# GATE 2026 Chemistry Question Paper with Solutions

ZOLLEGE

## 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:**

This question tests careful reading plus word meaning (vocabulary in context). The passage sets up a contrast: someone is criticized for making false claims, and then a general statement is made about what honesty does to trust. Each option must be checked against both blanks together, not one at a time.

1. **exaggerates; engenders**: "He often exaggerates the numbers" directly explains why "false claims are not going to help" follows right after it. "Honesty engenders trust" is a well known phrase, since engender means to bring something into existence. Both blanks fit.
2. **excels; encourages**: "Excels" is normally followed by "at" or "in", not used directly with an object like "the numbers", so this breaks grammatically before the meaning is even checked.
3. **aggravates; alleviates**: "Aggravates the numbers" is an odd, unnatural phrase, and "honesty alleviates trust" is backward in meaning, since alleviate means to lessen a burden, and trust is not a burden.
4. **diminishes; eliminates**: "Diminishes the numbers" could just about pass grammatically, but "honesty eliminates trust" says the opposite of what honesty actually does, so the sentence would contradict itself.

Only option (A) keeps the sentence grammatical and logically consistent in both blanks, so "exaggerates; engenders" is correct.

Let's summarize:

- The first blank needs a verb close in spirit to "making false claims", which points to "exaggerates".

- The second blank needs a verb meaning "creates" or "produces", which points to "engenders".

So the correct order of words is "exaggerates; engenders", option (A).

**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.

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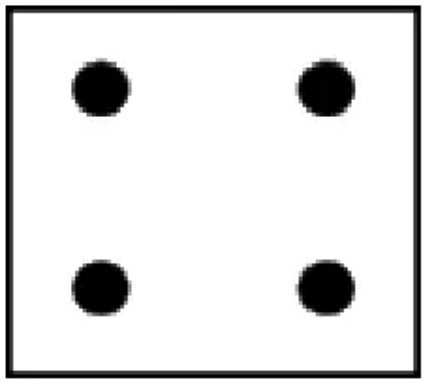
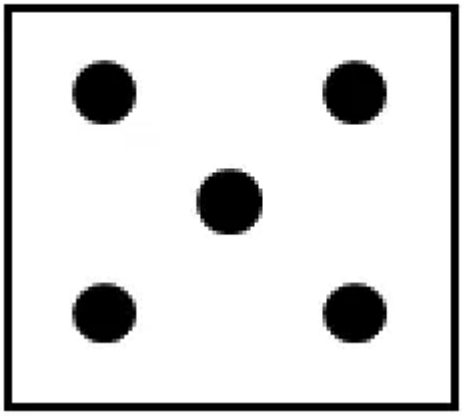
**2.** In the sequence of tiles shown below, the missing tile indicated by the question mark should be

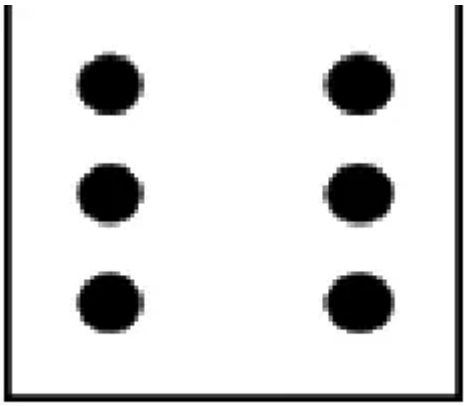
(A)



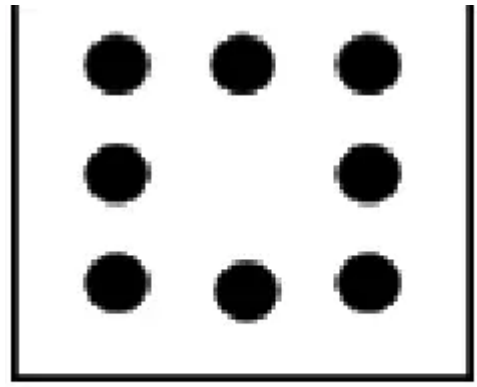
(B)



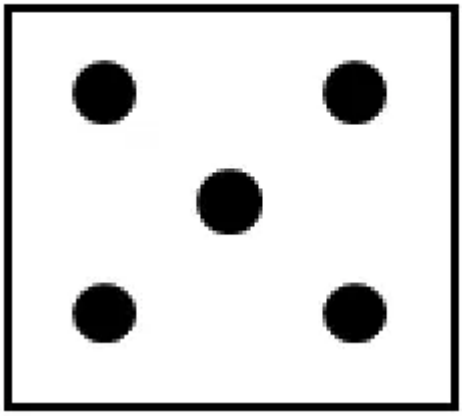
(C)



(D)



**Correct Answer:** (B)



**SOLUTION:**

Another way to solve this is to look at how the dot count grows from tile to tile instead of splitting the tiles into groups first, then confirm the jump into the answer using a second check.

1. **Tile 1 to tile 2**: dots go from 2 to 3, a rise of 1.
2. **Tile 4 to tile 5**: dots go from 6 to 10, a rise of 4. Since the tiles are not rising by a constant amount, the growth rate itself must be increasing, which is typical of a squared or "sum of small numbers" style rule rather than a simple addition rule.

3. **Testing $n^2 + 1$ on the 1st, 3rd, 5th tiles**: with $n = 1, 2, 3$ this gives $2, 5, 10$. The 1st and 5th values (2 and 10) already match the tiles we can see, so the middle value, 5, is the strongest candidate for the missing tile.
4. **Cross check with $n^2 + 2$ on the 2nd, 4th tiles**: with $n = 1, 2$ this gives $3, 6$, which matches both visible tiles exactly, so the same style of rule is confirmed to be running on the other set of positions too.

Since both parallel rules check out against every tile we can actually see, the missing tile must carry $2^2 + 1 = 5$ dots.

Let's summarize:

- Odd tiles (1st, 3rd, 5th) follow $n^2 + 1$: 2, 5, 10.
- Even tiles (2nd, 4th) follow $n^2 + 2$: 3, 6.

The missing tile has 5 dots, so the answer is option (B), the tile with the 2-1-2 dot pattern.

**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.

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**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:**

A quick way to see this is through the idea of an average. If 100 students are spread over 10 standards, the average number of students per standard is $100/10 = 10$. Whenever a set of whole numbers has an average of 10, at least one of them must be 10 or more, since it is impossible for every single value to sit strictly below the average.

1. **There are at least 10 students who belong to the same standard**: matches the averaging argument directly, since some standard must reach or cross the average of 10. This is always true.
2. **There is at least one student in each standard**: the 100 students could all be crammed into one standard, leaving the other 9 empty, so this can be false.
3. **There are at most 10 students in 10th standard**: the 10th standard alone could hold anywhere from 0 to 100 students, so a cap of 10 is not forced.
4. **The total from 1st to 5th standards is at least 50**: all 100 students could be pushed into standards 6 to 10, making the 1st to 5th total as low as 0.

Every option except the first can be broken by some valid distribution of the 100 students, which means only the first statement is guaranteed under every possible distribution.

Let's summarize:

- Average students per standard is 10, so some standard must have 10 or more.
- Every other option can be defeated by an extreme, uneven distribution of students.

The statement that always holds is "there are at least 10 students who belong to the same standard", 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.

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**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:**

This is a direct application of the permutation formula, and it helps to first be clear on which digits are even in play.

1. **Identify the digit pool**: single digit prime numbers are 2, 3, 5, 7, giving a pool of 4 digits, none of which is zero.
2. **Decide the counting rule**: since the three digits used in each number must be distinct, and order matters (237 and 273 are

different numbers), this calls for permutations, written $P(n, r)$ for choosing and arranging $r$ items out of $n$.

3. **Apply the formula**: here $n = 4$ and $r = 3$, so $P(4, 3) = \frac{4!}{(4-3)!} = \frac{4!}{1!} = \frac{24}{1} = 24$.
4. **Sanity check by direct multiplication**: the hundreds digit has 4 choices, the tens digit has 3 remaining choices, and the units digit has 2 remaining choices, giving $4 \times 3 \times 2 = 24$, which matches the formula.

Both the formula and the direct slot-by-slot count agree, so the number of valid 3-digit numbers is 24.

Let's summarize:

- There are 4 single digit primes: 2, 3, 5, 7.
- Choosing 3 distinct ones and arranging them gives $P(4, 3) = 24$.

The correct count is 24, option (B).

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

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**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:**

This problem is easiest to picture as a Venn diagram with two overlapping circles, one for Mathematics and one for English, sitting inside a rectangle that represents the whole group.

1. **Both subjects**: the overlap region has 4 students, since 4 students like both Mathematics and English.
2. **Only Mathematics**: out of the 10 who like Mathematics, 4 are shared with English, so $10 - 4 = 6$ students like only Mathematics.
3. **Only English**: out of the 12 who like English, 4 are shared with Mathematics, so $12 - 4 = 8$ students like only English.
4. **Neither subject**: given directly as 6 students, sitting outside both circles.

Adding up every region of the diagram gives the full group: only Mathematics (6) plus only English (8) plus both (4) plus neither (6), which is $6 + 8 + 4 + 6 = 24$.

Let's summarize:

- Only Mathematics: 6 students.
- Only English: 8 students.
- Both: 4 students.
- Neither: 6 students.

Adding all four non-overlapping regions gives a total group size of 24 students, option (C).

**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.

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**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:**

An analogy of the form "Charity : P :: Retaliation : Q" is asking for the adjective that describes someone who performs each action. Charity is an act of giving without expecting anything back, so P should mean generous. Retaliation is an act of hitting back at someone, so Q should mean vengeful. The right answer needs both words to fit their own term, not just one of the two.

1. **Parsimonious; Vengeful**: vengeful correctly matches retaliation, but parsimonious means unwilling to give, the reverse of a charitable person.
2. **Altruistic; Amicable**: altruistic correctly matches charity, but amicable just means friendly, which has nothing to do with striking back after being wronged.
3. **Resentful; Spiteful**: both words describe a bitter, grudge holding person, so neither one fits "charity" at all.

4. **Magnanimous; Vindictive**: magnanimous means big hearted and forgiving, matching charity, and vindictive means driven to get revenge, matching retaliation.

Only the fourth pair satisfies both halves of the analogy at once, so "Magnanimous; Vindictive" is correct.

Let's summarize:

- P must mean generous/forgiving, to match charity: magnanimous.
- Q must mean vengeful, to match retaliation: vindictive.

The correct pair is P = Magnanimous, Q = Vindictive, option (D).

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

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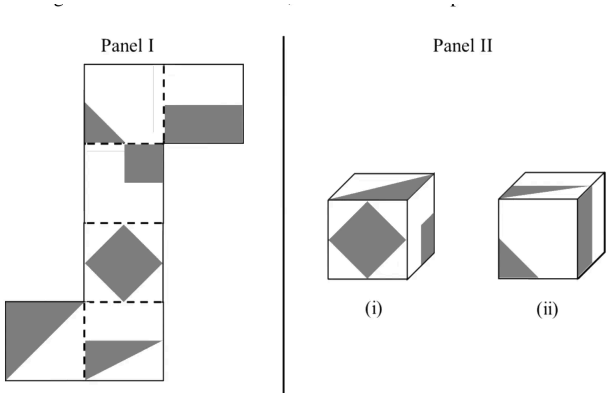
**7.** A paper shown in Panel I is folded along the dashed lines (- - -) to construct a cube. The shaded regions shown in Panel I appear on the outer surface of the cube. Referring to cubes shown in Panel II, which one of the options is correct?



(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:**

A second, complementary way to check this kind of question is to first work out which pairs of squares in the net become opposite faces of the cube (faces that can never be seen together in a single 2D picture of the cube), and then use that to rule out impossible pictures before even worrying about exact shading direction.

1. **Map out the net**: in a net made of a straight run of four squares plus one square attached on each side near the two ends, the two squares that are not in the straight run of four end up opposite each other once folded, and, within the run of four, the 1st and 3rd squares become opposite each other, and the 2nd and 4th squares become opposite each other.
2. **Locate the diamond and triangle squares**: using this rule on Panel I, the diamond square and the shaded triangle square that appear together as neighbors in cube (i) and (ii) are genuinely adjacent in the net, not opposite, so both can legally show up together on a single 2D cube drawing. This rules out rejecting either cube purely on adjacency grounds.
3. **Decide the remaining check with orientation**: since both faces are legally adjacent, the only thing left to test is whether the triangle's shaded corner sits on the correct side of the shared edge

with the diamond. Physically folding the net, without flipping it over, fixes this orientation uniquely, in the same sense it appears flat in Panel I.

4. **Apply the orientation test**: cube (i) preserves this fixed orientation between the diamond and the triangle, while cube (ii) shows the triangle shading as a mirror image of what a real fold would produce, something only possible if the sheet were turned over, which folding along a crease never does.

So adjacency alone does not settle the question, but the orientation of the shading across the shared edge does, and it rules out cube (ii) while confirming cube (i).

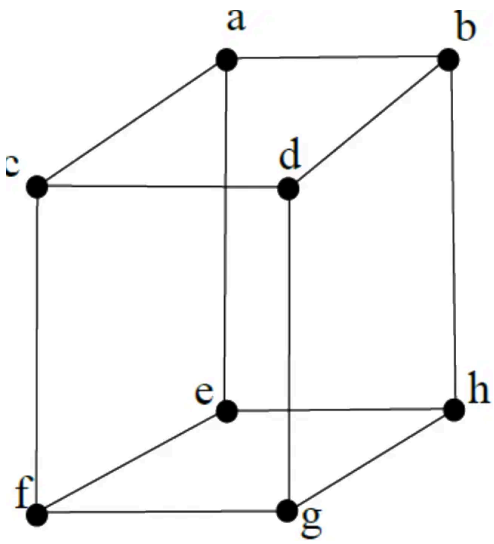
Let's summarize:

- The diamond and triangle faces are adjacent in the net, so both cubes are geometrically possible at first glance.
- Only the orientation of the shading across their shared edge, fixed by the actual fold, decides the answer.
- Cube (i) keeps the correct orientation; cube (ii) shows a mirrored, impossible orientation.

Only cube (i) can be produced by folding the net in Panel I, so the answer is option (A).

**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:**

Another way to find the minimum number of colors is to look directly at the cycles (closed loops of edges) in the cube graph, since the length and parity of those cycles decides the chromatic number for a graph like this one.

1. **Look at the shortest loops**: every face of the cube is a square, so walking around any one face traces a closed loop of exactly 4 edges. A loop of even length, like 4, never forces more than 2

colors on its own, since you can alternate two colors all the way around and land back on the start with no clash.

2. **Check for odd loops**: a graph needs 3 or more colors only if it contains at least one cycle with an odd number of edges (a triangle, a 5-loop, and so on). The cube's corners and edges only ever form loops of length 4 or 6, both even, and it has no triangles at all, since no three corners of a cube are all mutually joined by edges.
3. **Conclude bipartiteness**: a graph with only even length cycles is bipartite, which means its corners split cleanly into two sets with every edge crossing between the sets, and never staying inside one set.
4. **Assign colors directly**: take any corner, color it Red, then color every corner directly joined to it Blue, then every corner joined to those Red again, and so on outward. Because every cycle in the graph has even length, this alternating process never contradicts itself and finishes with a clean 2 coloring.

Since a single edge already forces its two ends to differ, at least 2 colors are always required, and the alternating process above shows 2 colors are also enough.

Let's summarize:

- The cube graph has only even length cycles (4-loops on faces, 6-loops around the cube) and no odd cycles.
- A graph with no odd cycles is bipartite and can always be colored with exactly 2 colors.

The minimum number of colors needed is 2, option (D).

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

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**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:**

This question is a placement puzzle. Instead of algebra, list the four positions from west to east as 1, 2, 3, 4 and place the hills by elimination, one clue at a time.

1. **Clues (i) and (ii) together**: $H_2$ and $H_3$ cannot be at position 1 (west end) or position 4 (east end), so they must both sit somewhere in the middle, at positions 2 and 3 in some order.

That forces $H_1$ and $H_4$ to take the two end positions, 1 and 4, in some order.

2. **Clue (iv)**: two hills sit west of $H_2$. Of the two middle slots (2 and 3), only position 3 has two positions (1 and 2) to its west. So $H_2$ is at position 3, and $H_3$ takes the only slot left in the middle, position 2.
3. **Clue (iii)**: the southernmost hill is not at position 1 or position 4. Since $H_1$ and $H_4$ occupy positions 1 and 4, neither of them can be the southernmost hill. That leaves $H_2$ (position 3) or $H_3$ (position 2) as candidates.
4. **Clue (v)**: the southernmost hill needs at least two hills to its east. $H_2$ sits at position 3, so only 1 hill (position 4) is east of it, too few. $H_3$ sits at position 2, so 2 hills (positions 3 and 4) are east of it, which is enough.

Only $H_3$ survives every clue, so $H_3$ is the southernmost hill.

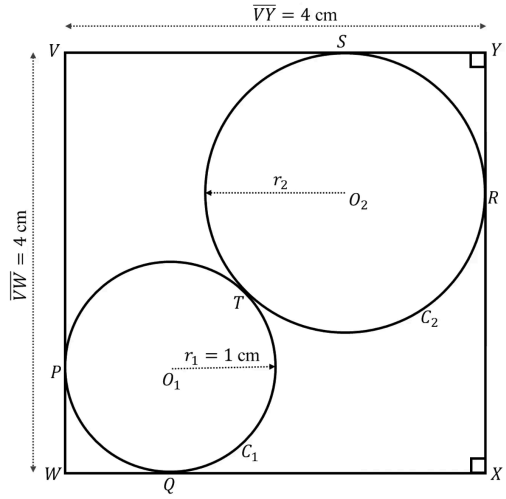
Let's summarize:

- $H_1$ and $H_4$ are stuck at the two ends (east and west), so clue (iii) rules them both out.
- $H_2$ sits third from the west, leaving only one hill to its east, which clue (v) rejects.
- $H_3$ sits second from the west, with two hills to its east, matching every clue.

