IChO 2026

Theory problems and solutions · Tashkent, Uzbekistan · 9 theory problems with complete solutions

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Problem 1: A journey through time: The secrets of Avicenna

T1. A journey through time: The secrets of Avicenna

7%

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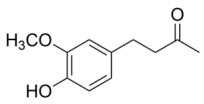
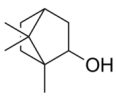
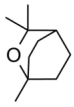
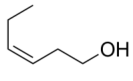
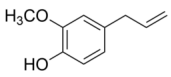
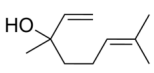
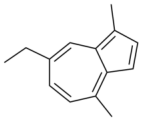
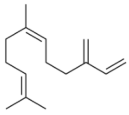
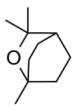


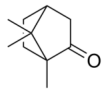
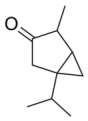
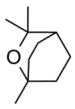
A chemist found herself in the 11th Century, where she met the renowned physician Avicenna. In Avicenna's laboratory, she discovered a blue elixir and a yellow mysterious stone. She brought them back to 2026. Determined to uncover their composition, she began her research.

Part 1. The blue elixir

At first, the chemist compiled a table listing the names of the only four plants which she saw in Avicenna's lab that could have been used to prepare the elixir, and the compounds that can be extracted from these plants.

Plants	Compounds that can be extracted		
Zingiber	**1** ($C_{11}H_{14}O_3$)	**2** ($C_{10}H_{18}O$)	**3** ($C_{10}H_{18}O$)
Hypericum	**4** ($C_6H_{12}O$)	**5** ($C_{10}H_{12}O_2$)	**6** ($C_{10}H_{18}O$)
Chamomilla	**7** ($C_{14}H_{16}$)	**8** ($C_{15}H_{24}$)	**3** ($C_{10}H_{18}O$)
Artemisia	**9** ($C_{10}H_{16}O$)	**10** ($C_{10}H_{18}O$)	**3** ($C_{10}H_{18}O$)

Plants	Compounds that can be extracted		
Zingiber			
	1 ($C_{11}H_{14}O_3$)	**2** ($C_{10}H_{18}O$)	**3** ($C_{10}H_{18}O$)
Hypericum			
	4 ($C_6H_{12}O$)	**5** ($C_{10}H_{12}O_2$)	**6** ($C_{10}H_{18}O$)
Chamomilla			
	7 ($C_{14}H_{16}$)	**8** ($C_{15}H_{24}$)	**3** ($C_{10}H_{18}O$)

Artemisia			
	9 ($C_{10}H_{16}O$)	**10** ($C_{10}H_{18}O$)	**3** ($C_{10}H_{18}O$)

Using chromatography, she determined that the elixir consists of four different substances (**X, Y, Z** and **W**).

The chemist then discovered that **X** can isomerise into **Y** in an acidic medium and that **Y** has a plane of symmetry.

1.1 Identify X and Y. — 3.0 pt

Chromatography also revealed it was substance **Z** that gave the elixir its blue colour. **Z** is a derivative of the well-known substance **A**, which has two perpendicular planes of symmetry. When heated, **A** isomerises into aromatic compound **B**, which has three mutually perpendicular planes of symmetry. When substance **Z** is chlorinated, a pair of peaks with an intensity ratio of 3:1 is observed in the mass spectrum at m/z 218 and 220, respectively.

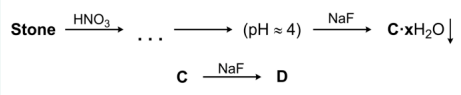
1.2 Identify Z and draw the structures of substances A and B. — 4.0 pt

The chemist extracted **W** from the elixir. When **W** was added to an aqueous Fe^{3+} solution, a characteristic colour change was observed. Mass spectrometric analysis of **W** revealed the intensity ratio of $[\mathrm{M}]^+ : [\mathrm{M}+1]^+ = 9:1$, where M is the molecular ion. Assume carbon consists exclusively of $^{12}\mathrm{C}$ and $^{13}\mathrm{C}$, the natural isotopic abundance of $^{12}\mathrm{C}$ is 98.9%, and all other elements are monoisotopic.

1.3 Determine the number of carbon atoms (n) from the mass spec data and identify W. Show your calculations. — 3.0 pt

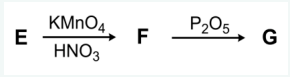
Part 2. The mysterious stone

Avicenna had told her the **stone** was a stoichiometric compound. She dissolved it in dilute nitric acid. After that, she adjusted the pH of the solution to ~4 and added NaF. This led to the formation of precipitate $\mathbf{C}\cdot x\mathrm{H_2O}$, which contained 39.16% water by mass. Anhydrous **C** reacts with an excess of NaF to yield compound **D**, which contains 32.85% sodium and 12.85% of metal **Q** by mass, and is used in the industrial production of **Q**.



1.4 Identify metal Q and compounds $\mathbf{C}\cdot x\mathrm{H_2O}$ and D. — 4.0 pt

Avicenna told her that he found the **stone** in a coal deposit. The **stone** contains the anion of a highly symmetrical acid **F**. Reaction of **F** with $\mathrm{P_2O_5}$ gives binary compound **G**, which contains 49.98% of oxygen by mass and has a three-fold symmetry axis. **F** can be prepared by oxidising compound **E** with potassium permanganate in an acidic solution. **E** contains 11.18% of hydrogen by mass and has a six-fold symmetry axis.

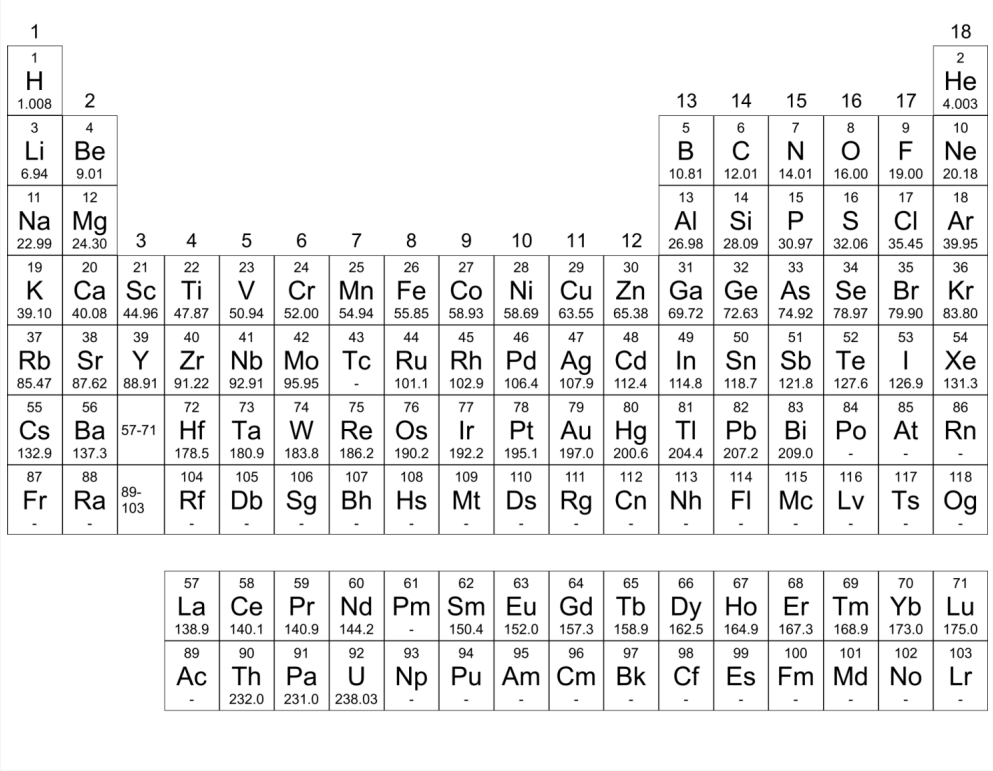


1.5 Draw the structures of E, F, and G. — 7.0 pt

Then, she analysed the **stone** thermogravimetrically in open air. A 10.00 g sample began to lose mass at approximately $100\ ^\circ\mathrm{C}$ and stopped at 5.75 g at $200\ ^\circ\mathrm{C}$. A second drop in mass was observed at $400\ ^\circ\mathrm{C}$, with a final mass of 1.50 g of compound **H** remaining constant at higher temperatures.

1.6 Determine the chemical formulae of the stone and compound H using thermogravimetric data. — 4.0 pt

Periodic Table of Elements



Official English text of the problem.

Answers

- **1.1: X = 6**, linalool; **Y = 3**, 1,8-cineole (eucalyptol).
- **1.2: Z = 7**, chamazulene; **A** is azulene; **B** is naphthalene.
- **1.3:** $n = \boxed{10}$; **W = 5**, eugenol.
- **1.4: Q** is aluminium; $\mathbf{C} \cdot x\mathrm{H_2O} = \boxed{\mathrm{AlF_3 \cdot 3\,H_2O}}$, so $x = 3$; **D** is cryolite, $\boxed{\mathrm{Na_3AlF_6}}$.
- **1.5: E** is hexamethylbenzene, $\mathrm{C_{12}H_{18}}$; **F** is mellitic acid, $\mathrm{C_6(COOH)_6}$; **G** is mellitic trianhydride, $\mathrm{C_{12}O_9}$.
- **1.6:** The **stone** is mellite, $\boxed{\mathrm{Al_2[C_6(COO)_6] \cdot 16\,H_2O}}$; **H** is aluminium oxide, $\boxed{\mathrm{Al_2O_3}}$.

Solution

1.1

X is compound 6, linalool, or 3,7-dimethylocta-1,6-dien-3-ol:

```
C=CC(C)(O)CCC=C(C)C
```

Y is compound 3, 1,8-cineole, also called eucalyptol:

```
CC12CCC(CC1)C(C)(C)O2
```

Linalool can undergo acid-catalysed rearrangement and cyclisation to 1,8-cineole. The net transformation conserves the molecular formula:

$$\mathrm{C_{10}H_{18}O} \xrightarrow{\mathrm{H^+}} \mathrm{C_{10}H_{18}O} \qquad (\mathbf{X} \longrightarrow \mathbf{Y}).$$

The acyclic diene alcohol becomes a saturated bicyclic ether: two double bonds are replaced by two rings.

In 1,8-cineole, a mirror plane contains the oxygen-containing bridge and the two bridgehead carbons, and exchanges the two equivalent carbon bridges. This satisfies the symmetry clue. Linalool's configuration is unspecified in the supplied drawing, so its SMILES does not assign an enantiomer.

1.2

The required parent compound is **A, azulene**, $\mathrm{C_{10}H_8}$:

```
C1=CC=C2C=CC=C2C=C1
```

Its structure consists of a five-membered ring fused to a seven-membered ring, with a delocalised aromatic 10π-electron system. To draw it, show these two rings sharing one edge and five double bonds in a valid Kekulé arrangement.

Azulene has two perpendicular mirror planes: the molecular plane and a plane perpendicular to it that bisects both rings.

On heating, azulene isomerises to **B, naphthalene**, $\mathrm{C_{10}H_8}$:

`c1ccc2ccccc2c1`

$$\mathrm{C_{10}H_8} \xrightarrow{\Delta} \mathrm{C_{10}H_8} \qquad (\mathbf{A} \longrightarrow \mathbf{B}).$$

Naphthalene consists of two fused six-membered aromatic rings. Its molecular plane and the two planes perpendicular to it through its long and short molecular axes are three mutually perpendicular mirror planes.

Thus the blue component is **Z, compound 7, chamazulene**, or 7-ethyl-1,4-dimethylazulene, $\mathrm{C_{14}H_{16}}$:

`CCC1=CC2=C(C)C=CC2=C(C)C=C1`

The chlorination data independently confirm this identification. A molecular-ion pair separated by two mass units with approximately $3:1$ intensities is characteristic of **one chlorine atom**, arising from $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$.

Monochlorination by substitution gives:

$$\mathrm{C_{14}H_{16} + Cl_2 \longrightarrow C_{14}H_{15}Cl + HCl}.$$

The nominal masses of the two chlorine isotopologues are

$$14(12) + 15(1) + 35 = 218,$$
$$14(12) + 15(1) + 37 = 220.$$

These are exactly the stated peaks. Their masses establish the chlorinated formula without requiring the chlorine substitution position.

1.3

Let

$$p = P(^{12}\mathrm{C}) = 0.989, \qquad q = P(^{13}\mathrm{C}) = 0.011.$$

For a molecule containing n carbon atoms, the probabilities of containing no $^{13}\mathrm{C}$ atoms and exactly one $^{13}\mathrm{C}$ atom are

$$P_0 = p^n, \qquad P_1 = nqp^{n-1}.$$

Therefore,

$$\frac{I(M+1)}{I(M)} = \frac{P_1}{P_0} = n\frac{q}{p} = \frac{1}{9}.$$

Hence

$$n = \frac{0.989}{9(0.011)} = 9.9899 \approx \boxed{10}.$$

The small departure from an integer reflects rounding of the supplied abundance and intensity ratio.

The characteristic colour with aqueous iron(III) identifies a **phenolic group**, through formation of coloured iron–phenolate complexes. Compounds **1** and **5** contain phenolic hydroxyl groups, but only **5** contains ten carbon atoms.

Thus **W is compound 5, eugenol**, or 2-methoxy-4-(prop-2-en-1-yl)phenol, $\mathrm{C_{10}H_{12}O_2}$:

`COc1cc(CC=C)ccc1O`

1.4

Compound **D** is a sodium–metal fluoride. Its fluorine mass percentage is

$$w_{\mathrm{F}} = 100.00 - 32.85 - 12.85 = 54.30\%.$$

For $100.00\ \mathrm{g}$ of **D**,

$$n_{\mathrm{Na}} = \frac{32.85\ \mathrm{g}}{22.99\ \mathrm{g\,mol^{-1}}} = 1.4289\ \mathrm{mol},$$
$$n_{\mathrm{F}} = \frac{54.30\ \mathrm{g}}{19.00\ \mathrm{g\,mol^{-1}}} = 2.8579\ \mathrm{mol}.$$

Thus $\mathrm{Na:F} = 1:2$. A formula written with one metal atom is consequently $\mathrm{Na}_a\mathrm{QF}_{2a}$, with the metal in oxidation state $+a$. Its atomic molar mass must satisfy

$$\frac{M_Q}{a} = \frac{12.85}{32.85}(22.99) = 8.993\ \mathrm{g\,mol^{-1}}.$$

For $a = 3$, this gives $M_Q = 26.98\ \mathrm{g\,mol^{-1}}$, identifying **aluminium**.

Thus **Q is aluminium**, Al, SMILES `[Al]`, and **D is cryolite**, sodium hexafluoroaluminate, $\mathrm{Na_3AlF_6}$.

Its molar mass is

$$M_D = 3(22.99) + 26.98 + 6(19.00) = 209.95\ \mathrm{g\,mol^{-1}}.$$

The calculated percentages are

$$w_{\mathrm{Na}} = \frac{68.97}{209.95}(100\%) = 32.85\%, \qquad w_{\mathrm{Al}} = \frac{26.98}{209.95}(100\%) = 12.85\%.$$

Cryolite is used as the molten electrolyte medium in aluminium production, agreeing with the industrial clue.

Its ionic-composition SMILES is:

`[Na+].[Na+].[Na+].[Al+3].[F-].[F-].[F-].[F-].[F-].[F-]`

Cryolite contains octahedral $[\mathrm{AlF_6}]^{3-}$ units. The disconnected SMILES records composition and charges, not this coordination geometry or the crystal lattice.

C is aluminium fluoride, $\mathrm{AlF_3}$:

```
[Al+3].[F-].[F-].[F-]
```

Since

$$M_{\mathrm{AlF_3}} = 26.98 + 3(19.00) = 83.98\ \mathrm{g\,mol^{-1}},$$

the hydrate's water fraction gives

$$\frac{18.016x}{83.98 + 18.016x} = 0.3916.$$

Therefore,

$$x = \frac{0.3916(83.98)}{0.6084(18.016)} = 3.0003 \approx \boxed{3}.$$

The precipitate is **aluminium fluoride trihydrate**, $\mathrm{AlF_3 \cdot 3\,H_2O}$:

```
[Al+3].[F-].[F-].[F-].O.O.O
```

The relevant balanced reactions are

$$\mathrm{Al^{3+} + 3\,F^- + 3\,H_2O \longrightarrow AlF_3 \cdot 3\,H_2O\,(s)}$$

and

$$\mathrm{AlF_3 + 3\,NaF \longrightarrow Na_3AlF_6}.$$

1.5

E is hexamethylbenzene, $\mathrm{C_{12}H_{18}}$:

```
Cc1c(C)c(C)c(C)c(C)c1C
```

To draw **E**, place a methyl group on every carbon of a benzene ring. The six equivalent substituents give the required sixfold symmetry of the substitution pattern about an axis perpendicular to the ring.

Its hydrogen mass percentage is

$$w_{\mathrm{H}} = \frac{18(1.008)}{12(12.01) + 18(1.008)}(100\%) = 11.1818\% \approx 11.18\%.$$

Oxidation of all six benzylic methyl groups to carboxyl groups produces **F, mellitic acid**, or benzenehexacarboxylic acid, $\mathrm{C_6(COOH)_6}$:

```
O=C(O)c1c(C(=O)O)c(C(=O)O)c(C(=O)O)c(C(=O)O)c1C(=O)O
```

To draw **F**, replace each methyl group in **E** by $-\mathrm{COOH}$.

Each methyl carbon undergoes a six-electron oxidation, giving 36 electrons per molecule of **E**. The balanced oxidation half-reaction is

$$\mathrm{C_{12}H_{18} + 12\,H_2O \longrightarrow C_{12}H_6O_{12} + 36\,H^+ + 36\,e^-}.$$

Combining this with acidic permanganate reduction gives

$$\mathrm{5\,C_{12}H_{18} + 36\,MnO_4^- + 108\,H^+ \longrightarrow 5\,C_{12}H_6O_{12} + 36\,Mn^{2+} + 84\,H_2O}.$$

Dehydration of three adjacent pairs of carboxyl groups gives **G, mellitic trianhydride**, $\mathrm{C_{12}O_9}$:

```
O=C1OC(=O)c2c1c1c(c3c2C(=O)OC3=O)C(=O)OC1=O
```

To draw **G**, retain the central benzene ring and form cyclic anhydrides from carboxyl pairs at positions $1,2$, $3,4$, and $5,6$. Each pair becomes a five-membered ring containing the linkage $-\mathrm{C(=O)-O-C(=O)^-}$, fused to one edge of the benzene ring. Rotation by 120° exchanges the three anhydride rings, giving a threefold axis perpendicular to the central ring.

Formally, **F** loses three water molecules:

$$\mathrm{C_{12}H_6O_{12} \longrightarrow C_{12}O_9 + 3\,H_2O}.$$

Including their uptake by the dehydrating agent, the net balance is

$$\mathrm{C_{12}H_6O_{12} + P_2O_5 \longrightarrow C_{12}O_9 + 2\,H_3PO_4}.$$

The oxygen percentage of **G** is

$$w_{\mathrm{O}} = \frac{9(16.00)}{12(12.01) + 9(16.00)}(100\%) = 49.9792\% \approx 49.98\%.$$

Thus both the elemental composition and symmetry agree.

1.6

Mellitic acid is hexabasic. Its fully deprotonated anion has charge $6-$, so charge balance with aluminium(III) gives the anhydrous salt

$$\mathrm{Al_2[C_6(COO)_6] = Al_2C_{12}O_{12}}.$$

Its molar mass is

$$M_{\text{anhydrous}} = 2(26.98) + 12(12.01) + 12(16.00) = 390.08\ \mathrm{g\,mol^{-1}}.$$

The first mass loss is dehydration:

$$m_{\text{water}} = 10.00 - 5.75 = 4.25\ \mathrm{g},$$
$$n_{\text{water}} = \frac{4.25}{18.016} = 0.2359\ \mathrm{mol}.$$

The amount of anhydrous salt is

$$n_{\text{salt}} = \frac{5.75}{390.08} = 0.0147406\ \text{mol}.$$

Therefore, the number of waters per formula unit is

$$x = \frac{0.235901}{0.0147406} = 16.0036 \approx \boxed{16}.$$

The stone is consequently **mellite**, aluminium mellitate hexadecahydrate:

$$\boxed{\mathrm{Al_2[C_6(COO)_6]\cdot 16\,H_2O}}.$$

Its formula-unit composition SMILES is:

```
[Al+3].[Al+3].O=C([O-])c1c(C(=O)[O-])c(C(=O)[O-])c(C(=O)[O-])c(C(=O)[O-])c1C(=O)[O-].O.O.O.O.O.O.O.O.O.O.O.O.O.O.O.O
```

This notation gives the two aluminium ions, mellitate anion, and sixteen waters; it does not assign their solid-state coordination.

The dehydration equation is

$$\mathrm{Al_2C_{12}O_{12}\cdot 16\,H_2O} \xrightarrow{\Delta} \mathrm{Al_2C_{12}O_{12} + 16\,H_2O}.$$

In air, the organic anion is oxidised, leaving **H, aluminium oxide**, $\mathrm{Al_2O_3}$:

```
[Al+3].[Al+3].[O-2].[O-2].[O-2]
```

The balanced oxidation is

$$\mathrm{2\,Al_2C_{12}O_{12} + 15\,O_2} \xrightarrow{\Delta} \mathrm{2\,Al_2O_3 + 24\,CO_2}.$$

Thus

$$M_{\mathrm{Al_2O_3}} = 2(26.98) + 3(16.00) = 101.96\ \mathrm{g\,mol^{-1}}.$$

Using

$$M_{\text{stone}} = 390.08 + 16(18.016) = 678.336\ \mathrm{g\,mol^{-1}},$$

the two predicted residue masses from 10.00 g are

$$m_{\text{anhydrous}} = 10.00\frac{390.08}{678.336} = 5.7505\ \text{g} \approx 5.75\ \text{g},$$
$$m_{\mathrm{Al_2O_3}} = 10.00\frac{101.96}{678.336} = 1.5031\ \text{g} \approx 1.50\ \text{g}.$$

Both agree with the measured plateaus. The second mass loss is a **net** loss: oxygen enters from the air while carbon dioxide leaves.

The earlier dissolution in nitric acid is also consistent with this formula:

$$\mathrm{Al_2C_{12}O_{12}\cdot 16\,H_2O + 6\,HNO_3 \longrightarrow 2\,Al(NO_3)_3 + C_{12}H_6O_{12} + 16\,H_2O}.$$

The solution was checked against the official solution.

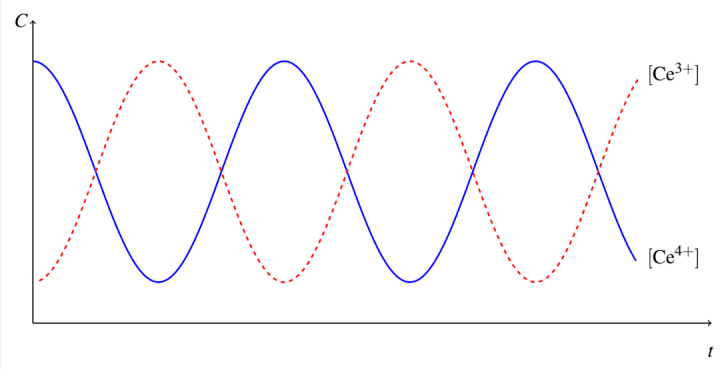
Problem 2: Kinetics of the Belousov-Zhabotinsky reaction

T2. Kinetics of the Belousov-Zhabotinsky reaction

6%

2.1	2.2	2.3	2.4	2.5	2.6	2.7	$\sum$
2	11	4	2	9	4	3	35

When the chemicals $\mathrm{KBrO_3}$, $\mathrm{CH_2(COOH)_2}$ (malonic acid, – MA), $\mathrm{Ce(SO_4)_2}$, and $\mathrm{H_2SO_4}$ are mixed, the concentration, C, of Ce species and the colour of the solution oscillates between yellow (due to $\mathrm{Ce^{4+}}$) and colourless (due to $\mathrm{Ce^{3+}}$). A schematic picture is given below:



2.1 — 2.0 pt

Write the overall balanced reaction equation of the Belousov-Zhabotinsky reaction (BZ reaction). Note: in this reaction, MA is oxidised to $\mathrm{CO_2}$, $\mathrm{BrO_3^-}$ is reduced to $\mathrm{Br^-}$, and Ce(IV) is a catalyst.

The mechanism of the BZ reaction is shown below (BMA – $\mathrm{CHBr(COOH)_2}$):

Process A	(1) $\mathrm{HBrO_2 + BrO_3^- + H^+ \xrightarrow{k_1} 2BrO_2^{\cdot} + H_2O}$ (2) $\mathrm{BrO_2^{\cdot} + Ce^{3+} + H^+ \xrightarrow{k_2} HBrO_2 + Ce^{4+}}$ (3) $\mathrm{2HBrO_2 \xrightarrow{k_3} BrO_3^- + HBrO + H^+}$
Process B	(4) $\mathrm{HBrO_2 + Br^- + H^+ \xrightarrow{k_4} 2HBrO}$ (5) $\mathrm{BrO_3^- + Br^- + 2H^+ \xrightarrow{k_5} HBrO + HBrO_2}$ (6) $\mathrm{HBrO + MA \xrightarrow{k_6} BMA + H_2O}$
Process C	(7) $\mathrm{Ce^{4+} + BMA \xrightarrow{k_7} Ce^{3+} + Br^-}$ + other products

$k_1 = 1.0 \times 10^4\ \mathrm{M^{-2}\,s^{-1}}$ $k_2 = 6.2 \times 10^4\ \mathrm{M^{-2}\,s^{-1}}$ $k_3 = 4.0 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}$
$k_4 = 2.0 \times 10^9\ \mathrm{M^{-2}\,s^{-1}}$ $k_5 = 2.1\ \mathrm{M^{-3}\,s^{-1}}$ $k_6 = 8.2\ \mathrm{M^{-1}\,s^{-1}}$
$k_7 = 1.0 \times 10^2\ \mathrm{M^{-1}\,s^{-1}}$

In the BZ reaction, **Process C** occurs continuously, while **Processes A and B** alternate with each other.

Assume that:

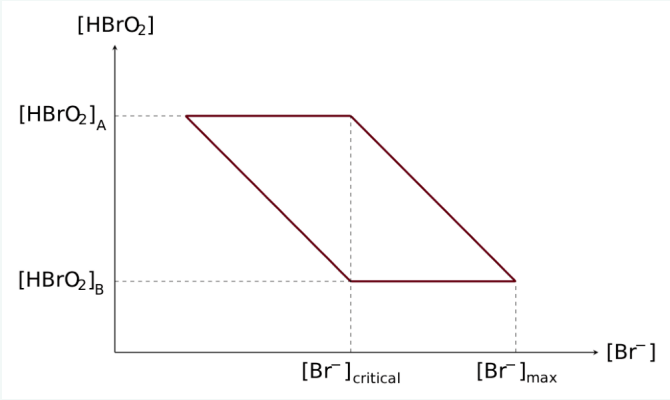
- when **Process A** occurs the solution is yellow and **Process B** practically does not occur;
- when **Process B** occurs the solution is colourless and **Process A** practically does not occur;
- $[\mathrm{BrO_3^-}]_0 = 0.06\ \mathrm{M}$, $[\mathrm{MA}]_0 = 0.1\ \mathrm{M}$, $[\mathrm{H^+}]_0 = 0.8\ \mathrm{M}$, $[\mathrm{Ce^{4+}}]_0 = 0.001\ \mathrm{M}$;
- the concentrations of the reactants (except $\mathrm{Ce^{4+}}$) and pH are maintained constant throughout the BZ reaction.

2.2 — 11.0 pt

Using the steady-state approximation, **calculate** the stationary molar concentrations of $\mathrm{HBrO_2}$ in **Processes A and B**, $[\mathrm{HBrO_2}]_\mathrm{A}$ and $[\mathrm{HBrO_2}]_\mathrm{B}$.

If you could not calculate $[\mathrm{HBrO_2}]_\mathrm{A}$ *and* $[\mathrm{HBrO_2}]_\mathrm{B}$*, you can use the values* $[\mathrm{HBrO_2}]_\mathrm{A} = 1 \times 10^{-5}\ \mathrm{M}$ *and* $[\mathrm{HBrO_2}]_\mathrm{B} = 1 \times 10^{-10}\ \mathrm{M}$ *for the following calculations.*

During the BZ reaction, the concentrations of $\mathrm{HBrO_2}$ and $\mathrm{Br^-}$ oscillate strictly in relation to each other, and this is sketched in the phase portrait of $[\mathrm{HBrO_2}]$ vs $[\mathrm{Br^-}]$:



Here $[\mathrm{Br^-}]_\mathrm{max}$ is the maximum concentration and $[\mathrm{Br^-}]_\mathrm{critical}$ is the critical concentration of $\mathrm{Br^-}$ at which there is a switch over in processes from **A to B** or from **B to A**. To switch **Process A to Process B**, the reaction rate of the elementary step (4) must exceed that of the elementary step (1) and vice versa.

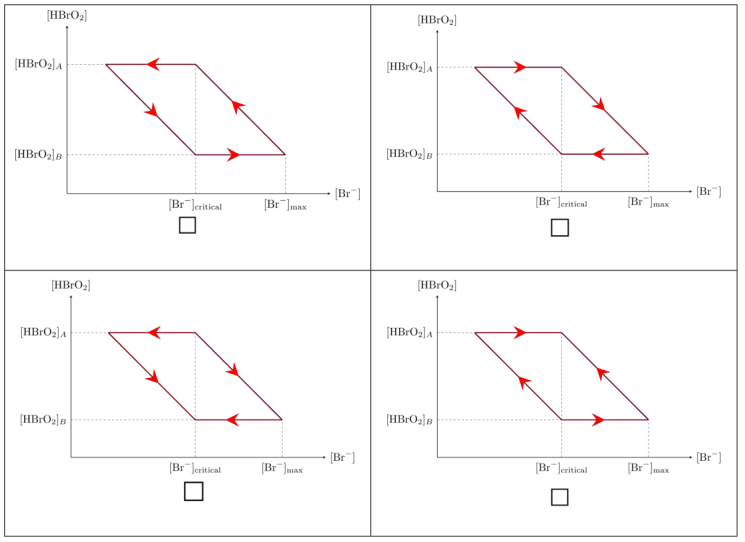
2.3 — 4.0 pt

Calculate $[\mathrm{Br^-}]_\mathrm{critical}$.

If you could not calculate $[\mathrm{Br^-}]_\mathrm{critical}$*, use* $[\mathrm{Br^-}]_\mathrm{critical} = 1 \times 10^{-7}\ \mathrm{M}$ *for the following calculations.*

2.4 — 2.0 pt

In **which direction** in the phase portrait of $[\mathrm{HBrO_2}]$ vs $[\mathrm{Br^-}]$ will the concentrations of $[\mathrm{HBrO_2}]$ and $[\mathrm{Br^-}]$ change over time? **Tick** the correct box.



The system does not traverse the phase portrait of $[\mathrm{HBrO_2}]$ vs $[\mathrm{Br^-}]$ at a constant velocity, that is the concentration of $[\mathrm{Br^-}]$ slowly decreases from $[\mathrm{Br^-}]_{\max} = 7.0 \times 10^{-4}\ \mathrm{M}$ to $[\mathrm{Br^-}]_{\text{critical}}$, and then almost immediately reaches $[\mathrm{Br^-}]_{\max}$ again.

2.5 — 9.0 pt

Calculate based on the data the period of oscillations, τ, of the BZ reaction, in seconds.

