INTERNATIONAL CHEMISTRY OLYMPIAD

IChO 2025

Theory problems and solutions · Dubai, United Arab Emirates · 9 theory problems with complete solutions

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Problem 1: Isocaryophyllene, clovene, and humulene

6% of the total

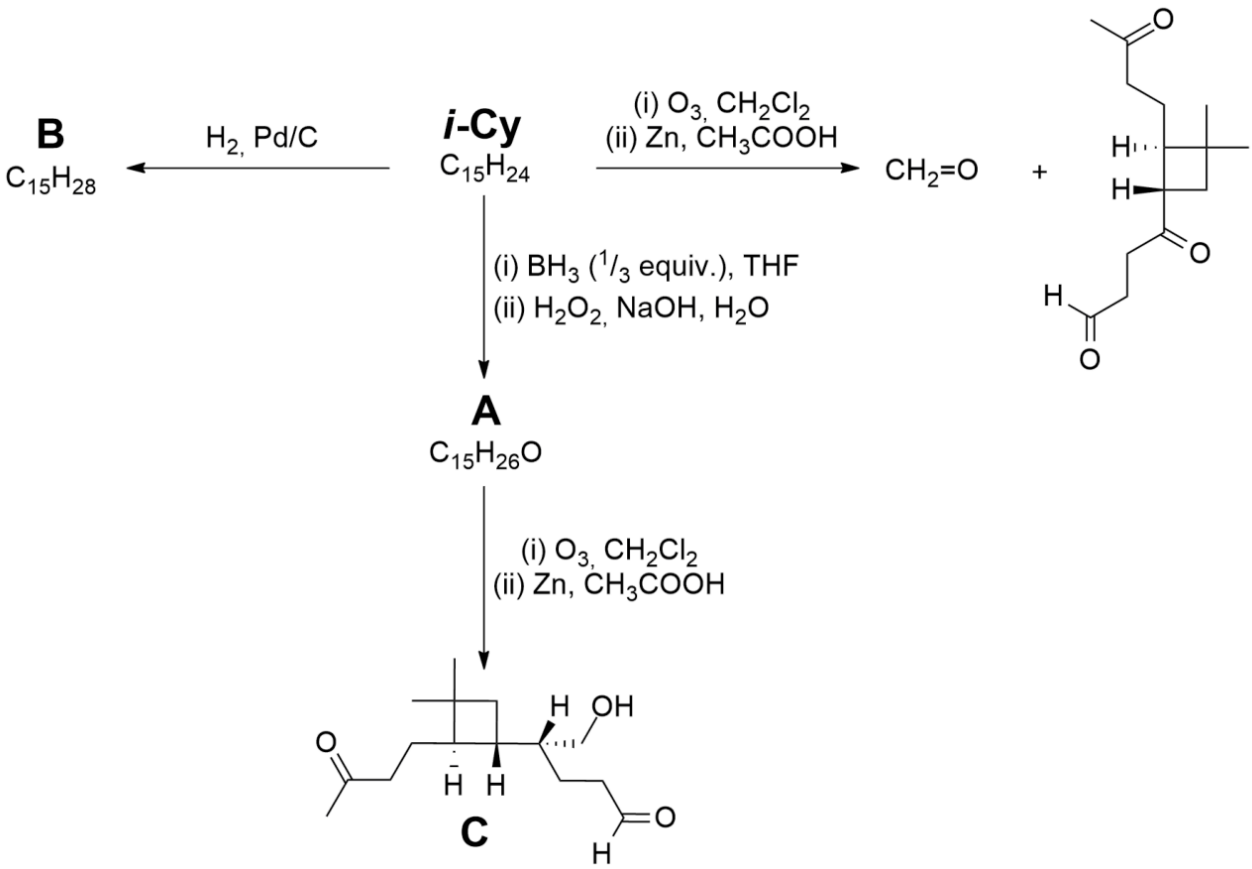
1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	Total
7	3	6	2	2	8	2	2	2	34



Sesquiterpenes have the formula $\mathrm{C_{15}H_{24}}$. They are secondary metabolites in plants and both deter insects which eat plants and attract animals which eat the insects.

Isocaryophyllene (**i-Cy**) is a sesquiterpene found in oregano, rosemary, pepper, and cloves.

The structural formula of **i-Cy** can be determined by performing various reactions and analysing the products as shown in the figure.

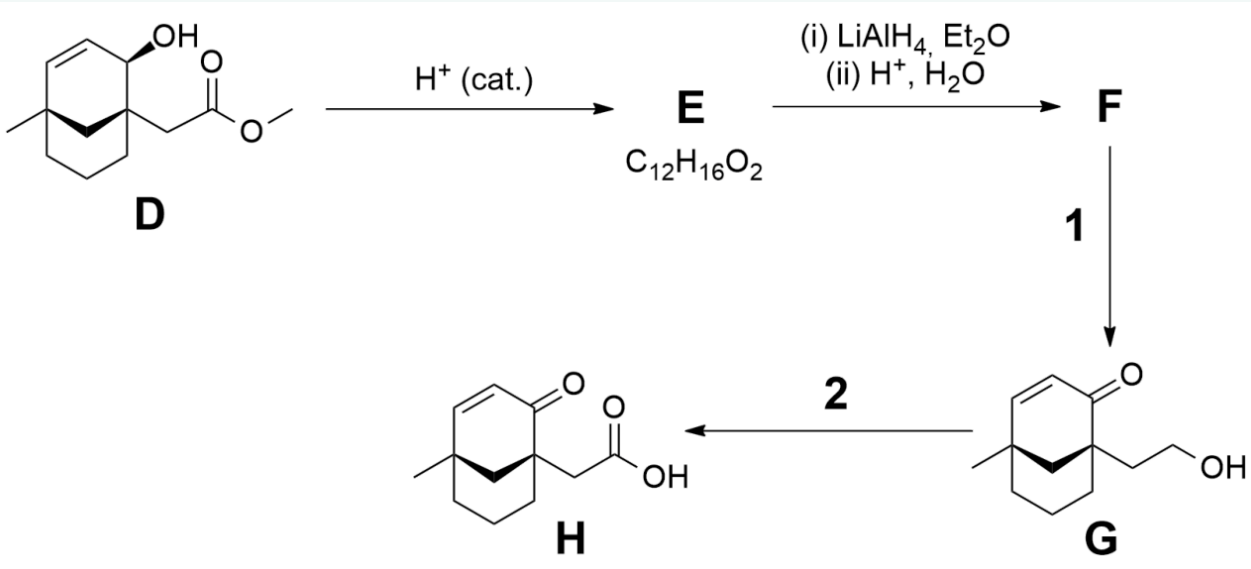


equiv. = translation 'equiv.'

1.1 Draw the structures of **i-Cy, A, and B**. Stereochemistry is not required.

1.2 Circle the stereocentres in compound **C** and **assign** them as R or S.

Clovene (**Cv**) can be synthesised from **i-Cy** under acid catalysis. The synthesis of **Cv** starts from compound **D**.

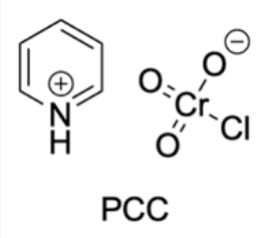


H^+ (cat.)="translation H^+ (cat.)"

1.3 Draw the structures of compounds **E** and **F**. Stereochemistry is not required.

For steps **'1'** and **'2'** several reagents could be considered. For example:

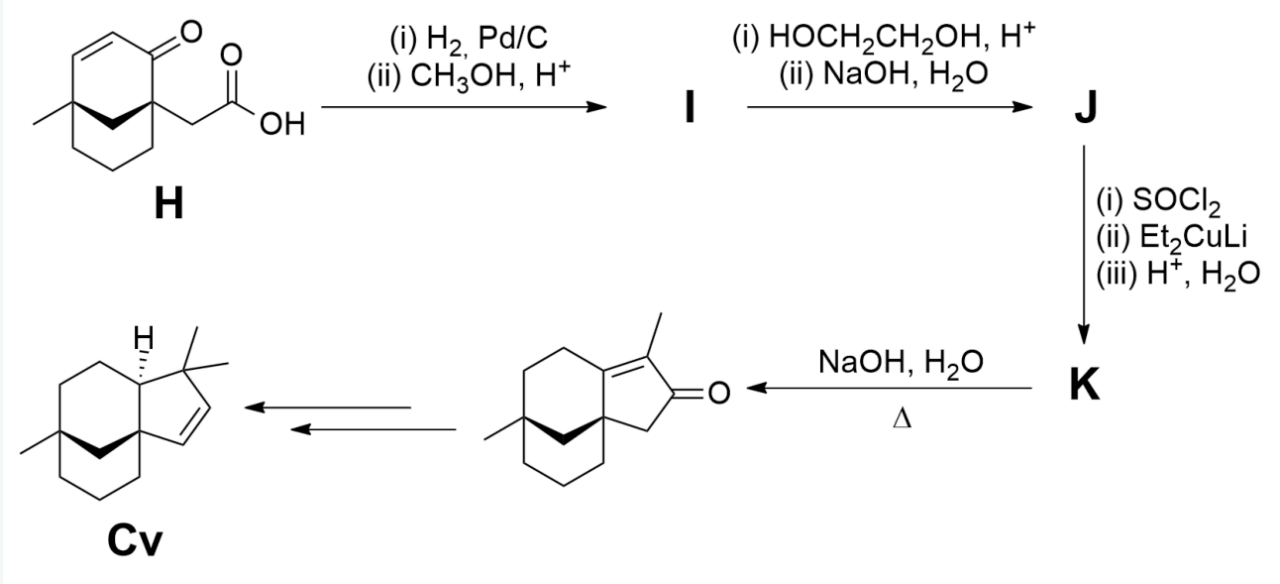
- □ PCC
- □ $K_2Cr_2O_7$, H_2SO_4, H_2O
- □ MnO_2
- □ (i) OsO_4, (ii) $KHSO_3$



1.4 From the reagents above, **tick** which one(s) would be suitable for step **'1'**.

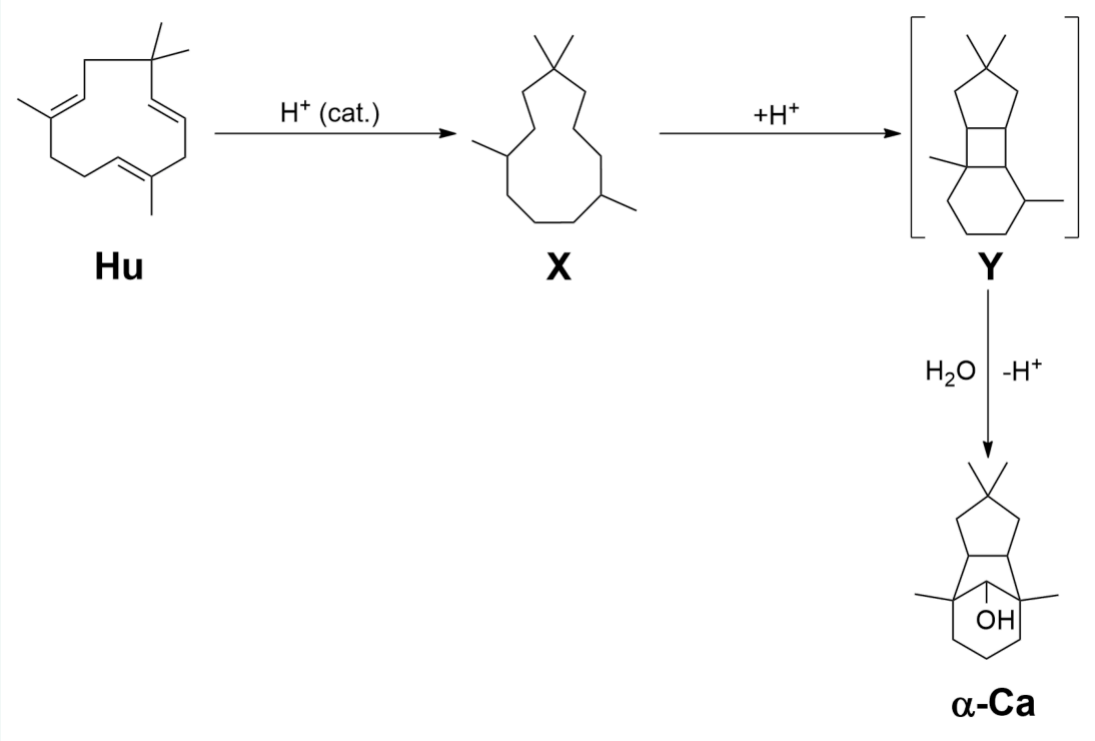
1.5 From the reagents above, **tick** which one(s) would be suitable for step **'2'**.

The final part of the synthesis is shown.



1.6 Draw the structures of compounds **I, J, and K**. Stereochemistry is not required.

Humulene (**Hu**) is another sesquiterpene. It can be converted to α-caryophyllene alcohol (**α-Ca**), which is similar in structure to **Cv**. This conversion is an acid-catalysed hydration reaction which takes place via multiple intermediate structures. Incomplete structures of some intermediates, **X** and **Y**, are shown.



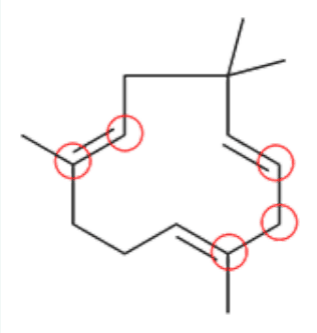
H^+ (cat.)="translation H^+ (cat.)"

The transformation from **Hu** to **X** is an acid-catalysed isomerisation reaction. Intermediate **Y** is charged.

1.7 Complete the structure of intermediate **X** by adding double bonds in the correct places.

1.8 Complete the structure of intermediate **Y** by adding a positive charge in the correct place.

Five carbon atoms are circled in **Hu**. Through understanding the mechanism we can determine where these five carbon atoms end up in **α-Ca**.



1.9 Circle the five corresponding carbon atoms in **α-Ca** which are circled in **Hu**.

Official English text of the problem.

Answers

- **1.1**

i-Cy — isocaryophyllene, 4,11,11-trimethyl-8-methylidenebicyclo[7.2.0]undec-4-ene: `CC1=CCCC(=C)C2CC(C)(C)C2CC1`

A — 8-(hydroxymethyl)-4,11,11-trimethylbicyclo[7.2.0]undec-4-ene:
`CC1=CCCC(CO)C2CC(C)(C)C2CC1`

B — tetrahydroisocaryophyllene, 2,6,10,10-tetramethylbicyclo[7.2.0]undecane:
`CC1CCCC(C)C2CC(C)(C)C2CC1`

- **1.2** Circle the **three consecutive stereocentres running from left to right across the lower edge of the cyclobutane and into the side chain**. Their configurations are R, S, R.

C — (4R)-5-hydroxy-4-[(1S,2R)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl]pentanal:
`CC(=O)CC[C@H]1C(C)(C)C[C@@H]1[C@H](CO)CCC=O`

- **1.3**

E — the five-membered lactone of 2-(2-hydroxy-5-methylbicyclo[3.3.1]non-3-en-1-yl)acetic acid:
`O=C1CC23C(O1)C=CC(C)(CCC2)C3`

F — 1-(2-hydroxyethyl)-5-methylbicyclo[3.3.1]non-3-en-2-ol:
`OCCC12C(O)C=CC(C)(CCC1)C2`

- **1.4** Tick $\mathrm{MnO_2}$ **only** — manganese(IV) oxide, formal ionic SMILES `[Mn+4].[O-2].[O-2]`. This represents its composition; the solid has an extended lattice.
- **1.5** Tick $\mathrm{K_2Cr_2O_7}$, $\mathrm{H_2SO_4}$, $\mathrm{H_2O}$ **only**:

Potassium dichromate `[K+].[K+].[O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]`; sulfuric acid `OS(=O)(=O)O`; water `O`.

- **1.6**

I — methyl 2-(5-methyl-2-oxobicyclo[3.3.1]nonan-1-yl)acetate:
`COC(=O)CC12C(=O)CCC(C)(CCC1)C2`

J — the ethylene ketal of 2-(5-methyl-2-oxobicyclo[3.3.1]nonan-1-yl)acetic acid:
`O=C(O)CC12C3(OCCO3)CCC(C)(CCC1)C2`

Under the stated alkaline hydrolysis conditions, J is present as its carboxylate; its sodium salt is:
`[Na+].O=C([O-])CC12C3(OCCO3)CCC(C)(CCC1)C2`

K — 5-methyl-1-(2-oxobutyl)bicyclo[3.3.1]nonan-2-one:
`CCC(=O)CC12C(=O)CCC(C)(CCC1)C2`

- **1.7 X — (1Z,3E,7E)-1,5,5,8-tetramethylcycloundeca-1,3,7-triene:**
  `CC1(C)/C=C/C=C(C)\CCC/C(C)=C/C1`

In the supplied X drawing, add double bonds to:

1. The upper-right sloping bond, one bond beyond the gem-dimethyl carbon.
2. The right-hand vertical bond ending at the methyl-bearing carbon.
3. The bond from the left methyl-bearing carbon to the next carbon above and to its right.

- **1.8** Put $+$ on the **lower-right methyl-bearing carbon of the six-membered ring**.

Y — the tricyclic tertiary cyclobutylcarbinyl carbocation:
`CC1(C)CC2C3[C+](C)CCCC3(C)C2C1`

- **1.9** In **α-caryophyllene alcohol**, circle:

1. Both carbons forming the bottom edge of the top five-membered ring.
2. Both methyl-bearing bridgeheads, on the left and right.
3. The central bridge carbon bearing OH.

α-Caryophyllene alcohol:
`CC1(C)CC2C(C1)C1(C)CCCC2(C)C1O`

Solution

1.1 — Reconstructing i-Cy, A, and B

The degree of unsaturation of $\mathrm{C_{15}H_{24}}$ is

$$\mathrm{DBE} = \frac{2(15) + 2 - 24}{2} = 4.$$

Hydrogenation gives $\mathrm{C_{15}H_{28}}$, whose DBE is 2. Thus hydrogenation removes two units of unsaturation. The ozonolysis products identify these as **two carbon–carbon double bonds**, leaving **two rings**.

The hydrogenation balance is

$$\mathrm{C_{15}H_{24} + 2\,H_2 \longrightarrow C_{15}H_{28}}.$$

Thus the uptake is $2\,\mathrm{mol}$ of hydrogen per mole of i-Cy.

The ozonolysis products determine how to reconnect the carbon skeleton:

- Methanal, `C=O`, identifies a terminal $=\mathrm{CH_2}$ group.
- Its former double-bond partner is the carbonyl carbon directly attached to the cyclobutane.
- The remaining aldehyde and methyl ketone must be reconnected by a double bond. This closes a nine-membered ring sharing one bond with the cyclobutane.

The supplied larger ozonolysis product is **4-[(1S,2R)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl]-4-oxobutanal**:

`CC(=O)CC[C@H]1C(C)(C)C[C@@H]1C(=O)CCC=O`

Its formula is $\mathrm{C_{14}H_{22}O_3}$. An atom-balanced representation of the reductive ozonolysis is

$$\mathrm{C_{15}H_{24} + 2\,O_3 + 2\,Zn + 4\,CH_3COOH \longrightarrow C_{14}H_{22}O_3 + CH_2O + 2\,Zn(CH_3COO)_2 + 2\,H_2O}.$$

This gives the i-Cy structure listed in the answers: a fused four-/nine-membered bicyclic system containing one internal alkene and one exocyclic methylene.

Borane, `[BH3]`, preferentially hydroborates the less hindered exocyclic double bond. Anti-Markovnikov addition places boron on the terminal carbon; oxidation with hydrogen peroxide, `OO`, replaces the carbon–boron bond with a carbon–oxygen bond. Consequently,

$$\mathrm{>C{=}CH_2 \longrightarrow >CH{-}CH_2OH}.$$

The internal alkene remains intact. Each borane molecule contains three B–H bonds, so $1/3$ equivalent supplies enough B–H bonds to hydroborate one double bond per substrate molecule. Using boric acid, `OB(O)O`, for neutral-work-up bookkeeping,

$$3\,\mathrm{C_{15}H_{24}} + \mathrm{BH_3} + 3\,\mathrm{H_2O_2} \longrightarrow 3\,\mathrm{C_{15}H_{26}O} + \mathrm{B(OH)_3}.$$

This identifies A. Its remaining internal double bond undergoes ozonolysis to give C:

$$\mathrm{C_{15}H_{26}O} + \mathrm{O_3} + \mathrm{Zn} + 2\,\mathrm{CH_3COOH} \longrightarrow \mathrm{C_{15}H_{26}O_3} + \mathrm{Zn(CH_3COO)_2} + \mathrm{H_2O}.$$

Complete hydrogenation of both double bonds instead gives B: the exocyclic methylene becomes a methyl group, and the internal double bond becomes a single bond.

1.2 — Absolute configurations in C

Label the three stereocentres from left to right in the supplied drawing as L, M, and R.

Centre	CIP priorities, highest to lowest	Assignment
L: left lower cyclobutane carbon	Gem-dimethyl ring carbon $>$ M $>$ methyl-ketone side chain $>$ H	R
M: right lower cyclobutane carbon	$R > L >$ ring methylene $>$ H	S
R: adjacent side-chain carbon	$\mathrm{CH_2OH} > M > \mathrm{CH_2CH_2CHO} >$ H	R

At L, the three carbon ligands initially give the comparison lists

$$[C, C, C] > [C, C, H] > [C, H, H].$$

Its hydrogen points away, so the clockwise $1 \to 2 \to 3$ sequence gives R.

At M, the two leading ligands initially tie. The right-hand ligand wins at the next comparison because its hydroxymethyl branch reaches oxygen. Hydrogen points towards the observer, so the apparent sense must be reversed, giving S.

At R, the hydroxymethyl carbon has the comparison list $[O, H, H]$, which outranks both carbon-only alternatives. Reversing the apparent sense because hydrogen points towards the observer gives R.

Therefore the required assignments are

$$\boxed{R,\ S,\ R \quad \text{from left to right.}}$$

The gem-dimethyl carbon is not stereogenic because its two methyl substituents are identical.

1.3 — Lactonization and reduction

D is **methyl 2-(2-hydroxy-5-methylbicyclo[3.3.1]non-3-en-1-yl)acetate**:

`COC(=O)CC12C(O)C=CC(C)(CCC1)C2`

Its allylic hydroxyl group is positioned to attack the ester intramolecularly. Acid catalysis activates the ester carbonyl, and loss of methanol, `CO`, produces a **five-membered lactone**.

The new lactone ring follows the sequence

$$\text{alcohol-bearing carbon} - \mathrm{O} - \mathrm{C(=O)} - \mathrm{CH_2} - \text{adjacent bridgehead}.$$

The formula balance is

$$\mathrm{C_{13}H_{20}O_3} \longrightarrow \mathrm{C_{12}H_{16}O_2} + \mathrm{CH_3OH},$$

which agrees exactly with the stated formula of E.

Lithium aluminium hydride, `[Li+].[AlH4-]`, reduces the lactone carbonyl and opens its acyl–oxygen bond. After work-up:

- The original alcohol oxygen becomes the secondary allylic hydroxyl group again.
- The former ester carbonyl carbon becomes the terminal carbon of a $-\mathrm{CH_2CH_2OH}$ substituent.
- The carbon–carbon double bond remains intact.

Thus F is the diol specified in the answers, with formula $\mathrm{C_{12}H_{20}O_2}$. A balanced reduction/work-up equation, omitting spectator lithium ions, is

$$2\,\mathrm{C_{12}H_{16}O_2} + \mathrm{AlH_4^-} + 4\,\mathrm{H^+} \longrightarrow 2\,\mathrm{C_{12}H_{20}O_2} + \mathrm{Al^{3+}}.$$

1.4 — Selective oxidation of F to G

G is **1-(2-hydroxyethyl)-5-methylbicyclo[3.3.1]non-3-en-2-one**:

`OCCC12C(=O)C=CC(C)(CCC1)C2`

The required transformation oxidizes the **secondary allylic alcohol** while preserving the **non-allylic primary alcohol**.

Manganese(IV) oxide performs this selective oxidation. In oxygen-equivalent notation, where $[\mathrm{O}]$ denotes one formal oxygen-atom oxidizing equivalent,

$$\mathrm{C_{12}H_{20}O_2} + [\mathrm{O}] \longrightarrow \mathrm{C_{12}H_{18}O_2} + \mathrm{H_2O}.$$

The other choices are unsuitable:

- **PCC** would also oxidize the primary alcohol to an aldehyde.
- **Acidified dichromate** would also oxidize the primary alcohol, ultimately to a carboxylic acid.
- **Osmium tetroxide followed by bisulfite work-up** would dihydroxylate the alkene.

Therefore, tick $\mathrm{MnO_2}$ **only**.

1.5 — Oxidation of G to H

H is **2-(5-methyl-2-oxobicyclo[3.3.1]non-3-en-1-yl)acetic acid**:

`O=C(O)CC12C(=O)C=CC(C)(CCC1)C2`

The primary alcohol must undergo the four-electron oxidation

$$-\mathrm{CH_2OH} \longrightarrow -\mathrm{COOH}.$$

Aqueous acidified dichromate gives this conversion. The balanced ionic equation is

$$3\,\mathrm{C_{12}H_{18}O_2} + 2\,\mathrm{Cr_2O_7^{2-}} + 16\,\mathrm{H^+} \longrightarrow 3\,\mathrm{C_{12}H_{16}O_3} + 4\,\mathrm{Cr^{3+}} + 11\,\mathrm{H_2O}.$$

PCC normally stops at the aldehyde under its standard anhydrous conditions. Manganese dioxide does not provide the required oxidation of this non-allylic primary alcohol, and osmium tetroxide targets the alkene.

Therefore, tick $\mathrm{K_2Cr_2O_7}$, $\mathrm{H_2SO_4}$, $\mathrm{H_2O}$ **only**.

1.6 — Identifying I, J, and K

For clarity, number the bicyclo[3.3.1]nonane framework so that the side-chain-bearing bridgehead is C1, the adjacent ketone carbon is C2, and the methyl-bearing opposite bridgehead is C5.

Formation of I. Hydrogenation removes the alkene in H while retaining the ketone. Methanol under acid catalysis then esterifies the carboxylic acid.

The overall organic balance is

$$\mathrm{C_{12}H_{16}O_3 + H_2 + CH_3OH \longrightarrow C_{13}H_{20}O_3 + H_2O.}$$

Thus I contains the saturated bicyclic ketone and a $-\mathrm{CH_2COOCH_3}$ substituent at C1.

Formation of J. Ethylene glycol, **ethane-1,2-diol** OCCO, protects the ring ketone as a five-membered cyclic ketal. Aqueous sodium hydroxide subsequently hydrolyses the methyl ester without removing this ketal.

The combined balance under the stated alkaline conditions is

$$\mathrm{C_{13}H_{20}O_3 + HOCH_2CH_2OH + OH^- \longrightarrow C_{14}H_{21}O_4^- + CH_3OH + H_2O.}$$

Acidification would give the neutral acid shown in the principal answer:

$$\mathrm{C_{14}H_{21}O_4^- + H^+ \longrightarrow C_{14}H_{22}O_4.}$$

Therefore J retains the ethylene ketal at C2 and has a $-\mathrm{CH_2COOH}$ group, or its carboxylate, at C1.

Formation of K. Thionyl chloride converts the carboxylic acid group into an acyl chloride. Lithium diethylcuprate then replaces the acyl chloride's chlorine with **one ethyl group**, producing a ketone.

Writing R for the ketal-protected remainder of J and $\mathrm{Et = C_2H_5}$,

$$\mathrm{RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl,}$$
$$\mathrm{RCOCl + LiCuEt_2 \longrightarrow RCOEt + EtCu + LiCl.}$$

The corresponding protected structures are:

Intermediate	SMILES
Ketal-protected acyl chloride derived from J	`O=C(Cl)CC12C3(OCCO3)CCC(C)(CCC1)C2`
Ethylene-ketal-protected K	`CCC(=O)CC12C3(OCCO3)CCC(C)(CCC1)C2`

Finally, aqueous acid hydrolyses the ketal and restores the original ring ketone:

$$\mathrm{C_{16}H_{26}O_3 + H_2O \longrightarrow C_{14}H_{22}O_2 + HOCH_2CH_2OH.}$$

Hence K contains two ketones: the ring ketone and the side chain

$$\mathrm{-CH_2-C(=O)-CH_2-CH_3.}$$

The following aldol condensation independently confirms this identification. The enolate formed on the **ethyl side** of the side-chain ketone attacks the ring ketone, closing a five-membered ring. Dehydration gives the depicted tricyclic enone:

`CC1=C2CCC3(C)CCCC2(CC1=O)C3`

Its formula balance is

$$\mathrm{C_{14}H_{22}O_2 \longrightarrow C_{14}H_{20}O + H_2O.}$$

The ethyl group's terminal methyl consequently becomes the methyl substituent on the new enone double bond.

1.7 — Double bonds in X

Use the following **atom-tracking labels**, which are independent of systematic nomenclature:

- Label the gem-dimethyl ring carbon of Hu **C1**.
- Proceed clockwise around the Hu drawing to label the other ring atoms **C2–C11**.
- The other methyl-bearing ring carbons are **C5** and **C9**.

Humulene is **(1E,4E,8E)-2,6,6,9-tetramethylcycloundeca-1,4,8-triene**. Its atom-mapped SMILES under this tracking convention is:

`C[C:1]1(C)/[CH:2]=[CH:3]/[CH2:4]/[C:5](C)=[CH:6]/[CH2:7][CH2:8]/[C:9](C)=[CH:10]/[CH2:11]1`

Its double bonds are therefore

$$\mathrm{C2}=\mathrm{C3}, \qquad \mathrm{C5}=\mathrm{C6}, \qquad \mathrm{C9}=\mathrm{C10}.$$

Acid-catalysed isomerization moves the C5=C6 bond to C4=C5:

1. Protonation at C6 gives a carbocation at C5.
2. Loss of a proton from C4 regenerates the acid catalyst and forms C4=C5.

The resulting conjugated diene enables the subsequent cyclization. Thus X has

$$\boxed{\mathrm{C2}=\mathrm{C3}, \qquad \mathrm{C4}=\mathrm{C5}, \qquad \mathrm{C9}=\mathrm{C10}.}$$

No atoms are gained or lost: Hu and X both have formula $\mathrm{C_{15}H_{24}}$. In the supplied X drawing, C4=C5 has Z geometry, while the other two double bonds have E geometry; these geometries are included in the answer SMILES.

1.8 — Positive charge in Y

Starting from X, the cyclization can be followed by three electron-flow steps:

1. **Protonation at C2** of C2=C3 leaves a carbocation at C3.
2. The C9=C10 π bond attacks through **C10**, forming the new **C3–C10** bond and leaving a carbocation at C9.
3. The C4=C5 π bond attacks through **C4**, forming the new **C4–C9** bond and leaving a carbocation at **C5**.

These two new carbon–carbon bonds produce exactly the fused five-, four-, and six-membered rings drawn for Y.

The balance is

$$\mathrm{C_{15}H_{24}} + \mathrm{H^+} \longrightarrow \mathrm{C_{15}H_{25}}^+.$$

C5 is the **lower-right methyl-bearing carbon in the six-membered ring**. It has three carbon–carbon σ bonds, no attached hydrogen, and the positive charge.

1.9 — Tracking the five circled carbons

Under the numbering above, the five circled atoms in Hu are

$$\boxed{\mathrm{C3},\ \mathrm{C4},\ \mathrm{C5},\ \mathrm{C9},\ \mathrm{C10}.}$$

The conversion of Y into α-caryophyllene alcohol involves a **Wagner–Meerwein rearrangement**:

1. The **C3–C4 σ bond migrates to the cationic C5**, forming a new **C3–C5** bond.
2. The positive charge moves from C5 to **C4**.
3. Water attacks C4, and deprotonation produces the alcohol.

This migration expands the four-membered ring and creates the bridged skeleton shown in the product. The hydroxyl-bearing carbon is therefore the original **C4**.

The hydration balance is

$$\mathrm{C_{15}H_{25}}^{+} + \mathrm{H_2O} \longrightarrow \mathrm{C_{15}H_{26}O} + \mathrm{H}^{+},$$

so the overall acid-catalysed reaction is

$$\mathrm{C_{15}H_{24}} + \mathrm{H_2O} \longrightarrow \mathrm{C_{15}H_{26}O}.$$

The atom-mapped SMILES of **α-caryophyllene alcohol** is:

```
C[C:1]1(C)[CH2:2][CH:3]2[CH:10]([CH2:11]1)[C:9]1(C)[CH2:8][CH2:7][CH2:6][C:5]2(C)[CH:4]1O
```

The required circles are therefore:

Original circled atom	Position in the supplied α-Ca drawing
C3	Lower-right corner of the top five-membered ring
C10	Lower-left corner of the top five-membered ring
C9	Left methyl-bearing bridgehead
C5	Right methyl-bearing bridgehead
C4	Central bridge carbon bearing OH

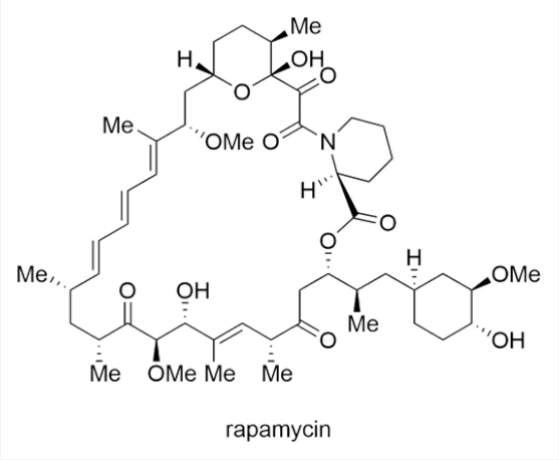
The mapped SMILES specifies atom identity and connectivity. The spatial arrangement of the bridges is conveyed by the supplied skeletal drawing; no additional absolute stereochemical assignment is requested in this part.

The answers were checked against the official answers published by the organisers.