The correct answer is $H_3$, option (C).

**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:**

Both circles sit snugly in opposite corners of the square, each tangent to the two sides meeting at that corner, and they touch each other. A quick way to solve this is to work along the diagonal of the square that passes through both corners, $W$ and $Y$.

1. The center of a circle tucked into a right-angle corner, tangent to both sides, always lies on the diagonal bisecting that corner angle,

at a distance $r\sqrt{2}$ from the corner, since the perpendicular distance to each side is $r$, and the diagonal makes a $45°$ angle with each side.

2. The diagonal $WY$ of the square has length $\sqrt{4^2+4^2} = 4\sqrt{2}$ cm.
3. Center $O_1$ (near corner $W$) lies at distance $r_1\sqrt{2} = 1 \cdot \sqrt{2} = \sqrt{2}$ cm from $W$, measured along $WY$.
4. Center $O_2$ (near corner $Y$) lies at distance $r_2\sqrt{2}$ cm from $Y$, so it is $4\sqrt{2} - r_2\sqrt{2}$ cm from $W$ along the same diagonal.
5. Since the circles touch, the gap between $O_1$ and $O_2$ along the diagonal equals $r_1 + r_2$:

$$\left(4\sqrt{2} - r_2\sqrt{2}\right) - \sqrt{2} = r_1 + r_2 = 1 + r_2$$

Simplify the left side:

$$4\sqrt{2} - \sqrt{2} - r_2\sqrt{2} = 3\sqrt{2} - r_2\sqrt{2}$$

So the equation becomes:

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

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

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

Multiply numerator and denominator by $(\sqrt{2} - 1)$ to rationalize:

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

This matches the coordinate-geometry method exactly, confirming $r_2 = 7 - 4\sqrt{2}$ cm, about 1.34 cm.

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

**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.

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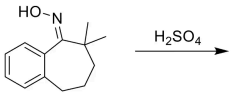
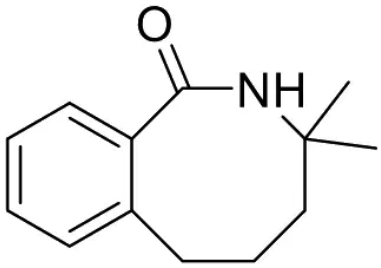
**11.** The major product formed in the following reaction is:



(A)

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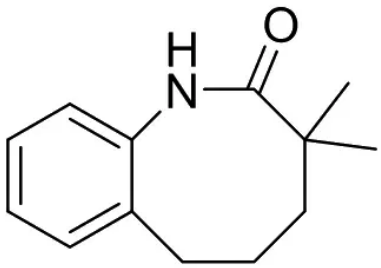


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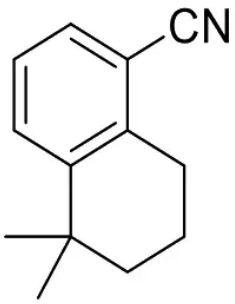

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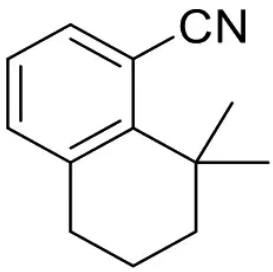
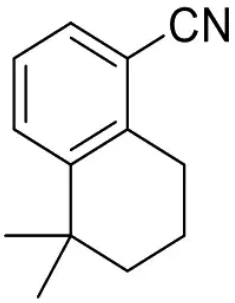



**Correct Answer:** (C)

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**SOLUTION:**

This is a Beckmann reaction, but the twist is that the substrate is set up to fragment rather than simply rearrange. Look at what sits next to the oxime carbon: one neighbor is the aromatic ring, and the other neighbor is a carbon carrying two methyl groups. That gem-dimethyl carbon is the key to the whole question.

1. **Normal Beckmann path**: if this were an ordinary oxime, protonating the OH and losing water would trigger the group anti to the leaving OH, here the gem-dimethyl carbon, to migrate onto nitrogen, giving a ring-expanded seven-membered lactam. That is exactly what options (A) and (B) show.

2. **Why that does not happen here**: migrating as a full alkyl group is only the low-energy path when there is no better option. Here, breaking off the gem-dimethyl carbon completely gives a tertiary carbocation, stabilized by the two flanking methyls. A tertiary cation is much more stable than the transition state for simple migration, so the molecule fragments instead, the bond between the oxime carbon and the gem-dimethyl carbon breaks fully.
3. **What each fragment becomes**: the oxime carbon keeps its bond to the aromatic ring and turns into a nitrile, $\mathbf{Ar{-}C{\equiv}N}$. The gem-dimethyl carbon becomes a free tertiary cation, still attached through three $\mathbf{CH_2}$ groups to the far side of the aromatic ring.
4. **Ring closure**: that tertiary cation gets trapped right back onto the same aromatic ring, an intramolecular Friedel-Crafts alkylation, forming a new six-membered ring. The seven-membered ring has effectively contracted to a six-membered ring, with a pendant nitrile group on the aromatic ring and the two methyls sitting on the new ring's quaternary carbon, on the far side of the ring from the nitrile.

That six-membered, nitrile-bearing bicyclic structure is option (C). Option (D) draws almost the same skeleton but puts the gem-dimethyl carbon right next to the nitrile-bearing aromatic carbon instead of across the ring, which is not where the ring-closing carbocation actually lands.

Let's summarize:

- A carbon anti to the leaving $\mathbf{OH}$ that can form a stabilized, here tertiary, cation favors Beckmann fragmentation over normal rearrangement.

- Fragmentation converts the oxime carbon into a nitrile and releases the other carbon as a cation.
- An electron-rich aromatic ring nearby traps that cation intramolecularly, closing a new, smaller ring.

The correct product is the ring-contracted nitrile in option (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.

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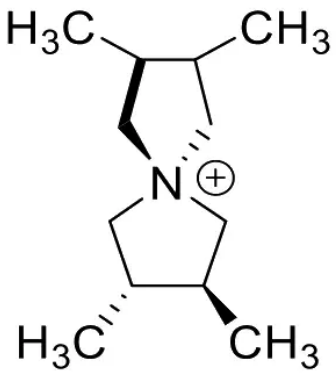
**12.** The correct statement about the following quaternary ammonium ion is:




(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:**

The trick in this question is not to stop at "how many stereocenters does it have," but to ask whether the whole molecule can be superimposed on its own mirror image. That is a question about symmetry elements, not about counting stereocenters.

1. **It has only $C_2$-symmetry, hence chiral**: a $C_2$ axis, a plain rotation axis, is indeed present here, running through **N** and the midpoint of the far $C$–$C$ bond. But a proper rotation axis by itself never makes a molecule chiral or achiral, chirality depends only on whether an improper element ($\sigma$, $i$, or $S_n$) exists. This option misses the improper axis that is actually present, so it wrongly calls the ion chiral.
2. **It has $S_4$-symmetry, hence achiral**: the four ring stereocenters are arranged as two methyls "up", next to **N**, and two methyls "down", further from **N**. A **90°** rotation about the axis through **N**, combined with a reflection, swaps the up-pair with the down-pair and reproduces the exact same structure. That rotation-plus-reflection is an $S_4$ operation, and any molecule with an $S_n$ axis is achiral by definition.
3. **It has no symmetry, hence chiral**: this ignores the very regular "up, down, down, up" pattern the wedges and hashes show. The methyls are not placed randomly, so "no symmetry" is not correct.
4. **It has a centre of symmetry, hence achiral**: a true inversion center $i$ would require every atom to have a matching atom directly opposite through one central point, which the puckered five-membered ring does not provide. The achirality here comes from $S_4$, not from $i$.

Only the $S_4$ description fits both the observed wedge and hash pattern and the correct rule for chirality, the presence of any improper symmetry element makes a molecule achiral.

Let's summarize:

- Four stereocenters do not automatically make a molecule chiral, symmetry is what decides it.
- Any $S_n$ axis, not just a mirror plane or inversion center, is enough to make a molecule achiral.
- The "up-up, down-down" methyl pattern here generates an $S_4$ axis through **N**.

The correct statement is that the ion has $S_4$ symmetry and is achiral, option (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:**

This sequence is a classic two-step method for turning a terminal alkyne into a single, stereodefined vinyl bromide: hydroboration sets the alkene geometry with boron in place, and the bromination/elimination step swaps that boron for bromine, flipping the geometry in the process.

1. **Step 1, hydroboration**: catecholborane delivers H and B to the triple bond on the same face, syn addition, with boron landing on the terminal, less hindered carbon. Because both new atoms arrive from one face, the hexyl chain, already on the alkyne, ends up trans to the boron group in the product alkene: this is the (E)-alkenylboronate, $C_6H_{13}CH=CHBcat$.
2. **Step 2, bromination then base**: $Br_2$ first adds across the double bond from one face, anti addition, giving a vicinal bromo compound that still carries the boron group. NaOMe then pulls out the boron and an adjacent bromide in a single anti-periplanar elimination step, which rebuilds the double bond.

3. **Net stereochemical outcome**: an addition followed by an anti-elimination at the same two carbons flips the original alkene geometry. Since boron started trans to the chain (E), bromine ends up cis to the chain in the new double bond, giving the (Z)-vinyl bromide.
4. **Why not the dibromides**: options with two bromines on the double bond, $C_6H_{13}CH{=}CBr_2$ or $C_6H_{13}CBr{=}CHBr$, would require an extra bromine to stay on the alkene permanently. Here bromine only ever occupies the position boron is leaving from, one bromine net stays, the rest is consumed as bromide leaving with the boron.

Only one candidate is both a monobromide and has the geometry consistent with inversion from the (E)-alkenylboronate: the (Z)-alkene, $C_6H_{13}CH{=}CHBr$ with the chain and bromine on the same side.

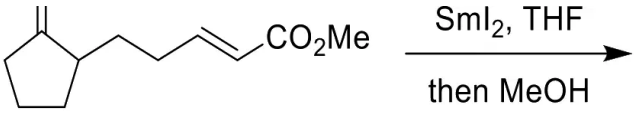
Let's summarize:

- Catecholborane hydroboration of a terminal alkyne gives the (E)-alkenylboronate (chain trans to boron).
- $Br_2$ then NaOMe swaps boron for bromine with net inversion of alkene geometry.
- The product therefore has the chain and bromine cis, the (Z)-vinyl bromide.

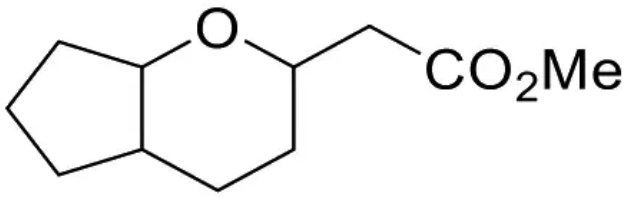
The major product is option (C), the (Z)-configured vinyl bromide.

**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.

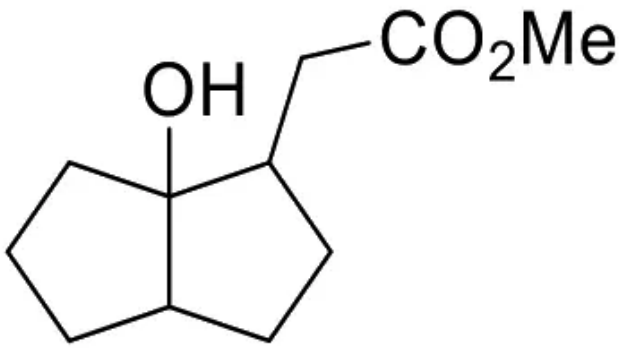
**14.** The major product formed in the following reaction is:



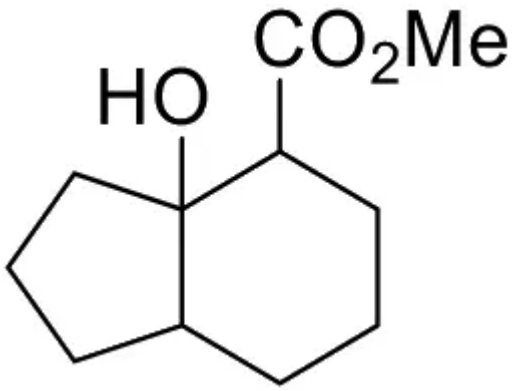
(A)



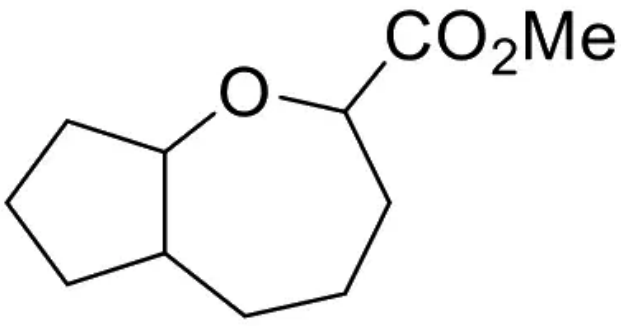

(B)



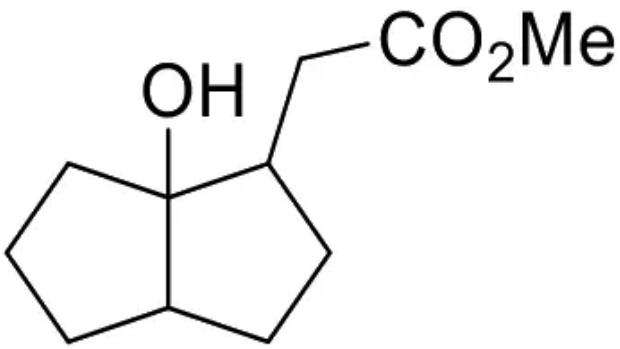

(C)




(D)



**Correct Answer:** (B)




**SOLUTION:**

$SmI_2$ is a one-electron reductant, and the classic move it makes with a ketone is to hand over an electron and generate a ketyl radical. When that ketone has an alkene hanging off it on a chain of the right length, the ketyl radical reaches over and forms a new ring by attacking the alkene. That is exactly the setup in this question.

1. **Where the radical starts**: the ketone carbon of the cyclopentanone becomes a radical, ketyl, after picking up one electron from $SmI_2$.
2. **Where the radical goes**: tracing the chain from that carbon, through the ring's substituted carbon, then two $CH_2$ groups, to the nearer carbon of the $C{=}C{-}CO_2Me$ alkene, that is a five-atom path. Radical cyclizations strongly prefer forming a five-membered ring this way, 5-exo-trig, over a six-membered one, so the ketyl radical attacks the nearer alkene carbon, not the one next to the ester.
3. **What is left after the new ring closes**: closing that five-membered ring uses up the double bond, leaving the radical, and eventually after a second reduction an anion stabilized by the ester, sitting on the carbon that was attached to $CO_2Me$. That carbon becomes a simple $CH_2$ once it picks up a proton.

4. **Where the proton comes from**: MeOH, added after the $SmI_2$ step, supplies the proton both to that ester-stabilized carbon, giving $-CH_2CO_2Me$, and indirectly through the samarium alkoxide, to the oxygen that was originally the ketone, giving a tertiary alcohol at the ring-fusion carbon.

Put together, the two original rings, the cyclopentanone ring and the newly closed five-membered ring, are now fused at the carbon that used to be the carbonyl carbon, which carries the new OH. The pendant group on the new ring is $-CH_2CO_2Me$, not a ring oxygen and not an ester carbon fused directly into the ring. That rules out the two oxygen-in-ring answers, they would need the oxygen, not the carbon, to attack the alkene, and the direct-fused-ester answer, it would need a 6-exo cyclization, which loses out to the favored 5-exo pathway here.

Let's summarize:

- $SmI_2$ converts the ketone to a ketyl radical, which cyclizes onto the tethered alkene, at carbon, not oxygen.
- The tether length favors a five-membered ring, 5-exo-trig, giving a fused bicyclic, hydrindane-type, skeleton.
- MeOH quench delivers protons to give a tertiary alcohol at the ring fusion and a $-CH_2CO_2Me$ pendant group.

The correct product is the fused bicyclic alcohol with the pendant ester arm, option (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:**

Beta-hydride elimination is often treated as if it just needs a beta-hydrogen, but that is only half the story. The metal also needs somewhere for the hydrogen to go, an open coordination site sitting cis to the alkyl group. Go through each complex checking both conditions.

1. $[Rh(C_5H_5)(PMe_3)(C_2H_5)]^+$: add up the electrons this Rh(III) center receives: 6 from $d^6$ Rh(III), 6 from $\eta^5$-cyclopentadienyl, 2 from $PMe_3$, 2 from ethyl, total 16. A 16-electron complex has a coordination gap, an open site the ethyl group's beta-hydrogen can swing toward. This complex satisfies both conditions and is the one that eliminates.
2. $[Rh(NH_3)_5(C_2H_5)]^{2+}$: six ligands fully occupy an octahedral Rh(III) center, giving 18 electrons with no gaps anywhere. The ethyl group has beta-hydrogens, but there is no empty site for them to reach, so nothing happens.
3. $[Pt(PPh_3)_2(C_6H_5)I]$: square-planar Pt(II) is 16-electron and does have an open site, but the group attached to platinum is phenyl, not a simple alkyl. The would-be beta-carbons are locked into an aromatic ring, pulling a hydrogen off one of them would destroy

the ring's aromaticity, so this pathway is blocked structurally, regardless of the open site.