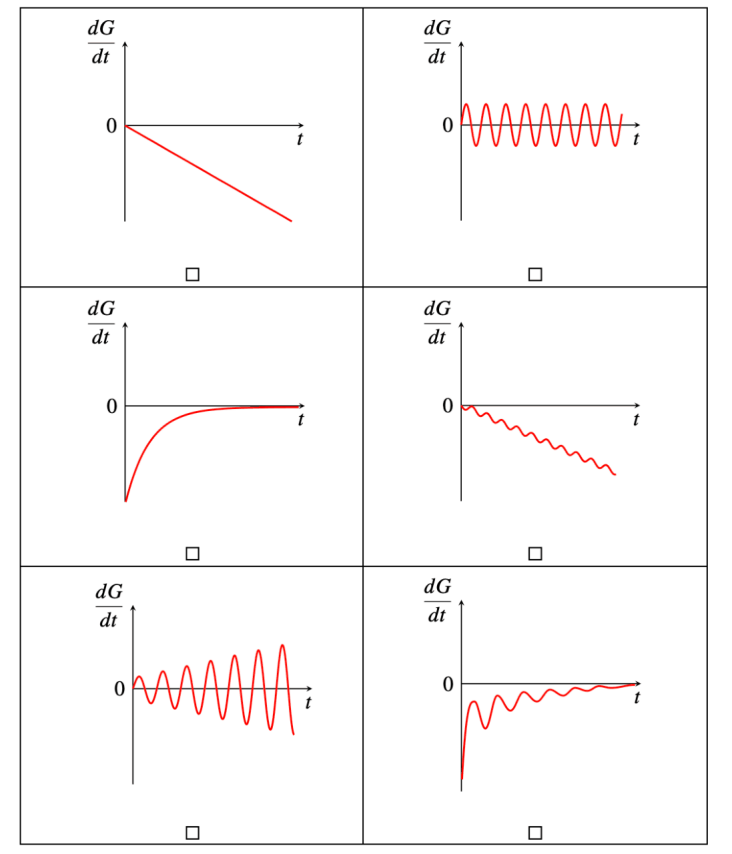
2.6 — 4.0 pt

What will be the effect if the following actions **(1-4)** are performed on an **open** system where a BZ reaction is taking place? **Tick** only one box **(a-e)** for each case.

1. Adding of small amount of $\mathrm{Ce^{4+}}$ during **Process A**. 2. Adding of a small amount of $\mathrm{Ag^+}$ during **Process B**. 3. Adding of a small amount of $\mathrm{Br^-}$ during **Process B**. 4. Continuous addition of $\mathrm{Br^-}$.	[a] prolongs **Process A** [b] prolongs **Process B** [c] **Process A** switches to **Process B** [d] **Process B** switches to **Process A** [e] oscillations stop

2.7 — 3.0 pt

Which graph qualitatively illustrates the rate of change of Gibbs energy $\left(\frac{dG}{dt}\right)$ of a **closed** system in which an oscillatory reaction occurs? **Tick** the correct box.



Official English text of the problem.

Answers

- **2.1:** $3\,\mathrm{CH_2(COOH)_2} + 4\,\mathrm{BrO_3^-} \longrightarrow 9\,\mathrm{CO_2} + 4\,\mathrm{Br^-} + 6\,\mathrm{H_2O}$.
- **2.2:** $[\mathrm{HBrO_2}]_\mathrm{A} = \boxed{6.0 \times 10^{-6}\ \mathrm{M}}$; $[\mathrm{HBrO_2}]_\mathrm{B} = \boxed{5.0 \times 10^{-11}\ \mathrm{M}}$.
- **2.3:** $[\mathrm{Br^-}]_\mathrm{critical} = \boxed{3.0 \times 10^{-7}\ \mathrm{M}}$.
- **2.4: Upper-right diagram** of the answer-sheet figure for 2.4: **clockwise** traversal.
- **2.5:** $\boxed{\tau \approx 48\ \mathrm{s}}$.
- **2.6:** Intended choices: **1–c; 2–d; 3–b; 4–e**, subject to sufficient perturbation strength as explained below.
- **2.7: Bottom-right graph** of the answer-sheet figure for 2.7: dG/dt undergoes damped oscillations below zero and approaches zero.

Solution

The species used below have the following names and SMILES.

Species	Name	SMILES
$\mathrm{CH_2(COOH)_2}$, MA	Malonic acid	`O=C(O)CC(=O)O`
$\mathrm{CHBr(COOH)_2}$, BMA	Bromomalonic acid	`O=C(O)C(Br)C(=O)O`
$\mathrm{BrO_3^-}$	Bromate ion	`[O-][Br](=O)=O`
$\mathrm{Br^-}$	Bromide ion	`[Br-]`
$\mathrm{HBrO_2}$	Bromous acid	`O[Br]=O`
HBrO	Hypobromous acid	`OBr`
$\mathrm{BrO_2^\bullet}$	Bromine dioxide radical	`O=[Br]=O`
$\mathrm{CO_2}$	Carbon dioxide	`O=C=O`
$\mathrm{H_2O}$	Water	`O`
$\mathrm{H^+}$	Hydrogen ion (proton)	`[H+]`
$\mathrm{Ce^{4+}}$	Cerium(IV) ion	`[Ce+4]`
$\mathrm{Ce^{3+}}$	Cerium(III) ion	`[Ce+3]`
$\mathrm{Ag^+}$	Silver(I) ion	`[Ag+]`
AgBr	Silver bromide	`[Ag+].[Br-]`

The silver bromide SMILES specifies its constituent ions, not the solid's crystal lattice. The ionic SMILES do not show solvation.

2.1

Complete oxidation of one molecule of malonic acid to three molecules of carbon dioxide releases eight electrons:

$$\mathrm{CH_2(COOH)_2} + 2\,\mathrm{H_2O} \longrightarrow 3\,\mathrm{CO_2} + 8\,\mathrm{H^+} + 8\,\mathrm{e^-}.$$

Reduction of bromate to bromide consumes six electrons:

$$\mathrm{BrO_3^-} + 6\,\mathrm{H^+} + 6\,\mathrm{e^-} \longrightarrow \mathrm{Br^-} + 3\,\mathrm{H_2O}.$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 4. Cancelling 24 electrons, 24 hydrogen ions, and the common water gives

$$\boxed{3\,\mathrm{CH_2(COOH)_2} + 4\,\mathrm{BrO_3^-} \longrightarrow 9\,\mathrm{CO_2} + 4\,\mathrm{Br^-} + 6\,\mathrm{H_2O}}.$$

Cerium cycles between its oxidation states and is regenerated, so it does not appear in the net equation.

2.2

Define

$$x = [\mathrm{HBrO_2}], \qquad r = [\mathrm{BrO_2^\bullet}], \qquad b = [\mathrm{Br^-}],$$
$$a = [\mathrm{BrO_3^-}] = 0.06\ \mathrm{M}, \qquad h = [\mathrm{H^+}] = 0.8\ \mathrm{M}.$$

Let v_i denote the reaction rate of elementary step i, with stoichiometric factors included separately in species balances.

For **Process A**,

$$v_1 = k_1 x a h, \qquad v_2 = k_2 r [\mathrm{Ce^{3+}}] h, \qquad v_3 = k_3 x^2.$$

Applying the steady-state approximation to the bromine dioxide radical gives

$$\frac{dr}{dt} = 2v_1 - v_2 \simeq 0 \quad \Longrightarrow \quad v_2 = 2v_1.$$

The bromous-acid balance is

$$\frac{dx}{dt} = -v_1 + v_2 - 2v_3 \simeq 0.$$

The factor 2 before v_3 is essential: each occurrence of step (3) consumes two molecules of bromous acid. Substituting $v_2 = 2v_1$,

$$k_1 x a h - 2k_3 x^2 = 0.$$

The nonzero stationary concentration corresponding to active Process A is therefore

$$x_{\mathrm{A}} = \frac{k_1 a h}{2k_3}.$$

Numerically,

$$x_{\mathrm{A}} = \frac{(1.0\times10^{4}\ \mathrm{M^{-2}s^{-1}})(0.06\ \mathrm{M})(0.8\ \mathrm{M})}{2(4.0\times10^{7}\ \mathrm{M^{-1}s^{-1}})} = \boxed{6.0\times10^{-6}\ \mathrm{M}}.$$

For **Process B**, step (5) produces bromous acid and step (4) consumes it:

$$v_4 = k_4 x b h, \qquad v_5 = k_5 a b h^2.$$

Thus

$$\frac{dx}{dt} = v_5 - v_4 \simeq 0,$$

and, cancelling the nonzero factors b and h,

$$x_{\mathrm{B}} = \frac{k_5 a h}{k_4}.$$

Hence

$$x_{\mathrm{B}} = \frac{(2.1\ \mathrm{M^{-3}s^{-1}})(0.06\ \mathrm{M})(0.8\ \mathrm{M})}{2.0\times10^{9}\ \mathrm{M^{-2}s^{-1}}} = 5.04\times10^{-11}\ \mathrm{M} \approx \boxed{5.0\times10^{-11}\ \mathrm{M}}.$$

2.3

At the switching threshold, steps (1) and (4) have equal rates:

$$k_1 x a h = k_4 x b_{\mathrm{critical}} h.$$

Cancelling x and h gives

$$b_{\mathrm{critical}} = \frac{k_1 a}{k_4} = \frac{1.0\times10^{4}}{2.0\times10^{9}}(0.06\ \mathrm{M}) = \boxed{3.0\times10^{-7}\ \mathrm{M}}.$$

Below this concentration, step (1) dominates and favours Process A. Above it, step (4) dominates and favours Process B.

2.4

During Process A, the solution contains appreciable cerium(IV), so Process C produces bromide. The bromide concentration increases along the upper branch until the system switches to Process B.

During Process B, bromide is consumed while the bromous-acid concentration remains low. The system moves left along the lower branch until bromide falls to the switching threshold and Process A resumes.

Consequently, the arrows must point:

- right along the upper horizontal edge;
- down and right along the right sloping edge;
- left along the lower horizontal edge;
- up and left along the left sloping edge.

This is **clockwise traversal**, shown in the **upper-right diagram of the answer-sheet figure for 2.4**.

2.5

The period is dominated by the slow decrease of bromide during Process B. The subsequent return to the maximum concentration is taken to require negligible time.

The full bromide balance during B is

$$\frac{db}{dt} = -v_4 - v_5 + v_7.$$

In the intended approximation, the colourless B interval has very little cerium(IV), so

$$v_7 = k_7[\mathrm{Ce^{4+}}][\mathrm{BMA}]$$

is neglected during this slow interval. From the steady-state calculation, $v_4 = v_5$. Therefore,

$$\frac{db}{dt} \simeq -2v_5 = -2k_5 a h^2 b.$$

Both steps (4) and (5) consume bromide; this supplies the factor 2.

The effective first-order decay constant is

$$k_{\mathrm{eff}} = 2k_5 a h^2 = 2(2.1\ \mathrm{M^{-3}s^{-1}})(0.06\ \mathrm{M})(0.8\ \mathrm{M})^2 = 0.16128\ \mathrm{s^{-1}}.$$

Integration gives

$$b(t) = b_{\max} e^{-k_{\mathrm{eff}} t}.$$

Setting $b(\tau) = b_{\mathrm{critical}}$,

$$\tau \simeq \frac{1}{k_{\mathrm{eff}}} \ln\left(\frac{b_{\max}}{b_{\mathrm{critical}}}\right).$$

Thus

$$\tau = \frac{\ln\left(\dfrac{7.0 \times 10^{-4}}{3.0 \times 10^{-7}}\right)}{0.16128\ \mathrm{s}^{-1}} = 48.0844\ \mathrm{s} \approx \boxed{48\ \mathrm{s}}.$$

2.6

1. **Adding cerium(IV) during Process A: (c).**
   Increasing $[\mathrm{Ce}^{4+}]$ accelerates Process C and therefore bromide production. If this raises bromide through its critical concentration, step (4) overtakes step (1), and **Process A switches to Process B**.
2. **Adding silver(I) during Process B: (d).**
   Silver(I) removes bromide by precipitation:
   $$\mathrm{Ag}^{+} + \mathrm{Br}^{-} \longrightarrow \mathrm{AgBr\,(s)}.$$
   If bromide falls below its critical concentration, step (1) becomes dominant, and **Process B switches to Process A**.
3. **Adding bromide during Process B: (b).**
   The bromide concentration is moved farther above the switching threshold. More time is needed to consume it down to that threshold, so the addition **prolongs Process B**.
4. **Continuous addition of bromide: (e).**
   A sufficient continuous supply maintains bromide above the critical concentration, sustaining Process B and preventing the alternating switches. The **oscillations stop**.

2.7

For a spontaneously reacting closed system at constant temperature and pressure,

$$\frac{dG}{dt} \leq 0.$$

The concentrations can oscillate, and the rate of Gibbs-energy decrease can vary, while Gibbs energy itself continues to decrease. As equilibrium is approached,

$$\frac{dG}{dt} \longrightarrow 0.$$

The intended graph therefore shows oscillations in dG/dt that remain below zero and diminish as the curve approaches zero: the **bottom-right graph of the answer-sheet figure for 2.7**.

The solution was checked against the official solution.

Problem 3: Into Reticular Chemistry

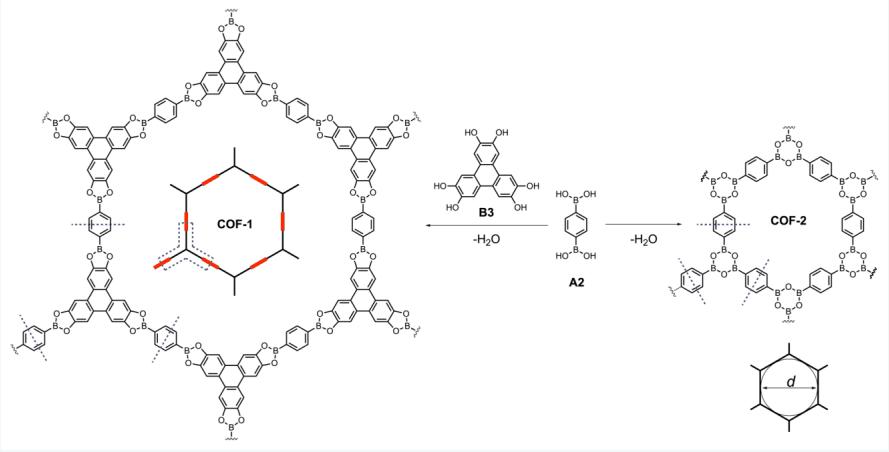
T3. Into Reticular Chemistry

7%

3.1	3.2	3.3	3.4	3.5	3.6	3.7	$\sum$
2	3	23	12	6	12	5	63

Covalent organic frameworks (COFs) are a class of polymers that form two- or three-dimensional structures through reactions between organic precursors, resulting in covalent bonds to afford porous, crystalline materials. Two examples of honeycomb type 2D-COFs formed by boronate ester and boroxine rings (repeat units indicated using dashed lines) are shown in the figure below.

The black and red bold lines represent different building blocks in all COF topology figures.



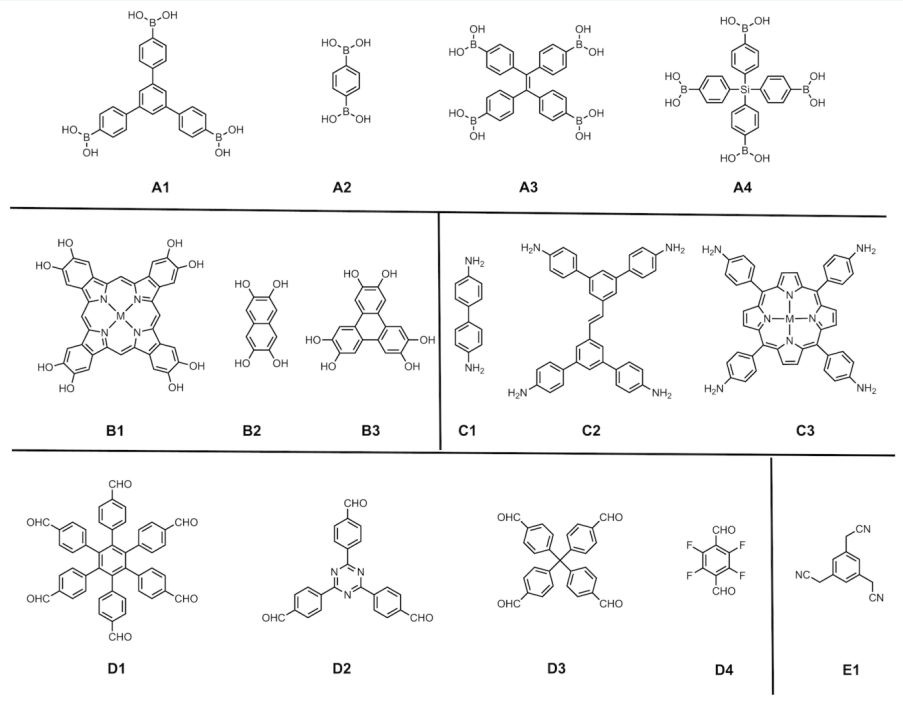
3.1 Determine the empirical formula of **COF-1** and calculate the mass percentage (%, to two decimal places) of carbon in **COF-1**. **2.0 pt**

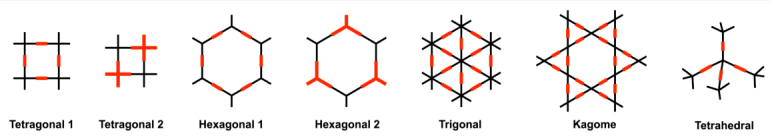
3.2 Calculate the internal diameter, d, in Å, of the honeycomb for **COF-2**, with the following assumptions: **3.0 pt**

- $\mathrm{C{-}C/C{=}C}$ (arenes) = 1.39 Å

- $\mathrm{C{-}B}$ = 1.56 Å
- $\mathrm{B{-}O}$ = 1.38 Å
- Note, the diameter of a circle, d, inscribed inside a hexagon, is given by $d = \sqrt{3}a$, where a is the side length of the hexagon.
- Neglect the width of the linkers.

The structures shown below can form 2D and 3D COFs. For this question consider only formation of COFs with boronate esters, imines, and $\mathrm{C{=}C}$ bonds through condensation reactions. **A–E** represent compound classes with different functional groups.



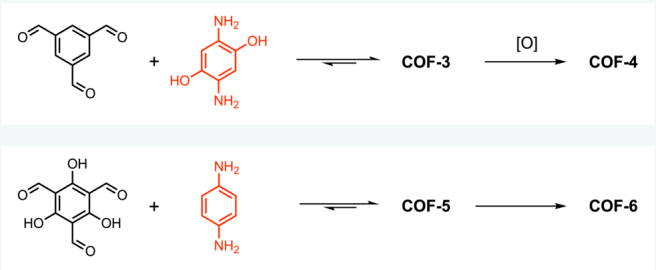


Tetragonal means *Tetragonal*, **Hexagonal** means *Hexagonal*, **Trigonal** means *Trigonal*, **Kagome** means *Kagome*, **Tetrahedral** means *Tetrahedral*.

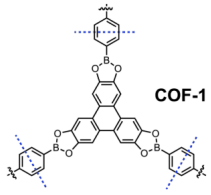
3.3 Fill all the table cells with either new examples of monomer combinations that give the topologies shown above or with **"XXX"** if you are certain that no additional combinations satisfy that topology. Both the combinations and the **"XXX"** entries will be graded. Incorrect answers (both combinations and **"XXX"** entries) will be penalised. Blank table cells will not be graded. **23.0 pt**

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetrahedral
■	■	A2 + B3	E1 + D2	■	C2 + D4	■

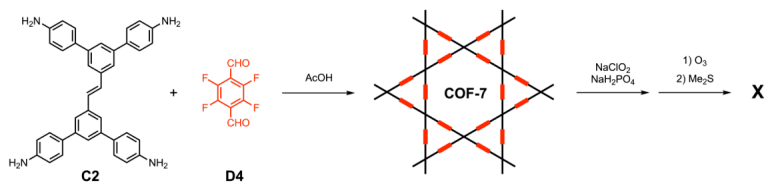
Whilst imine-based COFs are easily synthesised, they are also vulnerable to hydrolysis under strongly acidic and basic conditions. The addition of hydroxy groups to the aldehyde or amine monomers can overcome this. IR spectrum of **COF-3** contained stretches corresponding to the imine functional group, but **COF-4** did not. **COF-4** contains a different type of $\mathrm{C{=}N}$ bonds, and elemental analysis revealed a loss of six additional hydrogen atoms per repeat unit relative to **COF-3** as the only change. **COF-5** irreversibly isomerises to **COF-6**, which did not contain imine stretches in its IR spectrum.



3.4 Draw the repeat units for **COFs 3–6**. Indicate the edges of each repeat unit with a dashed line as shown for **COF-1** below. **12.0 pt**

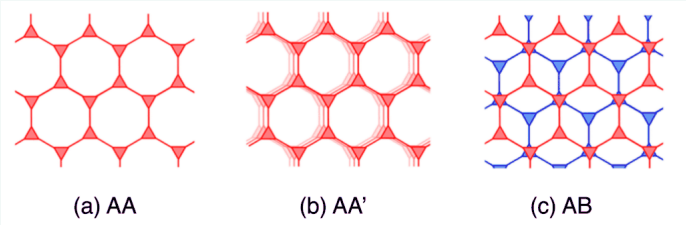


Macrocycle **X** was synthesised by post-synthetic modification of **COF-7 (C2 + D4)** followed by degradation.

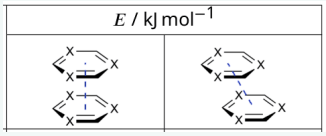


3.5 Draw the smallest repeat unit of macrocycle **X**. **6.0 pt**

π-π interactions result in different stacking modes of COF layers, some of which are shown below.

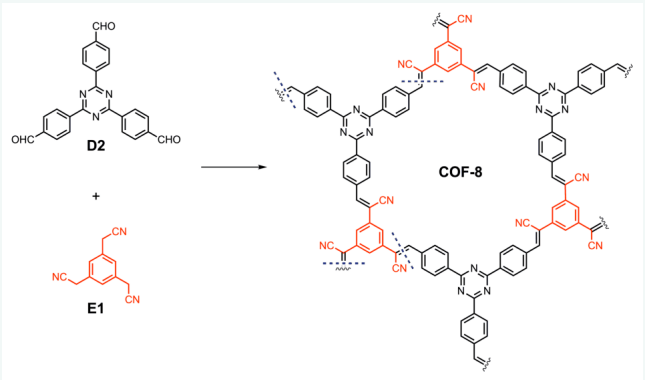


Depending on stacking geometry, the interaction energy can be different as shown below.



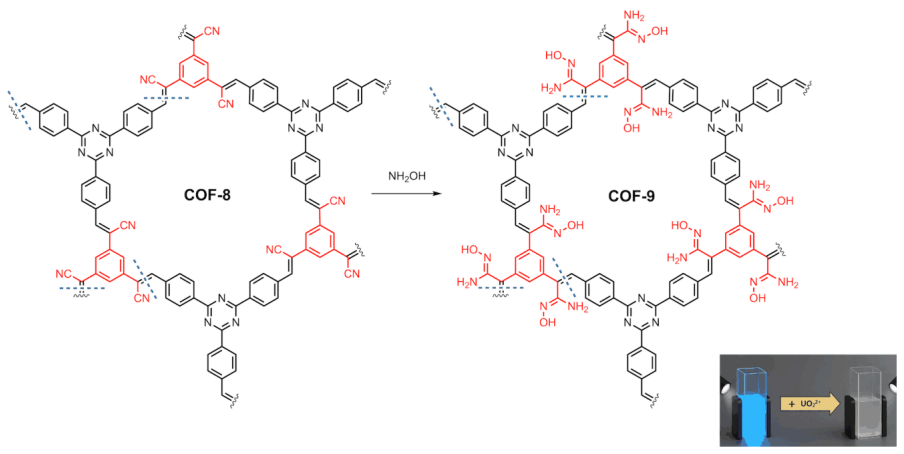
Interaction geometry	$E/\mathrm{kJ\,mol^{-1}}$	$E/\mathrm{kJ\,mol^{-1}}$
benzene ($\mathrm{X=CH}$) – benzene (b-b)	−7.9	−12.6
benzene-triazine ($\mathrm{X=N}$) (b-t)	−49.8	−55.6
triazine–triazine (t-t)	−6.7	−16.7

COF-8, synthesised from **(E1 + D2)**, is notable for its remarkable stability. The **AA'** slightly shifted mode of a **COF-8** bilayer has a π-π stacking interaction energy of $-67.1\ \mathrm{kJ\,mol^{-1}}$ between two layers of one repeat unit.



3.6 Calculate the π-π stacking energy between two layers of one repeat unit of **COF-8**, for the **AA, AB and AB'** arrangements. Assume π-π stacking happens only between aromatic units. **12.0 pt**

COF-9, obtained from **COF-8**, absorbs $\mathrm{UO_2}^{2+}$ ions and loses its fluorescence. In an experiment, a suspension of 5.000 mg **COF-9** in $19.90\ \mathrm{mg\,dm^{-3}}$ $\mathrm{UO_2}^{2+}$ solution (200.0 mL) was filtered after equilibrium was reached. The final concentration of $\mathrm{UO_2}^{2+}$ was $9.225\ \mathrm{mg\,dm^{-3}}$.



3.7 Calculate the equilibrium absorption capacity at a given temperature (q_e) in $\mathrm{mg\,g^{-1}}$ of **COF-9**. Indicate the number of $\mathrm{UO_2}^{2+}$ ions absorbed per pore. Assume that all uranium exists as $\mathrm{UO_2}^{2+}$ ions. **5.0 pt**

Periodic Table of Elements

1																	18
1 H 1.008	2											13	14	15	16	17	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 24.30	3	4	5	6	7	8	9	10	11	12	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 72.63	33 As 74.92	34 Se 78.97	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 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	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 -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	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

- **3.1:** Empirical formula $\boxed{\mathrm{C_9H_4BO_2}}$; carbon mass percentage $\boxed{69.77\%}$.
- **3.2:** $\boxed{d = 15.00\ \text{Å}}$.
- **3.3:** Fill the two empty rows as follows:

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetrahedral
A2 + B1	XXX	A1 + B2	A1 + B3	C1 + D1	A3 + B2	A4 + B2
C3 + D4	XXX	C1 + D2	XXX	XXX	XXX	C1 + D3

- **3.4: COF-3:** hydroxy-substituted imine framework; **COF-4:** benzobisoxazole framework; **COF-5:** enol–imine framework; **COF-6:** β-ketoenamine framework. Their precise connectivity, SMILES fragments and repeat boundaries are given below.
- **3.5:** The smallest repeat contains one **3,5-bis(4-aminophenyl)benzaldehyde-derived unit** and one **tetrafluoroterephthaloyl unit**, joined by amide bonds. Its formula is $\mathrm{C_{27}H_{14}F_4N_2O_3}$, and its attachment-point SMILES is `[*:1]Nc1ccc(cc1)-c1cc(C=O)cc(c1)-c1ccc(cc1)NC(=O)c1c(F)c(F)c(c(F)c1F)C(=O)[*:2]`.
- **3.6:** $\boxed{E_{\mathrm{AA}} = -38.3, \quad E_{\mathrm{AB}} = -49.8, \quad E_{\mathrm{AB'}} = -55.6\ \mathrm{kJ\,mol^{-1}}}$, per pair of repeat units.

- **3.7:** $\boxed{q_e = 427.0\ \mathrm{mg\,g^{-1}}}$; $\boxed{\text{approximately one } \mathrm{UO_2}^{2+} \text{ ion per pore}}$.

Solution

In the structural SMILES below, `[*]` denotes an attachment to the rest of the framework. These are finite structural fragments: ordinary SMILES does not itself specify an infinite periodic framework or its dashed repeat boundaries. Water, eliminated in the condensations, has SMILES `O`.

3.1 — Composition of COF-1

The monomers are:

- **A2, benzene-1,4-diboronic acid**, $\mathrm{C_6H_8B_2O_4}$: `OB(O)c1ccc(B(O)O)cc1`.
- **B3, triphenylene-2,3,6,7,10,11-hexol**, $\mathrm{C_{18}H_{12}O_6}$: `Oc1cc2c(cc1O)c1cc(O)c(O)cc1c1cc(O)c(O)cc21`.

Each B3 molecule contains three catechol groups, while A2 contains two boronic acid groups. Thus their stoichiometric ratio is

$$n(\mathrm{A2}) : n(\mathrm{B3}) = 3 : 2.$$

Formation of each cyclic boronate ester eliminates two water molecules. Six such linkages therefore give

$$3\,\mathrm{C_6H_8B_2O_4} + 2\,\mathrm{C_{18}H_{12}O_6} \longrightarrow \mathrm{C_{54}H_{24}B_6O_{12}} + 12\,\mathrm{H_2O}.$$

The product formula here denotes a framework composition, rather than an isolated molecule. Dividing its subscripts by six gives

$$\boxed{\mathrm{C_9H_4BO_2}}.$$

Using the supplied atomic masses,

$$M = 9(12.01) + 4(1.008) + 10.81 + 2(16.00) = 154.932\ \mathrm{g\,mol^{-1}}.$$

Consequently,

$$w_{\mathrm{C}} = \frac{9(12.01)}{154.932} \times 100\% = \boxed{69.77\%}.$$

3.2 — Internal diameter of COF-2

COF-2 contains **boroxine nodes**, whose substituted ring can be represented by `[*]B1OB([*])OB([*])O1`. Their formation follows the balanced condensation

$$3\,\mathrm{R{-}B(OH)_2} \longrightarrow (\mathrm{RBO})_3 + 3\,\mathrm{H_2O}.$$

Treating the boroxine ring as the regular hexagon drawn, its centre-to-boron distance equals its side length, 1.38 Å. The separation between opposite carbon atoms of a regular benzene ring is twice its side length.

The distance between two neighbouring boroxine centres—the honeycomb side length—is therefore

$$\begin{aligned} a &= 2r_{\mathrm{B{-}O}} + 2r_{\mathrm{C{-}B}} + 2r_{\mathrm{C{-}C}} \\ &= 2(1.38) + 2(1.56) + 2(1.39) \\ &= 8.66\ \text{Å}. \end{aligned}$$

Neglecting linker width as instructed,

$$d = \sqrt{3}\,a = \sqrt{3}(8.66) = \boxed{15.00\ \text{Å}}.$$

3.3 — Monomer combinations and topology

The allowed complementary functional groups are:

Combination	Linkage formed	Condensation stoichiometry
A + B	Cyclic boronate ester	One boronic acid group + one catechol group eliminates two water molecules
C + D	Imine	One amine + one aldehyde eliminates one water molecule
E + D	Cyano-substituted alkene	One activated methylene group + one aldehyde eliminates one water molecule

The latter two reactions can be written

$$\mathrm{R{-}CHO} + \mathrm{H_2N{-}R'} \longrightarrow \mathrm{R{-}CH{=}N{-}R'} + \mathrm{H_2O},$$
$$\mathrm{R{-}CHO} + \mathrm{R'{-}CH_2{-}CN} \longrightarrow \mathrm{R{-}CH{=}C(CN){-}R'} + \mathrm{H_2O}.$$

The idealized connection geometries in the supplied drawings are:

Connection geometry	Monomers
Linear, two connections	A2, B2, C1, D4
Trigonal, three connections	A1, B3, D2, E1
Square, four connections	B1, C3
Four connections suited to the Kagome arrangement	A3, C2
Planar, six connections	D1
Tetrahedral, four connections	A4, D3

These give the completed table:

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetrahedral
■	■	A2 + B3	E1 + D2	■	C2 + D4	■
A2 + B1	**XXX**	**A1 + B2**	**A1 + B3**	**C1 + D1**	**A3 + B2**	**A4 + B2**

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetrahedral
C3 + D4	XXX	C1 + D2	XXX	XXX	XXX	C1 + D3

The assignments follow directly from the geometry:

- **Tetragonal 1:** square nodes connected by linear linkers.
- **Tetragonal 2:** requires complementary square nodes of both colours. None of the supplied pairs meets this requirement: A3 has the Kagome-type connection geometry, while D3 is tetrahedral.
- **Hexagonal 1:** trigonal nodes connected by linear linkers.
- **Hexagonal 2:** alternating complementary trigonal nodes.
- **Trigonal:** six-connected D1 nodes joined through linear C1 linkers.
- **Kagome:** A3 and C2 supply the appropriate four-connected geometry; their compatible linear partners are B2 and D4, respectively.
- **Tetrahedral:** tetrahedral A4 or D3 nodes joined through compatible linear linkers.

E1 + D4 is another possible Hexagonal 1 combination; the two new examples entered above already fill its available cells.

For completeness, the names and SMILES identifying the monomers used in these assignments are listed below. A2 and B3 were specified in 3.1.