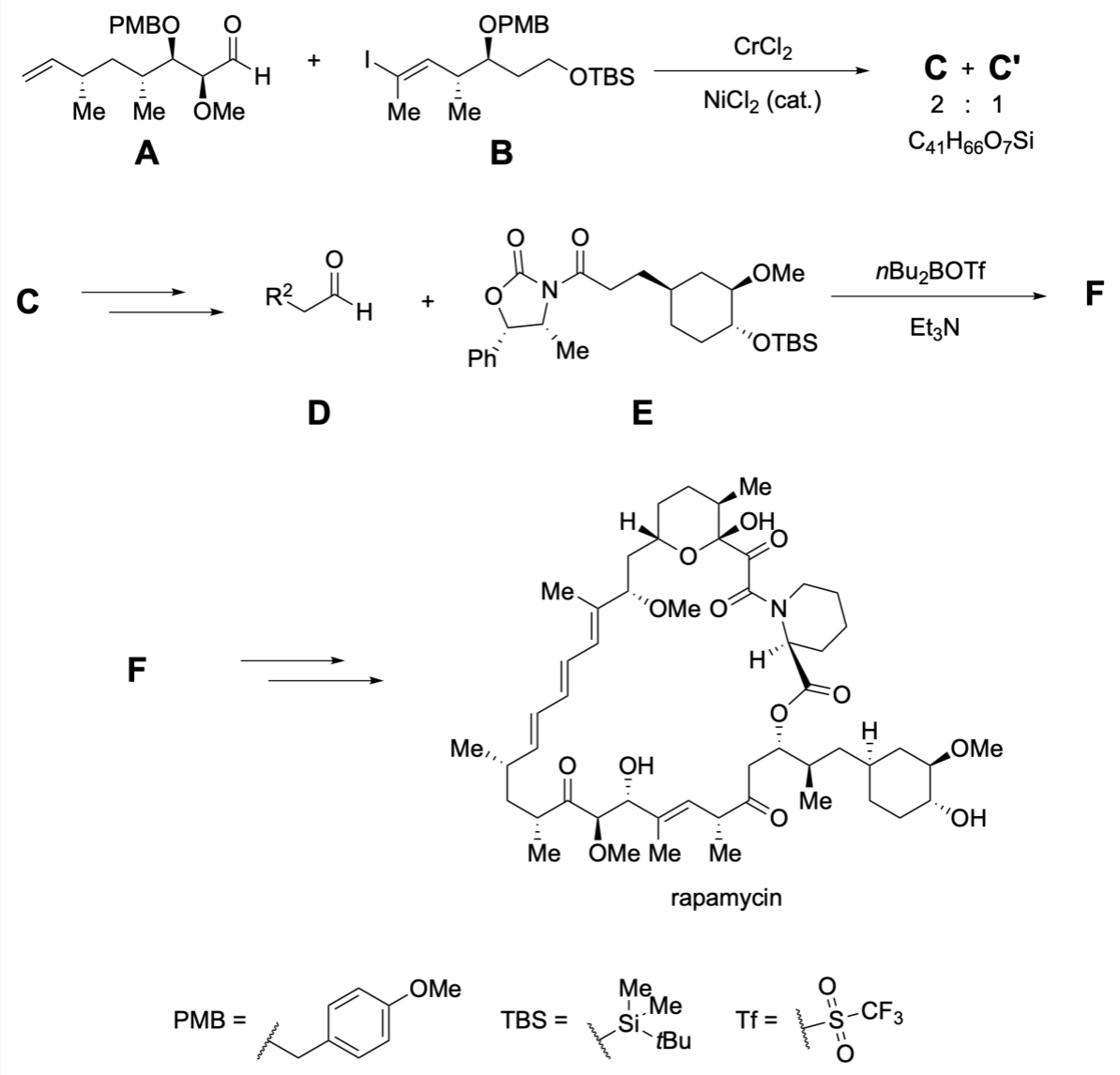
Problem 2: Rapamycin - A molecular glue

6.5% of the total

2.1	2.2	2.3	2.4	Total
12	19	18	18	67



Rapamycin was isolated from the bacterium *Streptomyces hygroscopicus* in 1972. It acts as a "molecular glue" and inhibits the activity of the protein mTOR through binding to another protein. It has been used to treat various diseases. The stereochemical complexity of rapamycin makes its total synthesis challenging. The figure shows part of the first total synthesis by the Nicolaou group.



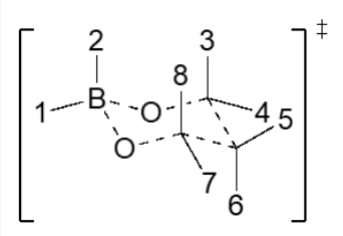
The major stereoisomer (**C**) is formed from the chromium-mediated coupling reaction of aldehyde **A** and vinyl iodide **B** and can be predicted using the Felkin-Anh model without chelation.

2.1a Draw a Newman projection showing the best approach of the nucleophile in this reaction. Use the labels =O, –H, –R^1, –OMe, and Nu.

2.1b Draw the full structure of the major diastereomer **C** showing all stereochemistry.

After a few transformations, **C** can be converted into an aldehyde **D** which reacts with **E** to form **F**. **F** can be further transformed into rapamycin.

2.2a Using the Zimmerman-Traxler model, **predict** the arrangement of the reactants as they come together to form the six-membered ring transition state in the reaction to form **F**. **Draw** the substituents at positions labelled with numbers. If a position does not have a substituent, put an "X" in the box. Boxes 1 and 2 have been filled in as an example. You may use the abbreviation R^2 as given in the scheme above.



2.2b Draw the structure of **F** showing all stereochemistry. You may use the abbreviation R^2 as given in the scheme above.

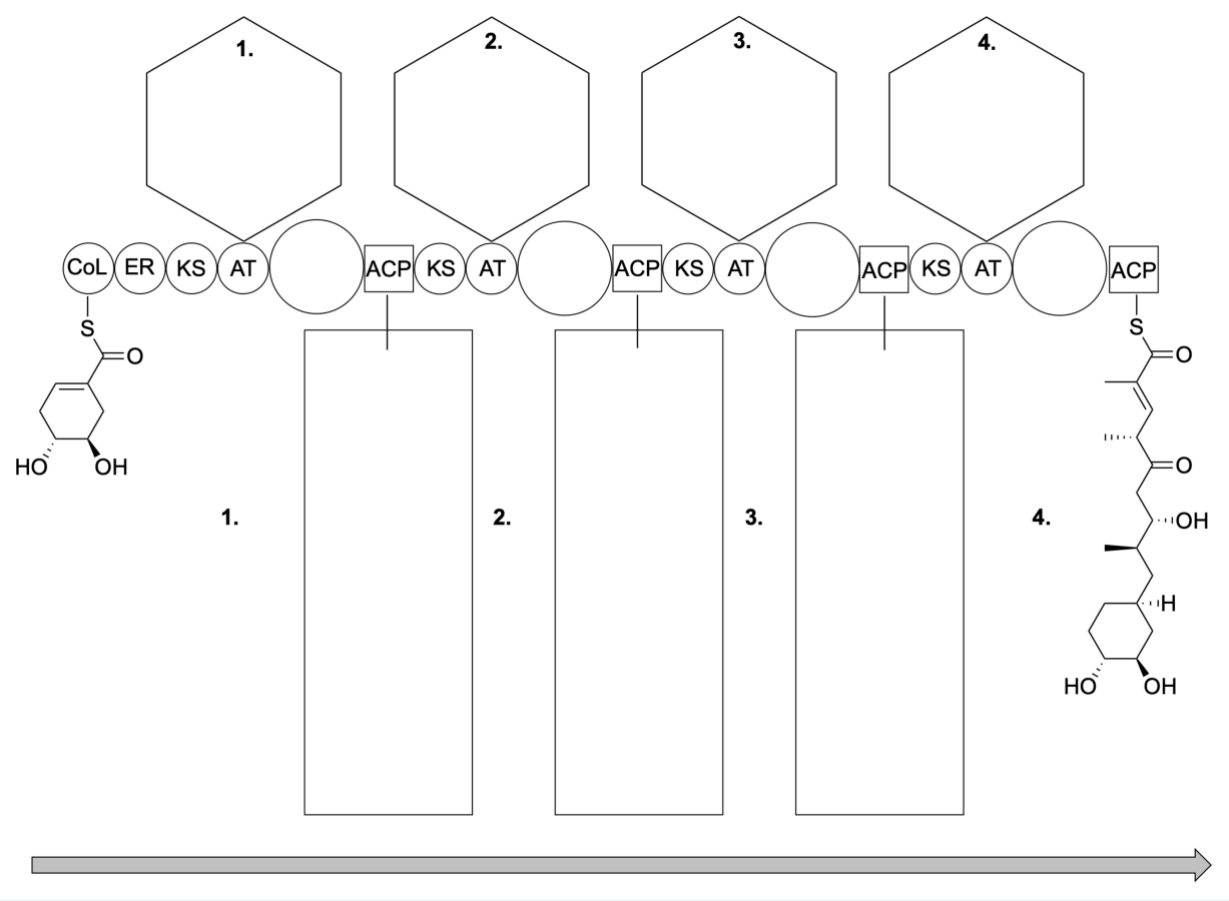
Whilst stereochemical control is challenging synthetically, the biological synthesis controls stereochemistry elegantly through an assembly line of various enzymes.

The carbon chain is built up through the addition of monomers. These units are connected via a thioester to Coenzyme A (CoA).

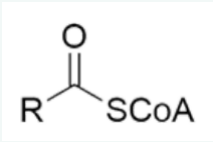
The functions of the various enzymes and proteins are shown in the table.

Abbreviation	Name	Function
ACP	Acyl-carrier protein	Carries growing chain between domains
CoL	CoA-Ligase	Activates a carboxylic acid substrate to be loaded onto the ACP
AT	Acyltransferase	Selects monomer and transfers to ACP
KS	Ketosynthase	Accepts growing chain from previous ACP and activates it for Claisen condensation with next monomer-loaded ACP
KR	Ketoreductase	Reduces carbonyl of a previous monomer to a hydroxyl
DH	Dehydratase	Forms α,β-unsaturated thioester via elimination on the previous monomer
ER	Enoylreductase	Reduces α,β-unsaturated thioester to saturated chain on the previous monomer

The first part of the assembly line is shown with blanks. The enzymes are shown in circles and act in the order of the arrow.



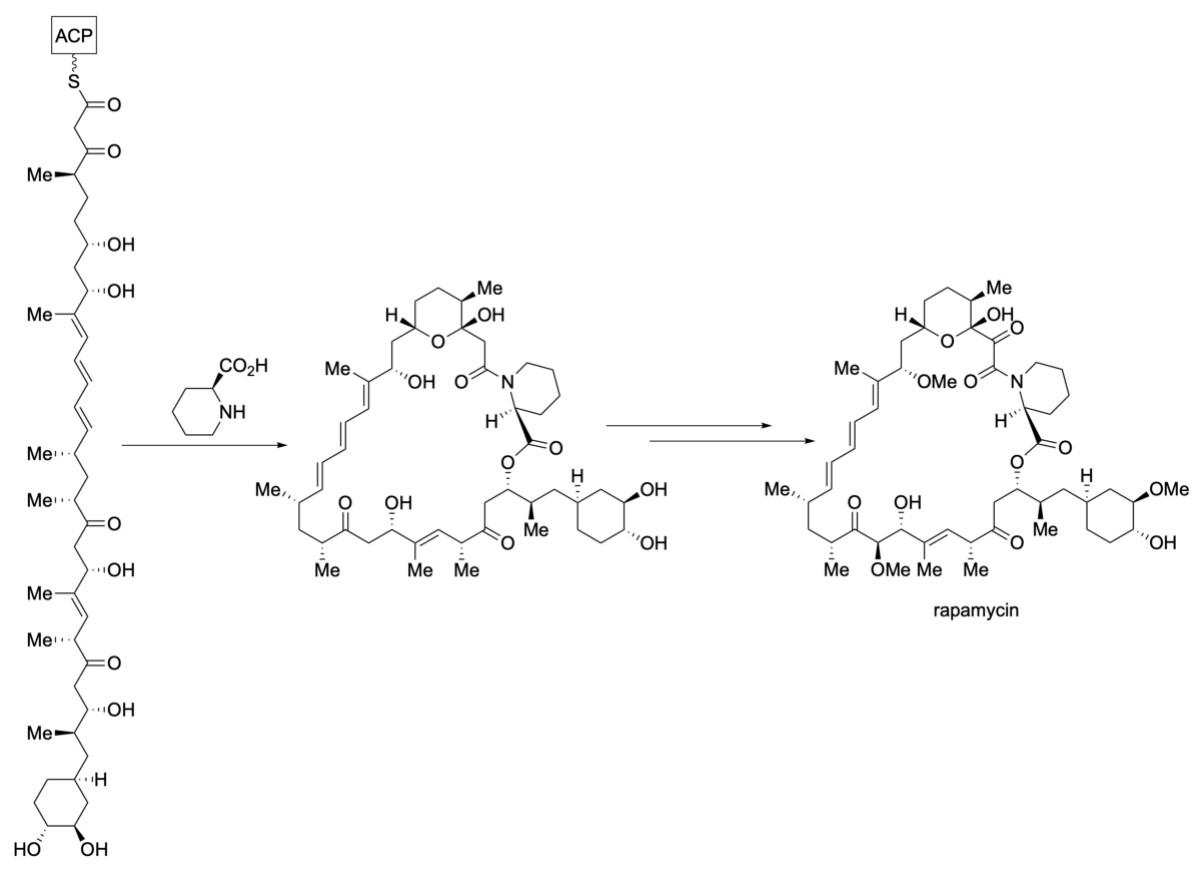
2.3a Draw in the hexagons the structure of the monomer needed by the enzyme AT at each of the points numbered **1-4**. Carbon dioxide is released when the monomers are incorporated. The monomers have the following general structure where the R group is anionic:



2.3b Fill in each circle with the abbreviations of enzyme(s) needed. Write “X” if no additional enzyme is needed.

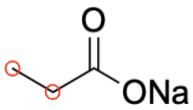
2.3c Complete the rectangles with the structure of the growing molecule attached to the enzyme.

The final steps of the enzymatic synthesis are shown below.

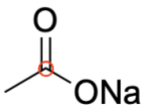


The building blocks involved were determined by feeding the bacterium with three different ^{13}C-labelled starting materials which are incorporated into the monomers (^{13}C are circled as shown below):

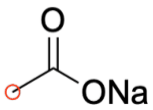
a.



b.



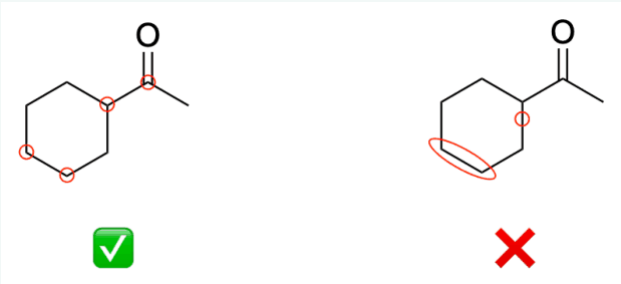
c.



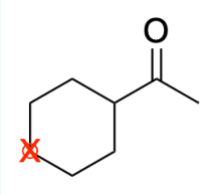
2.4 Circle the carbons in rapamycin that will be ^{13}C-labelled when the bacterium is fed with each of the three starting materials **a-c** in turn, following the guidelines on the next page. Incorrect circles will be penalised but there is no negative scoring.

Guidelines for circling carbon atoms:

- Each circle should clearly surround one carbon atom
- Do not include multiple carbon atoms in the same circle
- Do not circle any bonds



- If you would like to change your answer and cross-out a circle, put an “X” over the circle.



Official English text of the problem.

Answers

In the SMILES below, `[*:2]` represents the permitted abbreviation R^2. The macromolecular abbreviations are `S[*:90]` for SCoA and `S[*:91]` for SACP. Other asterisks mark a fragment's attachment point.

- **2.1a.** View **from the aldehyde carbon towards its adjacent stereogenic carbon**. Put the front $=\mathrm{O}$ at 9 o'clock and front H at 3 o'clock. On the rear carbon put OMe at 6 o'clock, R^1 at 10 o'clock, and H at 2 o'clock. Draw Nu approaching the front carbon from above, opposite the rear C–OMe bond, with the usual Bürgi–Dunitz approach.
- **2.1b.** The major Felkin–Anh coupling product **C** has the R configuration at the newly formed alcohol centre:

```
C=C[C@@H](C)C[C@@H](C)[C@@H](OCc1ccc(OC)cc1)[C@H](OC)[C@H](O)/C(C)=C/[C@@H]
(C)[C@@H](OCc1ccc(OC)cc1)CCO[Si](C)(C)C(C)(C)C
```

- **2.2a.** Fill the supplied chair as follows. The auxiliary is attached through its nitrogen; R^3 is the protected cyclohexylmethyl group defined in the solution.

Position	Entry
1	n-Bu
2	n-Bu
3	The N-attached $(4R,5S)$-4-methyl-5-phenyloxazolidin-2-one auxiliary
4	X
5	H
6	$R^3 = \mathrm{CH_2}$–protected cyclohexyl
7	$\mathrm{CH_2}R^2$
8	H

- **2.2b. F** is the $(2R,3S)$ **syn aldol adduct**, numbering its acyl chain from the auxiliary-bound carbonyl:

```
[*:2]C[C@H](O)[C@@H](C[C@H]1C[C@@H](OC)[C@H](O[Si](C)(C)C(C)
(C)C)CC1)C(=O)N1[C@H](C)[C@H](c2ccccc2)OC1=O
```

- **2.3a.** The monomers are:

Hexagon	Monomer	SMILES
1	Methylmalonyl-CoA carboxylate	`C[C@@H](C(=O)[O-])C(=O)S[*:90]`
2	Malonyl-CoA carboxylate	`O=C([O-])CC(=O)S[*:90]`
3	Methylmalonyl-CoA carboxylate	`C[C@@H](C(=O)[O-])C(=O)S[*:90]`
4	Methylmalonyl-CoA carboxylate	`C[C@@H](C(=O)[O-])C(=O)S[*:90]`

The methylmalonyl SMILES specifies the conventional $(2S)$ substrate; the problem itself does not give the extender's absolute configuration.

- **2.3b.** The circles, in order, contain **KR, DH, ER**; **KR**; **X**; **KR, DH**.
- **2.3c.** The three ACP-bound intermediates are:

Rectangle 1 — first extension product:

`[*:91]SC(=O)[C@H](C)C[C@H]1C[C@@H](O)[C@H](O)CC1`

Rectangle 2 — second extension product:

`[*:91]SC(=O)C[C@H](O)[C@H](C)C[C@H]1C[C@@H](O)[C@H](O)CC1`

Rectangle 3 — third extension product:

`[*:91]SC(=O)[C@@H](C)C(=O)C[C@H](O)[C@H](C)C[C@H]1C[C@@H](O)[C@H](O)CC1`

- **2.4.** Define P_1 as the polyketide-derived **amide carbonyl bonded to the pipecolate nitrogen**. Number consecutively along the carbon backbone to P_{29}, the methylene attached to the cyclohexyl ring. An atom-mapped SMILES specifying this numbering appears below.

Feed	Carbons to circle individually	Number of circles
a	$P_4, P_{10}, P_{16}, P_{18}, P_{22}, P_{24}, P_{28}$, **and the methyl carbon attached to each of these seven atoms**	**14**
b	$P_1, P_5, P_7, P_{11}, P_{13}, P_{19}, P_{25}$	**7**
c	$P_2, P_6, P_8, P_{12}, P_{14}, P_{20}, P_{26}$	**7**

Solution

2.1a — Felkin–Anh projection

The protected α-methoxy aldehyde **A** is:

`C=C[C@@H](C)C[C@@H](C)[C@@H](OCc1ccc(OC)cc1)[C@H](OC)C=O`

Its carbon adjacent to the aldehyde has the S configuration. Here R^1 denotes the rest of the carbon chain attached to that centre.

For the non-chelated, polar Felkin–Anh model, orient the C–OMe bond approximately perpendicular to the carbonyl plane. Nucleophilic attack occurs opposite this bond, along a Bürgi–Dunitz trajectory, with a nucleophile–carbonyl-carbon–oxygen angle of approximately 107°.

A precise Newman specification is:

Component	Position when looking from CHO towards the adjacent carbon
Front carbonyl oxygen	9 o'clock
Front aldehydic hydrogen	3 o'clock
Rear OMe	6 o'clock
Rear R^1	10 o'clock
Rear hydrogen	2 o'clock
Incoming Nu	Approaches from above the front carbon, opposite the rear OMe

The projection fixes both the substrate's handedness and the face of attack. Ordinary SMILES cannot specify this approach geometry; the substrate and product SMILES specify the corresponding configurations.

2.1b — Structure of C

The protected vinyl iodide **B** is:

`I/C(C)=C/[C@@H](C)[C@@H](OCc1ccc(OC)cc1)CCO[Si](C)(C)C(C)(C)C`

Chromium-mediated activation replaces the vinyl C–I bond by a nucleophilic carbon–chromium bond. That vinyl carbon attacks the aldehyde carbon of **A**. Protonation of the resulting alkoxide gives **C**.

The formal, atom- and charge-balanced reductive coupling is

$$\mathrm{RCHO} + \mathrm{R'I} + 2\,\mathrm{e^-} + \mathrm{H^+} \longrightarrow \mathrm{RCH(OH)R'} + \mathrm{I^-}.$$

Here RCHO represents **A**, and $\mathrm{R'I}$ represents **B**. The proton is `[H+]`, and the iodide ion is `[I-]`. This equation expresses the net redox balance without assigning particular chromium coordination species.

The resulting connectivity is

$$\begin{aligned}&\mathrm{CH_2{=}CH{-}CH(Me){-}CH_2{-}CH(Me){-}CH(OPMB){-}CH(OMe)}\\&\quad\mathrm{{-}CH(OH){-}C(Me){=}CH{-}CH(Me){-}CH(OPMB){-}CH_2{-}CH_2{-}OTBS.}\end{aligned}$$

All pre-existing stereogenic centres retain their spatial configurations, and the vinyl geometry is retained. The new alcohol centre is R, as specified by the complete SMILES in **Answers**.

To draw it with the left-hand portion of **A** kept in its original zigzag orientation, continue the chain through the former aldehyde carbon and draw its new OH bond **hashed and upward**. The adjacent OMe bond remains **solid-wedged and downward**.

The completed structure has molecular formula $\mathrm{C_{41}H_{66}O_7Si}$, matching the formula supplied in the scheme.

2.2a — Zimmerman–Traxler transition state

The aldehyde **D** is R^2-substituted ethanal:

`[*:2]CC=O`

The chiral N-acyl oxazolidinone **E** is:

`O=C(N1[C@H](C)[C@H](c2ccccc2)OC1=O)CC[C@H]1C[C@@H](OC)[C@H](O[Si](C)(C)C(C)(C)C)CC1`

Define the two substituents used in the chair:

Symbol or description	Name and attachment-point SMILES
Auxiliary at position 3	N-attached $(4R,5S)$-4-methyl-5-phenyloxazolidin-2-one: `*N1[C@H](C)[C@H](c2ccccc2)OC1=O`
R^3, at position 6	Protected cyclohexylmethyl group: `*C[C@H]1C[C@@H](OC)[C@H](O[Si](C)(C)C(C)(C)C)CC1`
n-Bu, at positions 1 and 2	Butan-1-yl group: `*CCCC`

The boron reagent and base produce the Z **boron enolate** of **E**. Its constitution and enolate geometry can be represented as:

`CCCCB(CCCC)O/C(N1[C@H](C)[C@H](c2ccccc2)OC1=O)=C\C[C@H]1C[C@@H](OC)[C@H](O[Si](C)(C)C(C)(C)C)CC1`

The aldehyde oxygen coordinates to boron, and the new carbon–carbon bond forms through a six-membered chair-like transition state. In the **particular perspective printed in the question**, the ring atoms run in this order:

$$\mathrm{B}-\mathrm{O}_E-\mathrm{C}_E-\mathrm{C}_\alpha-\mathrm{C}_D-\mathrm{O}_D-\mathrm{B}.$$

Consequently:

- The upper-right carbon bearing positions **3/4** is the **enolate carbonyl-derived carbon**.
- The right-hand carbon bearing **5/6** is the **enolate α-carbon**.
- The lower-middle carbon bearing **7/8** is the **aldehyde carbon**.

The entries therefore are:

Position	Substituent	Reason
1	n-Bu	First alkyl ligand on boron
2	n-Bu	Second alkyl ligand on boron
3	N-attached chiral auxiliary	Substituent on the enolate carbonyl-derived carbon
4	X	No fourth substituent at that carbon
5	H	Hydrogen on the enolate α-carbon
6	R^3	Original side chain of **E**
7	$\mathrm{CH_2}R^2$	Aldehyde substituent, in the favourable equatorial position
8	H	Aldehydic hydrogen

This assignment gives the $2R,3S$ product. The identification of positions **3/4 as the enolate carbon and 7/8 as the aldehyde carbon** is essential to preserving the handedness of the supplied chair.

2.2b — Structure of F

The aldol addition gives the connectivity

$$\mathrm{R}^2\mathrm{CH_2}-\mathrm{CH(OH)}-\mathrm{CH(R}^3)-\mathrm{C(=O)}-\mathrm{N(Aux)}.$$

No carbon atoms are lost. In generic form, the balanced aldol addition is

$$\mathrm{RCHO} + \mathrm{R'CH_2C(=O)N(Aux)} \longrightarrow \mathrm{RCH(OH)CH(R')C(=O)N(Aux)}.$$

The Z enolate gives the **syn** relationship between the new OH group and R^3. The auxiliary selects the face that gives $2R, 3S$, counting the auxiliary-bound carbonyl carbon as C1.

For a drawing, place the chain

$$\mathrm{C(=O)-CH(R^3)-CH(OH)-CH_2R^2}$$

as a conventional zigzag running left to right. Draw both R^3 and OH with **solid wedges**; their corresponding hydrogens point behind the plane. Retain the auxiliary's $(4R, 5S)$ configuration and all three cyclohexyl stereocentres. This drawing corresponds to the SMILES for **F** in **Answers**.

2.3a — Identification of the monomers

Let Q denote the cyclohexyl group with the ring stereochemistry shown in the supplied product. Reading the four-module product from the starter end towards ACP gives

$$\mathrm{Q-CH_2-CH(Me)-CH(OH)-CH_2-C(=O)-CH(Me)-CH{=}C(Me)-C(=O)-SACP}.$$

Every extension contributes two backbone carbons. A methylmalonyl unit also supplies a methyl branch on its newly introduced α-carbon.

The successive extensions therefore require:

Module	Substitution of the newly introduced α-carbon	Required extender
1	Methyl-substituted	Methylmalonyl-CoA
2	Unsubstituted	Malonyl-CoA
3	Methyl-substituted	Methylmalonyl-CoA
4	Methyl-substituted	Methylmalonyl-CoA

The generic decarboxylative chain extension, written after loading the extender onto its ACP, is

$$\mathrm{R-C(=O)-SACP} + {}^{-}\mathrm{OOC-CH(R')-C(=O)-SACP'} + \mathrm{H^+} \longrightarrow \mathrm{R-C(=O)-CH(R')-C(=O)-SACP'} + \mathrm{CO_2} + \mathrm{HSACP}.$$

Here $R' = \mathrm{H}$ for malonyl and $R' = \mathrm{Me}$ for methylmalonyl. Carbon dioxide is O=C=O. The released carbon is the extender's free carboxylate carbon.

As a carbon-count check, the seven-carbon starter plus these four extensions gives

$$7 + 3 + 2 + 3 + 3 = 18$$

carbons in the displayed four-module acyl chain, including its cyclohexyl ring and methyl branches.

2.3b — Identification of the enzymes

The processing domains act on the carbonyl that becomes the **β-carbonyl after the current extension**.

Module	Fate required for that carbonyl	Enzymes, in order
1	Ketone → alcohol → alkene → methylene	KR, DH, ER
2	Ketone → alcohol	KR
3	Carbonyl remains a ketone	X
4	Ketone → alcohol → alkene	KR, DH

Their net transformations can be written as balanced reduction half-reactions and dehydration:

$$\text{KR:}\quad \mathrm{RCOCH(R')COSACP} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{RCH(OH)CH(R')COSACP}$$

$$\text{DH:}\quad \mathrm{RCH(OH)CH(R')COSACP} \longrightarrow \mathrm{RCH{=}C(R')COSACP} + \mathrm{H_2O}$$

$$\text{ER:}\quad \mathrm{RCH{=}C(R')COSACP} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{RCH_2CH(R')COSACP}.$$

Water has SMILES O. These equations show the reducing-equivalent balance without introducing cofactors absent from the question.

2.3c — The growing ACP-bound chains

The initially supplied ER saturates the starter's ring double bond. The completed rectangles must then show:

Rectangle	Chain, written from the cyclohexyl end towards ACP	Configurations of acyl-chain stereocentres, numbered from the thioester carbonyl
1	$\mathrm{Q{-}CH_2{-}CH(Me){-}C(=O){-}SACP}$	$2R$
2	$\mathrm{Q{-}CH_2{-}CH(Me){-}CH(OH){-}CH_2{-}C(=O){-}SACP}$	$3S, 4R$
3	$\mathrm{Q{-}CH_2{-}CH(Me){-}CH(OH){-}CH_2{-}C(=O){-}CH(Me){-}C(=O){-}SACP}$	$2S, 5S, 6R$

In all three, the cyclohexyl group has the $(1S, 3R, 4R)$ configuration for the substituted ring as numbered in these products. The complete stereochemical SMILES are given in **Answers**.

For a drawing matching the vertical orientation of the supplied final chain:

- Retain the ring's dashed H, dashed OH and solid-wedged OH.
- Draw the methyl group introduced by module 1 on a solid wedge.
- Draw the alcohol generated by module 2 with a hashed bond.
- Draw the methyl group introduced by module 3 with a hashed bond.

After module 4, the resulting ACP-bound α,β-unsaturated thioester is:

```
[*:91]SC(=O)/C(C)=C/[C@@H](C)C(=O)C[C@H](O)[C@H](C)C[C@H]1C[C@@H](O)[C@H](O)CC1
```

Its E double bond, retained ketone, alcohol and methyl branches reproduce the product printed at the right of the assembly line.

2.4 — Carbon tracing

Use the following explicit numbering of rapamycin:

- P_1: the amide carbonyl directly bonded to the pipecolate nitrogen.
- P_2: the adjacent ketone carbonyl.
- P_3: the OH-bearing hemiketal carbon.
- Continue along the carbon backbone through the six-membered oxygen-containing ring, the triene and the lower portion of the macrocycle.
- P_{27}: the carbon whose oxygen forms the macrocyclic ester.
- P_{28}: the adjacent methyl-bearing side-chain carbon.

- P_{29}: the methylene directly attached to the cyclohexyl ring.

For complete positional identification, **rapamycin** has the following atom-mapped SMILES. Maps **1–29** are P_1–P_{29}; map $100 + i$ denotes the methyl attached to P_i:

```
[C:1]1(=O)[C:2](=O)[C@@:3]2(O)[C@H:4]([CH3:104])[CH2:5][CH2:6][C@H:7](O2)
[CH2:8][C@H:9](O[CH3:209])/[C:10]([CH3:110])=[CH:11]/[CH:12]=[CH:13]/[CH:14]=
[CH:15]/[C@@H:16]([CH3:116])[CH2:17][C@@H:18]([CH3:118])[C:19](=O)[C@H:20]
(O[CH3:220])[C@H:21](O)/[C:22]([CH3:122])=[CH:23]/[C@@H:24]([CH3:124])[C:25]
(=O)[CH2:26][C@@H:27]([C@H:28]([CH3:128])[CH2:29][C@H:30]2[CH2:31][C@@H:32]
(O[CH3:232])[C@H:33](O)[CH2:34][CH2:35]2)O[C:41](=O)[C@@H:36]2[CH2:37][CH2:38]
[CH2:39][CH2:40]N12
```

The formula of this structure is $\mathrm{C_{51}H_{79}NO_{13}}$.

The fourteen extender units supply consecutive carbon pairs. Each pair below is written as **(original acyl carbonyl carbon, original α-carbon)**:

Acetate-derived pairs	Propionate-derived pairs
(P_1, P_2)	(P_3, P_4)
(P_5, P_6)	(P_9, P_{10})
(P_7, P_8)	(P_{15}, P_{16})
(P_{11}, P_{12})	(P_{17}, P_{18})
(P_{13}, P_{14})	(P_{21}, P_{22})
(P_{19}, P_{20})	(P_{23}, P_{24})
(P_{25}, P_{26})	(P_{27}, P_{28})

Carboxylation converts the acetate- and propionate-derived acyl units into malonyl and methylmalonyl extenders. The **newly added carboxyl carbon** is subsequently lost as $\mathrm{CO_2}$; the original acyl carbonyl carbon remains in the product.

Subsequent reduction, dehydration, cyclization, oxidation and methylation alter functional groups but preserve the identities of the backbone carbons.

The carbon count closes as

$$\underbrace{7(2)}_{\text{acetate units}} + \underbrace{7(3)}_{\text{propionate units}} + \underbrace{7}_{\text{starter}} + \underbrace{6}_{\text{pipecolate}} + \underbrace{3}_{\text{O-methyl groups}} = 51.$$

Feed a: sodium [2,3-$^{13}\mathrm{C_2}$]propionate

Starting-material SMILES:

```
[13CH3][13CH2]C(=O)[O-].[Na+]
```

The labelled methylene carbon becomes the methyl-bearing backbone carbon, and the labelled terminal methyl remains its methyl branch. Therefore circle

$$P_4,\ P_{10},\ P_{16},\ P_{18},\ P_{22},\ P_{24},\ P_{28},$$

and the methyl attached to each one: **14 separate circles**.

The corresponding labelled rapamycin is:

```
C1(=O)C(=O)[C@@]2(O)[13C@H]([13CH3])CC[C@H](O2)C[C@H](OC)/[13C]
([13CH3])=C/C=C/C=C/[13C@@H]([13CH3])C[13C@@H]([13CH3])C(=O)[C@H](OC)[C@H]
(O)/[13C]([13CH3])=C/[13C@@H]([13CH3])C(=O)C[C@@H]([13C@H]
([13CH3])C[C@H]2C[C@@H](OC)[C@H](O)CC2)OC(=O)[C@@H]2CCCCN12
```

Feed b: sodium [1-^{13}C]acetate

Starting-material SMILES:

```
C[13C](=O)[O-].[Na+]
```

The labelled carboxyl carbon becomes the first member of each acetate-derived pair. Therefore circle

$$\boxed{P_1,\ P_5,\ P_7,\ P_{11},\ P_{13},\ P_{19},\ P_{25}}$$

for **7 separate circles**.

The corresponding labelled rapamycin is:

```
[13C]1(=O)C(=O)[C@@]2(O)[C@H](C)[13CH2]C[13C@H](O2)C[C@H](OC)/C(C)=[13CH]/C=
[13CH]/C=C/[C@@H](C)C[C@@H](C)[13C](=O)[C@H](OC)[C@H](O)/C(C)=C/[C@@H](C)[13C]
(=O)C[C@@H]([C@H](C)C[C@H]2C[C@@H](OC)[C@H](O)CC2)OC(=O)[C@@H]2CCCCN12
```

Feed c: sodium [2-^{13}C]acetate

Starting-material SMILES:

```
[13CH3]C(=O)[O-].[Na+]
```

The labelled methyl carbon becomes the second member of each acetate-derived pair. Therefore circle

$$\boxed{P_2,\ P_6,\ P_8,\ P_{12},\ P_{14},\ P_{20},\ P_{26}}$$

for **7 separate circles**.

