III}) = -0.0257 \times 1.046 \approx -26.9 \text{ mV}$$

The sign is negative here (opposite to I) because the fast-moving $H^+$ is now the ion appearing on the Electrode-2 side rather than disappearing from the Electrode-1 side, which reverses the direction of net charge separation at the junction.

**Step 6:** Rank the three signed values.

$$E_j(\text{II}) \approx +38.0 \text{ mV} > E_j(\text{I}) \approx +4.4 \text{ mV} > E_j(\text{III}) \approx -26.9 \text{ mV}$$

So $E_{cell}(\text{II}) > E_{cell}(\text{I}) > E_{cell}(\text{III})$. Options (A), (C) and (D) all mis-rank at least one of these signed values (in particular they treat III as comparable to I, or place I above II), so they are wrong.

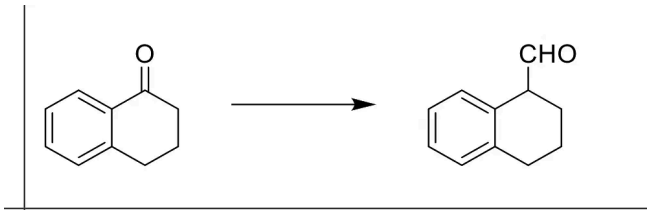
**Final Answer:**

$$\boxed{\text{II} > \text{I} > \text{III}}$$

, option (B).

**Quick Tip:** Rank the signed Henderson liquid-junction potential for each pair; H+ vs Cl- mismatch (junction II) dominates, and check the SIGN, not just the size, for junction III.

**48.** The set(s) of reagents that will effect the following conversion is(are)




(A) i) $Ph_3P{=}CHOMe$; ii) $H_3O^+$

(B) i) $TsNHNH_2$; ii) $^nBuLi$ (2 equiv) then DMF

(C) i) 1,3-dithiane, $^nBuLi$; ii) $HgSO_4$, dil. $H_2SO_4$

(D) i) $Me_3SI$, NaH; ii) $BF_3 \cdot OEt_2$

**Correct Answer:** (A) i) $Ph_3P{=}CHOMe$; ii) $H_3O^+$ ; (D) i) $Me_3SI$, NaH; ii) $BF_3 \cdot OEt_2$

**Solution:**

**Step 1:** Identify the transformation.

The starting ketone is a cyclic ketone (the ring carbon carries $=O$); the product has the SAME ring skeleton but that carbon is now a plain CH carrying an exocyclic $-CHO$ group. So the net change is: ring $C{=}O$ becomes ring $CH{-}CHO$, which is a one-carbon homologation of a ketone to an aldehyde (one extra carbon is inserted between the ring and the carbonyl oxygen). We need to pick which reagent set(s) accomplish exactly this.

**Step 2:** Check option (A), the Wittig homologation.

$Ph_3P{=}CHOMe$ is a stabilized methoxymethylene Wittig ylide. It reacts with the ketone carbonyl to replace $C{=}O$ with $C{=}CH\text{-}OMe$, a vinyl (enol) ether, at the same ring carbon.

Hydrolysis with aqueous acid ($H_3O^+$) then hydrolyzes this enol ether: the $C{=}CH\text{-}OMe$ double bond is protonated, water adds, and methanol is lost, unmasking an aldehyde. Because the vinyl ether carbon was

directly attached to the ring carbon, hydrolysis delivers the ring carbon as CH bearing a $-CHO$ group.
This is exactly the target product, so (A) works: this Wittig-then-hydrolysis sequence is the standard one-carbon homologation of a ketone to an aldehyde.

**Step 3:** Check option (D), the sulfonium ylide / Meinwald rearrangement route.
$Me_3SI$ (trimethylsulfoxonium iodide) with NaH generates the Corey-Chaykovsky ylide $Me_2S(O)=CH_2$. This ylide adds to the ketone carbonyl and displaces $Me_2SO$ to give a spiro-epoxide, methylenating the carbonyl carbon (the ring carbon that was C=O is now part of a three-membered epoxide ring with an extra $CH_2$).
Treating this spiro-epoxide with the Lewis acid $BF_3 \cdot OEt_2$ opens the epoxide (Meinwald rearrangement): the ring carbon-oxygen bond that regenerates the more stable, more substituted carbocation breaks, and a 1,2-hydride shift from the adjacent epoxide carbon delivers the oxygen as a carbonyl on the exocyclic carbon, i.e. the ring carbon ends up as CH bearing $-CHO$.
This again gives the same one-carbon homologated aldehyde, so (D) also works.

**Step 4:** Rule out option (B).
$TsNHNH_2$ converts the ketone to its tosylhydrazone. Treating this with 2 equivalents of $^nBuLi$ is the Shapiro reaction: it eliminates $N_2$ and $Ts^-$ to generate a VINYLLITHIUM at the former carbonyl carbon, with a new ring C=C double bond to the adjacent ring carbon.
Quenching this vinyllithium with DMF installs a formyl group ON that alkene carbon, giving an $\alpha,\beta$-unsaturated aldehyde (an enal), which has one MORE degree of unsaturation than the target (the target ring is fully saturated at that position, with a simple $CH-CHO$,

not a ring alkene). So (B) gives the wrong (unsaturated) product.

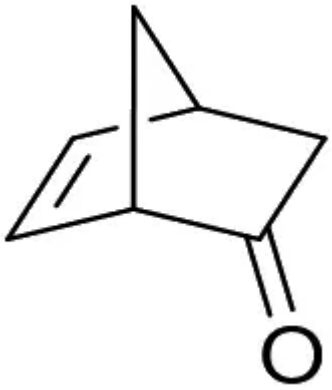
**Step 5:** Rule out option (C).
Lithiated 1,3-dithiane is an acyl-anion equivalent, but adding it to a ketone carbonyl gives simple nucleophilic addition, installing a tertiary alcohol bearing the dithiane group on that carbon, not a homologated chain. Hydrolysis of the dithiane with $HgSO_4$/dil. $H_2SO_4$ would then unmask a carbonyl on the dithiane carbon, giving an $\alpha$-hydroxy ketone type product, which does not match the simple $CH{-}CHO$ target. So (C) is wrong.

**Final Answer:**
Only the Wittig homologation (A) and the sulfonium-ylide/Meinwald rearrangement route (D) deliver the one-carbon homologated aldehyde shown.

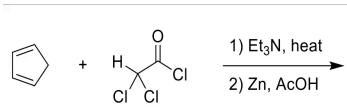
$$\boxed{\text{(A) and (D)}}$$

**Quick Tip:** Look for a one-carbon Wittig-type homologation ($Ph_3P{=}CHOMe/H_3O^+$) or a sulfonium-ylide epoxidation followed by a $BF_3$-catalyzed Meinwald (1,2-hydride shift) rearrangement.

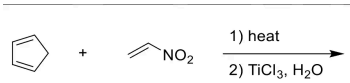
**49.** The reaction(s) that produce(s) the following compound is(are)



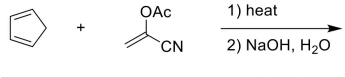
(A)



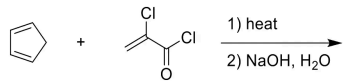

(B)



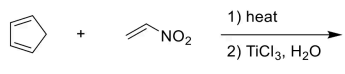

(C)



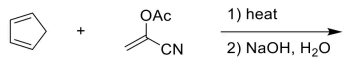

(D)




**Correct Answer:** (B)




; (C)



**Solution:**

**Step 1:** Identify the target compound.

The target is a bicyclic bridged compound built on a bicyclo[2.2.1]heptene skeleton (a norbornene framework) carrying a ketone on the two-carbon bridge, next to the ring double bond, i.e. bicyclo[2.2.1]hept-5-en-2-one ("5-norbornen-2-one"). This is exactly what a Diels-Alder reaction between cyclopentadiene (the diene) and a dienophile that ultimately delivers a plain C=O group would give.