Label	Name	SMILES
A1	1,3,5-Tris(4-boronophenyl)benzene	`c1(-c2ccc(B(O)O)cc2)cc(-c2ccc(B(O)O)cc2)cc(-c2ccc(B(O)O)cc2)c1`
A3	1,1,2,2-Tetrakis(4-boronophenyl)ethene	`C(=C(c1ccc(B(O)O)cc1)c1ccc(B(O)O)cc1)(c1ccc(B(O)O)cc1)c1ccc(B(O)O)cc1`
A4	Tetrakis(4-boronophenyl)silane	`[Si](c1ccc(B(O)O)cc1)(c1ccc(B(O)O)cc1)(c1ccc(B(O)O)cc1)c1ccc(B(O)O)cc1`
B1	Metal phthalocyanine bearing four peripheral catechol groups	Free-base ligand: `Oc1cc2c(cc1O)-c1nc-2nc2[nH]c(nc3nc(nc4[nH]c(n1)c1cc(O)c(O)cc41)-c1cc(O)c(O)cc1-3)c1cc(O)c(O)cc21`
B2	Naphthalene-2,3,6,7-tetrol	`Oc1cc2cc(O)c(O)cc2cc1O`
C1	Biphenyl-4,4′-diamine, or benzidine	`Nc1ccc(-c2ccc(N)cc2)cc1`
C2	(E)-1,2-Bis[3,5-bis(4-aminophenyl)phenyl]ethene	`Nc1ccc(-c2cc(-c3ccc(N)cc3)cc(/C=C/c3cc(-c4ccc(N)cc4)cc(-c4ccc(N)cc4)c3)c2)cc1`
C3	Metal meso-tetrakis(4-aminophenyl)porphyrin	Free-base ligand: `Nc1ccc(-c2c3nc(c(-c4ccc(N)cc4)c4ccc([nH]4)c(-c4ccc(N)cc4)c4nc(c(-c5ccc(N)cc5)c5ccc2[nH]5)C=C4)C=C3)cc1`
D1	Hexakis(4-formylphenyl)benzene	`c1(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c(-c2ccc(C=O)cc2)c1-c1ccc(C=O)cc1`
D2	2,4,6-Tris(4-formylphenyl)-1,3,5-triazine	`O=Cc1ccc(-c2nc(-c3ccc(C=O)cc3)nc(-c3ccc(C=O)cc3)n2)cc1`
D3	Tetrakis(4-formylphenyl)methane	`C(c1ccc(C=O)cc1)(c1ccc(C=O)cc1)(c1ccc(C=O)cc1)c1ccc(C=O)cc1`
D4	2,3,5,6-Tetrafluorobenzene-1,4-dicarbaldehyde	`O=Cc1c(F)c(F)c(C=O)c(F)c1F`
E1	1,3,5-Tris(cyanomethyl)benzene	`N#CCc1cc(CC#N)cc(CC#N)c1`

For B1 and C3, the figure does not identify the metal M. The listed SMILES therefore describe their free-base ligands. In the depicted metal complexes, the two inner N–H protons are replaced on metallation, and M coordinates the four inward-facing nitrogen atoms in an approximately planar $\mathrm{N_4}$ pocket.

3.4 — Repeat units of COFs 3–6

The additional starting compounds are:

Name	Formula	SMILES
Benzene-1,3,5-tricarbaldehyde	$\mathrm{C_9H_6O_3}$	`O=Cc1cc(C=O)cc(C=O)c1`
2,5-Diaminobenzene-1,4-diol	$\mathrm{C_6H_8N_2O_2}$	`Nc1c(O)cc(N)c(O)c1`
2,4,6-Trihydroxybenzene-1,3,5-tricarbaldehyde	$\mathrm{C_9H_6O_6}$	`O=Cc1c(O)c(C=O)c(O)c(C=O)c1O`
Benzene-1,4-diamine	$\mathrm{C_6H_8N_2}$	`Nc1ccc(N)cc1`

For each requested repeat drawing, place **one complete three-connected central node** in the middle, draw its three attached linkers, and draw a dashed boundary across the middle of each linker's central benzene ring. Thus each repeat contains one node and three half-linkers, just as in the supplied COF-1 example.

COF-3: hydroxy-substituted imine framework

Condensation produces three imine connections per central benzene node:

$$2\,\mathrm{C_9H_6O_3} + 3\,\mathrm{C_6H_8N_2O_2} \longrightarrow 2\,(\mathrm{C_{18}H_{12}N_3O_3})_{repeat} + 6\,\mathrm{H_2O}.$$

Each complete linker between central benzene nodes is

$$\mathrm{Ar{-}CH{=}N{-}C_6H_2(OH)_2{-}N{=}CH{-}Ar}.$$

The two imine nitrogen substituents are para to each other on the linker ring; each retained hydroxy group is ortho to one imine nitrogen substituent.

- **Three-connected benzene node:** `[*:1]c1cc([*:2])cc([*:3])c1`
- **Hydroxy-substituted bis(imine) linker:** `[*:1]/C=N/c1c(O)cc(/N=C/[*:2])c(O)c1`

The slashes show the extended imine configuration. The repeat composition is $\mathrm{C_{18}H_{12}N_3O_3}$.

COF-4: benzobisoxazole framework

Each ortho-hydroxy imine undergoes oxidative cyclization. The phenolic oxygen bonds to the neighbouring imine carbon, producing a fused five-membered **1,3-oxazole ring**.

At each site, the imine-carbon hydrogen and the phenolic hydrogen are lost overall. Three sites per repeat therefore remove six hydrogen atoms:

$$(\mathrm{C_{18}H_{12}N_3O_3})_{repeat} + 3\,[\mathrm{O}] \longrightarrow (\mathrm{C_{18}H_6N_3O_3})_{repeat} + 3\,\mathrm{H_2O}.$$

Here $[\mathrm{O}]$ denotes an oxidizing oxygen equivalent.

The central three-connected benzene node remains unchanged. Each linker becomes a benzene ring fused to an oxazole on each of two opposite edges:

- **Benzene-fused bis(1,3-oxazole) linker:** `[*:1]c1nc2cc3oc([*:2])nc3cc2o1`

Both external attachment points are at the carbon atoms between O and N in the respective oxazole rings.

This accounts for all the observations: no oxygen or nitrogen is lost, exactly six hydrogens disappear per repeat, and the remaining $\mathrm{C{=}N}$ bonds belong to aromatic oxazole rings rather than ordinary imine groups.

COF-5: enol–imine framework

Initial condensation retains the three phenolic hydroxy groups of the aldehyde monomer:

$$2\,\mathrm{C_9H_6O_6} + 3\,\mathrm{C_6H_8N_2} \longrightarrow 2\,(\mathrm{C_{18}H_{12}N_3O_3})_{repeat} + 6\,\mathrm{H_2O}.$$

Draw a central benzene ring with alternating OH groups and $-\mathrm{CH{=}N}-$ arms. The nitrogen atoms connect through para-phenylene linkers to adjacent nodes.

- **Hydroxylated three-connected node:** `Oc1c([*:1])c(O)c([*:2])c(O)c1[*:3]`
- **Para-phenylene bis(imine) linker:** `[*:1]/C=N/c1ccc(/N=C/[*:2])cc1`

The repeat formula is again $\mathrm{C_{18}H_{12}N_3O_3}$.

COF-6: β-ketoenamine framework

COF-5 undergoes proton transfer and bond rearrangement:

$$\mathrm{Ar{-}C(OH){=}C(-CH{=}N{-}R)^-} \longrightarrow \mathrm{Ar{-}C(=O){-}C(=CH{-}NH{-}R)^-}.$$

This is a tautomerization, so no atoms are added or removed:

$$\mathrm{COF\text{-}5} \longrightarrow \mathrm{COF\text{-}6}.$$

For the repeat drawing:

1. Replace the three phenolic $\mathrm{C{-}OH}$ groups by three $\mathrm{C{=}O}$ groups.
2. Replace each exocyclic $-\mathrm{CH{=}N{-}Ar}$ connection by $=\mathrm{CH{-}NH{-}Ar}$.
3. Draw the central six-membered ring with single bonds between its ring atoms.

Thus the central motif is **2,4,6-tris(arylaminomethylene)cyclohexane-1,3,5-trione**:

- **Ketoenamine node fragment:** `O=C1C(=CN[*:1])C(=O)C(=CN[*:2])C(=O)C1=CN[*:3]`
- **Connecting para-phenylene group:** `[*:1]c1ccc([*:2])cc1`

The repeat remains $\mathrm{C_{18}H_{12}N_3O_3}$. Its nitrogen atoms are now enamine NH atoms, explaining the absence of ordinary imine stretches.

3.5 — Smallest repeat unit of macrocycle X

There are two successive structural changes.

First, the imines of COF-7 are oxidized to **amides**:

$$\mathrm{R{-}CH{=}N{-}R' + [O] \longrightarrow R{-}C(=O){-}NH{-}R'}.$$

Consequently, every carbonyl carbon in these new amides comes from a D4 aldehyde, and every amide nitrogen comes from C2. The correct linkage orientation is therefore

$$\mathrm{(C_2){-}Ar{-}NH{-}C(=O){-}C_6F_4{-}C(=O){-}NH{-}Ar{-}(C_2)}.$$

The reagents are **sodium chlorite**, `[Na+].[O-]Cl=O`, and **sodium dihydrogen phosphate**, `[Na+].[O-]P(=O)(O)O`. Acetic acid, `CC(=O)O`, catalyses the preceding imine formation.

Second, reductive ozonolysis cleaves the central alkene of C2:

$$\mathrm{Ar{-}CH{=}CH{-}Ar + O_3 + (CH_3)_2S \longrightarrow 2\,Ar{-}CHO + (CH_3)_2SO}.$$

Here ozone is `[O-][O+]=O`, dimethyl sulfide is `CSC`, and dimethyl sulfoxide is `CS(C)=O`.

Each C2 half therefore becomes a **3,5-bis(4-aminophenyl)benzaldehyde-derived fragment**, with its amino groups already incorporated into amides. The corresponding free diamine is **3,5-bis(4-aminophenyl)benzaldehyde**, `O=Cc1cc(-c2ccc(N)cc2)cc(-c2ccc(N)cc2)c1`.

The smallest repeat of X consists of:

- one central benzene ring bearing a formyl group and two aryl substituents at alternating positions;
- a para-phenylene group on each aryl arm;
- two amide connections;
- one tetrafluorinated benzene ring bearing its two carbonyl groups para to each other.

Its unambiguous repeat-fragment SMILES is

`[*:1]Nc1ccc(cc1)-c1cc(C=O)cc(c1)-c1ccc(cc1)NC(=O)c1c(F)c(F)c(c(F)c1F)C(=O)[*:2]`

Join the terminal carbonyl carbon of one repeat to the initial nitrogen of the next. The surviving hexagonal circuit contains six such repeats, giving the **cyclic hexamer X**, $\mathrm{C_{162}H_{84}F_{24}N_{12}O_{18}}$. Its full molecular SMILES is

`N1c2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)Nc2ccc(cc2)-c2cc(C=O)cc(c2)-c2ccc(cc2)NC(=O)c2c(F)c(F)c(c(F)c2F)C(=O)1`

This specifies connectivity; it does not assert a unique three-dimensional conformation of the macrocycle.

3.6 — Stacking energies of COF-8

One primitive repeat contains one D2-derived node and one E1-derived node. Its aromatic rings are:

- three peripheral benzene rings from D2;
- one central 1,3,5-triazine ring from D2;
- one benzene ring from E1.

Thus there are **four benzene rings and one triazine ring** per repeat. Benzene is `c1ccccc1`; 1,3,5-triazine is `c1ncncn1`.

The given AA′ energy verifies this count:

$$4(-12.6) + (-16.7) = -67.1\ \mathrm{kJ\,mol^{-1}}.$$

For **AA**, all corresponding rings are directly superposed:

$$E_{\mathrm{AA}} = 4E_{\mathrm{b-b}} + E_{\mathrm{t-t}} = 4(-7.9) + (-6.7) = \boxed{-38.3\ \mathrm{kJ\,mol^{-1}}}.$$

For **AB**, the displacement places an E1-derived benzene node over a D2-derived triazine node. There is one such aromatic contact per primitive repeat. The other node lies over a pore, and the peripheral phenylene rings are not mutually registered.

Therefore,

$$E_{\mathrm{AB}} = E_{\mathrm{b-t}} = \boxed{-49.8\ \mathrm{kJ\,mol^{-1}}}.$$

For the slightly displaced **AB′** arrangement, use the displaced benzene–triazine interaction:

$$E_{\mathrm{AB'}} = \boxed{-55.6\ \mathrm{kJ\,mol^{-1}}}.$$

The contact accounting is:

Arrangement	b-b pairs	b-t pairs	t-t pairs	Energy / $\mathrm{kJ\,mol^{-1}}$
AA	4	0	1	−38.3
AA′, given check	4	0	1	−67.1
AB	0	1	0	−49.8
AB′	0	1	0	−55.6

Each aromatic pair is counted once, despite involving two layers.

3.7 — Uptake capacity and uranyl ions per pore

The absorbed uranyl mass is

$$\begin{aligned} m_{\mathrm{absorbed}} &= (C_0 - C_e)V \\ &= (19.90 - 9.225)\ \mathrm{mg\,dm^{-3}} \times 0.2000\ \mathrm{dm^3} \\ &= 2.135\ \mathrm{mg}. \end{aligned}$$

Hence

$$q_e = \frac{2.135\ \mathrm{mg}}{0.005000\ \mathrm{g}} = \boxed{427.0\ \mathrm{mg\,g^{-1}}}.$$

To determine the number of ions per pore, first find the framework mass associated with one pore.

D2 and E1 have formulas $\mathrm{C_{24}H_{15}N_3O_3}$ and $\mathrm{C_{12}H_9N_3}$, respectively. Three condensations per repeat give

$$\mathrm{C_{24}H_{15}N_3O_3} + \mathrm{C_{12}H_9N_3} \longrightarrow (\mathrm{C_{36}H_{18}N_6})_{repeat} + 3\,\mathrm{H_2O}.$$

Hydroxylamine, `NO`, converts each nitrile into an **amidoxime**, represented by `[*]C(=NO)N`:

$$\mathrm{R{-}C{\equiv}N} + \mathrm{NH_2OH} \longrightarrow \mathrm{R{-}C(=N{-}OH){-}NH_2}.$$

There are three nitriles per repeat, so

$$(\mathrm{C_{36}H_{18}N_6})_{repeat} + 3\,\mathrm{NH_2OH} \longrightarrow (\mathrm{C_{36}H_{27}N_9O_3})_{repeat}.$$

Therefore,

$$\begin{aligned} M_{\mathrm{COF-9,repeat}} &= 36(12.01) + 27(1.008) + 9(14.01) + 3(16.00) \\ &= 633.666\ \mathrm{g\,mol^{-1}}. \end{aligned}$$

A honeycomb pore has six vertices, each shared among three pores. It therefore corresponds to two complete nodes: one D2-derived node and one E1-derived node. Thus **one primitive repeat corresponds to one pore**.

The **uranyl ion**, `O=[U+2]=O`, has a linear $\mathrm{O{-}U{-}O}$ unit and molar mass

$$M_{\mathrm{UO_2^{2+}}} = 238.03 + 2(16.00) = 270.03\ \mathrm{g\,mol^{-1}}.$$

The amounts in the experiment are

$$n_{\mathrm{UO_2^{2+}}} = \frac{2.135 \times 10^{-3}}{270.03} = 7.907 \times 10^{-6}\ \mathrm{mol},$$
$$n_{\mathrm{pores}} = \frac{5.000 \times 10^{-3}}{633.666} = 7.891 \times 10^{-6}\ \mathrm{mol}.$$

Their ratio is

$$\frac{n_{\mathrm{UO_2^{2+}}}}{n_{\mathrm{pores}}} = 1.002 \approx \boxed{1\text{ uranyl ion per pore}}.$$

The solution was checked against the official solution.

Problem 4: The nuclear past of Uzbekistan

T4. The nuclear past of Uzbekistan

6%

4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	$\sum$
2	3	3	2	2	2	2	2	4	22

Natural uranium consists primarily of two isotopes, $^{235}\mathrm{U}$ and $^{238}\mathrm{U}$. $^{235}\mathrm{U}$ is responsible for sustaining nuclear fission reactions.

4.1 Calculate the atomic abundance of $^{235}\mathrm{U}$ in natural uranium, assuming it consists only of isotopes $^{235}\mathrm{U}$ (235.04 a.u.) and $^{238}\mathrm{U}$ (238.05 a.u.). **2.0 pt**

The main reaction occurring in nuclear power plants is the reaction where $^{235}\mathrm{U}$ absorbs a neutron and undergoes fission, releasing energy and producing three additional neutrons, thus sustaining a chain reaction.

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow \ldots + 3\,^{1}_{0}\mathrm{n}$$

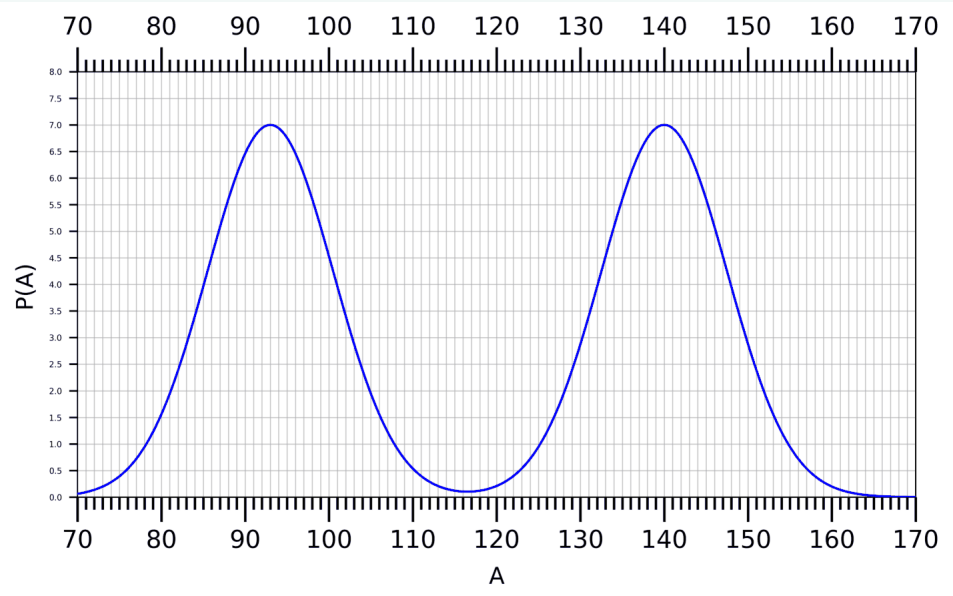
Neutrons that induce the chain reaction are produced by several ways:

a) Reaction of $^{11}\mathrm{B}$ with α-particles inside the reactor core

b) Interaction of γ rays with $^{2}\mathrm{D}$ nuclei present in the reactor coolant water

c) Reaction of $^{9}\mathrm{Be}$ with α-particles produced in an externally installed neutron source.

4.2 Write the nuclear reaction equations for **(a), (b), and (c)**. **3.0 pt**



The graph above displays the percentage yield, $P(A)$, of fission products by mass number, A, resulting from $^{235}\mathrm{U}$ fission.

4.3 Write the main nuclear fission equation for splitting of $^{235}\mathrm{U}$ upon neutron absorption. The pair of elements formed in this reaction are in the same group of Periodic Table. **3.0 pt**

4.4 Calculate the energy released in this reaction (ΔE, MeV), if the binding energy $BE(^{235}\mathrm{U}) = 7.59$ MeV/nucleon and average binding energy for fission products $BE(\mathrm{fis.}) = 8.45$ MeV/nucleon. *Neglect* the binding energy of free neutrons. **2.0 pt**

Fission neutrons are produced with an average energy of 2 MeV and slow down through many scatterings with nuclei. After several collisions, their speed decreases until their average kinetic energy matches that of the surrounding atoms or molecules.

The **logarithmic energy decrement**, ξ, shows the average decrease per collision in the logarithm of the neutron energy:

$$\xi = \ln\left(\frac{E_{initial}}{E_{final}}\right)$$

$E_{initial}$ and E_{final} are the initial and final neutron energies per collision.

ξ is a constant for each type of material and does not depend on the initial neutron energy.

4.5 Determine the average number of collisions required, n_c, to slow a neutron from 2 MeV to 0.012 eV, using water as the moderator. ξ (water)=0.948 **2.0 pt**

In 1963, the *Urtabulak* gas field suffered an uncontrolled natural gas well blowout, releasing enormous volumes of burning methane.

4.6 Calculate $\Delta_r H^\circ_{298}$ ($\mathrm{kJ\,mol^{-1}}$) for one mole of methane combustion reaction at 298 K. **Assume** all species are gaseous. Use the thermodynamic data below **2.0 pt**

$\Delta_f H^\circ_{298}(\mathrm{CH_4})$	$-74.8\ \mathrm{kJ\,mol^{-1}}$
$\Delta_f H^\circ_{298}(\mathrm{H_2O,\ gas})$	$-241.8\ \mathrm{kJ\,mol^{-1}}$
$\Delta_f H^\circ_{298}(\mathrm{CO_2})$	$-393.5\ \mathrm{kJ\,mol^{-1}}$
$C_P(\mathrm{CH_4})$	$35\ \mathrm{J\,mol^{-1}\,K^{-1}}$
$C_P(\mathrm{H_2O,\ gas})$	$34\ \mathrm{J\,mol^{-1}\,K^{-1}}$
$C_P(\mathrm{O_2})$	$29\ \mathrm{J\,mol^{-1}\,K^{-1}}$
$C_P(\mathrm{CO_2})$	$37\ \mathrm{J\,mol^{-1}\,K^{-1}}$

If you did not get an answer for 4.6, use $\Delta_r H^\circ_{298} = -750\ \mathrm{kJ\,mol^{-1}}$ *for further calculations.*

4.7 Calculate $\Delta_r H_{2000}$ ($\mathrm{kJ\,mol^{-1}}$) per mole of methane combustion reaction at 2000 K. **Assume** all species are gaseous. **2.0 pt**

If you did not get an answer for 4.7, use $\Delta_r H_{2000} = -700\ \mathrm{kJ\,mol^{-1}}$ *for further calculations.*

Assume that methane is flowing out the well at 101.325 kPa and 298 K with volumetric flow $Q = 2.2 \times 10^5\ \mathrm{m^3}$ per day before it catches fire.

4.8 Calculate the total energy released per day, E, (in $\mathrm{J\,day^{-1}}$) by complete isothermic combustion of methane at $T = 2000\ \mathrm{K}$ **2.0 pt**

The *Urtabulak* gas leak was ended by detonating a 30-kiloton in TNT equivalent underground nuclear explosion that collapsed the reservoir and sealed the leak. 1 ton of TNT equivalent is 4.184 GJ of energy.

4.9 Using the value from **4.4**, **calculate** the total number of fissions, TN, during the nuclear explosion. **Calculate** the mass, m, of enriched uranium used in the explosion (in kg), assuming it contained 90% by mass of the $^{235}\mathrm{U}$ isotope, and 33% of the $^{235}\mathrm{U}$ underwent fission.
If you did not get an answer for 4.4, use $\Delta E = 200\ \mathrm{MeV}$. **4.0 pt**

Physical Constants and Equations

Constants

Avogadro constant	$N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	$F = 96\,485\ \mathrm{C\,mol^{-1}}$
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	$e = 1.602 \times 10^{-19}\ \mathrm{C}$
Standard pressure	$P^\circ = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$
Ionic product of water at 25 °C	$K_w = 1.00 \times 10^{-14}$
Zero of the Celsius scale	$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
Electronvolt	$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
Watt	$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
Coulomb	$1\ \mathrm{C} = 1\ \mathrm{A\,s}$
Nanometre	$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
Ångstrom	$1\ \mathrm{Å} = 1 \times 10^{-10}\ \mathrm{m}$
metric ton	$1\ \mathrm{ton} = 1000\ \mathrm{kg}$
litre	$1\ \mathrm{L} = 1\ \mathrm{dm^3}$

Equations

Ideal gas law	$PV = nRT$
Dalton law	$P_i = x_i P$
Beer–Lambert law	$A = \log_{10}\frac{I_0}{I} = \varepsilon c l$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Heat and temperature change	$Q = nC_m\Delta T$
Gibbs energy definition	$G = H - TS$
Gibbs energy and equilibrium constant	$\Delta_r G^\circ = -RT\ln K$
Enthalpy change dependence on temperature (at $\Delta_r C_p = const$)	$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p(T_2 - T_1)$
Entropy change dependence on temperature (at $\Delta_r C_p = const$)	$\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln\frac{T_2}{T_1}$

Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$
Average reaction rate	$r = \frac{\Delta c}{\Delta t}$
The rate law	$r = k[A]^x[B]^y$
Arrhenius law	$k = A\exp\left(-\frac{E_a}{RT}\right)$
Integrated rate law for a 1st order reaction	$c = c_0 e^{-kt}$ $kt = \ln\frac{c_0}{c}$
Lifetime of a reagent in a 1st order reaction	$\tau = \frac{1}{k}$
Integrated rate law for n-th order reaction ($n \neq 1$)	$kt = \frac{1}{n-1}\left(c^{1-n} - c_0^{1-n}\right)$ for $n \neq 1$
Concentration of an intermediate in a consecutive reaction:	$[B] = \frac{k_1[A]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} D$$

The ratio of products in the competitive reactions:	$\frac{[B]}{[C]} = \frac{k_1}{k_2}$

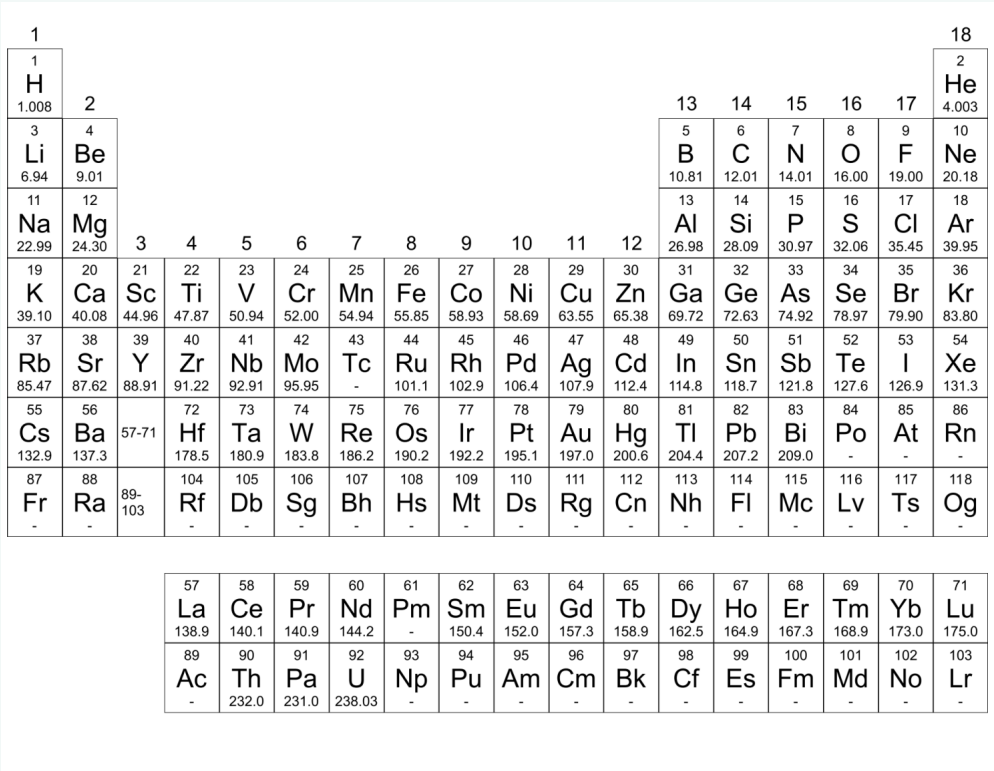
$$A \xrightarrow{k_1} B,\ A \xrightarrow{k_2} C$$

Michaelis–Menten equation	$r_0 = r_{\max}\frac{[S]_0}{K_M + [S]_0}$
Specific surface area	$s = \frac{S}{m}$
Progressions: arithmetic geometric	$a_n = a_1 + d(n-1)$ $a_n = a_1 q^{n-1}$
Sum of geometric progression	$\sum_{k=0}^{n} a_1 q^k = a_1\frac{q^{n+1}-1}{q-1}$
Volume of a sphere with radius r	$V = \frac{4}{3}\pi r^3$
Surface area of sphere with radius r	$S = 4\pi r^2$
Volume of a cone with base radius r and height h	$V = \frac{1}{3}\pi r^2 h$
Volume of a cylinder with base radius r and height h	$V = \pi r^2 h$

Consider all gases ideal.

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

Periodic Table of Elements



Official English text of the problem.

Answers

- **4.1:** The atomic abundance of $^{235}\mathrm{U}$ is $\boxed{0.664\% \approx 0.66\%}$.
- **4.2:**

  (a) $^{11}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n}$
  (b) $^{2}_{1}\mathrm{H} + \gamma \longrightarrow {}^{1}_{1}\mathrm{H} + {}^{1}_{0}\mathrm{n}$
  (c) $^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$
- **4.3:** The fragments are rubidium-93 and cesium-140, both group 1 elements:

  $$\boxed{^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{93}_{37}\mathrm{Rb} + {}^{140}_{55}\mathrm{Cs} + 3\,{}^{1}_{0}\mathrm{n}}$$
- **4.4:** $\boxed{\Delta E = 185.2\ \mathrm{MeV}}$ per fission.
- **4.5:** $\boxed{n_c = 19.97 \approx 20\ \text{collisions}}$.
- **4.6:** $\boxed{\Delta_r H^\circ_{298} = -802.3\ \mathrm{kJ\,mol^{-1}}}$.
- **4.7:** $\boxed{\Delta_r H_{2000} = -781.9\ \mathrm{kJ\,mol^{-1}}}$.
- **4.8:** $\boxed{E \approx 7.0 \times 10^{12}\ \mathrm{J\,day^{-1}}}$.
- **4.9:** $\boxed{TN \approx 4.23 \times 10^{24}\ \text{fissions}}$; the enriched uranium mass is $\boxed{m \approx 5.6\ \mathrm{kg}}$.

Solution

4.1 — Atomic abundance

The supplied periodic table gives the average atomic mass of natural uranium as 238.03 a.u. Let x be the atomic fraction of $^{235}\mathrm{U}$. The atomic fraction of $^{238}\mathrm{U}$ is then $1 - x$, so

$$238.03 = 235.04x + 238.05(1 - x).$$

Therefore,

$$x = \frac{238.05 - 238.03}{238.05 - 235.04} = \frac{0.02}{3.01} = 0.0066445.$$

Thus, using the supplied rounded atomic masses,

$$\boxed{100x = 0.66445\% \approx 0.66\%}.$$

4.2 — Neutron-producing reactions

In each nuclear reaction, both mass number A and atomic number Z are conserved. An α-particle is a helium-4 nucleus, $^{4}_{2}\mathrm{He}$.

(a) After emission of one neutron, the residual nucleus has

$$A = 11 + 4 - 1 = 14, \qquad Z = 5 + 2 = 7.$$

Atomic number 7 identifies nitrogen, so the product is nitrogen-14:

$$\boxed{^{11}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n}}.$$

(b) A deuterium nucleus, $^{2}_{1}\mathrm{H}$, contains one proton and one neutron. Absorption of a sufficiently energetic photon separates them:

$$\boxed{^{2}_{1}\mathrm{H} + \gamma \longrightarrow {}^{1}_{1}\mathrm{H} + {}^{1}_{0}\mathrm{n}}.$$

The hydrogen-1 nucleus is a proton.

(c) The residual nucleus has

$$A = 9 + 4 - 1 = 12, \qquad Z = 4 + 2 = 6.$$

Atomic number 6 identifies carbon, giving carbon-12:

$$\boxed{^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}}.$$

These nuclear equations specify nuclei; electron populations do not enter the balances.

4.3 — Identification of the fission fragments

The two maxima in the supplied graph occur at approximately

$$A_{\text{light}} = 93, \qquad A_{\text{heavy}} = 140.$$

Their sum is 233, consistent with the stated emission of three neutrons:

$$235 + 1 = 93 + 140 + 3.$$

Conservation of atomic number requires

$$Z_{\text{light}} + Z_{\text{heavy}} = 92.$$

Rubidium and cesium satisfy the same-group condition: both are group 1 elements, and

$$Z(\mathrm{Rb}) + Z(\mathrm{Cs}) = 37 + 55 = 92.$$

Assigning rubidium to the lighter fragment and cesium to the heavier fragment gives

$$\boxed{{}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{93}_{37}\mathrm{Rb} + {}^{140}_{55}\mathrm{Cs} + 3\,{}^{1}_{0}\mathrm{n}}.$$

Both mass number and atomic number are balanced.

4.4 — Energy released per fission

The energy released equals the increase in total nuclear binding energy.

Initially, the uranium nucleus contains 235 bound nucleons. The incoming neutron is free and contributes no binding energy under the stated approximation. Finally, the two fragments contain

$$93 + 140 = 233$$

bound nucleons; the three emitted neutrons are free.