4. $[Cr(CH_2Si(CH_3)_3)_4]$: the metal-bound carbon is $CH_2$, and one atom further out is silicon, not carbon. Beta-hydride elimination needs a hydrogen on a beta carbon, and there simply is no beta carbon here, only a beta silicon. This ligand is chosen specifically because it cannot eliminate.

Three of the four complexes fail one of the two requirements: (B) has the hydrogen but no open site, (C) has the open site but no usable beta-hydrogen, and (D) has neither a beta carbon nor, therefore, a beta-hydrogen. Only (A) has both an open coordination site and an ethyl group with real beta-hydrogens.

Let's summarize:

- Beta-hydride elimination needs both a beta-C-H bond and an open cis coordination site.
- Saturated 18-electron complexes, like the pentaammine ethyl rhodium, cannot eliminate even with a good beta-hydrogen present.
- Aryl, vinyl, and $CH_2SiMe_3$-type ligands have no usable beta-hydrogen at all.

The species that undergoes beta-elimination is the 16-electron cyclopentadienyl rhodium ethyl complex, option (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:**

Building the molecular orbital picture for an octahedral complex with a pure sigma-donor ligand set like $NH_3$ comes down to two separate counting jobs: filling the metal-ligand bonding orbitals with the ligand's own electrons, and then figuring out where the metal's own $d$ electrons land.

1. **Bonding orbitals come from symmetry matching**: the metal's $s$ orbital matches the totally symmetric ligand combination, giving the $a_{1g}$ bonding orbital. The three $p$ orbitals match a triply degenerate ligand combination, giving $t_{1u}$. Two of the five $d$ orbitals ($d_{z^2}$ and $d_{x^2-y^2}$) point straight at the ligands and match the remaining ligand combination, giving $e_g$. The other three $d$ orbitals ($d_{xy}, d_{xz}, d_{yz}$) point between the ligands and have no sigma partner, so they stay non-bonding, labeled $t_{2g}$.
2. **Energy order**: $a_{1g} < t_{1u} < e_g$ (bonding, filled mostly by ligand electrons) $< t_{2g}$ (non-bonding, purely metal $d$ character) $< e_g^*$ (antibonding).
3. **Filling with ligand electrons**: each of the six $NH_3$ ligands contributes a lone pair, 12 electrons total, and these exactly fill $a_{1g}^2\ t_{1u}^6\ e_g^4$.

4. **Filling with metal electrons**: Co(III) is $d^6$. $NH_3$ is a strong enough field ligand that $[Co(NH_3)_6]^{3+}$ is the well known diamagnetic, low-spin case, so all six $d$ electrons pair up in the lower, non-bonding $t_{2g}$ set before touching the antibonding $e_g^*$ set: $t_{2g}^6\ e_g^{*0}$.

Stacking these in the correct energy order gives $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^6\ e_g^{*0}$. Any answer that reorders $t_{2g}$ ahead of the bonding $e_g$, or swaps $a_{1g}$ and $t_{1u}$, has the energy ladder wrong, and any answer that splits the six metal electrons across $t_{2g}$ and $e_g^*$, like $t_{2g}^4 e_g^{*2}$, is describing a high-spin, paramagnetic complex, which does not match the known diamagnetic $[Co(NH_3)_6]^{3+}$.

Let's summarize:

- Sigma-only ligands like $NH_3$ give bonding MOs $a_{1g}, t_{1u}, e_g$ (in that energy order), a non-bonding $t_{2g}$, and an antibonding $e_g^*$.
- 12 ligand electrons fill the three bonding MOs completely.
- All 6 of Co(III)'s $d$ electrons pair up in non-bonding $t_{2g}$ because the complex is low-spin, leaving $e_g^*$ empty.

The correct configuration is $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^6\ e_g^{*0}$, option (A).

**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.

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**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:**

A different way to count electrons at a metal center is the covalent (neutral atom) method. Here the metal is treated as a neutral atom contributing its own group number of electrons, an X-type ligand (like a halide or H) contributes 1 electron because it forms a normal covalent bond, and an L-type neutral 2-electron donor (like *CO*, $PPh_3$, $NH_3$, or one end of a chelate like *en*) contributes 2 electrons. Any overall ionic charge on the complex is then added (for an anion) or subtracted (for a cation) as extra or missing electrons.

1. $[Rh(PPh_3)_3Cl]$: neutral *Rh* (group 9) gives 9 electrons, 3 $PPh_3$ give $3 \times 2 = 6$, *Cl* (X-type) gives 1. No overall charge to add. Total $= 9 + 6 + 1 = 16$, so this is a 16-electron complex, not 18.
2. $[Co(NH_3)_6]^{2+}$: neutral *Co* (group 9) gives 9 electrons, 6 $NH_3$ give $6 \times 2 = 12$. The complex is a 2+ cation, so subtract 2 electrons. Total $= 9 + 12 - 2 = 19$, an odd, non-18 count.
3. $[V(CO)_6]^{-}$: neutral *V* (group 5) gives 5 electrons, 6 *CO* give $6 \times 2 = 12$. The complex is a 1− anion, so add 1 electron. Total $= 5 + 12 + 1 = 18$, exactly the 18-electron count.
4. $[Ni(en)_3]^{2+}$: neutral *Ni* (group 10) gives 10 electrons, each bidentate *en* acts as two L-type donors so gives $2 \times 2 = 4$ electrons, three *en* give $3 \times 4 = 12$. The complex is 2+, so subtract 2. Total $= 10 + 12 - 2 = 20$, above 18.

Whichever method is used, ionic or covalent, only $[V(CO)_6]^-$ lands exactly on 18 valence electrons, so it is the species that follows the 18-electron rule.

Let's summarize:

- The covalent method always gives the same total electron count as the ionic method for a given real complex, since the two are just different bookkeeping of the same electrons.
- An odd total electron count (like 19 for the $Co(II)$ complex) can never satisfy the 18-electron rule, because it forces an unpaired electron.

The correct option is (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.

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**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:**

A quicker route than listing every element is to follow the standard point-group decision flow chart, starting from the shape of the molecule rather than from the symmetry elements directly.

1. **Is the molecule linear?** No. $CH_2 = C = CH_2$ has terminal $CH_2$ groups sticking out on either side of the central carbon, so the overall shape is not a straight line of atoms; the flow chart moves past the linear ($C_{\infty v}$ / $D_{\infty h}$) branch.
2. **Does it have two or more $C_n$ axes with $n > 2$ (a high-symmetry, cubic/tetrahedral/octahedral shape)?** No, allene has only one special axis (the $C = C = C$ line acting as an $S_4$ axis), so it is not one of the high symmetry point groups.
3. **Find the highest-order proper rotation axis $C_n$.** A simple 180 degree rotation about the $C = C = C$ axis does not by itself map the molecule onto itself (it would need the reflection too), but combining a 90 degree rotation with a reflection through the plane perpendicular to the axis does, so the molecule's improper axis is $S_4$, and the associated proper axis nested inside it is $C_2$ along the same line.
4. **Are there $n$ $C_2$ axes perpendicular to the principal axis?** Yes, two $C_2$ axes, one through each terminal $CH_2$ group, each perpendicular to the central $C = C = C$ axis.
5. **Is there a $\sigma_h$?** No, because that would force the two $CH_2$ planes to lie in the same plane, and they are twisted 90 degrees apart.
6. **Are there $n$ dihedral mirror planes $\sigma_d$?** Yes, one plane through each $CH_2$ group, containing the central axis.

A molecule with an $S_4$ axis, two perpendicular $C_2$ axes, two $\sigma_d$ planes, and no $\sigma_h$ is placed in the $D_{2d}$ point group by the flow chart, which is the same result reached by listing elements directly.

Let's summarize:

- Allene's perpendicular $CH_2$ ends are the key structural fact; they rule out any point group that needs a $\sigma_h$ or full planarity.
- The flow chart and the direct element count agree: the answer is $D_{2d}$.

The correct option is (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:**

Instead of deriving the rule from scratch, use the direct test: mutual exclusion between IR and Raman only ever happens in a molecule that possesses a center of symmetry, so this question reduces to spotting which one option is centrosymmetric.

1. $H_2O$: bent shape, point group $C_{2v}$. A $C_{2v}$ molecule never has an inversion center because an inversion would need atoms directly opposite the center in every direction, which a bent triatomic simply cannot provide. Not centrosymmetric.
2. **trans-planar** $H_2O_2$: laying the whole molecule flat with the two $O-H$ bonds pointing to opposite sides of the $O-O$ bond puts an inversion center exactly at the midpoint of the $O-O$ bond, since every atom (each $H$, each $O$) has an identical atom diagonally opposite through that point. Point group $C_{2h}$, which by definition contains $i$. Centrosymmetric.
3. **eclipsed ethane**: point group $D_{3h}$. $D_{3h}$ has a $\sigma_h$ and a $C_3$ axis but, because the two $CH_3$ groups are eclipsed rather than staggered, there is no point exactly opposite every atom through a single center. Not centrosymmetric (only the staggered form, $D_{3d}$, would qualify).
4. $CH_4$: tetrahedral, point group $T_d$. A regular tetrahedron has no inversion center (inverting one vertex through the middle does not land on another vertex). Not centrosymmetric.

Since trans-planar $H_2O_2$ is the only centrosymmetric species in the list, it is the only one where the IR active modes are guaranteed to be completely Raman silent and the Raman active modes completely IR silent.

Let's summarize:

- Mutual exclusion is a shortcut test for a center of inversion, nothing more.
- Bent, eclipsed, and tetrahedral shapes here all fail to have that center; only the flat, trans arrangement of $H_2O_2$ has it.

The correct option is (B), the trans-planar conformer of $H_2O_2$.

**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:**

A second way to reach the same result is to think of the pre-equilibrium step $A + B \rightleftharpoons X^{\ddagger}$ as an ordinary chemical equilibrium and use the standard relation between $K_p$ and $K_c$ (or equivalently between $\Delta H$ and $\Delta U$ for a reaction of gases).

1. For any reaction of ideal gases, $\Delta H = \Delta U + \Delta(PV)$, and since $PV = n_{gas}RT$ for each species, this becomes $\Delta H = \Delta U + (\Delta n_{gas})RT$, exactly the relation used to connect $K_p$ and $K_c$ through $K_p = K_c(RT)^{\Delta n_{gas}}$.

2. Count the moles of gas on each side of the activation step $A + B \rightarrow X^{\ddagger}$: 2 moles of gas go in ($A$ and $B$), 1 mole of gas comes out ($X^{\ddagger}$), so $\Delta n_{gas} = 1 - 2 = -1$.
3. Apply this to the activation quantities directly: $\Delta^{\ddagger}H^{o} = \Delta^{\ddagger}U^{o} + \Delta n^{\ddagger}RT = \frac{5}{2}RT + (-1)(RT)$.
4. Carrying out the subtraction: $\frac{5}{2}RT - \frac{2}{2}RT = \frac{3}{2}RT$.

This is the same numeric answer as before, reached by treating the activation step as a mole-counting problem on an equilibrium rather than a direct thermodynamic definition.

Let's summarize:

- Whenever the number of gas particles changes during a step, $\Delta H$ and $\Delta U$ for that step differ by $(\Delta n_{gas})RT$.
- Here two particles become one, so $\Delta n^{\ddagger} = -1$, and $\Delta^{\ddagger}H^{o}$ ends up $1RT$ smaller than $\Delta^{\ddagger}U^{o}$.

The correct option is (B), $\frac{3}{2}RT$.

**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.

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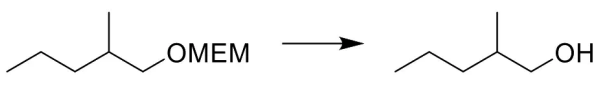
**21.** The reagent(s) that will effect the following transformation is(are)




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:**

A clean way to attack this question is to first sort all four protecting-group families that could appear on an exam, match each reagent in the options to the family it removes, and then see which families match "MEM ether."

1. $Pd/C, H_2$: this reagent pair is the classic deprotection for benzyl-type groups (*Bn*, *Cbz*) that have a benzylic C-O or C-N bond, through catalytic hydrogenolysis. A MEM ether has no benzylic bond and no double/triple bond, so this reagent simply does not react with it.
2. $ZnBr_2$: this is a mild oxophilic Lewis acid. Its textbook use is exactly to remove MEM ethers, by binding the acetal oxygen and helping the $C-O$ bond to the substrate alcohol break, releasing the free *ROH*. This matches the transformation shown.
3. **PPTS,** $^tBuOH$: PPTS is a weak acid catalyst (much milder than *TsOH*), commonly used in an alcohol solvent under heating to solvolyze acetal-based protecting groups such as *THP* and *MEM* ethers back to the free alcohol without disturbing acid sensitive parts of the rest of the molecule. This also matches.
4. $^nBu_4NF$: this delivers a naked fluoride ion, whose only job in synthesis is to attack silicon and cleave silyl ethers (*TMS*, *TES*,

*TBS*). There is no silicon anywhere in a MEM ether, so fluoride has nothing to react with here.

Matching reagent families to protecting group chemistry this way shows that only the Lewis acid ($ZnBr_2$) and the mild Bronsted acid in protic solvent (PPTS/$^tBuOH$) belong to the category of reagents that cleave acetal-type protecting groups like MEM.

Let's summarize:

- $Pd/C$, $H_2$ removes benzylic protecting groups, not acetals.
- $^nBu_4NF$ removes silyl protecting groups, not acetals.
- $ZnBr_2$ and PPTS/$^tBuOH$ both belong to the acid-catalyzed acetal cleavage family that removes MEM ethers.

The correct options are (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)

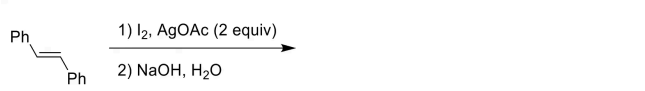

(B)


(C)


(D)


**Correct Answer:** (A)


; (D)




**SOLUTION:**

Another way to solve this is to mentally track what happens to just one face-defining feature, the relationship between the two phenyl groups, as each addition occurs, rather than quoting the general cis/trans-syn/anti rule from memory.

1. **cis-stilbene**: in the starting alkene the two phenyl groups sit on the same side of the double bond.

2. **trans-stilbene**: in the starting alkene the two phenyl groups sit on opposite sides of the double bond.
3. $OsO_4/NMO$ **(syn addition)**: both new $C-OH$ bonds form on the same face of the flat alkene. Starting from cis-stilbene, adding both $OH$ groups to one face keeps the two $Ph$ groups in a mirror-related arrangement in the product, which is exactly the internal-mirror-plane condition that defines a meso compound.
4. $I_2/AgOAc$ **then** $NaOH/H_2O$ **(net anti addition, Prevost)**: the two new $C-O$ bonds end up on opposite faces of what was the flat alkene. Starting from trans-stilbene, where the phenyls were already on opposite sides, adding the two oxygens to opposite faces again reconstructs the mirror-related, meso arrangement in the product.
5. The two "mismatched" combinations, cis-alkene with anti addition, and trans-alkene with syn addition, each end up putting the two stereocenters into a same-handed ($R,R$ or $S,S$) relationship instead, giving the chiral, optically active $d,l$ diol rather than the meso diol.

Checking the four options against this: (A) is cis-stilbene with syn ($OsO_4$) addition, a matched pair giving meso. (B) is trans-stilbene with syn addition, mismatched, giving $d,l$. (C) is cis-stilbene with anti (Prevost) addition, mismatched, giving $d,l$. (D) is trans-stilbene with anti (Prevost) addition, a matched pair giving meso.

Let's summarize:

- Meso hydrobenzoin needs the alkene geometry and the addition face-selectivity to be "matched" in the sense described above.
- That matching happens for cis-stilbene/syn and for trans-stilbene/anti, which are options (A) and (D).

The correct options are (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.

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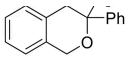
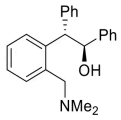
**23.** In the $^1$H NMR spectrum of compound **X**, the coupling constant ($J_{ab}$) between $H_a$ and $H_b$ is 3 Hz. The amino alcohol(s) that give(s) **X** on reaction with methyl iodide followed by heating is(are)

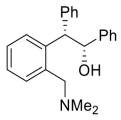



X

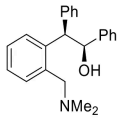
(A)



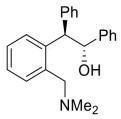

(B)



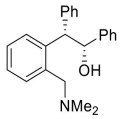

(C)



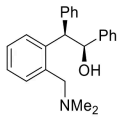

(D)




**Correct Answer:** (B)




; (C)




**SOLUTION:**

Approach this from the reaction type first, then bring in the NMR data only at the end, rather than jumping straight to the Karplus equation.

1. **Recognize the reaction as an intramolecular Williamson ether synthesis.** Methyl iodide is a strong, small alkylating agent; a tertiary amine like the $NMe_2$ group reacts with it fast and irreversibly to give a quaternary ammonium iodide. On warming, this quaternary center becomes an excellent intramolecular leaving group ($NMe_3$), and the nearby alcohol oxygen, positioned exactly right for a six-membered ring transition state, displaces it in a single $S_N2$ step. This is the standard way an ortho-(aminomethyl)benzylic alcohol like this is converted into a cyclic ether without needing any external base or catalyst.
2. **Track the stereochemistry through the mechanism.** An $S_N2$ step inverts configuration only at the carbon being attacked, here the benzylic $CH_2$ that is not a stereocenter to begin with (two identical $H$'s on it). The two carbons that do carry stereochemistry, the ones bearing the phenyl groups, are spectators in this step: their configurations, and therefore their relative configuration to each other, pass unchanged from starting amino alcohol into the isochroman product **X**.
3. **Bring in the NMR clue last.** Now that **X** is a rigid bicyclic ring, $J_{ab} = 3$ Hz is a small vicinal coupling, which by the Karplus curve means the $H_a - C - C - H_b$ dihedral in the ring is close to 90°. Only one of the two possible relative configurations of the phenyl-bearing stereocenters places the ring hydrogens near that dihedral once the ring is locked; the other diastereomer would push $H_a$ and $H_b$ closer to antiperiplanar and give a coupling several times larger.