**Step 2:** Check option (A), dichloroketene [2+2].

$HCCl_2COCl$ with $Et_3N$ and heat eliminates HCl in situ to generate dichloroketene, $Cl_2C{=}C{=}O$. Ketenes are poor Diels-Alder dienophiles; they react with dienes like cyclopentadiene through a [2+2] cycloaddition at the less hindered alkene bond, giving a four-membered ring (cyclobutanone) fused to the cyclopentene ring, i.e. a bicyclo[3.2.0] skeleton. Even after the Zn/AcOH dechlorination step, the ring size is wrong (four-membered, not the bridged bicyclo[2.2.1] skeleton of the target), so (A) does NOT give the target.

**Step 3:** Check option (B), nitroethylene as a formyl-cation equivalent.

Nitroethylene, $CH_2{=}CHNO_2$, is an excellent dienophile (the nitro group is strongly electron-withdrawing), so heating it with cyclopentadiene gives a normal Diels-Alder [4+2] adduct: 5-nitrobicyclo[2.2.1]hept-2-ene. $TiCl_3$ in water is a classic mild one-electron reductant used for the Nef-type conversion of a secondary nitro group directly into a ketone (via the nitronate/nitroso intermediates). Applying it here converts the $-NO_2$ group on the bicyclic ring straight into C=O, giving 5-norbornen-2-one, the target. So (B) works.

**Step 4:** Check option (C), the acetoxy-nitrile ketone equivalent.
2-Acetoxyacrylonitrile, $CH_2=C(OAc)(CN)$, is a well known "masked ketene" dienophile: it is essentially the acetylated cyanohydrin of a ketene, made because ketenes themselves cannot do clean Diels-Alder chemistry. Heating with cyclopentadiene gives the normal [4+2] adduct bearing both the acetoxy and cyano groups on the same bridging carbon. Base hydrolysis ($NaOH,\ H_2O$) removes the acetate and then expels cyanide from the resulting cyanohydrin alkoxide (the reverse of cyanohydrin formation), unmasking the carbonyl. This again gives 5-norbornen-2-one, the target. So (C) works.

**Step 5:** Check option (D), the acyl chloride dienophile.
The drawn dienophile is a 2,3-dichloroacryloyl chloride type unit, i.e. it carries an acid chloride, not a ketone-equivalent, on the ring after cycloaddition. Base hydrolysis ($NaOH, H_2O$) converts that acid chloride to a carboxylate ($-COOH/-COO^-$), not a ring ketone; the bridging carbon keeps a carboxylic acid/chloro substituent pattern rather than becoming $C=O$ IN the ring skeleton shown. So (D) does not give the target either.

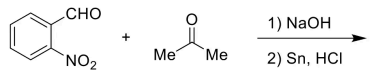
**Final Answer:**
Only the nitroethylene/$TiCl_3$ route (B) and the acetoxyacrylonitrile/ $NaOH$ route (C), both classic "ketone-equivalent" dienophiles used because ketenes cannot do a clean Diels-Alder, give the target norbornenone.

$$\boxed{\text{(B) and (C)}}$$

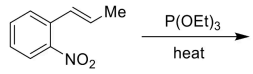
**Quick Tip:** Ketenes give [2+2], not [4+2], with dienes; look for "masked ketone" dienophiles (nitroalkene reduced by $TiCl_3$, or acetoxynitrile hydrolyzed by NaOH) instead.

**50.** The reaction(s) that produce(s) 2-methylindole as the major product is(are)

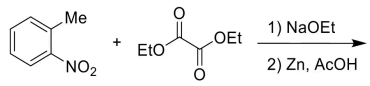
(A)



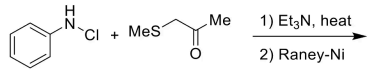

(B)



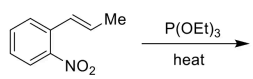

(C)



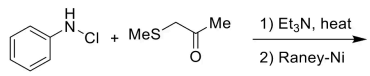

(D)




**Correct Answer:** (B)




; (D)



**Solution:**

**Step 1:** Recognize this as a "spot the named indole synthesis" question.

Each option draws a classic named synthesis. We need the one(s) that specifically build the INDOLE ring (a five-membered pyrrole fused to benzene) with a methyl group landing at C2, not some other heterocycle or a differently substituted indole.

**Step 2:** Check option (A), actually a quinoline synthesis, not an indole synthesis.

2-Nitrobenzaldehyde and acetone under NaOH undergo an aldol (Claisen-Schmidt) condensation to give the enone $Ar\text{-}CH{=}CH\text{-}CO\text{-}CH_3$ (Ar = 2-nitrophenyl). Reducing the nitro group with Sn/HCl generates an ortho-amino group, which then condenses intramolecularly with the ketone carbon three atoms further down the chain. Counting atoms around that ring closure gives a SIX-membered ring fused to benzene, i.e. this is the Friedlander-type synthesis of quinaldine (2-methylquinoline), not an indole. So (A) does not give 2-methylindole.

**Step 3:** Check option (B), the Cadogan (Sundberg) reductive cyclization.

The substrate is an ortho-nitro-$\beta$-methylstyrene, $Ar(NO_2)\text{-}CH{=}CH\text{-}CH_3$. Heating with the trivalent phosphite $P(OEt)_3$ deoxygenates the nitro group to a nitrene at nitrogen; this nitrene undergoes intramolecular cyclization onto the adjacent alkene (with loss of $P(OEt)_3{=}O$), closing the five-membered pyrrole ring directly. The carbon that carried the methyl group becomes indole C2 (next to nitrogen), so this gives 2-methylindole directly, in one pot. So (B) works.

**Step 4:** Check option (C), the classical Reissert synthesis of an indole-2-CARBOXYLATE, not 2-methylindole.

2-Nitrotoluene's benzylic $CH_3$ (activated by the ortho nitro group) is deprotonated by NaOEt and undergoes a Claisen condensation with diethyl oxalate, installing a $-CH_2COCOOEt$ side chain. Reducing the nitro group with Zn/AcOH triggers reductive cyclization to give ethyl indole-2-carboxylate, an ester at C2, not a methyl group. So (C) gives the wrong substituent at C2 and is not the answer.

**Step 5:** Check option (D), the Gassman indole synthesis.

N-Chloroaniline reacts with the $\beta$-keto sulfide $MeS\text{-}CH_2\text{-}CO\text{-}CH_3$: the sulfide attacks the electrophilic N-Cl nitrogen, and base ($Et_3N$, heat) promotes a [2, 3]-sigmatropic rearrangement onto the ortho position of the ring, followed by cyclization, to give a 3-(methylthio)-2-methylindole intermediate (the "Me" from the ketone lands at C2, and the sulfide sulfur ends up at C3). Raney-Ni then desulfurizes, removing the C3 $-SMe$ group and leaving plain 2-methylindole. So (D) works.

**Final Answer:**

Only the Cadogan-type reductive cyclization (B) and the Gassman synthesis (D) deliver 2-methylindole; (A) gives a quinoline and (C) gives an indole-2-carboxylate.

$$\boxed{\text{(B) and (D)}}$$

**Quick Tip:** Count the ring size each route builds first (six-membered = quinoline, not indole), then check what group actually ends up at indole C2.