Consequently,

$$\begin{aligned}\Delta E &= BE_{\text{products}} - BE_{\text{reactants}} \\ &= 233(8.45) - 235(7.59) \\ &= 1968.85 - 1783.65 \\ &= \boxed{185.2\ \mathrm{MeV}}.\end{aligned}$$

The positive value is the energy released per fission.

4.5 — Average number of collisions

The moderator is water, $\mathrm{H_2O}$, SMILES `O`.

Because the logarithmic energy decrements add over successive collisions,

$$\ln\left(\frac{E_0}{E_f}\right) = n_c \xi.$$

Using the same energy unit in numerator and denominator,

$$E_0 = 2\ \mathrm{MeV} = 2 \times 10^{6}\ \mathrm{eV}.$$

Therefore,

$$n_c = \frac{\ln\left(\dfrac{2 \times 10^{6}}{0.012}\right)}{0.948} = 19.9699.$$

Thus,

$$\boxed{n_c \approx 20 \text{ collisions}}.$$

4.6 — Methane combustion at 298 K

The molecular species are methane, $\mathrm{CH_4}$, SMILES `C`; dioxygen, $\mathrm{O_2}$, SMILES `O=O`; carbon dioxide, $\mathrm{CO_2}$, SMILES `O=C=O`; and water, $\mathrm{H_2O}$, SMILES `O`.

Complete combustion of one mole of methane is

$$\mathrm{CH_4\,(g)} + 2\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} + 2\,\mathrm{H_2O\,(g)}.$$

By Hess's law,

$$\Delta_r H^\circ_{298} = \sum_{\text{products}} \nu_i \Delta_f H^\circ_i - \sum_{\text{reactants}} \nu_i \Delta_f H^\circ_i.$$

The standard enthalpy of formation of $\mathrm{O_2\,(g)}$, an element in its reference state, is zero. Hence

$$\begin{aligned}\Delta_r H^\circ_{298} &= [-393.5 + 2(-241.8)] - [-74.8 + 2(0)] \\ &= \boxed{-802.3\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

The negative sign indicates an exothermic reaction.

4.7 — Methane combustion at 2000 K

For the same balanced combustion reaction,

$$\begin{aligned}\Delta_r C_P &= C_P(\mathrm{CO_2}) + 2C_P(\mathrm{H_2O}) - C_P(\mathrm{CH_4}) - 2C_P(\mathrm{O_2}) \\ &= 37 + 2(34) - 35 - 2(29) \\ &= 12\ \mathrm{J\,mol^{-1}\,K^{-1}} \\ &= 0.012\ \mathrm{kJ\,mol^{-1}\,K^{-1}}.\end{aligned}$$

Treating the supplied heat capacities as constant, Kirchhoff's law gives

$$\begin{aligned}\Delta_r H_{2000} &= \Delta_r H^\circ_{298} + \Delta_r C_P (2000 - 298) \\ &= -802.3 + 0.012(1702) \\ &= -781.876\ \mathrm{kJ\,mol^{-1}}.\end{aligned}$$

Thus,

$$\boxed{\Delta_r H_{2000} \approx -781.9\ \mathrm{kJ\,mol^{-1}}}.$$

4.8 — Energy released per day

The volumetric flow is specified at $298\ \mathrm{K}$, so that temperature must be used to convert the gas volume to an amount of methane.

From the ideal gas law, the molar flow is

$$\begin{aligned}\dot{n} &= \frac{pQ}{RT} \\ &= \frac{(101325\ \mathrm{Pa})(2.2\times10^{5}\ \mathrm{m^3\,day^{-1}})}{(8.314\ \mathrm{J\,mol^{-1}\,K^{-1}})(298\ \mathrm{K})} \\ &= 8.9973\times10^{6}\ \mathrm{mol\,day^{-1}}.\end{aligned}$$

Here, $\mathrm{Pa\,m^3} = \mathrm{J}$. The energy released is the positive magnitude of the combustion enthalpy:

$$\begin{aligned}E &= -\dot{n}\,\Delta_r H_{2000} \\ &= (8.9973\times10^{6}\ \mathrm{mol\,day^{-1}})(781876\ \mathrm{J\,mol^{-1}}) \\ &= 7.0348\times10^{12}\ \mathrm{J\,day^{-1}}.\end{aligned}$$

To two significant figures, consistent with the volumetric flow,

$$\boxed{E = 7.0\times10^{12}\ \mathrm{J\,day^{-1}}}.$$

4.9 — Number of fissions and uranium mass

The total energy represented by 30 kilotons of TNT is

$$\begin{aligned}E_{\text{explosion}} &= (30\times10^{3}\ \mathrm{ton})(4.184\times10^{9}\ \mathrm{J\,ton^{-1}}) \\ &= 1.2552\times10^{14}\ \mathrm{J}.\end{aligned}$$

Using the result from 4.4, the energy per fission in joules is

$$\begin{aligned}\varepsilon_{\text{fission}} &= (185.2\ \mathrm{MeV})(10^{6}\ \mathrm{eV\,MeV^{-1}})(1.602\times10^{-19}\ \mathrm{J\,eV^{-1}}) \\ &= 2.966904\times10^{-11}\ \mathrm{J}.\end{aligned}$$

Therefore, the total number of fissions is

$$TN = \frac{E_{\text{explosion}}}{\varepsilon_{\text{fission}}} = \frac{1.2552\times10^{14}}{2.966904\times10^{-11}} = \boxed{4.23\times10^{24}\ \text{fissions}}.$$

Each fission consumes one $^{235}\mathrm{U}$ nucleus. Thus, the mass of $^{235}\mathrm{U}$ that actually underwent fission is

$$\begin{aligned}m_{\text{fissioned}} &= \frac{TN}{N_A}M(^{235}\mathrm{U}) \\ &= \frac{4.23067\times10^{24}}{6.022\times10^{23}\ \mathrm{mol^{-1}}}(235.04\ \mathrm{g\,mol^{-1}}) \\ &= 1651.24\ \mathrm{g} = 1.65124\ \mathrm{kg}.\end{aligned}$$

If m is the initial mass of enriched uranium, its initial $^{235}\mathrm{U}$ mass is $0.90m$. Since 33% of that isotope underwent fission,

$$m_{\text{fissioned}} = 0.33(0.90m).$$

Hence

$$m = \frac{1.65124}{0.33\times0.90} = 5.5597\ \mathrm{kg}.$$

With sensible rounding,

$$\boxed{m \approx 5.6\ \mathrm{kg}}.$$

The solution was checked against the official solution.

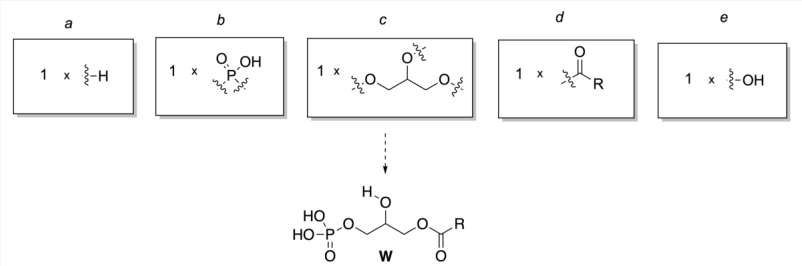
Problem 5: Cardiolipins

T5. Cardiolipins

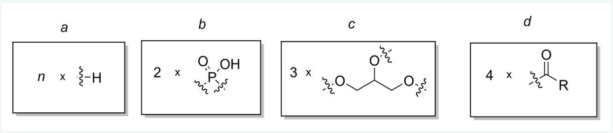
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5.1	5.2	5.3	5.4	5.5	5.6	Σ
1	6	4	2	2	3	18

In this problem you are asked to be creative and build molecules from fragments. For instance, if you are required to draw a chiral phospholipid such as **W** using fragments *a*-*e*, it can be assembled as shown below.



Cardiolipins are a family of acyclic phospholipids differing in fatty acid residues. They are essential for energy production and membrane stability. Defects can lead to certain diseases. **PL1** belongs to this family. Using only the structural elements *a-d* in the quantities stated below, it is possible to assemble the non-ionised form of **PL1**. R is a hydrocarbon substituent in the fatty acid structure.



PL1 does not contain any peroxide bonds.

5.1 **Tick** one correct statement regarding the value of n (number of type a fragments). **1.0 pt**

(a) n is an even number,
(b) n is an odd number,
(c) n can be either an odd or an even number.

Some cardiolipins are chiral molecules, even if they contain four identical fatty acid residues, as in the case of **PL1**. One enantiomer of **PL1** is found in prokaryotes and eukaryotes, and the other only in archaea. All other diastereomers of **PL1** are achiral molecules, since they have a plane of symmetry. Do not consider the chirality of phosphorus atoms as stereocentres.

PL1 is a diprotic acid with the same acidic groups. Its second deprotonation is less favourable ($pK_{a_2} \gg pK_{a_1}$) due to the special, stable structure of monoanion **Y**.

5.2 **Draw** the structure of one enantiomer of **PL1**. **Draw** the structure of **Y** in a way that shows the stabilisation that explains the difference between pK_{a_1} and pK_{a_2}. Use the abbreviation R for the fatty acid residues. **6.0 pt**

A series of experiments was conducted to identify the fatty acid (RCOOH) in **PL1** found predominantly in mammalian hearts. During reductive ozonolysis, RCOOH forms three different organic products in equimolar amounts.

5.3 **Determine** the molecular formula of the fatty acid (RCOOH), if the non-ionised form of **PL1** contains 255 σ and π bonds between atoms in total. **Support** your answer with calculations. **4.0 pt**

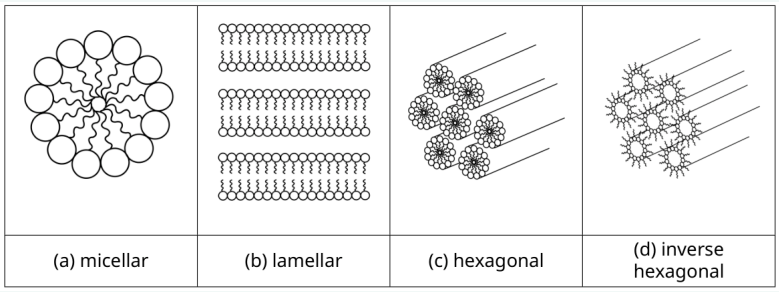
If you were unable to find the structural formula of PL1, you can use a-d fragments from 5.1.

100 g of RCOOH reacts with 181.0 g of iodine. RCOOH also reacts in similar way with **X** and forms an adduct with an iodine mass fraction of 36.57%.

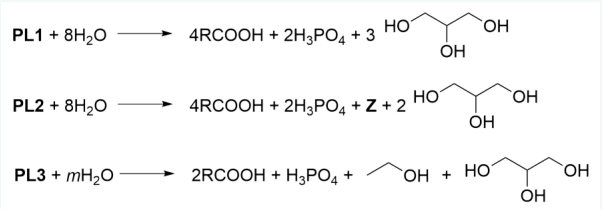
5.4 **Determine** the molecular formula of **X**. **Support** your answer with calculations. **2.0 pt**

The phase behavior of **PL1** depends on pH. In physiological conditions, **PL1** is a dianion and it forms a lamellar phase.

5.5 Which lipid phase is formed by **PL1** when both acid residues in it are protonated? **2.0 pt**
Note that knowledge of **PL1** structure is not required to solve this question.
Tick the correct answer.



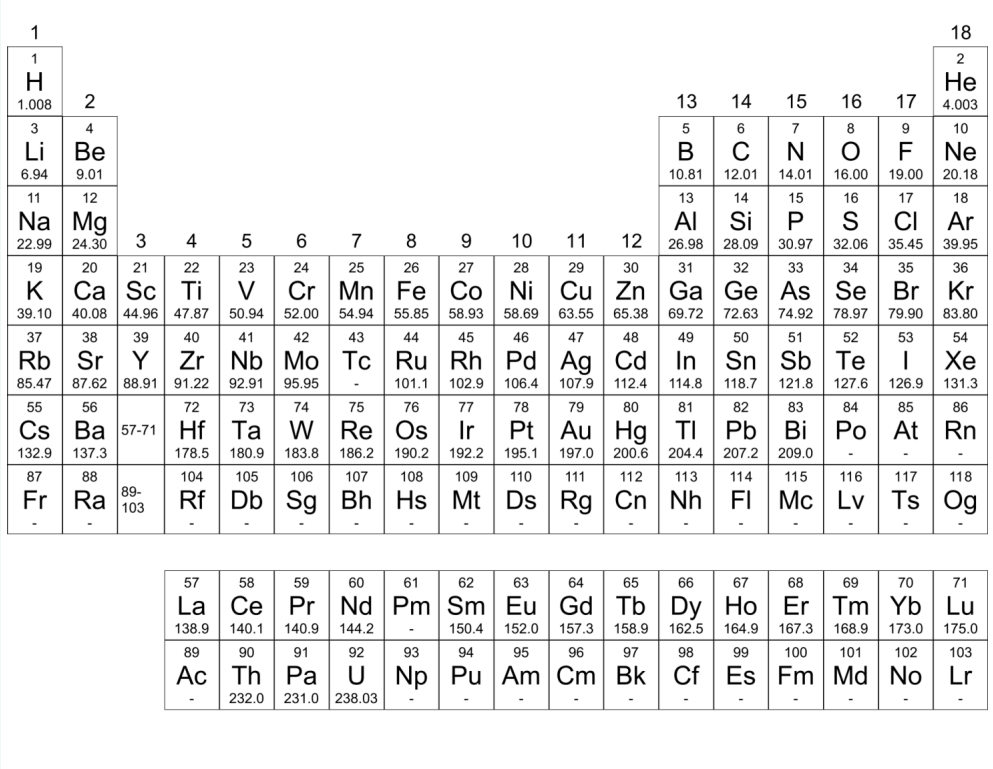
The following balanced reaction equations show the hydrolysis of phospholipids **PL1-PL3**:



- The non-ionised form of **PL2** contains 254 σ and π bonds between atoms in total. It is a chiral and a more symmetrical molecule than **PL1**,
- **Z** contains C, H, and O only, and it doesn't react with H_2 in the presence of a catalyst,
- Phospholipid **PL3** is a charged molecule at physiological pH values, and it exists as pair of enantiomers.

5.6 **Draw** the structures of **PL2** and **PL3** using R to show the fatty acid residues. **Show** stereochemistry where appropriate. **3.0 pt**

Periodic Table of Elements



Official English text of the problem.

Answers

In the generic structural SMILES below, every `*` denotes the same hydrocarbon substituent R. Phosphorus stereochemistry is omitted as instructed.

- **5.1: (b), n is odd.** Specifically, $n = 1$.
- **5.2: PL1 is cardiolipin, 1,3-bis(phosphatidyl)glycerol.** One enantiomer, with both outer glycerol stereocentres S, is
  `*C(=O)OC[C@H](OC(=O)*)COP(=O)(O)OCC(O)COP(=O)(O)OC[C@@H](OC(=O)*)COC(=O)*`

Y is the cardiolipin monoanion. One proton-localized representation is
`*C(=O)OC[C@H](OC(=O)*)COP(=O)(O)OC[C@H](O)COP(=O)([O-])OC[C@@H](OC(=O)*)COC(=O)*`

Draw two intramolecular hydrogen bonds: phosphate $\mathrm{O{-}H}$ donates to the central glycerol oxygen, whose $\mathrm{O{-}H}$ donates to the other phosphate's negatively charged oxygen.

- **5.3:** $\boxed{\mathrm{C_{18}H_{32}O_2}}$, an **octadecadienoic acid**. A compatible representative is **linoleic acid**, $(9Z,12Z)$-octadeca-9,12-dienoic acid:
  `CCCCC/C=C\C/C=C\CCCCCCCC(=O)O`
  The supplied data do not uniquely establish the double-bond positions or geometry.
- **5.4:** $\boxed{\mathrm{IBr}}$, **iodine monobromide**, `IBr`.
- **5.5: (d), inverse hexagonal phase.**
- **5.6: PL2 is 2′-deoxycardiolipin**, containing a propane-1,3-diol bridge. One enantiomer is
  `*C(=O)OC[C@H](OC(=O)*)COP(=O)(O)OCCCOP(=O)(O)OC[C@@H](OC(=O)*)COC(=O)*`

Z is propane-1,3-diol, `OCCCO`.

PL3 is phosphatidylethanol. One enantiomer of its physiological monoanion is
`CCOP(=O)([O-])OC[C@@H](OC(=O)*)COC(=O)*`

Its other enantiomer has `@` in place of `@@`. The hydrolysis coefficient is $\boxed{m = 4}$.

Solution

5.1 — Number of hydrogen fragments

Each glycerol fragment has three attachment sites, each phosphorus fragment has two, and each acyl fragment has one. Including the hydrogen fragments, the number of attachment sites is therefore

$$3(3) + 2(2) + 4(1) + n = 17 + n.$$

Each new bond consumes two attachment sites, so $17 + n$ must be even. Consequently, n **is odd**, giving answer **(b)**.

The exact value follows from acyclicity. There are $9 + n$ fragments, and connecting them into one acyclic molecule requires $8 + n$ interfragment bonds:

$$\frac{17+n}{2} = 8+n \quad \Longrightarrow \quad \boxed{n=1}.$$

In the resulting cardiolipin, this hydrogen completes the central glycerol hydroxyl group. The two phosphate hydroxyl hydrogens are already present in fragments b.

5.2 — PL1, its stereochemistry, and stabilization of Y

For the requested drawing, use a central glycerol unit whose two terminal hydroxyl groups form phosphate esters. Its secondary hydroxyl remains free.

Each phosphate has:

- one $\mathrm{P{=}O}$ bond;
- one acidic $\mathrm{P{-}OH}$ group;
- one ester linkage to the central glycerol;
- one ester linkage to a terminal oxygen of an outer glycerol.

Each outer glycerol carries two fatty acyl esters: one on its secondary oxygen and one on its remaining terminal oxygen. This uses exactly three glycerol fragments, two phosphate fragments, four acyl fragments, and one additional hydrogen.

The two outer glycerol stereocentres must have the **same absolute configuration**: either (S,S), as encoded in the answer SMILES, or (R,R). These structures are enantiomers. With identical arms, the central glycerol carbon in neutral PL1 is not a stereocentre. Opposite outer configurations allow the achiral, internally reflection-symmetric alternatives described in the question.

For **Y**, remove one phosphate proton and fold the central head group to form the hydrogen-bond sequence

$$\underbrace{\mathrm{P{-}O{-}H}}_{\text{one phosphate}} \quad \cdots \quad \underbrace{\mathrm{O{-}H}}_{\text{central glycerol hydroxyl}} \quad \cdots \quad \underbrace{\mathrm{O^{-}\,{-}P}}_{\text{other phosphate}} \quad .$$

The central oxygen **accepts** the first hydrogen bond and **donates** the second. Together with the covalent glycerol–phosphate framework, these interactions close two seven-membered hydrogen-bonded rings, counting the bridging hydrogen in each ring.

This cooperative hydrogen bonding stabilizes the monoanion. Removing the remaining phosphate proton removes a hydrogen-bond donor and creates a second negative charge in the compact head group. Thus the second deprotonation is substantially less favourable:

$$\boxed{pK_{a_2} \gg pK_{a_1}}.$$

The SMILES specifies connectivity, formal charge, and a proton-localized stereochemical representation; it does **not** encode this folded conformation or the hydrogen bonds.

5.3 — Molecular formula of the fatty acid

Reductive ozonolysis retains the original carboxyl group in one product. Since there is only one carboxyl group per fatty-acid molecule, the carboxyl-containing product is formed once per molecule.

The three products occur in equimolar amounts, so each fatty-acid molecule produces three fragments. For an acyclic fatty acid, this requires **two carbon–carbon double bonds**.

An acyclic monocarboxylic acid containing c carbon atoms and two carbon–carbon double bonds therefore has formula

$$\mathrm{C}_c\mathrm{H}_{2c-4}\mathrm{O}_2.$$

Let B denote the total number of σ and π bonds, counting a double bond as two. From the usual valences,

$$B_{\text{fatty acid}} = \frac{4c + (2c-4) + 2(2)}{2} = 3c.$$

The small molecules in the hydrolysis are water, `O`; glycerol, `OCC(O)CO`; and phosphoric acid, `OP(=O)(O)O`. Their bond totals are

$$B_{\mathrm{H_2O}} = 2, \qquad B_{\text{glycerol}} = 13, \qquad B_{\mathrm{H_3PO_4}} = 8.$$

The balanced hydrolysis is

$$\mathrm{PL}_1 + 8\,\mathrm{H_2O} \longrightarrow 4\,\mathrm{RCOOH} + 2\,\mathrm{H_3PO_4} + 3\,\mathrm{C_3H_8O_3}.$$

Hydrolysis replaces each ester linkage by two bonds to the atoms of water, preserving the total bond-order sum across this equation. Hence

$$\begin{gathered} 255 + 8(2) = 4B_{\text{fatty acid}} + 2(8) + 3(13), \\ 271 = 4B_{\text{fatty acid}} + 55, \\ B_{\text{fatty acid}} = 54. \end{gathered}$$

Therefore,

$$3c = 54, \qquad c = 18,$$

and

$$\boxed{\mathrm{RCOOH} = \mathrm{C_{18}H_{32}O_2}}.$$

As an independent check, condensation of the hydrolysis products gives

$$\mathrm{PL}_1 = \mathrm{C_{81}H_{142}O_{17}P_2}.$$

Its total bond count is

$$B_{\mathrm{PL1}} = \frac{4(81) + 142 + 2(17) + 5(2)}{2} = \boxed{255}.$$

Here phosphorus has bond-order sum five, consistent with the supplied $\mathrm{P{=}O}$ drawings.

The linoleic-acid SMILES in the answer is a compatible structural representative. Formula determination alone does not establish its particular double-bond positions or Z configurations.

5.4 — Identification of X

Using the supplied atomic masses,

$$M(\mathrm{C_{18}H_{32}O_2}) = 18(12.01) + 32(1.008) + 2(16.00) = 280.436\ \mathrm{g\,mol^{-1}}.$$

Iodine is $\mathrm{I_2}$, SMILES `II`, with

$$M(\mathrm{I_2}) = 253.8\ \mathrm{g\,mol^{-1}}.$$

The amount of iodine consumed per mole of fatty acid is

$$\frac{n(\mathrm{I_2})}{n(\text{fatty acid})} = \frac{181.0/253.8}{100/280.436} = 2.000.$$

This agrees with addition across two double bonds:

$$\mathrm{C_{18}H_{32}O_2 + 2\,I_2 \longrightarrow C_{18}H_{32}I_4O_2}.$$

For addition of an iodine-containing interhalogen, two reagent molecules introduce two iodine atoms per fatty-acid molecule. Thus

$$0.3657 = \frac{2(126.9)}{280.436 + 2M(X)}.$$

Solving,

$$M(X) = \frac{253.8/0.3657 - 280.436}{2} = 206.79\ \mathrm{g\,mol^{-1}}.$$

The mass remaining after accounting for one iodine atom is

$$206.79 - 126.9 = 79.89\ \mathrm{g\,mol^{-1}},$$

which matches bromine, $79.90\ \mathrm{g\,mol^{-1}}$. Therefore,

$$\boxed{X = \mathrm{IBr}},$$

iodine monobromide, `IBr`.

The balanced addition is

$$\mathrm{C_{18}H_{32}O_2 + 2\,IBr \longrightarrow C_{18}H_{32}Br_2I_2O_2}.$$

Checking the iodine fraction,

$$w_\mathrm{I} = \frac{253.8}{280.436 + 2(126.9 + 79.90)} = 0.365687 \approx \boxed{36.57\%}.$$

For the compatible linoleic-acid representative, constitutional representations of the addition products are **9,10,12,13-tetraiodooctadecanoic acid**, `CCCCCC(I)C(I)CC(I)C(I)CCCCCCCC(=O)O`, and **9,12-dibromo-10,13-diiodooctadecanoic acid**, `CCCCCC(I)C(Br)CC(I)C(Br)CCCCCCCC(=O)O`. These SMILES leave addition-product stereochemistry unspecified; neither stereochemistry nor alternative interhalogen regiochemistry affects the mass calculation.

5.5 — Lipid phase after protonation

Protonating both phosphate groups reduces electrostatic repulsion and hydration of the polar head group, decreasing its effective cross-sectional area. The four hydrocarbon tails retain their large volume.

Consequently, the packing parameter

$$p = \frac{v}{a_0 l_c}$$

increases as the head-group area a_0 decreases. This favours curvature around aqueous channels and formation of the **inverse hexagonal phase**.

Tick **(d)**. In that drawing, polar heads face inward toward water-filled cylindrical channels, while hydrocarbon tails extend outward into the surrounding lipid region.

5.6 — Structures of PL2 and PL3

For **PL2**, compare its hydrolysis with that of PL1. The fatty acids, phosphoric acid, and water coefficients are unchanged; one glycerol molecule is replaced by Z. Therefore,

$$B(Z) - B(\text{glycerol}) = B(\mathrm{PL2}) - B(\mathrm{PL1}) = -1,$$

so

$$B(Z) = 13 - 1 = \boxed{12}.$$

For an acyclic saturated diol, $\mathrm{C_kH_{2k+2}O_2}$,

$$B(Z) = \frac{4k + (2k+2) + 4}{2} = 3k + 3.$$

Thus

$$3k + 3 = 12 \quad\Longrightarrow\quad k = 3.$$

The required symmetry places the two hydroxyl groups at equivalent terminal positions, giving **propane-1,3-diol**, $\mathrm{HOCH_2CH_2CH_2OH}$, `OCCCO`.

A central carbonyl alternative, **dihydroxyacetone**, `OCC(=O)CO`, would also reduce the bond total by one relative to glycerol, but it would undergo catalytic hydrogenation. The stated nonreactivity excludes it.

Accordingly, draw **PL2** by replacing the central $-\mathrm{CH(OH)^-}$ group of PL1 with $-\mathrm{CH_2}-$, retaining the same two outer glycerol configurations. This gives **2′-deoxycardiolipin**, whose SMILES is listed in the answers. Replacing the central hydroxyl by hydrogen allows greater symmetry, including a conformation with a twofold rotation exchanging the two identical halves.

Its neutral molecular formula and balanced hydrolysis are

$$\mathrm{PL_2} = \mathrm{C_{81}H_{142}O_{16}P_2},$$
$$\mathrm{C_{81}H_{142}O_{16}P_2} + 8\,\mathrm{H_2O} \longrightarrow 4\,\mathrm{C_{18}H_{32}O_2} + 2\,\mathrm{H_3PO_4} + \mathrm{C_3H_8O_2} + 2\,\mathrm{C_3H_8O_3}.$$

Removing one oxygen from PL1 lowers the bond-order sum by one:

$$B_{\mathrm{PL2}} = \frac{4(81) + 142 + 2(16) + 5(2)}{2} = \boxed{254}.$$

For **PL3**, the hydrolysis products identify two fatty acyl groups, one glycerol, one phosphate, and ethanol, CCO.

Draw a glycerol with fatty acyl esters on its secondary oxygen and one terminal oxygen. Connect its other terminal oxygen to a phosphate group, and connect ethanol through oxygen to that same phosphate. The phosphate retains one acidic hydroxyl:

$$\mathrm{R{-}C(=O){-}O{-}CH_2{-}CH[O{-}C(=O){-}R]{-}CH_2{-}O{-}P(=O)(OH){-}O{-}CH_2{-}CH_3}.$$

This is **phosphatidylethanol**. One enantiomer of its neutral acid form is

`CCOP(=O)(O)OC[C@@H](OC(=O)*)COC(=O)*`

At physiological pH, its remaining phosphate hydroxyl is deprotonated, giving the monoanion shown in the answers. A phosphate on the central glycerol oxygen, with identical acyl groups on both terminal oxygens, would instead give an achiral structure; this is excluded by the stated enantiomeric pair.

There are two carboxylic ester linkages and two phosphate ester linkages to hydrolyse, requiring four water molecules:

$$\boxed{m = 4}.$$

For the neutral acid form, the balanced equation is

$$\mathrm{C_{41}H_{73}O_8P} + 4\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{C_{18}H_{32}O_2} + \mathrm{H_3PO_4} + \mathrm{C_2H_6O} + \mathrm{C_3H_8O_3}.$$

The solution was checked against the official solution.

Problem 6: Carbon Nanorings

T6. Carbon Nanorings

7%

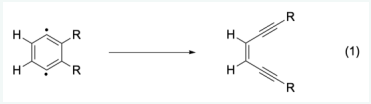
6.1	6.2	6.3	6.4	6.5	6.6	6.7	$\sum$
10	11	2	12	24	20	4	83

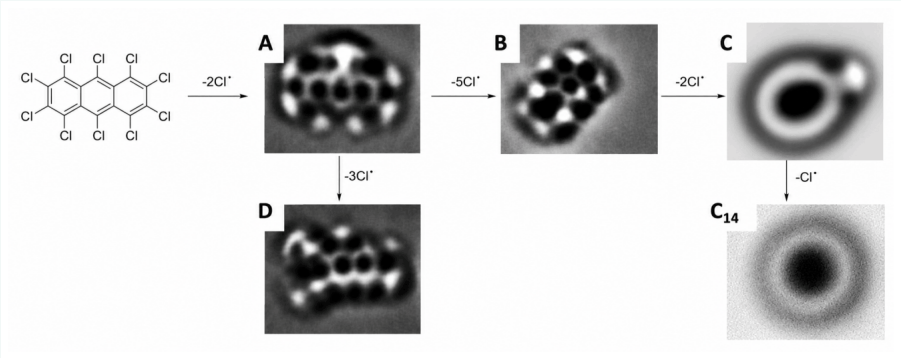
In 2019, $\mathrm{C_{18}}$, the first example of a new class of carbon allotropes called cyclo[n]carbons ($\mathrm{C_n}$) was detected. Cyclocarbons are monocyclic, all-carbon compounds with high strain energy and low stability. They can be generated and analysed by bond-resolved Atomic Force Microscopy (AFM). Cyclocarbons have interesting aromatic properties based on their π systems. $\mathrm{C_{13}}$ has triplet ($^3\mathrm{C_{13}}$, spin $S = 1$), and singlet ($^1\mathrm{C_{13}}$, spin $S = 0$) forms.

6.1 Based on Hückel's rule, **fill in** the table with the number of distinct aromatic (**A**) and anti-aromatic (**AA**) π-systems present in each of $\mathrm{C_{18}}$, $\mathrm{C_{16}}$, $^3\mathrm{C_{13}}$, and $^1\mathrm{C_{13}}$. **Fill in all blanks. 10.0 pt**

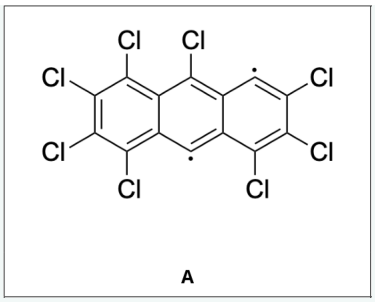
	$\mathrm{C_{18}}$	$\mathrm{C_{16}}$	$^3\mathrm{C_{13}}$	$^1\mathrm{C_{13}}$
A				
AA				

Later, cyclo[n]carbons $\mathrm{C_{10}}$, $\mathrm{C_{12}}$, $\mathrm{C_{14}}$, $\mathrm{C_{20}}$, and $\mathrm{C_{26}}$ were generated by a combination of dehalogenation and retro-Bergman (1) reactions on a surface. AFM images taken during the synthesis of $\mathrm{C_{14}}$ are shown below:





6.2 Draw structures **B-D**. Note they may contain one or more unpaired electrons. The structure of **A** is given as an example. **11.0 pt**

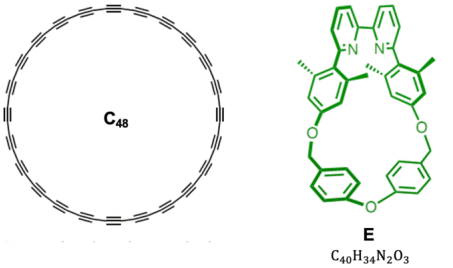


A

6.3 The voltages applied during the AFM-mediated synthesis of C_n may vary. Using the given C–X bond energies, **choose** the possible halogen(s) in the halogenated reagent for C_{18} synthesis via a retro-Bergman reaction with a voltage of 2.5 V acting on the electrons. **2.0 pt**

Bond (C–X)	Bond Dissociation Energy / $\mathrm{kJ\,mol^{-1}}$
C–F	467
C–Cl	346
C–Br	290
C–I	228

In 2025, the first relatively stable cyclo[48]carbon was synthesised. The molecule was stabilised by catenation (forming interlocking rings) with macrocycle **E** and was first characterised by electrospray mass spectrometry in positive mode.