4. **Bring back the starting materials.** Because the relative configuration is preserved (step 2) and only relative configuration controls $J$ (step 3), whichever amino alcohol diastereomer has the correct relative disposition of the two phenyls is the one that answers the question, and its mirror image (enantiomer) answers it equally well, since enantiomers give identical, superimposable NMR spectra.

Reading the four drawn structures as two enantiomeric pairs, the pair carrying the relative configuration consistent with $J_{ab} = 3$ Hz is B and C; A and D belong to the other, non-matching diastereomeric pair.

Let's summarize:

- The cyclization is a simple intramolecular Williamson ether synthesis at a non-stereogenic carbon.
- Relative stereochemistry survives the reaction untouched, so the NMR coupling constant of the product directly reports on the starting diastereomer.
- Both enantiomers of the correct diastereomer, B and C, are valid answers.

The correct options are (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.

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**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:**

A useful way to check facts about a metalloprotein is to compare it against the other classic metalloprotein families, since most wrong statements in this type of question are true facts, just borrowed from a different protein class.

1. **"It is an electron transfer protein"**: plastocyanin belongs to the same functional category as cytochromes and ferredoxins, proteins whose only job is to move a single electron along a chain, here specifically between cytochrome $b_6f$ and photosystem I in photosynthesis. It does not bind or activate a substrate the way an enzyme does. This statement is correct.
2. **"It is intensely colored in its oxidised form"**: this is the defining feature of the "blue copper" (type 1 copper) protein family that plastocyanin belongs to, named for exactly this property; the intense blue comes from a cysteine-sulfur to $Cu(II)$ charge transfer band that is only present when the copper is oxidised, and vanishes on reduction to colorless $Cu(I)$. Correct.
3. **"Its central metal ion has a distorted tetrahedral geometry"**: type 1 copper sites, unlike the square planar geometry typical of most $Cu(II)$ complexes, are held in a distorted

(compressed) tetrahedral geometry by the rigid protein scaffold, a geometry that is actually a compromise favoring fast electron transfer over ideal bonding for either oxidation state. Correct.

4. **"It contains $S^{2-}$ bridged metal cluster"**: bridging sulfide ions connecting two or more metal centers is the hallmark of iron-sulfur proteins, like $2Fe-2S$ or $4Fe-4S$ ferredoxins, a completely different protein family from blue copper proteins. Plastocyanin has exactly one metal (copper) and no sulfide bridge; its sulfur atoms come only from cysteine and methionine side chains binding that single copper. This statement describes the wrong protein family and is incorrect for plastocyanin.

Sorting the four statements this way confirms that three of them (electron transfer role, color tied to oxidation state, distorted tetrahedral copper site) are genuine, well known features of plastocyanin, while the fourth borrows a fact that belongs to iron-sulfur cluster proteins instead.

Let's summarize:

- Plastocyanin = single copper, blue in the oxidised $Cu(II)$ state, distorted tetrahedral site, pure electron shuttle.
- Sulfide-bridged clusters are a different protein family (iron-sulfur proteins), not plastocyanin.

The correct options are (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:**

Mossbauer spectroscopy is a nuclear technique. To judge each statement, remember three ideas: which isotope pair produces the right gamma energy, what causes quadrupole splitting, and what controls isomer shift.

1. **Option A ($^{57}Co$ as source):** Iron Mossbauer spectroscopy runs on the $^{57}Fe$ nucleus. $^{57}Co$ is the parent isotope: it captures an electron and decays into excited $^{57}Fe$, which emits the gamma-ray used to probe the sample. This makes $^{57}Co$ the standard, correct source. True.
2. **Option B (14.4 keV resonance energy):** The nuclear excited state of $^{57}Fe$ reached from $^{57}Co$ decay sits 14.4 keV above the ground state. The gamma-ray released when this state relaxes, and the one resonantly absorbed by $^{57}Fe$ nuclei in the sample, has exactly this 14.4 keV energy. True.
3. **Option C (large quadrupole splitting in $K_2[Fe(CN)_5NO]$):** Quadrupole splitting needs an uneven charge distribution around

the nucleus. The nitrosyl ligand NO is electronically very different from the five cyanide ligands around it, so the ligand field is strongly distorted along the Fe-NO direction. This large asymmetry produces one of the biggest quadrupole splittings seen among iron complexes. True.

4. **Option D (isomer shift comparison):** Isomer shift falls as s-electron density at the nucleus rises. High spin $Fe^{2+}$ in $FeSO_4 \cdot 7H_2O$ carries more d-electron shielding, so s-density at the nucleus is lower and the isomer shift is larger (roughly 1.2 to 1.4 mm/s). Low spin $Fe^{3+}$ in $K_3[Fe(CN)_6]$ has less shielding, so its isomer shift is small, near zero. So the isomer shift of $FeSO_4 \cdot 7H_2O$ is bigger, not smaller. False.

Putting the four checks together, A, B and C hold and D fails.

Let's summarize:

- $^{57}Co$ is the source isotope and 14.4 keV is the fixed resonance energy for $^{57}Fe$ Mossbauer work.
- Asymmetric ligand fields, like NO next to five CN groups, give large quadrupole splitting.
- More d-electron shielding means lower s-density at the nucleus and a larger isomer shift, so high spin Fe(II) beats low spin Fe(III) in isomer shift, not the other way round.

The correct statements are A, B and 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:**

The Wacker process is the industrial route from ethylene to acetaldehyde, run with a palladium and copper catalyst pair. Working out which metal oxidation states change tells us which options are right.

1. **Pd(II)/Pd(0):** Palladium starts as Pd(II), binds the alkene, and once the alkene is converted to acetaldehyde, the metal is released as Pd(0). This is the productive, alkene-consuming step of the cycle. True.
2. **Cu(II)/Cu(I):** Pd(0) cannot restart the cycle by itself, it needs reoxidation. Cu(II) chloride does this job, picking up the electrons from Pd(0) and becoming Cu(I) while palladium returns to Pd(II). True.
3. **Pd(IV)/Pd(II):** A Pd(IV) state belongs to other palladium catalytic cycles built on oxidative addition chemistry, not to the redox-relay mechanism of the Wacker process, where palladium only ever sits at Pd(II) or Pd(0). False.
4. **Cu(II)/Cu(0):** Copper is only ever a one-electron shuttle here, moving between Cu(II) and Cu(I); it is reoxidised by $O_2$ back to Cu(II) rather than being reduced further to metallic copper. False.

So the real redox pairs at work are palladium moving between +2 and 0, and copper moving between +2 and +1, while oxygen finally regenerates the Cu(II) used up in the cycle.

Let's summarize:

- Palladium is the alkene-activating metal and cycles between Pd(II) and Pd(0).
- Copper is the electron shuttle to atmospheric oxygen and cycles between Cu(II) and Cu(I).
- Neither Pd(IV) nor metallic Cu(0) appears in this cycle.

The correct interconversions are A and 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.

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**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:**

This question checks four different properties of a given spatial function: whether it is a stationary quantum state, whether it has odd symmetry, whether it belongs to a particle on a ring, and whether it is a momentum eigenfunction.

1. **Stationary state (A):** $\Phi = x(a - x)$ is a function of $x$ only, it carries no time label $t$. Time-independent spatial wavefunctions like this are exactly what go into the stationary-state ansatz $\Psi(x, t) = \Phi(x)e^{-iEt/\hbar}$, whose probability density $|\Psi|^2 = \Phi(x)^2$ stays fixed as $t$ runs. Since $\Phi$ here has no time dependence at all, the state it describes is stationary. True.
2. **Odd function (B):** Expand $\Phi = ax - x^2$. Odd functions have only odd powers of $x$ and satisfy $\Phi(-x) = -\Phi(x)$. Here $\Phi(-x) = -ax - x^2$, but $-\Phi(x) = -ax + x^2$; the $x^2$ terms carry opposite signs, so the two are not equal anywhere except $x = 0$. Shifting to the natural center $x = a/2$ also turns $\Phi$ into $a^2/4 - \xi^2$, an even function of $\xi$. So $\Phi$ is not odd. False.
3. **Particle on a ring (C):** Wavefunctions on a ring must repeat every $2\pi$ in the angle $\phi$, so they take the exponential form $e^{im\phi}$. $\Phi = x(a - x)$ is a plain polynomial in a straight-line coordinate, it has no periodicity and is not even written in an angular variable. So it cannot be a ring wavefunction. False.
4. **Momentum eigenfunction (D):** Apply $\hat{p} = -i\hbar\, d/dx$:

   $$\hat{p}\Phi = -i\hbar(a - 2x)$$

   For $\Phi$ to be a momentum eigenfunction, this result would need to equal a constant times $\Phi$, but $(a - 2x)$ is not a constant multiple of $x(a - x)$. Only plane waves $e^{ikx}$ are momentum eigenfunctions. False.

Working through the algebra on all four statements leaves only the stationary-state claim standing.

Let's summarize:

- A wavefunction written with no time variable, like $\Phi = x(a - x)$, is the time-independent part of a stationary state.
- $\Phi$ is neither odd, nor periodic like a ring wavefunction, nor an eigenfunction of momentum, since applying $\hat{p}$ to it does not return a multiple of itself.

The correct statement is 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.

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**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:**

Spherical harmonics $Y_l^m$ are the standard angular functions used for anything with a central potential, from the rigid rotor to the hydrogen

atom. Each statement here tests a core property of these functions.

1. **All complex (A):** The $\phi$-dependence of $Y_l^m$ sits in the factor $e^{im\phi}$. For $m = 0$ this factor is just 1, and the harmonic collapses to a real Legendre-polynomial function of $\cos\theta$ alone, for instance $Y_0^0$ and $Y_1^0$ are both real. So the word "all" makes this statement false.
2. **Eigenfunctions of $\hat{L}^2$ (B):** The defining equation of the spherical harmonics is $\hat{L}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m$; this is how $l$ is defined as a quantum number in the first place. True.
3. **Eigenfunctions of $\hat{L}_z$ (C):** They also satisfy $\hat{L}_z Y_l^m = m\hbar Y_l^m$, which is how the second quantum number $m$ is defined. $\hat{L}^2$ and $\hat{L}_z$ commute, so sharing simultaneous eigenfunctions is expected. True.
4. **Degeneracy of $Y_1^1$ and $Y_1^{-1}$ (D):** For any spherically symmetric potential, the energy does not depend on $m$ at all, only on $l$. $Y_1^1$ and $Y_1^{-1}$ both have $l = 1$, differing only in $m$, so they carry the same energy unless an external field like a magnetic field breaks the spherical symmetry. True.

Three of the four statements survive the check, with only the "all" in option A being too strong a claim.

Let's summarize:

- $Y_l^m$ is real only when $m = 0$; otherwise it is complex because of the $e^{im\phi}$ factor.
- $\hat{L}^2$ and $\hat{L}_z$ both act on $Y_l^m$ as eigenoperators, giving eigenvalues $l(l+1)\hbar^2$ and $m\hbar$.
- Energy in a central potential depends only on $l$, so different $m$ states at the same $l$, like $Y_1^1$ and $Y_1^{-1}$, are degenerate.

The correct statements are B, C and 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:**

A cleaner way to count gauche interactions is to build each conformer from a reference and count what changes, using the well known fact that a single axial methyl on cyclohexane carries 2 gauche (1,3-diaxial type) interactions relative to an equatorial one, worth about 1.8 kcal/mol combined (the methyl A-value), while two adjacent (1,2) equatorial substituents are gauche to each other, worth about 0.9 kcal/mol on their own.

1. **Diaxial conformer:** Both methyl groups point axial. On a 1,2 pair of carbons, axial-axial substituents are anti to one another (dihedral 180 degrees), so the methyls do not form a gauche pair between themselves. Each axial methyl still clashes with the axial hydrogens on the carbons two bonds away, giving 2 gauche interactions per methyl. With two axial methyls that is $2 \times 2 = 4$ gauche interactions.
2. **Diequatorial conformer:** Both methyl groups point equatorial. On adjacent (1,2) carbons, equatorial-equatorial

substituents sit gauche to each other (dihedral 60 degrees), giving exactly 1 methyl-methyl gauche interaction. Equatorial groups have no 1,3-diaxial type clash with the ring, so there is nothing more to add. Total: 1 gauche interaction.

Comparing the two counts, $4 - 1 = 3$. This also matches the experimentally known conformational preference of trans-1,2-dimethylcyclohexane for the diequatorial form, worth roughly $3 \times 0.9 \approx 2.7$ kcal/mol, close to the measured value.

Let's summarize:

- Diaxial trans-1,2-dimethylcyclohexane: 0 methyl-methyl gauche interaction (anti pair) plus 4 axial-ring gauche interactions, total 4.
- Diequatorial trans-1,2-dimethylcyclohexane: 1 methyl-methyl gauche interaction (gauche pair) plus 0 axial-ring interactions, total 1.

The difference in gauche interactions is 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:**

Both ions start from an octahedral ML6 skeleton, so the fastest route is to identify each point group from its ligand pattern and pull the operation count straight from the character table order.

1. **$[PdCl_6]^{2-}$:** All six ligands are identical chlorides, so nothing breaks the symmetry of a perfect octahedron. This is the parent $O_h$ point group. $O_h$ is the point group of highest order among common coordination geometries, with $x = 48$ symmetry operations (identity, rotations, improper rotations, mirror planes and the centre of inversion, all counted together).
2. **trans-$[PdBr_2Cl_4]^{2-}$:** Replacing a trans pair of Cl by Br singles out one of the three fourfold axes of the parent octahedron as special (the Br-Pd-Br axis), while the four remaining Cl ligands stay equivalent in the perpendicular plane. This lowers the symmetry from $O_h$ down to $D_{4h}$, the standard point group of any trans-$MA_4B_2$ octahedral complex, which has $y = 16$ symmetry operations.

A useful check: $D_{4h}$ is a subgroup of $O_h$, and the index of this subgroup, $48/16 = 3$, equals the number of distinct fourfold axes in the parent octahedron (one for each pair of trans positions the two Br ligands could occupy). This confirms $y = 16$ is consistent with $x = 48$.

Let's summarize:

- $[PdCl_6]^{2-}$: perfect octahedron, point group $O_h$, order 48.
- trans-$[PdBr_2Cl_4]^{2-}$: axially disubstituted octahedron, point group $D_{4h}$, order 16.
- $x - y = 48 - 16 = 32$.

The value of $x - y$ is 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:**

Since path length and wavelength stay the same for both solutions, the Beer-Lambert law $A = \varepsilon cl$ says absorbance is directly proportional to concentration. That means we do not even need to solve for $\varepsilon$ separately, doubling the concentration simply doubles the absorbance.

1. **Get the absorbance at 0.005 M from the given transmittance:** 80% transmittance means $T = 0.80$, and $A = -\log_{10} T$, so

$$A_1 = -\log_{10}(0.80) = -\log_{10}(4/5) = \log_{10}(5/4) = \log_{10}(1.25)$$

   Working this out, $\log_{10}(1.25) \approx 0.09691$, so $A_1 \approx 0.0969$.
2. **Scale by the concentration ratio:** The second solution is 0.01 M, exactly twice 0.005 M, and path length and compound (hence $\varepsilon$) are unchanged. So

$$A_2 = A_1 \times \frac{c_2}{c_1} = 0.09691 \times \frac{0.01}{0.005} = 0.09691 \times 2 = 0.19382$$

Rounding **0.19382** to three decimal places gives **0.194**.

Let's summarize:

- Transmittance and absorbance are linked by $A = -\log_{10} T$.
- At fixed path length, absorbance scales linearly with concentration, so doubling concentration doubles absorbance directly, without needing $\varepsilon$ as an intermediate number.

The absorbance of the 0.01 M solution is 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** $\mathbf{cm^{-1}}$. 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 $s^{-1}$)

**Correct Answer:** 0.93

**SOLUTION:**

Another way to get the same answer is to switch everything to frequency units before touching the moment of inertia formula, instead of carrying $B$ in $\mathbf{cm^{-1}}$ all the way through.

The rotational lines of a rigid diatomic sit at $\tilde{\nu} = 2B(J+1)$ in wavenumber units, and the paper tells us consecutive lines are $41.11\ \text{cm}^{-1}$ apart, so $B = 20.555\ \text{cm}^{-1}$.

Turn this into an ordinary frequency using $\nu = cB$ (with $c$ in $\text{cm s}^{-1}$):

$$\nu = (2.998 \times 10^{10}\ \text{cm s}^{-1})(20.555\ \text{cm}^{-1}) = 6.1638 \times 10^{11}\ \text{Hz}$$

The rotational energy levels are $E_J = \frac{\hbar^2}{2I}J(J+1)$, which turns the same spacing rule into $\nu = h/(4\pi^2 I)$ in ordinary frequency form. Rearranging for $I$:

$$I = \frac{h}{4\pi^2\nu} = \frac{6.626 \times 10^{-34}}{4\pi^2 \times 6.1638 \times 10^{11}} = 1.3618 \times 10^{-47}\ \text{kg m}^2$$

This is the same moment of inertia as before, as it must be, since it is just a different bookkeeping of the same $B$.

