

General Instructions

- This exam has **9 problems**.
- You may begin working when the **START** signal is given. You have **5 hours** to complete the exam.
- All results must be written **in the appropriate answer boxes** with pen **on the answer sheets**. Use the back of the question sheets if you need scrap paper. Remember that **answers written outside the answer boxes will not be graded**. If you run out of space raise your question card.
- **Write** relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- For the multiple choice questions, **if you want to change your answer, shade in** the tick box completely and then make **a new box next to it**.
- Use only the pen and calculator provided.
- The official English version of the exam is available upon request for clarification only.
- The supervisors will announce a **30-minute** warning before the **STOP** signal.
- You must stop your work immediately when the **STOP** signal is announced. Failure to stop writing can lead to nullification of your exam.
- After the supervisor tells you to do so, put **all sheets** back into the envelope. **Do not seal** the envelope.
- You are not allowed to leave your working place without permission. If you need any assistance, raise the corresponding non-verbal communication card.

		
I need a toilet break.	I have questions, or want the official English version for clarification.	I need to grab water, a snack, or take a break.

Meanings of the non-verbal communication cards.

GOOD LUCK!

Theory

Problems and Grading Information

	Title	Question Pages	Answer Pages	Total Points	Percentage
1	A Journey through Time: The Secrets of Avicenna	3	5	25	7
2	Kinetics of the Belousov-Zhabotinsky reaction	4	6	35	6
3	Into Reticular Chemistry	7	5	63	7
4	The Nuclear Past of Uzbekistan	3	4	24	6
5	Cardiolipins	3	4	18	6
6	Carbon Nanorings	5	6	83	7
7	Nitrogen Fixation	4	5	60	7
8	Recycling of Carbon Dioxide	5	7	84	7
9	Cyclodextrin Chemistry	4	5	53	7
				Total	60

Theory

Physical Constants and Equations

Constants

Avogadro constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 96\,485 \text{ C mol}^{-1}$
Planck constant	$h = 6.626 \times 10^{-34} \text{ J s}$
Speed of light in vacuum	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Mass of electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Charge of electron	$e = 1.602 \times 10^{-19} \text{ C}$
Standard pressure	$P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$
Ionic product of water at 25 °C	$K_w = 1.00 \times 10^{-14}$
Zero of the Celsius scale	$0^\circ\text{C} = 273.15 \text{ K}$
Electronvolt	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
Watt	$1 \text{ W} = 1 \text{ J s}^{-1}$
Coulomb	$1 \text{ C} = 1 \text{ A s}$
Nanometre	$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$
Ångstrom	$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$

Theory

Equations

Ideal gas law	$PV = nRT$
Dalton law	$P_i = x_i P$
Beer-Lambert law	$A = \log_{10} \frac{I_0}{I} = \epsilon c l$
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 $\Delta_r C_p = \text{const}$)	$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$
Entropy change dependence on temperature (at $\Delta_r C_p = \text{const}$)	$\Delta_r S_{T_2} = \Delta_r S_{T_1} + \Delta_r C_p \ln \frac{T_2}{T_1}$
Henderson-Hasselbalch equation	$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$
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 ($n \neq 1$)	$kt = \frac{1}{n-1} (c^{1-n} - c_0^{1-n})$ for $n \neq 1$
Concentration of an intermediate in a consecutive reaction: $A \xrightarrow{k_1} B \xrightarrow{k_2} D$	$[B] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$
The ratio of products in the competitive reactions: $A \xrightarrow{k_1} B, A \xrightarrow{k_2} C$	$\frac{[B]}{[C]} = \frac{k_1}{k_2}$
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 mol dm^{-3}

Periodic Table of Elements

[illegible]

T1. A journey through time: The secrets of Avicenna

7%						
1.1	1.2	1.3	1.4	1.5	1.6	Σ
3	4	3	4	7	4	25



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.