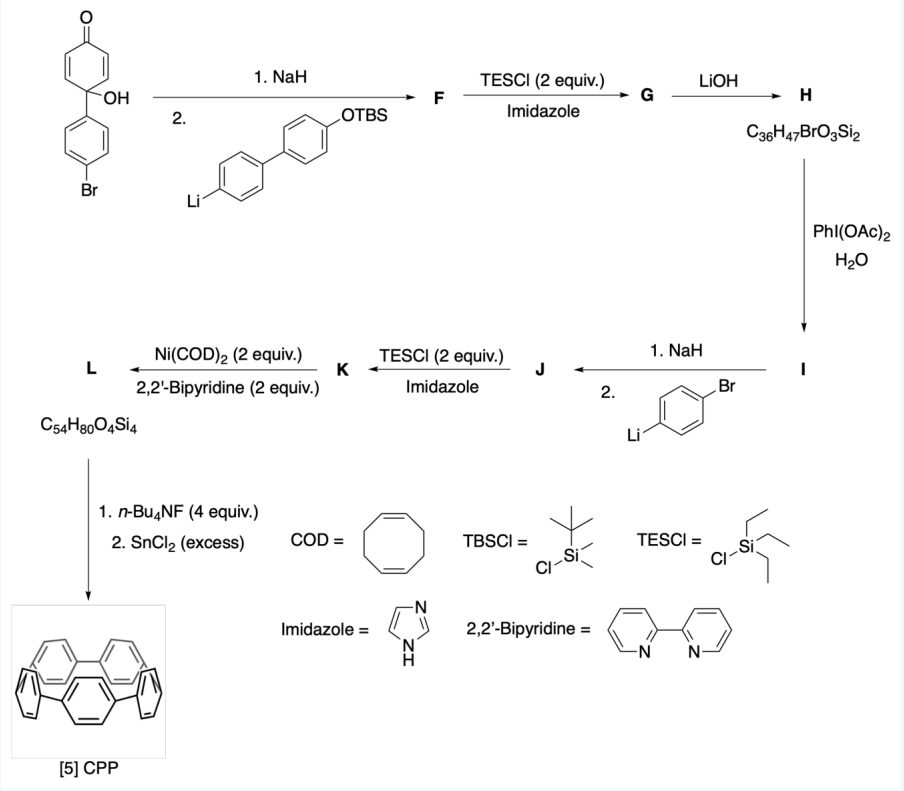
E

$\mathrm{C_{40}H_{34}N_2O_3}$

6.4 In the mass spectrum obtained, four intense peaks were observed m/z: 591, 783, 879, and 1174. **Suggest** the identity of these ions. **Use** integer atomic masses and **assume** no fragmentation happened. The ion corresponding to $m/z = 591$ is given as an example. **12.0 pt**

m/z	591	783	879	1174
	$[\mathbf{E}+\mathrm{H}]^+$			

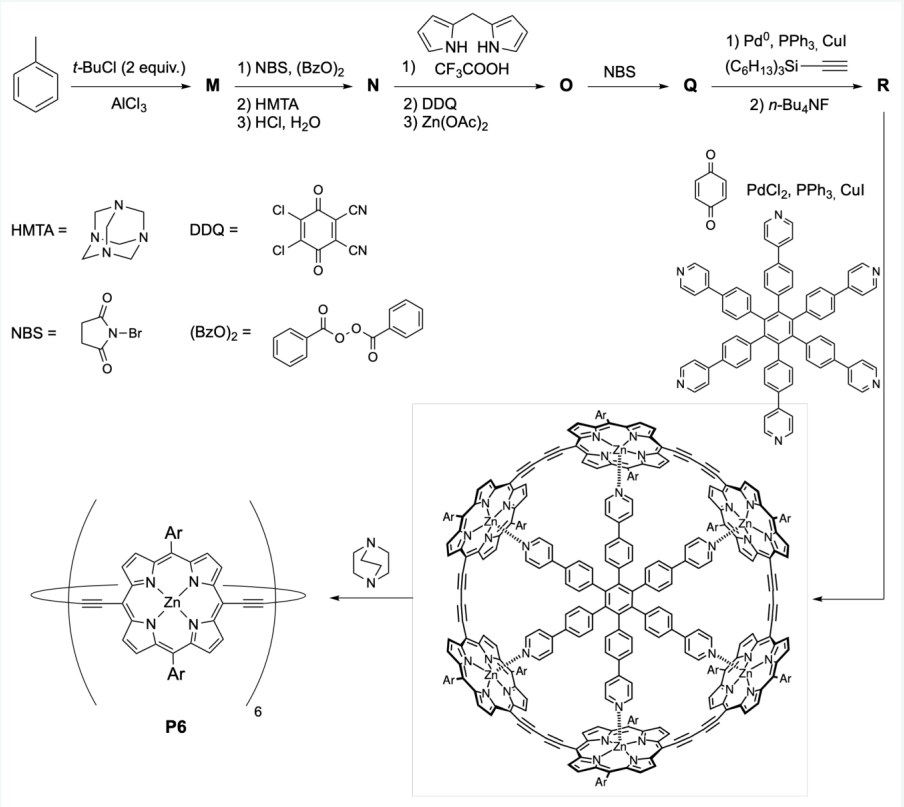
Cycloparaphenylene (CPP) is another cyclic, highly-strained molecule commonly called a carbon nanohoop. The synthesis of the smallest known member, [5]CPP, is shown below, where $\mathrm{PhI(OAc)_2}$ acts as a two electron oxidant.



(equiv. = Equivalent, excess = Excess)

6.5 Draw the structures of **F-L**. **24.0 pt**

Next generation nanobelts were constructed from porphyrin rings and triple bonds using the template synthesis method. *Hint:* **M** is the thermodynamic product and has four types of protons.

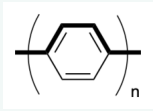


(equiv. = Equivalent)

6.6 Draw the structures of **M-R**. **20.0 pt**

When aromatic rings are joined to form a macrocycle, oxidation or reduction can produce global aromaticity, in which π electrons are delocalised around the entire macrocycle. Only the π system forming the continuous conjugated pathway around the ring participates in this delocalisation. As an example, [n]CPPs can become globally aromatic upon addition or removal of electrons. The number of π electrons is counted only along the bold

pathway shown below.



When **P6** is oxidised, it can exhibit global aromaticity and global anti-aromaticity.

6.7 Based on Hückel's rule, **find** the minimum number of electrons, $n(e)$, from **P6** that should be removed to achieve global aromaticity. **Write** the total number of π electrons, $n(t)$, in the global aromatic system. **4.0 pt**

Physical Constants and Equations

Constants

Constant	Value
Avogadro constant	$N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	$F = 96\,485\ \mathrm{C\,mol^{-1}}$
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	$e = 1.602 \times 10^{-19}\ \mathrm{C}$
Standard pressure	$P^\circ = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$
Ionic product of water at 25 °C	$K_w = 1.00 \times 10^{-14}$
Zero of the Celsius scale	$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
Electronvolt	$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
Watt	$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
Coulomb	$1\ \mathrm{C} = 1\ \mathrm{A\,s}$
Nanometre	$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
Ångstrom	$1\ \text{Å} = 1 \times 10^{-10}\ \mathrm{m}$
metric ton	$1\ \mathrm{ton} = 1000\ \mathrm{kg}$
litre	$1\ \mathrm{L} = 1\ \mathrm{dm^3}$

Official English text of the problem.

Answers

The structures named here are specified explicitly by SMILES in the corresponding Solution entries.

- **6.1:** In the order $\mathrm{C_{18}}$, $\mathrm{C_{16}}$, $^{3}\mathrm{C_{13}}$, $^{1}\mathrm{C_{13}}$:
  A: $2,\ 0,\ 0,\ 1.$
  AA: $0,\ 2,\ 0,\ 1.$
- **6.2:**
  B: A benzene-fused ten-membered ring containing four triple bonds; the retained benzenoid ring has chlorine at C5, C6 and C7, and a radical at C8. Formula $\mathrm{C_{14}Cl_3}$, one unpaired electron.
  C: A monocyclic $\mathrm{C_{14}Cl}$ radical containing six triple bonds and an adjacent $\mathrm{C(Cl){=}C^{\bullet}}$ pair.
  D: 1,6,7-Trichloro-2,3-bis(chloroethynyl)naphthalene-4,5,8-triyl, $\mathrm{C_{14}Cl_5}$, three unpaired electrons.
- **6.3:** $X = \mathrm{I}$, **iodine only**.
- **6.4:**
  $591:\ [\mathrm{E+H}]^{+}.$
  $783:\ [\mathrm{C_{48}+3\,E+3\,H}]^{3+}.$
  $879:\ [\mathrm{C_{48}+2\,E+2\,H}]^{2+}.$
  $1174:\ [\mathrm{C_{48}+3\,E+2\,H}]^{2+}.$
- **6.5:**
  F: The cis cyclohexadiene diol formed by addition of the TBS-protected biphenylyllithium reagent.
  G: Its bis-TES ether.
  H: The terminal phenol obtained by selective TBS removal.
  I: The terminal para-quinol obtained by oxidative dearomatisation of H.
  J: The second cis diol, formed by addition of 4-bromophenyllithium to I.
  K: The tetra-TES-protected dibromide.
  L: The cyclic product formed by coupling K's two terminal brominated aryl carbons.

- **6.6:**
  M: 3,5-Di-tert-butyltoluene.
  N: 3,5-Di-tert-butylbenzaldehyde.
  O: Zinc(II) 5,15-bis(3,5-di-tert-butylphenyl)porphyrin.
  Q: Its 10,20-dibromo derivative.
  R: Its 10,20-diethynyl derivative.
- **6.7:** $\boxed{n(e) = 2, \qquad n(t) = 82}$.

Solution

6.1 — Separate counts for the two perpendicular π systems

Each cyclocarbon has two perpendicular sets of π orbitals: one perpendicular to the molecular plane and one lying in that plane.

Hückel's electron-counting criterion is applied **separately** to each system:

$$4k + 2 \text{ π electrons: aromatic,} \qquad 4k \text{ π electrons: anti-aromatic.}$$

The electron distributions in the idealised configurations considered here are:

Species	π electrons in the two systems	A	AA
C_{18}	$18,\ 18$	2	0
C_{16}	$16,\ 16$	0	2
$^{3}\mathrm{C}_{13}$	$13,\ 13$	0	0
$^{1}\mathrm{C}_{13}$	$14,\ 12$	1	1

For C_{18}, $18 = 4(4) + 2$, so both systems are aromatic. For C_{16}, $16 = 4(4)$, so both are anti-aromatic.

In the triplet C_{13} configuration, each system has an odd electron count and one unpaired electron; neither satisfies the stated closed-shell Hückel counts. In the paired singlet configuration, the 26 π electrons are distributed as 14 and 12, giving one aromatic and one anti-aromatic system.

6.2 — Ring-opened intermediates

Retro-Bergman reactions break C–C bonds of the original fused framework and generate new triple bonds. Chlorine loss and carbon valence must both be respected.

In the following SMILES, bracketed `[c]` and `[C]` atoms identify the carbon radicals through their explicitly unsatisfied valence.

B — Trichlorinated benzene-fused cyclodecatetrayne radical

SMILES: `Clc1c(Cl)c(Cl)[c]c2c1C#CC#CC#CC#C2`

Retain one six-membered benzenoid ring. Its four nonfusion positions, numbered C5–C8 consecutively, carry:

- C5: chlorine;
- C6: chlorine;
- C7: chlorine;
- C8: one unpaired electron, adjacent to a fusion carbon.

The two fusion carbons are also connected by the eight-carbon chain

$$-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{C}{\equiv}\mathrm{C}^{-},$$

forming a fused ten-membered ring. Thus B contains **four triple bonds, three chlorine atoms and one radical**, with formula $\mathrm{C}_{14}\mathrm{Cl}_3$.

C — Monochlorocyclo[14]carbon radical

SMILES: `ClC1=[C]C#CC#CC#CC#CC#CC1`

Draw a single fourteen-membered carbon ring with six alternating triple bonds and one double bond. One carbon of the double bond carries chlorine; the other carries the unpaired electron:

$$-\mathrm{C}(\mathrm{Cl}){=}\mathrm{C}^{\bullet}-.$$

The remaining bonds between these unsaturated units are single bonds. C therefore has formula $\mathrm{C}_{14}\mathrm{Cl}$, with the radical **next to the chlorine-bearing carbon**.

D — 1,6,7-Trichloro-2,3-bis(chloroethynyl)naphthalene-4,5,8-triyl

SMILES: `Clc1c(C#CCl)c(C#CCl)[c]c2[c]c(Cl)c(Cl)[c]c12`

Use the standard naphthalene numbering:

- C2 and C3 each carry a chloroethynyl arm, $-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{Cl}$.
- C1, C6 and C7 each carry chlorine.
- C4, C5 and C8 each carry one unpaired electron.

The naphthalene core remains intact, while the opened third ring supplies the two chloroethynyl arms. The formula is $\mathrm{C}_{14}\mathrm{Cl}_5$, with three radicals.

The chlorine balances for the displayed sequence are:

$$\begin{aligned}
\mathrm{C_{14}Cl_{10}} &\longrightarrow \mathrm{C_{14}Cl_8} + 2\,\mathrm{Cl^\bullet} && \text{formation of A,}\\
\mathrm{C_{14}Cl_8} &\longrightarrow \mathrm{C_{14}Cl_3} + 5\,\mathrm{Cl^\bullet} && \text{A to B,}\\
\mathrm{C_{14}Cl_3} &\longrightarrow \mathrm{C_{14}Cl} + 2\,\mathrm{Cl^\bullet} && \text{B to C,}\\
\mathrm{C_{14}Cl_8} &\longrightarrow \mathrm{C_{14}Cl_5} + 3\,\mathrm{Cl^\bullet} && \text{A to D,}\\
\mathrm{C_{14}Cl} &\longrightarrow \mathrm{C_{14}} + \mathrm{Cl^\bullet} && \text{C to cyclo[14]carbon.}
\end{aligned}$$

The final cyclo[14]carbon has seven alternating triple bonds.

Name: **cyclo[14]carbon**.
SMILES: `C1#CC#CC#CC#CC#CC#CC#C1`

6.3 — Electron energy and bond dissociation

An electron accelerated through a potential difference U gains energy eU. Per mole of electrons,

$$E_{\mathrm{mol}} = FU = (96\,485\ \mathrm{C\,mol^{-1}})(2.5\ \mathrm{J\,C^{-1}}) = 241\,212.5\ \mathrm{J\,mol^{-1}}.$$

Thus the available energy is approximately

$$E_{\mathrm{mol}} = 241\ \mathrm{kJ\,mol^{-1}} \approx 2.4 \times 10^{2}\ \mathrm{kJ\,mol^{-1}}.$$

Only the C–I bond energy lies below this value:

$$228 < 241 < 290 < 346 < 467 \qquad (\mathrm{kJ\,mol^{-1}}).$$

Therefore,

$$\boxed{X = \mathrm{I}}.$$

6.4 — Masses, stoichiometries and charge states

Using the supplied formula of E,

$$M(E) = 40(12) + 34(1) + 2(14) + 3(16) = 590\ \mathrm{Da}.$$

For cyclo[48]carbon,

$$M(\mathrm{C_{48}}) = 48(12) = 576\ \mathrm{Da}.$$

For a complex containing one carbon ring, a macrocycles E and z added protons,

$$\frac{m}{z} = \frac{576 + 590a + z}{z}.$$

The assignments are:

m/z	Assignment	Calculation
591	$[\mathrm{E} + \mathrm{H}]^{+}$	$590 + 1 = 591$
783	$[\mathrm{C_{48}} + 3\,\mathrm{E} + 3\,\mathrm{H}]^{3+}$	$(576 + 3 \times 590 + 3)/3 = 783$
879	$[\mathrm{C_{48}} + 2\,\mathrm{E} + 2\,\mathrm{H}]^{2+}$	$(576 + 2 \times 590 + 2)/2 = 879$
1174	$[\mathrm{C_{48}} + 3\,\mathrm{E} + 2\,\mathrm{H}]^{2+}$	$(576 + 3 \times 590 + 2)/2 = 1174$

The following are explicit component SMILES for these ions. A dot separates **covalently disconnected rings**; SMILES does not encode their mechanical interlocking. The protonated pyridyl nitrogens shown are representative protonation sites.

$m/z = 591$: monoprotonated bipyridine-containing macrocycle E

SMILES: `[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1`

$m/z = 783$: triprotonated [4]catenane containing cyclo[48]carbon and three E rings

SMILES: `C1#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#C1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1`

$m/z = 879$: diprotonated [3]catenane containing cyclo[48]carbon and two E rings

SMILES: `C1#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#C1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1`

$m/z = 1174$: diprotonated [4]catenane containing cyclo[48]carbon and three E rings

SMILES: `C1#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#CC#C1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1.[nH+]1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1.n1c(-c2c(C)cc(O3)cc2C)cccc1-c1cccc(-c2c(C)cc(OCc4ccc(Oc5ccc(C3)cc5)cc4)cc2C)n1`

Their respective formulas are $\mathrm{C_{40}H_{35}N_2O_3}^{+}$, $\mathrm{C_{168}H_{105}N_6O_9}^{3+}$, $\mathrm{C_{128}H_{70}N_4O_6}^{2+}$, and $\mathrm{C_{168}H_{104}N_6O_9}^{2+}$.

6.5 — Construction of [5]CPP

The useful cyclohexadiene building blocks have their two aryl substituents **cis** to one another; the two oxygen substituents are correspondingly cis on the other face. These bent units allow macrocyclisation before the highly strained aromatic nanohoop is generated.

The paired `@` symbols below specify this relative stereochemistry. They do not specify a unique overall macrocycle conformation.

F — cis-1-(4-Bromophenyl)-4-[4′-(tert-butyldimethylsiloxy)biphenyl-4-yl]cyclohexa-2,5-diene-1,4-diol

SMILES: `Brc1ccc([C@]2(O)C=C[C@](O)(c3ccc(-c4ccc(O[Si](C)(C)C(C)(C)C)cc4)cc3)C=C2)cc1`

First, sodium hydride deprotonates the existing alcohol:

$$\mathrm{ROH} + \mathrm{NaH} \longrightarrow \mathrm{RONa} + \mathrm{H_2}.$$

The aryllithium reagent then adds to the ketone carbonyl. After work-up, that carbonyl becomes a tertiary alcohol:

$$\mathrm{R_2C{=}O} + \mathrm{ArLi} + \mathrm{H_2O} \longrightarrow \mathrm{R_2C(OH)Ar} + \mathrm{LiOH}.$$

The original alkoxide is also protonated during work-up. F therefore has two free hydroxyl groups and retains the terminal TBS-protected phenol.

G — Bis(triethylsilyl) ether of F

SMILES: `Brc1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c3ccc(-c4ccc(O[Si](C)(C)C(C)(C)C)cc4)cc3)C=C2)cc1`

Two equivalents of TESCl protect both tertiary alcohols. With Im denoting imidazole, each protection has the balance

$$\mathrm{ROH} + \mathrm{Et_3SiCl} + \mathrm{Im} \longrightarrow \mathrm{ROSiEt_3} + [\mathrm{ImH}]\mathrm{Cl}.$$

The terminal phenolic TBS ether remains present.

H — Terminal phenol obtained by selective TBS deprotection of G

SMILES: `Brc1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c3ccc(-c4ccc(O)cc4)cc3)C=C2)cc1`

LiOH hydrolyses the phenolic TBS ether:

$$\mathrm{ArOSiMe_2}(t\text{-Bu}) + \mathrm{H_2O} \xrightarrow{\mathrm{LiOH}} \mathrm{ArOH} + \mathrm{HOSiMe_2}(t\text{-Bu}).$$

The two tertiary TES ethers remain. This gives exactly the supplied formula:

$$\boxed{\mathrm{C_{36}H_{47}BrO_3Si_2}}.$$

I — Terminal para-quinol formed by oxidative dearomatisation of H

SMILES: `Brc1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c3ccc(C4(O)C=CC(=O)C=C4)cc3)C=C2)cc1`

The terminal phenol becomes a cyclohexa-2,5-dien-1-one. Its para carbon, already carrying the rest of the molecule, acquires an OH group.

The two-electron oxidation is balanced by

$$\mathrm{C_{36}H_{47}BrO_3Si_2} + \mathrm{PhI(OAc)_2} + \mathrm{H_2O} \longrightarrow \mathrm{C_{36}H_{47}BrO_4Si_2} + \mathrm{PhI} + 2\,\mathrm{CH_3COOH}.$$

Thus I contains the original protected cyclohexadiene unit and a new hydroxycyclohexadienone unit.

J — Second cis-diol addition product

SMILES: `Brc1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c3ccc([C@]4(O)C=C[C@](O)(c5ccc(Br)cc5)C=C4)cc3)C=C2)cc1`

NaH deprotonates I's newly formed OH group. Then 4-bromophenyllithium adds to the remaining ketone, as in the formation of F.

The five-ring chain now has the sequence

bromophenyl–protected diene–phenylene–diol diene–bromophenyl.

J has formula $\mathrm{C_{42}H_{52}Br_2O_4Si_2}$.

K — Tetra-TES-protected dibromide precursor

SMILES: `Brc1ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c3ccc([C@]4(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c5ccc(Br)cc5)C=C4)cc3)C=C2)cc1`

Two more equivalents of TESCl protect J's two free hydroxyl groups. K therefore contains four TES ethers and two terminal aryl bromides:

$$\mathrm{C_{54}H_{80}Br_2O_4Si_4}.$$

L — Tetra-TES-protected, doubly dearomatised [5]cycloparaphenylene

SMILES: `c1%10ccc([C@]2(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c3ccc([C@]4(O[Si](CC)(CC)CC)C=C[C@](O[Si](CC)(CC)CC)(c5ccc-%10cc5)C=C4)cc3)C=C2)cc1`

Nickel-mediated intramolecular coupling joins the two aromatic carbons that originally carried bromine. This closes the five-unit hoop.

The net coupling balance is

$$\mathrm{C_{54}H_{80}Br_2O_4Si_4} + \mathrm{Ni} \longrightarrow \mathrm{C_{54}H_{80}O_4Si_4} + \mathrm{NiBr_2}.$$

The resulting formula agrees with the problem:

$$\boxed{\mathrm{C_{54}H_{80}O_4Si_4}}.$$

The two equivalents of nickel complex shown are the experimental reagent loading; the net redox balance consumes one equivalent of $\mathrm{Ni}(0)$.

Finally, fluoride removes all four TES groups. For each group, a hydrolytic work-up can be represented by

$$\mathrm{ROSiEt_3} + \mathrm{F^-} + \mathrm{H_2O} \longrightarrow \mathrm{ROH} + \mathrm{Et_3SiF} + \mathrm{OH^-}.$$

The resulting tetrol has formula $\mathrm{C_{30}H_{24}O_4}$. Reductive aromatisation then gives [5]CPP. Its balanced reduction half-equation is

$$\mathrm{C_{30}H_{24}O_4} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longrightarrow \mathrm{C_{30}H_{20}} + 4\,\mathrm{H_2O}.$$

Tin(II) supplies the electrons:

$$2\,\mathrm{Sn^{2+}} \longrightarrow 2\,\mathrm{Sn^{4+}} + 4\,\mathrm{e^-}.$$

Name: **[5]cycloparaphenylene**.
SMILES: `c1%10ccc(-c2ccc(-c3ccc(-c4ccc(-c5ccc-%10cc5)cc4)cc3)cc2)cc1`

6.6 — Porphyrin building block

Define Ar here as **3,5-di-tert-butylphenyl**.

M — 3,5-Di-tert-butyltoluene

SMILES: `Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1`

Under the thermodynamic alkylation conditions, the bulky substituents adopt the alternating 1,3,5 arrangement, avoiding adjacent methyl/tert-butyl substitution.

The net alkylation is

$$\mathrm{C_6H_5CH_3} + 2\,\mathrm{(CH_3)_3CCl} \xrightarrow{\mathrm{AlCl_3}} \mathrm{C_6H_3(CH_3)[C(CH_3)_3]_2} + 2\,\mathrm{HCl}.$$

M has the required four proton environments:

1. the methyl group, 3 H;
2. the two equivalent tert-butyl groups, 18 H;
3. aromatic H2 and H6, 2 H;
4. aromatic H4, 1 H.

N — 3,5-Di-tert-butylbenzaldehyde

SMILES: `O=Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1`

NBS with peroxide initiator brominates the benzylic methyl group:

$$\mathrm{ArCH_3} + \mathrm{NBS} \longrightarrow \mathrm{ArCH_2Br} + \mathrm{succinimide}.$$

The intermediate is **3,5-di-tert-butylbenzyl bromide**.

SMILES: `BrCc1cc(C(C)(C)C)cc(C(C)(C)C)c1`

HMTA followed by acidic hydrolysis effects the Sommelet conversion to the aldehyde. Writing the amine hydrolysis products in their neutral forms gives the balanced net equation

$$\mathrm{ArCH_2Br} + \mathrm{C_6H_{12}N_4} + 6\,\mathrm{H_2O} \longrightarrow \mathrm{ArCHO} + 5\,\mathrm{HCHO} + \mathrm{CH_3NH_2} + 3\,\mathrm{NH_3} + \mathrm{HBr}.$$

In the acidic reaction medium, the amines are protonated.

O — Zinc(II) 5,15-bis(3,5-di-tert-butylphenyl)porphyrin

SMILES: `CC(C)(C)c1cc(-c2c3[n]4->[Zn+2]56<-[n]7c(cc8ccc2[n-]->58)C=Cc7c(-c2cc(C(C)(C)C)cc(C(C)(C)C)c2)c2ccc(cc4C=C3)[n-]->62)cc(C(C)(C)C)c1`

Two aldehydes and two dipyrromethanes furnish the porphyrin framework. The aldehyde-derived carbons become two opposite meso carbons bearing Ar. The other two meso positions retain hydrogen.

Condensation and oxidation by DDQ have the overall balance

$$2\,\mathrm{C_{15}H_{22}O} + 2\,\mathrm{C_9H_{10}N_2} + 3\,\mathrm{DDQ} \longrightarrow \mathrm{C_{48}H_{54}N_4} + 2\,\mathrm{H_2O} + 3\,\mathrm{DDQH_2}.$$

Zinc insertion then replaces the two inner N–H protons:

$$\mathrm{C_{48}H_{54}N_4} + \mathrm{Zn(OAc)_2} \longrightarrow \mathrm{C_{48}H_{52}N_4Zn} + 2\,\mathrm{CH_3COOH}.$$

The SMILES explicitly includes N-to-Zn dative bonds. The four porphyrin nitrogens coordinate zinc in an approximately square-planar arrangement; that geometry is not specified by the SMILES itself.

Q — Zinc(II) 10,20-dibromo-5,15-bis(3,5-di-tert-butylphenyl)porphyrin

SMILES: `CC(C)(C)c1cc(-c2c3[n]4->[Zn+2]56<-[n]7c(c(Br)c8ccc2[n-]->58)C=Cc7c(-c2cc(C(C)(C)C)cc(C(C)(C)C)c2)c2ccc(c(Br)c4C=C3)[n-]->62)cc(C(C)(C)C)c1`

NBS replaces the two remaining meso hydrogens by bromine. The net balance is

$$\mathrm{C_{48}H_{52}N_4Zn} + 2\,\mathrm{NBS} \longrightarrow \mathrm{C_{48}H_{50}Br_2N_4Zn} + 2\,\mathrm{succinimide}.$$

R — Zinc(II) 10,20-diethynyl-5,15-bis(3,5-di-tert-butylphenyl)porphyrin

SMILES: `C#Cc1c2[n]3->[Zn+2]45<-[n]6c(c(C#C)c7ccc(c(-c8cc(C(C)(C)C)cc(C(C)(C)C)c8)c3C=C2)[n-]->47)C=Cc6c(-c2cc(C(C)(C)C)cc(C(C)(C)C)c2)c2ccc1[n-]->52`

Each meso bromide undergoes Sonogashira coupling with trihexylsilyl-protected acetylene:

$$\mathrm{P{-}Br} + \mathrm{HC{\equiv}C{-}Si(C_6H_{13})_3} \longrightarrow \mathrm{P{-}C{\equiv}C{-}Si(C_6H_{13})_3} + \mathrm{HBr},$$

where P denotes the remaining porphyrin framework.

Fluoride then removes both silyl protecting groups. Per ethynyl group,

$$\mathrm{P{-}C{\equiv}C{-}Si(C_6H_{13})_3} + \mathrm{F^-} + \mathrm{H_2O} \longrightarrow \mathrm{P{-}C{\equiv}CH} + \mathrm{(C_6H_{13})_3SiF} + \mathrm{OH^-}.$$

R therefore contains two opposite terminal ethynyl groups and has formula $\mathrm{C_{52}H_{52}N_4Zn}$. Oxidative coupling of these terminal groups subsequently generates the butadiyne connections between porphyrins in P6.

6.7 — Global π-electron count

Count only the orbitals belonging to one continuous conjugated route around the entire nanoring.

Each porphyrin contributes **10 π electrons** along the route between its two opposite linker-bearing meso positions. Each butadiyne bridge,

$$\mathrm{-C{\equiv}C{-}C{\equiv}C^-},$$

contributes **4 π electrons**: only one of the two perpendicular π systems of each triple bond belongs to the global conjugation pathway.

With six porphyrins and six butadiyne bridges,

$$N_\pi = 6(10) + 6(4) = 84.$$

After removing $n(e)$ electrons, the Hückel condition is

$$84 - n(e) = 4k + 2.$$

Removing one electron gives 83, which does not satisfy the condition. Removing two gives

$$82 = 4(20) + 2.$$

Therefore, under the Hückel-counting criterion requested,

$$\boxed{n(e) = 2, \qquad n(t) = 82}.$$

The solution was checked against the official solution.

Problem 7: Nitrogen Fixation

T7. Nitrogen Fixation

7%

7.1	7.2	7.3	7.4	7.5	7.6	7.7	$\sum$
3	8	15	3	6	6	13	54

The Haber–Bosch process is the principal industrial method for ammonia production. A simplified diagram of an ammonia synthesis plant is shown below.

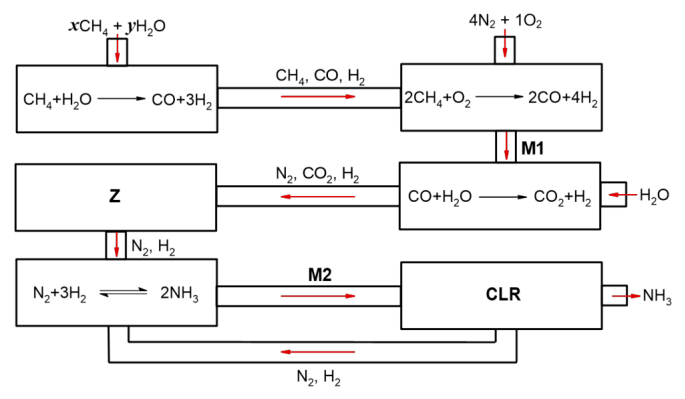


Fig. 1. **M1** - Mixture 1, **M2** - Mixture 2, **Z** – CO_2 scrubber, **CLR** - cooler

In the following calculations, assume that all reactions in **Fig. 1**, except NH_3 formation, are quantitative.

7.1 Tick the gases contained in **M1** and **M2**; and **tick** the correct relationship between x and y. **3.0 pt**

	CH_4	H_2O	CO	O_2	H_2	N_2	NH_3	CO_2
M1								
M2								

$x > y$	$x = y$	$x < y$

An ammonia production complex with a capacity of 660,000 tons per year was commissioned at the *Navoiazot* plant in Uzbekistan, which operates with a 97.0% of overall yield.

7.2 Calculate the mass of CH_4 (tons) required annually to produce 660,000 tons of ammonia, if the *Navoiazot* operates according to the **Fig. 1**. **8.0 pt**

Consider a model of a real reaction system, which includes recirculation of reagents. An open system operates in a cyclic mode. Each cycle consists of four steps:

1. A stoichiometric $N_2 : H_2 = 1 : 3$ mixture with a total amount of n_0 mol is fed into the reactor after each cycle.
2. The reaction proceeds with a constant yield of $\eta = 0.150$.
3. Ammonia is separated by liquification.
4. Unreacted gases are returned into the reactor.

The cycle is repeated until the required overall yield is reached.