Now find the reduced mass in kg using the atomic masses and the amu-to-kg conversion together:

$$\mu = \frac{(1.008)(18.998)}{1.008 + 18.998} \times 1.661 \times 10^{-27} = 0.9572 \times 1.661 \times 10^{-27} = 1.5899 \times 10^{-27}\ \text{kg}$$

Since $I = \mu r^2$,

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.3618 \times 10^{-47}}{1.5899 \times 10^{-27}}} = 9.25 \times 10^{-11}\ \text{m} = 0.93\ \text{Å}$$

The H-F bond length comes out to $0.93$ Å, the same value reached through the wavenumber route, a good check that both approaches agree.

**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:**

A different way to reach the same number is to work out the absolute frequency of each peak first, then subtract, instead of scaling the ppm difference in one shot.

First get the spectrometer frequency from the proton's gyromagnetic ratio:

$$\nu_0 = \frac{\gamma B_0}{2\pi} = \frac{(2.675 \times 10^{8})(14.1)}{2\pi} = 6.0028 \times 10^{8}\ \text{Hz} = 600.28\ \text{MHz}$$

By definition, a peak at $\delta$ ppm sits $\delta \times 10^{-6}$ of the operating frequency away from the reference, so its absolute frequency is $\nu(\delta) = \nu_0(1 + \delta \times 10^{-6})$.

For the peak at 1.25 ppm:

$$\nu_1 = 600.28\ \text{MHz} + 750.35\ \text{Hz}$$

For the peak at 5.75 ppm:

$$\nu_2 = 600.28\ \text{MHz} + 3451.6\ \text{Hz}$$

The separation is just the difference of the two added-on Hz terms, since the common 600.28 MHz cancels:

$$\Delta\nu = 3451.6 - 750.35 = 2701.3\ \text{Hz}$$

This matches scaling the $(5.75 - 1.25) = 4.50$ ppm gap by $\nu_0$ directly, confirming that shortcut. The two peaks are 2701.3 Hz apart, well inside the accepted band of 2699 to 2703 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:**

Here is a quicker route to the same result: start from the constant-pressure free energy change $\Delta G$, then correct it for the fact that the gas volume shrinks during the reaction.

Since $G = H - TS$ and $A = U - TS$, the two differ by $G - A = PV$, and for an ideal-gas change at constant $T$, $\Delta(PV) = \Delta n_{gas} RT$. That gives a direct shortcut:

$$\Delta A = \Delta G - \Delta n_{gas} RT$$

First compute $\Delta G$ the ordinary way:

$$\Delta G = \Delta H - T\Delta S = -890.01 - (298.15)(-241.60 \times 10^{-3}) = -890.01 + 72.03 = -817.98\ \text{kJ}$$

Now find $\Delta n_{gas}$ for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$: 3 mol of gas before, only 1 mol of gas after (water condenses), so $\Delta n_{gas} = 1 - 3 = -2$.

Apply the correction:

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

$$\Delta A = -817.98 - (-4.958) = -813.02 \text{ kJ}$$

This lands on the same number as computing $\Delta U$ first, since both routes are the same rearrangement done in a different order. The maximum total work obtainable from burning 1 mol of methane at constant pressure and 25°C is about 813.0 kJ, and the gap between this and the naive $|\Delta G| \approx 818.0$ kJ is exactly the $PV$ work tied up in the 2 mol drop in gas amount.

**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:**

A more direct way to see this is to skip the Nernst-Einstein detour and use Stokes' law for the ion's terminal drift velocity under an electric field directly.

Under a field $E$, an ion of charge $ze$ feels an electric force $zeE$. In steady drift this force is balanced by the viscous drag from Stokes' law, $6\pi\eta r v$. Setting them equal:

$$zeE = 6\pi\eta r v \quad \Rightarrow \quad u = \frac{v}{E} = \frac{ze}{6\pi\eta r}$$

The elementary charge is the Faraday constant divided by Avogadro's number, $e = F/N_A$. Since $R = N_A k$, $N_A = R/k$, so $e = Fk/R$, which folds back into the same $u = zFk/(6\pi\eta r R)$ formula, just built up from the drift-velocity picture instead of the diffusion-coefficient picture.

Put in the numbers for $z = 1$, $F = 96500\ \text{C mol}^{-1}$, $k = 1.38 \times 10^{-23}\ \text{J K}^{-1}$, $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$:

$$e = \frac{Fk}{R} = \frac{(96500)(1.38 \times 10^{-23})}{8.314} = 1.602 \times 10^{-19}\ \text{C}$$

which is (as a sanity check) the textbook value of the electron charge, confirming the constants are being combined correctly.

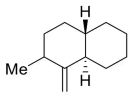
$$u = \frac{(1)(1.602 \times 10^{-19})}{6\pi(8.94 \times 10^{-4})(1.5 \times 10^{-10})} = \frac{1.602 \times 10^{-19}}{2.5277 \times 10^{-12}} = 6.34 \times 10^{-8}\ \text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$$

So $y \approx 6.34$ to $6.35$, matching the answer from the diffusion-coefficient route, since both are just two ways of writing the same physics.

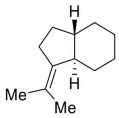
**Quick Tip:** Combine Stokes' law for the diffusion coefficient with the Nernst-Einstein relation between mobility and diffusion coefficient: $u = zFk/(6\pi\eta r R)$, since $k/R = 1/N_A$.

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

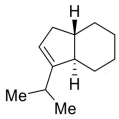

(A)



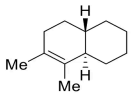

(B)



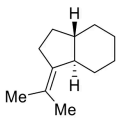

(C)




(D)




**Correct Answer:** (B)




**SOLUTION:**

Another way to pick the right structure is to work backward from alkene stability instead of forward from the mechanism step by step.

Acid treatment of an alcohol is a standard way to build an alkene by E1 dehydration: protonate the OH, lose water to make a carbocation, then lose an adjacent proton to form the double bond. Since the reaction runs under acidic, reversible conditions, the alkene that ends up as the major product is whichever one is the most stable, not necessarily the first one formed.

1. **Option (A)**: a terminal =CH2 exocyclic double bond, disubstituted overall, the least stable choice.
2. **Option (B)**: an exocyclic isopropylidene double bond fully flanked by ring carbons and the two methyls, a well conjugated, more substituted alkene, the most stable of the four.
3. **Option (C)**: keeps an isopropyl group but also draws in an extra ring double bond, which would need loss of a second molecule of water or an oxidation step, not a simple single dehydration.
4. **Option (D)**: a more substituted-looking ring alkene, but positioned so it is not conjugated with the isopropylidene fragment the way (B) is, the product of elimination toward the wrong side of the rearranged cation.

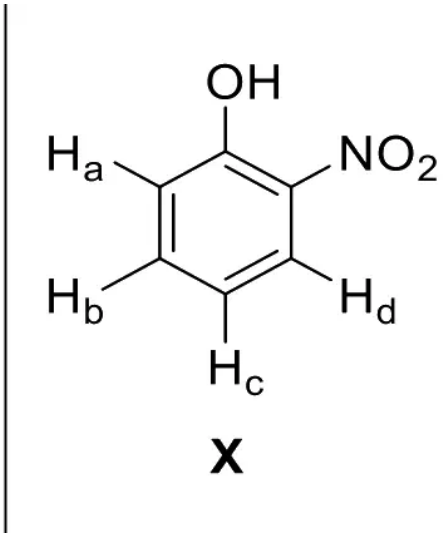
Acid-catalyzed dehydrations of polycyclic alcohols like this one are well known to proceed with skeletal (Wagner-Meerwein) rearrangement of the intermediate cation before the final proton loss, so the system can reach the most substituted, most stable alkene rather than stopping at whatever alkene sits closest to the original OH position.

Ranking the four candidates by alkene stability puts option (B) on top, which is why it is the major product formed under these acidic, thermodynamically controlled dehydration conditions.

**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:**

A second way to reach the same match is to estimate each proton's shift with rough substituent increments, instead of only ranking pairs qualitatively.

Take benzene's base shift as about **7.26** ppm and add typical increments for **−OH** and **$-NO_2$**: **−OH** shifts a proton by roughly **−0.5** (ortho), **−0.1** (meta), **−0.4** (para); **$-NO_2$** shifts a proton by roughly **+0.95** (ortho), **+0.26** (meta), **+0.38** (para).

Numbering the ring **C1 = OH**, **C2 = $NO_2$**, **C3 = $H_d$**, **C4 = $H_c$**, **C5 = $H_b$**, **C6 = $H_a$**:

- $H_d$ (C3): ortho to **$NO_2$**, meta to **OH**: **$7.26 + 0.95 - 0.1 \approx 8.1$** ppm.
- $H_c$ (C4): meta to **$NO_2$**, para to **OH**: **$7.26 + 0.26 - 0.4 \approx 7.1$** ppm.
- $H_b$ (C5): para to **$NO_2$**, meta to **OH**: **$7.26 + 0.38 - 0.1 \approx 7.5$** ppm.
- $H_a$ (C6): meta to **$NO_2$**, ortho to **OH**: **$7.26 + 0.26 - 0.5 \approx 7.0$** to **7.2** ppm.

These rough numbers line up with the four experimental values: $H_d$ (about 8.1) matches **IV** (8.12), $H_b$ (about 7.5) matches **III** (7.59), $H_c$ (about 7.1) matches **I** (7.00), and $H_a$ (about 7.0 to 7.2) matches **II** (7.17).

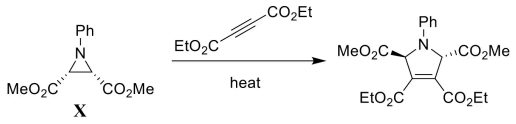
The splitting patterns confirm this independently: $H_a$ and $H_d$ sit next to a substituted carbon on one side, so they only pick up one ortho and one meta coupling (dd), while $H_b$ and $H_c$ sit between two **CH** carbons and pick up a third coupling (ddd), matching **I**/**III** as the ddd pair and **II**/**IV** as the dd pair.

Both the shift estimate and the splitting-pattern logic converge on $P \rightarrow II$, $Q \rightarrow III$, $R \rightarrow I$, $S \rightarrow IV$, option (A).

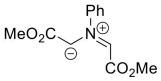
**Quick Tip:** A proton flanked by ring CH on both sides gives ddd (three J's); one flanked on only one side gives dd (two J's). Substituent effects then fix which is more upfield or downfield: OH shields ortho/para, NO2 deshields ortho/para.

• • •

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



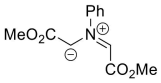
(A)



is formed through conrotatory opening of **X**

is formed through conrotatory opening of **X**

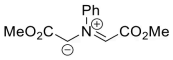
(B)



is formed through disrotatory opening of **X**

is formed through disrotatory opening of **X**

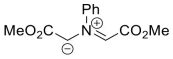
(C)



is formed through conrotatory opening of **X**

is formed through conrotatory opening of **X**

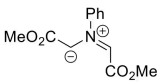
(D)



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:**

The same answer can be reached by thinking about orbital symmetry directly, instead of just quoting the $4\pi$/conrotatory rule from memory.

When the C – C sigma bond of the aziridine breaks to open the ring, the two electrons in that bond become the terminal p-orbitals of the new 3-atom pi system (the azomethine ylide), together with the C = N pi bond and the nitrogen lone pair contribution. Counting all the electrons delocalised over this 3-atom, 3-orbital system gives 4 electrons, so the ring-opening is governed by the same 4-electron ($4\pi$) electrocyclic selection rules as the butadiene-to-cyclobutene interconversion.

For a $4\pi$ electrocyclic process, only one rotation mode keeps the terminal lobes overlapping with the right sign as the sigma bond stretches into the two new p-orbitals. Under thermal activation that mode is conrotatory; disrotatory opening only becomes symmetry-allowed once the system is promoted to an excited state by light. Since this problem runs on heat, not light, conrotatory is the mode in play, ruling out options (B) and (D).

Between the two remaining structures, the conrotatory pathway keeps the two ring substituents rotating the same way as the ring opens, walking the two $CO_2Me$ groups out to opposite, extended ends of the newly linear 2-azaallyl cation, the geometry drawn in option (A). Option (C) shows a folded arrangement that this particular conrotatory opening does not produce; that folded shape would instead be the disrotatory outcome.

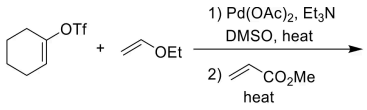
So orbital symmetry (thermal, 4 electrons, conrotatory) and the geometric consequence of that rotation both point to option (A) as the correct intermediate.

**Quick Tip:** Aziridine ring-opening to an azomethine ylide is a $4\pi$-electron electrocyclic process; under thermal conditions the Woodward-Hoffmann

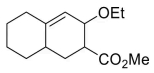
rules require conrotatory ring-opening, and the resulting ylide geometry follows from that rotation sense.

• • •

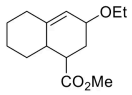
**39.** The major product formed in the following reaction sequence is:



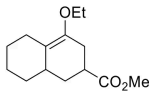

(A)



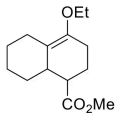

(B)



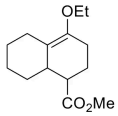

(C)




(D)




**Correct Answer:** (D)



**SOLUTION:**

**Step 1:** Spot the two reaction classes hidden in the scheme.
There are two separate events here, not one. Reagent set 1 ($Pd(OAc)_2$, $Et_3N$, DMSO, heat) is a Heck-coupling recipe: it needs a vinyl leaving group, here the vinylic triflate, and an alkene coupling partner, here ethyl vinyl ether. Reagent set 2, methyl propiolate under heat with no metal, is the signature of a Diels-Alder cycloaddition.

**Step 2:** Build the diene from the Heck step.
Pd(0) oxidatively adds into the vinyl-OTf bond, carbopalladates the vinyl ether so Pd sits next to the oxygen-bearing carbon (oxygen stabilizes the incipient positive charge), and beta-hydride elimination on the far side restores an alkene. The net outcome is a new $C=C-OEt$ unit hung directly off the ring's original alkene carbon, so the ring alkene and the new alkene are conjugated: a semicyclic 1-ethoxy-1,3-diene.

**Step 3:** Run the Diels-Alder and count atoms.
Methyl propiolate, $HC\equiv C-CO_2Me$, is a strong dienophile because the ester group withdraws electron density from the triple bond. Heating drives the [4+2]: the diene's terminal carbons bond to the two alkyne carbons, forming a new six-membered ring fused to the cyclohexane, giving a bicyclic octahydronaphthalene framework carrying only OEt and $CO_2Me$ as substituents, matching the substitution count in every one of the four answer choices.

**Step 4:** Use electronics to fix the regiochemistry.
The largest HOMO coefficient of an electron-rich, C1-oxygenated diene lies at the terminus away from oxygen, and the largest LUMO coefficient of an ester-activated alkyne dienophile lies at the carbon

away from the ester. These large-coefficient ends bond preferentially to each other, fixing where **OEt** and **$CO_2Me$** land relative to the new ring fusion, matching the connectivity drawn in option (D) rather than the alternative regiochemistries in (A), (B) or (C).

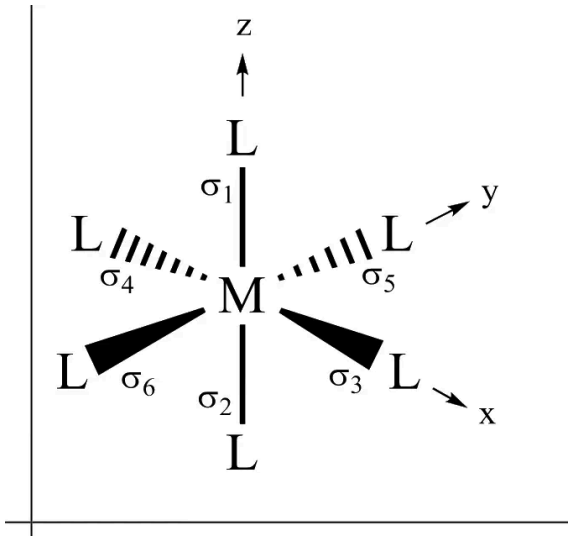
**Step 5:** Conclusion.
Cross-checking the mechanism, Heck then Diels-Alder, against the drawn structures confirms the product is option (D).

**Option (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:** Reduce the sigma representation.

For six sigma-only ligands on an octahedron, the reducible representation of the six sigma bonds reduces as $\Gamma_\sigma = a_{1g} + e_g + t_{1u}$. The $e_g$ piece transforms exactly like the pair $(d_{z^2}, d_{x^2-y^2})$, so the LGO matching $d_{z^2}$ is one specific combination inside this $e_g$ block.

**Step 2:** Use the sign pattern of $d_{z^2}$ directly.

Write $d_{z^2}$ as proportional to $2z^2 - x^2 - y^2$. Each ligand contributes its sigma orbital weighted by this function along its bond direction: along $+z$ and $-z$ the value is $2(1)^2 = 2$, and along $\pm x, \pm y$ the value is $-(1)^2 = -1$. Reading these off gives the unnormalized LGO $2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$, with $\sigma_1, \sigma_2$ axial and $\sigma_3$ to $\sigma_6$ equatorial.

**Step 3:** Normalize by summing squared coefficients.

$2^2 + 2^2 + (-1)^2 + (-1)^2 + (-1)^2 + (-1)^2 = 12$, so divide by $\sqrt{12}$:

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

**Step 4:** Check orthogonality with the other $e_g$ partner and with $a_{1g}$. The $d_{x^2-y^2}$ partner is $\frac{1}{2}(\sigma_3 - \sigma_4 + \sigma_5 - \sigma_6)$, with no axial terms at all since $x^2 - y^2$ vanishes on the $z$-axis, and it is orthogonal to $\psi_{z^2}$ by inspection. The totally symmetric $a_{1g}$ combination is $\frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$, all-positive and equal, a different orbital (option D), not the $d_{z^2}$ match. This confirms only the $(2, 2, -1, -1, -1, -1)$ pattern with $\frac{1}{\sqrt{12}}$ works.