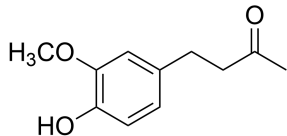
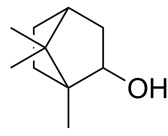
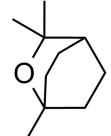
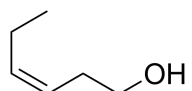
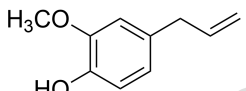
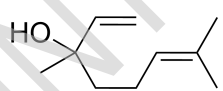
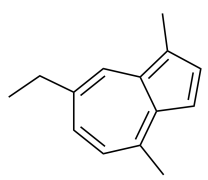
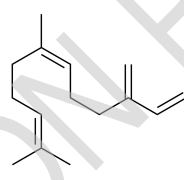
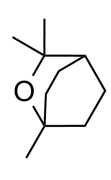
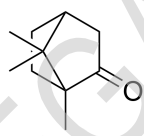
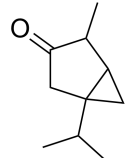
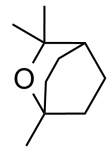
Part 1. The blue elixir

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.

Theory

Q1-2

English (Official)

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 ₆ H 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

SOLUTION:

X: 2 pt

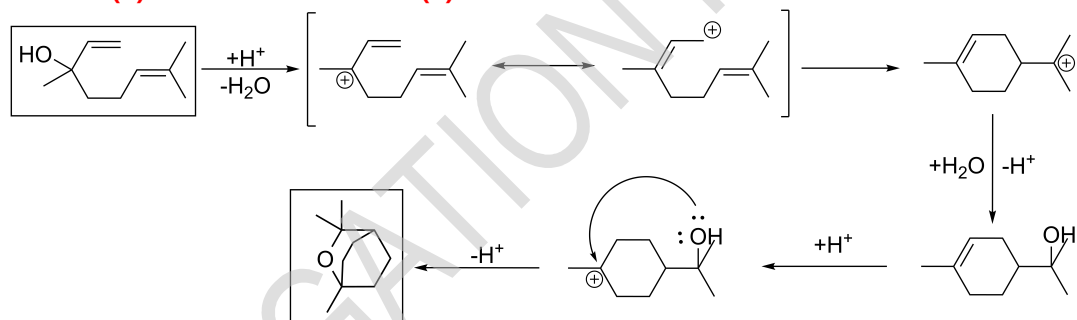
☐ 1	☐ 2	☐ 3	☐ 4	☐ 5
☒ 6	☐ 7	☐ 8	☐ 9	☐ 10

Y: 1pt

☐ 1	☐ 2	☒ 3	☐ 4	☐ 5
☐ 6	☐ 7	☐ 8	☐ 9	☐ 10

1 pt will be given if student switched X and Y.

Linalool (6) isomerises to cineole (3) in acidic solution as follows:



Theory

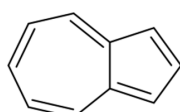
Chromatography also revealed it was substance **Z** that gave the elixir its blue colour. **Z** is a derivative of the well-known substance **A**, which has two perpendicular planes of symmetry. When heated, **A** isomerises into aromatic compound **B**, which has three mutually perpendicular planes 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

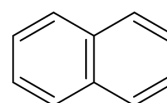
SOLUTION:

Chlorination of compound **Z** yields a monochlorinated product whose mass spectrum shows peaks at m/z 218 and 220 in a 3:1 ratio, characteristic of a molecule containing one chlorine atom (reflecting the natural abundance of ^{35}Cl and ^{37}Cl). Therefore, the molecular ion (M) of the ^{35}Cl monochlorinated product is 218, indicating that the non-chlorinated precursor **Z** has a molecular mass of 184 ($218 - 35 + 1 = 184$). Compound **A** is azulene, a hydrocarbon distinguished by its deep blue colour – an uncommon property among organic molecules. Compound **Z** ($M = 184 \text{ g mol}^{-1}$) is identified as chamazulene. Upon heating, azulene (**A**) isomerises into naphthalene (**B**), a thermodynamically more stable isomer.