The corresponding labelled rapamycin is:

```
C1(=O)[13C](=O)[C@@]2(O)[C@H](C)C[13CH2][C@H](O2)[13CH2][C@H]
(OC)/C(C)=C/[13CH]=C/[13CH]=C/[C@@H](C)C[C@@H](C)C(=O)[13C@H](OC)[C@H]
(O)/C(C)=C/[C@@H](C)C(=O)[13CH2][C@@H]([C@H](C)C[C@H]2C[C@@H](OC)[C@H]
(O)CC2)OC(=O)[C@@H]2CCCCN12
```

Under the building-block incorporation model in the question, the starter-derived carbons, pipecolate carbons and three O-methyl carbons receive none of these labels.

The answers were checked against the official answers published by the organisers.

Problem 3: Lanterns and the Burj Khalifa

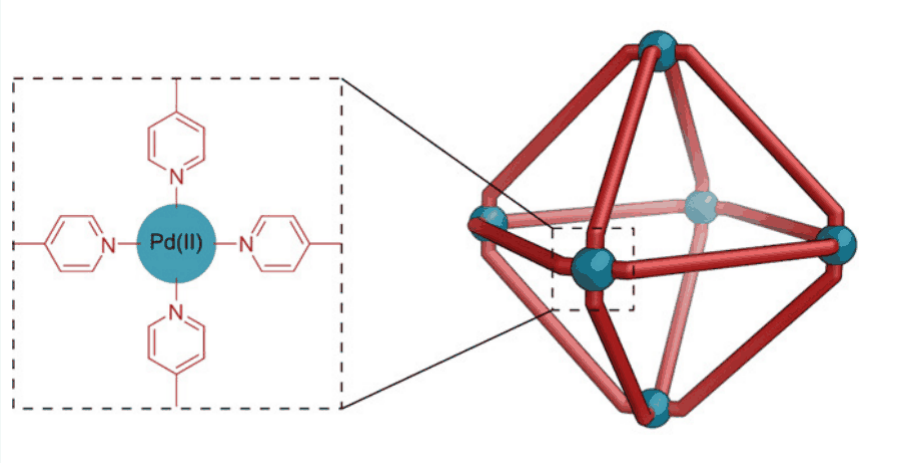
7.5% of the total

3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
6	4	4	5	40	20	32	111

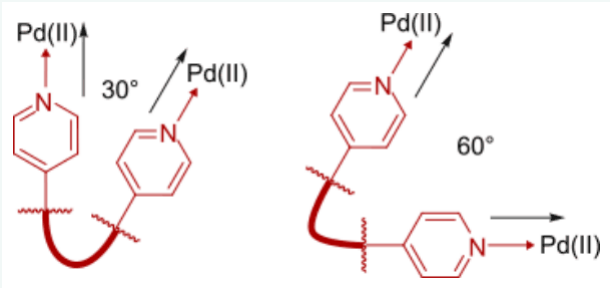


At 829.8 m, Dubai’s Burj Khalifa is the world's tallest structure. To simplify construction, many floors were made from similar pieces. Some artificial "molecular skyscrapers" can be made through coordination chemistry of just two pieces: metal ions and organic ligands.

In these 3D structures, every vertex contains a square planar $\mathrm{Pd(II)}$ ion coordinated to four pyridine ligands. Along each edge is a bent organic ligand consisting of two pyridines linked together.

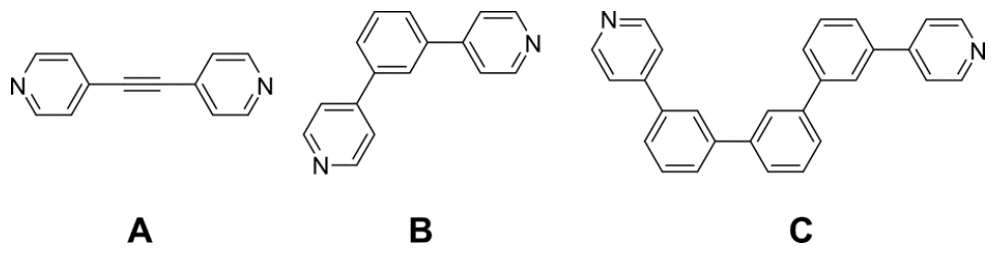


The angle between the two $\mathrm{N} \longrightarrow \mathrm{Pd}$ bonds from the same ligand controls which structure forms. Larger angles give larger structures.

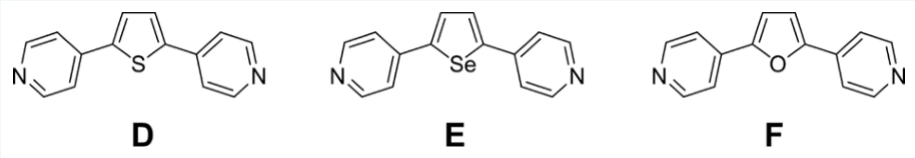


Where free rotation around a bond is possible, the ligand adopts a conformation to form a structure with the smallest possible angle.

3.1 Tick the smallest angle (approximately) between the $\mathrm{N} \longrightarrow \mathrm{Pd}$ bonds which could be achieved by ligands **A, B, and C**.



3.2 Using "<", **rank** ligands **D, E, and F**, from smallest angle to largest angle between the $\mathrm{N} \longrightarrow \mathrm{Pd}$ bonds that they could form.

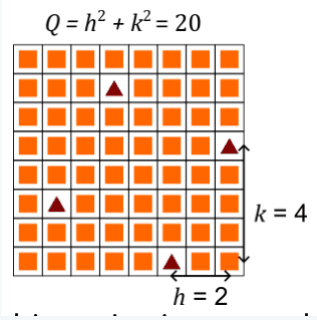


One series of structures can be modelled as polyhedra with tetracoordinated $\mathrm{Pd(II)}$ ions at the vertices. All structures have eight triangular faces (F_3), with various numbers of square faces (F_4).

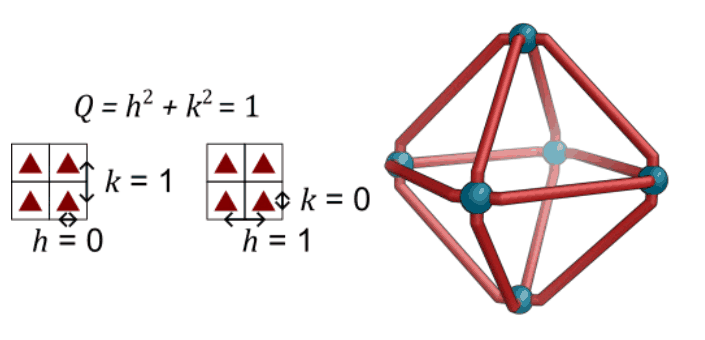
The triangular and square faces can be placed onto a square grid, where the relative position of two nearest triangles is described with integer coordinates h and k. Q is then given by the equation:

$$Q = h^2 + k^2$$

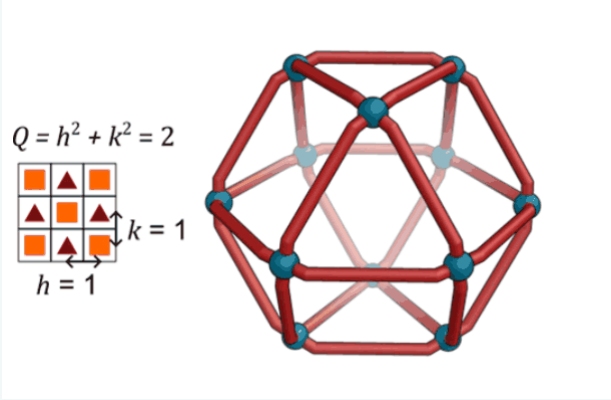
Part of the grid for a structure with $h = 2$ and $k = 4$ is shown below.



The smallest possible structure in this series is an octahedron, where $Q = 1$, and $(h, k) = (0, 1)$ or $(1, 0)$. It has six vertices, eight triangular faces, and 12 edges. Nearest triangles are a move of one face in one direction apart.



The second smallest structure is a cuboctahedron, where $Q = 2$. Nearest triangles are a move of one face in each direction apart.



3.3 Complete the column in the table for $Q = 2$, describing the number of vertices, V, number of edges E, the total number of faces, F, and the number of square faces, F_4.

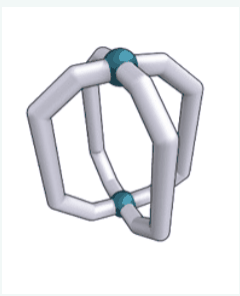
Q	1	2
(h, k)	$(0, 1)$ or $(1, 0)$	$(1, 1)$
V	6	
E	12	
F	8	
F_3	8	8
F_4	0	

All structures obey the following rules:

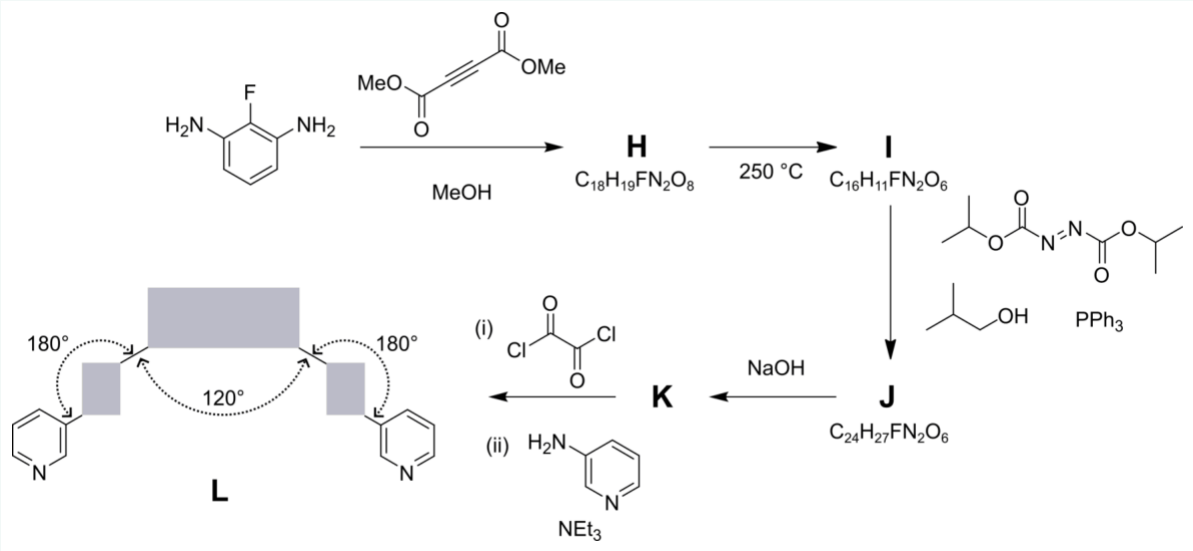
$$V - E + F = 2$$
$$V = 6Q$$
$$F - V = 2$$

3.4 Complete the table for the third smallest structure, where $Q = 4$.

Q	4
(h, k)	
V	
E	
F	
F_3	8
F_4	



In contrast to these large structures, the smallest structures contain two metals and four ligands and are called lanterns. They are similar in shape to the traditional lanterns seen at the Dubai light festival. Lanterns are formed by ligands such as **L**, which make two parallel $\mathrm{N} \longrightarrow \mathrm{Pd}$ bonds. Ligand **L** has two planes of symmetry and can adopt a planar conformation with the angles shown.

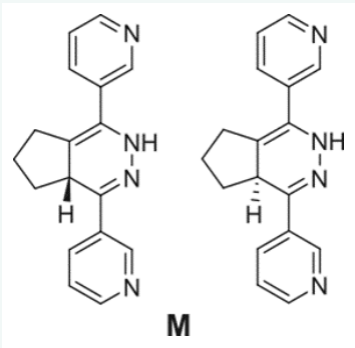


Hint:

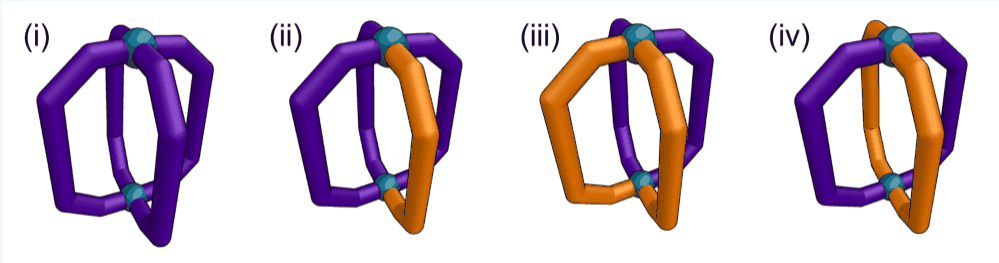
- The transformation from **H** to **I** could also be achieved by Lewis acid catalysis.

3.5 Draw the structures of compounds **H, I, J, K**, and ligand **L**.

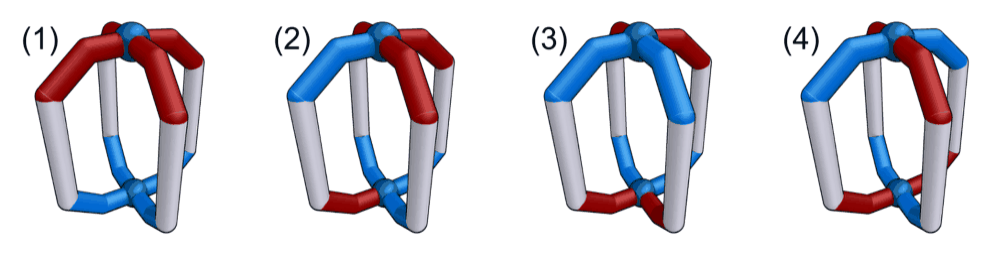
Unlike symmetrical ligand **L**, chiral ligand **M** lacks symmetry and exists as a pair of R and S enantiomers.



Multiple lantern isomers can be formed from ligand **M**. We can group these isomers in two ways. Firstly we categorise by the number of each type of ligand in the lantern: (i) all the same ($RRRR$ or $SSSS$), (ii) one different ($RRRS$ or $SSSR$), (iii) *cis*-$RRSS$, and (iv) *trans*-$RSRS$.



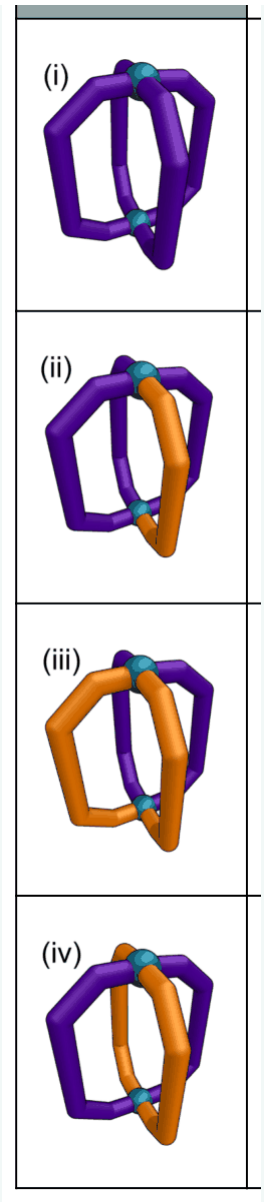
Secondly, the two ends of ligand **M** are not the same; the ligand has a head (H) and a tail (T). There are four categories of structure considering head-to-tail orientation: (1) all up (HHHH), (2) three up (HHHT), (3) *cis*-HHTT, and (4) *trans*-HTHT.



The 16 possible combinations of these categories are represented by empty cells in the table. Some combinations have only one possible isomer, whereas others have multiple possible isomers. In any one combination, all possible isomers are either chiral or achiral.

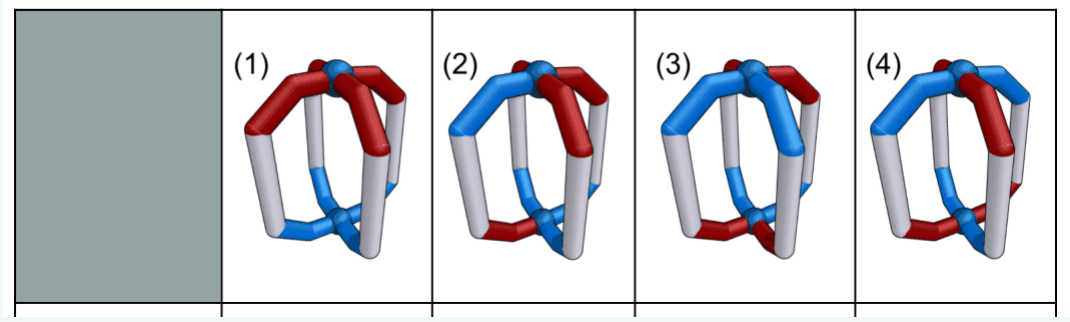
3.6 Complete the table by writing **"C"** for chiral and **"A"** for achiral. **Note**, in this part you will be awarded points for each correct answer but deducted points for each incorrect answer down to a minimum of zero. There is no penalty for empty cells.

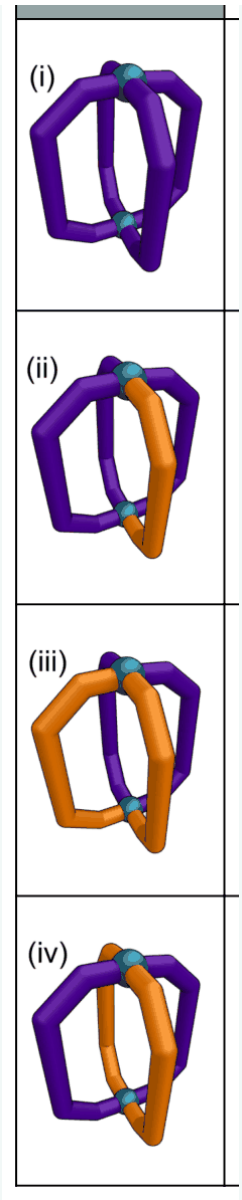
(1)	(2)	(3)	(4)



	(1)	(2)	(3)	(4)
(i)				
(ii)				
(iii)				
(iv)				

3.7 Complete the table with the number of possible isomers of each combination.





	(1)	(2)	(3)	(4)
(i)		2		
(ii)			4	
(iii)				
(iv)				

Official English text of the problem.

Answers

- **3.1:** $\boxed{A : 180^\circ, \quad B : 120^\circ, \quad C : 0^\circ}$.
- **3.2:** $\boxed{F < D < E}$.
- **3.3:** $\boxed{V = 12,\ E = 24,\ F = 14,\ F_4 = 6}$.
- **3.4:** $\boxed{(h, k) = (0, 2) \text{ or } (2, 0),\ V = 24,\ E = 48,\ F = 26,\ F_3 = 8,\ F_4 = 18}$.

- **3.5:** The following structures specify the required drawings.

H — Tetramethyl (2Z,2′Z)-2,2′-[(2-fluorobenzene-1,3-diyl)bis(azanediyl)]bis(but-2-enedioate), the double aza-Michael adduct:

```
COC(=O)/C=C(\Nc1cccc(N/C(=C\C(=O)OC)C(=O)OC)c1F)C(=O)OC
```

I — Dimethyl 9-fluoro-4,5-dihydroxy-1,8-diazaanthracene-2,7-dicarboxylate, shown in its hydroxy tautomer:

```
COC(=O)c1cc(O)c2cc3c(O)cc(C(=O)OC)nc3c(F)c2n1
```

J — Dimethyl 9-fluoro-4,5-bis(2-methylpropoxy)-1,8-diazaanthracene-2,7-dicarboxylate:

```
COC(=O)c1cc(OCC(C)C)c2cc3c(OCC(C)C)cc(C(=O)OC)nc3c(F)c2n1
```

K — 9-Fluoro-4,5-bis(2-methylpropoxy)-1,8-diazaanthracene-2,7-dicarboxylic acid, after acid work-up:

```
O=C(O)c1cc(OCC(C)C)c2cc3c(OCC(C)C)cc(C(=O)O)nc3c(F)c2n1
```

L — 9-Fluoro-4,5-bis(2-methylpropoxy)-N^2,N^7-bis(pyridin-3-yl)-1,8-diazaanthracene-2,7-dicarboxamide:

```
O=C(Nc1cccnc1)c1cc(OCC(C)C)c2cc3c(OCC(C)C)cc(C(=O)Nc4cccnc4)nc3c(F)c2n1
```

- **3.6:** Columns and rows follow the problem's numbering.

Ligand configurations	(1) HHHH	(2) HHHT	(3) cis-HHTT	(4) trans-HTHT
(i) RRRR or SSSS	C	C	C	C
(ii) RRRS or SSSR	C	C	C	C
(iii) cis-RRSS	A	C	A	C
(iv) trans-RSRS	A	C	A	A

- **3.7:** Enantiomers are counted separately.

Ligand configurations	(1) HHHH	(2) HHHT	(3) cis-HHTT	(4) trans-HTHT
(i) RRRR or SSSS	2	2	2	2
(ii) RRRS or SSSR	2	8	4	2
(iii) cis-RRSS	1	4	3	2
(iv) trans-RSRS	1	2	1	1

There are **39 stereoisomers: 7 achiral structures and 16 enantiomeric pairs**.

Solution

3.1 — Minimum angles

The donor direction of a 4-pyridyl group lies along the line joining its nitrogen and its para substituent. Rotating that ring about its attachment bond therefore does not change the donor direction.

- **A**, 1,2-bis(pyridin-4-yl)ethyne, `n1ccc(C#Cc2ccncc2)cc1`, has a linear ethynyl connection. Its two donor vectors point in opposite directions:

$$\boxed{\theta_A = 180^\circ}.$$

- **B**, 1,3-bis(pyridin-4-yl)benzene, `c1cc(-c2ccncc2)cc(-c2ccncc2)c1`, has two outward substituent directions separated by approximately 120° at the central meta-substituted benzene:

$$\boxed{\theta_B = 120^\circ}.$$

- **C**, 1,3-bis[3-(pyridin-4-yl)phenyl]benzene, `c1cc(-c2cccc(-c3ccncc3)c2)cc(-c2cccc(-c3ccncc3)c2)c1`, contains three meta-phenylene bends. Rotation about the inter-ring single bonds permits a folded conformation in which the successive 60° changes of chain direction all have the same sense. The terminal donor vectors then point in the same direction:

$$\boxed{\theta_C = 0^\circ}.$$

For the required drawing of C's minimum-angle conformation, fold the aromatic chain into a U-shaped arrangement with the two terminal $\mathrm{N} \longrightarrow \mathrm{Pd}$ arrows parallel and pointing the same way.

3.2 — Heterocycle-dependent angles

The ligands are:

Ligand	Name	SMILES
D	2,5-Bis(pyridin-4-yl)thiophene	`s1c(-c2ccncc2)ccc1-c1ccncc1`
E	2,5-Bis(pyridin-4-yl)selenophene	`[se]1c(-c2ccncc2)ccc1-c1ccncc1`
F	2,5-Bis(pyridin-4-yl)furan	`o1c(-c2ccncc2)ccc1-c1ccncc1`

The internal $\mathrm{C{-}X{-}C}$ angle at the heteroatom decreases in the order oxygen, sulfur, selenium. The outward directions of the two pyridyl substituents consequently spread farther apart.

In an idealized trigonal-carbon construction, their angle is approximately

$$\theta_{\text{donors}} \simeq 240^\circ - \angle\mathrm{C{-}X{-}C}.$$

Thus,

$$\boxed{F < D < E}.$$

3.3 — Cuboctahedron

The metal is palladium(II), `[Pd+2]`; its four donors are pyridine nitrogens, with pyridine represented by `n1ccccc1`. The local coordination geometry is square planar.

Each vertex has degree four. Counting edge ends gives

$$4V = 2E, \qquad E = 2V.$$

Euler's equation then gives

$$F = 2 - V + E = V + 2.$$

Since eight faces are triangular,

$$F_4 = F - 8 = V - 6.$$

For $Q = 2$,

$$V = 6Q = 12, \qquad E = 24, \qquad F = 14, \qquad F_4 = 6.$$

The completed column is therefore:

Quantity	$Q = 2$
(h, k)	$(1, 1)$
V	12
E	24
F	14
F_3	8
F_4	6

3.4 — Third-smallest structure

For nonnegative grid coordinates,

$$h^2 + k^2 = 4$$

has the solutions $(0, 2)$ and $(2, 0)$. Reversing coordinate directions gives equivalent signed choices.

Using the same relations,

$$V = 6(4) = 24, \qquad E = 2(24) = 48,$$
$$F = 24 + 2 = 26, \qquad F_4 = 26 - 8 = 18.$$

These are the counts of a rhombicuboctahedron.

3.5 — Synthesis and structural identification

The SMILES in **Answers** specify the connectivity of each product.

Formation of H. The starting materials are 2-fluorobenzene-1,3-diamine, `Nc1cccc(N)c1F`, and dimethyl acetylenedicarboxylate, `COC(=O)C#CC(=O)OC`.

Each amino group adds across one electron-poor alkyne. Nitrogen attacks an alkyne carbon, and proton transfer gives an enamine arm:

$$\mathrm{Ar{-}NH{-}C(CO_2Me){=}CH{-}CO_2Me}.$$

Thus two equivalents of the alkyne are incorporated without elimination:

$$\mathrm{C_6H_7FN_2} + 2\,\mathrm{C_6H_6O_4} \longrightarrow \mathrm{C_{18}H_{19}FN_2O_8}.$$

This reproduces H's supplied molecular formula. Draw two identical enamine arms on the original amino nitrogens. In the cyclization-competent arrangement, each nitrogen and the distal ester are on the same side of the alkene.

Formation of I. Each enamine arm cyclizes at the unoccupied ortho position of its attached benzene ring. Fluorine occupies the other ortho position.

The aromatic carbon forms a bond to the **distal ester carbonyl carbon**, closing a six-membered ring. Acyl substitution and proton transfer eliminate methanol, CO, and produce a quinolin-4-one unit. Its hydroxy tautomer is a 4-hydroxyquinoline unit.

Both sides undergo this reaction:

$$\mathrm{C_{18}H_{19}FN_2O_8} \xrightarrow{\Delta} \mathrm{C_{16}H_{11}FN_2O_6} + 2\,\mathrm{CH_3OH}.$$

The formula difference is exactly two methanol molecules. The two new rings share opposite edges of the original benzene, giving the linear 1,8-diazaanthracene framework. Lewis acid activation of the ester carbonyl provides the alternative cyclization route mentioned in the hint.

For the drawing, retain fluorine on the central ring; place ester groups at positions 2 and 7 and hydroxy groups at positions 4 and 5. The corresponding doubly lactamized tautomer represents the same tautomeric system.

Formation of J. I assign this as Mitsunobu etherification of both hydroxy groups with 2-methylpropan-1-ol, `CC(C)CO`.

The reagents are triphenylphosphine, `P(c1ccccc1)(c1ccccc1)c1ccccc1`, and diisopropyl azodicarboxylate, `CC(C)OC(=O)N=NC(=O)OC(C)C`.

Each hydroxy oxygen attacks the activated primary alcohol carbon, installing

$$-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH(CH_3)_2}.$$

Replacing two hydroxy hydrogens with two isobutyl groups adds $\mathrm{C_8H_{16}}$:

$$\mathrm{C_{16}H_{11}FN_2O_6} \longrightarrow \mathrm{C_{24}H_{27}FN_2O_6}.$$

The complete Mitsunobu material balance is

$$\begin{aligned}\mathrm{C_{16}H_{11}FN_2O_6} + 2\,\mathrm{C_4H_{10}O} + 2\,\mathrm{C_{18}H_{15}P} + 2\,\mathrm{C_8H_{14}N_2O_4} \\ \longrightarrow \mathrm{C_{24}H_{27}FN_2O_6} + 2\,\mathrm{C_{18}H_{15}OP} + 2\,\mathrm{C_8H_{16}N_2O_4}.\end{aligned}$$

The additional products are triphenylphosphine oxide, `O=P(c1ccccc1)(c1ccccc1)c1ccccc1`, and diisopropyl hydrazine-1,2-dicarboxylate, `CC(C)OC(=O)NNC(=O)OC(C)C`.

Formation of K. Hydroxide, `[OH-]`, saponifies the two methyl esters:

$$\mathrm{C_{24}H_{27}FN_2O_6} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{C_{22}H_{21}FN_2O_6}^{2-} + 2\,\mathrm{CH_3OH}.$$

The resulting dicarboxylate is

`O=C([O-])c1cc(OCC(C)C)c2cc3c(OCC(C)C)cc(C(=O)[O-])nc3c(F)c2n1`

Acidification with protons, `[H+]`, gives the diacid K:

$$\mathrm{C_{22}H_{21}FN_2O_6}^{2-} + 2\,\mathrm{H^+} \longrightarrow \mathrm{C_{22}H_{23}FN_2O_6}.$$

The alkoxy substituents remain intact.

Formation of L. Oxalyl chloride, `O=C(Cl)C(=O)Cl`, first converts both carboxylic acids to acid chlorides:

$$\mathrm{C_{22}H_{23}FN_2O_6} + 2\,\mathrm{(COCl)_2} \longrightarrow \mathrm{C_{22}H_{21}Cl_2FN_2O_4} + 2\,\mathrm{CO} + 2\,\mathrm{CO_2} + 2\,\mathrm{HCl}.$$

The intermediate is K’s dicarbonyl dichloride:

`O=C(Cl)c1cc(OCC(C)C)c2cc3c(OCC(C)C)cc(C(=O)Cl)nc3c(F)c2n1`

The byproducts are carbon monoxide, `[C-]#[O+]`, carbon dioxide, `O=C=O`, and hydrogen chloride, `Cl`.

Reaction with two equivalents of pyridin-3-amine, `Nc1cccnc1`, forms the two amides. Triethylamine, `CCN(CC)CC`, captures the hydrogen chloride:

$$\mathrm{C_{22}H_{21}Cl_2FN_2O_4} + 2\,\mathrm{C_5H_6N_2} + 2\,\mathrm{NEt_3} \longrightarrow \mathrm{C_{32}H_{31}FN_6O_4} + 2\,\mathrm{[HNEt_3]Cl}.$$

Triethylammonium chloride is `CC[NH+](CC)CC.[Cl-]`.

Each terminal connection in L must therefore be

$$\mathrm{core}-\mathrm{C}(=\mathrm{O})-\mathrm{NH}-(\text{pyridin-3-yl}).$$

For the requested ligand drawing, place the two amide–pyridyl arms as mirror-related arms on the fused core. Use the indicated 120° relationship between the core's exit directions and the indicated 180° arrangements in the arms. Orient the terminal pyridine rings so that their two $\mathrm{N} \longrightarrow \mathrm{Pd}$ vectors are parallel. These conformational choices are not encoded by ordinary connectivity SMILES.

3.6 — Chirality of the lanterns

The supplied ligand M is a cyclopentane-fused dipyridyl dihydropyridazine. Its enantiomers can be represented as:

- R**-M:** `C1(c2cccnc2)=C2CCC[C@H]2C(c2cccnc2)=NN1`
- S**-M:** `C1(c2cccnc2)=C2CCC[C@@H]2C(c2cccnc2)=NN1`

Number the four ligand positions $0, 1, 2, 3$ around the metal–metal axis. At each position record two attributes: R/S, and whether the head or tail lies at the upper metal.

There are eight proper rotations that can identify arrangements:

1. Four rotations about the metal–metal axis, giving cyclic permutations.
2. Four half-turns about perpendicular axes. These reverse cyclic order and interchange upper and lower ends, so they also interchange H and T.

Proper rotations **never interchange** R **and** S.

To test chirality, reflect the cage through its equatorial plane. This interchanges $R \leftrightarrow S$ and H↔T at every position. An arrangement is achiral precisely when a proper rotation superposes it on this reflected arrangement.

For rows **(i)** and **(ii)**, reflection changes the numbers of R and S ligands. A rotation cannot undo that change. Every entry in these rows is therefore **C**.

For the two balanced rows:

- **HHHH:** Both cis-RRSS and trans-RSRS permit a vertical reflection exchanging the appropriate R and S positions. Both are **A**.
- **HHHT:** The unique reversed ligand prevents a symmetry operation from exchanging all R and S positions while preserving the head pattern. Both are **C**.
- **cis-HHTT:** With cis-RRSS, inversion exchanges both pairs of attributes correctly. With trans-RSRS, a suitable vertical reflection does so. Both are **A**.
- **trans-HTHT:** The cis-RRSS combination lacks the required improper symmetry and is **C**. The trans-RSRS combination has an improper fourfold rotation, S_4, and is **A**.

The last case illustrates why absence of an obvious mirror plane alone does not establish chirality: an S_4 operation also makes a structure achiral.

3.7 — Number of isomers

We identify arrangements only under the eight **proper rotations** described above. Mirror-related structures remain separate unless superposable.

Before rotational identification, the numbers of head patterns in columns (1)–(4) are

$$\mathbf{n} = (2, 8, 4, 2).$$

These count HHHH/TTTT, the eight three-to-one patterns, the four adjacent two-to-two patterns, and the two alternating patterns.

Row (i): all configurations the same.

For fixed RRRR, all head patterns within each column are equivalent under rotations. Thus there is one arrangement per column. SSSS supplies its distinct enantiomer:

$$\boxed{(2, 2, 2, 2)}.$$

Row (ii): one configuration different.

Fix the position of the unique S ligand in RRRS. Two proper rotations preserve this R/S pattern: the identity and a perpendicular half-turn through the unique ligand and the opposite ligand.

The half-turn complements the head pattern and fixes none of the labeled head assignments. There are consequently $\mathbf{n}/2$ arrangements for RRRS. The SSSR enantiomeric composition doubles this:

$$\boxed{(2, 8, 4, 2)}.$$

Row (iii): cis-RRSS.

Fix the cyclic pattern RRSS. Its preserving rotation group has two elements. The nonidentity element exchanges the two R positions, exchanges the two S positions, and complements H/T.

Its numbers of fixed head assignments are

$$\mathbf{f} = (0, 0, 2, 2).$$

Burnside's counting formula gives

$$\frac{\mathbf{n} + \mathbf{f}}{2} = \frac{(2, 8, 4, 2) + (0, 0, 2, 2)}{2} = \boxed{(1, 4, 3, 2)}.$$

Row (iv): trans-RSRS.

The alternating R/S pattern has four preserving proper rotations. Apart from the identity, the axial half-turn fixes

$$\mathbf{g} = (2, 0, 0, 2)$$

head assignments. Neither perpendicular half-turn fixes a head assignment, because each would have to complement H/T at a position it leaves fixed.

Thus,

$$\frac{\mathbf{n} + \mathbf{g}}{4} = \frac{(2, 8, 4, 2) + (2, 0, 0, 2)}{4} = \boxed{(1, 2, 1, 1)}.$$

As an independent check, there are initially $2^4 \times 2^4 = 256$ labeled assignments. Burnside's formula over all eight proper rotations gives

$$N = \frac{256 + 2(4) + 16 + 2(0) + 2(16)}{8} = \boxed{39}.$$

Summing the entries marked A gives seven achiral structures. The remaining $39 - 7 = 32$ structures form sixteen enantiomeric pairs.