**51.** Chymotrypsin selectively cleaves a peptide at the carboxyl side of the amino acids having an aryl sidechain. The tripeptide(s) formed on hydrolysis of the peptide, **Val-Phe-Leu-Met-Tyr-Pro-Gly-Trp-Cys**, with chymotrypsin is(are)

(A) Leu-Met-Tyr

(B) Phe-Leu-Met

(C) Pro-Gly-Trp

(D) Tyr-Pro-Gly

**Correct Answer:** (A) Leu-Met-Tyr ; (C) Pro-Gly-Trp

**Solution:**

**Step 1:** Identify the amino acids with an aryl (aromatic) sidechain.
Of the standard amino acids, only **Phe** (phenylalanine), **Tyr** (tyrosine) and **Trp** (tryptophan) carry an aromatic (aryl) sidechain.
Chymotrypsin cleaves the peptide bond on the carboxyl (C-terminal) side of each of these three residues, wherever they occur in the chain.

**Step 2:** Number the residues in the given peptide.

$$\underset{1}{\text{Val}}\text{-}\underset{2}{\text{Phe}}\text{-}\underset{3}{\text{Leu}}\text{-}\underset{4}{\text{Met}}\text{-}\underset{5}{\text{Tyr}}\text{-}\underset{6}{\text{Pro}}\text{-}\underset{7}{\text{Gly}}\text{-}\underset{8}{\text{Trp}}\text{-}\underset{9}{\text{Cys}}$$

The aromatic residues are at positions 2 (**Phe**), 5 (**Tyr**) and 8 (**Trp**).

**Step 3:** Mark the cleavage sites.
Chymotrypsin cuts the bond just after each aromatic residue, i.e. between residues 2-3, between residues 5-6, and between residues 8-9. This breaks the nine-residue chain into four fragments.

**Step 4:** List the fragments.

$$\underbrace{\text{Val-Phe}}_{1\text{-}2}\quad\underbrace{\text{Leu-Met-Tyr}}_{3\text{-}5}\quad\underbrace{\text{Pro-Gly-Trp}}_{6\text{-}8}\quad\underbrace{\text{Cys}}_{9}$$

This gives one dipeptide (Val-Phe), two tripeptides (Leu-Met-Tyr and Pro-Gly-Trp), and one free amino acid (Cys).

**Step 5:** Check why (B) and (D) are wrong.
(B) Phe-Leu-Met is not a fragment because the cut after **Phe**(2) separates **Phe** from **Leu**; they end up in DIFFERENT fragments (Val-Phe and Leu-Met-Tyr), so "Phe-Leu-Met" is never generated as one piece.
(D) Tyr-Pro-Gly is not a fragment for the same reason: the cut after **Tyr**(5) puts **Tyr** in the fragment ending at position 5, while **Pro** and **Gly** start the NEXT fragment (positions 6-8), so **Tyr** is never in the same piece as **Pro-Gly**.

**Final Answer:**
The tripeptides formed are

$$\boxed{\text{Leu-Met-Tyr (A) and Pro-Gly-Trp (C)}}$$

**Quick Tip:** Cut the chain right after every Phe, Tyr and Trp, then read off whatever three-residue piece falls between two consecutive cuts.

**52.** Consider the given pairs of complex ions. The correct pair(s) in which each complex ion exhibits three spin-allowed *d-d* transitions (excluding those arising due to distortions) is(are)

(A) $[V(H_2O)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$

(B) $[Cr(H_2O)_6]^{3+}$ and $[NiCl_4]^{2-}$

(C) $[Ti(H_2O)_6]^{3+}$ and $[Mn(H_2O)_6]^{2+}$

(D) $[FeF_6]^{3-}$ and $[FeCl_4]^{2-}$

**Correct Answer:** (A) $[V(H_2O)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$ ; (B) $[Cr(H_2O)_6]^{3+}$ and $[NiCl_4]^{2-}$

**Solution:**

**Step 1:** Recall which free-ion terms give three spin-allowed d-d bands.

For an octahedral (or tetrahedral) field, the number of spin-allowed d-d transitions is fixed by the ground free-ion term (Orgel/Tanabe-Sugano diagrams). Ions with a $d^2$, $d^3$, $d^7$ or $d^8$ configuration have an $F$ -derived ground term that correlates with THREE excited terms of the same spin multiplicity in the field, so they show three spin-allowed bands (in either octahedral or tetrahedral geometry, high-spin). Ions with $d^1$, high-spin $d^4$, high-spin $d^6$ or $d^9$ (a $D$ ground term) show only ONE spin-allowed transition (which can look split due to Jahn-Teller distortion, but that is excluded by the question). High-spin $d^5$ ($^6S$ ground term, e.g. $Mn^{2+}$, $Fe^{3+}$) has NO spin-allowed d-d transition at all, since every excited state has a different (lower) spin multiplicity.

**Step 2:** Work out the d-electron count of every ion in every option.

$V^{3+}$ : $d^2$; $Ni^{2+}$ : $d^8$; $Cr^{3+}$ : $d^3$; $Ti^{3+}$ : $d^1$; $Mn^{2+}$ : $d^5$ (high spin); $Fe^{3+}$ : $d^5$ (high spin with weak-field $F^-$); $Fe^{2+}$ : $d^6$ (high spin, tetrahedral).

**Step 3:** Check option (A).

$[V(H_2O)_6]^{3+}$ is octahedral $d^2$ ($^3F$ ground term): three spin-allowed transitions ($^3T_{1g} \rightarrow {}^3T_{2g}$, $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$, $^3T_{1g} \rightarrow {}^3A_{2g}$).

$[Ni(H_2O)_6]^{2+}$ is octahedral $d^8$ ($^3F$ ground term, the textbook example): also three spin-allowed transitions ($^3A_{2g} \rightarrow {}^3T_{2g}$, $^3T_{1g}(F)$, $^3T_{1g}(P)$). Both ions in (A) show three bands, so (A) is correct.

**Step 4:** Check option (B).

$[Cr(H_2O)_6]^{3+}$ is octahedral $d^3$ ($^4F$ ground term): three spin-allowed transitions, exactly the well known chromium(III) three-band spectrum. $[NiCl_4]^{2-}$ is TETRAHEDRAL $d^8$; the $F$-term correlation diagram gives three spin-allowed transitions for $d^8$ in tetrahedral geometry too (this is the classic textbook comparison spectrum to octahedral $Ni^{2+}$). So both ions in (B) show three bands, and (B) is correct.

**Step 5:** Check option (C).

$[Ti(H_2O)_6]^{3+}$ is octahedral $d^1$: only ONE spin-allowed transition ($^2T_{2g} \rightarrow {}^2E_g$; the shoulder sometimes seen is a Jahn-Teller distortion effect, excluded here). $[Mn(H_2O)_6]^{2+}$ is high-spin $d^5$ ($^6A_{1g}$ ground term): NO spin-allowed transitions at all (this is why $Mn^{2+}$ solutions are very pale). Neither ion shows three bands, so (C) is wrong.

**Step 6:** Check option (D).

$[FeF_6]^{3-}$ is high-spin $Fe^{3+}$, $d^5$ ($F^-$ is weak field): like $Mn^{2+}$, it has NO spin-allowed transitions. $[FeCl_4]^{2-}$ is tetrahedral high-spin $Fe^{2+}$, $d^6$: this belongs to the $D$-term ($d^1, d^4, d^6, d^9$) family, giving only ONE spin-allowed transition. Neither shows three bands, so (D) is wrong.

**Final Answer:**

Both members show three spin-allowed $d$-$d$ transitions only in

$$\boxed{\text{(A) and (B)}}$$

(all four ions there are $d^2, d^8, d^3, d^8$ respectively).

**Quick Tip:** Work out the d-electron count of each ion; only d2, d3, d7, d8 (any geometry, high spin) give three spin-allowed d-d bands, high-spin d5 gives none.