**Final Answer:**

Option (A) is the correct $\sigma$-LGO of $e_g$ symmetry matching $d_{z^2}$.

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

**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:** Start from the known physical fact: ferrocene is diamagnetic. Ferrocene has no unpaired electrons, confirmed by experiment. This rules out any option that leaves electrons unpaired across two different-energy sets, and means all six $d$-electrons of $Fe^{2+}$ ($d^6$) must sit fully paired.

**Step 2:** Use the geometry of each orbital relative to the two Cp rings. Picture the rings as flat pentagons above and below the metal, with the sandwich axis as $z$. $d_{xy}$ and $d_{x^2-y^2}$ lie entirely in the equatorial $xy$ plane, roughly between the ring carbon positions, so they barely interact with the ring $\pi$ clouds: a spectator pair, lowest in energy. $d_{z^2}$ points directly up and down the $z$-axis toward the ring centroids, giving a small $\sigma$-type interaction, a middle-energy orbital. $d_{xz}$ and $d_{yz}$ tilt toward the ring carbons and interact most strongly with the filled ring $\pi$ orbitals, pushing this pair highest.

**Step 3:** Fill six electrons from the bottom up, respecting degeneracy. The lowest doubly-degenerate pair ($d_{xy}, d_{x^2-y^2}$) takes 4 electrons, the next single orbital ($d_{z^2}$) takes the remaining 2, and the highest doubly-degenerate pair ($d_{xz}, d_{yz}$) is left empty. Every electron is paired, consistent with diamagnetism.

**Step 4:** Write the final configuration and confirm against options.

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

Option (B) puts the near-nonbonding pair as highest energy, contradicting the weak-overlap argument. Option (C) removes the distinct level for $d_{z^2}$. Option (D) lists four levels instead of the

required 2:1:2 degeneracy pattern. Only (A) survives.

**Final Answer:**
Option (A) is correct.

$$\boxed{d_{xy}^2 = d_{x^2-y^2}^2 < d_{z^2}^2 < d_{xz}^0 = d_{yz}^0}$$

**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:** Frame the question as a bond-reorganization comparison.
Outer-sphere electron transfer needs both partner ions to reach a matching geometry before the electron hops. So the slowest pair is the one whose two oxidation states look most different structurally: biggest change in $M-L$ bond length, and worse, a change in $e_g$ electron occupancy.

**Step 2:** Work out the *d*-electron count and spin state for each metal in each option.

$Co^{3+}$ ($d^6$) with $NH_3$ is low spin, $t_{2g}^6 e_g^0$; $Co^{2+}$ ($d^7$) is high spin, $t_{2g}^5 e_g^2$. $Fe^{3+}$ ($d^5$) and $Fe^{2+}$ ($d^6$) with water are both high spin. $Ru^{3+}$ ($d^5$) and $Ru^{2+}$ ($d^6$) with $NH_3$ are both low spin, since second/third-row metals have a much larger field splitting. Mn(III) $d^4$ and Mn(II) $d^5$ with cyanide are both low spin.

**Step 3:** Score each pair on how many $e_g$ electrons change.

Cobalt pair: $e_g$ occupancy jumps from 0 to 2, stretching the bond by roughly 0.2 angstrom. Iron pair: both stay high spin with $e_g$ occupancy unchanged at 2; only $t_{2g}$ changes by one electron, a smaller effect. Ruthenium pair: both low spin, $e_g$ stays empty in both; only $t_{2g}$ changes by one, minimal bond-length change. Manganese cyanide pair: both low spin, $e_g$ stays empty in both, a small change.

**Step 4:** Rank the reorganization energies.

The cobalt pair has by far the biggest jump in $e_g$ occupancy among all four options, needing the most nuclear reorganization before electron transfer, giving the largest activation barrier. All other pairs keep $e_g$ occupancy fixed and change only $t_{2g}$ population, a much smaller perturbation.

**Final Answer:**

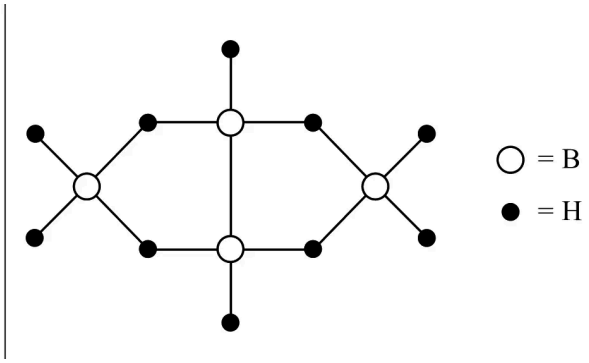
The cobalt ammine pair, option (A), has the largest reorganization energy and the slowest outer-sphere self-exchange rate.

$$\boxed{[Co(NH_3)_6]^{3+} \text{ and } [Co(NH_3)_6]^{2+}}$$

**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:** Count total valence electrons and pairs.
Each boron contributes 3 valence electrons and each hydrogen contributes 1. For $B_4H_{10}$: total electrons $= 4(3) + 10(1) = 12 + 10 = 22$, so there are 11 electron pairs to place.

**Step 2:** Subtract the electrons used for the default terminal $B-H$ bonds.
Every one of the 4 borons must have at least one normal terminal $B-H$ bond, using 4 pairs, leaving $11 - 4 = 7$ pairs for bridge bonds,

extra $B-B$ bonds, 3-centre bonds, and extra terminal hydrogens. This matches $s+t+y+x=(2p+q)/2=7$.

**Step 3:** Use the remaining hydrogen count to split $s$ and $x$.
Total H is 10, and 4 are already used as one-per-boron terminal hydrogens, leaving 6 extra. Each bridge hydrogen ($s$) and each second terminal hydrogen on a $BH_2$ group ($x$) accounts for one of these 6, so $s+x=6$. From the drawing, the 4 bridging positions give $s=4$, leaving $x=6-4=2$.

**Step 4:** Solve for $t$ and $y$ using the remaining pair count.
From Step 2, $s+t+y+x=7$. Substituting $s=4, x=2$: $t+y=1$. The drawn structure shows one direct $B-B$ bond linking the two bridgehead borons and no closed 3-centre triangle in the open, butterfly-shaped $B_4$ skeleton, so $y=1, t=0$.

**Step 5:** Assemble and cross-check.
$s,t,y,x=4,0,1,2$. Cross-check with $2s+3t+2y+x=3p$: $2(4)+0+2(1)+2=12=3(4)$, correct.

**Final Answer:**
The styx number is 4012, option (A).

$$\boxed{4012}$$

**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:** List every phase separately, don't lump solids together.
A common mistake is assuming all solids form one phase. That's wrong unless they form a single homogeneous solid solution. Here $Pb_3O_4(s)$ and $PbO(s)$ are two different compounds with distinct crystal structures, so they're two separate solid phases. The gas, $O_2(g)$, is always one phase. Total: $P = 2\,(\text{solids}) + 1\,(\text{gas}) = 3$.

**Step 2:** Count species and subtract for the reaction constraint.
Species present: $Pb_3O_4$, $PbO$, $O_2$, so 3 species, tied together by the single equilibrium $2Pb_3O_4 \rightleftharpoons 6PbO + O_2$. The general rule is:

$$C = (\text{species}) - (\text{independent reaction equilibria}) - (\text{extra restrictions})$$

There is 1 reaction and no further restriction, so $C = 3 - 1 - 0 = 2$.

**Step 3:** Plug into the phase rule and solve for $F$.
$F = C - P + 2 = 2 - 3 + 2 = 1$.

**Step 4:** Interpret the answer physically as a check.
$F = 1$ means this is univariant: exactly one intensive variable, say temperature, can be chosen freely, and everything else, including the equilibrium $O_2$ partial pressure, is then fixed. This matches the known behavior of solid-solid-gas decomposition equilibria of this type.

**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 down the normalized ground-state wavefunction.
The ground-state wavefunction of the 1D harmonic oscillator is a Gaussian:

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \qquad \alpha = \frac{2\pi m\nu}{h}$$

where $m$ is the oscillator mass.

**Step 2:** Compute the average potential energy directly.
The potential is $V(x) = \frac{1}{2}m\omega^2 x^2$ with $\omega = 2\pi\nu$. Using $\langle x^2\rangle = \frac{\hbar}{2m\omega}$ for this normalized $\psi_0$:

$$\langle V\rangle = \frac{1}{2}m\omega^2 \cdot \frac{\hbar}{2m\omega} = \frac{\hbar\omega}{4} = \frac{h\nu}{4}$$

since $\hbar\omega = h\nu$.

**Step 3:** Get the average kinetic energy from the total minus potential.
The ground-state total energy is $E_0 = \frac{1}{2}h\nu$ regardless of how it splits. Since $\langle T\rangle + \langle V\rangle = E_0$:

$$\langle T\rangle = E_0 - \langle V\rangle = \frac{h\nu}{2} - \frac{h\nu}{4} = \frac{h\nu}{4}$$

This matches a direct momentum-space computation, $\langle p^2\rangle/2m$ for the same Gaussian also gives $\hbar\omega/4$, confirming the two averages are equal by explicit integration.

**Step 4:** Match to the options.
Both $\langle T\rangle$ and $\langle V\rangle$ equal $h\nu/4$, so the two averages are equal and each is a quarter of $h\nu$, not half.

**Final Answer:**

Option (C): $h\nu/4$ and $h\nu/4$, respectively.

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

**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:**

This question uses the Smoluchowski model for a diffusion-controlled bimolecular reaction, but it is easier to solve by first writing

everything as a ratio to the radius of Y, since only the ratio of the two radii is given.

The diffusion-limited rate constant for two spherical, neutral reactants is $k = 4\pi(D_X + D_Y)(r_X + r_Y)$, and each diffusion coefficient obeys the Stokes-Einstein law $D = kT/(6\pi\eta r)$. Let $r_Y = r$, so the diameter condition "diameter of X is five times that of Y" gives $r_X = 5r$.

Write both diffusion coefficients in terms of $r$:

$$D_X = \frac{kT}{6\pi\eta(5r)} = \frac{kT}{30\pi\eta r}, \qquad D_Y = \frac{kT}{6\pi\eta r}$$

Add them by putting both over a denominator of $30\pi\eta r$:

$$D_X + D_Y = \frac{kT}{30\pi\eta r} + \frac{5kT}{30\pi\eta r} = \frac{6kT}{30\pi\eta r} = \frac{kT}{5\pi\eta r}$$

The sum of radii is $r_X + r_Y = 5r + r = 6r$. Multiply the two pieces into the Smoluchowski formula:

$$k = 4\pi \times \frac{kT}{5\pi\eta r} \times 6r = \frac{4 \times 6}{5} \cdot \frac{kT}{\eta} = \frac{24kT}{5\eta}$$

Notice that both the $\pi$ and the $r$ cancel exactly, which is exactly why the problem only needed to tell us the RATIO of the diameters (5:1) rather than an absolute size, a useful check that the algebra is on the right track.

So the rate constant is $k = \frac{24kT}{5\eta}$, which is option (C). The equal-size textbook result $8kT/3\eta$ (option A) would only apply if $r_X = r_Y$, which is not the case here, and dropping $D_X$ entirely (as in option B, $4kT/\eta$) under-counts the diffusive flux since both molecules move relative to each other.

**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:**

A quicker route to the same ranking looks at WHICH ion is out of balance at each junction and how badly, without writing the full Henderson formula from scratch each time.

All three cells share the same two electrodes, so differences in $E_{cell}$ come only from the liquid junction potential $E_j$ set up where the two solutions meet. A junction potential arises whenever a cation and an anion diffuse across the boundary at different rates, leaving a small charge imbalance.

1. **Junction II (0.1 M HCl against 0.01 M HCl):** the electrolyte is the same on both sides but ten times more concentrated on the

Electrode-1 side, so $H^+$ and $Cl^-$ both diffuse from the concentrated to the dilute side. $H^+$ (limiting conductance about 350 $S\,cm^2\,mol^{-1}$) is far faster than $Cl^-$ (about 76), so $H^+$ races ahead, the dilute side becomes momentarily positive, and this gives the largest junction potential of the three, about +38 mV.

2. **Junction I (0.1 M KCl against 0.1 M NaCl, same concentration):** here $Cl^-$ is common to both sides so it does not contribute a net gradient; the only mismatch is between $K^+$ (about 73.5) and $Na^+$ (about 50.1), which are much closer to each other than $H^+$ and $Cl^-$ are. This gives a small positive junction potential, about +4.4 mV, which is why KCl and NaCl are considered a comparatively "well matched" pair for this kind of boundary.
3. **Junction III (0.01 M KCl against 0.01 M HCl, same concentration):** again $Cl^-$ is common, so the mismatch is between $K^+$ (about 73.5) and $H^+$ (about 350), which is an even bigger mismatch than in junction I. Working through the same Henderson-type expression gives about −27 mV, and the sign comes out negative because the very mobile $H^+$ now sits on the Electrode-2 side, which pushes the potential the opposite way to junction I.

Putting the three signed numbers side by side, +38.0 mV (II), +4.4 mV (I), and −27 mV (III), the order from highest to lowest is II, then I, then III.

Let's summarize:

- Same electrolyte, different concentration, with $H^+$ involved (junction II) gives by far the biggest junction potential.
- Same concentration, common anion, different cations (junctions I and III) give smaller potentials, sized by how different the two

cation mobilities are, and the sign depends on which side the faster ion sits.

So the correct order is $E_{cell}(\text{II}) > E_{cell}(\text{I}) > E_{cell}(\text{III})$, 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.

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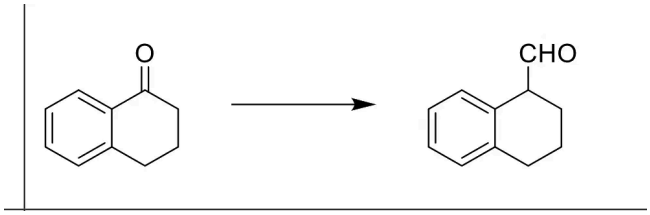
**48.** The set(s) of reagents that will effect the following conversion is(are)




(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:**

Instead of working through each mechanism in full, it helps to first count atoms: the product has exactly one more carbon than the ketone starting material, and that extra carbon carries the new –CHO group while the original carbonyl oxygen is gone. Any correct reagent set has to (1) add one carbon to the carbonyl carbon and (2) end up delivering

that carbon as an aldehyde, with the original ring carbon left as a plain CH.

1. **(A) $Ph_3P{=}CHOMe$, then $H_3O^+$:** this ylide is a one-carbon Wittig reagent carrying a masked aldehyde (as a methyl enol ether). Olefination puts a =CHOMe group directly on the old carbonyl carbon, and aqueous acid simply unmasks that enol ether to the free aldehyde. Carbon count and functional group both match the product, so this route works.
2. **(B) $TsNHNH_2$, then 2 eq $^n$BuLi/DMF:** this is the Shapiro sequence, which turns the carbonyl carbon into an alkene carbon (vinyllithium), then formylates it. The product keeps the new ring double bond, so it is more unsaturated than the target and is not the right structure.
3. **(C) 1,3-dithiane/$^n$BuLi, then $HgSO_4$/dil. $H_2SO_4$:** lithiodithiane simply adds to the ketone as a nucleophile, giving an alcohol with the dithiane hanging off the same carbon; hydrolyzing the dithiane later just converts that group into a new carbonyl, giving a hydroxy-ketone rather than the target aldehyde with a plain CH at the ring position.
4. **(D) $Me_3SI$/NaH, then $BF_3 \cdot OEt_2$:** the sulfoxonium ylide methylenates the carbonyl to a spiro-epoxide (again adding exactly one carbon), and $BF_3$ then triggers a Meinwald rearrangement, a Lewis-acid-promoted 1,2-hydride shift that converts the epoxide straight into the homologated aldehyde. This also matches the target exactly.

Only (A) and (D) add the correct one carbon AND land on an aldehyde with the ring carbon as a plain CH; (B) leaves an extra double bond and (C) leaves an extra hydroxyl, so both are structurally wrong.

So the reagent sets that work are (A) and (D).

**Quick Tip:** Look for a one-carbon Wittig-type homologation (Ph3P=CHOMe/H3O+) or a sulfonium-ylide epoxidation followed by a BF3-catalyzed Meinwald (1,2-hydride shift) rearrangement.

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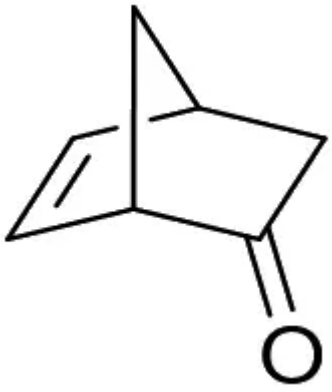
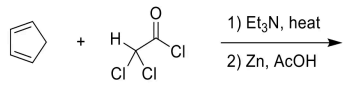
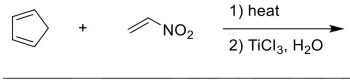
**49.** The reaction(s) that produce(s) the following compound is(are)



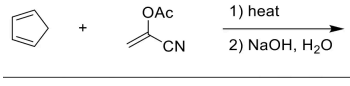
(A)



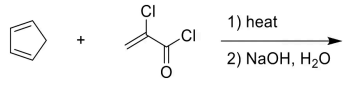

(B)



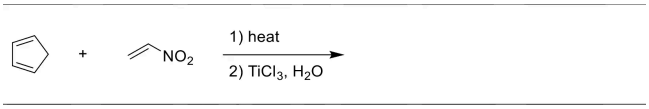

(C)



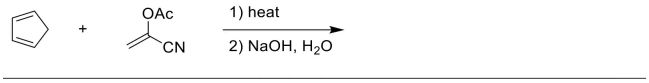

(D)



**Correct Answer:** (B)




; (C)




**SOLUTION:**

The fastest way to solve this is to recognize that plain ketenes ( $R_2C{=}C{=}O$) are notoriously bad Diels-Alder partners: they almost always react with dienes through a [2+2] pathway instead of the wanted [4+2], so organic chemists use "ketone equivalent" dienophiles that behave like a normal alkene in the Diels-Alder step and only reveal the carbonyl afterwards, on workup.