azulene

A



naphthalene

B

Z: 1 pt

☐ 1	☐ 2	☐ 3	☐ 4	☐ 5
☐ 6	☒ 7	☐ 8	☐ 9	☐ 10

1 pt for **A**
2 pt for **B**

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 $[M]^+ : [M + 1]^+ = 9:1$, where M is the molecular ion. Assume carbon consists exclusively of ^{12}C and ^{13}C , the natural isotopic abundance of ^{12}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

SOLUTION:

Since **W** gives a colour upon reaction with Fe^{3+} , it contains a phenol group. Two possible candidates with phenol group are eugenol ($\text{C}_{10}\text{H}_{12}\text{O}_2$) and zingerone ($\text{C}_{11}\text{H}_{14}\text{O}_3$). From mass spec data:

$$\frac{0.989^n}{0.989^{n-1} \times 0.011n} = 9 \quad (1)$$

(n is the number of C atoms in **W**)

$$n = \frac{0.989}{0.011 \times 9} = 10$$

meaning that compound **W** has 10 carbon atoms. Thus, **W** is eugenol.

☐ 1	☐ 2	☐ 3	☐ 4	☒ 5
☐ 6	☐ 7	☐ 8	☐ 9	☐ 10

1 pt for Equation 1

(other logically true equations to find carbons atoms will be also considered as true)

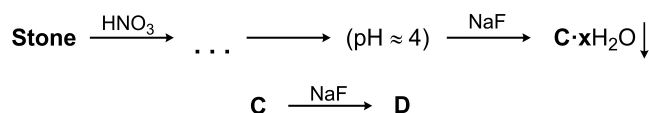
1 pt for carbon atoms (n)

W: 1 pt

If student struggled to find number of carbon atoms and choose one of the two options (zingerone or eugenol), 1 pt will be given

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 **C** $\cdot$ $x\text{H}_2\text{O}$, 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 **C** · xH₂O and **D**.

4.0 pt

SOLUTION:

When NaF is added to the solution, precipitate **C** forms, which dissolves in an excess of NaF. This behaviour suggests the formation of a fluoride complex. Since **D** is used in the production of a metal, and only a few metals are obtained from fluoride complexes, the most probable candidates is aluminum. Considering, the ratio of Na:**Q** in **D** is $a : 1$

$$M(\mathbf{Q}) = \frac{23a}{0.3285} \times 0.1285 = 9a \quad (2)$$

Option $a = 3$, where **Q** is aluminum, perfectly fits the conditions.

C · xH₂O is most probably hydrate of aluminum fluoride. To find number of water molecules(x), we can use mass fraction of water,

$$0.3916 = \frac{(1.008 \times 2 + 16) \times x}{(1.008 \times 2 + 16) \times x + 26.98 + 19 \times 3}, \quad x = 3$$

Thus, **C** · xH₂O is AlF₃ · 3H₂O.

$$M(\mathbf{D}) = \frac{27}{0.1285} = 210 \text{ g mol}^{-1}$$

Thus, **D** is Na₃AlF₆.

Q – Al

C · xH₂O – AlF₃ · 3H₂O

D – Na₃AlF₆

1 pt for Equation 2. 1 pt for each correct of **Q**, **C**, and **D**.

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 P₂O₅ 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

SOLUTION:

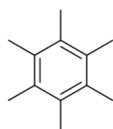
The highly symmetrical nature of the unknown compounds suggests that these are carboxylic derivatives of benzene, which form anhydrides when treated with phosphorus pentoxide. Thus, for **G**:

$$\text{C:O} = \frac{50.02}{12.01} : \frac{49.98}{16} = \frac{1.333}{1}$$

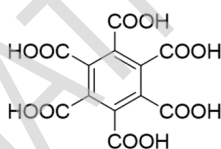
The corresponding minimum integer ratio is 4:3 (C_4O_3). Considering that **F** is a carboxylic acid and **G** is its anhydride, the presence of symmetry, and the aromatic nature of these compounds, one can propose that: **G** is C_{12}O_9 , mellitic acid anhydride. **F** is $\text{C}_6(\text{COOH})_6$, mellitic acid. Treatment of **E** with potassium permanganate leads to **F** (mellitic acid), indicating that **E** is a hexasubstituted benzene.

$$0.1118 = \frac{1.008x}{1.008x + 12.01y} \quad (3)$$

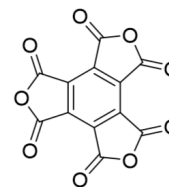
Solving this equation gives, $x:y=9:6$. Thus, the empirical formula of **E** is C_6H_9 . The number of H atoms must be even, so, $\text{C}_{12}\text{H}_{18}$ or $(\text{C}_6(\text{CH}_3))_6$ ideally fits the conditions. Thus, **E** is $(\text{C}_6(\text{CH}_3))_6$.