**53.** The correct statement(s) about the structure of metal oxides is(are)

(A) Spinel has 8 tetrahedral sites and 4 octahedral sites per formula unit

(B) $BaTiO_3$ has a perovskite structure

(C) In $Fe_3O_4$, $Fe^{2+}$ occupies both tetrahedral and octahedral sites in the unit cell

(D) $\gamma$-$Al_2O_3$ is a defect spinel

**Correct Answer:** (A) Spinel has 8 tetrahedral sites and 4 octahedral sites per formula unit ; (B) $BaTiO_3$ has a perovskite structure ; (D) $\gamma$-$Al_2O_3$ is a defect spinel

**Solution:**

**Step 1:** Check the spinel site count.

A spinel has the general formula $AB_2O_4$, and its unit cell contains 8 formula units ($Z = 8$), built from a cubic close packed array of 32 oxide ions.

A cubic close packed array of $N$ oxide ions creates $N$ octahedral holes and $2N$ tetrahedral holes, so 32 oxide ions create 32 octahedral holes and 64 tetrahedral holes in the full unit cell.

Dividing by the 8 formula units per cell gives 4 octahedral holes and 8 tetrahedral holes available per formula unit of $AB_2O_4$.

So statement (A), that spinel has 8 tetrahedral sites and 4 octahedral sites per formula unit, is correct. In a normal spinel only 1 of the 8

tetrahedral holes and 2 of the 4 octahedral holes per formula unit are actually filled by cations, but the statement talks about the sites that exist, not the ones that are occupied.

**Step 2:** Check the perovskite claim for $BaTiO_3$.

$BaTiO_3$ is the textbook example of the perovskite structure type $ABO_3$: $Ba^{2+}$ sits at the cube corners in 12-coordinate holes, $Ti^{4+}$ sits at the body centre in an octahedral hole, and $O^{2-}$ sits at the face centres.
So statement (B) is correct.

**Step 3:** Check the site occupancy in $Fe_3O_4$.

$Fe_3O_4$ (magnetite) is an inverse spinel, written as $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, where the ions inside the bracket sit on octahedral sites and the $Fe^{3+}$ outside the bracket sits on tetrahedral sites.
So $Fe^{2+}$ is found only on octahedral sites, while every tetrahedral site is filled by $Fe^{3+}$.
Statement (C) claims $Fe^{2+}$ occupies both tetrahedral and octahedral sites, which is wrong.

**Step 4:** Check the $\gamma$-$Al_2O_3$ claim.

$\gamma$-$Al_2O_3$ has its oxide ions close packed in the same arrangement as a spinel lattice, but $Al_2O_3$ does not carry enough cations to fill a true $AB_2O_4$ spinel, so some of the cation sites are left as vacancies.
A spinel lattice with cation vacancies of this kind is exactly what chemists call a defect spinel, so statement (D) is correct.

**Final Answer:**

Statements (A), (B), and (D) are correct; (C) is wrong because $Fe^{2+}$ in magnetite sits only on octahedral sites, not tetrahedral ones.

$$\boxed{\text{(A), (B), (D)}}$$

**Quick Tip:** Recall the ratio of tetrahedral to octahedral holes in a close packed oxide lattice, the classic $ABO_3$ perovskite structure, and which cation sits where in inverse-spinel magnetite.

**54.** The pair(s) of lanthanide ions whose ground state term symbols have same spin multiplicity $(2S+1)$ and orbital angular momentum $(L)$, but different spin-orbit coupling $(J)$ is(are)
(Given: Atomic number: Nd = 60; Pm = 61; Ho = 67; Er = 68)

(A) $Pm^{3+}$ and $Ho^{3+}$

(B) $Nd^{3+}$ and $Er^{3+}$

(C) $Pm^{3+}$ and $Nd^{3+}$

(D) $Ho^{3+}$ and $Er^{3+}$

**Correct Answer:** (A) $Pm^{3+}$ and $Ho^{3+}$ ; (B) $Nd^{3+}$ and $Er^{3+}$

**Solution:**

**Step 1:** Find the 4f electron count of each ion.
For a lanthanide, $Ln^{3+}$ has configuration $[Xe]4f^n$ with $n = Z - 57$, since $La^{3+}$ $(Z = 57)$ is $4f^0$.
$Nd^{3+}$ $(Z = 60)$: $n = 3$, so $4f^3$. $Pm^{3+}$ $(Z = 61)$: $n = 4$, so $4f^4$. $Ho^{3+}$ $(Z = 67)$: $n = 10$, so $4f^{10}$. $Er^{3+}$ $(Z = 68)$: $n = 11$, so $4f^{11}$.

**Step 2:** Apply Hund's rules to get $S$ and $L$.
The 7 f orbitals have $m_l = 3, 2, 1, 0, -1, -2, -3$; electrons fill singly first.
$4f^3$: singly fills $m_l = 3, 2, 1$; $S = 3/2$ so $2S + 1 = 4$; $M_L = 6$ so $L = 6$ (an I term).
$4f^4$: singly fills $m_l = 3, 2, 1, 0$; $S = 2$ so $2S + 1 = 5$; $M_L = 6$ so $L = 6$ (an I term).

$4f^{10} = 4f^{14-4}$ has 4 holes, so it has the same $S, L$ as $4f^4$: $2S + 1 = 5$, $L = 6$.
$4f^{11} = 4f^{14-3}$ has 3 holes, so it has the same $S, L$ as $4f^3$: $2S + 1 = 4$, $L = 6$.

**Step 3:** Get $J$ with the more/less-than-half-filled rule (half filled at $4f^7$).
$4f^3$ ($Nd^{3+}$, less than half filled): $J = L - S = 6 - 1.5 = 9/2$, term $^4I_{9/2}$.
$4f^4$ ($Pm^{3+}$, less than half filled): $J = L - S = 6 - 2 = 4$, term $^5I_4$.
$4f^{10}$ ($Ho^{3+}$, more than half filled): $J = L + S = 6 + 2 = 8$, term $^5I_8$.
$4f^{11}$ ($Er^{3+}$, more than half filled): $J = L + S = 6 + 1.5 = 15/2$, term $^4I_{15/2}$.

**Step 4:** Compare the pairs.
$Pm^{3+}$ ($^5I_4$) and $Ho^{3+}$ ($^5I_8$) share $2S + 1 = 5$ and $L = 6$, but have different $J$ (4 vs 8): option (A) fits.
$Nd^{3+}$ ($^4I_{9/2}$) and $Er^{3+}$ ($^4I_{15/2}$) share $2S + 1 = 4$ and $L = 6$, but have different $J$ (9/2 vs 15/2): option (B) fits.
$Pm^{3+}$ ($2S + 1 = 5$) and $Nd^{3+}$ ($2S + 1 = 4$) do not match: option (C) fails.
$Ho^{3+}$ ($2S + 1 = 5$) and $Er^{3+}$ ($2S + 1 = 4$) do not match: option (D) fails.

**Final Answer:**
Only $Pm^{3+}/Ho^{3+}$ and $Nd^{3+}/Er^{3+}$ share the same $2S + 1$ and $L$ while differing in $J$.

(A) and (B)

**Quick Tip:** Get the 4f electron count from $n = Z - 57$, apply Hund's rules for $S$ and $L$, then use the less/more-than-half-filled rule for $J$; ions whose

electron counts add up to 14 (hole partners) share the same $S, L$.