The answers were checked against the official answers published by the organisers.

Problem 4: The life of tennis balls

6% of the total

4.1	4.2	4.3	4.4	Total
3	16	5	16	40



This problem honours the incredible Rafael Nadal, a true tennis icon who concluded his remarkable career in 2024.

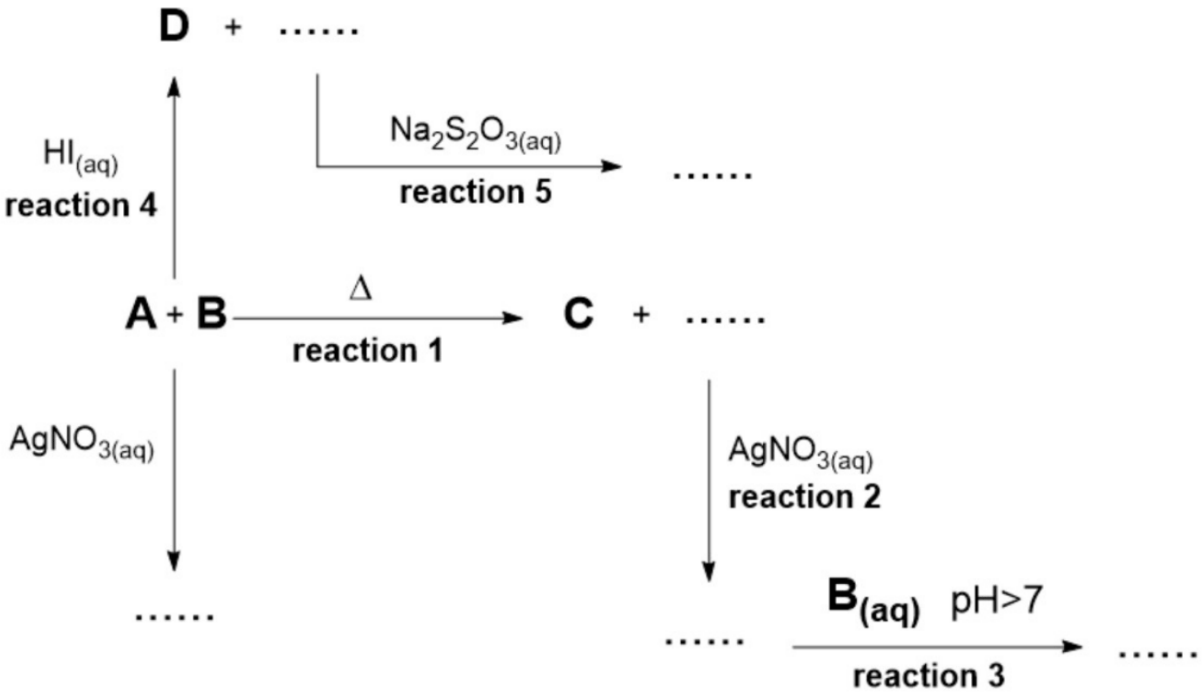
The Dubai Tennis Championships is a prestigious tournament held annually in UAE. Many of the world's top players, including Rafael Nadal, Roger Federer, Novak Djokovic, and Andy Murray have won titles there.

The composition of tennis balls has evolved over hundreds of years. To ensure a good bounce, the inside of modern tennis balls is pressurised above atmospheric pressure. However, old hollow tennis balls just contained air at atmospheric pressure.

In this problem, assume tennis balls have an inner radius of $R = 3.0\,\mathrm{cm}$ that remains constant throughout the pressurisation process. Assume that the composition of air is 20% $\mathrm{O_2}$ and 80% $\mathrm{N_2}$ by volume. Consider that overpressure does not expand the ball.

4.1 Calculate the mass m (in g) of air inside an old tennis ball at $T_0 = 25\,^{\circ}\mathrm{C}$.

Chemists then discovered how to pressurise a ball above atmospheric pressure using a reaction between compounds **A** and **B**, which forms gas **C** (to create additional inner pressure) plus other non-gaseous products.



A capsule with a quantity $m_{\text{mix}} = 0.3389\,\text{g}$ of a stoichiometric mixture of two white inorganic compounds **A** and **B** was placed inside a ball filled with air at atmospheric pressure. They reacted completely inside the ball upon heating to form gas **C** and other products (**reaction 1**) to produce an overall pressure inside the ball of $p = 1.600\,\text{atm}$ (at $25\,^{\circ}\text{C}$). Once this ball was opened, all residue inside was collected and dissolved in water. The dropping of silver nitrate in that solution gave a white precipitate (**reaction 2**). This collected precipitate could be partially dissolved in a concentrated aqueous solution of **B**. By increasing the pH of this mixture, the precipitate dissolved completely (**reaction 3**). If the same initial capsule of **A+B** is dissolved in water and concentrated solution of silver nitrate added, $m_{\text{precipitate}} = 0.8224\,\text{g}$ of white precipitate formed which was approximately twice the mass of precipitate formed in **reaction 2**.

When the capsule of **A+B** dissolved in a solution of HI the formation of gas **D** started, and the solution turned brown (**reaction 4**). Upon further addition of sodium thiosulfate this colour disappeared (**reaction 5**).

The densities of gases **C** and **D** differ by no more than 10%.

4.2 Write the chemical formulae of compounds **A–D**.

4.3 Write equations for **reactions 1–5**.

The pressure inside modern tennis balls is $p_0 = 1.80\,\text{atm}$. They are sold in a pressurised can, with the same pressure in the can as in the ball to stop gas coming out during storage.

Standard balls contain air and premium balls contain pure N_2. Once the can is opened, depressurisation begins, and the gas diffuses out of the balls until the internal pressure reaches atmospheric pressure. Assume there is no diffusion of gas into the balls at any point. The activation energy for the depressurisation of a premium ball is $E_A = 50.0\,\text{kJ}\,\text{mol}^{-1}$.

The rate of ball depressurisation (pressure/time) could be described by similar equations of those used in chemical kinetics. At $T_0 = 25.0\ ^\circ\mathrm{C}$, once the can is opened, the premium balls depressurise to $p_1 = 1.40\ \mathrm{atm}$ after $t_1 = 241\ \mathrm{h}$ and to $p_2 = 1.19\ \mathrm{atm}$ after about $t_2 = 21$ days. The initial depressurisation rate of regular balls is 10% faster than premium balls.

4.4a Demonstrate that the depressurisation process follows the first kinetic order by **calculating** the depressurisation rate constant $k_{\mathrm{N_2}}$ for $\mathrm{N_2}$ in $\mathrm{h^{-1}}$.

Note: If you couldn't calculate the answer, use $k_{\mathrm{N_2}} = 10^{-3}\ \mathrm{h^{-1}}$ in further calculations.

4.4b Calculate the (depressurisation) rate constant $k_{\mathrm{O_2}}$ for $\mathrm{O_2}$ in $\mathrm{h^{-1}}$, **assuming** the rates for both gases are additive.

As well as today being the IChO 2025 theory paper, it is also (perhaps less importantly) the Semi-Finals day at Wimbledon. Amanda Anisimova will start a match in $t_{\mathrm{match}} = 12.0\ \mathrm{h}$ from now. The weather today in Wimbledon is predicted to be a constant $T_W = 30.0\ ^\circ\mathrm{C}$. Assume a new set of **premium balls**, which were manufactured and placed in the can at $T_0 = 25.0\ ^\circ\mathrm{C}$, are opened now and quickly change to $T_W = 30.0\ ^\circ\mathrm{C}$.

4.4c Calculate the pressure p_{start} (in atm) of the balls at the start of the match.

Periodic table and data sheet

Physical constants and formulae

Avogadro constant	N_A	$6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
molar gas constant	R	$8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	F	$96485\ \mathrm{C\,mol^{-1}}$
Planck constant	h	$6.626 \times 10^{-34}\ \mathrm{J\,s}$
speed of light in vacuum	c	$2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}$
mass of electron	m_e	$9.109 \times 10^{-31}\ \mathrm{kg}$
charge of electron	e	$1.602 \times 10^{-19}\ \mathrm{C}$
atmospheric pressure	p_{atm}	$101325\ \mathrm{Pa}$
ionic product of water at 298 K	K_W	10^{-14}

$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
$1\ \mathrm{Å} = 1 \times 10^{-10}\ \mathrm{m}$
$1\ \mathrm{pm} = 1 \times 10^{-12}\ \mathrm{m}$
$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
$1\ \mathrm{kWh} = 3600\ \mathrm{kJ}$
$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
$1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$

area of triangle	$A = \frac{1}{2}ab \cdot \sin C$
volume of cube	$V = a^3$
volume of sphere	$V = \frac{4}{3}\pi r^3$

surface area of sphere	$S = 4\pi r^2$
ideal gas equation	$pV = nRT$
frequency of light	$\nu = \frac{c}{\lambda}$
energy of a photon	$E = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon c d$
spin-only magnetic moment	$\mu = \sqrt{n(n+2)}\,\mathrm{BM}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
0^{th} order integrated rate law	$[A] = [A]_0 - kt$
1^{st} order integrated rate law	$\ln[A] = \ln[A]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-E_a/(RT)}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}}$
Clausius-Clapeyron equation	$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
specific heat	$Q = mC_p\Delta T$
boiling point elevation	$\Delta T = iK_b m_i$
freezing point depression	$\Delta T = iK_f m_i$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of $1\,\mathrm{mol\,dm^{-3}}$.

Periodic table

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Official English text of the problem.

Answers

- **4.1:** $m = 0.133\ \mathrm{g}$, or $0.13\ \mathrm{g}$ to two significant figures.
- **4.2: A:** $\mathrm{NaNO_2}$, sodium nitrite, `[Na+].[O-]N=O`; **B:** $\mathrm{NH_4Cl}$, ammonium chloride, `[NH4+].[Cl-]`; **C:** $\mathrm{N_2}$, nitrogen, `N#N`; **D:** NO, nitrogen monoxide (nitric oxide), `[N]=O`.
- **4.3:** Balanced equations, using net ionic forms where appropriate:

$$\begin{aligned}
&(1)\quad \mathrm{NaNO_2 + NH_4Cl \xrightarrow{\Delta} N_2 + NaCl + 2\,H_2O}\\
&(2)\quad \mathrm{Ag^+ + Cl^- \longrightarrow AgCl(s)}\\
&(3)\quad \mathrm{AgCl(s) + 2\,NH_4{}^+ + 2\,OH^- \longrightarrow [Ag(NH_3)_2]^+ + Cl^- + 2\,H_2O}\\
&(4)\quad \mathrm{2\,NO_2{}^- + 4\,H^+ + 2\,I^- \longrightarrow 2\,NO(g) + I_2 + 2\,H_2O}\\
&(5)\quad \mathrm{I_2 + 2\,S_2O_3{}^{2-} \longrightarrow 2\,I^- + S_4O_6{}^{2-}}
\end{aligned}$$

  Names and SMILES for the additional species are supplied in the solution.
- **4.4a:** First order in excess pressure $p - p_{\mathrm{atm}}$, with

$$\boxed{k_{\mathrm{N_2}} = 2.88 \times 10^{-3}\ \mathrm{h^{-1}}}.$$

- **4.4b:**

$$\boxed{k_{\mathrm{O_2}} = 4.31 \times 10^{-3}\ \mathrm{h^{-1}}}.$$

- **4.4c:**

$$\boxed{p_{\mathrm{start}} = 1.79\ \mathrm{atm}}.$$

Solution

4.1

To distinguish the ball radius from the gas constant, write the radius as $r = 0.030\ \mathrm{m}$. The internal volume is

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (0.030\ \mathrm{m})^3 = 1.13097 \times 10^{-4}\ \mathrm{m^3}.$$

At $T_0 = 298.15\ \mathrm{K}$, the amount of air is

$$n_{\mathrm{air}} = \frac{p_{\mathrm{atm}} V}{R T_0} = \frac{101325 (1.13097 \times 10^{-4})}{8.314 (298.15)} = 4.62300 \times 10^{-3}\ \mathrm{mol}.$$

For ideal gases, volume fractions equal mole fractions. The components are oxygen, $\mathrm{O_2}$, `O=O`, and nitrogen, $\mathrm{N_2}$, `N#N`. Thus

$$\overline{M} = 0.20 (2 \times 16.00) + 0.80 (2 \times 14.01) = 28.816\ \mathrm{g\,mol^{-1}}.$$

Therefore,

$$m = n_{\mathrm{air}} \overline{M} = (4.62300 \times 10^{-3})(28.816) = 0.133216\ \mathrm{g}.$$

$$\boxed{m \approx 0.133\ \mathrm{g} \approx 0.13\ \mathrm{g}\ \text{to two significant figures.}}$$

4.2

The additional pressure comes from gas **C**. Because the volume and final temperature are unchanged,

$$n_C = \frac{(p - p_{\mathrm{atm}})V}{RT_0} = 0.600\, n_{\mathrm{air}} = 2.77380 \times 10^{-3}\,\mathrm{mol}.$$

The qualitative observations identify the reactants as follows.

The white precipitate from the final residue is consistent with silver chloride, AgCl. Its dissolution upon increasing the pH in a solution of **B** indicates ammonia complex formation: raising the pH converts ammonium ions into ammonia, which dissolves silver chloride as the diamminesilver(I) ion. This points to ammonium chloride as **B**.

The other reactant must generate a gas with ammonium ions on heating and oxidize iodide to iodine in acid. Nitrite satisfies both requirements:

$$\mathrm{NH_4{}^+ + NO_2{}^- \xrightarrow{\Delta} N_2 + 2\,H_2O},$$

while acidified nitrite oxidizes iodide and is reduced to nitrogen monoxide. Consequently, **C** is nitrogen and **D** is nitrogen monoxide.

Their molar masses are

$$M_C = 28.02\,\mathrm{g\,mol^{-1}}, \qquad M_D = 30.01\,\mathrm{g\,mol^{-1}}.$$

At equal temperature and pressure, gas density is proportional to molar mass, so

$$\frac{\rho_D - \rho_C}{\rho_C} = \frac{30.01 - 28.02}{28.02} = 0.0710 = 7.10\%,$$

which satisfies the stated limit.

The silver-precipitation data identify the cation of **A**. Before heating, both chloride and nitrite precipitate:

$$\mathrm{Ag^+ + Cl^- \longrightarrow AgCl\,(s)}, \qquad \mathrm{Ag^+ + NO_2{}^- \longrightarrow AgNO_2\,(s)}.$$

For a 1:1 mixture of a monovalent metal nitrite and ammonium chloride, each mole of reaction mixture gives one mole of each precipitate. Their molar masses are

$$M(\mathrm{AgCl}) = 107.87 + 35.45 = 143.32\,\mathrm{g\,mol^{-1}},$$
$$M(\mathrm{AgNO_2}) = 107.87 + 14.01 + 32.00 = 153.88\,\mathrm{g\,mol^{-1}}.$$

Thus the initial precipitate corresponds to

$$n = \frac{0.8224}{143.32 + 153.88} = 2.76716 \times 10^{-3}\,\mathrm{mol}.$$

Since

$$M(\mathrm{NH_4Cl}) = 14.01 + 4(1.008) + 35.45 = 53.492\,\mathrm{g\,mol^{-1}},$$

the inferred molar mass of **A** is

$$M_A = \frac{0.3389}{2.76716 \times 10^{-3}} - 53.492 = 68.980\,\mathrm{g\,mol^{-1}}.$$

Subtracting the nitrite contribution gives the cation mass:

$$68.980 - (14.01 + 32.00) = 22.970\,\mathrm{g\,mol^{-1}},$$

matching sodium, $22.99\,\mathrm{g\,mol^{-1}}$. Hence **A** is sodium nitrite.

The complete identification is therefore:

Compound	Formula	Name	SMILES
A	$\mathrm{NaNO_2}$	Sodium nitrite	`[Na+].[O-]N=O`
B	$\mathrm{NH_4Cl}$	Ammonium chloride	`[NH4+].[Cl-]`
C	$\mathrm{N_2}$	Nitrogen	`N#N`
D	NO	Nitrogen monoxide (nitric oxide)	`[N]=O`

A direct check using the proposed mixture gives

$$n_{\text{reaction}} = \frac{0.3389}{69.00 + 53.492} = 2.76671 \times 10^{-3}\,\text{mol}.$$

This predicts

$$m_{\text{initial precipitate}} = n_{\text{reaction}}(143.32 + 153.88) = 0.82227\,\text{g},$$

in agreement with $0.8224\,\text{g}$. After heating, only the chloride precipitate remains:

$$m_{\text{reaction 2}} = n_{\text{reaction}}(143.32) = 0.39653\,\text{g}.$$

Their ratio is

$$\frac{0.82227}{0.39653} = 2.0737,$$

consistent with “approximately twice.” The predicted final pressure is $1.5985\,\text{atm}$, consistent with the stated $1.600\,\text{atm}$ given the two-significant-figure radius.

4.3

Reaction 1: thermal production of nitrogen

$$\boxed{\mathrm{NaNO_2 + NH_4Cl \xrightarrow{\Delta} N_2\,(g) + NaCl + 2\,H_2O}}$$

Nitrogen in ammonium has oxidation state -3, while nitrogen in nitrite has oxidation state $+3$. Both become nitrogen in oxidation state zero. At the final temperature, water is treated as a condensed product under the problem's stated model.

Reaction 2: precipitation of silver chloride

$$\boxed{\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)}}$$

The sodium chloride residue supplies the chloride ions.

Reaction 3: dissolution through ammonia complex formation

Increasing the pH releases ammonia:

$$\mathrm{NH_4{}^+\,(aq) + OH^-\,(aq) \longrightarrow NH_3\,(aq) + H_2O\,(l)}.$$

Ammonia binds silver(I), shifting the dissolution equilibrium:

$$\boxed{\mathrm{AgCl\,(s) + 2\,NH_3\,(aq) \rightleftharpoons [Ag(NH_3)_2]^+\,(aq) + Cl^-\,(aq)}}.$$

Combining these equations gives an equivalent overall equation that explicitly includes **B**'s ammonium ions and the added base:

$$\mathrm{AgCl(s) + 2\,NH_4^+(aq) + 2\,OH^-(aq) \longrightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq) + 2\,H_2O(l)}.$$

Reaction 4: oxidation of iodide by acidified nitrite

Nitrite is reduced from nitrogen oxidation state $+3$ to $+2$, while iodide is oxidized to iodine:

$$\mathrm{NO_2^- + 2\,H^+ + e^- \longrightarrow NO + H_2O},$$
$$\mathrm{2\,I^- \longrightarrow I_2 + 2\,e^-}.$$

Adding the half-reactions gives

$$\boxed{\mathrm{2\,NO_2^-(aq) + 4\,H^+(aq) + 2\,I^-(aq) \longrightarrow 2\,NO(g) + I_2(aq) + 2\,H_2O(l)}}.$$

The liberated iodine accounts for the brown colour.

Reaction 5: reduction of iodine by thiosulfate

$$\boxed{\mathrm{I_2(aq) + 2\,S_2O_3^{2-}(aq) \longrightarrow 2\,I^-(aq) + S_4O_6^{2-}(aq)}}.$$

Iodine is reduced to iodide, while thiosulfate is oxidized to tetrathionate, removing the brown colour.

The additional species used above have the following names and SMILES:

Formula	Name	SMILES
NaCl	Sodium chloride	`[Na+].[Cl-]`
$\mathrm{H_2O}$	Water	`O`
$\mathrm{Ag^+}$	Silver(I) ion	`[Ag+]`
$\mathrm{Cl^-}$	Chloride ion	`[Cl-]`
AgCl	Silver(I) chloride	`[Ag+].[Cl-]`
$\mathrm{AgNO_2}$	Silver(I) nitrite	`[Ag+].[O-]N=O`
$\mathrm{NH_4^+}$	Ammonium ion	`[NH4+]`
$\mathrm{OH^-}$	Hydroxide ion	`[OH-]`
$\mathrm{NH_3}$	Ammonia	`N`
$\mathrm{[Ag(NH_3)_2]^+}$	Diamminesilver(I) ion	`[NH3]->[Ag+]<-[NH3]`
$\mathrm{NO_2^-}$	Nitrite ion	`[O-]N=O`
$\mathrm{H^+}$	Hydrogen ion, proton	`[H+]`
$\mathrm{I^-}$	Iodide ion	`[I-]`
$\mathrm{I_2}$	Iodine	`II`
$\mathrm{S_2O_3^{2-}}$	Thiosulfate ion	`[O-]S(=O)(=O)[S-]`
$\mathrm{S_4O_6^{2-}}$	Tetrathionate ion	`[O-]S(=O)(=O)SSS(=O)(=O)[O-]`

Dot-separated salt SMILES specify constituent ions rather than a crystal lattice. The dative-bond SMILES for diamminesilver(I) does not specify its approximately linear $\mathrm{N{-}Ag{-}N}$ coordination geometry.

4.4a

The pressure approaches atmospheric pressure. The quantity that decays to zero is therefore the excess pressure

$$q = p - p_{\mathrm{atm}}.$$

For first-order depressurisation,

$$-\frac{dq}{dt} = k_{\mathrm{N_2}} q, \qquad q(t) = q_0 e^{-k_{\mathrm{N_2}} t}.$$

Hence

$$k_{\mathrm{N_2}} = \frac{1}{t} \ln\left(\frac{p_0 - p_{\mathrm{atm}}}{p(t) - p_{\mathrm{atm}}}\right).$$

Using the first measurement,

$$k_{\mathrm{N_2}} = \frac{1}{241\,\mathrm{h}} \ln\left(\frac{1.80 - 1.00}{1.40 - 1.00}\right) = \frac{\ln 2}{241\,\mathrm{h}} = 2.87613 \times 10^{-3}\,\mathrm{h^{-1}}.$$

Using the second measurement, with $21\,\mathrm{days} = 504\,\mathrm{h}$,

$$k_{\mathrm{N_2}} = \frac{1}{504\,\mathrm{h}} \ln\left(\frac{1.80 - 1.00}{1.19 - 1.00}\right) = 2.85236 \times 10^{-3}\,\mathrm{h^{-1}}.$$

These values agree within about 0.8%, consistent with the approximate second time and rounded pressures. In particular, the first value predicts

$$p(504\,\mathrm{h}) = 1.00 + 0.80 e^{-(2.87613\times10^{-3})(504)} = 1.18774\,\mathrm{atm},$$

which rounds to the stated $1.19\,\mathrm{atm}$.

Thus the data support first-order decay of excess pressure, with

$$\boxed{k_{\mathrm{N_2}} = 2.88 \times 10^{-3}\,\mathrm{h^{-1}}}.$$

4.4b

At the same initial excess pressure q_0, the premium ball has initial rate

$$v_{\mathrm{premium},0} = k_{\mathrm{N_2}} q_0.$$

For the stated additive-rate model, the initial rate for air is the composition-weighted sum:

$$v_{\mathrm{air},0} = (0.80 k_{\mathrm{N_2}} + 0.20 k_{\mathrm{O_2}}) q_0.$$

The air-filled ball initially depressurises 10% faster, so

$$0.80 k_{\mathrm{N_2}} + 0.20 k_{\mathrm{O_2}} = 1.10 k_{\mathrm{N_2}}.$$

Therefore,

$$k_{\mathrm{O_2}} = \frac{1.10 - 0.80}{0.20} k_{\mathrm{N_2}} = 1.50 k_{\mathrm{N_2}},$$

and

$$\boxed{k_{\mathrm{O_2}} = 1.50(2.87613 \times 10^{-3}) = 4.31 \times 10^{-3}\,\mathrm{h^{-1}}}.$$

4.4c

First, calculate the rate constant at $30.0\,^{\circ}\mathrm{C}$:

$$T_0 = 298.15\,\mathrm{K}, \qquad T_W = 303.15\,\mathrm{K}.$$

The Arrhenius equation gives

$$\ln\left(\frac{k_W}{k_0}\right) = \frac{E_A}{R}\left(\frac{1}{T_0} - \frac{1}{T_W}\right).$$

Therefore,

$$\frac{k_W}{k_0} = \exp\left[\frac{50000}{8.314}\left(\frac{1}{298.15} - \frac{1}{303.15}\right)\right] = 1.39471,$$

$$k_W = (2.87613 \times 10^{-3})(1.39471) = 4.01137 \times 10^{-3}\,\mathrm{h}^{-1}.$$

The rapid temperature change also raises the pressure immediately. At constant volume and before appreciable gas loss,

$$p(0^+) = p_0\frac{T_W}{T_0} = 1.80\frac{303.15}{298.15} = 1.83019\,\mathrm{atm}.$$

The resulting excess pressure then decays for $12.0\,\mathrm{h}$:

$$p_{\mathrm{start}} = p_{\mathrm{atm}} + \left[p(0^+) - p_{\mathrm{atm}}\right]e^{-k_W t_{\mathrm{match}}}.$$

Substitution gives

$$p_{\mathrm{start}} = 1.000 + (1.83019 - 1.000)e^{-(4.01137\times10^{-3})(12.0)} = 1.79117\,\mathrm{atm}.$$

$$\boxed{p_{\mathrm{start}} = 1.79\,\mathrm{atm}}.$$

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 5: Solar-powered multi-stage flash desalination

6.5% of the total

5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	Total
2	2	3	2	2	2	1	2	16

Freshwater is scarce in the arid climate of the UAE. The country relies on solar-powered desalination plants to produce freshwater. A Dubai desalination plant uses a multi-stage flash (MSF) desalination process. In MSF desalination, seawater is heated by passing through a series of heat exchangers to raise its temperature, reaching its saturation temperature at a high pressure. When pressure is reduced, this superheated seawater gives off pure water vapour to become saturated again, a process known as flashing.



Assume seawater in Dubai is at $T_0 = 25.00\,^\circ\mathrm{C}$ and is an aqueous solution of 3.45 % mass NaCl. Assume complete ionisation of NaCl in water.

The boiling point of seawater is higher than pure water. The boiling point elevation constant, $K_\mathrm{b} = 0.5120\,\mathrm{K\,kg\,mol^{-1}}$.

5.1 Calculate the boiling point, T, (in °C) of Dubai seawater at atmospheric pressure.

If you couldn't calculate the answer, use a temperature of 373.50 K for further calculations.

5.2 Calculate the percentage mass of NaCl, w_{NaCl}, in water that has a boiling point, $T_{\mathrm{b}} = 378.00\,\mathrm{K}$.

5.3 The boiling point of seawater also increases as pressure increases. **Calculate** the boiling point, T, (in °C) of the **initial Dubai seawater** at a pressure, $p = 2.50\,\mathrm{atm}$. The latent heat of vaporisation of water, $E_{\mathrm{vap}} = 2260\,\mathrm{kJ\,kg^{-1}}$ (40.716 kJ/mol). Assume this is the same for seawater.

In the plant, a flash chamber (of volume, $V = 100\,\mathrm{L}$) contains a mass of 1.00 kg of seawater (l) at $T_1 = 90.0\,^{\circ}\mathrm{C}$.

Another mass of 1.00 kg of seawater is then overheated to $T_2 = 110.0\,^{\circ}\mathrm{C}$ at high pressure before being added to this chamber, where a reduction in pressure causes some water to turn into steam.

After equilibrium was established, the temperature in the chamber was $T_{\mathrm{f}} = 97.0\,^{\circ}\mathrm{C}$. Assume there was no loss of energy, and that the latent heat of vaporisation is independent of temperature.

The specific heat capacity of seawater, $C_{\mathrm{p}} = 3.85\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$, assumed to be independent of temperature. The density of seawater, $d = 1025\,\mathrm{kg\,m^{-3}}$.

5.4 Calculate the amount, n, (in mol) of water that vapourised, assuming that the latent heat of vaporization does not depend on pressure, and that the heat capacity of water vapor in the chamber is negligible.

If you couldn't calculate the answer, use 0.56 mol for further calculations.

5.5 Assuming the **initial** vapour pressure before addition of the overheated water in the chamber was $p_{\mathrm{i}} = 0.690\,\mathrm{atm}$, **calculate** the final vapour pressure, p_{f}, (in atm) in the chamber assuming the water vapour behaves as an ideal gas.

5.6 Calculate the thermal energy, E, (in kWh) required to heat a mass of 1.00 kg of seawater from $T_1 = 25.0\,^{\circ}\mathrm{C}$ to $T_2 = 110.0\,^{\circ}\mathrm{C}$.

If you couldn't calculate the answer, use 0.1 kWh for further calculations.

5.7 A plant produces 50,000 $\mathrm{m^3}$ of pure water per day. The plant passes Dubai seawater through 30 flash cycles and overall can extract 85% of the water present. **Calculate** the mass, m, (in kg) of Dubai seawater needed per day.

If you couldn't calculate the answer, use 6.0×10^7 *kg for further calculations.*

Plants make efficient use of heat exchangers to save energy. We can assume the total energy required by the plant is the same as the energy needed to heat all the seawater from $T_1 = 25.0\,^{\circ}\mathrm{C}$ to $T_2 = 110.0\,^{\circ}\mathrm{C}$.

5.8 Assuming a 10 $\mathrm{m^2}$ solar panel has a power of 2.00 kW averaged during the 12 operational hours every day and the efficiency of using energy is 67%, **calculate** the number of panels, N, required for the plant.

Periodic table and data sheet

Physical constants and formulae

Avogadro constant	N_A	$6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
molar gas constant	R	$8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	F	$96485\ \mathrm{C\,mol^{-1}}$
Planck constant	h	$6.626 \times 10^{-34}\ \mathrm{J\,s}$
speed of light in vacuum	c	$2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}$
mass of electron	m_e	$9.109 \times 10^{-31}\ \mathrm{kg}$
charge of electron	e	$1.602 \times 10^{-19}\ \mathrm{C}$
atmospheric pressure	p_atm	$101325\ \mathrm{Pa}$
ionic product of water at 298 K	K_w	10^{-14}

$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
$1\ \text{Å} = 1 \times 10^{-10}\ \mathrm{m}$
$1\ \mathrm{pm} = 1 \times 10^{-12}\ \mathrm{m}$
$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
$1\ \mathrm{kWh} = 3600\ \mathrm{kJ}$
$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
$1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$

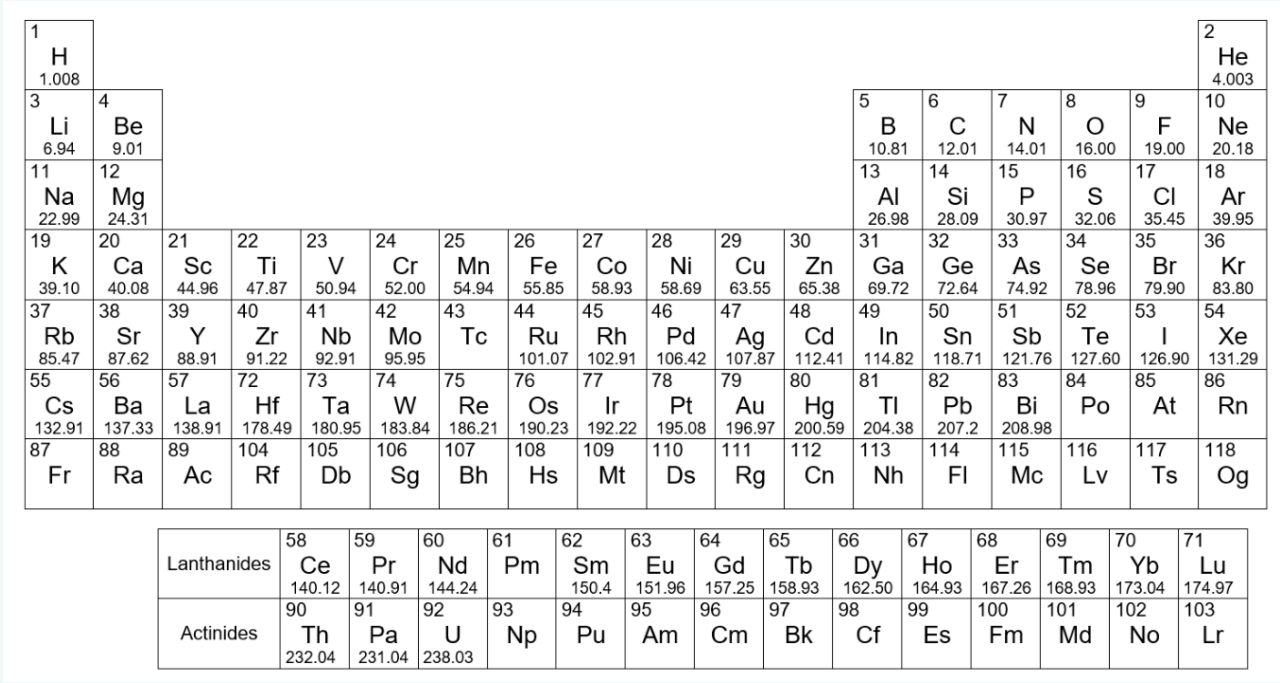
area of triangle	$A = \frac{1}{2}ab \cdot \sin C$
volume of cube	$V = a^3$
volume of sphere	$V = \frac{4}{3}\pi r^3$
surface area of sphere	$S = 4\pi r^2$
ideal gas equation	$pV = nRT$
frequency of light	$\nu = \frac{c}{\lambda}$
energy of a photon	$E = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon c d$
spin-only magnetic moment	$\mu = \sqrt{n(n+2)}\ \mathrm{BM}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
0^th order integrated rate law	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
1^st order integrated rate law	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-E_\mathrm{a}/RT}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_\mathrm{r}G^\circ = -RT\ln K = -nFE^\circ_\mathrm{cell}$

Clausius-Clapeyron equation	$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
specific heat	$Q = mC_{\text{p}}\Delta T$
boiling point elevation	$\Delta T = iK_{\text{b}}m_i$
freezing point depression	$\Delta T = iK_{\text{f}}m_i$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of $1\,\text{mol}\,\text{dm}^{-3}$.

Periodic table



Official English text of the problem.

Answers

- **5.1:** $T = 100.63\,^{\circ}\text{C}$.
- **5.2:** $w_{\text{NaCl}} = 21.7\%$ by mass.
- **5.3:** $T = 128.7\,^{\circ}\text{C}$.
- **5.4:** $n = 0.567\,\text{mol}$.
- **5.5:** $p_{\text{f}} = 0.886\,\text{atm}$, accounting for the volume occupied by liquid.
- **5.6:** $E = 0.0909\,\text{kWh}$.
- **5.7:** $m \approx 6.1 \times 10^{7}\,\text{kg}$ of seawater per day.
- **5.8:** $N \approx 3.4 \times 10^{5}$ panels; the nominal calculation gives a minimum of **344,422 panels**.

Parts 5.7–5.8 use $\rho_{\text{pure water}} = 1000\,\text{kg}\,\text{m}^{-3}$.