E



F



G

0.5 pt for finding C:O ratio in **G**

2 pt for structure of **G**

2 pt for structure of **F**

0.5 pt for Equation 3

0.5 pt for empirical formula of **E**

1.5 pt for structure of **E**

(full marks will be given if student did not show calculations but did find all structures correctly)

Then, she analysed the **stone** thermogravimetrically in open air. A 10.00 g sample began to lose mass at approximately 100 °C and stopped at 5.75 g at 200 °C. A second drop in mass was observed at 400 °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

SOLUTION:

Thermogravimetric data indicate that the mineral is a hydrate, as it starts to lose mass at about 100 °C. Thus, the molecular formula of the stone would be $\text{Al}_2(\text{C}_6(\text{COO})_6) \cdot n\text{H}_2\text{O}$. Thus,

$$\frac{4.25}{(1.008 \times 2 + 16)n} = \frac{5.75}{26.98 \times 2 + 12.01 \times 12 + 16 \times 12} \quad (4)$$

$$n = 16$$

The final decomposition product is most likely aluminum oxide. To confirm this:

$$\frac{1.50}{M} = \frac{5.75}{26.98 \times 2 + 12.01 \times 12 + 16 \times 12} \quad (5)$$

$M = 101.8 \text{ g mol}^{-1}$, which is very close to the molar mass of Al_2O_3 .

Thus, **H** - Al_2O_3

Stone: $\text{Al}_2(\text{C}_6(\text{COO})_6) \cdot 16\text{H}_2\text{O}$ (Honeystone)

1 pt for Equation 4

1 pt for Equation 5

1 pt for the formula of the **stone**

1 pt for the formula of the compound **H**

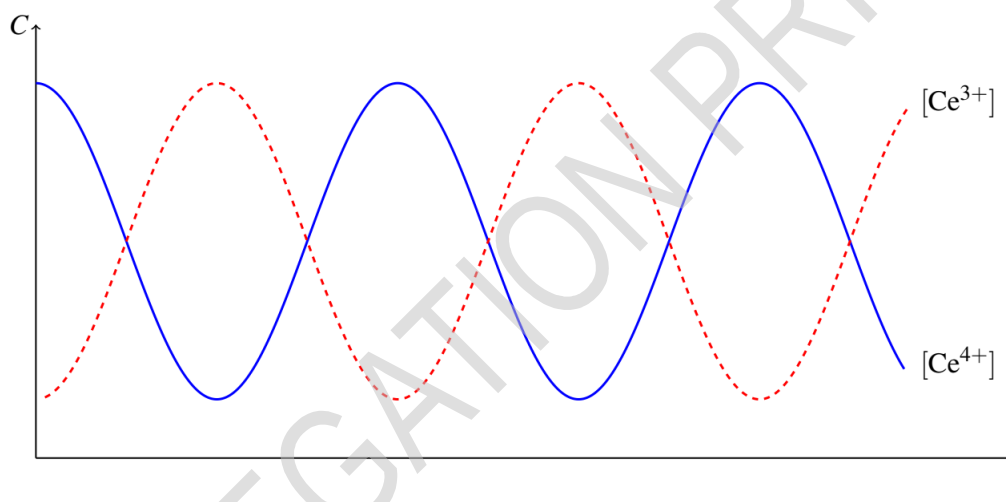
(full marks will be given if student found both formulae correctly without showing any equations).

If student has incorrect **Q** and/or incorrect **F** then credit can be given only if they propose an alternative answer that is **consistent with the data and chemically sensible**.