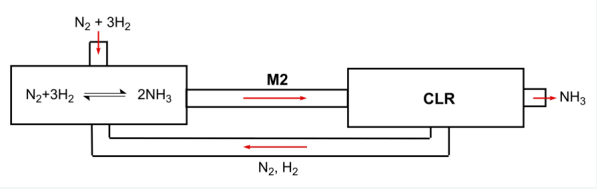


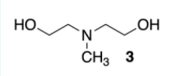
Fig. 2. **M2.** – Mixture 2, **CLR** - cooler.

7.3

a) **Calculate** the amount of nitrogen, present in the system after the 58th cycle (before the addition of 59th portion of mixture), if $n_0 = 4$ mol. **Provide** 4 decimal places. *Hint: a formula for the sum of the terms of a geometric progression is needed.*

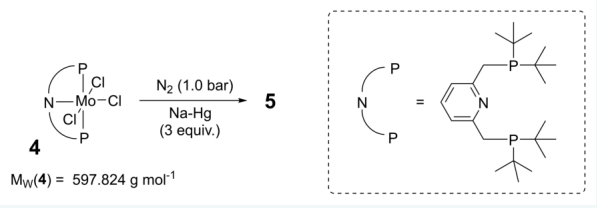
b) **Calculate** the number of cycles needed to increase the overall yield from 15.0% to 97.0%. **15.0 pt**

An aqueous solution of **3** is being used to remove $\mathrm{CO_2}$ from the mixture.



7.4 Write the equation for this reaction. **3.0 pt**

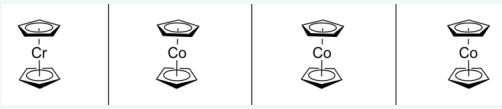
Complex **5** is obtained through the fixation of the molecular nitrogen according to the scheme below.



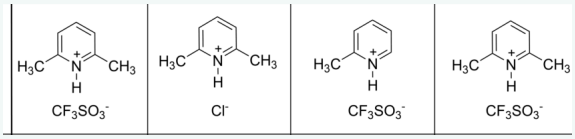
7.5 Draw the structure of **5** using simplified scheme for the ligand. Note that 1.00 g of **4** will react stoichiometrically with 94.97 $\mathrm{cm^3}$ of $\mathrm{N_2}$ at 273.15 K and 1.0 bar. **6.0 pt**

The effect of different reductants and additives on the yield of $\mathrm{NH_3}$ was examined. The different Red and Ad combinations, their respective E° and pK_a, together with the resulting $\mathrm{NH_3}$ yield are presented below.

Red



Ad



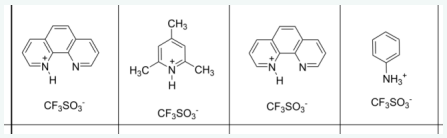
#	1	2	3	4
E° (V)	−0.88	−1.15	−1.15	−1.15
pK_a	14.4	14.4	13.9	14.4
$\mathrm{NH_3}$ yield (mole)	0	0.7	9.1	11.8

7.6 Rank the following **Red/Ad** combinations **A-D** by the decrease in ammonia yield. **6.0 pt**

Red



Ad



#	A	B	C	D
E° (V)	−0.09	−1.10	−1.10	−1.10
pK_a	13.7	15.0	13.7	10.6

Nitrogen fixation can also be achieved via binary nitrides (compounds containing N^{3-}). Such nitrides **7, 8, 9** were obtained from pure elements. When they are heated together with $\mathrm{SiO_2}$, red crystals of a stable compound **10** are formed as the single product. The minimal possible formula, describing the structure of compound **10** is $\mathrm{Q}_\alpha\mathrm{R}_\beta\mathrm{S}_2\mathrm{T}[\mathrm{Si}_{12}\mathrm{N}_{24}]$. In addition:

1. Mass fractions of nitrogen are $w(\mathrm{N})_7 = 9.16\%$, $w(\mathrm{N})_8 = 18.90\%$, $w(\mathrm{N})_9 = 39.94\%$
2. **Q** and **R** are metal cations in their highest oxidation state.
3. **S** is a monoatomic anion.
4. **T** is an anion with tetrahedral configuration.
5. For the quantitative formation of **10**, the mass ratio **7 : 8 : 9** : $\mathrm{SiO_2}$ = 5.09 : 2.96 : 3.27 : 1.00.

7.7 Identify the empirical formulae of **7–10**. **Specify** the composition of anions **S** and **T**. **13.0 pt**

Physical Constants and Equations

Constants

Constant	Value
Avogadro constant	$N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
Universal gas constant	$R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	$F = 96\,485\ \mathrm{C\,mol^{-1}}$
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	$e = 1.602 \times 10^{-19}\ \mathrm{C}$
Standard pressure	$P^\circ = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$
Ionic product of water at 25 °C	$K_w = 1.00 \times 10^{-14}$
Zero of the Celsius scale	$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
Electronvolt	$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
Watt	$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
Coulomb	$1\ \mathrm{C} = 1\ \mathrm{A\,s}$
Nanometre	$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
Ångstrom	$1\ \text{Å} = 1 \times 10^{-10}\ \mathrm{m}$
metric ton	$1\ \mathrm{ton} = 1000\ \mathrm{kg}$
litre	$1\ \mathrm{L} = 1\ \mathrm{dm^3}$

Equations

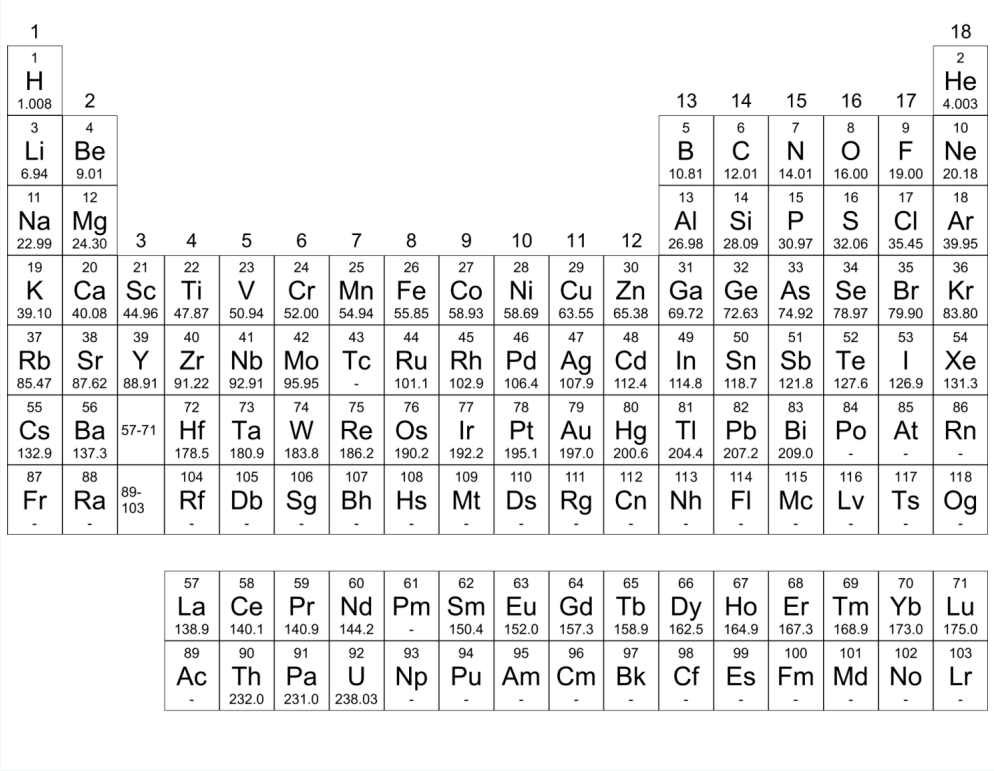
Equation	Expression
Ideal gas law	$PV = nRT$
Dalton law	$P_i = x_i P$
Beer–Lambert law	$A = \log_{10}\dfrac{I_0}{I} = \varepsilon c l$
Energy of a photon	$E = h\nu = \dfrac{hc}{\lambda}$
Heat and temperature change	$Q = nC_m\Delta T$
Gibbs energy definition	$G = H - TS$
Gibbs energy and equilibrium constant	$\Delta_r G^\circ = -RT\ln K$
Enthalpy change dependence on temperature (at $\Delta_r C_p = \text{const}$)	$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$
Entropy change dependence on temperature (at $\Delta_r C_p = \text{const}$)	$\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln\dfrac{T_2}{T_1}$
Henderson–Hasselbalch equation	$pH = pK_a + \log_{10}\dfrac{[\mathrm{A^-}]}{[\mathrm{HA}]}$
Average reaction rate	$r = \dfrac{\Delta c}{\Delta t}$
The rate law	$r = k[A]^x[B]^y$
Arrhenius law	$k = A\exp\left(-\dfrac{E_a}{RT}\right)$
Integrated rate law for a 1st order reaction	$c = c_0 e^{-kt}$; $kt = \ln\dfrac{c_0}{c}$
Lifetime of a reagent in a 1st order reaction	$\tau = \dfrac{1}{k}$
Integrated rate law for n-th order reaction ($n \neq 1$)	$kt = \dfrac{1}{n-1}\left(c^{1-n} - c_0^{1-n}\right)$, for $n \neq 1$
Concentration of an intermediate in a consecutive reaction: $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{D}$	$[B] = \dfrac{k_1[A]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$
The ratio of products in the competitive reactions: $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$, $\mathrm{A} \xrightarrow{k_2} \mathrm{C}$	$\dfrac{[B]}{[C]} = \dfrac{k_1}{k_2}$

Equation	Expression
Michaelis–Menten equation	$r_0 = r_{\max}\dfrac{[S]_0}{K_M + [S]_0}$
Specific surface area	$s = \dfrac{S}{m}$
Progressions: arithmetic geometric	$a_n = a_1 + d(n-1)$; $a_n = a_1 q^{n-1}$
Sum of geometric progression	$\sum_{k=0}^{n} a_1 q^k = a_1 \dfrac{q^{n+1}-1}{q-1}$
Volume of a sphere with radius r	$V = \dfrac{4}{3}\pi r^3$
Surface area of sphere with radius r	$S = 4\pi r^2$
Volume of a cone with base radius r and height h	$V = \dfrac{1}{3}\pi r^2 h$
Volume of a cylinder with base radius r and height h	$V = \pi r^2 h$

Consider all gases ideal.

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

Periodic Table of Elements



Official English text of the problem.

Answers

- **7.1:** Tick CO, $\mathrm{H_2}$, and $\mathrm{N_2}$ for **M1**; tick $\mathrm{H_2}$, $\mathrm{N_2}$, and $\mathrm{NH_3}$ for **M2**. Tick $x > y$.
- **7.2:** $\boxed{2.80 \times 10^5 \text{ tons of } \mathrm{CH_4} \text{ per year}}$.
- **7.3(a):** $\boxed{5.6662\ \mathrm{mol\ of\ N_2}}$.
- **7.3(b):** $\boxed{189 \text{ total cycles}}$, or **188 additional cycles after the first cycle**, which gives 15.0%.
- **7.4:**

$$\boxed{\mathrm{CH_3N(CH_2CH_2OH)_2 + CO_2 + H_2O \rightleftharpoons [CH_3NH(CH_2CH_2OH)_2]^+ + HCO_3^-}}$$

- **7.5: 5** is $\boxed{[\mathrm{Mo_2(L)_2(N_2)_5}]}$: two octahedral molybdenum(0) centres, each bearing one tridentate PNP ligand L and two terminal dinitrogen ligands, joined by one end-on/end-on bridging dinitrogen ligand.
- **7.6:** $\boxed{\mathrm{B > C > D > A}}$, in decreasing ammonia yield.
- **7.7: 7** = lanthanum(III) nitride, LaN; **8** = calcium nitride, $\mathrm{Ca_3N_2}$; **9** = silicon nitride, $\mathrm{Si_3N_4}$. **10** has empirical formula $\boxed{\mathrm{Ca_9La_5Si_{13}N_{25}O_5}}$, written structurally as $\boxed{\mathrm{Ca_9La_5O_2[SiNO_3][Si_{12}N_{24}]}}$. Thus **S** is $\mathrm{O^{2-}}$, and **T** is tetrahedral $[\mathrm{SiNO_3}]^{5-}$.

Solution

7.1 — Gases in the two mixtures

The molecular species used in the process are methane `C`, water `O`, carbon monoxide `[C-]#[O+]`, dioxygen `O=O`, dihydrogen `[H][H]`, dinitrogen `N#N`, ammonia `N`, and carbon dioxide `O=C=O`.

The first reactor carries out steam reforming:

$$\mathrm{CH_4 + H_2O \longrightarrow CO + 3\,H_2}.$$

Its outlet contains unreacted methane, carbon monoxide, and hydrogen. Water has been consumed, whereas methane remains; therefore,

$$\boxed{x > y}.$$

The remaining methane then reacts quantitatively with the oxygen introduced alongside nitrogen:

$$\mathrm{2\,CH_4 + O_2 \longrightarrow 2\,CO + 4\,H_2}.$$

Consequently, immediately after this reactor,

$$\boxed{\mathrm{M1:\ CO,\ H_2,\ N_2}}.$$

The subsequent water–gas shift reaction is

$$\mathrm{CO + H_2O \longrightarrow CO_2 + H_2}.$$

The scrubber removes the resulting carbon dioxide, leaving nitrogen and hydrogen for ammonia synthesis:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3}.$$

Because ammonia formation is incomplete, its reactor outlet contains product and unreacted reagents:

$$\boxed{\mathrm{M2:\ H_2,\ N_2,\ NH_3}}.$$

No other boxes should be ticked.

7.2 — Annual methane requirement

Use a basis of $1\ \mathrm{mol}$ of oxygen supplied with $4\ \mathrm{mol}$ of nitrogen.

In the first reactor, y mol of methane react with y mol of water. The remaining methane is $x - y$ mol. The second reactor consumes 2 mol of methane per mole of oxygen, so

$$x - y = 2.$$

Before the shift reaction, the amounts are

$$n(\mathrm{CO}) = y + 2, \qquad n(\mathrm{H_2}) = 3y + 4.$$

Converting all carbon monoxide into carbon dioxide produces a further $y + 2$ mol of hydrogen. Hence

$$n(\mathrm{H_2}) = 4y + 6.$$

The $4\ \mathrm{mol}$ of nitrogen require $12\ \mathrm{mol}$ of hydrogen for stoichiometric ammonia synthesis:

$$4y + 6 = 12, \qquad y = 1.5, \qquad x = 3.5.$$

Thus $3.5\ \mathrm{mol}$ of methane supply the reagents for $8\ \mathrm{mol}$ of ammonia. With integer coefficients, the overall theoretical reaction is

$$\boxed{\mathrm{7\,CH_4 + 10\,H_2O + 2\,O_2 + 8\,N_2 \longrightarrow 7\,CO_2 + 16\,NH_3}}.$$

The molar masses calculated from the supplied table are

$$M(\mathrm{CH_4}) = 12.01 + 4(1.008) = 16.042\ \mathrm{g\,mol^{-1}},$$
$$M(\mathrm{NH_3}) = 14.01 + 3(1.008) = 17.034\ \mathrm{g\,mol^{-1}}.$$

Accounting for the overall yield,

$$m(\mathrm{CH_4}) = \frac{660\,000\ \mathrm{tons}}{0.970}\,\frac{7}{16}\,\frac{16.042}{17.034} = 280\,344.6\ \mathrm{tons}.$$

Therefore,

$$\boxed{m(\mathrm{CH_4}) = 2.80 \times 10^5\ \mathrm{tons\,year^{-1}}}.$$

7.3(a) — Nitrogen remaining after 58 cycles

Each fresh portion contains

$$a = \frac{n_0}{4} = 1\ \mathrm{mol}$$

of nitrogen. Let r_k be the amount of unreacted nitrogen after cycle k, after ammonia removal and before the next addition. The unreacted fraction per cycle is

$$q = 1 - \eta = 0.850.$$

The recurrence is

$$r_k = q(r_{k-1} + a), \qquad r_0 = 0.$$

Therefore,

$$r_k = a(q + q^2 + \cdots + q^k) = a\frac{q(1 - q^k)}{1 - q}.$$

For $k = 58$,

$$r_{58} = (1\ \text{mol})\frac{0.85(1-0.85^{58})}{0.15} = 5.6662099726\ \text{mol}.$$

To four decimal places,

$$\boxed{r_{58} = 5.6662\ \text{mol of } \mathrm{N_2}}.$$

7.3(b) — Cycles needed for 97.0% overall yield

After k cycles, the total amount of nitrogen introduced is ka, and the amount converted is $ka - r_k$. Consequently, the cumulative ammonia yield is

$$Y_k = \frac{2(ka - r_k)}{2ka} = 1 - \frac{q(1-q^k)}{k(1-q)}.$$

Thus

$$Y_k = 1 - \frac{0.85(1-0.85^k)}{0.15k}.$$

The required condition is $Y_k \geq 0.970$. The two consecutive values surrounding the threshold are

$$Y_{188} = 0.9698581560 = 96.9858\%,$$
$$Y_{189} = 0.9700176367 = 97.0018\%.$$

The overall yield increases with the number of cycles, so the minimum is

$$\boxed{189\ \text{total cycles}}.$$

Since the first cycle gives 15.0%, this is **188 additional cycles after the first**. Fresh reagent is added every cycle; a calculation for repeatedly recycling a single initial charge would describe a different system.

7.4 — Carbon dioxide absorption

Compound **3** is **N-methyldiethanolamine**, SMILES `CN(CCO)CCO`.

It is a tertiary amine. In aqueous solution it accepts a proton as dissolved carbon dioxide forms hydrogencarbonate:

$$\boxed{\mathrm{CH_3N(CH_2CH_2OH)_2 + CO_2 + H_2O \rightleftharpoons [CH_3NH(CH_2CH_2OH)_2]^+ + HCO_3^-}}.$$

The products are **N-methyldiethanolammonium**, SMILES `C[NH+](CCO)CCO`, and **hydrogencarbonate (bicarbonate)**, SMILES `O=C([O-])O`.

The amine has no nitrogen-bound hydrogen initially, so the appropriate net absorption product is hydrogencarbonate rather than an ordinary amine carbamate.

7.5 — Structure of complex 5

Denote the neutral pincer ligand by L. Its name is **2,6-bis[(di-tert-butylphosphino)methyl]pyridine**, and its SMILES is:

`n1c(CP(C(C)(C)C)C(C)(C)C)cccc1CP(C(C)(C)C)C(C)(C)C`

It coordinates through both phosphorus atoms and the pyridine nitrogen, giving a meridional κ^3-P,N,P arrangement.

Starting complex **4** is **trichlorido(L)molybdenum(III)**, $[\mathrm{MoCl_3(L)}]$. A dative-bond SMILES representation is:

`[Cl-]->[Mo+3]12(<-[Cl-])(<-[Cl-])<-n3c(CP->1(C(C)(C)C)C(C)(C)C)cccc3CP->2(C(C)(C)C)C(C)(C)C`

The amount of **4** is

$$n(4) = \frac{1.00\ \text{g}}{597.824\ \text{g mol}^{-1}} = 1.672733 \times 10^{-3}\ \text{mol}.$$

For nitrogen,

$$n(\mathrm{N_2}) = \frac{PV}{RT} = \frac{(1.0 \times 10^5\ \text{Pa})(94.97 \times 10^{-6}\ \text{m}^3)}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(273.15\ \text{K})} = 4.181915 \times 10^{-3}\ \text{mol}.$$

Therefore,

$$\frac{n(\mathrm{N_2})}{n(4)} = 2.50005 \approx \frac{5}{2}.$$

The simplest product unit thus contains **two molybdenum atoms and five dinitrogen molecules**.

Three equivalents of sodium reduce each molybdenum(III) centre to molybdenum(0), removing the three chlorides as sodium chloride. The balanced preparation is

$$2\,[\mathrm{MoCl_3(L)}] + 6\,\mathrm{Na} + 5\,\mathrm{N_2} \longrightarrow [\mathrm{Mo_2(L)_2(N_2)_5}] + 6\,\mathrm{NaCl}.$$

Sodium chloride has formula-unit SMILES `[Na+].[Cl-]`; mercury serves as the amalgam medium.

The expected structure is **μ-dinitrogen-bis[bis(dinitrogen)(L)molybdenum(0)]**:

- Draw two molybdenum centres joined by a linear, end-on/end-on $\mathrm{Mo{-}N{\equiv}N{-}Mo}$ bridge.
- Attach one tridentate PNP ligand to each molybdenum.
- Attach two additional, terminal, end-on dinitrogen ligands to each molybdenum.
- Each molybdenum is approximately octahedral. The two terminal dinitrogen ligands are mutually trans; the bridging dinitrogen is trans to the pyridine nitrogen.

Each metal is then an 18-electron centre:

$$6 \quad (d^6\ \text{Mo(0)}) + 6 \quad (L) + 4 \quad (\text{two terminal dinitrogens}) + 2 \quad (\text{bridging dinitrogen}) = 18.$$

A dative-bond SMILES specifying this connectivity is:

`[Mo]12(<-N#N)(<-N#N)(<-N#N->[Mo]45(<-N#N)(<-N#N)<-n6c(CP->4(C(C)(C)C)C(C)(C)C)cccc6CP->5(C(C)(C)C)C(C)(C)C)<-n3c(CP->1(C(C)(C)C)C(C)(C)C)cccc3CP->2(C(C)(C)C)C(C)(C)C`

This SMILES specifies donor–metal connectivity; the octahedral and trans relationships are supplied by the drawing instructions above.

7.6 — Ranking the reductant/additive combinations

Comparing combinations 1 and 4 in the supplied experimental table shows that the stronger reductant, with the more negative potential, supports ammonia formation. Combination A has a much less negative potential, $-0.09\ \mathrm{V}$, so it is predicted to give the lowest yield.

B, C, and D have the same reductant potential and the same counterion. The comparison of experimental combinations 3 and 4 associates the higher additive pK_a, corresponding to the weaker acid, with the higher ammonia yield. Applying that trend gives

$$pK_a(\mathrm{B}) = 15.0 > pK_a(\mathrm{C}) = 13.7 > pK_a(\mathrm{D}) = 10.6.$$

The intended decreasing-yield ranking is therefore

$$\boxed{\mathrm{B} > \mathrm{C} > \mathrm{D} > \mathrm{A}}.$$

7.7 — Identification of the nitrides and compound 10

For a binary nitride $\mathrm{E}_a\mathrm{N}_b$, let the oxidation state of element E be $+z$. Since nitrogen is present as nitride,

$$az = 3b.$$

Its nitrogen mass fraction is

$$w(\mathrm{N}) = \frac{14.01b}{aM(E) + 14.01b}.$$

Using $a/b = 3/z$,

$$\frac{M(E)}{z} = \frac{14.01}{3}\left(\frac{1}{w(\mathrm{N})} - 1\right).$$

The three supplied percentages give the following identifications:

Compound	$M(E)/z$, $\mathrm{g\,mol^{-1}}$	Identification	Formula	Calculated nitrogen mass fraction
7	46.3125	$z = 3$, $M(E) \approx 138.94$: lanthanum	LaN	9.1623%
8	20.0390	$z = 2$, $M(E) \approx 40.078$: calcium	$\mathrm{Ca_3N_2}$	18.8992%
9	7.02254	$z = 4$, $M(E) \approx 28.090$: silicon	$\mathrm{Si_3N_4}$	39.9401%

Thus **7** is **lanthanum(III) nitride**, formula-unit SMILES `[La+3].[N-3]`; **8** is **calcium nitride**, formula-unit SMILES `[Ca+2].[Ca+2].[Ca+2].[N-3].[N-3]`; and **9** is **silicon nitride**. A formal charge-separated composition for the latter is `[Si+4].[Si+4].[Si+4].[N-3].[N-3].[N-3].[N-3]`. These disconnected strings express compositions, not crystal connectivity; silicon nitride is an extended covalent solid.

Their formation from the elements is represented by

$$\begin{aligned} 2\,\mathrm{La} + \mathrm{N_2} &\longrightarrow 2\,\mathrm{LaN}, \\ 3\,\mathrm{Ca} + \mathrm{N_2} &\longrightarrow \mathrm{Ca_3N_2}, \\ 3\,\mathrm{Si} + 2\,\mathrm{N_2} &\longrightarrow \mathrm{Si_3N_4}. \end{aligned}$$

To find the composition of **10**, convert the given mass ratio to a molar ratio:

$$\begin{aligned} M(\mathrm{LaN}) &= 152.91\ \mathrm{g\,mol^{-1}}, \\ M(\mathrm{Ca_3N_2}) &= 148.26\ \mathrm{g\,mol^{-1}}, \\ M(\mathrm{Si_3N_4}) = 140.31\ \mathrm{g\,mol^{-1}}, &\qquad M(\mathrm{SiO_2}) = 60.09\ \mathrm{g\,mol^{-1}}. \end{aligned}$$

Hence

$$n(\mathrm{LaN}) : n(\mathrm{Ca_3N_2}) : n(\mathrm{Si_3N_4}) : n(\mathrm{SiO_2}) = \frac{5.09}{152.91} : \frac{2.96}{148.26} : \frac{3.27}{140.31} : \frac{1.00}{60.09}.$$

Normalizing gives

$$2.00025 : 1.19969 : 1.40043 : 1 \approx 10 : 6 : 7 : 5.$$

These quantities contain

$$\mathrm{La_{10}Ca_{18}Si_{26}N_{50}O_{10}},$$

which reduces to the empirical formula

$$\boxed{\mathrm{Ca_9La_5Si_{13}N_{25}O_5}}.$$

The prescribed structural formula already contains $\mathrm{Si_{12}N_{24}}$. Subtracting this unit leaves one silicon, one nitrogen, and five oxygen atoms in addition to the metal cations.

The two identical monoatomic anions must therefore be oxide ions:

$$\boxed{\mathrm{S = O^{2-}}},$$

named **oxide**, SMILES `[O-2]`.

After assigning two oxygen atoms to these oxide ions, the tetrahedral anion has composition $\mathrm{SiNO_3}$. Its charge is

$$(+4) + (-3) + 3(-2) = -5,$$

so

$$\boxed{\mathrm{T} = [\mathrm{SiNO_3}]^{5-}}.$$

This is **nitridotrioxidosilicate(5–)**, SMILES `[N-2][Si]([O-])([O-])[O-]`. Draw silicon at the centre of a tetrahedron, bonded to one nitrogen and three oxygen atoms. The formal charges in this bonded SMILES sum to -5; nitrogen's oxidation state remains -3.

Thus **10**, a **calcium lanthanum oxonitridosilicate**, is

$$\boxed{\mathrm{Ca_9La_5O_2[SiNO_3][Si_{12}N_{24}]}}.$$

One assignment is $Q = \mathrm{Ca^{2+}}$, $\alpha = 9$, $R = \mathrm{La^{3+}}$, and $\beta = 5$. The cation SMILES are `[Ca+2]` and `[La+3]`, respectively.

The charge balance confirms the result:

$$9(2) + 5(3) = 33,$$
$$2(-2) + (-5) + \left[12(4) + 24(-3)\right] = -4 - 5 - 24 = -33.$$

The balanced synthesis is

$$\boxed{10\,\mathrm{LaN} + 6\,\mathrm{Ca_3N_2} + 7\,\mathrm{Si_3N_4} + 5\,\mathrm{SiO_2} \longrightarrow 2\,\mathrm{Ca_9La_5O_2[SiNO_3][Si_{12}N_{24}]}}.$$

The extended $[\mathrm{Si_{12}N_{24}}]^{24-}$ framework's connectivity is not supplied, so a unique structural SMILES for the complete crystalline compound **10** cannot be inferred from its formula.

The solution was checked against the official solution.

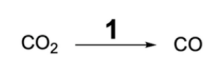
Problem 8: Recycling of Carbon Dioxide

T8. Recycling of Carbon Dioxide

7%

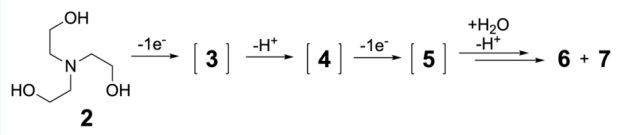
8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10	$\sum$
2	16	2	29	5	10	2	4	12	2	84

Removing $\mathrm{CO_2}$ gas from the atmosphere is key to combat climate change. One promising solution is the photocatalytic reduction of $\mathrm{CO_2}$ to CO using molecular catalyst **1**.



8.1 Write the half equation for the reduction of $\mathrm{CO_2}$ to CO in an acidic medium. **2.0 pt**

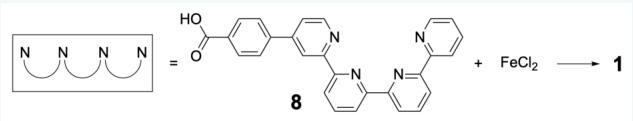
The conjugate oxidation reaction occurs with sacrificial reductant **2** in aqueous solution with the following mechanism:



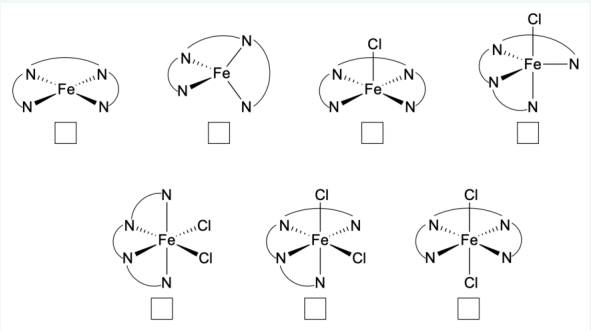
Species **3**, **4**, and **5** are short-lived ionic and/or radical intermediates. **7** yields a silver mirror with the $[\mathrm{Ag(NH_3)_2}]\mathrm{OH}$ test.

8.2 Draw the structures of **3**-**7**. **16.0 pt**

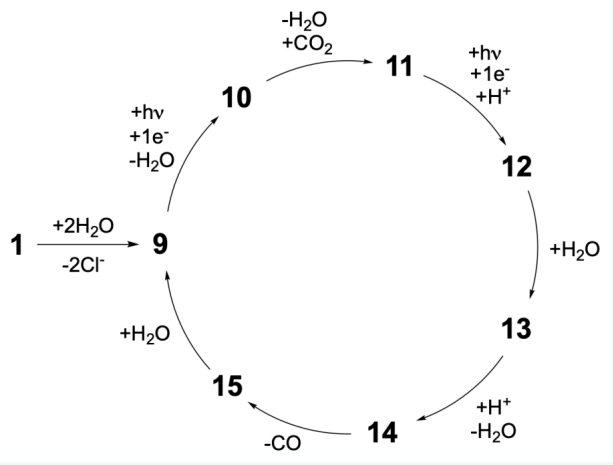
Catalyst **1** can be synthesised with the following reaction.



8.3 Tick the correct geometry for the structure of **1**. **2.0 pt**



When **1** is loaded on crystalline carbon nitride ($\mathrm{C_3N_4}$) support material, it can reduce $\mathrm{CO_2}$ via the following mechanism.