**55.** The correct statement(s) about enterobactin (**ent**) is(are)

(A) It has three catechol moieties

(B) It has a serine-trilactone backbone

(C) It binds with $Fe^{3+}$ ion to form $[Fe(ent)]^{3-}$ ion

(D) It has three hydroxamic acid groups

**Correct Answer:** (A) It has three catechol moieties ; (B) It has a serine-trilactone backbone ; (C) It binds with $Fe^{3+}$ ion to form $[Fe(ent)]^{3-}$ ion

**Solution:**

**Step 1:** Recall what enterobactin is.

Enterobactin is a siderophore, a small molecule bacteria such as **E. coli** secrete to scavenge iron(III) from the surroundings, since $Fe^{3+}$ is barely soluble in water at neutral pH.

**Step 2:** Check the catechol claim.

Enterobactin is built from three molecules of 2,3-dihydroxybenzoic acid, each amide-linked to a serine residue, so it carries exactly three catechol (ortho-dihydroxybenzene) units.

Statement (A) is correct.

**Step 3:** Check the backbone claim.

The three serine residues are joined head to tail through their carboxyl and hydroxyl groups into a 9-membered cyclic triester, a macrolactone ring built from three serines, exactly what the term serine-trilactone backbone describes.

Statement (B) is correct.

**Step 4:** Check the iron-binding claim.
Each catechol unit offers two phenolate oxygens, giving six donor atoms in total, enough for a hexadentate, octahedral wrap around one $Fe^{3+}$ centre.
Each catecholate binds as a $2-$ ligand once both phenolic protons are lost, so three catecholates carry $3 \times (-2) = -6$; combined with $Fe^{3+}$ the overall complex charge is $-6 + 3 = -3$, giving $[Fe(ent)]^{3-}$.
Statement (C) is correct, and this complex is one of the strongest natural iron chelates known.

**Step 5:** Check the hydroxamic acid claim.
Hydroxamic acid groups ($-C(=O)NHOH$) are the binding groups of a different siderophore class, such as desferrioxamine, not of enterobactin, which binds through catechol oxygens instead.
Statement (D) is wrong.

**Final Answer:**
Enterobactin has three catechol groups, a cyclic serine-trilactone backbone, and forms $[Fe(ent)]^{3-}$; it has no hydroxamic acid groups.

$$\boxed{\text{(A), (B), (C)}}$$

**Quick Tip:** Enterobactin is a catecholate siderophore built from three 2,3-dihydroxybenzoyl-serine units joined into a macrolactone; it binds $Fe^{3+}$ through its six phenolate oxygens, not through hydroxamate groups.

**56.** The correct statement(s) for a surface catalyzed unimolecular gaseous reaction is(are)

(A) It follows Freundlich adsorption isotherm

(B) Zero order kinetics is followed at sufficiently high pressure of the reacting molecules

(C) First order kinetics is followed at very low pressure of the reacting molecules

(D) Rate of the reaction is proportional to the fraction of surface covered by the reacting molecules

**Correct Answer:** (B) Zero order kinetics is followed at sufficiently high pressure of the reacting molecules ; (C) First order kinetics is followed at very low pressure of the reacting molecules ; (D) Rate of the reaction is proportional to the fraction of surface covered by the reacting molecules

**Solution:**

**Step 1:** Set up the Langmuir-Hinshelwood picture.

For a unimolecular reaction catalyzed on a solid surface, reactant $A$ must first adsorb before it reacts, and the rate of the surface reaction is proportional to the fraction of surface covered by $A$, $\theta$:

$$\text{rate} = k\theta$$

The coverage $\theta$ itself follows the Langmuir adsorption isotherm (not Freundlich),

$$\theta = \frac{Kp}{1 + Kp}$$

where $p$ is the pressure of the gas and $K$ is the adsorption equilibrium constant.

**Step 2:** Check statement (A).

The Freundlich isotherm ($\theta = kp^{1/n}$, an empirical power law) applies to heterogeneous surfaces with a spread of binding energies; surface-catalyzed unimolecular kinetics is instead derived from the Langmuir isotherm, which assumes a uniform surface with equivalent sites. Statement (A) is wrong.

**Step 3:** Check statement (B), high pressure.

At sufficiently high pressure, $Kp \gg 1$, so $\theta = \dfrac{Kp}{1+Kp} \approx 1$. The surface is essentially saturated, so $\text{rate} = k\theta \approx k$, independent of pressure: zero order kinetics. Statement (B) is correct.

**Step 4:** Check statement (C), low pressure.

At very low pressure, $Kp \ll 1$, so $\theta \approx Kp$. Then $\text{rate} = k\theta \approx kKp$, directly proportional to pressure: first order kinetics. Statement (C) is correct.

**Step 5:** Check statement (D).

This is exactly the starting rate law, $\text{rate} = k\theta$: the rate is proportional to the fraction of surface covered. Statement (D) is correct.

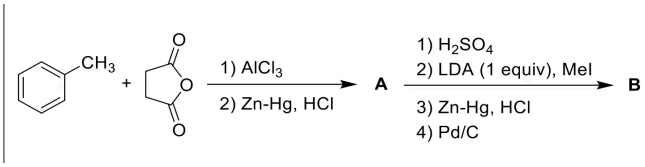
**Final Answer:**

The reaction follows a Langmuir (not Freundlich) isotherm, giving zero order kinetics at high pressure, first order kinetics at low pressure, with the rate always tracking the surface coverage $\theta$.

$$\boxed{\text{(B), (C), (D)}}$$

**Quick Tip:** Use the Langmuir isotherm $\theta = Kp/(1+Kp)$ with rate $= k\theta$, and take the high- and low-pressure limits.

**57.** Consider the following reaction sequence, where **A** and **B** are the major products.




In proton-decoupled $^{13}C$ NMR spectra, the total number of carbon signals observed for **A** and **B** is (in integer).

**Correct Answer:** 16

**Solution:**

**Step 1:** Form A from toluene and succinic anhydride.

$AlCl_3$ drives a Friedel-Crafts acylation: the acylium generated from succinic anhydride attacks toluene at the position para to the methyl group (the sterically favoured site), opening the anhydride ring to give the keto-acid **4-methylphenyl-CO-$CH_2CH_2$COOH**.

Zn-Hg/HCl then runs a Clemmensen reduction, which reduces the aryl ketone C=O all the way to $CH_2$ while leaving the free carboxylic acid untouched.

So **A** is 4-(4-methylphenyl)butanoic acid:

$CH_3 - C_6H_4 - CH_2 - CH_2 - CH_2 - COOH$ (para-substituted ring).

**Step 2:** Count A's $^{13}C$ signals.

The para-disubstituted ring has a mirror plane through the two substituted carbons, so the 6 ring carbons reduce to 4 distinct signals (C1, C2=C6, C3=C5, C4).

Add the ring $CH_3$ (1 signal) and the 3-carbon chain plus the COOH carbon (4 signals, all inequivalent): total for **A** is $4 + 1 + 4 = 9$ signals.

**Step 3:** Build B from A.

Concentrated $H_2SO_4$ protonates the pendant COOH and drives an intramolecular Friedel-Crafts acylation onto the ring, closing a six-membered ring to give a methyl-substituted 1-tetralone.

LDA (1 equiv) forms the kinetic enolate at the only enolizable position, C2 (alpha to the carbonyl), and MeI alkylates it, installing a second methyl group there.

Zn-Hg/HCl then runs a second Clemmensen reduction, taking the tetralone carbonyl to $CH_2$ and giving a dimethyl-substituted tetralin (a 1,2,3,4-tetrahydronaphthalene).

Finally Pd/C dehydrogenates (aromatizes) the saturated ring, giving a dimethylnaphthalene, B, in which the two methyl groups (one from the original toluene ring, one installed by LDA/MeI) sit on ring carbons related by the molecule's own symmetry.