T2. Kinetics of the Belousov-Zhabotinsky reaction

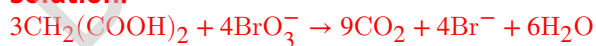
6%							
2.1	2.2	2.3	2.4	2.5	2.6	2.7	Σ
2	11	4	2	9	4	3	35

When the chemicals KBrO_3 , $\text{CH}_2(\text{COOH})_2$ (malonic acid, – MA), $\text{Ce}(\text{SO}_4)_2$, and H_2SO_4 are mixed, the concentration, C , of Ce species and the colour of the solution oscillates between yellow (due to Ce^{4+}) and colourless (due to Ce^{3+}). A schematic picture is given below:

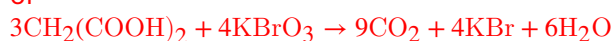


- 2.1** **Write** the overall balanced reaction equation of the Belousov-Zhabotinsky reaction (BZ reaction). Note: in this reaction, MA is oxidised to CO_2 , BrO_3^- is reduced to Br^- , and Ce(IV) is a catalyst. 2.0 pt

Solution:



or



For fully correct reaction equation: 2 points.

If only coefficient of H_2O is wrong: 1 point.

Theory

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

Process A $\left\{ \begin{array}{l} (1) \text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \xrightarrow{k_1} 2\text{BrO}_2^\cdot + \text{H}_2\text{O} \\ (2) \text{BrO}_2^\cdot + \text{Ce}^{3+} + \text{H}^+ \xrightarrow{k_2} \text{HBrO}_2 + \text{Ce}^{4+} \\ (3) 2\text{HBrO}_2 \xrightarrow{k_3} \text{BrO}_3^- + \text{HBrO} + \text{H}^+ \end{array} \right.$	$k_1 = 1.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ $k_2 = 6.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ $k_3 = 4.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
Process B $\left\{ \begin{array}{l} (4) \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \xrightarrow{k_4} 2\text{HBrO} \\ (5) \text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \xrightarrow{k_5} \text{HBrO} + \text{HBrO}_2 \\ (6) \text{HBrO} + \text{MA} \xrightarrow{k_6} \text{BMA} + \text{H}_2\text{O} \end{array} \right.$	$k_4 = 2.0 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ $k_5 = 2.1 \text{ M}^{-3} \text{ s}^{-1}$ $k_6 = 8.2 \text{ M}^{-1} \text{ s}^{-1}$
Process C $\left\{ \begin{array}{l} (7) \text{Ce}^{4+} + \text{BMA} \xrightarrow{k_7} \text{Ce}^{3+} + \text{Br}^- + \text{other products} \end{array} \right.$	$k_7 = 1.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$

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;
- $[\text{BrO}_3^-]_0 = 0.06 \text{ M}$, $[\text{MA}]_0 = 0.1 \text{ M}$, $[\text{H}^+]_0 = 0.8 \text{ M}$, $[\text{Ce}^{4+}]_0 = 0.001 \text{ M}$;
- the concentrations of the reactants (except Ce^{4+}) and pH are maintained constant throughout the BZ reaction.

- 2.2** Using the steady-state approximation, **calculate** the stationary molar concentrations of HBrO_2 in **Processes A** and **B**, $[\text{HBrO}_2]_{\text{A}}$ and $[\text{HBrO}_2]_{\text{B}}$. 11.0 pt

SOLUTION:

$$\frac{d[\text{BrO}_2^\cdot]}{dt} = 2k_1[\text{HBrO}_2][\text{BrO}_3^-][\text{H}^+] - k_2[\text{BrO}_2^\cdot][\text{Ce}^{3+}][\text{H}^+] = 0 \quad (\text{eq.2.1})$$

$$\frac{d[\text{HBrO}_2]}{dt} = -k_1[\text{HBrO}_2][\text{BrO}_3^-][\text{H}^+] + k_2[\text{BrO}_2^\cdot][\text{Ce}^{3+}][\text{H}^+] - 2k_3[\text{HBrO}_2]^2 = 0 \quad (\text{eq.2.2})$$