8.4 Draw the structures of **9-15**. Use the cartoon structure for ligand **8** shown above. For **9-15**, **specify** the oxidation state, OS, coordination number, CN, and number of valence electrons, VE, of Fe, along with the total charge of corresponding complex structures, Z. Note: Some information is provided on the answer sheet. **29.0 pt**

9 $Z =$ _____ $OS =$ _____ $CN =$ _____ $VE =$ _____	**10** $Z =$ _____ $OS =$ _____ $CN =$ _____ $VE =$ _____
11 $Z =$ _____ $OS = +3$ $CN = 6$ $VE =$ _____	**12** $Z =$ _____ $OS =$ _____ $CN = 5$ $VE =$ _____

13 $Z =$ _____ $OS = +2$ $CN =$ _____ $VE =$ _____	**14** $Z =$ _____ $OS =$ _____ $CN =$ _____ $VE =$ _____
15 $Z =$ _____ $OS =$ _____ $CN =$ _____ $VE = 16$	

8.5 Calculate the number of catalytic molecules per nm^2, N_{cat}, of $\mathrm{C_3N_4}$ loaded with **1**, when the mass fraction of catalyst, $\omega_{\mathrm{cat}} = 3.8\%$, if the specific surface area of $\mathrm{C_3N_4}$ is $17.8\ \mathrm{m^2\,g^{-1}}$. $M_{\mathrm{cat}} = 557.21\ \mathrm{g\,mol^{-1}}$. **5.0 pt**

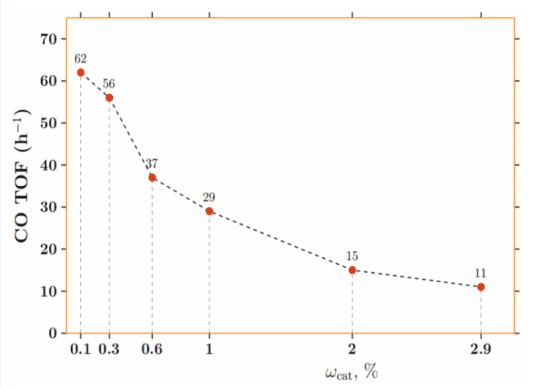
The Turnover Frequency of a catalyst (TOF) is the number of product molecules formed per active catalyst molecule per hour. Under LED illumination ($\lambda = 390\ \mathrm{nm}$) with power of $50\ \mathrm{mW}$, there was a TOF of $8\ \mathrm{h^{-1}}$ for $10\ \mathrm{mg}$ of $\mathrm{C_3N_4}$, loaded with **1** with $\omega_{\mathrm{cat}} = 3.8\%$

The formula for calculating the quantum yield is given below:

$$\varphi = \frac{\textit{number of reacted electrons}}{\textit{number of incident photons}} \cdot 100\%$$

8.6 Calculate the quantum yield, $\varphi(\%)$, for CO formation. **10.0 pt**

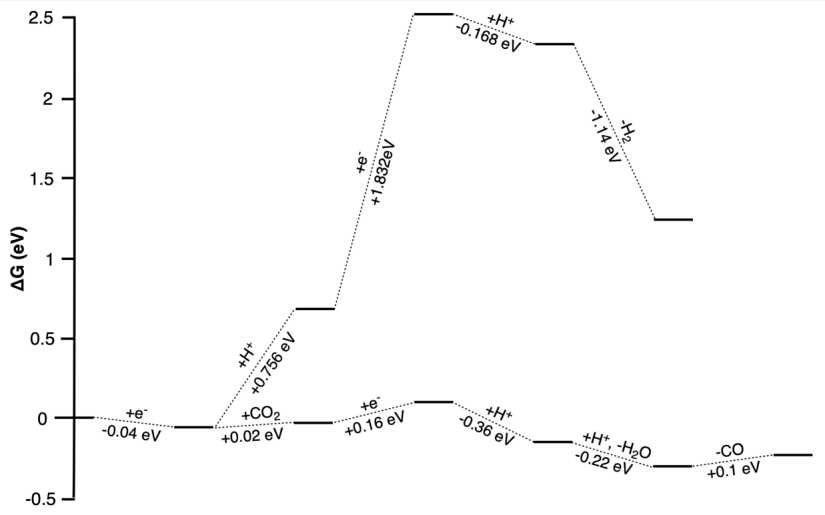
The diagram below shows the change in the TOF of CO as ω_{cat} is varied.



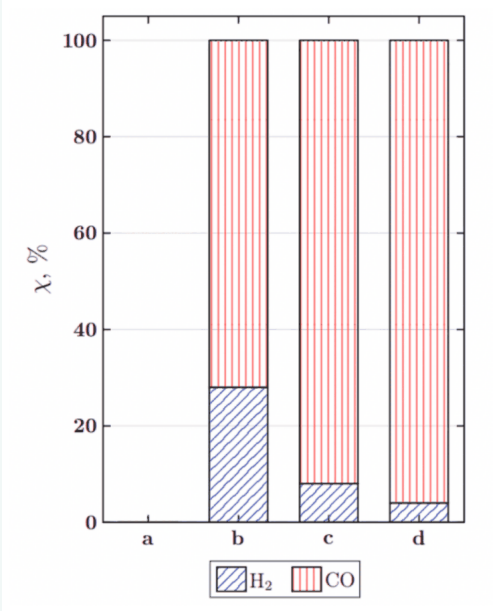
8.7 How does the overall rate of CO formation per gram of $\mathrm{C_3N_4}$ loaded with **1** change with increasing ω_{cat}, within the range $0.1 \leq \omega_{\mathrm{cat}} \leq 2.9$? **Tick** the correct box. **2.0 pt**

a) increases
b) decreases
c) doesn't change

The reduction of CO_2 can be accompanied by the reduction of additional protons. The changes in Gibbs energy during these two reactions are shown in the diagram.



The system was irradiated using different LEDs. The diagram below shows the mole percentages, χ, of H_2 and CO produced during the reduction of CO_2 under four different conditions: no irradiation (N) and irradiation with red (R), green (G), and blue (B) light.



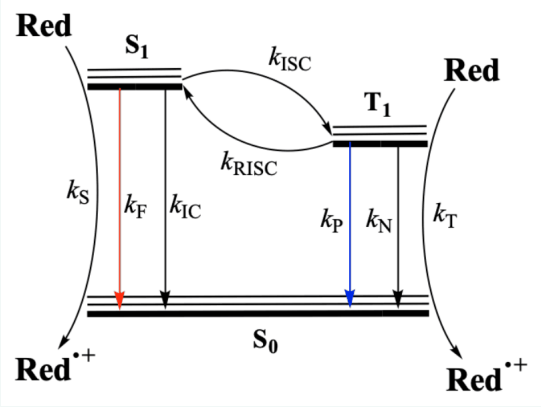
8.8 Tick which of the four conditions, mentioned above, corresponds to **a**, **b**, **c** and **d** in the diagram. **4.0 pt**

Photosensitisers (PS) offer some advantages over C_3N_4 for the reduction of CO_2. Mn(I)-containing complexes combined with PS can achieve ~23% quantum yield. In this system, reductive quenching of the *singlet* (S_1) and *triplet* (T_1) excited states of a PS by reductant (Red) forms $PS^{\bullet-}$, which donates electrons to CO_2 through the Mn(I)-containing complex.

$$PS_{(S_1)} + Red \xrightarrow{k_S} PS^{\bullet-} + Red^{\bullet+} \quad k_S = 2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$PS_{(T_1)} + Red \xrightarrow{k_T} PS^{\bullet-} + Red^{\bullet+} \quad k_T = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

The following Jablonski diagram describes the processes occurring in the PS:



$\tau_0(\mathbf{S}_1) = 2.9\ \mathrm{ns}$ and $\tau_0(\mathbf{T}_1) = 84\ \mu\mathrm{s}$, where τ_0 is the emission lifetime in the absence of the quencher.

8.9 Calculate the percentage of quenching, η_q, (in %) of $\mathbf{S}_1$ and $\mathbf{T}_1$ states, when $[\mathrm{Red}] = 0.1\ \mathrm{M}$. Note: here the values of k_{ISC} and k_{RISC} are negligible. **12.0 pt**

8.10 How do the emission lifetimes of $\mathbf{S}_1$ and $\mathbf{T}_1$ states change when $[\mathrm{Red}]$ increases?
Tick the correct box. **2.0 pt**

a) increases
b) decreases
c) doesn't change

Physical Constants and Equations

Constants

Constant	Value
Avogadro constant	$N_A = 6.022 \times 10^{23}\ \mathrm{mol}^{-1}$
Universal gas constant	$R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	$F = 96\,485\ \mathrm{C\,mol^{-1}}$
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	$e = 1.602 \times 10^{-19}\ \mathrm{C}$
Standard pressure	$P^\circ = 1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$
Ionic product of water at 25 °C	$K_w = 1.00 \times 10^{-14}$
Zero of the Celsius scale	$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
Electronvolt	$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$
Watt	$1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$
Coulomb	$1\ \mathrm{C} = 1\ \mathrm{A\,s}$
Nanometre	$1\ \mathrm{nm} = 1 \times 10^{-9}\ \mathrm{m}$
Ångstrom	$1\ \mathrm{Å} = 1 \times 10^{-10}\ \mathrm{m}$
metric ton	$1\ \mathrm{ton} = 1000\ \mathrm{kg}$
litre	$1\ \mathrm{L} = 1\ \mathrm{dm}^3$

Equations

Equation	Expression
Ideal gas law	$PV = nRT$
Dalton law	$P_i = x_i P$
Beer–Lambert law	$A = \log_{10} \frac{I_0}{I} = \varepsilon c l$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Heat and temperature change	$Q = nC_m\Delta T$
Gibbs energy definition	$G = H - TS$
Gibbs energy and equilibrium constant	$\Delta_r G^\circ = -RT\ln K$
Enthalpy change dependence on temperature (at $\Delta_r C_p = const$)	$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$
Entropy change dependence on temperature (at $\Delta_r C_p = const$)	$\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_a + \log_{10} \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$
Average reaction rate	$r = \frac{\Delta c}{\Delta t}$

Equation	Expression
The rate law	$r = k[A]^x[B]^y$
Arrhenius law	$k = A\exp\left(-\frac{E_a}{RT}\right)$
Integrated rate law for a 1st order reaction	$c = c_0 e^{-kt}$, $kt = \ln\frac{c_0}{c}$
Lifetime of a reagent in a 1st order reaction	$\tau = \frac{1}{k}$
Integrated rate law for n-th order reaction ($n \neq 1$)	$kt = \frac{1}{n-1}\left(c^{1-n} - c_0^{1-n}\right)$ for $n \neq 1$
Concentration of an intermediate in a consecutive reaction: $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{D}$	$[B] = \frac{k_1[A]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$
The ratio of products in the competitive reactions: $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$, $\mathrm{A} \xrightarrow{k_2} \mathrm{C}$	$\frac{[B]}{[C]} = \frac{k_1}{k_2}$
Michaelis–Menten equation	$r_0 = r_{\max}\frac{[S]_0}{K_M + [S]_0}$
Specific surface area	$s = \frac{S}{m}$
Progressions: arithmetic geometric	$a_n = a_1 + d(n-1)$, $a_n = a_1 q^{n-1}$
Sum of geometric progression	$\sum_{k=0}^{n} a_1 q^k = a_1\frac{q^{n+1} - 1}{q - 1}$
Volume of a sphere with radius r	$V = \frac{4}{3}\pi r^3$
Surface area of sphere with radius r	$S = 4\pi r^2$
Volume of a cone with base radius r and height h	$V = \frac{1}{3}\pi r^2 h$
Volume of a cylinder with base radius r and height h	$V = \pi r^2 h$

Consider all gases ideal.

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

Official English text of the problem.

Answers

- **8.1.**

$$\boxed{\mathrm{CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O}}$$

- **8.2.**

Species	Identification	SMILES
3	Triethanolamine radical cation; radical and positive charge on nitrogen	`[N+](CCO)(CCO)CCO`
4	Triethanolamine-derived α-amino carbon radical	`OCCN(CCO)[CH]CO`
5	N,N-Bis(2-hydroxyethyl)-2-hydroxyethaniminium ion	`[N+](CCO)(CCO)=CCO`
6	Diethanolamine	`OCCNCCO`
7	Glycolaldehyde, or 2-hydroxyethanal	`OCC=O`

- **8.3.** Tick the **bottom-right, seventh structure**: octahedral **trans-dichlorido(L)iron(II)**, with four nitrogen donors in the equatorial plane and two mutually trans chlorido ligands. Here L is ligand **8**.
- **8.4.** All four nitrogen atoms of neutral L remain coordinated. Full coordination SMILES and drawing descriptions are given in the Solution.

Species	Structure and binding mode	OS	CN	VE	Z
9	$[\mathrm{Fe(L)(H_2O)_2}]^{2+}$	$+2$	6	18	$+2$
10	$[\mathrm{Fe(L)(H_2O)}]^{+}$	$+1$	5	17	$+1$
11	$[\mathrm{Fe(L)(CO_2)}]^{+}$; C,O-bound $\mathrm{CO_2}^{2-}$, forming an Fe–C–O ring	$+3$	6	17	$+1$
12	$[\mathrm{Fe(L)(COOH)}]^{+}$; carbon-bound hydroxycarbonyl	$+2$	5	16	$+1$
13	$[\mathrm{Fe(L)(COOH)(H_2O)}]^{+}$; carbon-bound hydroxycarbonyl	$+2$	6	18	$+1$
14	$[\mathrm{Fe(L)(CO)(H_2O)}]^{2+}$; carbon-bound carbonyl	$+2$	6	18	$+2$
15	$[\mathrm{Fe(L)(H_2O)}]^{2+}$	$+2$	5	16	$+2$

- **8.5.** $\boxed{N_{\mathrm{cat}} \approx 2.40\ \mathrm{molecules\,nm^{-2}}}$, treating 3.8% as the mass fraction in the composite and $17.8\ \mathrm{m^2\,g^{-1}}$ as the area per gram of bare support. If the surface area is instead per gram of loaded material, the result is $2.31\ \mathrm{molecules\,nm^{-2}}$.
- **8.6.** $\boxed{\varphi \approx 1.93\%}$ for $10\ \mathrm{mg}$ of bare support. If $10\ \mathrm{mg}$ denotes the total loaded material, $\boxed{\varphi \approx 1.86\%}$. Both are approximately 1.9%.
- **8.7.** $\boxed{\text{a) increases}}$.

- **8.8.** $\boxed{\mathrm{a=N,\quad b=B,\quad c=G,\quad d=R}}$.
- **8.9.**

$$\boxed{\eta_q(\mathrm{S_1}) = 43.9\%, \qquad \eta_q(\mathrm{T_1}) = 99.92\%}$$

- **8.10.** $\boxed{\text{b) decreases}}$ for both states.

Solution

8.1 — Reduction half-equation

Carbon changes from oxidation state $+4$ in carbon dioxide to $+2$ in carbon monoxide, so two electrons are required. Balancing oxygen with water and hydrogen with protons gives

$$\boxed{\mathrm{CO_2 + 2\,H^+ + 2\,e^- \longrightarrow CO + H_2O}}.$$

Both atoms and charge are balanced.

The small molecular species used throughout the solution are carbon dioxide `O=C=O`, carbon monoxide `[C-]#[O+]`, water `O`, dihydrogen `[H][H]`, the proton `[H+]`, and chloride `[Cl-]`.

8.2 — Oxidation of the sacrificial reductant

Compound **2** is **triethanolamine**, `OCCN(CCO)CCO`. Write R for a 2-hydroxyethyl group, $-\mathrm{CH_2CH_2OH}$, so **2** is $\mathrm{R_3N}$.

The first oxidation removes one electron from the nitrogen lone pair:

$$\mathrm{R_3N \longrightarrow [R_3N]^{\bullet +} + e^-}.$$

Thus **3** is the nitrogen-centred radical cation given in the Answers.

Deprotonation occurs at a carbon directly attached to nitrogen. All three arms are equivalent, so choosing any one gives the same constitutional intermediate:

$$\mathrm{[R_3N]^{\bullet +} \longrightarrow R_2N{-}CH^{\bullet}{-}CH_2OH + H^+}.$$

This produces **4**, with the unpaired electron on the α-carbon. Loss of a second electron gives the iminium ion **5**:

$$\mathrm{R_2N{-}CH^{\bullet}{-}CH_2OH \longrightarrow [R_2N{=}CH{-}CH_2OH]^+ + e^-}.$$

Water attacks the electrophilic iminium carbon. Proton transfer and cleavage of its carbon–nitrogen bond give the secondary amine **6** and aldehyde **7**:

$$\mathrm{[R_2N{=}CH{-}CH_2OH]^+ + H_2O \longrightarrow R_2NH + HOCH_2CHO + H^+}.$$

Therefore **6** is diethanolamine and **7** is glycolaldehyde. The aldehyde group of **7** accounts for its positive silver-mirror test.

The overall oxidation half-equation is

$$\boxed{\mathrm{N(CH_2CH_2OH)_3 + H_2O \longrightarrow HN(CH_2CH_2OH)_2 + HOCH_2CHO + 2\,H^+ + 2\,e^-}}.$$

For the requested drawings, show the nitrogen radical cation in **3**, the α-carbon radical in **4**, and the positively charged nitrogen–carbon double bond in **5**. The SMILES in the Answers specify their connectivity and radical locations.

8.3 — Geometry of catalyst 1

Ligand **8**, denoted L, is **4-(4-carboxyphenyl)-2,2′:6′,2″:6″,2‴-quaterpyridine**. Its SMILES is

`O=C(O)c1ccc(-c2ccnc(-c3cccc(-c4cccc(-c5ccccn5)n4)n3)c2)cc1`

Its four pyridine nitrogen atoms provide four neutral donor sites. Together with two chlorido ligands, they give an iron coordination number of six. The quaterpyridine donor arrangement places the four nitrogen atoms around the equatorial plane, leaving the two axial sites for mutually trans chlorido ligands.

Therefore **1** is **trans-dichlorido(L)iron(II)**, and the correct choice is the **bottom-right structure**.

Coordination SMILES:

`[Cl-]->[Fe+2]6789<-[Cl-].O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

The coordination SMILES used here and below employ dative bonds, `->` and `<-`. Matching ring numbers connect the ligand to iron across the dot. These strings specify connectivity and formal charges; the coordination geometry is specified in words.

8.4 — Catalytic intermediates and electron counting

The pendant carboxylic acid group of L remains unchanged, so L is neutral and donates $4 \times 2 = 8$ electrons.

For iron, a group-8 metal,

$$d\text{-electron count} = 8 - OS.$$

Each coordinated water, carbonyl, nitrogen donor, or X-type donor contributes two electrons in the ionic counting method.

9 — Diaqua(L)iron(II) ion

Both chlorido ligands of **1** are replaced by water:

$$\mathrm{[Fe(L)Cl_2] + 2\,H_2O \longrightarrow [Fe(L)(H_2O)_2]^{2+} + 2\,Cl^-}.$$

Draw four nitrogen donors around iron and two water ligands in the positions previously occupied by chloride.

SMILES:

`[OH2]->[Fe+2]6789<-[OH2].O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

All ligands are neutral, so $Z = OS = +2$. The electron count is

$$VE = 6 + 8 + 2(2) = 18, \qquad CN = 6.$$

10 — Aqua(L)iron(I) ion

One-electron reduction of **9**, accompanied by loss of one water ligand, gives **10**:

$$[\mathrm{Fe(L)(H_2O)_2}]^{2+} + \mathrm{e^-} \longrightarrow [\mathrm{Fe(L)(H_2O)}]^{+} + \mathrm{H_2O}.$$

Draw the four nitrogen donors and one water ligand.

SMILES:

`[OH2]->[Fe+]6789.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

Thus

$$OS = +1, \quad Z = +1, \quad CN = 5, \quad VE = 7 + 8 + 2 = 17.$$

11 — C,O-bound carbonite complex of iron(III)

The remaining water is displaced by carbon dioxide. The answer-sheet information specifies $OS = +3$ and $CN = 6$. Because four coordination sites come from L, carbon dioxide must bind through two atoms.

Draw an **Fe–C–O three-membered ring**, with the carbon also double-bonded to the second oxygen. This is the C,O-bound, formally two-electron-reduced carbon dioxide ligand, $\mathrm{CO_2}^{2-}$, often called carbonite.

SMILES:

`[Fe+3]16789<-[O-][C-](=O)->1.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

Formation of this ligand formally transfers two electrons from iron(I) to carbon dioxide, giving iron(III). Consequently,

$$Z = (+3) + (-2) = +1,$$
$$CN = 4 + 2 = 6, \qquad VE = 5 + 8 + 4 = 17.$$

12 — Hydroxycarbonyl(L)iron(II) ion

Addition of one electron reduces iron(III) to iron(II). Protonation of the coordinated oxygen opens the Fe–C–O ring, leaving a carbon-bound hydroxycarbonyl ligand.

Draw the connectivity

$$\mathrm{Fe{-}C(=O){-}OH},$$

with all four nitrogen donors still attached and no water ligand.

SMILES:

`[Fe+2]6789<-[C-](=O)O.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

The hydroxycarbonyl ligand has formal charge -1, so

$$OS = +2, \quad Z = +1, \quad CN = 5, \quad VE = 6 + 8 + 2 = 16.$$

13 — Aqua(hydroxycarbonyl)(L)iron(II) ion

Water coordinates to **12**:

$$[\mathrm{Fe(L)(COOH)}]^{+} + \mathrm{H_2O} \longrightarrow [\mathrm{Fe(L)(COOH)(H_2O)}]^{+}.$$

Draw the same carbon-bound hydroxycarbonyl group, with one additional water ligand.

SMILES:

`[OH2]->[Fe+2]6789<-[C-](=O)O.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

Water coordination changes neither charge nor oxidation state:

$$OS = +2, \quad Z = +1, \quad CN = 6, \quad VE = 6 + 8 + 2 + 2 = 18.$$

14 — Aqua(carbonyl)(L)iron(II) ion

Protonation of the hydroxycarbonyl group permits loss of water, producing a carbonyl ligand:

$$[\mathrm{Fe(L)(COOH)(H_2O)}]^{+} + \mathrm{H^+} \longrightarrow [\mathrm{Fe(L)(CO)(H_2O)}]^{2+} + \mathrm{H_2O}.$$

Draw carbon monoxide attached through carbon, together with the retained water ligand.

SMILES:

`[OH2]->[Fe+2]6789<-[C-]#[O+].O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

Carbon monoxide is a neutral two-electron donor. Therefore

$$OS = +2, \quad Z = +2, \quad CN = 6, \quad VE = 6 + 8 + 2 + 2 = 18.$$

15 — Aqua(L)iron(II) ion

Carbon monoxide dissociates:

$$[\mathrm{Fe(L)(CO)(H_2O)}]^{2+} \longrightarrow [\mathrm{Fe(L)(H_2O)}]^{2+} + \mathrm{CO}.$$

Draw iron coordinated to the four nitrogen donors and one water ligand.

SMILES:

`[OH2]->[Fe+2]6789.O=C(O)c1ccc(-c2ccn->6c(-c3cccc(-c4cccc(-c5ccccn5->7)n4->8)n3->9)c2)cc1`

Hence

$$OS = +2, \quad Z = +2, \quad CN = 5, \quad VE = 6 + 8 + 2 = 16,$$

consistent with the supplied electron count. Addition of water regenerates **9**.

Summing the cycle gives the reduction half-equation in **8.1**.

8.5 — Surface density of catalyst molecules

Use the standard definition of mass fraction:

$$w = \omega_{\mathrm{cat}} = \frac{m_{\mathrm{cat}}}{m_{\mathrm{cat}} + m_{\mathrm{support}}} = 0.038.$$

Taking $1.000\ \mathrm{g}$ of loaded material gives

$$m_{\mathrm{cat}} = 0.038\ \mathrm{g}, \qquad m_{\mathrm{support}} = 0.962\ \mathrm{g}.$$

The number of catalyst molecules is

$$N = \frac{0.038\ \mathrm{g}}{557.21\ \mathrm{g\,mol^{-1}}}(6.022 \times 10^{23}\ \mathrm{mol^{-1}}) = 4.1068 \times 10^{19}.$$

If the stated specific surface area is per gram of bare $\mathrm{C_3N_4}$, its area is

$$S = (0.962\ \mathrm{g})(17.8\ \mathrm{m^2\,g^{-1}}) = 17.1236\ \mathrm{m^2} = 1.71236 \times 10^{19}\ \mathrm{nm^2}.$$

Thus

$$\boxed{N_{\mathrm{cat}} = \frac{wN_A}{(1-w)M_{\mathrm{cat}} s\, 10^{18}} = 2.398 \approx 2.4\ \text{molecules}\,\mathrm{nm^{-2}}}.$$

If $17.8\ \mathrm{m^2\,g^{-1}}$ is instead the area per gram of **loaded material**, the factor $1 - w$ is absent:

$$\boxed{N_{\mathrm{cat}} = \frac{wN_A}{M_{\mathrm{cat}} s\, 10^{18}} = 2.307 \approx 2.3\ \text{molecules}\,\mathrm{nm^{-2}}}.$$

8.6 — Quantum yield

Each molecule of carbon monoxide requires two electrons.

First interpret the stated $10\ \mathrm{mg}$ as the mass of the bare support. The catalyst mass is then

$$m_{\mathrm{cat}} = \frac{w}{1-w} m_{\mathrm{support}} = \frac{0.038}{0.962}(0.010\ \mathrm{g}) = 3.9501 \times 10^{-4}\ \mathrm{g}.$$

Consequently,

$$n_{\mathrm{cat}} = \frac{3.9501 \times 10^{-4}}{557.21} = 7.0891 \times 10^{-7}\ \mathrm{mol}.$$

In one hour,

$$n_{\mathrm{CO}} = (8\ \mathrm{h^{-1}})(7.0891 \times 10^{-7}\ \mathrm{mol})(1\ \mathrm{h}) = 5.6713 \times 10^{-6}\ \mathrm{mol}.$$

The number of reacted electrons is

$$N_e = 2n_{\mathrm{CO}} N_A = 6.8305 \times 10^{18}.$$

The energy of each incident photon is

$$E_\gamma = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \mathrm{J\,s})(2.998 \times 10^{8}\ \mathrm{m\,s^{-1}})}{390 \times 10^{-9}\ \mathrm{m}} = 5.0935 \times 10^{-19}\ \mathrm{J}.$$

The incident energy in one hour is

$$Pt = (0.050\ \mathrm{J\,s^{-1}})(3600\ \mathrm{s}) = 180\ \mathrm{J},$$

so

$$N_\gamma = \frac{180}{5.0935 \times 10^{-19}} = 3.5339 \times 10^{20}.$$

Therefore

$$\boxed{\varphi = \frac{6.8305 \times 10^{18}}{3.5339 \times 10^{20}} \times 100\% = 1.93\%}.$$

If $10\ \mathrm{mg}$ denotes the **total loaded material**, then

$$m_{\mathrm{cat}} = (0.038)(0.010\ \mathrm{g}) = 3.80 \times 10^{-4}\ \mathrm{g},$$

and the same calculation gives

$$\boxed{\varphi = 1.86\%}.$$

The result is approximately 1.9% under either interpretation.

8.7 — Overall rate versus catalyst loading

TOF is the rate per catalyst molecule. The amount of catalyst per gram of loaded material increases in proportion to its mass fraction, so

$$r_{\mathrm{CO}} = \frac{w}{M_{\mathrm{cat}}}\,\mathrm{TOF}.$$

It is therefore the product $w\,\mathrm{TOF}$, not TOF alone, that determines the overall rate.

Catalyst loading	TOF / $\mathrm{h^{-1}}$	$w\,\mathrm{TOF}$ / $\mathrm{h^{-1}}$
0.1%	62	0.062
0.3%	56	0.168
0.6%	37	0.222
1.0%	29	0.290
2.0%	15	0.300
2.9%	11	0.319

The product increases throughout the plotted range. Normalizing to bare support instead introduces the factor $1/(1-w)$, which also increases and does not change the conclusion.

$$\boxed{\text{a) increases}}$$

8.8 — Identification of irradiation conditions

The empty position **a** corresponds to no irradiation, **N**.

Photon energies follow

$$E_{\mathrm{blue}} > E_{\mathrm{green}} > E_{\mathrm{red}},$$

because $E = hc/\lambda$.

The hydrogen-evolution branch has substantially larger uphill free-energy changes, including a $+1.832\ \mathrm{eV}$ step. In the qualitative interpretation intended by the problem, higher-energy illumination permits a larger contribution from this competing pathway.

The hydrogen fractions decrease from **b** to **c** to **d**, approximately 28%, 8%, and 4%. Accordingly,

$$\boxed{\mathrm{a = N}, \qquad \mathrm{b = B}, \qquad \mathrm{c = G}, \qquad \mathrm{d = R}}.$$

8.9 — Quenching efficiencies

With intersystem crossing and reverse intersystem crossing neglected, each excited state has two competing types of decay:

- intrinsic decay, with total rate constant $k_0 = 1/\tau_0$;
- reductive quenching, with pseudo-first-order rate constant $k_q[\mathrm{Red}]$.

The probability that an excited molecule is quenched is therefore

$$\eta_q = \frac{k_q[\mathrm{Red}]}{k_0 + k_q[\mathrm{Red}]} \times 100\% = \frac{k_q[\mathrm{Red}]\tau_0}{1 + k_q[\mathrm{Red}]\tau_0} \times 100\%.$$

For the singlet state,

$$k_S[\mathrm{Red}]\tau_0(\mathrm{S_1}) = (2.7 \times 10^9\ \mathrm{M^{-1}s^{-1}})(0.1\ \mathrm{M})(2.9 \times 10^{-9}\ \mathrm{s}) = 0.783.$$

Thus

$$\boxed{\eta_q(\mathrm{S_1}) = \frac{0.783}{1 + 0.783} \times 100\% = 43.9\%}.$$

For the triplet state,

$$k_T[\mathrm{Red}]\tau_0(\mathrm{T_1}) = (1.5 \times 10^8\ \mathrm{M^{-1}s^{-1}})(0.1\ \mathrm{M})(84 \times 10^{-6}\ \mathrm{s}) = 1260.$$

Hence

$$\boxed{\eta_q(\mathrm{T_1}) = \frac{1260}{1261} \times 100\% = 99.92\%}.$$

Although the triplet quenching rate constant is smaller, its much longer unquenched lifetime makes quenching nearly quantitative.

8.10 — Dependence of emission lifetime on reductant concentration

The observed lifetime is

$$\boxed{\tau = \frac{1}{k_0 + k_q[\mathrm{Red}]} = \frac{\tau_0}{1 + k_q[\mathrm{Red}]\tau_0}}.$$

Increasing reductant concentration increases the total decay rate and therefore decreases the lifetime of both excited states.

At the concentration used in **8.9**, the lifetimes are

$$\tau(\mathrm{S_1}) = \frac{2.9\ \mathrm{ns}}{1.783} = 1.63\ \mathrm{ns},$$

$$\tau(\mathrm{T_1}) = \frac{84\ \mu\mathrm{s}}{1261} = 0.0666\ \mu\mathrm{s} = 66.6\ \mathrm{ns}.$$

Thus the correct choice is

$$\boxed{\text{b) decreases, for both states}}.$$

The solution was checked against the official solution.

Problem 9: Cyclodextrin Chemistry

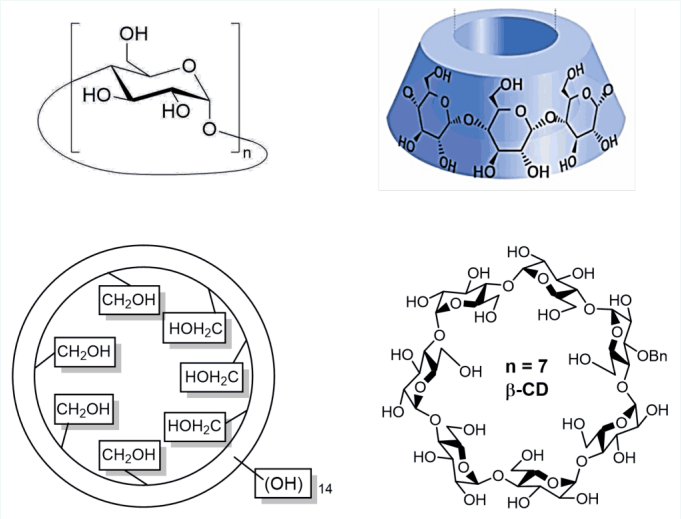
T9. Cyclodextrin Chemistry

7%

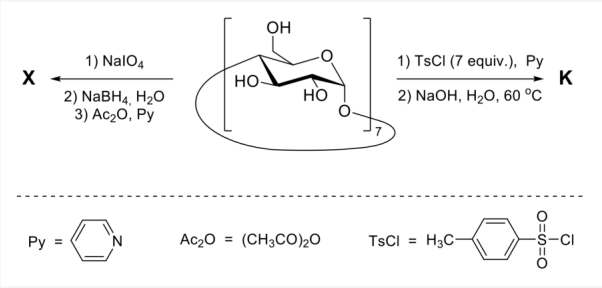
9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9	$\sum$
2	6	8	3	2	4	6	18	4	53

Cyclodextrins (CD) are a family of cyclic oligosaccharides, consisting of glucose subunits joined by α-1,4-glycosidic bonds. The three most common cyclodextrins (α-, β-, γ-cyclodextrin) contain 6, 7, and 8 α-D-glucopyranoside units, respectively.