The target is the norbornenone skeleton, bicyclo[2.2.1]hept-5-en-2-one, i.e. cyclopentadiene's Diels-Alder adduct with a dienophile that eventually becomes a plain C=O group.

1. **(A):** dichloroacetyl chloride plus base generates dichloroketene in situ. Real ketenes give [2+2] adducts (four-membered rings), not the bridged [2.2.1] skeleton, so even after removing the chlorines with Zn/AcOH the ring size is wrong. Rejected.
2. **(B):** nitroethylene is a normal, very reactive dienophile (the $NO_2$ group activates it), so the Diels-Alder step is clean [4+2]. $TiCl_3/H_2O$ is a standard reagent for turning a secondary nitro group into a ketone (a Nef-type reduction). This delivers the target directly. Accepted.
3. **(C):** 2-acetoxyacrylonitrile is the textbook masked-ketene dienophile, an acetylated cyanohydrin of a ketene. It undergoes normal [4+2] cycloaddition, and base hydrolysis afterwards strips

off the acetate and then the cyanide (reverse cyanohydrin formation), unmasking the same carbonyl. Accepted.

4. **(D):** the dienophile here is a chloro-substituted acryloyl chloride; the Diels-Alder step works, but base hydrolysis converts the acid chloride into a carboxylic acid/carboxylate group, not a ring ketone, so the final functional group is wrong even though the ring skeleton is right. Rejected.

Let's summarize:

- A dienophile has to look like a normal alkene during the cycloaddition and only reveal the carbonyl on workup, since ketenes themselves give [2+2], not [4+2].
- Nitroethylene (with $TiCl_3/H_2O$) and 2-acetoxyacrylonitrile (with $NaOH/H_2O$) are both classic ketone-equivalent dienophiles; an acid chloride dienophile gives an acid, not a ketone.

So the reactions that give the target compound are (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.

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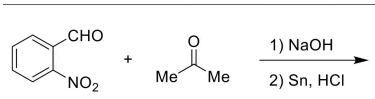
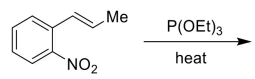
**50.** The reaction(s) that produce(s) 2-methylindole as the major product is(are)

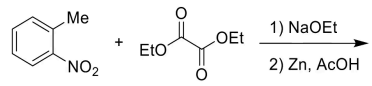
(A)



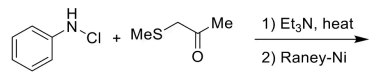

(B)



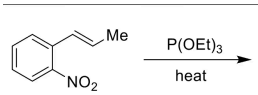

(C)



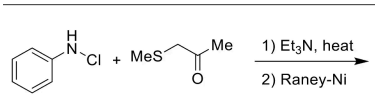

(D)




**Correct Answer:** (B)




; (D)




**SOLUTION:**

A good way through this question is to first sort the four routes by WHICH ring size they build, since that alone eliminates one option before even worrying about the methyl group position.

1. **(A):** aldol condensation of 2-nitrobenzaldehyde with acetone, then reduction of the nitro group, is the standard Friedlander route to quinaldine (2-methylquinoline). Counting the chain atoms between the new amino nitrogen and the ketone carbon it condenses with shows a six-membered ring forms, not the five-membered pyrrole ring of an indole. Wrong ring size, so this is rejected outright.
2. **(B):** an ortho-nitrostyrene bearing a $\beta$-methyl group, heated with $P(OEt)_3$, is the classic Cadogan-Sundberg reductive cyclization: the phosphite deoxygenates the nitro group to a nitrene, which closes directly onto the alkene to build the five-membered ring in one step, with the methyl substituent landing at C2. This is a textbook one-pot synthesis of 2-methylindole.
3. **(C):** 2-nitrotoluene condensed with diethyl oxalate, then reduced, is the original 1897 Reissert indole synthesis, but it installs an ester group ($-COOEt$) at C2, not a methyl group, giving ethyl indole-2-carboxylate. Right ring, wrong substituent, so rejected.
4. **(D):** N-chloroaniline plus a $\beta$-keto sulfide is the Gassman indole synthesis: a $[2, 3]$-sigmatropic rearrangement of the intermediate sulfonium species builds the pyrrole ring with the ketone's methyl group at C2 and the sulfide's methylthio group temporarily at C3. Raney nickel then strips out that C3 sulfur, leaving 2-methylindole as the final product.

Let's summarize:

- Option (A) actually builds a six-membered ring (a quinoline), so it can never give an indole regardless of substituents.
- Option (C) builds the right five-membered ring but puts an ester, not a methyl group, at C2.

- Options (B) and (D) both build the indole ring with a methyl group correctly placed at C2, one directly via nitrene cyclization, the other via a sigmatropic rearrangement followed by desulfurization.

So the reactions that give 2-methylindole are (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:**

An easier way to see this is to mark a cut symbol directly after every aromatic residue in the sequence, then just read off the pieces between the cuts.

The sequence is **Val-Phe-Leu-Met-Tyr-Pro-Gly-Trp-Cys**. The three aromatic (aryl-sidechain) amino acids are phenylalanine, tyrosine and tryptophan, so a cut goes right after each one:

Val-Phe | Leu-Met-Tyr | Pro-Gly-Trp | Cys

Reading the four pieces left to right: **Val-Phe** (a dipeptide), **Leu-Met-Tyr** (a tripeptide), **Pro-Gly-Trp** (a tripeptide) and **Cys** alone (a single residue).

Now check each answer option against this list directly:

1. **Leu-Met-Tyr:** matches the second piece exactly. Correct.
2. **Phe-Leu-Met:** this string straddles the first cut point (it takes Phe from the first piece and Leu-Met from the second), so it can never appear as a single fragment. Incorrect.
3. **Pro-Gly-Trp:** matches the third piece exactly. Correct.
4. **Tyr-Pro-Gly:** this straddles the second cut point (Tyr from the second piece, Pro-Gly from the third), so it is likewise never a real fragment. Incorrect.

So the tripeptides actually formed are Leu-Met-Tyr and Pro-Gly-Trp.

**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:**

The quickest route here is to reduce every complex to a single number, its $d$-electron count, and remember a short rule: only $d^2$, $d^3$, $d^7$ and $d^8$ configurations (with an $F$ ground term) give three spin-allowed $d$-$d$ bands, in EITHER octahedral or tetrahedral geometry, since the same $F$-term correlation diagram is used for all four. Configurations $d^1$, high-spin $d^4$, high-spin $d^6$ and $d^9$ (a $D$ term) give just one band, and high-spin $d^5$ gives none at all, because its $^6S$ ground state has no other sextet state to go to.

Work out the $d$-count for each metal ion in turn:

- $V^{3+} = d^2$, $Ni^{2+} = d^8$, $Cr^{3+} = d^3$, $Ti^{3+} = d^1$, $Mn^{2+} = d^5$ (HS), $Fe^{3+} = d^5$ (HS with $F^-$), $Fe^{2+} = d^6$ (HS, tetrahedral).

Now sort the four option pairs by this rule:

1. **(A) $[V(H_2O)_6]^{3+}$ ($d^2$) and $[Ni(H_2O)_6]^{2+}$ ($d^8$):** both in the three-band group. Every complex in this pair qualifies.
2. **(B) $[Cr(H_2O)_6]^{3+}$ ($d^3$, octahedral) and $[NiCl_4]^{2-}$ ($d^8$, tetrahedral):** both again fall in the three-band group; the tetrahedral geometry does not change which group $d^8$ belongs to, it only changes the exact term labels and band positions, not the count of three.
3. **(C) $[Ti(H_2O)_6]^{3+}$ ($d^1$) and $[Mn(H_2O)_6]^{2+}$ ($d^5$, HS):** $d^1$ gives one band and high-spin $d^5$ gives zero bands (its ground term $^6A_{1g}$ has no other sextet term to jump to). Neither is a three-band ion.
4. **(D) $[FeF_6]^{3-}$ ($d^5$, HS) and $[FeCl_4]^{2-}$ ($d^6$, HS, tetrahedral):** the first gives zero bands for the same reason as $Mn^{2+}$ above, and

the second is a *D*-term ion, giving only one band.

Let's summarize:

- The "three spin-allowed bands" club is exactly $d^2, d^3, d^7, d^8$, regardless of octahedral or tetrahedral geometry.
- High-spin $d^5$ is the special case with zero spin-allowed bands, which is why $Mn^{2+}$ and high-spin $Fe^{3+}$ salts look almost colorless.

So the pairs where BOTH complexes show three spin-allowed transitions are (A) and (B).

**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:**

This question checks four separate facts about oxide structures: the site count in a spinel lattice, the structure type of $BaTiO_3$, the cation distribution in magnetite, and the nature of $\gamma$-alumina.

1. **Spinel has 8 tetrahedral sites and 4 octahedral sites per formula unit**: Correct. A spinel unit cell holds 32 oxide ions in a cubic close packed lattice, which always generates twice as many tetrahedral holes as octahedral holes, giving 64 tetrahedral and 32 octahedral holes in total. Divided across the 8 $AB_2O_4$ formula units in that cell, that works out to 8 tetrahedral and 4 octahedral sites per formula unit, matching the statement.
2. $BaTiO_3$ **has a perovskite structure**: Correct. This is one of the defining perovskite oxides, with the large $Ba^{2+}$ ion at the cube corners, the small $Ti^{4+}$ ion at the body centre in an octahedral oxide hole, and the oxide ions at the face centres.
3. **In** $Fe_3O_4$**,** $Fe^{2+}$ **occupies both tetrahedral and octahedral sites**: Wrong. Magnetite is an inverse spinel, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$, so the tetrahedral holes are filled only by $Fe^{3+}$, while the octahedral holes carry the remaining $Fe^{3+}$ together with all of the $Fe^{2+}$. $Fe^{2+}$ never sits in a tetrahedral hole here.
4. $\gamma$-$Al_2O_3$ **is a defect spinel**: Correct. Its oxide ions pack the same way as in a spinel, but since the $Al^{3+}$ to $O^{2-}$ ratio of $Al_2O_3$ does not match a normal $AB_2O_4$ spinel, some cation sites stay empty. A vacancy-containing spinel lattice like this is what is meant by a defect spinel.

So the true statements describe the spinel site count, the perovskite structure of $BaTiO_3$, and the defect spinel nature of $\gamma$-$Al_2O_3$; the statement about $Fe^{2+}$ in magnetite is false.

Let's summarize:

- A spinel cell has 8 tetrahedral and 4 octahedral sites per formula unit, from its close packed oxide ions.
- $BaTiO_3$ is a classic $ABO_3$ perovskite.
- Magnetite is an inverse spinel where $Fe^{2+}$ sits only on octahedral sites.
- $\gamma$-$Al_2O_3$ is a cation-deficient (defect) spinel.

The correct options are (A), (B), and (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:** Set up the 4f count using $n = Z - 57$ for $Ln^{3+}$.
$Nd^{3+}(Z = 60) \rightarrow 4f^3$, $Pm^{3+}(Z = 61) \rightarrow 4f^4$, $Ho^{3+}(Z = 67) \rightarrow 4f^{10}$, $Er^{3+}(Z = 68) \rightarrow 4f^{11}$.

**Step 2:** Use electron-hole pairing to shortcut $S$ and $L$.
The 4f shell is half full at $4f^7$. A configuration $4f^{7+k}$ has the same $S$ and $L$ as $4f^{7-k}$, because both have the same number of unpaired electrons filling the $m_l$ slots from the outside in.
$4f^{10} = 4f^{7+3}$ pairs with $4f^4 = 4f^{7-3}$, so $Ho^{3+}$ shares $S, L$ with $Pm^{3+}$.
$4f^{11} = 4f^{7+4}$ pairs with $4f^3 = 4f^{7-4}$, so $Er^{3+}$ shares $S, L$ with $Nd^{3+}$.
This already flags the two candidate matching pairs: $\{Pm^{3+}, Ho^{3+}\}$ and $\{Nd^{3+}, Er^{3+}\}$.

**Step 3:** Confirm $S$ and $L$ for the base configurations.
$4f^3$: unpaired electrons in $m_l = 3, 2, 1$ give $S = 3/2$, $M_L = 6$, so $L = 6$, term ${}^4I$.
$4f^4$: unpaired electrons in $m_l = 3, 2, 1, 0$ give $S = 2$, $M_L = 6$, so $L = 6$, term ${}^5I$.

**Step 4:** Apply Hund's third rule for $J$, since the pairs only match in $S, L$, not $J$.
$Nd^{3+}$ ($4f^3$, less than half filled): $J = L - S = 6 - 1.5 = 9/2$, term ${}^4I_{9/2}$.
$Er^{3+}$ ($4f^{11}$, more than half filled): $J = L + S = 6 + 1.5 = 15/2$, term ${}^4I_{15/2}$. These differ in $J$, confirming pair (B).
$Pm^{3+}$ ($4f^4$, less than half filled): $J = L - S = 6 - 2 = 4$, term ${}^5I_4$.
$Ho^{3+}$ ($4f^{10}$, more than half filled): $J = L + S = 6 + 2 = 8$, term ${}^5I_8$.
These differ in $J$, confirming pair (A).

**Step 5:** Rule out the cross pairs.
$Pm^{3+}$ and $Nd^{3+}$ come from different base configurations ($4f^4$ vs $4f^3$), so their $2S + 1$ (5 vs 4) do not match; the same applies to $Ho^{3+}$ and $Er^{3+}$.

**Final Answer:**

The hole-pairing shortcut pins down the two matching pairs directly: $Pm^{3+}/Ho^{3+}$ and $Nd^{3+}/Er^{3+}$.

**(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:**

Enterobactin is the classic catecholate-type siderophore made by bacteria like **E. coli** to capture iron(III) from the surroundings. Each statement can be checked against its known structure.

1. **It has three catechol moieties**: True. Enterobactin is built from three units of 2,3-dihydroxybenzoic acid, so it carries three catechol (1,2-dihydroxybenzene) rings.
2. **It has a serine-trilactone backbone**: True. The three catechol-bearing acid units are each attached to one serine, and

the three serines link through ester bonds into a 9-membered macrocyclic triester, the trilactone ring that forms the core scaffold of the molecule.

3. **It binds with $Fe^{3+}$ ion to form $[Fe(ent)]^{3-}$ ion**: True. The three catechol groups fully deprotonate and wrap around one $Fe^{3+}$ centre using all six phenolate oxygens, giving an octahedral hexadentate complex. Three catecholate(2−) ligands carry a total charge of $-6$, so with $Fe^{3+}$ the complex charge works out to $-6 + 3 = -3$, matching $[Fe(ent)]^{3-}$.
4. **It has three hydroxamic acid groups**: False. Hydroxamate donor groups belong to a separate family of siderophores, such as ferrioxamine; enterobactin uses catechol oxygens for iron binding, not hydroxamic acid groups.

So enterobactin is correctly described by its three catechol groups, its serine-trilactone ring, and the $[Fe(ent)]^{3-}$ complex it forms; it does not contain hydroxamic acid groups.

Let's summarize:

- Three 2,3-dihydroxybenzoyl (catechol) units are attached to a cyclic tri-serine lactone core.
- The six catecholate oxygens give hexadentate, octahedral binding to $Fe^{3+}$, forming $[Fe(ent)]^{3-}$.
- Enterobactin has no hydroxamic acid groups; that feature belongs to a different siderophore class.

The correct options are (A), (B), and (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.

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**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:** Write the general Langmuir-Hinshelwood rate law.

$$\text{rate} = k\theta, \qquad \theta = \frac{Kp}{1 + Kp}$$

This equation already shows the surface follows a Langmuir isotherm, not the empirical Freundlich isotherm proposed in option (A), so (A) is false right away.

**Step 2:** Take the two limiting cases of pressure.
High pressure ($Kp \gg 1$): $1 + Kp \approx Kp$, so $\theta \approx 1$ and rate $\approx k$, independent of $p$. A rate independent of concentration is zero order, so option (B) holds.

Low pressure ($Kp \ll 1$): $1 + Kp \approx 1$, so $\theta \approx Kp$ and rate $\approx kKp$, directly proportional to $p$. A rate directly proportional to concentration is first order, so option (C) holds.

**Step 3:** Read off option (D) directly.
The rate law rate $= k\theta$ already says the rate is proportional to the surface coverage $\theta$, which is exactly option (D); it is simply the defining relationship of the mechanism, so it is true.

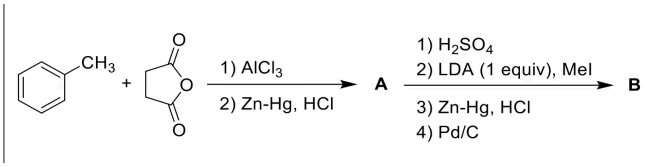
**Step 4:** Physical picture behind the two limits.
At high pressure nearly every active site is filled, so adding more gas cannot speed the reaction further, giving the pressure-independent regime. At low pressure most sites are empty, so the number of adsorbed molecules grows directly with the gas supplied, giving the first order regime.