When adding equations 2.1 and 2.2 we get the following:

$$k_1[\text{HBrO}_2][\text{BrO}_3^-][\text{H}^+] - 2k_3[\text{HBrO}_2]^2 = 0 \quad (\text{eq.2.3})$$

$$[\text{HBrO}_2]_{\text{A}} = \frac{k_1}{2k_3}[\text{BrO}_3^-][\text{H}^+] \quad (\text{eq.2.4})$$

$$[\text{HBrO}_2]_{\text{A}} = \frac{1.0 \times 10^4}{2 \times 4.0 \times 10^7} \times 0.06 \times 0.8 = 6.0 \times 10^{-6} \text{ M}$$

The steady-state approximation for **Process B**:

$$\frac{d[\text{HBrO}_2]}{dt} = -k_4[\text{HBrO}_2][\text{Br}^-][\text{H}^+] + k_5[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 = 0 \quad (\text{eq.2.5})$$

$$[\text{HBrO}_2]_{\text{B}} = \frac{k_5}{k_4}[\text{BrO}_3^-][\text{H}^+] \quad (\text{eq.2.6})$$

$$[\text{HBrO}_2]_{\text{B}} = \frac{2.1}{2.0 \times 10^9} \times 0.06 \times 0.8 = 5.04 \times 10^{-11} \text{ M}$$

$$[\text{HBrO}_2]_{\text{A}} = 6.0 \times 10^{-6} \text{ M} \quad [\text{HBrO}_2]_{\text{B}} = 5.04 \times 10^{-11} \text{ M}$$

For fully correct equations 2.1, 2.2 and 2.5: 2 points each.

If only one incorrect coefficient in front of the rate constant in equations 2.1, 2.2 and 2.5: 1 point each.

For corresponding equations 2.3, 2.4 and 2.6: 1 point each.

For calculated $[\text{HBrO}_2]_{\text{A}}$ and $[\text{HBrO}_2]_{\text{B}}$ values: 1 point each.

For correct calculation without formula derivation: full marks.

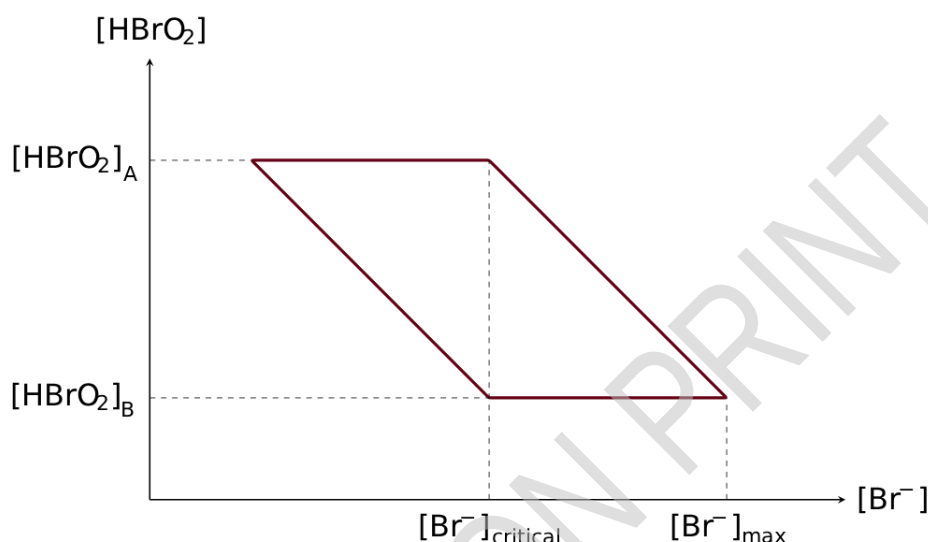
If you could not calculate $[\text{HBrO}_2]_{\text{A}}$ and $[\text{HBrO}_2]_{\text{B}}$, you can use the values $[\text{HBrO}_2]_{\text{A}} = 1 \times 10^{-5} \text{ M}$ and $[\text{HBrO}_2]_{\text{B}} = 1 \times 10^{-10} \text{ M}$ for the following calculations.