Solution

The relevant species are water, $\mathrm{H_2O}$, SMILES `O`; sodium ion, $\mathrm{Na^+}$, SMILES `[Na+]`; and chloride ion, $\mathrm{Cl^-}$, SMILES `[Cl-]`. Sodium chloride, NaCl, has the ionic SMILES representation `[Na+].[Cl-]`.

5.1 — Boiling point at atmospheric pressure (2 points)

Complete ionisation gives two ions per formula unit:

$$\mathrm{NaCl(s)} \longrightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}.$$

Thus the van 't Hoff factor is $i = 2$. From the periodic table,

$$M(\mathrm{NaCl}) = 22.99 + 35.45 = 58.44\,\mathrm{g\,mol^{-1}}.$$

Take $100.00\,\mathrm{g}$ of seawater. It contains $3.45\,\mathrm{g}$ of salt and $96.55\,\mathrm{g} = 0.09655\,\mathrm{kg}$ of water. Its molality is

$$b = \frac{3.45\,\mathrm{g}/(58.44\,\mathrm{g\,mol^{-1}})}{0.09655\,\mathrm{kg}} = 0.611444\,\mathrm{mol\,kg^{-1}}.$$

The boiling point elevation is

$$\Delta T_\mathrm{b} = iK_\mathrm{b}b = 2(0.5120)(0.611444) = 0.626119\,\mathrm{K}.$$

Pure water boils at $100.00\,^\circ\mathrm{C}$ at atmospheric pressure, so

$$\boxed{T = 100.63\,^\circ\mathrm{C}}.$$

The corresponding absolute temperature, retained for part 5.3, is $373.776119\,\mathrm{K}$.

5.2 — Salt mass percentage for a boiling point of 378.00 K (2 points)

At atmospheric pressure,

$$\Delta T_\mathrm{b} = 378.00 - 373.15 = 4.85\,\mathrm{K}.$$

Therefore,

$$b = \frac{\Delta T_\mathrm{b}}{iK_\mathrm{b}} = \frac{4.85}{2(0.5120)} = 4.736328\,\mathrm{mol\,kg^{-1}}.$$

For $1.000\,\mathrm{kg}$ of water, the required salt mass is

$$m_\mathrm{NaCl} = (4.736328\,\mathrm{mol})(58.44\,\mathrm{g\,mol^{-1}}) = 276.791\,\mathrm{g}.$$

The mass percentage uses the total solution mass:

$$w_\mathrm{NaCl} = \frac{276.791}{1000 + 276.791} \times 100\% = 21.6786\%.$$

$$\boxed{w_\mathrm{NaCl} = 21.7\%}.$$

5.3 — Boiling point at 2.50 atm (3 points)

Use the boiling point of the initial seawater from part 5.1 as the reference:

$$P_\mathrm{ref} = 1.00\,\mathrm{atm}, \qquad T_\mathrm{ref} = 373.776119\,\mathrm{K}.$$

With the given constant molar enthalpy of vaporisation,

$$\Delta H_\mathrm{vap} = 40716\,\mathrm{J\,mol^{-1}},$$

the Clausius–Clapeyron equation gives

$$\ln\left(\frac{P}{P_{\mathrm{ref}}}\right) = \frac{\Delta H_{\mathrm{vap}}}{R}\left(\frac{1}{T_{\mathrm{ref}}} - \frac{1}{T}\right).$$

Rearranging,

$$T = \left[\frac{1}{T_{\mathrm{ref}}} - \frac{R}{\Delta H_{\mathrm{vap}}}\ln\left(\frac{P}{P_{\mathrm{ref}}}\right)\right]^{-1}.$$

Substitution yields

$$T = \left[\frac{1}{373.776119} - \frac{8.314}{40716}\ln(2.50)\right]^{-1} = 401.881381\,\mathrm{K}.$$

Thus,

$$\boxed{T = 128.7\,^{\circ}\mathrm{C}}.$$

5.4 — Amount of water vaporised (2 points)

The hot seawater releases heat as it cools from $110.0\,^{\circ}\mathrm{C}$ to $97.0\,^{\circ}\mathrm{C}$:

$$Q_{\mathrm{hot}} = m_2 C_{\mathrm{p}}(T_2 - T_{\mathrm{f}}) = (1.00)(3.85)(110.0 - 97.0) = 50.05\,\mathrm{kJ}.$$

Heating the initial seawater from $90.0\,^{\circ}\mathrm{C}$ to $97.0\,^{\circ}\mathrm{C}$ consumes

$$Q_{\mathrm{cold}} = m_1 C_{\mathrm{p}}(T_{\mathrm{f}} - T_1) = (1.00)(3.85)(97.0 - 90.0) = 26.95\,\mathrm{kJ}.$$

With no heat loss and negligible heat capacity of the vapour, the remaining energy causes vaporisation:

$$\mathrm{H_2O\,(l)} \longrightarrow \mathrm{H_2O\,(g)}.$$

Consequently,

$$n\Delta H_{\mathrm{vap}} = Q_{\mathrm{hot}} - Q_{\mathrm{cold}} = 23.10\,\mathrm{kJ}.$$

$$n = \frac{23.10\,\mathrm{kJ}}{40.716\,\mathrm{kJ\,mol^{-1}}} = 0.567345\,\mathrm{mol}.$$

$$\boxed{n = 0.567\,\mathrm{mol}}.$$

The corresponding mass evaporated is

$$m_{\mathrm{evap}} = \frac{23.10}{2260} = 0.0102212\,\mathrm{kg}.$$

5.5 — Final vapour pressure (2 points)

The initial vapour remains in the chamber, and the newly evaporated water adds to it. Both the temperature change and the change in vapour-space volume must be included.

Initially,

$$T_{\mathrm{i}} = 363.15\,\mathrm{K}, \qquad V_{\mathrm{g,i}} = V - \frac{m_1}{d} = 0.100 - \frac{1.00}{1025} = 0.0990244\,\mathrm{m^3}.$$

The initial amount of vapour is therefore

$$n_{\mathrm{i}} = \frac{p_{\mathrm{i}} V_{\mathrm{g,i}}}{R T_{\mathrm{i}}} = \frac{(0.690 \times 101325)(0.0990244)}{(8.314)(363.15)} = 2.29304\,\mathrm{mol}.$$

The final liquid mass is

$$m_{\mathrm{l,f}} = 1.00 + 1.00 - m_{\mathrm{evap}} = 1.989779\,\mathrm{kg}.$$

Using the given liquid density,

$$V_{\mathrm{g,f}} = 0.100 - \frac{1.989779}{1025} = 0.0980588\,\mathrm{m^3}.$$

At $T_{\mathrm{f}} = 370.15\,\mathrm{K}$,

$$n_{\mathrm{f}} = n_{\mathrm{i}} + n = 2.29304 + 0.567345 = 2.86039\,\mathrm{mol}.$$

Thus,

$$p_{\mathrm{f}} = \frac{n_{\mathrm{f}} R T_{\mathrm{f}}}{V_{\mathrm{g,f}}} = \frac{(2.86039)(8.314)(370.15)}{0.0980588} = 8.9769 \times 10^4\,\mathrm{Pa},$$

and

$$\boxed{p_{\mathrm{f}} = 0.886\,\mathrm{atm}}.$$

If the liquid volume is neglected and the vapour volume is approximated as $100\,\mathrm{L}$ throughout, the corresponding approximation is

$$p_{\mathrm{f}} = p_{\mathrm{i}}\frac{T_{\mathrm{f}}}{T_{\mathrm{i}}} + \frac{nRT_{\mathrm{f}}}{V} = 0.876\,\mathrm{atm}.$$

5.6 — Energy required to heat 1.00 kg of seawater (2 points)

The temperature increase is

$$\Delta T = 110.0 - 25.0 = 85.0\,\mathrm{K}.$$

Therefore,

$$E = mC_{\mathrm{p}}\Delta T = (1.00\,\mathrm{kg})(3.85\,\mathrm{kJ\,kg^{-1}\,K^{-1}})(85.0\,\mathrm{K}) = 327.25\,\mathrm{kJ}.$$

Using $1\,\mathrm{kWh} = 3600\,\mathrm{kJ}$,

$$E = \frac{327.25}{3600} = 0.0909028\,\mathrm{kWh}.$$

$$\boxed{E = 0.0909\,\mathrm{kWh}}.$$

5.7 — Daily seawater requirement (1 point)

Using the usual approximation $\rho_{\text{pure water}} = 1000\,\mathrm{kg\,m^{-3}}$, the daily product mass is

$$m_{\mathrm{product}} = (50000\,\mathrm{m^3})(1000\,\mathrm{kg\,m^{-3}}) = 5.0000 \times 10^7\,\mathrm{kg}.$$

The water mass fraction of the feed is

$$w_{\mathrm{water}} = 1 - 0.0345 = 0.9655.$$

Since 85% of this water is recovered,

$$m_{\mathrm{product}} = 0.85(0.9655)m.$$

Hence,

$$m = \frac{5.0000 \times 10^7}{0.85(0.9655)} = 6.09255 \times 10^7\,\mathrm{kg}.$$

$$\boxed{m \approx 6.1 \times 10^7\,\mathrm{kg\,per\,day}}.$$

The stated 85% is the overall recovery across all 30 cycles, so it is applied once.

5.8 — Number of solar panels (2 points)

Under the stated heat-recovery assumption, the daily thermal requirement is the energy needed to heat the entire daily seawater feed once:

$$E_{\text{day}} = m\left(0.0909028\,\text{kWh}\,\text{kg}^{-1}\right) = 5.53829 \times 10^{6}\,\text{kWh}.$$

Each panel supplies useful energy per day of

$$E_{\text{panel}} = (2.00\,\text{kW})(12\,\text{h})(0.67) = 16.08\,\text{kWh}.$$

The given $2.00\,\text{kW}$ is already the power of one complete $10\,\text{m}^2$ panel.

Therefore,

$$N = \frac{E_{\text{day}}}{E_{\text{panel}}} = \frac{5.53829 \times 10^{6}}{16.08} = 344421.23.$$

Rounding upward to a whole number gives the nominal minimum:

$$\boxed{N_{\text{min}} = 344422\ \text{panels}}.$$

At the precision of the supplied efficiency,

$$\boxed{N \approx 3.4 \times 10^{5}\ \text{panels}}.$$

The solution was checked against the official solution.

Problem 6: Solar energy conversion by CO2 reduction

6. Solar energy conversion by CO_2 reduction

6% of the total

6.1	6.2	6.3	6.4	6.5	6.6	6.7	Total
5	2	3	3	3	2	4	22

Use the following data to solve this problem. Assume enthalpy and entropy changes of reactions do not depend on temperature.

	$\text{CO}_2\,(\text{g})$	$\text{CO}\,(\text{g})$	$\text{O}_2\,(\text{g})$	$\text{Zn}\,(\text{s})$	$\text{Zn}\,(\text{l})$	$\text{Zn}\,(\text{g})$	$\text{ZnO}\,(\text{s})$
$\Delta_{\text{f}}H^{\circ}_{298}\,/\,\text{kJ}\,\text{mol}^{-1}$	−393.5	−110.5			6.5	130.4	−350.5
$S^{\circ}_{298}\,/\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$	213.8	197.7	205.1	41.7	50.8	161.0	43.7
Melting Point / K				692.7			2247
Boiling Point / K					1180		

Photochemical reduction of carbon dioxide is a promising approach both for solar energy conversion and for reduction of CO_2 content in the atmosphere. There are several ways to convert CO_2 to CO and other useful substances.

Direct decomposition

Direct decomposition of CO_2 to CO and O_2 is a highly endothermic process which requires a large amount of energy – from heat or from light.

6.1 Estimate the temperature (in K) at which half of $\mathrm{CO_2}$ decomposes at equilibrium at a total pressure of 1 bar.

Catalytic decomposition

The use of metal/metal oxide catalytic systems allows the temperature of $\mathrm{CO_2}$ decomposition to be significantly reduced and eases the separation of the gaseous products by using thermochemical cycles.

Consider a catalytic cycle based on the $\mathrm{Zn/ZnO}$ system and containing two reactions. The net reaction is $\mathrm{CO_2}$ decomposition into CO and $\mathrm{O_2}$. **Reaction 1** is exothermic, while **Reaction 2** is highly endothermic – the reactants should be heated to the required temperature.

6.2 Write equations for **Reaction 1** and **Reaction 2**.

The operating temperature for **Reaction 1** is 1073 K.

6.3 Calculate the equilibrium constant, K, for **Reaction 1** and **find** the degree of $\mathrm{CO_2}$ conversion, x, at this temperature.

Reaction 2 is performed at the much higher temperature of 2000 K.

6.4 Calculate the equilibrium pressure of oxygen, $p(\mathrm{O_2})$, in bar, at this temperature.

Photocatalytic reduction

Photocatalytic reduction of $\mathrm{CO_2}$ with water is akin to natural photosynthesis. Plants convert $\mathrm{CO_2}$ to carbohydrates as an energy source, but human civilisation needs hydrocarbons to produce energy. On the way from $\mathrm{CO_2}$ to $\mathrm{C}_x\mathrm{H}_y$ there are many possible intermediate products of $\mathrm{CO_2}$ reduction.

6.5 Complete the table with the formulae of the **one-carbon** species from $\mathrm{CO_2}$ reduction, containing only H and/or O atoms in addition to the **one** C. The oxidation number of the carbon in each species is shown. For the oxidation state +2 give the formulae of both an anion **"anion"** and a neutral molecule **"neutral molecule"**. **Indicate** only **one** species in each box.

+3	+2 (anion)	+2 (neutral molecule)	0	−2	−4

Visible light ($400\,\mathrm{nm} < \lambda < 700\,\mathrm{nm}$) makes up >40% of the total solar radiation reaching Earth. Light can be absorbed by semiconductors or dyes, leading to electronic excitation which can promote redox reactions. The band gaps of some common semiconductors are listed.

Semiconductor	CdS	Ge	Si	SiC	$\mathrm{WO_3}$	$\mathrm{ZrO_2}$
Band gap / eV	2.4	0.67	1.1	3.2	2.8	5.0

6.6 Tick which semiconductor(s) can be excited by visible light to serve as a potential photocatalyst(s). **Support** your answer with calculations.

In an early photocatalysis experiment, SiC semiconductor was suspended in $V = 100\,\mathrm{mL}$ of water, and $\mathrm{CO_2}$ was bubbled through at a rate of $v = 3.0\,\mathrm{L\,min^{-1}}$ ($T = 25\,^\circ\mathrm{C}$, $p = 1\,\mathrm{atm}$). The suspension was irradiated by a $P = 500\,\mathrm{W}$ lamp ($\lambda = 365\,\mathrm{nm}$) for $t = 7\,\mathrm{h}$. After irradiation, the solution contained $c(\mathrm{HCHO}) = 1.0 \times 10^{-3}\,\mathrm{M}$ and $c(\mathrm{CH_3OH}) = 5.4 \times 10^{-3}\,\mathrm{M}$.

The apparent quantum yield ϕ is defined as:

$$\phi = \frac{N_e}{N_i},$$

where N_e is the number of electrons transferred and N_i is the number of incident photons.

6.7 Calculate the total degree of $\mathrm{CO_2}$ conversion, η, and the apparent quantum yield of photocatalytic reduction, ϕ.

Periodic table and data sheet

Physical constants and formulae

Avogadro constant	N_A	$6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
molar gas constant	R	$8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$
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ionic product of water at 298 K	K_{W}	10^{-14}

$1\,\mathrm{nm} = 1 \times 10^{-9}\,\mathrm{m}$
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$0\,^{\circ}\mathrm{C} = 273.15\,\mathrm{K}$
$1\,\mathrm{kWh} = 3600\,\mathrm{kJ}$
$1\,\mathrm{W} = 1\,\mathrm{J\,s^{-1}}$
$1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$
$1\,\mathrm{bar} = 10^{5}\,\mathrm{Pa}$

area of triangle	$A = \frac{1}{2}ab \cdot \sin C$
volume of cube	$V = a^3$
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1^{st} order integrated rate law	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$

Arrhenius equation	$k = A \cdot e^{-E_a/(RT)}$
enthalpy	$H = U + pV$
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specific heat	$Q = mC_p\Delta T$
boiling point elevation	$\Delta T = iK_b m_i$
freezing point depression	$\Delta T = iK_f m_i$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of $1\ \mathrm{mol\,dm^{-3}}$.

Official English text of the problem.

Answers

- **6.1:** $\boxed{T \approx 3.04 \times 10^3\ \mathrm{K}}$.
- **6.2:** At the stated operating temperatures:
- Reaction 1: $\boxed{\mathrm{Zn\,(l) + CO_2\,(g) \longrightarrow ZnO\,(s) + CO\,(g)}}$.
- Reaction 2: $\boxed{\mathrm{ZnO\,(s) \longrightarrow Zn\,(g) + \tfrac{1}{2}\,O_2\,(g)}}$.
- **6.3:** For Reaction 1 as written, $\boxed{K = 2.46 \times 10^2}$ and $\boxed{x = 0.99595 \approx 99.6\%}$.
- **6.4:** $\boxed{p(\mathrm{O_2}) = 0.121\ \mathrm{bar}}$.
- **6.5:** Fill the boxes, from left to right, with: $\mathrm{CO_2^{\bullet-}}$ — carbon dioxide radical anion, `[O-][C]=O`; $\mathrm{HCOO^-}$ — formate, `O=C[O-]`; CO — carbon monoxide, `[C-]#[O+]`; HCHO — formaldehyde, `C=O`; $\mathrm{CH_3OH}$ — methanol, `CO`; $\mathrm{CH_4}$ — methane, `C`.
- **6.6:** Tick $\boxed{\mathrm{CdS},\ \mathrm{Ge},\ \mathrm{Si},\ \mathrm{WO_3}}$.
- **6.7:** $\boxed{\eta \approx 1.2 \times 10^{-5} = 0.0012\%}$ and $\boxed{\phi \approx 9.5 \times 10^{-5} = 0.0095\%}$.

Solution

Use the standard pressure $p^\circ = 1\ \mathrm{bar}$, dimensionless gas activities p_i/p°, and unit activities for pure solid and liquid phases. The standard formation enthalpies of $\mathrm{O_2\,(g)}$ and $\mathrm{Zn\,(s)}$ are zero.

The molecular species appearing in the reaction equations include carbon dioxide, $\mathrm{CO_2}$, `O=C=O`; carbon monoxide, CO, `[C-]#[O+]`; dioxygen, $\mathrm{O_2}$, `O=O`; and water, $\mathrm{H_2O}$, `O`. The dioxygen SMILES does not encode its triplet electronic ground state. The metals, metal oxides and other solid semiconductors are extended phases whose crystal structures are not represented by molecular SMILES.

6.1

Write the decomposition per mole of carbon dioxide:

$$\mathrm{CO_2\,(g)} \rightleftharpoons \mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)}.$$

Starting with $1.00\,\mathrm{mol}$ of pure carbon dioxide, 50% decomposition gives

$$n(\mathrm{CO_2}) = 0.50\,\mathrm{mol}, \qquad n(\mathrm{CO}) = 0.50\,\mathrm{mol}, \qquad n(\mathrm{O_2}) = 0.25\,\mathrm{mol}.$$

The total amount is $1.25\,\mathrm{mol}$. At a total pressure of $1\,\mathrm{bar}$,

$$p(\mathrm{CO_2}) = 0.40\,\mathrm{bar}, \qquad p(\mathrm{CO}) = 0.40\,\mathrm{bar}, \qquad p(\mathrm{O_2}) = 0.20\,\mathrm{bar}.$$

Therefore, the required equilibrium constant is

$$K = \frac{[p(\mathrm{CO})/p^\circ]\,[p(\mathrm{O_2})/p^\circ]^{1/2}}{p(\mathrm{CO_2})/p^\circ} = \frac{0.40\sqrt{0.20}}{0.40} = \sqrt{0.20} = 0.447214.$$

The standard reaction enthalpy and entropy are

$$\Delta_\mathrm{r}H^\circ = -110.5 - (-393.5) = 283.0\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_\mathrm{r}S^\circ = 197.7 + \frac{1}{2}(205.1) - 213.8 = 86.45\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

Using

$$\Delta_\mathrm{r}H^\circ - T\Delta_\mathrm{r}S^\circ = -RT\ln K,$$

we obtain

$$T = \frac{\Delta_\mathrm{r}H^\circ}{\Delta_\mathrm{r}S^\circ - R\ln K} = \frac{283000}{86.45 - 8.314\ln(0.447214)} = 3038.4\,\mathrm{K}.$$

Thus,

$$\boxed{T \approx 3.04 \times 10^3\,\mathrm{K}}.$$

6.2

In Reaction 1, zinc is oxidized from oxidation state 0 to $+2$, while carbon is reduced from $+4$ in carbon dioxide to $+2$ in carbon monoxide:

$$\boxed{\mathrm{Zn\,(l)} + \mathrm{CO_2\,(g)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{CO\,(g)}}.$$

Zinc is liquid at $1073\,\mathrm{K}$, since

$$692.7 < 1073 < 1180.$$

Zinc oxide remains solid. The enthalpy change is

$$\begin{aligned}\Delta_\mathrm{r}H_1^\circ &= [-350.5 + (-110.5)] - [6.5 + (-393.5)] \\ &= -74.0\,\mathrm{kJ\,mol^{-1}},\end{aligned}$$

confirming that Reaction 1 is exothermic.

Reaction 2 regenerates zinc by decomposing zinc oxide:

$$\boxed{\mathrm{ZnO\,(s)} \longrightarrow \mathrm{Zn\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)}}.$$

At $2000\,\mathrm{K}$, zinc is gaseous because this temperature exceeds its boiling point, while zinc oxide is still solid because $2000 < 2247\,\mathrm{K}$. Its reaction enthalpy is

$$\Delta_\mathrm{r}H_2^\circ = 130.4 - (-350.5) = 480.9\,\mathrm{kJ\,mol^{-1}},$$

so it is highly endothermic.

The zinc vapor is cooled and condensed before reuse in Reaction 1. Including this physical recycling step, $\mathrm{Zn\,(g)} \longrightarrow \mathrm{Zn\,(l)}$, the net chemical reaction is

$$\mathrm{CO_2\,(g)} \longrightarrow \mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)}.$$

6.3

For Reaction 1,

$$\Delta_\mathrm{r} S_1^\circ = 43.7 + 197.7 - 50.8 - 213.8 = -23.2\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

At $1073\,\mathrm{K}$,

$$\begin{aligned}\Delta_\mathrm{r} G_1^\circ &= \Delta_\mathrm{r} H_1^\circ - T\Delta_\mathrm{r} S_1^\circ \\ &= -74000 - 1073(-23.2) \\ &= -49106.4\,\mathrm{J\,mol^{-1}}.\end{aligned}$$

Hence,

$$K = \exp\left(-\frac{\Delta_\mathrm{r} G_1^\circ}{RT}\right) = \exp\left(\frac{49106.4}{8.314(1073)}\right) = 245.83.$$

Thus,

$$\boxed{K = 2.46 \times 10^2}.$$

With pure liquid zinc and solid zinc oxide present,

$$K = \frac{p(\mathrm{CO})}{p(\mathrm{CO_2})}.$$

Starting with carbon dioxide and no carbon monoxide, let x be the fraction of carbon dioxide converted. The carbon monoxide and remaining carbon dioxide amounts are proportional to x and $1 - x$, respectively. Therefore,

$$K = \frac{x}{1-x}, \qquad x = \frac{K}{1+K}.$$

This gives

$$\boxed{x = \frac{245.83}{246.83} = 0.99595 \approx 99.6\%}.$$

This equilibrium conversion assumes sufficient zinc is available.

6.4

For

$$\mathrm{ZnO\,(s)} \rightleftharpoons \mathrm{Zn\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)},$$

the entropy change is

$$\Delta_\mathrm{r} S_2^\circ = 161.0 + \frac{1}{2}(205.1) - 43.7 = 219.85\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

At $2000\,\mathrm{K}$,

$$\Delta_\mathrm{r} G_2^\circ = 480900 - 2000(219.85) = 41200\,\mathrm{J\,mol^{-1}}.$$

Thus,

$$K_2 = \exp\left(-\frac{41200}{8.314(2000)}\right) = 0.083932.$$

Because zinc is gaseous, its partial pressure must appear in the equilibrium expression:

$$K_2 = \frac{p(\mathrm{Zn})}{p^\circ}\left(\frac{p(\mathrm{O_2})}{p^\circ}\right)^{1/2}.$$

For gases generated solely by zinc oxide decomposition, the stoichiometry gives

$$n(\mathrm{Zn}) = 2n(\mathrm{O_2}), \qquad p(\mathrm{Zn}) = 2p(\mathrm{O_2}).$$

Consequently,

$$K_2 = 2\left(\frac{p(\mathrm{O_2})}{p^\circ}\right)^{3/2},$$

and

$$p(\mathrm{O_2}) = p^\circ\left(\frac{K_2}{2}\right)^{2/3} = (1\ \mathrm{bar})\left(\frac{0.083932}{2}\right)^{2/3}.$$

Therefore,

$$\boxed{p(\mathrm{O_2}) = 0.121\ \mathrm{bar}}.$$

6.5

Assign hydrogen oxidation number $+1$ and oxygen oxidation number -2. The sum of the oxidation numbers equals the overall charge.

Carbon oxidation number	Species to enter	Name and SMILES	Oxidation-number check
$+3$	$\mathrm{CO_2^{\bullet -}}$	Carbon dioxide radical anion, `[O-][C]=O`	$+3 + 2(-2) = -1$
$+2$, anion	$\mathrm{HCOO^-}$	Formate ion, `O=C[O-]`	$+2 + 1 + 2(-2) = -1$
$+2$, neutral molecule	CO	Carbon monoxide, `[C-]#[O+]`	$+2 - 2 = 0$
0	HCHO	Formaldehyde (methanal), `C=O`	$0 + 2(+1) - 2 = 0$
-2	$\mathrm{CH_3OH}$	Methanol, `CO`	$-2 + 4(+1) - 2 = 0$
-4	$\mathrm{CH_4}$	Methane, `C`	$-4 + 4(+1) = 0$

The $+3$ species results from one-electron reduction of carbon dioxide. Its SMILES represents one localized Lewis structure; it does not encode the bent geometry or resonance delocalization. The formal charges in carbon monoxide's SMILES are distinct from its oxidation numbers.

6.6

The energy of a photon is

$$E = \frac{hc}{\lambda}.$$

Using the supplied constants,

$$E\,(\mathrm{eV}) = \frac{(6.626 \times 10^{-34})(2.998 \times 10^{8})}{\lambda\,(\mathrm{nm}) \times 10^{-9}(1.602 \times 10^{-19})} \approx \frac{1240}{\lambda\,(\mathrm{nm})}.$$

At the boundaries of the visible range,

$$E(400\,\text{nm}) \approx 3.10\,\text{eV}, \qquad E(700\,\text{nm}) \approx 1.77\,\text{eV}.$$

A photon can excite an electron across the band gap when $E \geq E_g$. Equivalently, the longest wavelength capable of excitation is

$$\lambda_{\max}\,(\text{nm}) \approx \frac{1240}{E_g\,(\text{eV})}.$$

Semiconductor	E_g / eV	Approximate $\lambda_{\max}$ / nm	Visible-light excitation
Cadmium sulfide, CdS	2.4	517	Tick
Germanium, Ge	0.67	1850	Tick
Silicon, Si	1.1	1130	Tick
Silicon carbide, SiC	3.2	388	Leave unticked
Tungsten(VI) oxide, WO_3	2.8	443	Tick
Zirconium(IV) oxide, ZrO_2	5.0	248	Leave unticked

Thus,

$$\boxed{\text{CdS, Ge, Si, WO}_3}.$$

Germanium and silicon qualify because visible photons have more energy than their band gaps. This calculation establishes optical excitation; band gaps alone do not establish the suitability of the band-edge potentials for a particular redox reaction.

6.7

The irradiation and gas-flow duration is

$$t = 7(60) = 420\,\text{min} = 25200\,\text{s}.$$

The total volume of carbon dioxide supplied, measured at the stated inlet conditions, is

$$V_{\text{feed}} = (3.0\,\text{L min}^{-1})(420\,\text{min}) = 1260\,\text{L} = 1.260\,\text{m}^3.$$

At $25\,^\circ\text{C} = 298.15\,\text{K}$ and $1\,\text{atm} = 101325\,\text{Pa}$,

$$n_{\text{feed}}(\text{CO}_2) = \frac{pV_{\text{feed}}}{RT} = \frac{101325(1.260)}{8.314(298.15)} = 51.50\,\text{mol}.$$

The product amounts in $0.100\,\text{L}$ of solution are

$$n(\text{HCHO}) = (1.0 \times 10^{-3}\,\text{mol L}^{-1})(0.100\,\text{L}) = 1.0 \times 10^{-4}\,\text{mol},$$
$$n(\text{CH}_3\text{OH}) = (5.4 \times 10^{-3}\,\text{mol L}^{-1})(0.100\,\text{L}) = 5.4 \times 10^{-4}\,\text{mol}.$$

Each product molecule contains one carbon atom, so

$$n_{\text{converted}}(\text{CO}_2) = 1.0 \times 10^{-4} + 5.4 \times 10^{-4} = 6.4 \times 10^{-4}\,\text{mol}.$$

Therefore,

$$\eta = \frac{n_{\text{converted}}(\text{CO}_2)}{n_{\text{feed}}(\text{CO}_2)} = \frac{6.4 \times 10^{-4}}{51.50} = 1.2426 \times 10^{-5}.$$

To two significant figures,

$$\boxed{\eta = 1.2 \times 10^{-5} = 0.0012\%}.$$

For the quantum yield, reduction from carbon oxidation state $+4$ to 0 in formaldehyde requires four electrons per molecule; reduction to -2 in methanol requires six electrons per molecule. The corresponding overall reactions with water are

$$\mathrm{CO_2 + H_2O \longrightarrow HCHO + O_2},$$
$$\mathrm{CO_2 + 2\,H_2O \longrightarrow CH_3OH + \tfrac{3}{2}\,O_2}.$$

Thus, the amount of electrons transferred is

$$\begin{aligned} n_e &= 4n(\mathrm{HCHO}) + 6n(\mathrm{CH_3OH}) \\ &= 4(1.0 \times 10^{-4}) + 6(5.4 \times 10^{-4}) \\ &= 3.64 \times 10^{-3}\,\mathrm{mol}. \end{aligned}$$

The number of transferred electrons is

$$N_e = n_e N_A = (3.64 \times 10^{-3})(6.022 \times 10^{23}) = 2.1920 \times 10^{21}.$$

The energy per incident photon is

$$E_\gamma = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^{8})}{365 \times 10^{-9}} = 5.4424 \times 10^{-19}\,\mathrm{J}.$$

Using the stated lamp power as the incident monochromatic radiant power,

$$E_{\text{incident}} = Pt = (500\,\mathrm{J\,s^{-1}})(25200\,\mathrm{s}) = 1.260 \times 10^{7}\,\mathrm{J}.$$

Therefore,

$$N_i = \frac{Pt}{E_\gamma} = \frac{1.260 \times 10^{7}}{5.4424 \times 10^{-19}} = 2.3152 \times 10^{25}.$$

Finally,

$$\phi = \frac{N_e}{N_i} = \frac{2.1920 \times 10^{21}}{2.3152 \times 10^{25}} = 9.4681 \times 10^{-5}.$$

To two significant figures,

$$\boxed{\phi = 9.5 \times 10^{-5} = 0.0095\%}.$$

The solution was checked against the official solution.

Problem 7: Dubai crude oil

7% of the total

7.1	7.2	7.3	7.4	7.5	Total
8	2	3	1	8	22

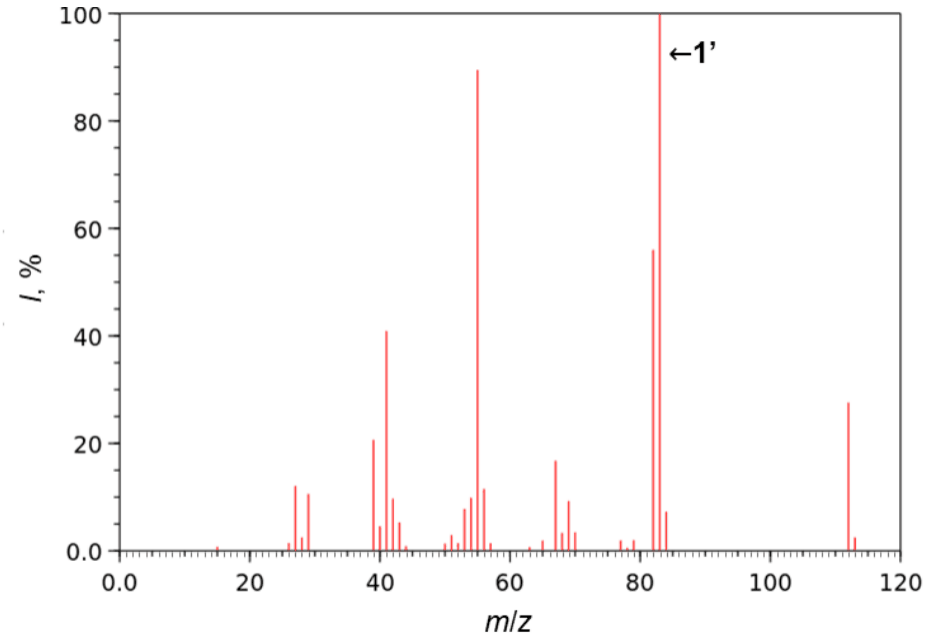
The petroleum industry plays an important role in the UAE economy. The oil called “Dubai Crude” is a benchmark for global oil prices. Crude oil is a complex mixture of organic compounds, mainly hydrocarbons, along with smaller amounts of S, N, and O-containing compounds.

The hydrocarbon composition of oil is characterised by the PONA number. The abbreviation stands for *P* – paraffins (alkanes), *O* – olefins (alkenes), *N* – naphthenes (cycloalkanes), and *A* – aromatics (arenes). One method to determine the composition of oil is gas chromatography–mass

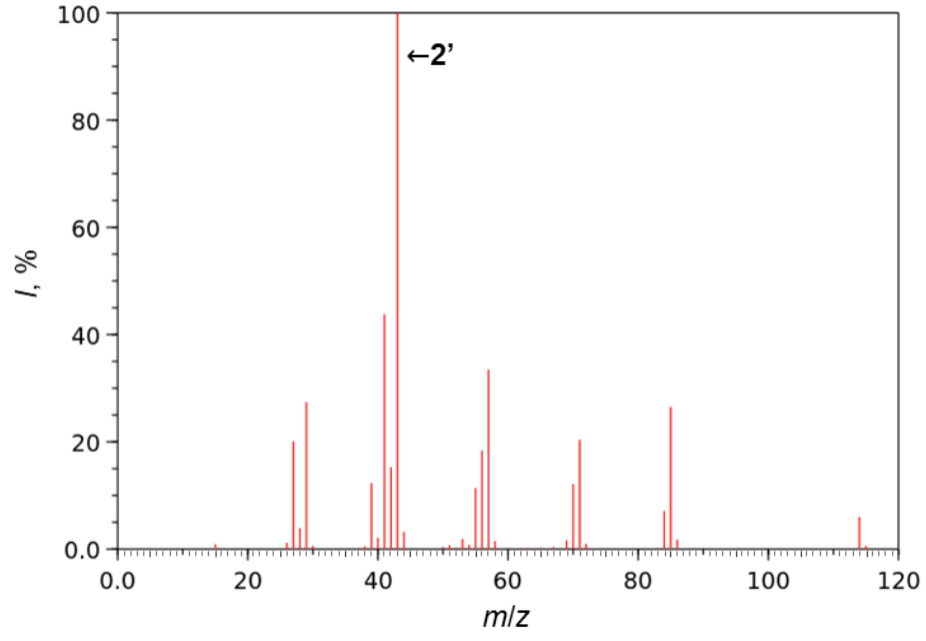
spectrometry (GC–MS).