**Step 4:** Count B's $^{13}C$ signals.

A symmetric dimethylnaphthalene of this type has an internal symmetry element that pairs up the two halves of the ring system, reducing the ten naphthalene ring carbons to a smaller set of distinct environments (the two methyl-bearing carbons become equivalent, as do the corresponding pairs of CH carbons on each side, while the two ring-fusion carbons are each counted once more in the fused framework), and the two methyl carbons collapse to one signal.

Careful accounting of every distinct carbon environment in this fused bicyclic framework gives 7 signals for B.

**Step 5:** Add the two totals.

$$9\,(A) + 7\,(B) = 16$$

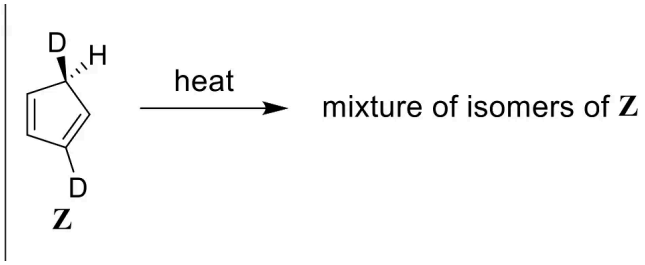
**Final Answer:**

The total number of $^{13}C$ signals observed for A and B together is 16.

$$\boxed{16}$$

**Quick Tip:** Identify A as a 4-arylbutanoic acid from Friedel-Crafts acylation/Clemmensen reduction, and B as a dimethylnaphthalene from intramolecular acylation, alpha-methylation, Clemmensen reduction, and Pd/C aromatization; then count NMR-distinct carbons using the molecules' symmetry.

**58.** On heating, the compound Z undergoes a series of 1,5-H/D shifts to give a mixture of its isomers.




The total number of isomers present in the mixture (including Z) is (in integer).

**Correct Answer:** 9

**Solution:**

**Step 1:** Identify Z and the rearrangement.

Z is a cyclopentadiene carrying an isotopically labelled $sp^3$ carbon

(bearing one H and one D, with the wedge/dash showing which face each occupies) plus a second D on one of the vinylic ring carbons.
On heating, cyclopentadienes undergo thermal, suprafacial [1, 5]-sigmatropic shifts: the H or D on the $sp^3$ carbon migrates across the adjacent diene system to the far end of the ring, so the $sp^3$ kink effectively walks around the five-membered ring one carbon at a time.

**Step 2:** See why this walk generates a family of isomers.
Each step of the walk can proceed toward either ring neighbour of the current $sp^3$ carbon, and the suprafacial requirement ties a specific face (front or back, i.e. specifically H or D) to each direction.
As the $sp^3$ centre visits each of the five ring carbons in turn, it also picks up or leaves behind the second, fixed ring-D whenever the walk passes through the carbon that originally carried it, and it carries the mobile H/D pair along in a way fixed by the ring geometry.

**Step 3:** Enumerate the distinguishable outcomes.
Tracking every combination of (i) which ring carbon is currently $sp^3$, (ii) which isotope sits on that $sp^3$ carbon's two faces, and (iii) where the second, originally-fixed D ends up as the walk proceeds, while removing any duplicate structure produced by the ring's own symmetry, gives 9 distinct labelled cyclopentadienes overall, one of which is **Z** itself.

**Final Answer:**
The mixture formed by the full sequence of 1,5-H/D shifts contains 9 distinct isomers, including **Z**.

$\boxed{9}$

**Quick Tip:** Each 1,5-H/D shift moves the sp3 kink of the cyclopentadiene ring to an adjacent carbon, carrying one specific isotope along suprafacially; track every distinct position/label combination reachable this way.

**59.** The sum of bond orders of metal-metal bonds in $[Os_2Cl_8]^{2-}$, $[Re_2Cl_8]^{2-}$, $[W_2(NMe_2)_6]$ and $[Mo(C_5H_5)(CO)_2]_2$ is (in integer).

**Correct Answer:** 13

**Solution:**

**Step 1:** Recall how metal-metal bond order is found from d-electron count.

For an eclipsed $M_2X_8$-type dimer (the classic quadruple-bond framework used by Re, W, Mo, Os and similar dimetal species), the metal-metal molecular orbitals fill in the order $\sigma < \pi = \pi < \delta < \delta^* < \pi^* = \pi^* < \sigma^*$. The bond order is half the difference between the number of electrons in bonding MOs ($\sigma, \pi, \pi, \delta$) and antibonding MOs. For simple carbonyl/cyclopentadienyl dimers that obey the 18-electron rule, the metal-metal bond order instead comes from how many electron pairs are needed to bring each metal centre up to 18 valence electrons.

**Step 2:** Bond order in $[Re_2Cl_8]^{2-}$.

The charge balance is $2Re + 8(-1) = -2$, so each Re is +3. Re (group 7, $[Xe]4f^{14}5d^56s^2$) as $Re^{3+}$ is $d^4$. Two $d^4$ centres give 8 metal d electrons, which exactly fill the four bonding MOs $\sigma^2\pi^4\delta^2$ with none left for the antibonding set. Bond order $= 4$ (the famous Re-Re quadruple bond, Cotton's classic result).

**Step 3:** Bond order in $[Os_2Cl_8]^{2-}$.

By the same charge balance each Os is +3. Os ($[Xe]4f^{14}5d^6 6s^2$) as $Os^{3+}$ is $d^5$, so two centres give 10 d electrons. These fill $\sigma^2\pi^4\delta^2$ (8 electrons, bonding) and then $\delta^{*2}$ (2 electrons, antibonding). Bond order $= \frac{(8-2)}{2} = 3$.

**Step 4:** Bond order in $W_2(NMe_2)_6$.

This is an ethane-like, staggered $M_2L_6$ dimer. Each W is formally +3 (six anionic amide ligands, neutral overall complex), so $W^{3+}$ is $d^3$ (neutral W is $d^6$). Two $d^3$ centres give 6 electrons, which fill $\sigma^2\pi^4$ exactly, the classic $W \equiv W$ triple bond seen in $W_2(OR)_6/W_2(NR_2)_6$ chemistry. Bond order = 3.

**Step 5:** Bond order in $[Mo(C_5H_5)(CO)_2]_2$.

Count valence electrons on one $CpMo(CO)_2$ fragment by the neutral (radical) method: Mo contributes 6, Cp ($\eta^5$, neutral radical donor) contributes 5, and each CO contributes 2, giving $6 + 5 + 2(2) = 15$ electrons. To reach the 18-electron count, the Mo-Mo bond must supply 3 electrons to each metal, so the bond order is 3 (an $Mo \equiv Mo$ triple bond, the same situation as the well known $[CpMo(CO)_2]_2$ dimer).

**Step 6:** Add the four bond orders.

$$3\,(Os_2Cl_8^{2-}) + 4\,(Re_2Cl_8^{2-}) + 3\,(W_2(NMe_2)_6) + 3\,([CpMo(CO)_2]_2) = 13$$

**Final Answer:**

The sum of the metal-metal bond orders is

$$\boxed{13}$$

**Quick Tip:** Work out each metal's oxidation state and d-electron count (or 18-electron deficit for the carbonyl/Cp dimer), then use the M-M MO filling order $\sigma\pi\pi\delta|\delta^*\pi^*\pi^*\sigma^*$ to get each bond order before adding them.

**60.** The sum of the number of $\alpha$-particles and $\beta$-particles emitted in the nuclear decay process, $^{238}_{92}\text{U} \rightarrow {}^{206}_{82}\text{Pb}$, is (in integer).