Theory

Q2-4

English (Official)

During the BZ reaction, the concentrations of HBrO_2 and Br^- oscillate strictly in relation to each other, and this is sketched in the phase portrait of $[\text{HBrO}_2]$ vs $[\text{Br}^-]$:



Here $[\text{Br}^-]_{\text{max}}$ is the maximum concentration and $[\text{Br}^-]_{\text{critical}}$ is the critical concentration of 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 Calculate $[\text{Br}^-]_{\text{critical}}$.

4.0 pt

SOLUTION:

During the switching process the following equality is observed:

$$k_1[\text{HBrO}_2][\text{BrO}_3^-][\text{H}^+] = k_4[\text{HBrO}_2][\text{Br}^-][\text{H}^+] \quad (\text{eq.3.1})$$

$$[\text{Br}^-]_{\text{critical}} = \frac{k_1}{k_4}[\text{BrO}_3^-] \quad (\text{eq.3.2})$$

$$[\text{Br}^-]_{\text{critical}} = \frac{1.0 \times 10^4}{2.0 \times 10^9} \cdot 0.06 = 3.0 \times 10^{-7} \text{ M}$$

$$[\text{Br}^-]_{\text{critical}} = 3.0 \times 10^{-7} \text{ M}$$

For fully correct equation 3.1: 1 point.

For fully correct equation 3.2: 2 points.

For calculated $[\text{Br}^-]_{\text{critical}}$ value: 1 point.

For correct calculation without formula derivation: full marks.

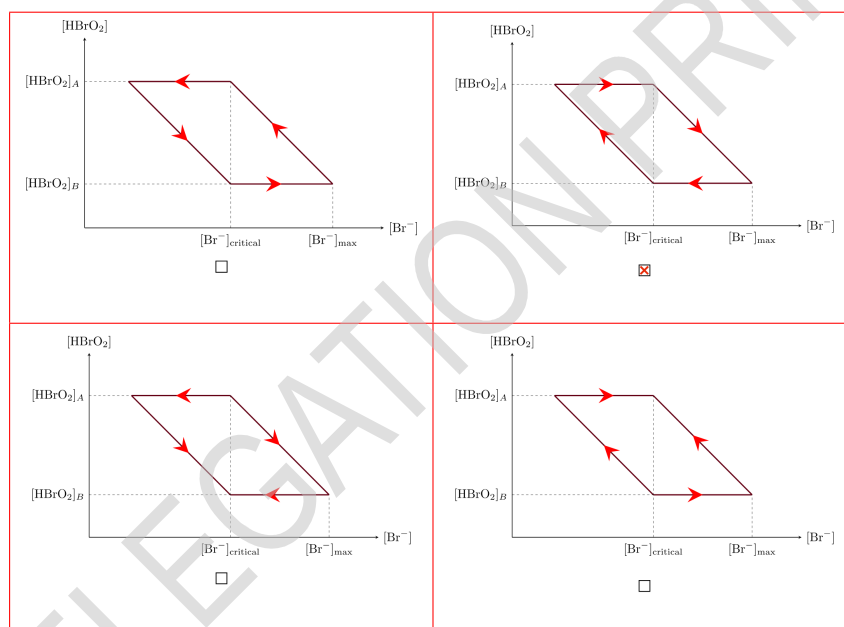
If you could not calculate $[\text{Br}^-]_{\text{critical}}$, use $[\text{Br}^-]_{\text{critical}} = 1 \times 10^{-7} \text{ M}$ for the following calculations.

- 2.4 In **which direction** in the phase portrait of $[\text{HBrO}_2]$ vs $[\text{Br}^-]$ will the concentrations of $[\text{HBrO}_2]$ and $[\text{Br}^-]$ change over time? **Tick** the correct box. 2.0 pt

SOLUTION:

As the process should be cyclic and not converge in equilibrium points, options **c** and **d** do not fit this criterion.