Below are mass spectra (electron impact ionisation, I – relative intensity) of four hydrocarbons **1–4** of Dubai Crude oil. They include **linear** alkane **P**, **linear** alkene **O**, **monosubstituted** cycloalkane **N**, and arene **A**. Alkene **O does not** have *cis–trans* isomers. **1′–4′** are selected fragmentation products.

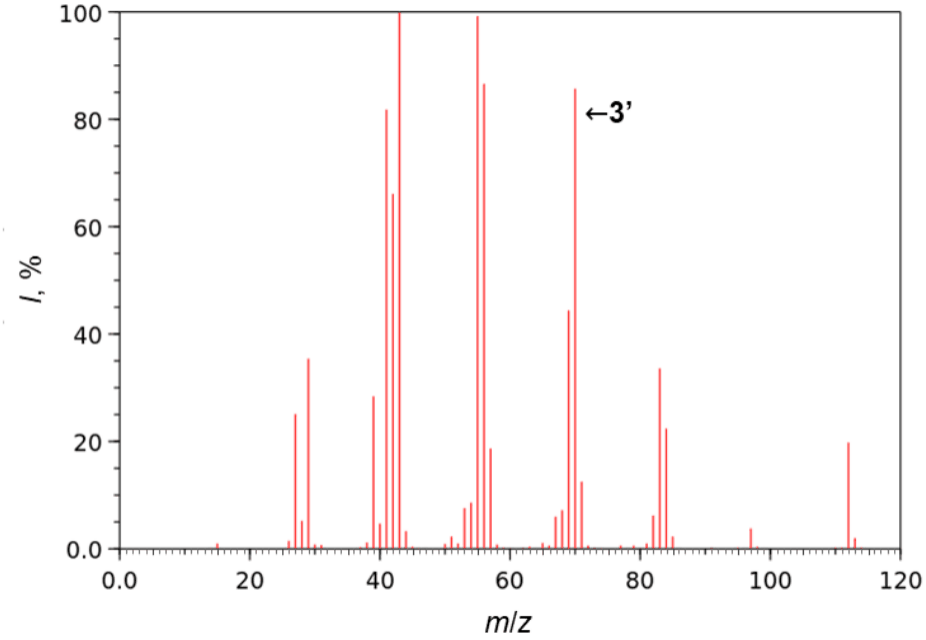
Compound 1



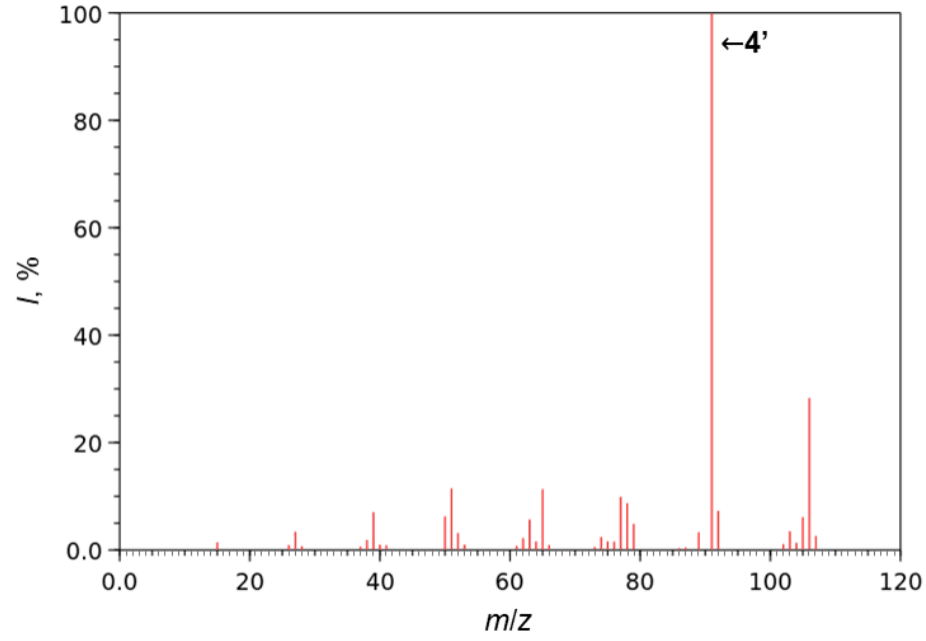
Compound 2



Compound 3



Compound 4

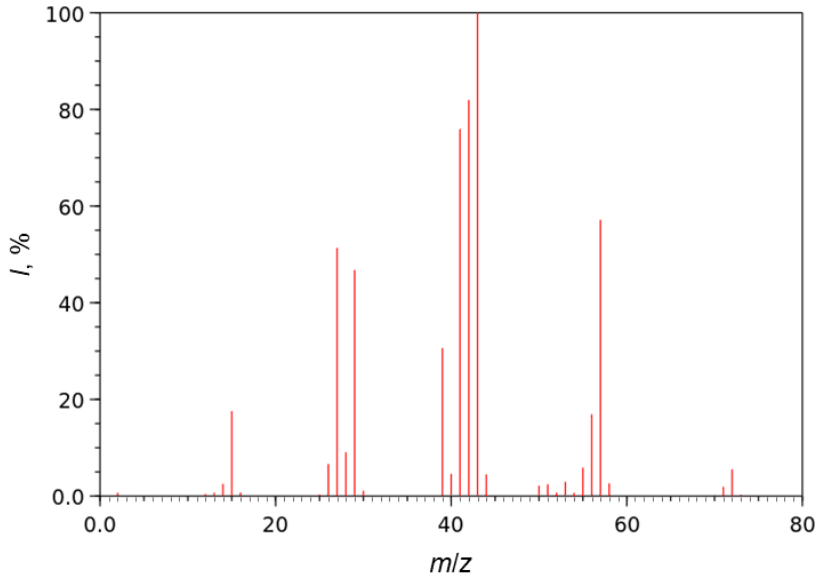


7.1 Draw the structures of **1–4** and **1′–4′**. If you cannot determine the structure(s) of **1–4**, **write** the corresponding letter code (**P/O/N/A**) and the molecular formula.

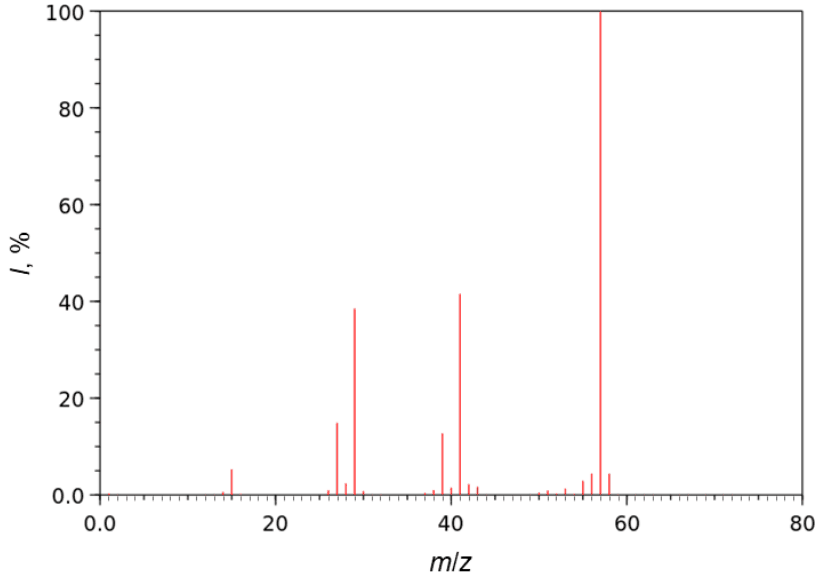
Hint: Species 3′ is formed by a rearrangement of the molecular ion by the McLafferty mechanism.

To differentiate isoparaffins (isoalkanes, *I*) from *n*-alkanes, the PIONA number may be used for a more precise description of crude oil composition. Below are two mass spectra of branched alkanes **5** and **6**. In the mass spectrum of **6**, the $[\mathrm{M}_1^+]^+$ peak has an intensity of *ca.* 5.4% relative to the intensity of the $[\mathrm{M}]^+$ peak of the molecular ion.

Compound 5



Compound 6



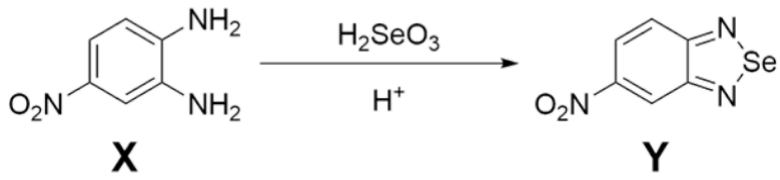
7.2 Draw the structures of compounds **5** and **6**.

Crude oil is classified by the sulfur content as either sweet (<0.5 wt%) or sour (>0.5 wt%). A $V = 115\ \mu\mathrm{L}$ sample of Dubai Crude oil ($\rho = 871\ \mathrm{g\,dm^{-3}}$) was completely burnt. The resulting gas mixture was passed through a $\mathrm{H_2O_2}$ solution containing an excess of $\mathrm{Ba(OH)_2}$, leading to the formation of $m = 1.395\ \mathrm{g}$ of white precipitate. Upon acidification with $\mathrm{HNO_3}$, the precipitate's mass decreased by 98.95%.

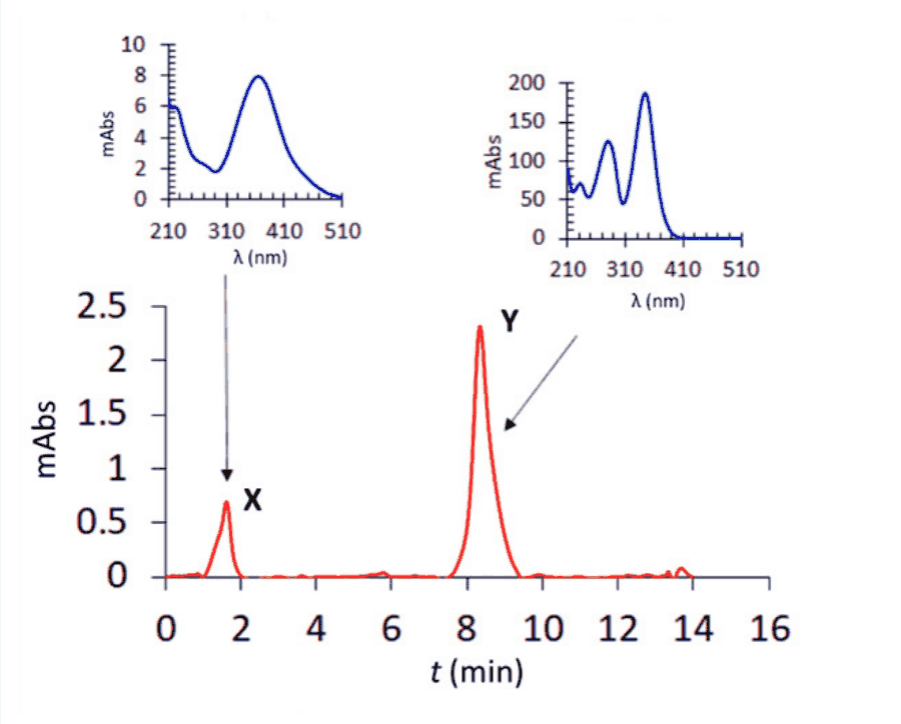
7.3 Calculate the sulfur content ($w(\mathrm{S})$, wt%) of Dubai Crude oil.

In addition to sulfur, crude oil contains trace amounts of selenium, which transfers into the water used during refining. In aqueous solutions, selenium exists as $\mathrm{SeO_3^{2-}}$ and $\mathrm{SeO_4^{2-}}$.

The concentration of $\mathrm{SeO_3^{2-}}$ can be determined chromatographically by its selective reaction with diamine **X** under acidic conditions, forming piazoselenol **Y**. This reaction is complete only at the right pH range.



X and **Y** elute at different times (t) on the chromatogram shown below. The absorption spectra (1 mAbs corresponds to absorbance $A = 0.001$) of **X** and **Y** are also provided.



7.4 Tick the optimal wavelength (λ) for the absorbance measurements in the chromatogram.

□ 270 nm □ 300 nm □ 350 nm □ 510 nm

Acidified water from the refining process, containing $\mathrm{SeO_3}^{2-}$ and $\mathrm{SeO_4}^{2-}$ (**solution 1**), was analysed as follows. A 9.50 mL sample was mixed with 0.50 mL of an aqueous solution of **X** (300 µM, excess) to form **solution 2**.

The area, S, under each chromatogram peak was measured. These areas are proportional to the amount of the respective species in the peak. In a blank experiment under the same conditions with Se-free water, the peak area of **X**, $S(\mathbf{X})$ from the free diamine, was 0.825 mAbs·min. Running identical measurements with known amounts of $\mathrm{SeO_3}^{2-}$ showed that the peak area for **Y** (mAbs·min) depends on Se concentration (µM) as follows: $S(\mathbf{Y}) = 1.21 \cdot c(\mathrm{Se})$.

The measurements for the Se-containing sample (**solution 2**) were carried out at different pH values, adjusted by adding four different strong acids. The ratios $S(\mathbf{X})/S(\mathbf{Y})$ of the area under peak **X** to the area under peak **Y** for these measurements are shown in **the table below**. Assume all reactions have reached equilibrium.

Table. $S(\mathbf{X})/S(\mathbf{Y})$ measured at different pH values with four strong acids

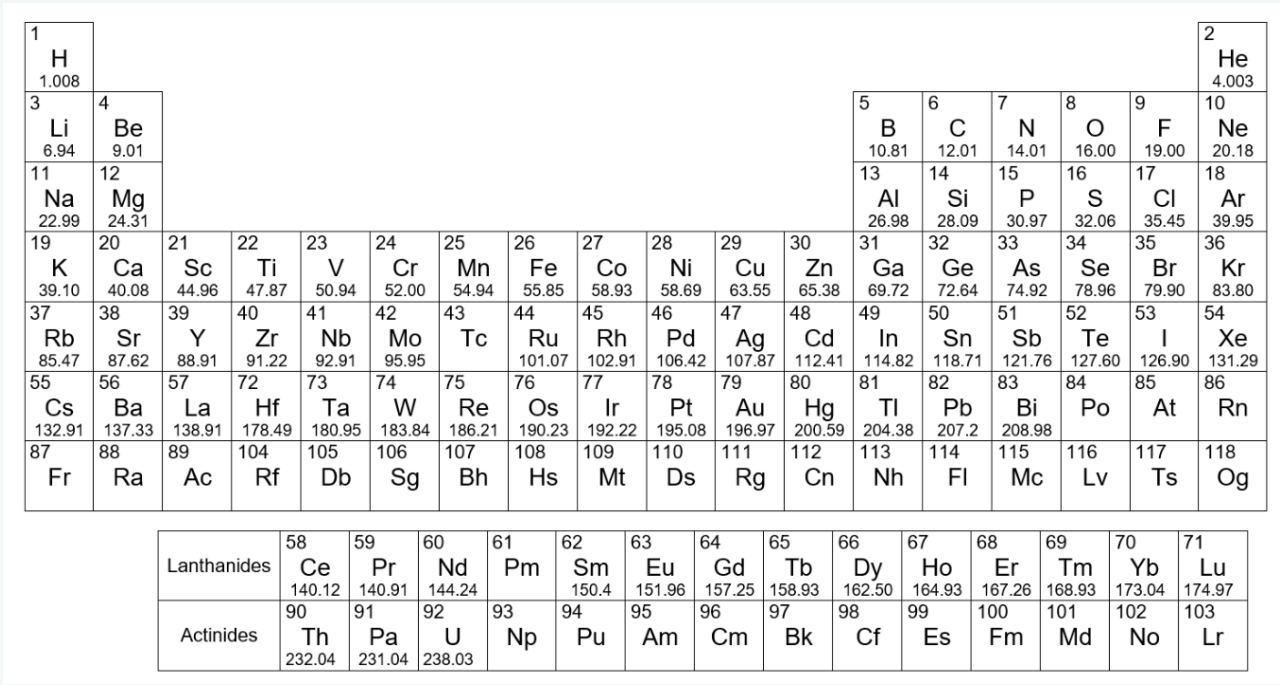
pH	3.0	2.0	1.5	1.0	0	−0.50
$\mathrm{HNO_3}$	1.523	3.334	5.454	7.783	10.232	13.450

pH	3.0	2.0	1.5	1.0	0	−0.50
HCl	0.634	0.538	0.523	0.523	0.581	0.782
HBr	0.523	0.377	0.368	0.368	0.399	0.546
HI	1.722	2.223	5.114	8.123	11.736	15.780

Hint: You need only two values from the table to solve this question.

7.5 Calculate the concentrations of selenium species ($c_0(\mathrm{SeO_3}^{2-})$, $c_0(\mathrm{SeO_4}^{2-})$, in μM) in **solution 1**.

Periodic table



Official English text of the problem.

Answers

- **7.1**

Compound	Assignment	Molecular formula	SMILES
1	**N**, ethylcyclohexane	$\mathrm{C_8H_{16}}$	`CCC1CCCCC1`
2	**P**, *n*-octane	$\mathrm{C_8H_{18}}$	`CCCCCCCC`
3	**O**, oct-1-ene	$\mathrm{C_8H_{16}}$	`C=CCCCCCC`
4	**A**, ethylbenzene, the preferred assignment	$\mathrm{C_8H_{10}}$	`CCc1ccccc1`

Fragment	m/z	Assignment	SMILES
1′	83	Cyclohexyl cation, $\mathrm{C_6H_{11}}^+$	`[CH+]1CCCCC1`
2′	43	Propyl cation, $\mathrm{C_3H_7}^+$: propan-1-ylium from direct cleavage, capable of rearranging to propan-2-ylium	`CC[CH2+]`; rearranged form `C[CH+]C`

Fragment	m/z	Assignment	SMILES
3′	70	Pent-1-ene radical cation, $\mathrm{C_5H_{10}}^{+\bullet}$	`[CH2][CH+]CCC`, a localized charge/radical representation
4′	91	Tropylium cation, $\mathrm{C_7H_7}^{+}$	`[CH+]1C=CC=CC=C1`

- **7.2:** **5** is **2-methylbutane**, `CC(C)CC`; **6** is **2,2-dimethylpropane (neopentane)**, `CC(C)(C)C`.
- **7.3:** $\boxed{w(\mathrm{S}) = 2.01\ \mathrm{wt\%}}$. Dubai Crude is therefore **sour**.
- **7.4:** Tick **350 nm**.
- **7.5:** In **solution 1**:
- Selenite, $\mathrm{SeO_3}^{2-}$, `[O-][Se](=O)[O-]`: $\boxed{c_0 = 1.26\ \mu\mathrm{M}}$.
- Selenate, $\mathrm{SeO_4}^{2-}$, `[O-][Se](=O)(=O)[O-]`: $\boxed{c_0 = 0.473\ \mu\mathrm{M}}$, approximately $0.47\ \mu\mathrm{M}$.

Solution

7.1 — Identification of compounds and fragments

The molecular-ion peaks occur at nominal $m/z = 112,\ 114,\ 112$, and 106 for **1–4**, respectively. The isotope peaks immediately above these masses are not separate molecular ions.

Compound	Molecular-ion m/z	Formula	Degree of unsaturation
1	112	$\mathrm{C_8H_{16}}$	1
2	114	$\mathrm{C_8H_{18}}$	0
3	112	$\mathrm{C_8H_{16}}$	1
4	106	$\mathrm{C_8H_{10}}$	4

Here the degree of unsaturation is

$$\mathrm{DBE} = \frac{2n_\mathrm{C} + 2 - n_\mathrm{H}}{2}.$$

Compound 1 and fragment 1′. The prominent fragment at $m/z = 83$ is $\mathrm{C_6H_{11}}^{+}$. Its formation from the molecular ion corresponds to loss of an ethyl radical:

$$\mathrm{C_8H_{16}}^{+\bullet} \longrightarrow \mathrm{C_6H_{11}}^{+} + \mathrm{C_2H_5}^{\bullet}.$$

The ethyl radical is `C[CH2]`. Cleavage of the bond between an ethyl substituent and a six-membered ring gives the secondary **cyclohexyl cation**, whose structure is listed in the answers. Thus **1** is assigned as **ethylcyclohexane**, the naphthene **N**.

On the answer sheet, draw a cyclohexane ring carrying one ethyl substituent for **1**. For **1′**, draw the six-membered ring with a positive charge on the ring carbon from which the ethyl group was removed; that carbon retains one hydrogen.

Compound 2 and fragment 2′. A molecular mass of 114 matches the linear alkane:

$$14n + 2 = 114 \quad \Longrightarrow \quad n = 8.$$

Consequently, **2** is n**-octane**, **P**. The peaks at $m/z = 43,\ 57,\ 71$, and 85 belong to the characteristic alkyl-cation series, differing by successive $\mathrm{CH_2}$ units.

The selected $m/z = 43$ fragment has formula $\mathrm{C_3H_7}^+$. Direct chain cleavage can be written as

$$\mathrm{C_8H_{18}}^{+\bullet} \longrightarrow \mathrm{C_3H_7}^+ + \mathrm{C_5H_{11}}^\bullet,$$

where the neutral cofragment is the **pentan-1-yl radical**, `[CH2]CCCC`.

Direct cleavage gives **propan-1-ylium**, `CC[CH2+]`. A subsequent 1,2-hydride shift gives the more stable secondary **propan-2-ylium**, `C[CH+]C`. The mass of this peak alone does not distinguish these ion structures.

Compound 3 and fragment 3′. This compound has formula $\mathrm{C_8H_{16}}$ and is the specified linear alkene. An internal double bond in a linear eight-carbon monoalkene would permit *cis–trans* isomerism. Therefore the double bond must be terminal: **3 is oct-1-ene**, **O**.

The marked fragment is at $m/z = 70$, corresponding to $\mathrm{C_5H_{10}}^{+\bullet}$. Its formation involves loss of neutral **propene**, `C=CC`:

$$\mathrm{C_8H_{16}}^{+\bullet} \longrightarrow \mathrm{C_5H_{10}}^{+\bullet} + \mathrm{C_3H_6}.$$

Number the oct-1-ene chain from the double-bond end, so the initial double bond is between C1 and C2. In the McLafferty rearrangement:

1. A hydrogen on C5 transfers to C1 through a six-membered arrangement involving C1–C5 and the transferred hydrogen.
2. The C3–C4 bond breaks.
3. Double bonds form between C2–C3 and C4–C5.

The C1–C3 portion becomes neutral propene. The C4–C8 portion becomes the **pent-1-ene radical cation**, **3′**.

For the requested drawing, show the pent-1-ene structure in brackets with $+\bullet$ outside the brackets. The SMILES `[CH2][CH+]CCC` gives one localized charge/radical representation; the ion's electronic structure is delocalized over the original alkene unit. SMILES does not show the folded rearrangement geometry or the coupled electron movement described above.

Compound 4 and fragment 4′. The molecular ion at $m/z = 106$ gives $\mathrm{C_8H_{10}}$, consistent with an arene. The dominant $m/z = 91$ peak is characteristic of the resonance-stabilized $\mathrm{C_7H_7}^+$ ion.

The preferred assignment is **ethylbenzene**, **A**. Loss of a **methyl radical**, `[CH3]`, gives a **benzyl cation**, `[CH2+]c1ccccc1`, which can rearrange to the **tropylium cation**:

$$\mathrm{C_8H_{10}}^{+\bullet} \longrightarrow \mathrm{C_7H_7}^+ + \mathrm{CH_3}^\bullet.$$

For **4′**, draw a seven-membered carbon ring with three alternating double bonds and an overall positive charge. The positive charge is delocalized; the ring contains six π electrons. The SMILES in the answer represents one Kekulé form.

7.2 — Identification of the branched alkanes

For **5**, the molecular-ion peak at $m/z = 72$ gives

$$14n + 2 = 72 \quad \Longrightarrow \quad n = 5,$$

so its formula is $\mathrm{C_5H_{12}}$.

There are two branched alkane structures with this formula: **2-methylbutane**, `CC(C)CC`, and **2,2-dimethylpropane**, `CC(C)(C)C`.

The strong $m/z = 43$ peak of **5** is consistent with cleavage of 2-methylbutane to the secondary propan-2-ylium ion:

$$\mathrm{C_5H_{12}}^{+\bullet} \longrightarrow \mathrm{C_3H_7}^{+} + \mathrm{C_2H_5}^{\bullet}.$$

Thus **5 is 2-methylbutane**.

For **6**, the usual natural-abundance contribution of $^{13}\mathrm{C}$ is approximately 1.1% to the $M+1$ peak per carbon atom. Hence

$$n_{\mathrm{C}} \approx \frac{5.4}{1.1} \approx 5.$$

As an alkane, **6** therefore also has formula $\mathrm{C_5H_{12}}$. Its dominant $m/z = 57$ peak corresponds to a **tert-butyl cation**, `C[C+](C)C`:

$$\mathrm{C_5H_{12}}^{+\bullet} \longrightarrow \mathrm{C_4H_9}^{+} + \mathrm{CH_3}^{\bullet}.$$

All four carbon–carbon bonds of neopentane are equivalent, and cleavage of any one produces this stabilized tertiary carbocation. This accounts for the dominant fragment and the very weak molecular ion.

Thus **6 is 2,2-dimethylpropane**. Draw one central carbon bonded to four methyl groups.

7.3 — Sulfur content

Combustion produces carbon dioxide and sulfur oxides. In the alkaline peroxide solution, carbon is collected as **barium carbonate**, `[Ba+2].[O-]C(=O)[O-]`, and sulfur as **barium sulfate**, `[Ba+2].[O-]S(=O)(=O)[O-]`.

The relevant balanced collection reactions are

$$\mathrm{CO_2} + \mathrm{Ba(OH)_2} \longrightarrow \mathrm{BaCO_3\,(s)} + \mathrm{H_2O},$$
$$\mathrm{SO_2} + \mathrm{H_2O_2} + \mathrm{Ba(OH)_2} \longrightarrow \mathrm{BaSO_4\,(s)} + 2\,\mathrm{H_2O}.$$

Nitric acid dissolves the carbonate:

$$\mathrm{BaCO_3\,(s)} + 2\,\mathrm{HNO_3} \longrightarrow \mathrm{Ba(NO_3)_2} + \mathrm{CO_2\,(g)} + \mathrm{H_2O}.$$

Barium sulfate remains as the acid-insoluble precipitate.

The other species in these equations are carbon dioxide `O=C=O`, sulfur dioxide `O=S=O`, hydrogen peroxide `OO`, barium hydroxide `[Ba+2].[OH-].[OH-]`, water `O`, nitric acid `O=[N+]([O-])O`, and barium nitrate `[Ba+2].[O-][N+](=O)[O-].[O-][N+](=O)[O-]`. The disconnected ionic SMILES specify composition, not crystal structures.

The remaining precipitate mass is

$$m(\mathrm{BaSO_4}) = 1.395(1 - 0.9895) = 0.0146475\,\mathrm{g}.$$

Using the supplied atomic masses,

$$M(\mathrm{BaSO_4}) = 137.33 + 32.06 + 4(16.00) = 233.39\,\mathrm{g\,mol^{-1}}.$$

Each mole of barium sulfate contains one mole of sulfur, so

$$m(\mathrm{S}) = 0.0146475\,\mathrm{g}\,\frac{32.06}{233.39} = 2.01208 \times 10^{-3}\,\mathrm{g}.$$

The original oil mass is

$$m_{\text{oil}} = \rho V = (871\,\text{g}\,\text{dm}^{-3})(1.15 \times 10^{-4}\,\text{dm}^3) = 0.100165\,\text{g}.$$

Therefore,

$$w(\text{S}) = \frac{2.01208 \times 10^{-3}}{0.100165} \times 100\% = 2.00876\%.$$

$$\boxed{w(\text{S}) = 2.01\,\text{wt}\%}.$$

Since this exceeds $0.5\,\text{wt}\%$, the oil is **sour**.

7.4 — Detection wavelength

Choose

$$\boxed{\lambda = 350\,\text{nm}}.$$

The absorption spectrum of **Y** has its strongest maximum near this wavelength, giving the highest sensitivity for the selenium-containing derivative among the listed choices. The other wavelengths give weaker absorption by **Y**; at 510 nm its absorption is essentially zero.

7.5 — Selenium speciation

The derivatizing reagent **X** is **4-nitrobenzene-1,2-diamine**, `Nc1ccc([N+](=O)[O-])cc1N`. Product **Y** is **5-nitro-2,1,3-benzoselenadiazole**, `O=[N+]([O-])c1ccc2n[se]nc2c1`.

The condensation with **selenous acid**, `O[Se](=O)O`, is

$$\text{C}_6\text{H}_7\text{N}_3\text{O}_2 + \text{H}_2\text{SeO}_3 \xrightarrow{\text{H}^+} \text{C}_6\text{H}_3\text{N}_3\text{O}_2\text{Se} + 3\,\text{H}_2\text{O}.$$

Thus **one mole of X is consumed for each mole of Y formed**, and each mole of **Y** contains one mole of selenium.

The two useful ratios are the constant minimum values at pH 1.0–1.5:

$$R_{\text{HCl}} = 0.523, \qquad R_{\text{HBr}} = 0.368.$$

These are the conditions for quantitative derivatization. In hydrochloric acid, chloride, `[Cl-]`, does not reduce selenate under these conditions, so the signal measures the original selenium(IV).

Bromide, `[Br-]`, reduces selenium(VI) to selenium(IV):

$$\text{SeO}_4{}^{2-} + 2\,\text{Br}^- + 2\,\text{H}^+ \longrightarrow \text{SeO}_3{}^{2-} + \text{Br}_2 + \text{H}_2\text{O}.$$

Here bromine is `BrBr`, and the proton is `[H+]`. The HBr measurement therefore measures the **sum** of the original selenium(IV) and selenium(VI).

First calculate the concentration of **X** introduced into solution 2:

$$c_{\mathbf{X},0} = 300\,\mu\text{M}\,\frac{0.50\,\text{mL}}{10.00\,\text{mL}} = 15.0\,\mu\text{M}.$$

The blank establishes the response coefficient for free **X**:

$$k_{\mathbf{X}} = \frac{0.825\,\text{mAbs}\,\text{min}}{15.0\,\mu\text{M}} = 0.0550\,\text{mAbs}\,\text{min}\,\mu\text{M}^{-1}.$$

Let y, expressed in µM, be the concentration of **Y** formed in solution 2. The remaining free diamine concentration is $15.0 - y$. Therefore,

$$S(\mathbf{X}) = 0.0550(15.0 - y), \qquad S(\mathbf{Y}) = 1.21y,$$

with both peak areas in mAbs·min.

Consequently,

$$R = \frac{S(\mathbf{X})}{S(\mathbf{Y})} = \frac{0.0550(15.0 - y)}{1.21y},$$

and

$$y = \frac{0.825}{0.0550 + 1.21R} = \frac{15.0}{1 + 22.0R}\ \mu\mathrm{M}.$$

For the HCl measurement,

$$y_{\mathrm{HCl}} = \frac{15.0}{1 + 22.0(0.523)} = 1.199424\ \mu\mathrm{M}.$$

This is the original selenite concentration after dilution into solution 2.

For the HBr measurement,

$$y_{\mathrm{HBr}} = \frac{15.0}{1 + 22.0(0.368)} = 1.649077\ \mu\mathrm{M}.$$

This is the total selenium concentration in solution 2. Thus the original selenate contribution in solution 2 is

$$1.649077 - 1.199424 = 0.449652\ \mu\mathrm{M}.$$

Finally, correct for dilution from 9.50 mL of solution 1 to 10.00 mL of solution 2:

$$c_0(\mathrm{SeO_3}^{2-}) = 1.199424\frac{10.00}{9.50} = 1.262552\ \mu\mathrm{M},$$

$$c_0(\mathrm{SeO_4}^{2-}) = 0.449652\frac{10.00}{9.50} = 0.473318\ \mu\mathrm{M}.$$

Hence

$$\boxed{c_0(\mathrm{SeO_3}^{2-}) = 1.26\ \mu\mathrm{M}}, \qquad \boxed{c_0(\mathrm{SeO_4}^{2-}) = 0.473\ \mu\mathrm{M}}.$$

The last value is about $0.47\ \mu\mathrm{M}$, allowing for the rounding of the tabulated ratios.

The solution was checked against the official solution.

Problem 8: Carbon monoxide: deadly poison or promising therapeutic agent?

7.5% of the total

8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	Total
4	1	6	3	2	2	4	8	5	35

Carbon monoxide is a toxic gas because it binds to haemoglobin and blocks oxygen binding. A major source of CO is incomplete combustion of engine fuel. Therefore, many exhausts are fitted with catalytic converters which remove CO and other hazardous compounds including unburnt

hydrocarbons and nitrogen oxides (NO_x), forming mainly water vapour, carbon dioxide, and nitrogen.

8.1 Write the equations for the reactions of the following in a converter. **Tick** the box to indicate whether the carbon or nitrogen atom(s) have been oxidised by oxygen, **"Ox"**, been reduced **"Red"**, or stayed at the same oxidation state **"Same"**. Please ignore any reactions between the exhaust gases.

(a) CO
(b) Unburnt hydrocarbon $\mathrm{C}_x\mathrm{H}_y$
(c) Nitrogen oxides NO_x

Catalytic converters contain nanoparticles of noble metals which act as catalysts, immobilised on a cheap high surface area material such as $\mathrm{Al_2O_3}$.

In one experiment, $m(\mathrm{cat.}) = 0.10\,\mathrm{g}$ of catalyst containing $w(\mathrm{Pd}) = 10\,\mathrm{wt\%}$ was used in a tube reactor. Gases were passed over the catalyst under continuous flow. The flow rate of CO gas was $v(\mathrm{CO}) = 10\,\mathrm{mL\,min^{-1}}$, which was mixed with a second flow of air (assume 20% $\mathrm{O_2}$, 80% $\mathrm{N_2}$), at $T = 273.15\,\mathrm{K}$ and $p = 1.00\,\mathrm{atm}$, before entering the reactor.