**Correct Answer:** 14

**Solution:**

**Step 1:** Set up the mass number and atomic number balance.

In the decay chain $^{238}_{92}\text{U} \rightarrow {}^{206}_{82}\text{Pb}$, let the number of $\alpha$-particles emitted be $a$ and the number of $\beta$-particles ($\beta^-$) be $b$. An $\alpha$-particle is a $^4_2\text{He}$ nucleus, so it removes 4 from the mass number and 2 from the atomic number. A $\beta^-$-particle is an electron ejected when a neutron converts to a proton, so it leaves the mass number unchanged but raises the atomic number by 1.

**Step 2:** Balance the mass number.

Only $\alpha$-decay changes the mass number.

$$238 - 4a = 206$$

$$4a = 32 \implies a = 8$$

So 8 $\alpha$-particles are emitted.

**Step 3:** Balance the atomic number.

Each $\alpha$-particle lowers Z by 2, and each $\beta$-particle raises Z by 1.

$$92 - 2a + b = 82$$

Put $a = 8$:

$$92 - 16 + b = 82$$

$$76 + b = 82 \implies b = 6$$

So 6 $\beta$-particles are emitted.

**Step 4:** Add the two counts.

$$a + b = 8 + 6 = 14$$

**Final Answer:**

The sum of $\alpha$ and $\beta$-particles emitted is

$$\boxed{14}$$

**Quick Tip:** Alpha decay drops mass number by 4 and atomic number by 2; beta decay keeps mass number fixed but raises atomic number by 1. Balance both numbers separately, then add the two particle counts.

**61.** The positions of two atoms in spherical polar coordinates $(r, \theta, \Phi)$ are $(1, \frac{\pi}{2}, \frac{\pi}{2})$ and $(1, \frac{\pi}{4}, \frac{3\pi}{2})$, where the distance is in Å and the angles are in radian. The interatomic distance (in Å) is (rounded off to two decimal places).

**Correct Answer:** 1.85

**Solution:**

**Step 1:** Write down the spherical-to-Cartesian conversion.

For a point at $(r, \theta, \Phi)$ in spherical polar coordinates, the Cartesian coordinates are

$$x = r\sin\theta\cos\Phi, \quad y = r\sin\theta\sin\Phi, \quad z = r\cos\theta$$

Here $\theta$ is measured from the $z$-axis and $\Phi$ is the azimuthal angle in the $xy$-plane.

**Step 2:** Convert atom 1, $(1, \pi/2, \pi/2)$.

$\sin(\pi/2) = 1, \cos(\pi/2) = 0.$

$$x_1 = 1(1)\cos(\pi/2) = 0, \quad y_1 = 1(1)\sin(\pi/2) = 1, \quad z_1 = 1(0) = 0$$

So atom 1 is at $(0, 1, 0)$.

**Step 3:** Convert atom 2, $(1, \pi/4, 3\pi/2)$.

$\sin(\pi/4) = \cos(\pi/4) = \dfrac{1}{\sqrt{2}} \approx 0.7071; \cos(3\pi/2) = 0, \sin(3\pi/2) = -1.$

$$x_2 = 1(0.7071)(0) = 0, \quad y_2 = 1(0.7071)(-1) = -0.7071, \quad z_2 = 1(0.7071) = 0.7071$$

So atom 2 is at $(0, -0.7071, 0.7071)$.

**Step 4:** Apply the distance formula.

$$d = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$$

$$d = \sqrt{(0 - 0)^2 + (-0.7071 - 1)^2 + (0.7071 - 0)^2}$$

$$d = \sqrt{(-1.7071)^2 + (0.7071)^2} = \sqrt{2.9142 + 0.5000} = \sqrt{3.4142}$$

$$d \approx 1.8477\ \text{Å}$$

**Final Answer:**

Rounded to two decimal places, the interatomic distance is

$$\boxed{1.85\ \text{Å}}$$

**Quick Tip:** Convert each point to Cartesian using $x = r\sin\theta\cos\Phi$, $y = r\sin\theta\sin\Phi$, $z = r\cos\theta$, then use the 3D distance formula (or the spherical law of cosines directly).

**62.** If the translational partition function for $H_2$ confined in a 1 L vessel at 300 K is $y \times 10^{27}$, then the value of $y$ is (rounded off to one decimal place). (Given: Atomic mass (in amu): H = 1.008; 1 amu = $1.661 \times 10^{-27}$ kg; $h = 6.626 \times 10^{-34}$ J s; $k = 1.381 \times 10^{-23}$ J $K^{-1}$)

**Correct Answer:** 2.8

**Solution:**

**Step 1:** Write the translational partition function formula.

For a particle of mass $m$ free to move in a volume $V$, the translational partition function is

$$q_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

Here $m$ is the mass of one molecule (not the molar mass), $k$ is Boltzmann's constant, $T$ is the temperature, and $h$ is Planck's constant.

**Step 2:** Find the mass of one $H_2$ molecule.

Molar mass of $H_2$ in amu: $2 \times 1.008 = 2.016$ amu. Convert to kg using $1\ \text{amu} = 1.661 \times 10^{-27}$ kg:

$$m = 2.016 \times 1.661 \times 10^{-27}\ \text{kg} = 3.3486 \times 10^{-27}\ \text{kg}$$

**Step 3:** Compute $2\pi mkT$.

$$kT = (1.381 \times 10^{-23})(300) = 4.143 \times 10^{-21}\ \text{J}$$

$$m\,kT = (3.3486 \times 10^{-27})(4.143 \times 10^{-21}) = 1.3873 \times 10^{-47}$$

$$2\pi\, m\, kT = 6.2832 \times 1.3873 \times 10^{-47} = 8.7168 \times 10^{-47}$$

**Step 4:** Divide by $h^2$.

$$h^2 = (6.626 \times 10^{-34})^2 = 4.3904 \times 10^{-67}$$

$$\frac{2\pi mkT}{h^2} = \frac{8.7168 \times 10^{-47}}{4.3904 \times 10^{-67}} = 1.9854 \times 10^{20}\ \text{m}^{-2}$$

**Step 5:** Raise to the power 3/2 and multiply by V.

$$(1.9854 \times 10^{20})^{3/2} = (1.9854)^{3/2} \times 10^{30} = 2.7976 \times 10^{30}\ \text{m}^{-3}$$

Convert $V = 1\ \text{L} = 1 \times 10^{-3}\ \text{m}^3$:

$$q_{trans} = 2.7976 \times 10^{30} \times 1 \times 10^{-3} = 2.7976 \times 10^{27}$$

**Final Answer:**

Comparing with $q_{trans} = y \times 10^{27}$, and rounding to one decimal place,

$$\boxed{y \approx 2.8}$$

**Quick Tip:** Use $q_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$ with $m$ as the mass of one $H_2$ molecule in kg and $V$ converted to $m^3$.