**Final Answer:**
Since the mechanism runs on a Langmuir isotherm, with zero order kinetics at high pressure, first order kinetics at low pressure, and the rate always tracking the surface coverage, the true statements are (B), (C), and (D).

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

**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:**

This problem is really two structure-elimination puzzles chained together, followed by a symmetry count. Work out **A**, then push it through the second sequence to get **B**, then count carbons in each.

1. **Toluene + succinic anhydride,** $AlCl_3$: This is a Friedel-Crafts acylation. The anhydride opens at the ring, attaching an aroyl group para to the methyl (steric preference) and leaving a free $-CH_2CH_2COOH$ tail, giving the keto-acid 4-oxo-4-(p-tolyl)butanoic acid.
2. **Zn-Hg, HCl (Clemmensen)**: Reduces only the aryl ketone, not the carboxylic acid, giving **A** = 4-(4-methylphenyl)butanoic acid, a para-disubstituted ring carrying a $-CH_2CH_2CH_2COOH$ chain.
3. $H_2SO_4$: Protonates the COOH of **A** and closes a new six-membered ring onto the arene by intramolecular Friedel-Crafts acylation, giving a methyltetralone.
4. **LDA (1 equiv), MeI**: The only alpha-hydrogen available for kinetic enolate formation is at C2 next to the carbonyl;

methylation there installs a second methyl group on the saturated ring.

5. **Zn-Hg, HCl**: A second Clemmensen reduction removes the tetralone carbonyl, giving a dimethyltetralin (saturated ring fused to the original aromatic ring).
6. **Pd/C**: Dehydrogenates the saturated ring to full aromaticity, giving the dimethylnaphthalene B, with the two methyls on ring positions related by the molecule's symmetry.

Now count carbons. In A, the para-substituted ring gives 4 distinct ring signals (by the mirror symmetry through the two substituted positions), plus 1 for the ring methyl and 4 for the $-CH_2CH_2CH_2COOH$ chain (three inequivalent $CH_2$ groups plus the carboxyl carbon), for $4 + 1 + 4 = 9$ signals total.

In B, the symmetric dimethylnaphthalene skeleton folds its ten ring carbons and two methyl carbons down through the molecule's own symmetry; working through every distinct environment in the fused ring system gives 7 signals for B.

Let's summarize:

- A = 4-(4-methylphenyl)butanoic acid, 9 distinct $^{13}C$ signals.
- B = a symmetric dimethylnaphthalene formed by cyclization, alpha-methylation, reduction, and aromatization, 7 distinct $^{13}C$ signals.
- Total: $9 + 7 = 16$.

The total number of carbon signals observed for A and B is 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.

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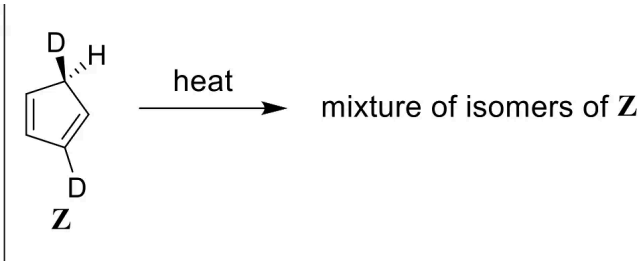
**58.** On heating, the compound **Z** undergoes a series of 1,5-H/D shifts to give a mixture of its isomers.




The total number of isomers present in the mixture (including **Z**) is (in integer).

**Correct Answer:** 9

**SOLUTION:**

This question is about the classic degenerate rearrangement of cyclopentadiene, where the single $sp^3$ carbon of the ring walks all the way around through a chain of thermal **[1, 5]**-sigmatropic H (or D) shifts.

1. **Starting point**: **Z** has an $sp^3$ ring carbon carrying one H and one D on two distinct faces (shown by the wedge and dash bonds), plus a second, separate D sitting on one of the four vinylic ring carbons.
2. **Mechanism**: In a **[1, 5]**-shift, the migrating atom on the $sp^3$ carbon moves suprafacially across the adjacent conjugated diene to the far ring carbon, which becomes the new $sp^3$ centre; the

carbon that is left behind becomes part of the new diene, keeping whichever of H or D did not migrate.

3. **Effect of the ring closure**: because the $sp^3$ carbon is bonded to both ends of the diene system, the walk can proceed toward either ring neighbour, with the suprafacial requirement locking a specific face (and hence a specific isotope) to each direction of travel.
4. **Repeating the walk**: sending the $sp^3$ position all the way around the five ring carbons, and tracking whenever it meets and interacts with the second, originally fixed ring D, generates a set of distinct isotopically labelled cyclopentadienes.

Collecting every position/label combination this walk reaches, and merging any pair of structures that are secretly identical by the unlabelled ring's own symmetry, leaves 9 distinguishable isotopomers in the final mixture, with **Z** counted as one of them.

Let's summarize:

- Thermal **[1, 5]**-H/D shifts move the $sp^3$ carbon of a cyclopentadiene around the ring one position at a time.
- With two isotopic labels present (the H/D pair on the mobile carbon and the fixed ring D), the walk generates several distinguishable structures rather than just one.
- The full accessible set, including the starting compound **Z**, has 9 members.

The total number of isomers present in the mixture, including **Z**, is 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.

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**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:**

Each of these four dimers is a textbook case of a metal-metal multiple bond, and the trick is counting the relevant electrons correctly for each bonding scheme (crystal-field d-count for the halide dimers, 18-electron count for the carbonyl/Cp dimer).

1. $[Re_2Cl_8]^{2-}$: Overall charge $-2$ with 8 chloride ($-1$ each) fixes Re at $+3$, a $d^4$ ion. Stacking two $d^4$ centres face to face gives 8 electrons, which is exactly enough to fill one $\sigma$, two $\pi$, and one $\delta$ bonding orbital, nothing left over for antibonding orbitals. That is a full quadruple bond, bond order 4, the historic Re-Re bond that first proved metal-metal quadruple bonding exists.
2. $[Os_2Cl_8]^{2-}$: Same charge bookkeeping puts Os at $+3$, but Os sits one group to the right of Re in the same row, so $Os^{3+}$ is $d^5$, one electron richer than $Re^{3+}$. Two $d^5$ centres supply 10 electrons: 8 fill the bonding set (same as above) and the extra 2 must go into the antibonding $\delta^*$ level. Losing one bonding pair's worth of order, bond order $= 4 - 1 = 3$.
3. $W_2(NMe_2)_6$: This is a staggered, ethane-shaped $M_2L_6$ molecule with six anionic amide ligands and a neutral overall complex, so each W is $+3$. Neutral tungsten contributes 6 valence electrons, so $W^{3+}$ is $d^3$. Two $d^3$ centres give 6 electrons, filling $\sigma^2\pi^4$ with no $\delta$ overlap available in the staggered geometry, a clean W ≡ W triple bond, order 3.

4. $[Mo(C_5H_5)(CO)_2]_2$: Use the 18-electron rule on one $CpMo(CO)_2$ unit. Neutral-atom counting gives Mo = 6 electrons, $\eta^5$-Cp (radical) = 5 electrons, two CO = 4 electrons, total 15. Each metal is 3 electrons short of 18, and the only source is the metal-metal bond, so the bond must be a triple bond (order 3) to supply those 3 electrons to each Mo.

Adding the four bond orders: $3 + 4 + 3 + 3 = 13$.

Let's summarize:

- Halide-bridged $d^n$-$d^n$ dimers (Re, Os) get their bond order from how many of the four bonding MOs ($\sigma, \pi, \pi, \delta$) fill before electrons spill into $\delta^*$.
- Ligand-supported organometallic dimers (W-amide, Mo-Cp-carbonyl) get their bond order from whatever multiplicity is needed to complete the 18-electron count at each metal.

So the sum of all four 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, $^{238}_{92}U \rightarrow {}^{206}_{82}Pb$, is (in integer).

**Correct Answer:** 14

**SOLUTION:**

A nuclear decay chain must conserve both mass number (top number) and atomic number (bottom number) at every step, so instead of writing individual equations, tabulate the total change needed and split it between the two particle types.

1. **Total mass number drop**: $238 - 206 = 32$. Only $\alpha$-emission changes mass number, and each $\alpha$ carries away 4 mass units. So the number of $\alpha$-particles is $32/4 = 8$.
2. **Total atomic number drop**: $92 - 82 = 10$. But $\alpha$-emission alone would drop $Z$ by $2 \times 8 = 16$, which overshoots the required drop of 10 by $16 - 10 = 6$.
3. **Beta correction**: every $\beta^-$ emitted pushes $Z$ back up by 1 (a neutron becomes a proton plus an ejected electron), so exactly 6 $\beta$-particles are needed to cancel that overshoot and land exactly on $Z = 82$.

So the decay uses 8 $\alpha$-particles and 6 $\beta$-particles.

Let's summarize:

- Mass number balance alone fixes the alpha count: $(238 - 206)/4 = 8$.
- Atomic number balance then fixes the beta count once alpha's contribution is subtracted: $2(8) - (92 - 82) = 6$.

Adding them, $8 + 6 = 14$, so the total number of 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:**

Instead of converting both points fully into Cartesian coordinates, this method finds the angle between the two position vectors directly using the spherical law of cosines, then applies the law of cosines for the two known radii.

1. **Angle between the vectors**: for two points at $(r_1, \theta_1, \Phi_1)$ and $(r_2, \theta_2, \Phi_2)$, the angle $\gamma$ between the vectors from the origin satisfies $\cos\gamma = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\Phi_1 - \Phi_2)$.
2. **Plug in the given angles**: $\theta_1 = \pi/2$, $\theta_2 = \pi/4$, $\Phi_1 = \pi/2$, $\Phi_2 = 3\pi/2$. Then $\cos\theta_1 = 0$, $\cos\theta_2 = \sin\theta_2 = 0.7071$, $\sin\theta_1 = 1$, and $\Phi_1 - \Phi_2 = -\pi$ so $\cos(\Phi_1 - \Phi_2) = -1$.
3. **Compute** $\cos\gamma$: $\cos\gamma = (0)(0.7071) + (1)(0.7071)(-1) = -0.7071$, which is $\cos 135°$, so the two position vectors are $135°$ apart.
4. **Law of cosines for the distance**: with $r_1 = r_2 = 1$ Å, $d^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma = 1 + 1 - 2(1)(1)(-0.7071) = 2 + 1.4142 = 3.4142$.

Taking the square root, $d = \sqrt{3.4142} = 1.8478$ Å, which agrees with a direct Cartesian conversion of both points.

Let's summarize:

- The spherical law of cosines gives the angle between two direction vectors straight from their $\theta$ and $\Phi$ values, no need to write out

$x, y, z$.

- Once the angle is known, the ordinary law of cosines on the triangle formed by the two radii and the connecting segment gives the distance.

So the interatomic distance, rounded to two decimal places, 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:**

A cleaner way to get the same number is through the thermal de Broglie wavelength $\Lambda$, since $q_{trans} = V/\Lambda^3$ is just a repackaged form of the same formula.

1. **Molecule mass**: $m(H_2) = 2(1.008)$ amu $= 2.016$ amu $= 2.016 \times 1.661 \times 10^{-27}$ kg $= 3.3486 \times 10^{-27}$ kg.
2. **Thermal wavelength formula**: $\Lambda = \dfrac{h}{\sqrt{2\pi mkT}}$. First get $2\pi mkT$ as before: $kT = 4.143 \times 10^{-21}$ J, so $2\pi mkT = 8.7168 \times 10^{-47}$ (SI units).
3. **Square root**: $\sqrt{8.7168 \times 10^{-47}} = 9.3364 \times 10^{-24}$.

4. **Wavelength**: $\Lambda = \dfrac{6.626 \times 10^{-34}}{9.3364 \times 10^{-24}} = 7.0966 \times 10^{-11}$ m.
5. **Cube it**: $\Lambda^3 = (7.0966 \times 10^{-11})^3 = 3.574 \times 10^{-31}$ m$^3$.
6. **Divide the volume**: $V = 1$ L $= 1 \times 10^{-3}$ m$^3$, so $q_{trans} = \dfrac{1 \times 10^{-3}}{3.574 \times 10^{-31}} = 2.798 \times 10^{27}$.

Let's summarize:

- $q_{trans} = V/\Lambda^3$ is the same physics as the $(2\pi mkT/h^2)^{3/2}V$ formula, just grouped through the de Broglie wavelength.
- Both routes give the same number because they use the identical mass, temperature, and volume inputs.

So $q_{trans} = 2.80 \times 10^{27}$, meaning $\boxed{y = 2.8}$.

**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:**

Since the pH meter is Nernstian, we do not need to find the full calibration constant $K$ at all. A change in pH just produces a

proportional drop in the measured potential, so the second reading can be found directly from the first one and the pH difference.

1. **Get the acetic acid pH first**: solve the acid dissociation quadratic $x^2 + K_a x - K_a C = 0$ with $K_a = 1.75 \times 10^{-5}$, $C = 4.0 \times 10^{-3}$ M (the simple $\sqrt{K_a C}$ shortcut is not accurate enough, since $x$ turns out to be about 6% of $C$). This gives $[H^+] = 2.560 \times 10^{-4}$ M, so $pH = -\log(2.560 \times 10^{-4}) = 3.592$.
2. **Use the Nernst response directly**: for a glass electrode combination cell, $E = K - 0.059\,pH$, so between any two readings $E_2 - E_1 = -0.059(pH_2 - pH_1)$. There is no need to solve for $K$ separately.
3. **Plug in the two states**: state 1 is the pH 4.01 buffer at $E_1 = 0.814$ V, state 2 is the acid solution at $pH_2 = 3.592$. The pH change is $pH_2 - pH_1 = 3.592 - 4.01 = -0.418$.
4. **Apply the shift**: $E_2 = 0.814 - 0.059(-0.418) = 0.814 + 0.02466 = 0.83866$ V.

Let's summarize:

- The calibration point only fixes the line's slope-intercept relationship; you can jump straight between any two points on it using $\Delta E = -0.059\,\Delta(pH)$.
- A lower pH (more acidic than the buffer) gives a higher potential here, since $E$ and pH move in opposite directions on this electrode.

So the measured potential, rounded to three decimal places, is $\boxed{0.839\text{ V}}$.

**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.

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**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:**

Instead of finding $V_m$ and the molecule count as two separate steps, this route folds the volume-to-area conversion into a single constant first, then applies it once to $V_m$.

1. **Get $V_m$ from the BET plot**: for the linear BET plot $\frac{z}{(1-z)V}$ against $z$, the sum of slope and intercept always equals $1/V_m$ (the $C$ term cancels), so $V_m = \frac{1}{\text{slope+intercept}} = \frac{1}{6\times10^{-4}+4\times10^{-6}} = \frac{1}{6.04\times10^{-4}} = 1655.63$ mm$^3$.
2. **Build one conversion factor**: each mm$^3$ of gas holds $2.7 \times 10^{16}$ molecules, and each molecule covers 0.16 nm$^2$ $= 1.6 \times 10^{-19}$ m$^2$. So one mm$^3$ of monolayer gas corresponds to a surface area of $2.7 \times 10^{16} \times 1.6 \times 10^{-19} = 4.32 \times 10^{-3}$ m$^2$.

3. **Apply the factor to $V_m$**: $A = V_m \times 4.32 \times 10^{-3}\ \text{m}^2/\text{mm}^3$ $= 1655.63 \times 4.32 \times 10^{-3} = 7.152\ \text{m}^2$.
4. **Report per gram**: the whole measurement used a 1.0 g adsorbent sample, so this area is already the specific surface area, $7.152\ \text{m}^2\ \text{g}^{-1}$.

Let's summarize:

- Slope plus intercept of the BET plot always gives $1/V_m$ directly, no need to solve for the BET constant $C$ separately.
- Wrapping the molecules-per-volume and area-per-molecule data into one combined conversion factor avoids carrying two large exponents through the last step.

So the BET surface area, rounded to one decimal place, 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-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:**

The vector model pictures $\mathbf{L}$ as a cone of fixed length precessing around the $z$-axis, with $L_z$ as its fixed projection. Getting the

minimum tilt angle just needs the two extreme lengths of that picture, the full vector length and its largest possible projection.

1. **Find $l$ from the given length**: $|\mathbf{L}| = \sqrt{l(l+1)}\hbar = \sqrt{12}\hbar$ means $l(l+1) = 12$. Since $l$ must be a non-negative integer, checking small values ($l = 2$ gives 6, $l = 3$ gives 12) shows $l = 3$.
2. **Longest possible projection**: $L_z = m_l\hbar$ can only take integer values from $-l$ to $l$, so the largest projection on the $z$-axis is at $m_l = l = 3$, giving $L_z = 3\hbar$.
3. **Picture the right triangle**: the vector $\mathbf{L}$ (length $\sqrt{12}\hbar$), its projection $L_z$ (length $3\hbar$), and the angle $\theta$ between them form a right triangle where $L_z$ is the adjacent side, so $\cos\theta = L_z/|\mathbf{L}|$. A longer projection means a smaller tilt angle, so the biggest $L_z$ (that is, $m_l = +l$) gives the smallest possible $\theta$.
4. **Evaluate**: $\cos\theta_{min} = \dfrac{3\hbar}{\sqrt{12}\hbar} = \dfrac{3}{2\sqrt{3}} = \dfrac{\sqrt{3}}{2}$. This is a standard trigonometric value: $\cos 30° = \sqrt{3}/2$.

Let's summarize:

- The quantum number $l$ comes straight from matching $\sqrt{l(l+1)}$ to the given coefficient of $\hbar$.
- The minimum tilt of $\mathbf{L}$ away from the $z$-axis always happens at the extreme value $m_l = +l$, never at $m_l = 0$.

So the minimum angle, rounded to one decimal place, is $\boxed{30.0°}$.

**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.