9.1 Calculate the molar mass of β-CD. **Assume** $M_w(\text{glucose}) = 180.16\ \text{g mol}^{-1}$. **2.0 pt**

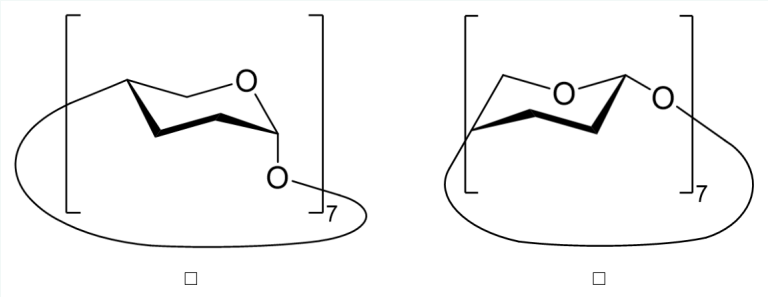


CDs combine macrocyclic properties with glucose chemistry, which was demonstrated in the synthesis of **X**. Primary and secondary hydroxy groups show different reactivity due to being a part of CDs. Stoddart *et al.* synthesised compound **K**, where only one OH group remained free per glucopyranoside unit.



equiv.= equivalent

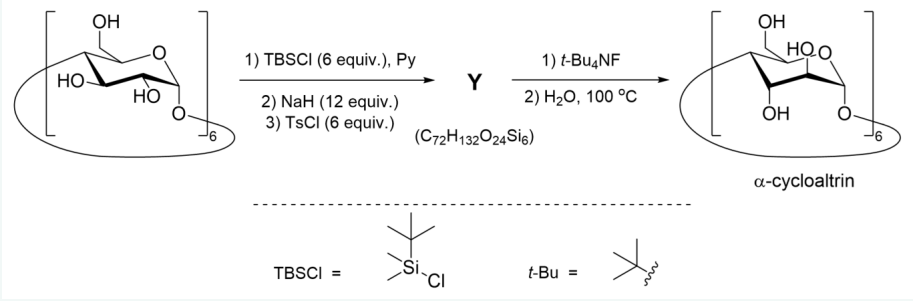
9.2 Tick the favorable chair conformation and **draw** the structure of **K** by completing the CD template. **Show** stereochemistry unambiguously. **6.0 pt**



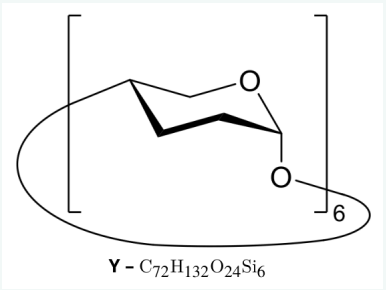
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9.3 Determine the ring size, rs, of macrocycle **X**. **Give** the number of stereocentres, sc, in **X**. **8.0 pt**

α-Cycloaltrin, a synthetic analogue of α-CD, was synthesised as follows.

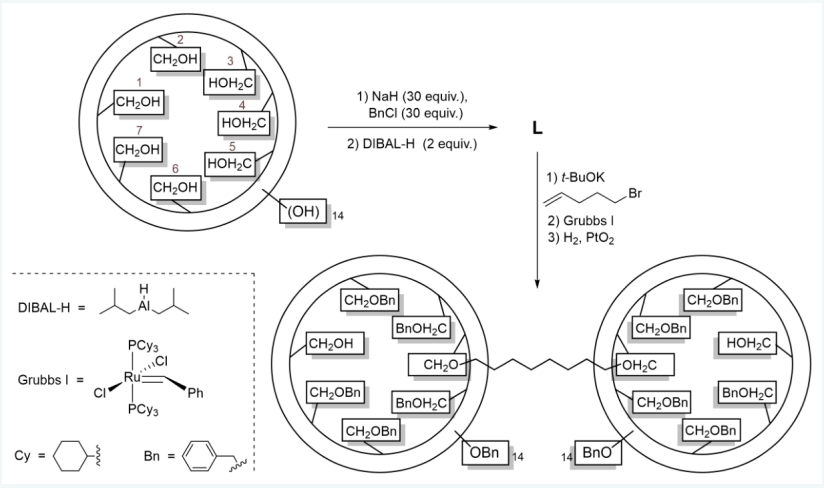


9.4 Draw the structure of **Y** with stereochemistry by completing the CD template. **3.0 pt**

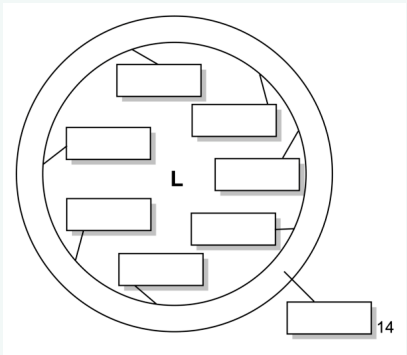


Y – $C_{72}H_{132}O_{24}Si_6$

In 2000, Sinay *et al.* demonstrated that a single protic group (NH and OH) at unit 1 directs the **next** reductive debenzylation of a primary OH group to unit 4 in the macrocyclic ring (or to unit 3 if the unit 4 position is not available). This allowed the synthesis of the following β-CD dimer as a mixture of constitutional linkage isomers.

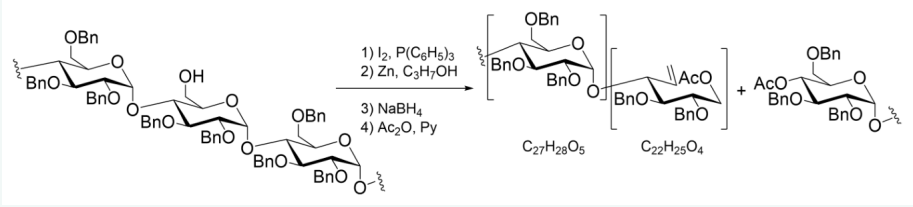


9.5 Draw the structure of **L** on the β-CD template. **Fill in** all the boxes. **2.0 pt**



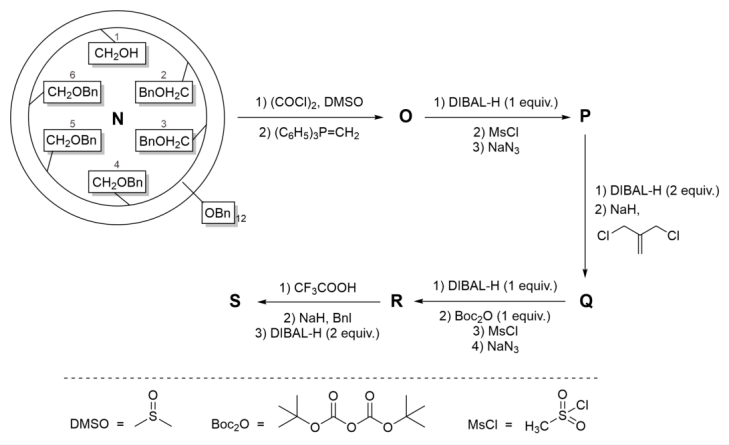
9.6 Determine the number of isomers of the β-CD dimer that can form during the synthesis by Sinay *et. al.* **4.0 pt**

To confirm the positions of debenzylation, **L** was subjected to the “hexo-5-enose degradation” reaction, as shown below. The products were then analysed by mass spectrometry.

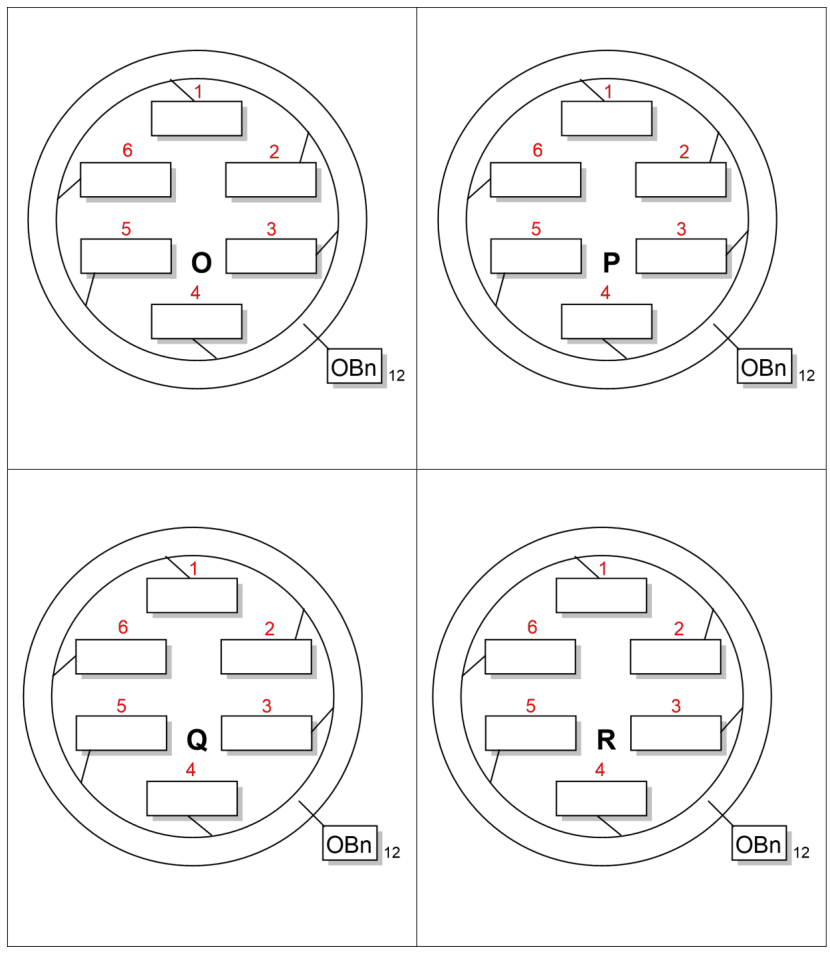


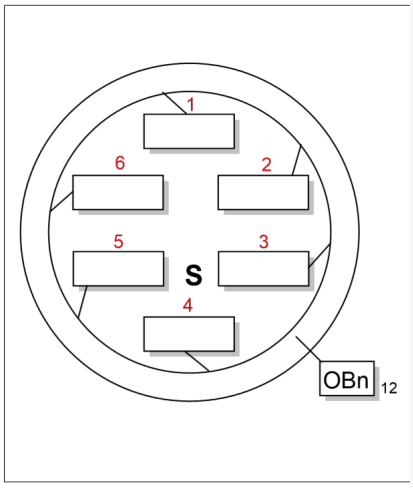
9.7 Calculate the m/z value for the two $[M^+Na]^+$ peaks that were observed for the degradation products from **L**. **Use** integer values of atomic mass. **6.0 pt**

Later, Sollogoub *et al.* applied the ability of alkenes to direct the debenzylation to the "*ortho*"-glucopyranose unit for the synthesis of hexadifferentiated α-CD **S**:



9.8 Draw the structures of **O–S** on the α-CD templates. **Fill in** all the boxes. You may draw structures outside the boxes if appropriate. **Assume** 1,2-unit modification happens **clockwise**, while 1,3-unit modification happens **counterclockwise**. Protic groups have stronger directing effects than alkenes. **18.0 pt**





9.9 Determine the number of all possible arrangements of the functional groups on a hexadifferentiated α-CD (**assume** only the $\mathrm{CH_2OH}$ groups have been modified). **4.0 pt**

Periodic Table of Elements

1																	18
1 H 1.008	2											13	14	15	16	17	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 24.30	3	4	5	6	7	8	9	10	11	12	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 72.63	33 As 74.92	34 Se 78.97	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 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	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 -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	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

- **9.1:** $\boxed{M(\beta\text{-CD}) = 1135.0\ \mathrm{g\,mol^{-1}}}$.
- **9.2:** Tick the **right-hand chair**, $^1C_4$. **K** is heptakis(3,6-anhydro)-β-cyclodextrin: every residue has a C3–O–C6 bridge and a free C2–OH.
- **9.3:** $\boxed{rs = 35, \quad sc = 21}$.
- **9.4: Y** is the per-6-O-TBS-protected, per-2,3-anhydro **manno** derivative of α-CD. Each epoxide oxygen lies on the same face as the C5–$\mathrm{CH_2OTBS}$ substituent.
- **9.5: L:** primary boxes 1 and 4 contain $\mathrm{CH_2OH}$; boxes 2, 3, 5, 6, and 7 contain $\mathrm{CH_2OBn}$; the external box contains OBn, repeated 14 times.
- **9.6:** $\boxed{3}$ constitutional linkage isomers.
- **9.7:** $\boxed{m/z = 1299 \text{ and } 1731}$.
- **9.8:** The complete substitution patterns are given below. All twelve secondary oxygen substituents remain OBn.
- **9.9:** $\boxed{120}$ arrangements.

For **9.8**, the numbers identify glucose **units**, clockwise as on the answer sheet. Each entry is the substituent attached to that unit's C5.

Compound	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6
O	$\mathrm{CH{=}CH_2}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$
P	$\mathrm{CH{=}CH_2}$	$\mathrm{CH_2N_3}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$
Q	$\mathrm{CH{=}CH_2}$	$\mathrm{CH_2NH}$, bridge end	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2O}$, bridge end	$\mathrm{CH_2OBn}$
R	$\mathrm{CH{=}CH_2}$	$\mathrm{CH_2N(Boc)}$, bridge end	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2O}$, bridge end	$\mathrm{CH_2N_3}$
S	$\mathrm{CH{=}CH_2}$	$\mathrm{CH_2N(Bn)}$, bridge end	$\mathrm{CH_2OH}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2O}$, bridge end	$\mathrm{CH_2NH_2}$

In **Q**, **R**, and **S**, join the indicated nitrogen at unit 2 to the oxygen at unit 5 through

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

Thus the complete bridge runs from unit 2 to unit 5 as

$$\mathrm{CH_2{-}N(R){-}CH_2{-}C(=CH_2){-}CH_2{-}O{-}CH_2},$$

where $R = \mathrm{H}$, Boc, and Bn in **Q**, **R**, and **S**, respectively.

Solution

The SMILES below specify complete molecular connectivity and stereochemistry. Chair conformations and the positions on the printed templates are specified separately in words.

The substituent abbreviations are benzyl, Bn, `*Cc1ccccc1`; acetyl, Ac, `*C(=O)C`; tert-butyldimethylsilyl, TBS, `*[Si](C)(C)C(C)(C)C`; and tert-butoxycarbonyl, Boc, `*C(=O)OC(C)(C)C`. Here `*` marks the attachment point of a substituent.

9.1

A cyclic assembly of seven glucose molecules contains **seven** glycosidic bonds. Consequently, formation of β-CD eliminates seven water molecules:

$$7\,\mathrm{C_6H_{12}O_6} \longrightarrow \mathrm{C_{42}H_{70}O_{35}} + 7\,\mathrm{H_2O}.$$

Using the supplied atomic masses,

$$M(\mathrm{H_2O}) = 2(1.008) + 16.00 = 18.016\ \mathrm{g\,mol^{-1}},$$

and therefore

$$\begin{aligned} M(\beta\text{-CD}) &= 7(180.16) - 7(18.016) \\ &= 1135.008\ \mathrm{g\,mol^{-1}} \\ &\approx \boxed{1135.0\ \mathrm{g\,mol^{-1}}}. \end{aligned}$$

Glucose in the α-D-glucopyranose form has SMILES `OC[C@H]1O[C@H](O)[C@H](O)[C@@H](O)[C@@H]1O`; water has SMILES `O`.

β-Cyclodextrin, $\mathrm{C_{42}H_{70}O_{35}}$, has SMILES:

```
OC[C@H]1O[C@@H]2O[C@@H]3[C@H](O)[C@@H](O)[C@@H](O[C@@H]4[C@H](O)[C@@H](O)[C@@H](O[C@@H]5[C@H](O)[C@@H](O)[C@@H](O[C@@H]6[C@H](O)[C@@H](O)[C@@H](O[C@@H]7[C@H](O)[C@@H](O)[C@@H](O[C@@H]8[C@H](O)[C@@H](O)[C@@H](O[C@@H]1[C@H](O)[C@H]2O)O[C@@H]8CO)O[C@@H]7CO)O[C@@H]6CO)O[C@@H]5CO)O[C@@H]4CO)O[C@@H]3CO
```

9.2

The seven equivalents of tosyl chloride preferentially activate the seven primary C6 hydroxyl groups. Under basic conditions, the C3 alkoxide of each glucose residue attacks its own C6 carbon by intramolecular $S_\mathrm{N}2$ displacement of tosylate. This produces a **3,6-anhydro ether bridge**.

The C2 hydroxyl group remains free. Substitution occurs at the non-stereogenic C6 carbon, so the existing configurations of the glucose stereocentres are retained.

The 3,6 bridge requires the inverted ${}^1C_4$ **chair**, which is the **right-hand template**. To complete it:

- Place the C5–C6 substituent above the ring.
- Connect C6 through oxygen to C3, also on the upper face.
- Draw the remaining C2–OH **axial down**.
- Retain the α-glycosidic connections already shown.

K, heptakis(3,6-anhydro)-β-cyclodextrin, has formula $\mathrm{C_{42}H_{56}O_{28}}$ and SMILES:

```
O[C@H]1[C@H]2O[C@@H]3[C@@H]4OC[C@H]3O[C@H](O[C@@H]3[C@@H]5OC[C@H]3O[C@H](O[C@@H]3[C@@H]6OC[C@H]3O[C@H](O[C@@H]3[C@@H]7OC[C@H]3O[C@H](O[C@@H]3[C@@H]8OC[C@H]3O[C@H](O[C@@H]3[C@@H]9OC[C@H]3O[C@H](O[C@@H]3[C@@H]1OC[C@H]3O2)[C@@H]9O)[C@@H]8O)[C@@H]7O)[C@@H]6O)[C@@H]5O)[C@@H]4O
```

9.3

Periodate cleaves the C2–C3 bond of every glucose residue because C2 and C3 bear a vicinal diol. The corresponding general atom balance is

$$\mathrm{R{-}CH(OH){-}CH(OH){-}R' + IO_4{}^- \longrightarrow R{-}CHO + R'{-}CHO + IO_3{}^- + H_2O}.$$

Borohydride reduces both aldehydes to primary alcohols. Acetic anhydride then acetylates the hydroxyl groups at the original C2, C3, and C6 positions.

After C2–C3 cleavage, the surviving macrocyclic path through each residue is

$$\mathrm{C1 - O5 - C5 - C4 - O4},$$

followed by C1 of the next residue along that path. There are five macrocyclic atoms per glucose-derived unit:

$$\boxed{rs = 7 \times 5 = 35}.$$

C2 and C3 become $\mathrm{CH_2OAc}$ groups and lose their stereochemistry. The configurations at C1, C4, and C5 remain:

$$\boxed{sc = 7 \times 3 = 21}.$$

X, the peracetylated, periodate-cleaved and reduced β-cyclodextrin derivative, has formula $\mathrm{C_{84}H_{126}O_{56}}$ and SMILES:

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

9.4

TBS chloride protects the six primary C6 hydroxyl groups. Sodium hydride deprotonates the twelve remaining secondary hydroxyl groups.

Tosylation at O2 followed by intramolecular attack of O3 at C2 produces a **2,3-epoxide**, with inversion at C2. Consequently, the epoxide has the **manno configuration**: its oxygen lies above the ring, on the same face as the C5–$\mathrm{CH_2OTBS}$ group.

To complete the template, draw:

- $\mathrm{CH_2OTBS}$ at C5, with the original D configuration;
- an oxygen bonded to **both C2 and C3 on the upper face**;
- no free hydroxyl groups.

The formula provides an independent check. Before epoxide formation, the six TBS-protected residues give $\mathrm{C_{72}H_{144}O_{30}Si_6}$. Formation of six epoxides corresponds to loss of six water equivalents from the carbohydrate framework:

$$\mathrm{C_{72}H_{144}O_{30}Si_6} \longrightarrow \mathrm{C_{72}H_{132}O_{24}Si_6} + 6\,\mathrm{H_2O}.$$

Subsequent fluoride treatment removes the TBS groups. Water opens the epoxide at C3 with inversion, giving the C2-up/C3-down hydroxyl arrangement of the drawn α-cycloaltrin.

Y, hexakis(2,3-anhydro-6-O-tert-butyldimethylsilyl)-α-cyclomannin, has SMILES:

```
CC(C)(C)[Si](C)(C)OC[C@H]1O[C@@H]2O[C@@H]3[C@@H]4O[C@@H]4[C@@H](O[C@@H]4[C@@H]5O[C@@H]5[C@@H]
(O[C@@H]5[C@@H]6O[C@@H]6[C@@H](O[C@@H]6[C@@H]7O[C@@H]7[C@@H](O[C@@H]7[C@@H]8O[C@@H]8[C@@H]
(O[C@@H]1[C@@H]1O[C@H]21)O[C@@H]7CO[Si](C)(C)C(C)(C)C)O[C@@H]6CO[Si](C)(C)C(C)(C)C)O[C@@H]5CO[Si](C)(C)C(C)
(C)C)O[C@@H]4CO[Si](C)(C)C(C)(C)C)O[C@@H]3CO[Si](C)(C)C(C)(C)C
```

9.5

The first reaction benzylates all 21 hydroxyl groups of β-CD.

The first reductive debenzylation can be designated as occurring at unit 1, since all units were initially equivalent. Its newly formed primary OH directs the second debenzylation to unit 4.

Thus **L** contains two primary hydroxyl groups and nineteen benzyl ethers:

Unit	1	2	3	4	5	6	7
Primary substituent	$\mathrm{CH_2OH}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OH}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$	$\mathrm{CH_2OBn}$

The external box is OBn, with the printed multiplier 14.

L, the 1,4-primary-diol derivative of per-O-benzyl-β-cyclodextrin, has formula $\mathrm{C_{175}H_{184}O_{35}}$ and SMILES:

```
OC[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4ccccc4)[C@@H](OCc4ccccc4)[C@@H](O[C@@H]4[C@H](OCc5ccccc5)[C@@H](OCc5ccccc5)[C@@H]
(O[C@@H]5[C@H](OCc6ccccc6)[C@@H](OCc6ccccc6)[C@@H](O[C@@H]6[C@H](OCc7ccccc7)[C@@H](OCc7ccccc7)[C@@H](O[C@@H]7[C@H]
(OCc8ccccc8)[C@@H](OCc8ccccc8)[C@@H](O[C@@H]8[C@H](OCc9ccccc9)[C@@H](OCc9ccccc9)[C@@H](O[C@@H]1[C@H](OCc1ccccc1)
[C@H]2OCc1ccccc1)O[C@@H]8COCc1ccccc1)O[C@@H]7COCc1ccccc1)O[C@@H]6CO)O[C@@H]5COCc1ccccc1)O[C@@H]4COCc1ccccc1)O[C@@H]3COC
```

9.6

The two free primary hydroxyl groups in **L** are constitutionally distinguishable on the directed cyclodextrin scaffold. Linking two molecules therefore permits the combinations

$$1-1', \qquad 1-4', \qquad 4-4'.$$

The combination $4-1'$ is identical to $1-4'$ after exchanging the two identical cyclodextrin components.

Any alkene E/Z distinction generated during metathesis disappears upon hydrogenation. Therefore,

$$\boxed{N_{\text{isomers}} = 3}.$$

9.7

Degradation at units 1 and 4 divides the seven-unit ring into fragments containing **three** and **four** original glucose units.

For a fragment containing n original units, the depicted product contains:

- $n-1$ intact protected residue blocks, each $\mathrm{C_{27}H_{28}O_5}$;
- one degraded terminal block, $\mathrm{C_{22}H_{25}O_4}$;
- one additional acetoxy end group, $\mathrm{C_2H_3O_2}$, at the other end.

Their integer masses are

$$\begin{aligned} M(\mathrm{C_{27}H_{28}O_5}) &= 27(12) + 28 + 5(16) = 432, \\ M(\mathrm{C_{22}H_{25}O_4}) &= 22(12) + 25 + 4(16) = 353, \\ M(\mathrm{C_2H_3O_2}) &= 2(12) + 3 + 2(16) = 59. \end{aligned}$$

Thus

$$M_n = 432(n-1) + 353 + 59.$$

For the three-unit fragment,

$$M_3 = 2(432) + 353 + 59 = 1276,$$

and for the four-unit fragment,

$$M_4 = 3(432) + 353 + 59 = 1708.$$

Adding one sodium ion of integer mass 23 and charge $+1$,

$$\boxed{\left(\frac{m}{z}\right)_3 = 1276 + 23 = 1299}, \qquad \boxed{\left(\frac{m}{z}\right)_4 = 1708 + 23 = 1731}.$$

The neutral fragments have formulas $\mathrm{C_{78}H_{84}O_{16}}$ and $\mathrm{C_{105}H_{112}O_{21}}$, respectively.

Sodium adduct of the three-unit degradation fragment, $[\mathrm{C_{78}H_{84}O_{16} + Na}]^+$, has SMILES:

```
C=C[C@H](O[C@H]1O[C@H](COCc2ccccc2)[C@H](O[C@H]2O[C@H](COCc3ccccc3)[C@H](OC(C)=O)[C@H](OCc3ccccc3)[C@H]2OCc2ccccc2)
[C@H](OCc2ccccc2)[C@H]1OCc1ccccc1)[C@H](OCc1ccccc1)[C@H](COC(C)=O)OCc1ccccc1.[Na+]
```

Sodium adduct of the four-unit degradation fragment, $[\mathrm{C_{105}H_{112}O_{21} + Na}]^+$, has SMILES:

```
C=C[C@H](O[C@H]1O[C@H](COCc2ccccc2)[C@H](O[C@H]2O[C@H](COCc3ccccc3)[C@H](O[C@H]3O[C@H](COCc4ccccc4)[C@H](OC(C)=O)[C@H]
(OCc4ccccc4)[C@H]3OCc3ccccc3)[C@H](OCc3ccccc3)[C@H]2OCc2ccccc2)[C@H](OCc2ccccc2)[C@H]1OCc1ccccc1)[C@H](OCc1ccccc1)[C@H]
(COC(C)=O)OCc1ccccc1.[Na+]
```

The disconnected sodium component in these SMILES specifies the adduct composition; the problem does not establish a particular sodium coordination geometry.

9.8

Throughout this sequence, the twelve secondary benzyl ethers remain intact.

Formation of O. Swern oxidation converts the free $\mathrm{CH_2OH}$ group at unit 1 into an aldehyde. Wittig methylenation then converts that side chain into $\mathrm{CH{=}CH_2}$. Units 2–6 retain $\mathrm{CH_2OBn}$.

O, the unit-1-vinyl α-cyclodextrin derivative, has SMILES:

```
C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4ccccc4)[C@@H](OCc4ccccc4)[C@@H](O[C@@H]4[C@H](OCc5ccccc5)[C@@H](OCc5ccccc5)[C@@H]
(O[C@@H]5[C@H](OCc6ccccc6)[C@@H](OCc6ccccc6)[C@@H](O[C@@H]6[C@H](OCc7ccccc7)[C@@H](OCc7ccccc7)[C@@H](O[C@@H]7[C@H]
(OCc8ccccc8)[C@@H](OCc8ccccc8)[C@@H](O[C@@H]1[C@H](OCc1ccccc1)
[C@H]2OCc1ccccc1)O[C@@H]7COCc1ccccc1)O[C@@H]6COCc1ccccc1)O[C@@H]5COCc1ccccc1)O[C@@H]4COCc1ccccc1)O[C@@H]3COCc1ccccc1
```

Formation of P. The alkene at unit 1 directs the first debenzylation to its clockwise neighbour, unit 2. Mesylation followed by azide displacement converts the resulting $\mathrm{CH_2OH}$ into $\mathrm{CH_2N_3}$.

P, the unit-2-azidomethyl derivative of **O**, has SMILES:

```
C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4ccccc4)[C@@H](OCc4ccccc4)[C@@H](O[C@@H]4[C@H](OCc5ccccc5)[C@@H](OCc5ccccc5)[C@@H]
(O[C@@H]5[C@H](OCc6ccccc6)[C@@H](OCc6ccccc6)[C@@H](O[C@@H]6[C@H](OCc7ccccc7)[C@@H](OCc7ccccc7)[C@@H](O[C@@H]7[C@H]
(OCc8ccccc8)[C@@H](OCc8ccccc8)[C@@H](O[C@@H]1[C@H](OCc1ccccc1)
[C@H]2OCc1ccccc1)O[C@@H]7COCc1ccccc1)O[C@@H]6COCc1ccccc1)O[C@@H]5COCc1ccccc1)O[C@@H]4COCc1ccccc1)O[C@@H]3CN=[N+]=[N-]
```

Formation of Q. DIBAL-H first reduces the azide at unit 2 to a primary amine. Its protic NH group then directs debenzylation to the opposite unit, **unit 5**.

The two available groups are consequently $\mathrm{CH_2NH_2}$ at unit 2 and $\mathrm{CH_2OH}$ at unit 5. Reaction with **1,3-dichloro-2-methylenepropane**, `C=C(CCl)CCl`, joins them through an N,O bridge:

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

One N–H bond remains, so the nitrogen can direct the next debenzylation.

Q, the unit-2/unit-5 N,O-bridged α-cyclodextrin derivative, has SMILES:

```
C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4ccccc4)[C@@H](OCc4ccccc4)[C@H]4O[C@@H]5[C@H](OCc6ccccc6)[C@@H](OCc6ccccc6)[C@@H]
(O[C@@H]6[C@H](OCc7ccccc7)[C@@H](OCc7ccccc7)[C@@H](O[C@@H]7[C@H](OCc8ccccc8)[C@@H](OCc8ccccc8)[C@@H](O[C@@H]8[C@H]
(OCc9ccccc9)[C@@H](OCc9ccccc9)[C@@H](O[C@@H]1[C@H](OCc1ccccc1)
[C@H]2OCc1ccccc1)O[C@@H]8COCc1ccccc1)O[C@@H]7COCC(=C)CNC[C@H]3O4)O[C@@H]6COCc1ccccc1)O[C@@H]5COCc1ccccc1
```

Formation of R. The secondary NH at unit 2 is the strongest directing group. Its usual 1,4 target, unit 5, is already incorporated into the bridge and has no benzyl ether to remove.

The fallback is therefore a 1,3 modification **counterclockwise** from unit 2:

$$2 \longrightarrow 1 \longrightarrow 6.$$

DIBAL-H unveils the primary OH at unit 6. Boc protection blocks the bridge nitrogen, while mesylation and azide displacement convert the newly exposed unit-6 side chain into $\mathrm{CH_2N_3}$.

R, the N-Boc-protected, unit-6-azidomethyl derivative of **Q**, has SMILES:

```
C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4ccccc4)[C@@H](OCc4ccccc4)[C@H]4O[C@@H]5[C@H](OCc6ccccc6)[C@@H](OCc6ccccc6)[C@@H]
(O[C@@H]6[C@H](OCc7ccccc7)[C@@H](OCc7ccccc7)[C@@H](O[C@@H]7[C@H](OCc8ccccc8)[C@@H](OCc8ccccc8)[C@@H](O[C@@H]8[C@H]
(OCc9ccccc9)[C@@H](OCc9ccccc9)[C@@H](O[C@@H]1[C@H](OCc1ccccc1)[C@H]2OCc1ccccc1)O[C@@H]8CN=[N+]=
[N-])O[C@@H]7COCC(=C)CN(C(=O)OC(C)(C)C)C[C@H]3O4)O[C@@H]6COCc1ccccc1)O[C@@H]5COCc1ccccc1
```

Formation of S. Trifluoroacetic acid removes Boc. Benzylation then converts the bridge nitrogen into a tertiary N-benzyl amine, eliminating its N–H directing group.

DIBAL-H reduces the azide at unit 6 to $\mathrm{CH_2NH_2}$. This newly formed protic group directs debenzylation to the opposite unit, **unit 3**, giving $\mathrm{CH_2OH}$ there. Unit 4 retains its primary benzyl ether.

The final six side chains are therefore all differentiated: vinyl, bridged N-benzylamino, hydroxymethyl, benzyloxymethyl, bridged oxymethyl, and aminomethyl, in that clockwise order.

S, the hexadifferentiated α-cyclodextrin derivative, has SMILES:

```
C=C[C@H]1O[C@@H]2O[C@@H]3[C@H](OCc4ccccc4)[C@@H](OCc4ccccc4)[C@H]4O[C@@H]5[C@H](OCc6ccccc6)[C@@H](OCc6ccccc6)[C@@H](O[C@@H]6[C@H](OCc7ccccc7)[C@@H](OCc7ccccc7)[C@@H](O[C@@H]7[C@H](OCc8ccccc8)[C@@H](OCc8ccccc8)[C@@H](O[C@@H]8[C@H](OCc9ccccc9)[C@@H](OCc9ccccc9)[C@@H](O[C@@H]1[C@H](OCc1ccccc1)[C@H]2OCc1ccccc1)O[C@@H]8CN)O[C@@H]7COCC(=C)CN(Cc1ccccc1)C[C@H]3O4)O[C@@H]6COCc1ccccc1)O[C@@H]5CO
```

9.9

Six different substituents can be assigned to six labelled sites in $6!$ ways. Rotating the whole α-CD ring does not produce a new arrangement, so each arrangement has been counted six times:

$$N = \frac{6!}{6} = 5! = \boxed{120}.$$

There is no further division by two. Reversing the cyclic order is not a symmetry operation of the directed, chiral α-D-glucopyranoside scaffold.

The solution was checked against the official solution.