**63.** In a calibrated pH meter comprising of glass electrode-standard calomel electrode, the potential for a buffer solution of pH 4.01 is measured as 0.814 V at 25°C. For a $4.0 \times 10^{-3}$ M solution of acetic acid, the measured potential (in V) is (rounded off to three decimal places).
(Given: $K_a$ of acetic acid at 25°C = $1.75 \times 10^{-5}$; $2.303RT/F = 0.059$;
Assume: $a_{H^+} = [H^+]$)

**Correct Answer:** 0.839

**Solution:**

**Step 1:** Find $[H^+]$ for the acetic acid solution from $K_a$.

Acetic acid is a weak acid, $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$, with $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$. Let $x = [H^+]$ at equilibrium, starting from $C = 4.0 \times 10^{-3}$ M:

$$K_a = \frac{x^2}{C - x}$$

$$x^2 + K_a x - K_a C = 0$$

**Step 2:** Solve the quadratic (the simple $x = \sqrt{K_a C}$ approximation is not accurate enough here since $x/C$ works out to about 6%).

$$x^2 + (1.75 \times 10^{-5})x - (1.75 \times 10^{-5})(4.0 \times 10^{-3}) = 0$$

$$x^2 + 1.75 \times 10^{-5}x - 7.00 \times 10^{-8} = 0$$

$$x = \frac{-1.75 \times 10^{-5} + \sqrt{(1.75 \times 10^{-5})^2 + 4(7.00 \times 10^{-8})}}{2}$$

$$x = \frac{-1.75 \times 10^{-5} + \sqrt{2.803 \times 10^{-7}}}{2} = \frac{-1.75 \times 10^{-5} + 5.2944 \times 10^{-4}}{2}$$

$$x = [H^+] = 2.5597 \times 10^{-4}\ \text{M}$$

**Step 3:** Convert to pH.

$$pH = -\log_{10}(2.5597 \times 10^{-4}) = 4 - \log_{10}(2.5597) = 4 - 0.4082 = 3.5918$$

**Step 4:** Use the calibration line of the glass-calomel cell.

A glass-calomel pH cell responds Nernstianly to pH: $E = K - (2.303RT/F)\ pH$, so $E$ falls by 0.059 V for every unit rise in pH. Use the pH 4.01 calibration point to find the cell constant $K$:

$$0.814 = K - (0.059)(4.01)$$

$$K = 0.814 + 0.23659 = 1.05059\ \text{V}$$

**Step 5:** Apply the same line to the acetic acid solution's pH.

$$E = K - 0.059\,(pH) = 1.05059 - 0.059(3.5918)$$

$$E = 1.05059 - 0.21192 = 0.83867\ \text{V}$$

**Final Answer:**

Rounded to three decimal places, the measured potential is

$$\boxed{E \approx 0.839\ \text{V}}$$

**Quick Tip:** First find the pH of the $4.0 \times 10^{-3}$ M acetic acid solution by solving the $K_a$ quadratic exactly (not the simple square-root approximation), then use the Nernstian line $E = K - 0.059\ pH$ calibrated at pH 4.01.

**64.** The Brunauer-Emmett-Teller (BET) surface area measurement data for adsorption of $N_2$ gas at 77 K on 1.0 g of an adsorbent fits into a straight line, when $\frac{z}{(1-z)V}$ is plotted against $z$. The slope and intercept of the straight line are $6 \times 10^{-4}$ mm$^{-3}$ and $4 \times 10^{-6}$ mm$^{-3}$, respectively. The surface area (in m$^2$ g$^{-1}$) of the adsorbent is (rounded off to one decimal place).

(Given: 1 mm$^3$ of $N_2$ gas corresponds to $2.7 \times 10^{16}$ molecules and each molecule occupies 0.16 nm$^2$. $V$ is the volume of gas adsorbed in mm$^3$, $z$ is $p/p_o$, where $p$ is the pressure of the $N_2$ gas and $p_o$ is equilibrium vapour pressure of liquid $N_2$)

**Correct Answer:** 7.2

**Solution:**

**Step 1:** Write the BET equation in linear form.

The BET adsorption isotherm, in the linear form used for this plot, is

$$\frac{z}{(1-z)V} = \frac{1}{V_m C} + \frac{C-1}{V_m C} z$$

So intercept $= \frac{1}{V_m C}$ and slope $= \frac{C-1}{V_m C}$, where $V_m$ is the monolayer volume of gas (per gram of adsorbent here, since the sample is 1.0 g) and $C$ is the BET constant.

**Step 2:** Add slope and intercept to eliminate $C$.

$$\text{slope} + \text{intercept} = \frac{C-1}{V_m C} + \frac{1}{V_m C} = \frac{C}{V_m C} = \frac{1}{V_m}$$

$$V_m = \frac{1}{\text{slope} + \text{intercept}} = \frac{1}{(6 \times 10^{-4}) + (4 \times 10^{-6})} = \frac{1}{6.04 \times 10^{-4}}$$

$$V_m = 1655.63 \text{ mm}^3$$

This is the monolayer volume of $N_2$ gas (at the measurement conditions) adsorbed on the 1.0 g sample.

**Step 3:** Convert $V_m$ into the number of molecules in the monolayer.
Given: 1 $\text{mm}^3$ of $N_2$ gas corresponds to $2.7 \times 10^{16}$ molecules.

$$N = V_m \times 2.7 \times 10^{16} = 1655.63 \times 2.7 \times 10^{16} = 4.4702 \times 10^{19} \text{ molecules}$$

**Step 4:** Convert molecule count to surface area.
Each $N_2$ molecule covers $0.16 \text{ nm}^2 = 0.16 \times 10^{-18} \text{ m}^2$.

$$A = N \times 0.16 \times 10^{-18} \text{ m}^2 = (4.4702 \times 10^{19})(1.6 \times 10^{-19}) = 7.1523 \text{ m}^2$$

**Step 5:** State per-gram surface area.
Since this area belongs to the 1.0 g adsorbent sample used in the measurement, the specific surface area is directly $7.1523 \text{ m}^2 \text{ g}^{-1}$.

**Final Answer:**
Rounded to one decimal place, the BET surface area is

$$\boxed{7.2 \text{ m}^2 \text{ g}^{-1}}$$

**Quick Tip:** Slope + intercept of the BET plot equals $1/V_m$; convert $V_m$ (mm $^3$) to molecules using the given molecules-per-$\text{mm}^3$ figure, then multiply by

the area per molecule.

**65.** The orbital angular momentum ($\mathbf{L}$) of an electron is $\sqrt{12}\,\hbar$. The minimum angle between $\mathbf{L}$ and its $z$-component (in degrees) is (rounded off to one decimal place).

**Correct Answer:** 30.0

**Solution:**

**Step 1:** Identify the azimuthal quantum number $l$.

The magnitude of the orbital angular momentum vector is given by

$$|\mathbf{L}| = \sqrt{l(l+1)}\,\hbar$$

We are told $|\mathbf{L}| = \sqrt{12}\,\hbar$, so

$$l(l+1) = 12$$

Testing integers, $l = 3$ gives $3 \times 4 = 12$, which works. So $l = 3$.

**Step 2:** Recall the z-component of angular momentum.

The z-component is quantised as $L_z = m_l\hbar$, where $m_l$ runs from $-l$ to $+l$ in integer steps. For $l = 3$, the allowed $m_l$ values are $-3, -2, -1, 0, 1, 2, 3$.

**Step 3:** Find the angle between $\mathbf{L}$ and the z-axis.

By the vector model, the angle $\theta$ between $\mathbf{L}$ and the $z$-axis satisfies

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_l\hbar}{\sqrt{l(l+1)}\,\hbar} = \frac{m_l}{\sqrt{l(l+1)}}$$

Since $\sqrt{l(l+1)}$ is fixed, $\theta$ is smallest when $\cos\theta$ is largest, which happens at the largest allowed $m_l$, namely $m_l = +l = 3$.

**Step 4:** Compute the minimum angle.

$$\cos\theta_{min} = \frac{l}{\sqrt{l(l+1)}} = \frac{3}{\sqrt{12}} = \frac{3}{2\sqrt{3}} = \frac{\sqrt{3}}{2} = 0.8660$$

$$\theta_{min} = \cos^{-1}(0.8660) = 30.0^\circ$$

**Final Answer:**

The minimum angle between **L** and its z-component is

$$\boxed{30.0^\circ}$$

**Quick Tip:** Find $l$ from $\sqrt{l(l+1)} = \sqrt{12}$, then use $\cos\theta = m_l/\sqrt{l(l+1)}$ with the largest allowed $m_l = l$ to get the minimum angle.