8.2 Calculate the flow rate v (in $\mathrm{mL\,min^{-1}}$) of air required for the reactants to be present in a stoichiometric ratio.

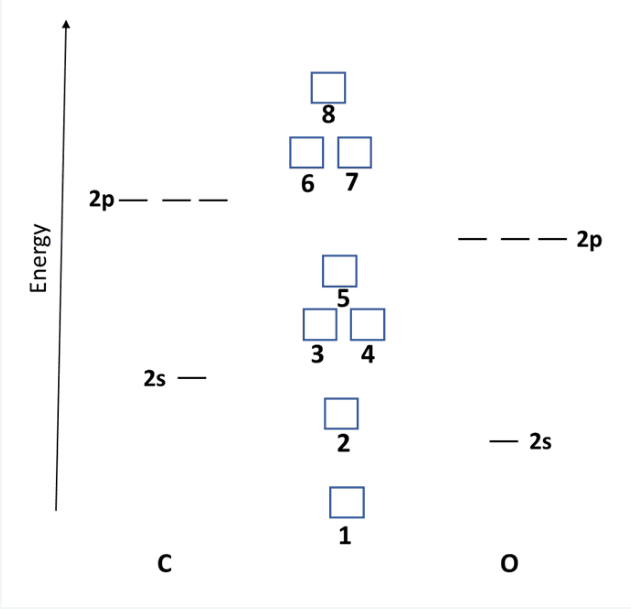
Assume 10% of the Pd atoms in the nanoparticles are exposed on the surface. Assume the conversion of CO to $\mathrm{CO_2}$ was $\eta = 70\%$.

8.3 Calculate the number of $\mathrm{CO_2}$ molecules, N, formed after $t = 1\,\mathrm{h}$ per surface Pd atom.

Ruthenium nanoparticles are efficient catalysts for CO combustion. The bonding interactions between CO molecules and the surface Ru atoms are of two types:

1. σ-bonding through a lone pair on the carbon atom;
2. π-interaction through an overlap between the Ru valence d-orbitals and CO molecular orbitals.

8.4 Complete the MO diagram for CO with electrons and the following table with the type (σ/π) of overlap for forming each MO.



MO	1	2	3	4	5	6	7	8
Type of overlap								

8.5 What is the effect of the $\mathrm{Ru-CO}$ π-interaction on the $\mathrm{Ru-CO}$ and the $\mathrm{C-O}$ bond strengths? **Tick** the correct answer.

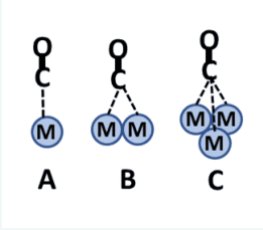
(i) $\mathrm{Ru-CO}$ bond strength:

□ increases **"in"**
□ decreases **"dec"**
□ no change **"nc"**

(ii) $\mathrm{C-O}$ bond strength:

□ increases **"in"**
□ decreases **"dec"**
□ no change **"nc"**

Adsorbed CO molecules have strong IR absorptions due to $\mathrm{C-O}$ stretching vibrations. Three binding modes for CO adsorbed on a metal surface are shown, where CO can interact with one or more metal atoms. IR peaks in the spectra of free CO and the three binding modes of adsorbed CO were observed at values of 1850, 1930, 2100, and $2143\ \mathrm{cm^{-1}}$.

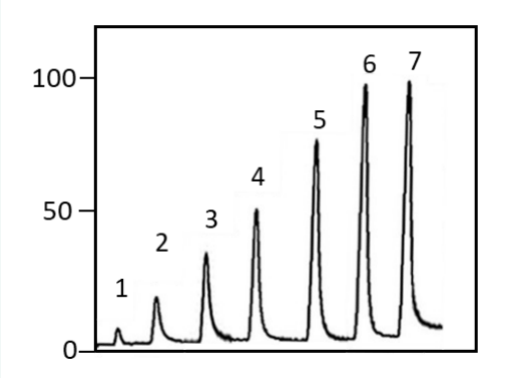


8.6 Tick which wavenumber corresponds to each adsorption mode (**A, B, and C**) and to free CO.

Dispersion of a metal catalyst refers to the percentage of its atoms exposed on the surface. Dispersion can be determined by pulse chemisorption of CO since it adsorbs selectively onto surface atoms. Equal pulses of known amounts of CO are injected and a certain amount is

adsorbed from each pulse. The amount remaining is measured by a detector and a peak, the area under which correlates with the amount of unadsorbed CO from each pulse, is plotted as shown below. Injections continue until no more CO adsorbs.

One experiment used $50\ \mu\mathrm{L}$ pulses consisting of 10% vol CO in He, at $25\ ^{\circ}\mathrm{C}$ and $100\ \mathrm{kPa}$. $15\ \mathrm{mg}$ catalyst was used, composed of 10 wt% Ni on an $\mathrm{Al_2O_3}$ support. Assume one CO molecule adsorbs on each surface Ni atom.



Pulse # (x axis)	1	2	3	4	5	6	7
% of pulse unadsorbed (y axis)	4	10	20	50	80	100	100

8.7 Calculate the percentage of Ni atoms exposed on the surface, $\%_{\mathrm{Ni}}$.

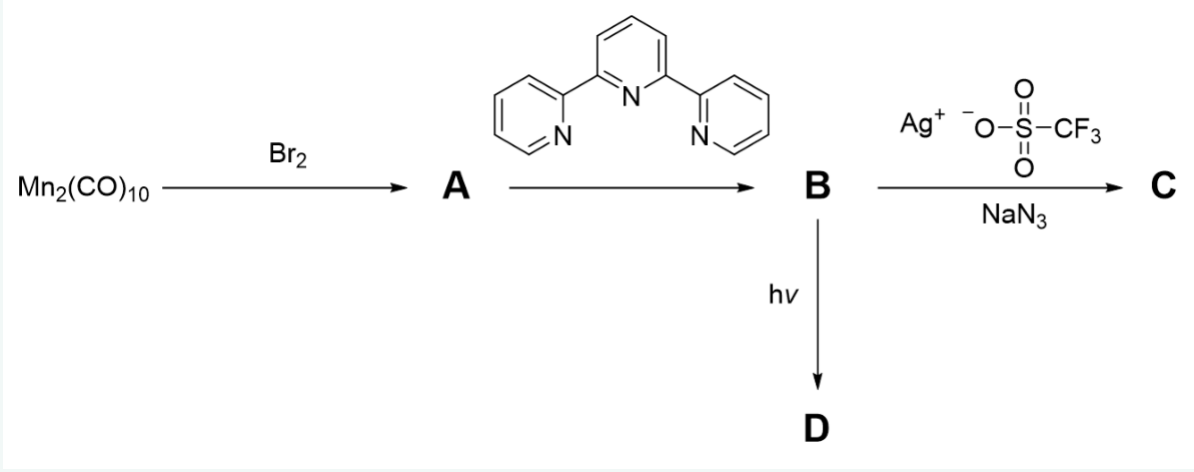
Despite being toxic at higher concentrations, at a concentration of 10-250 ppm, CO shows anti-inflammatory properties. Prodrugs known as CO releasing molecules (CORMs) target the delivery of effective dosages of CO to tissues in response to a trigger. Mn(I) carbonyl complexes have shown promise as PhotoCORMs as they can release CO when exposed to light.

Compounds **A-D** are all neutral Mn(I) carbonyl complexes.

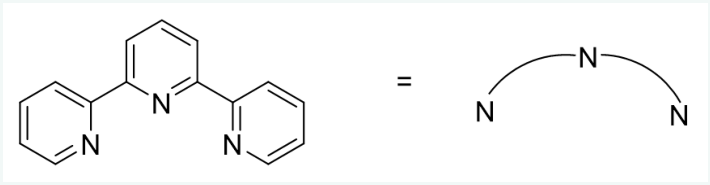
B, C, and D do not contain two CO ligands in a *trans* arrangement.

The IR spectrum of **C** contains a band at $2042\ \mathrm{cm^{-1}}$ in addition to the CO stretching bands. The table with the number of CO stretching bands in the IR spectra of metal carbonyl complexes is given in the data sheet section at the beginning of the exam.

Compound	%Mn by mass	Number of CO stretching bands
A	19.98	3
B	12.15	3
C	13.26	3
D	12.95	2



For simplicity, the ligand can be drawn as:



8.8 Draw the structures of compounds **A-D**, ensuring the three-dimensional shape is clear. If the compound is chiral, only one enantiomer needs to be drawn.

Compound **C** reacts with alkynes and this can be used to tag proteins. This is known as an Inorganic Click (iClick) reaction.



During the conversion of **C** to **E**, the $2042\ \mathrm{cm^{-1}}$ band in the IR spectrum of **C** disappears. The IR spectrum of **E** has two new $\mathrm{C{=}O}$ bands in the range of 1735-1725 $\mathrm{cm^{-1}}$. After a further 6 h, compound **E** converts to compound **F** which only has one $\mathrm{C{=}O}$ band in the range of 1735-1725 $\mathrm{cm^{-1}}$. Compound **G** does not contain manganese and has two planes of symmetry.

8.9 Draw the structures of compounds **E, F, and G**, ensuring the three-dimensional shape is clear. If the compound is chiral, only one enantiomer needs to be drawn.

Periodic table and data sheet

Physical constants and formulae

Avogadro constant	N_A	$6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
molar gas constant	R	$8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	F	$96485\ \mathrm{C\,mol^{-1}}$
Planck constant	h	$6.626 \times 10^{-34}\ \mathrm{J\,s}$
speed of light in vacuum	c	$2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}$
mass of electron	m_e	$9.109 \times 10^{-31}\ \mathrm{kg}$

charge of electron	e	$1.602 \times 10^{-19}\ \mathrm{C}$
atmospheric pressure	p_{atm}	$101325\ \mathrm{Pa}$
ionic product of water at 298 K	K_w	10^{-14}

$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
$1\ \mathrm{Å} = 1 \times 10^{-10}\ \mathrm{m}$
$1\ \mathrm{pm} = 1 \times 10^{-12}\ \mathrm{m}$
$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
$1\ \mathrm{kWh} = 3600\ \mathrm{kJ}$
$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
$1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$

area of triangle	$A = \frac{1}{2}ab \cdot \sin C$
volume of cube	$V = a^3$
volume of sphere	$V = \frac{4}{3}\pi r^3$
surface area of sphere	$S = 4\pi r^2$
ideal gas equation	$pV = nRT$
frequency of light	$\nu = \frac{c}{\lambda}$
energy of a photon	$E = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon c d$
spin-only magnetic moment	$\mu = \sqrt{n(n+2)}\ \mathrm{BM}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
0^{th} order integrated rate law	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
1^{st} order integrated rate law	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-E_a/(RT)}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\circ = -RT\ln K = -nFE^\circ_{\mathrm{cell}}$
Clausius-Clapeyron equation	$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\mathrm{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
specific heat	$Q = mC_p\Delta T$
boiling point elevation	$\Delta T = iK_b m_i$
freezing point depression	$\Delta T = iK_f m_i$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of $1\ \mathrm{mol\,dm^{-3}}$.

IR absorption data

Bond stretching frequencies

Bond type		Wavenumber $(\mathrm{cm^{-1}})$
$\mathrm{C-H}$	Alkane	3000-2850
	Alkene	3100-3000
	Aromatic	3150-3050
	Alkyne	~ 3300
	Aldehyde	2900-2700
$\mathrm{C=C}$	Alkene	1680-1600
	Aromatic	1600-1400
$\mathrm{C\equiv C}$	Alkyne	2250-2100
$\mathrm{C=O}$	Aldehyde	1740-1720
	Ketone	1725-1705
	Carboxylic acid	1725-1700
	Ester	1750-1720
	Amide	1670-1640
	Anhydride	1810, 1760
$\mathrm{C-O}$	Alcohol, ether, ester, carboxylic acid, anhydride	1300-800
$\mathrm{O-H}$	Alcohol, phenol, free	3600-3200
	Hydrogen bonded	3500-3200
	Carboxylic acid	3400-2500
$\mathrm{N-H}$	Primary and secondary amine and amide	3500-3100
$\mathrm{C-N}$	Amine	1350-1000
$\mathrm{C=N}$	Imine and oxime	1690-1640
$\mathrm{C\equiv N}$	Nitrile	2260-2240
$\mathrm{N=O}$	Nitro $(\mathrm{R-NO_2})$	1600-1500, 1400-1300
$\mathrm{S=O}$	Sulfoxide	1050
	Sulfate, sulfonamide	1200-1140

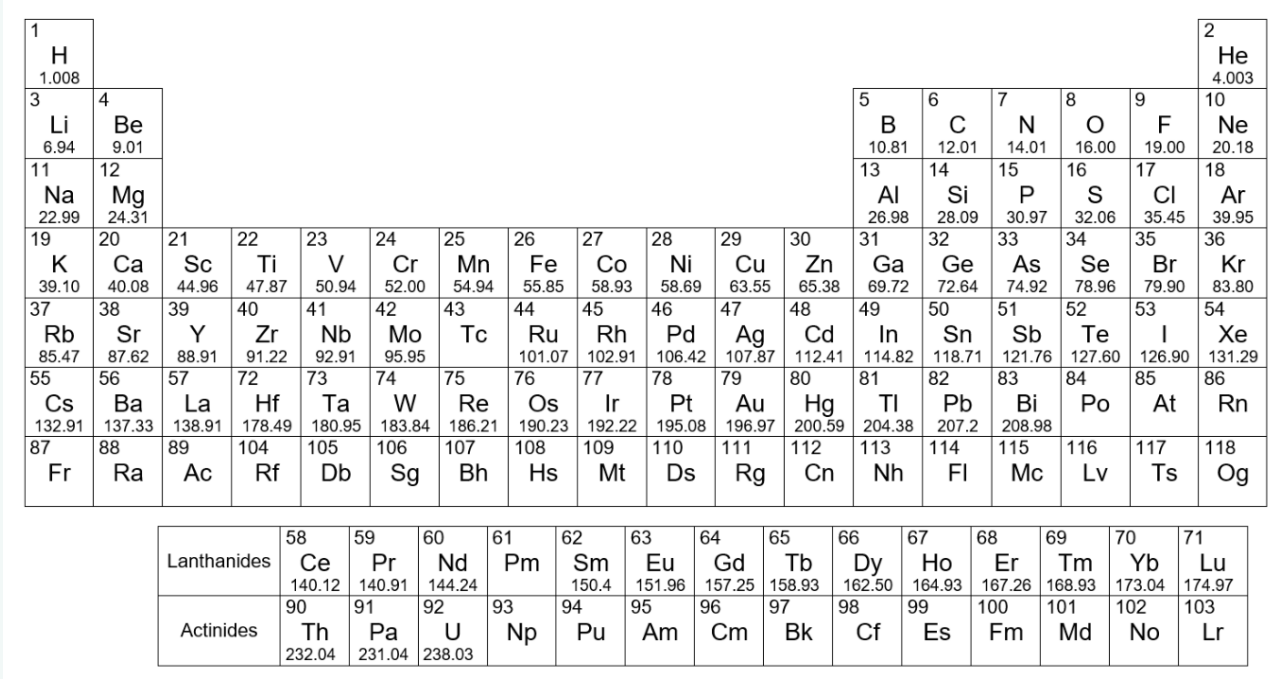
Characteristic bond stretching frequencies of anionic species

Anion	Wavenumber $(\mathrm{cm^{-1}})$
$\mathrm{SO_4{}^{2-}}$	1100-1200 (ν_{as})
$\mathrm{ClO_4{}^-}$	1050-1170 (ν_{as})
$\mathrm{NO_3{}^-}$	1370 (ν_{as})
$\mathrm{CN^-}$	2089
$\mathrm{SCN^-}$	2053 $(\nu_{\mathrm{C-N}})$, 748 $(\nu_{\mathrm{C-S}})$
$\mathrm{N_3{}^-}$	2042 (ν_{as}), 1343 (ν_{s})
$\mathrm{CNO^-}$	2052 $(\nu_{\mathrm{C-N}})$, 1057 $(\nu_{\mathrm{N-O}})$

Number of CO stretching bands in the IR spectra of metal carbonyl complexes

Complex	Number of bands
$\mathrm{M(CO)_6}$	1
$\mathrm{M(CO)_5X}$	3
cis-$\mathrm{M(CO)_4X_2}$	4
$trans$-$\mathrm{M(CO)_4X_2}$	1
fac-$\mathrm{M(CO)_3X_3}$	2
mer-$\mathrm{M(CO)_3X_3}$	3
fac-$\mathrm{M(CO)_3X_2Y}$	3
cis-$\mathrm{M(CO)_2X_4}$	2
$trans$-$\mathrm{M(CO)_2X_4}$	1

Periodic table



Official English text of the problem.

Answers

- **8.1 — 4 points**

(a) $2\,\mathrm{CO} + \mathrm{O_2} \longrightarrow 2\,\mathrm{CO_2}$: **Ox**.

(b) $\mathrm{C}_x\mathrm{H}_y + (\mathrm{x}^{+}\mathrm{y}/4)\mathrm{O_2} \longrightarrow x\,\mathrm{CO_2} + (\tfrac{y}{2})\mathrm{H_2O}$: **Ox**.

(c) $2\,\mathrm{NO}_x \longrightarrow \mathrm{N_2} + x\,\mathrm{O_2}$: **Red**.

The molecular species are carbon monoxide `[C-]#[O+]`, oxygen `O=O`, carbon dioxide `O=C=O`, water `O`, and nitrogen `N#N`. The variable formulas $\mathrm{C}_x\mathrm{H}_y$ and NO_x specify families, so neither has a unique SMILES.

- **8.2 — 1 point**

$$\boxed{v(\text{air}) = 25\,\text{mL}\,\text{min}^{-1}}$$

- **8.3 — 6 points**

$$\boxed{N = 1.994 \times 10^{3} \approx 2.0 \times 10^{3} \text{ molecules of } \text{CO}_2 \text{ per surface Pd atom}}$$

- **8.4 — 3 points**

MO	1	2	3	4	5	6	7	8
Electrons	↑↓	↑↓	↑↓	↑↓	↑↓	Empty	Empty	Empty
Type of overlap	σ	σ	π	π	σ	π	π	σ

- **8.5 — 2 points**

(i) $\text{Ru}-\text{CO}$ bond strength: **increases, “in”**.
(ii) $\text{C}-\text{O}$ bond strength: **decreases, “dec”**.

- **8.6 — 2 points**

Species or adsorption mode	Wavenumber (cm^{-1})	SMILES or schematic coordination SMILES
A: terminal carbon monoxide	**2100**	`[C-](->*)#[O+]`
B: doubly bridging carbon monoxide	**1930**	`[C-](->*)(->*)#[O+]`
C: triply bridging carbon monoxide	**1850**	`[C-](->*)(->*)(->*)#[O+]`
Free carbon monoxide	**2143**	`[C-]#[O+]`

Here `*` denotes an unspecified surface metal atom. These fragments describe connectivity; they do not represent the metal surface or its π-backbonding electronically.

- **8.7 — 4 points**

$$\boxed{\%_{\text{Ni}} = 2.65\% \quad \text{(approximately } 2.7\%\text{)}}$$

- **8.8 — 8 points**

Write **tpy** for **2,2′:6′,2″-terpyridine**, `n1c(-c2ccccn2)cccc1-c3ccccn3`.

All four complexes are octahedral. The coordination SMILES use donor-to-metal arrows; the `@OH` descriptors specify the octahedral arrangement. Explicit spatial descriptions are supplied in the Solution.

A: Bromidopentacarbonylmanganese(I), $[\text{MnBr}(\text{CO})_5]$.
SMILES: `[Br-]->[Mn+](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+]`

B: fac-Bromidotricarbonyl(κ²-terpyridine)manganese(I), fac-$[\mathrm{MnBr(CO)_3(tpy)}]$. The central pyridyl nitrogen and one terminal pyridyl nitrogen bind; the other terminal nitrogen remains unbound.
SMILES: `[O+]#[C-]->[Mn@OH3+]1(<-[C-]#[O+])(<-[C-]#[O+])(<-[Br-])<-[n]2c(-c3cccc[n]->13)cccc2-c1ccccn1`

C: fac-Azidotricarbonyl(κ²-terpyridine)manganese(I), fac-$[\mathrm{Mn(N_3)(CO)_3(tpy)}]$. Azide binds through a terminal nitrogen.
SMILES: `[O+]#[C-]->[Mn@OH3+]1(<-[C-]#[O+])(<-[C-]#[O+])(<-[N-]=[N+]=[N-])<-[n]2c(-c3cccc[n]->13)cccc2-c1ccccn1`

D: cis-Bromidodicarbonyl(κ³-terpyridine)manganese(I), cis-$[\mathrm{MnBr(CO)_2(tpy)}]$. All three terpyridine nitrogens bind in a meridional arrangement.
SMILES: `[O+]#[C-]->[Mn@OH9+]12(<-[C-]#[O+])(<-[Br-])<-[n]3c(-c4cccc[n]->14)cccc3-c1cccc[n]->21`

- **8.9 — 5 points**

E: fac-Tricarbonyl(κ²-terpyridine)(4,5-bis(methoxycarbonyl)-1,2,3-triazolato-κN¹)manganese(I). The triazolate binds through an end nitrogen of its three-nitrogen sequence.
SMILES: `[O+]#[C-]->[Mn@OH3+]1(<-[C-]#[O+])(<-[C-]#[O+])(<-[n-]2nnc(C(=O)OC)c2C(=O)OC)<-[n]2c(-c3cccc[n]->13)cccc2-c1ccccn1`

F: fac-Tricarbonyl(κ²-terpyridine)(4,5-bis(methoxycarbonyl)-1,2,3-triazolato-κN²)manganese(I). The triazolate now binds through the middle nitrogen of its three-nitrogen sequence.
SMILES: `[O+]#[C-]->[Mn@OH3+]1(<-[C-]#[O+])(<-[C-]#[O+])(<-[n-]2nc(C(=O)OC)c(C(=O)OC)n2)<-[n]2c(-c3cccc[n]->13)cccc2-c1ccccn1`

G: Dimethyl 2H-1,2,3-triazole-4,5-dicarboxylate. The hydrogen is on the middle nitrogen, N2.
SMILES: `COC(=O)c1n[nH]nc1C(=O)OC`

Solution

8.1

Carbon monoxide is oxidised to carbon dioxide:

$$\boxed{2\,\mathrm{CO} + \mathrm{O_2} \longrightarrow 2\,\mathrm{CO_2}}$$

The oxidation state of carbon increases from $+2$ to $+4$, so the correct box is **Ox**.

Complete combustion of an unburnt hydrocarbon gives carbon dioxide and water:

$$\boxed{\mathrm{C}_x\mathrm{H}_y + (\mathrm{x}^{+}\mathrm{y}/4)\mathrm{O_2} \longrightarrow x\,\mathrm{CO_2} + (\tfrac{y}{2})\mathrm{H_2O}}$$

The products contain x carbon atoms, y hydrogen atoms, and $2x + y/2$ oxygen atoms. Thus the oxygen coefficient is $x + y/4$. The average carbon oxidation state rises from $-y/x$ to $+4$, so the correct box is **Ox**.

With reactions between exhaust gases excluded, the requested formal conversion of nitrogen oxides is:

$$\boxed{2\,\mathrm{NO}_x \longrightarrow \mathrm{N_2} + x\,\mathrm{O_2}}$$

Nitrogen changes from an average oxidation state $+2x$ to zero, so the correct box is **Red**. For example:

$$2\,\mathrm{NO} \longrightarrow \mathrm{N_2} + \mathrm{O_2}$$
$$2\,\mathrm{NO_2} \longrightarrow \mathrm{N_2} + 2\,\mathrm{O_2}$$

Here nitrogen monoxide is `[N]=O`, and nitrogen dioxide is `O=[N+][O-]`. These equations follow the problem’s instruction to exclude reduction by other exhaust constituents.

8.2

The combustion equation requires one mole of oxygen for every two moles of carbon monoxide. At the same temperature and pressure, gas volume flow rates have the same ratio:

$$v(\mathrm{O_2}) = \frac{1}{2}v(\mathrm{CO}) = \frac{1}{2}(10) = 5.0\,\mathrm{mL\,min^{-1}}.$$

Air contains 20% oxygen by volume, so

$$0.20\,v(\mathrm{air}) = 5.0\,\mathrm{mL\,min^{-1}},$$

giving

$$\boxed{v(\mathrm{air}) = 25\,\mathrm{mL\,min^{-1}}}.$$

8.3

In one hour, the inlet volume of carbon monoxide is

$$V(\mathrm{CO}) = (10\,\mathrm{mL\,min^{-1}})(60\,\mathrm{min}) = 600\,\mathrm{mL} = 6.00\times10^{-4}\,\mathrm{m^3}.$$

Each converted carbon monoxide molecule produces one carbon dioxide molecule. Therefore,

$$n(\mathrm{CO_2}) = \eta\frac{pV(\mathrm{CO})}{RT} = \frac{0.70(101325)(6.00\times10^{-4})}{(8.314)(273.15)} = 1.87394\times10^{-2}\,\mathrm{mol}.$$

The total palladium mass is

$$m(\mathrm{Pd}) = (0.10\,\mathrm{g})(0.10) = 0.010\,\mathrm{g}.$$

Since 10% of the palladium atoms are surface atoms,

$$n(\mathrm{Pd})_{\mathrm{surface}} = 0.10\frac{0.010\,\mathrm{g}}{106.42\,\mathrm{g\,mol^{-1}}} = 9.39673\times10^{-6}\,\mathrm{mol}.$$

Avogadro’s constant cancels in the ratio:

$$N = \frac{n(\mathrm{CO_2})N_A}{n(\mathrm{Pd})_{\mathrm{surface}}N_A} = \frac{1.87394\times10^{-2}}{9.39673\times10^{-6}} = 1994.24.$$

Thus,

$$\boxed{N \approx 2.0\times10^{3}\ \text{carbon dioxide molecules per surface Pd atom}}.$$

8.4

Carbon contributes four valence electrons and oxygen contributes six, giving **ten valence electrons**.

Fill the supplied levels from lowest to highest energy. Orbitals 1 and 2 each receive two electrons, the degenerate pair 3 and 4 receives four electrons in total, and orbital 5 receives the remaining two. Orbitals 6, 7, and 8 remain empty.

The valence configuration, using the usual orbital labels, is

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^2.$$

Taking the molecular axis as z, end-on overlap produces σ orbitals and side-on overlap produces π orbitals. Therefore:

MO	Occupancy	Overlap type
1	2	σ
2	2	σ
3	2	π
4	2	π
5	2	σ
6	0	π
7	0	π
8	0	σ

In the requested drawing, place an opposite-spin electron pair in each of boxes 1–5 and leave boxes 6–8 empty.

8.5

The π-interaction is **metal-to-carbonyl back-donation**: occupied ruthenium d orbitals donate electron density into the empty carbon monoxide π^* orbitals, represented by levels 6 and 7.

This interaction is bonding between ruthenium and the carbonyl ligand, but antibonding within carbon monoxide. Consequently:

$$\boxed{\mathrm{Ru{-}CO}\text{ strengthens; }\mathrm{C{-}O}\text{ weakens.}}$$

8.6

For a stretching vibration,

$$\widetilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}},$$

where k is the bond force constant and μ is the reduced mass. As the atoms remain carbon and oxygen, the frequency ordering mainly reflects the $\mathrm{C{-}O}$ force constant.

Free carbon monoxide has the strongest internal bond and therefore the highest wavenumber, $2143\ \mathrm{cm^{-1}}$. Metal back-donation weakens that bond. In the adsorption modes shown, increasing the number of interacting metal atoms gives progressively lower stretching wavenumbers:

$$\boxed{\begin{aligned}\text{Free carbon monoxide}&: \ 2143\ \mathrm{cm^{-1}},\\ \text{A, terminal}&: \ 2100\ \mathrm{cm^{-1}},\\ \text{B, two-metal bridge}&: \ 1930\ \mathrm{cm^{-1}},\\ \text{C, three-metal bridge}&: \ 1850\ \mathrm{cm^{-1}}.\end{aligned}}$$

All three adsorption modes bind through the carbon end.

8.7

Each pulse contains

$$V_{\mathrm{CO,pulse}} = (50\,\mu\mathrm{L})(0.10) = 5.0\,\mu\mathrm{L} = 5.0 \times 10^{-9}\,\mathrm{m}^3.$$

At $T = 298.15\,\mathrm{K}$ and $p = 1.00 \times 10^5\,\mathrm{Pa}$,

$$n_{\mathrm{CO,pulse}} = \frac{pV}{RT} = \frac{(1.00 \times 10^5)(5.0 \times 10^{-9})}{(8.314)(298.15)} = 2.01709 \times 10^{-7}\,\mathrm{mol}.$$

The adsorbed fractions are obtained by subtracting each unadsorbed fraction from one:

Pulse	Adsorbed fraction
1	0.96
2	0.90
3	0.80
4	0.50
5	0.20
6	0
7	0

Their sum is

$$0.96 + 0.90 + 0.80 + 0.50 + 0.20 = 3.36.$$

Thus the total adsorbed amount is

$$n_{\mathrm{CO,ads}} = 3.36(2.01709 \times 10^{-7}) = 6.77742 \times 10^{-7}\,\mathrm{mol}.$$

One adsorbed molecule corresponds to one surface nickel atom, so this is also the amount of surface nickel atoms.

The total nickel amount is

$$n_{\mathrm{Ni,total}} = \frac{(15 \times 10^{-3}\,\mathrm{g})(0.10)}{58.69\,\mathrm{g\,mol^{-1}}} = 2.55580 \times 10^{-5}\,\mathrm{mol}.$$

Therefore,

$$\boxed{\%_{\mathrm{Ni}} = 100\frac{6.77742 \times 10^{-7}}{2.55580 \times 10^{-5}} = 2.65178\% \approx 2.65\%.}$$

8.8

The terpyridine ligand has formula $\mathrm{C_{15}H_{11}N_3}$ and molar mass

$$M(\mathrm{tpy}) = 15(12.01) + 11(1.008) + 3(14.01) = 233.268\,\mathrm{g\,mol^{-1}}.$$

Also,

$$M(\mathrm{CO}) = 28.01\,\mathrm{g\,mol^{-1}}.$$

The proposed compositions give:

Compound	Composition	Calculated molar mass $(\mathrm{g\,mol^{-1}})$	Calculated Mn mass percentage
A	$[\mathrm{MnBr(CO)_5}]$	274.890	19.986%

Compound	Composition	Calculated molar mass $(\mathrm{g\,mol^{-1}})$	Calculated Mn mass percentage
B	$[\mathrm{MnBr(CO)_3(tpy)}]$	452.138	12.151%
C	$[\mathrm{Mn(N_3)(CO)_3(tpy)}]$	414.268	13.262%
D	$[\mathrm{MnBr(CO)_2(tpy)}]$	424.128	12.954%

These agree with the supplied compositions, apart from the insignificant last-decimal discrepancy for A.

Identification of A. Bromine cleaves the manganese–manganese bond, oxidising both manganese atoms from Mn(0) to Mn(I):

$$\mathrm{Mn_2(CO)_{10} + Br_2 \longrightarrow 2\,[MnBr(CO)_5]}.$$

Bromine has SMILES `BrBr`. The starting material, **decacarbonyldimanganese(0)**, has a manganese–manganese bond and five terminal carbonyls on each metal; its coordination SMILES is:

`[Mn](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])-[Mn](<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])(<-[C-]#[O+])<-[C-]#[O+]`

A is an octahedral $\mathrm{M(CO)_5X}$ complex, consistent with its **three carbonyl stretching bands**.

Identification of B. Addition of one terpyridine ligand replaces two carbonyls:

$$\mathrm{A + tpy \longrightarrow B + 2\,CO}.$$

The mass percentage requires three retained carbonyls and one bromide ligand. These occupy four coordination sites, leaving two sites for terpyridine. Hence terpyridine binds through the central nitrogen and one terminal nitrogen; the other terminal pyridyl group remains pendant.

The absence of trans carbonyls requires a **facial carbonyl arrangement**. Its three carbonyl bands agree with the supplied $\mathit{fac}\text{-}\mathrm{M(CO)_3X_2Y}$ pattern.

Identification of C. Silver removes bromide as silver bromide, and azide replaces it:

$$\mathrm{B + AgCF_3SO_3 + NaN_3 \longrightarrow C + AgBr + NaCF_3SO_3}.$$

The species in this substitution are **silver(I) triflate** `[Ag+].[O-]S(=O)(=O)C(F)(F)F`, **sodium azide** `[Na+].[N-]=[N+]=[N-]`, **silver(I) bromide** `[Ag+].[Br-]`, and **sodium triflate** `[Na+].[O-]S(=O)(=O)C(F)(F)F`.

The $2042\,\mathrm{cm^{-1}}$ band identifies the **azide ion**, `[N-]=[N+]=[N-]`. Its replacement of bromide also explains the mass change:

$$79.90 - 3(14.01) = 37.87\,\mathrm{g\,mol^{-1}}.$$

C retains the facial tricarbonyl group and κ²-terpyridine. The azide binds end-on through a terminal nitrogen.

Identification of D. Photolysis removes one carbonyl:

$$\mathrm{B} \xrightarrow{\mathrm{h}\nu} \mathrm{D + CO}.$$

The previously unbound terminal pyridyl nitrogen then occupies the vacant site. Thus D contains **κ³-terpyridine**, two carbonyls, and bromide.

Terpyridine binds meridionally: its two terminal nitrogen donors are trans to one another. The two carbonyls are cis, as required by the question and supported by the **two carbonyl stretching bands**.

All four structures are consistent with an 18-electron Mn(I), d^6, centre.

Precise three-dimensional descriptions. Put manganese at the origin and its six donor atoms along the $\pm x, \pm y, \pm z$ axes. Opposite signs on the same axis are trans; all other site pairs are cis. Let N_c denote the central terpyridine nitrogen, N_t the first terminal nitrogen, and N_u the other terminal nitrogen.

Compound	$+x$	$-x$	$+y$	$-y$	$+z$	$-z$
A	CO	CO	CO	CO	CO	Br
B	CO	N_c	CO	N_t	CO	Br
C	CO	N_c	CO	N_t	CO	Terminal N of azide
D	CO	N_c	N_u	N_t	CO	Br

Every carbonyl binds through carbon. In B and C, N_u is uncoordinated. In D it occupies the site vacated by the $+y$ carbonyl. Connect N_c to each terminal pyridyl ring through the actual terpyridine skeleton given in the SMILES.

This specifies one allowed stereoisomer of B and C; their mirror images are equally acceptable.

8.9

The alkyne is **dimethyl acetylenedicarboxylate**, also called **dimethyl but-2-ynedioate**, with SMILES `COC(=O)C#CC(=O)OC`.

Formation of E. The coordinated azide undergoes a $[3+2]$ cycloaddition with the alkyne. The three azide nitrogen atoms and the two alkyne carbon atoms become the five atoms of a **1,2,3-triazolate ring**:

$$\mathrm{C} + \mathrm{C_6H_6O_4} \longrightarrow \mathrm{E}.$$

The original azide functionality is consumed, explaining the disappearance of its $2042\ \mathrm{cm^{-1}}$ band. The two ester groups remain intact.

Number the ring consecutively **N1–N2–N3–C4–C5**, with C5 bonded back to N1. Both C4 and C5 carry a methoxycarbonyl group, $-\mathrm{C(=O)OCH_3}$.

In **E**, manganese remains bonded to the azide nitrogen that becomes **N1**. N1 is adjacent to C5, whereas the opposite end nitrogen N3 is adjacent to C4. This binding arrangement distinguishes the two ester-bearing sides of the ring and is consistent with the **two new ester carbonyl bands**.

Conversion of E to F. The metal attachment migrates from the end nitrogen N1 to the middle nitrogen N2:

$$\mathrm{E} \longrightarrow \mathrm{F}.$$

In **F**, the triazolate's two ester-substituted sides are related by the symmetry of the N2-bound ligand fragment, consistent with the reported **single ester carbonyl band**. E and F are therefore **N1-bound and N2-bound coordination isomers**, respectively; the ester groups have not been removed.

In both E and F, manganese retains its facial tricarbonyl group and κ²-terpyridine. Their octahedral arrangements are the same as C in the table above, with the $-z$ site occupied by:

- **E:** triazolate N1;
- **F:** triazolate N2.

The ring is aromatic and approximately planar. Its rotational conformation about the metal–nitrogen bond is not fixed by the SMILES or by the supplied data.

Formation of G. Hydrobromic acid protonates the triazolate ligand and supplies bromide to regenerate B:

$$\mathrm{F} + \mathrm{HBr} \longrightarrow \mathrm{B} + \mathrm{G}.$$

Hydrogen bromide has molecular SMILES `Br`; its aqueous dissociation can be represented as `[H+].[Br-]`.

The product G is the **2H tautomer**: the hydrogen is attached to **N2**, the middle nitrogen. Its formula is $\mathrm{C_6H_7N_3O_4}$, and its SMILES is `COC(=O)c1n[nH]nc1C(=O)OC`.

For the requested drawing, make the triazole ring planar and draw the two identical ester groups in matching, symmetry-related conformations. The two mirror planes are:

1. The plane of the triazole ring and the planar ester framework.
2. A plane perpendicular to the ring, passing through N2–H and the midpoint of the C4–C5 bond. This exchanges N1 with N3, C4 with C5, and the two ester groups.

An N1-protonated tautomer would destroy the second of these planes, so the stated symmetry selects the **2H tautomer**.

The solution was checked against the official solution.

Problem 9: Enzymes and cofactors

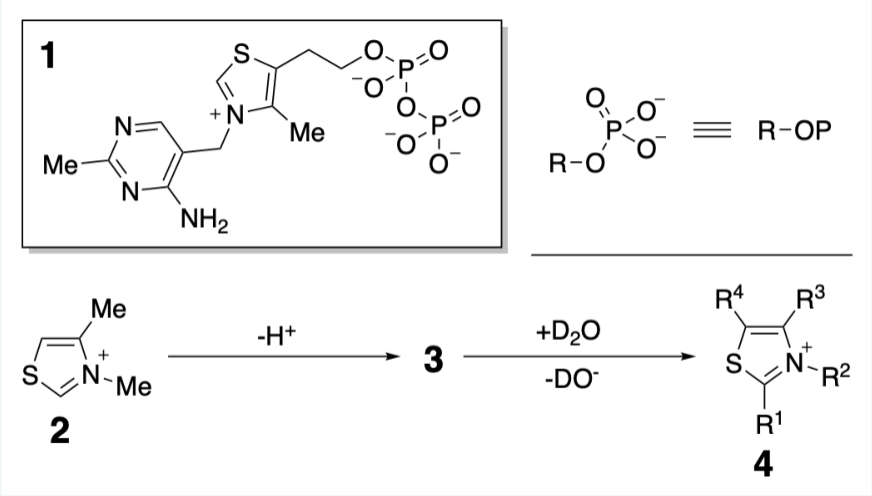
7% of the total

9.1	9.2	9.3	9.4	9.5	9.6	Total
2	6	2	6	10	10	36

In any answer for this task, **stereochemistry is not required** and the phosphate group can be abbreviated as "OP" (see the scheme below).

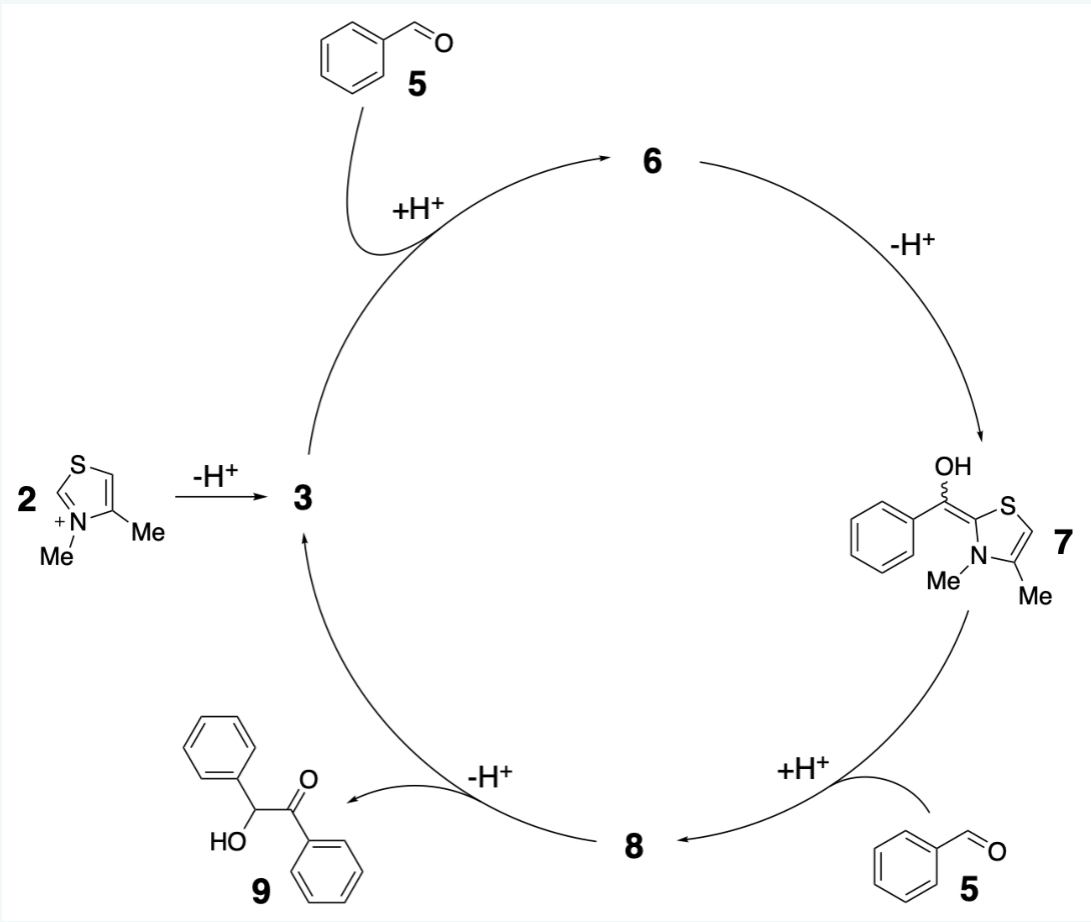
Transketolase (TK) and transaldolase (TA) are enzymes that catalyse C–C bond cleavage. TK contains the cofactor thiamine pyrophosphate **1**, a derivative of vitamin B1, in the active site.

Breslow and coworkers studied cation **2**, a model of cofactor **1**, to demonstrate the relatively acidic properties of thiamine. Cation **2** underwent a **single** H/D exchange in $\mathrm{D_2O}$, which yielded **4** via intermediate **3**.



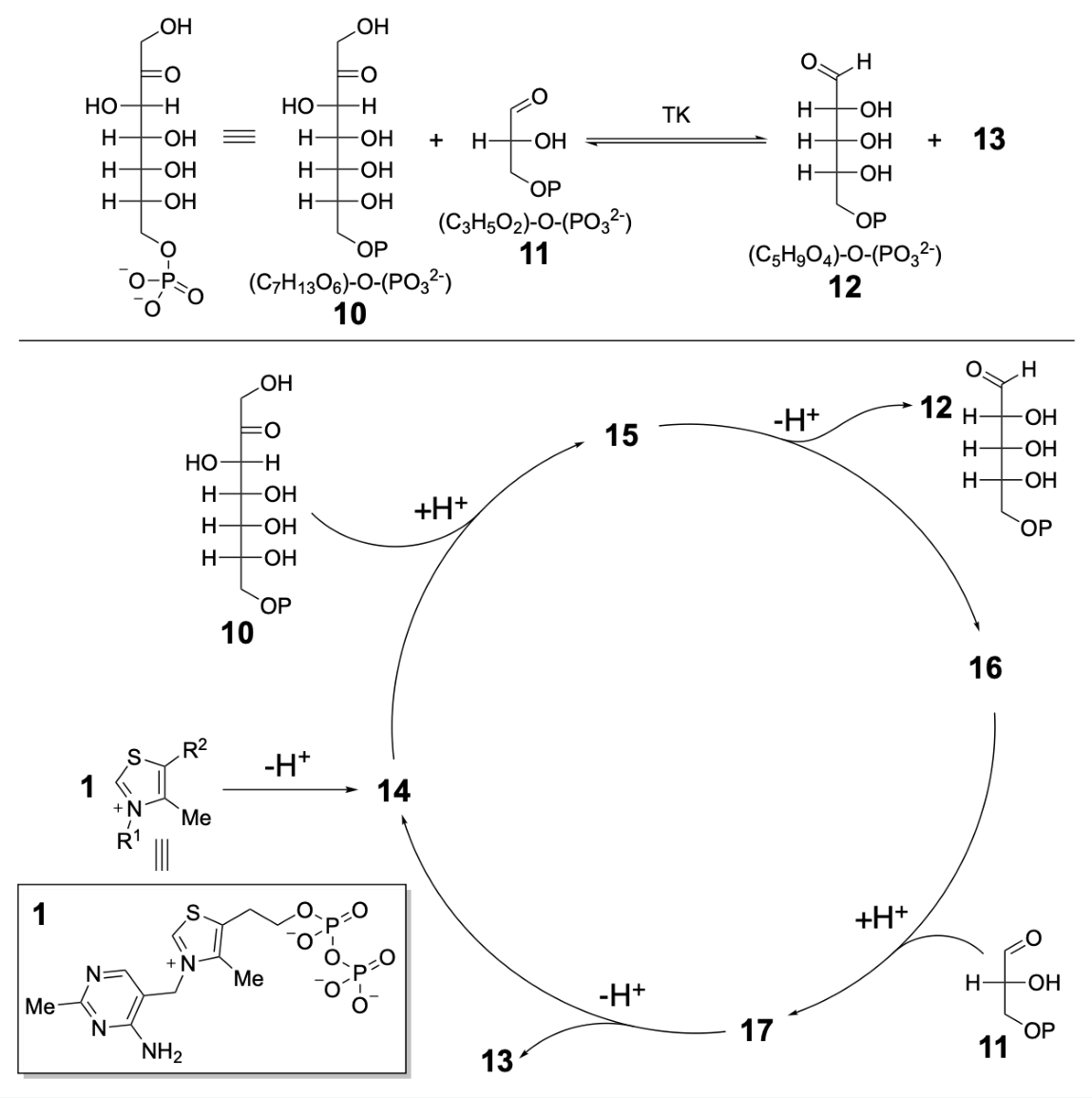
9.1 From the structures in the answer sheet, **choose** the one that corresponds to compound **4**.

Compounds such as **3** have many applications in organocatalysis. When a catalytic amount of **3** is generated in a solution of benzaldehyde **5**, a condensation reaction leads to product **9** via the catalytic cycle shown.



9.2 Draw the structures of compounds **3, 6, and 8**. Intermediates **6** and **8** are cations. There is no rearrangement in this catalytic cycle.

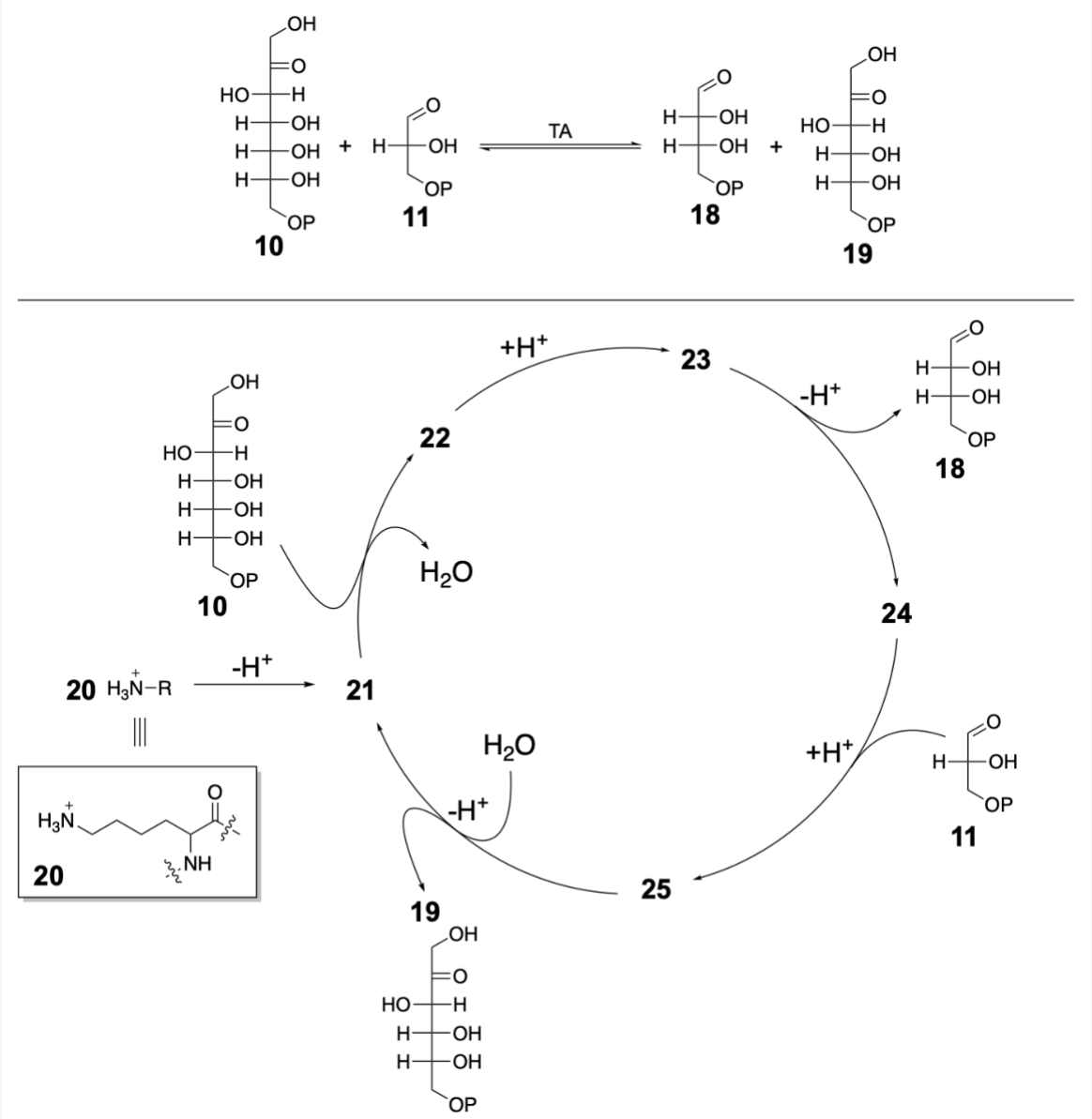
An aldose is a sugar containing an aldehyde. A ketose is a sugar containing a ketone. Enzyme TK contains **1** as a cofactor which catalyses the transfer of a two-carbon fragment from a ketose to an aldose by the catalytic cycle presented below.



9.3 Draw the structure of **13**.

9.4 Draw the structures of intermediates **15-17**.

Enzyme TA catalyses the transfer of a three-carbon fragment from a ketose to an aldose. The residue of amino acid lysine **20** in the active site of TA is responsible for the enzyme activity.

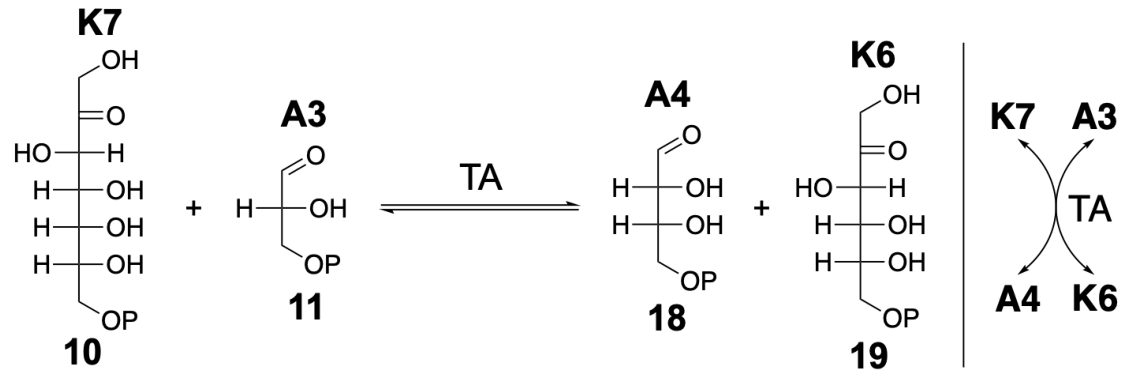


9.5 Draw the structures of intermediates **21-25**. **23** and **25** have the same functional groups.

TK and TA are used in some organisms to transform **five molecules of three-carbon** sugars into **three molecules of a five-carbon** sugars.

9.6 Propose a reaction sequence for this transformation. **Label** all sugars with a letter followed by a number. **Use** the letter **A** for any aldose and the letter **K** for any ketose. **Use** the number corresponding to the number of carbon atoms in the sugar; see the example below (e.g., present structure **10** as **K7**; using full structural formulae is not required). The number of carbon atoms in the sugar intermediates is **between 3 and 7**. There are **no non-enzymatic steps** in the pathway.

Write either TA or TK as the catalyst for each step. **Ignore** any phosphorylation, dephosphorylation, and isomerisation reactions. Beside transaldolase activity, TA exhibits aldolase activity resulting in only one product. Any five-carbon sugar (A5 or K5) is an acceptable product. **Use** the same style as shown in the figure below.



Official English text of the problem.

Answers

Stereochemistry is omitted throughout, as permitted. Phosphate charges in the SMILES follow the drawings. For **21–25**, `[*:1]` represents the unchanged protein substituent R attached to the lysine nitrogen.

- **9.1 — 2 points.**
  4 is **2-deuterio-3,4-dimethylthiazolium**, with D on the ring carbon between S and N:
  `C[N+]1=C([2H])SC=C1C`

In the figure's notation:

$$\boxed{R^1 = \mathrm{D}, \qquad R^2 = R^3 = \mathrm{CH_3}, \qquad R^4 = \mathrm{H}.}$$

- **9.2 — 6 points.**

3: 3,4-Dimethylthiazol-2-ylidene, shown as its neutral, charge-separated thiazolium-ylide resonance form:
`C[N+]1=[C-]SC=C1C`

6: 2-[Hydroxy(phenyl)methyl]-3,4-dimethylthiazolium, the first aldehyde adduct:
`C[N+]1=C(C(O)c2ccccc2)SC=C1C`

8: 2-(1,2-Dihydroxy-1,2-diphenylethyl)-3,4-dimethylthiazolium, the coupled diol adduct:
`C[N+]1=C(C(O)(c2ccccc2)C(O)c2ccccc2)SC=C1C`

- **9.3 — 2 points.**
  13 is **ketopentose 5-phosphate**, conventionally xylulose 5-phosphate:

  $$\boxed{\mathrm{HOCH_2{-}C(=O){-}CH(OH){-}CH(OH){-}CH_2OP}}$$

  SMILES: `OCC(=O)C(O)C(O)COP(=O)([O-])[O-]`

- **9.4 — 6 points.**

15: Sedoheptulose 7-phosphate–TPP covalent adduct; donor sugar C2 bears OH and is bonded to thiazolium C2:
`Cc1ncc(C[N+]2=C(C(O)(CO)C(O)C(O)C(O)C(O)COP(=O)([O-])[O-])SC(CCOP(=O)`

`([O-])OP(=O)([O-])[O-])=C2C)c(N)n1`

16: Dihydroxyethyl-TPP enaminol; the thiazole C2 is double-bonded to the external carbon bearing OH and $\mathrm{CH_2OH}$:
`Cc1ncc(CN2C(=C(O)CO)SC(CCOP(=O)([O-])OP(=O)([O-])[O-])=C2C)c(N)n1`

17: Ketopentose 5-phosphate–TPP covalent adduct, immediately before ketopentose release:
`Cc1ncc(C[N+]2=C(C(O)(CO)C(O)C(O)COP(=O)([O-])[O-])SC(CCOP(=O)([O-])OP(=O)([O-])[O-])=C2C)c(N)n1`

- **9.5 — 10 points.**

21: Neutral lysine ε-amine, $\mathrm{RNH_2}$:
`[*:1]N`

22: Sedoheptulose 7-phosphate–lysine ketimine, with an uncharged imine nitrogen:
`[*:1]N=C(CO)C(O)C(O)C(O)C(O)COP(=O)([O-])[O-]`

23: N-Protonated sedoheptulose 7-phosphate–lysine ketimine, an iminium intermediate:
`[*:1][NH+]=C(CO)C(O)C(O)C(O)C(O)COP(=O)([O-])[O-]`

24: Lysine-bound three-carbon enamine, $\mathrm{RNH{-}C(CH_2OH){=}CH(OH)}$:
`[*:1]NC(CO)=CO`

25: N-Protonated fructose 6-phosphate–lysine ketimine, an iminium intermediate:
`[*:1][NH+]=C(CO)C(O)C(O)C(O)C(O)COP(=O)([O-])[O-]`

- **9.6 — 10 points.**
  A valid four-step sequence is

$$\begin{aligned}
\mathrm{K_3} + \mathrm{A_3} &\xrightarrow{\mathrm{TA}} \mathrm{K_6} \\
\mathrm{K_6} + \mathrm{A_3} &\xrightarrow{\mathrm{TK}} \mathrm{A_4} + \mathrm{K_5} \\
\mathrm{K_3} + \mathrm{A_4} &\xrightarrow{\mathrm{TA}} \mathrm{K_7} \\
\mathrm{K_7} + \mathrm{A_3} &\xrightarrow{\mathrm{TK}} \mathrm{A_5} + \mathrm{K_5}.
\end{aligned}$$

  TA acts as an **aldolase** in the first and third steps. The net transformation is

$$\boxed{2\,\mathrm{K_3} + 3\,\mathrm{A_3} \longrightarrow \mathrm{A_5} + 2\,\mathrm{K_5}.}$$

Solution

9.1

Compound **2** is **3,4-dimethylthiazolium**, `C[N+]1=CSC=C1C`. Its most readily exchanged hydrogen is attached to **C2, the carbon between sulfur and the positively charged nitrogen**.

Removing this proton gives **3**, a resonance-stabilized thiazolium ylide/N-heterocyclic carbene. The SMILES in the answers uses the ylide representation: N carries $+1$, C2 carries -1, and the molecule is neutral overall.

Reaction of this carbon centre with heavy water, $\mathrm{D_2O}$, `[2H]O[2H]`, installs D at C2. Neither methyl group nor the other ring C–H position changes. The balanced net isotope exchange is

$$\mathrm{C_5H_8NS^+ + D_2O \rightleftharpoons C_5H_7DNS^+ + HDO},$$

where HDO is hydrogen deuterium oxide, `[2H]O`.

Thus the required drawing is the original thiazolium ring with its C2 hydrogen replaced by D.

9.2

The additional structures needed to follow the cycle are:

Compound	Name	SMILES
5	Benzaldehyde	`O=Cc1ccccc1`
7	Breslow enaminol intermediate	`CN1C(=C(O)c2ccccc2)SC=C1C`
9	Benzoin, 2-hydroxy-1,2-diphenylethan-1-one	`O=C(c1ccccc1)C(O)c1ccccc1`

Let C_T denote C2 of the thiazole ring, and let Ph denote phenyl.

Formation of 6. The nucleophilic carbon of **3** attacks the carbonyl carbon of benzaldehyde. The carbonyl π electrons move to oxygen, which is then protonated. Therefore, draw a single bond from C_T to a $\mathrm{CH(OH)Ph}$ group. The thiazolium nitrogen remains positively charged.

Formation of 7. Intermediate **6** loses the proton on its **benzylic carbon**, not the hydroxyl proton. The resulting electron redistribution creates an exocyclic double bond between that carbon and C_T, while the ring $\mathrm{N{=}C_T}$ bond becomes single. The nitrogen becomes neutral. This is the Breslow intermediate, an acyl-anion equivalent.

Formation of 8. The external enaminol carbon of **7** attacks the carbonyl carbon of a second benzaldehyde molecule. Protonation of the newly formed alkoxide gives **8**. Its side-chain connectivity is

$$C_\mathrm{T}\mathrm{-C(OH)(Ph)-CH(OH)Ph}.$$

The carbon directly attached to the catalyst has **no hydrogen**: it is bonded to OH, Ph, the second aldehyde-derived carbon, and C_T. The ring nitrogen is again positively charged.

Release of 9. Deprotonation of the hydroxyl directly adjacent to the catalyst allows that oxygen to form a carbonyl. Cleavage of the bond to C_T releases benzoin and regenerates **3**.

The balanced overall reaction is

$$\boxed{2\,\mathrm{C_6H_5CHO} \xrightarrow{3} \mathrm{C_6H_5COCH(OH)C_6H_5}.}$$

Although called a benzoin condensation, this net reaction does **not** eliminate water.

9.3

The given sugar identities and their open-chain structures are:

Compound	Name	SMILES
10	Sedoheptulose 7-phosphate	`OCC(=O)C(O)C(O)C(O)C(O)COP(=O)([O-])[O-]`
11	Glyceraldehyde 3-phosphate	`O=CC(O)COP(=O)([O-])[O-]`
12	Ribose 5-phosphate	`O=CC(O)C(O)C(O)COP(=O)([O-])[O-]`

Number the carbons of **10** from its unphosphorylated $\mathrm{CH_2OH}$ end. TK removes its **C1–C2 two-carbon unit** by breaking the C2–C3 bond. The remaining original C3–C7 fragment becomes the five-carbon aldose **12**.

The transferred two-carbon unit then combines with the three-carbon aldose **11**. Its carbonyl carbon becomes C2 of the new ketose, giving

$$\mathrm{HOCH_2{-}C(=O){-}CH(OH){-}CH(OH){-}CH_2OP},$$

which is **13**, a ketopentose 5-phosphate.

The balanced molecular equation, using the phosphate ionization shown in the question, is

$$\mathrm{C_7H_{13}O_{10}P^{2-} + C_3H_5O_6P^{2-} \overset{TK}{\rightleftharpoons} C_5H_9O_8P^{2-} + C_5H_9O_8P^{2-}}.$$

The two products have the same molecular formula but different carbonyl positions: **12** is an aldose and **13** a ketose.

9.4

Cofactor **1** is **thiamine diphosphate**, represented in the protonation state drawn in the question by:

```
Cc1ncc(C[N+]2=CSC(CCOP(=O)([O-])OP(=O)([O-])[O-])=C2C)c(N)n1
```

Its C2-deprotonated form **14**, the **thiamine diphosphate ylide**, is:

```
Cc1ncc(C[N+]2=[C-]SC(CCOP(=O)([O-])OP(=O)([O-])[O-])=C2C)c(N)n1
```

The chemistry parallels the benzoin cycle.

Intermediate 15. The nucleophilic thiazole C2 of **14** attacks sugar C2, the ketone carbon of **10**. Protonation of oxygen gives a tetrahedral alcohol.

For the drawing, retain all thiamine substituents and attach its thiazolium C2 to the second carbon of this chain:

$$\mathrm{HOCH_2{-}C(OH)(T){-}CH(OH){-}CH(OH){-}CH(OH){-}CH(OH){-}CH_2OP},$$

where T marks the single bond to the thiazolium ring. The ring nitrogen carries $+1$.

Intermediate 16. Break the bond between sugar C2 and C3. The hydroxyl on original C3 becomes the aldehyde oxygen of **12**, with loss of its proton. The C1–C2 fragment remains attached to TPP.

Electron redistribution gives an exocyclic double bond from thiazole C2 to the retained carbon bearing OH and $\mathrm{CH_2OH}$. The thiazole C2–N bond is now single and N is neutral. This is the two-carbon enaminol **16**.

Intermediate 17. The external enaminol carbon attacks the aldehyde carbon of **11**. Protonation of the new alkoxide produces the five-carbon adduct:

$$\mathrm{HOCH_2{-}C(OH)(T){-}CH(OH){-}CH(OH){-}CH_2OP}.$$

The thiazolium nitrogen again carries $+1$.

Finally, deprotonation of the hydroxyl at sugar C2 and formation of its carbonyl cleave the bond to the catalyst, releasing **13** and regenerating **14**.

The positive nitrogen charges in **15** and **17** refer to the thiazolium ring; their complete structures also contain negatively charged phosphate groups.

9.5

The enzyme-bound lysine ammonium group **20** is represented by `[*:1][NH3+]`. Deprotonation gives the neutral ε-amine **21**, $\mathrm{RNH_2}$.

The sugars released in this cycle are:

Compound	Name	SMILES
18	Erythrose 4-phosphate	`O=CC(O)C(O)COP(=O)([O-])[O-]`
19	Fructose 6-phosphate	`OCC(=O)C(O)C(O)C(O)COP(=O)([O-])[O-]`

Formation of 22. The lysine amine attacks the ketone carbon, C2, of **10**. Loss of water, `O`, gives a Schiff base. Thus, replace the C2 carbonyl oxygen of **10** by $\mathrm{N{-}R}$:

$$\mathrm{HOCH_2{-}C(=N{-}R){-}CH(OH){-}CH(OH){-}CH(OH){-}CH(OH){-}CH_2OP}.$$

The imine nitrogen of **22** has no hydrogen and no formal charge.

Formation of 23. Protonation occurs at the imine nitrogen:

$$\mathrm{HOCH_2{-}C(=[NH^+]{-}R){-}CH(OH){-}CH(OH){-}CH(OH){-}CH(OH){-}CH_2OP}.$$

The resulting iminium group facilitates the following C–C cleavage.

Formation of 24. Cleavage occurs between original sugar **C3 and C4**. The hydroxyl on C4 becomes an aldehyde, releasing the C4–C7 fragment as erythrose 4-phosphate **18**.

The retained C1–C3 fragment becomes the enamine

$$\boxed{\mathrm{HOCH_2{-}C(NH{-}R){=}CH(OH)}}.$$

The C2=C3 double bond is formed as the iminium π electrons move onto nitrogen. The nitrogen is therefore neutral and retains its hydrogen.

Formation of 25. The terminal enamine carbon, original C3, attacks the aldehyde carbon of **11**. The new alkoxide is protonated, and the iminium bond is restored. The resulting six-carbon structure is

$$\mathrm{HOCH_2{-}C(=[NH^+]{-}R){-}CH(OH){-}CH(OH){-}CH(OH){-}CH_2OP}.$$

Thus **23 and 25 both contain an iminium group, alcohol groups, and a phosphate ester**, as required. They differ in carbon-chain length.

Hydrolysis of **25** consumes water and restores the ketone, releasing fructose 6-phosphate **19**, neutral lysine amine **21**, and a proton, $\mathrm{H^+}$, `[H+]`.

Water released during Schiff-base formation is consumed during hydrolysis. The balanced overall transformation is

$$\boxed{\mathrm{C_7H_{13}O_{10}P^{2-} + C_3H_5O_6P^{2-} \overset{\mathrm{TA}}{\rightleftharpoons} C_4H_7O_7P^{2-} + C_6H_{11}O_9P^{2-}}.}$$

9.6

Choose **two K3 molecules and three A3 molecules** as the five starting trioses. For this part, phosphorylation is suppressed as instructed. Representative sugar identities are:

Label	Representative sugar	SMILES without stereochemistry or phosphate
A3	Glyceraldehyde	`O=CC(O)CO`

Label	Representative sugar	SMILES without stereochemistry or phosphate
K3	Dihydroxyacetone	`OCC(=O)CO`
A4	Erythrose	`O=CC(O)C(O)CO`
A5	Ribose	`O=CC(O)C(O)C(O)CO`
K5	Xylulose	`OCC(=O)C(O)C(O)CO`
K6	Fructose	`OCC(=O)C(O)C(O)C(O)CO`
K7	Sedoheptulose	`OCC(=O)C(O)C(O)C(O)C(O)CO`

The sequence works as follows:

Step	Reaction	Explanation
1	$\mathrm{K}_3 + \mathrm{A}_3 \xrightarrow{\mathrm{TA}} \mathrm{K}_6$	TA's aldolase activity joins two trioses, producing one six-carbon ketose.
2	$\mathrm{K}_6 + \mathrm{A}_3 \xrightarrow{\mathrm{TK}} \mathrm{A}_4 + \mathrm{K}_5$	TK transfers two carbons from K6 to A3. Retain the K5 as a final product.
3	$\mathrm{K}_3 + \mathrm{A}_4 \xrightarrow{\mathrm{TA}} \mathrm{K}_7$	TA's aldolase activity joins the remaining K3 to A4, producing one seven-carbon ketose.
4	$\mathrm{K}_7 + \mathrm{A}_3 \xrightarrow{\mathrm{TK}} \mathrm{A}_5 + \mathrm{K}_5$	TK transfers two carbons from K7 to the remaining A3, giving two further pentoses.

For the answer-sheet diagram, connect these four steps in order through **K6**, **A4**, and **K7**. Draw a **K5 output branch at step 2**, and terminate step 4 with **A5 and K5**. Label the successive reactions **TA, TK, TA, TK**.

Cancelling the intermediates gives

$$2\,\mathrm{K}_3 + 3\,\mathrm{A}_3 \longrightarrow \mathrm{A}_5 + 2\,\mathrm{K}_5.$$

With phosphorylation suppressed, the molecular balance is

$$5\,\mathrm{C_3H_6O_3} \longrightarrow 3\,\mathrm{C_5H_{10}O_5}.$$

Hence

$$5 \times 3 = 3 \times 5 = 15$$

carbon atoms are conserved. Every sugar contains between three and seven carbons, and every displayed reaction is enzymatic. The two aldolase steps are additions; they do not involve net elimination of water.

The answers were checked against the official answers published by the organisers.