If $r_1 > r_4$ (relatively low concentration of bromide) **Process B** switches to **Process A**, otherwise if $r_1 < r_4$ (relatively high concentration of bromide) **Process A** switches to **Process B**. During **process A** concentration of bromide increases (due to conjugate **process C**), while during **process B** it decreases. So the right option should account for the change in concentrations in such a way that fits this scenario. Therefore, the correct answer is a clockwise phase portrait.



Only for correct answer: 2 points.

The system does not traverse the phase portrait of $[\text{HBrO}_2]$ vs $[\text{Br}^-]$ at a constant velocity, that is the concentration of $[\text{Br}^-]$ slowly decreases from $[\text{Br}^-]_{\text{max}} = 7.0 \times 10^{-4} \text{ M}$ to $[\text{Br}^-]_{\text{critical}}$, and then almost immediately reaches $[\text{Br}^-]_{\text{max}}$ again.

- 2.5** **Calculate** based on the data the period of oscillations, τ , of the BZ reaction, in seconds. 9.0 pt

SOLUTION:

From the conditions of the problem, it can be understood that the period of oscillations, τ (s), is equal to the time it takes for the concentration of bromide to decrease from the maximum to the critical value. The decrease in bromide concentration occurs during **Process B**.

Let's write a kinetic equation for the change of $[\text{Br}^-]$ considering

$[\text{Ce}^{4+}] \approx 0 \rightarrow k_7 [\text{Ce}^{4+}] [\text{BMA}] \approx 0$ (eq.5.1) during **Process B**:

$$-\frac{d[\text{Br}^-]}{dt} = k_4[\text{HBrO}_2][\text{Br}^-][\text{H}^+] + k_5[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 \quad (\text{eq.5.2})$$

$$-\frac{d[\text{Br}^-]}{dt} = \left(k_4[\text{HBrO}_2]_B[\text{H}^+] + k_5[\text{BrO}_3^-][\text{H}^+]^2 \right) [\text{Br}^-] = k^*[\text{Br}^-]$$

where

$$k^* = k_4[\text{HBrO}_2]_B[\text{H}^+] + k_5[\text{BrO}_3^-][\text{H}^+]^2 \quad (\text{eq.5.3})$$

Thus, we obtain a first order kinetic equation. For this equation:

$$k^* = 2.0 \times 10^9 \times 5.04 \times 10^{-11} \times 0.8 + 2.1 \times 0.06 \times 0.8^2 = 0.16128 \text{ s}^{-1}$$

$$[\text{Br}^-]_{\text{critical}} = [\text{Br}^-]_{\text{max}} \cdot e^{-k^* \tau}$$

$$\tau = \frac{\ln([\text{Br}^-]_{\text{max}}/[\text{Br}^-]_{\text{critical}})}{k^*} \quad (\text{eq.5.4})$$

$$\tau = \frac{\ln(7.0 \times 10^{-4} / (3.0 \times 10^{-7}))}{0.16128 \text{ s}^{-1}} = 48 \text{ s}$$

For values $[\text{HBrO}_2]_B = 1.0 \times 10^{-10} \text{ M}$ and $[\text{Br}^-]_{\text{critical}} = 1.0 \times 10^{-7} \text{ M}$:

$$k^* = 2.0 \times 10^9 \times 1.0 \times 10^{-10} \times 0.8 + 2.1 \times 0.06 \times 0.8^2 = 0.24064 \text{ s}^{-1}$$

$$\tau = \frac{\ln\left(\frac{[\text{Br}^-]_{\text{max}}}{[\text{Br}^-]_{\text{critical}}}\right)}{k^*} = \frac{\ln(7.0 \times 10^{-4} / (1.0 \times 10^{-7}))}{0.24064 \text{ s}^{-1}} = 37 \text{ s}$$

For correct equations 5.1, 5.2 and 5.3: 2 points each.

For correct equation 5.4: 1 point.

For calculated k^* value: 1 point.

For calculated τ value: 1 point.

For correct calculation without formula derivation: full marks.

- 2.6** 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. 4.0 pt

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

SOLUTION:

	[a]	[b]	[c]	[d]	[e]
1.			×		
2.				×	
3.		×			
4.					×

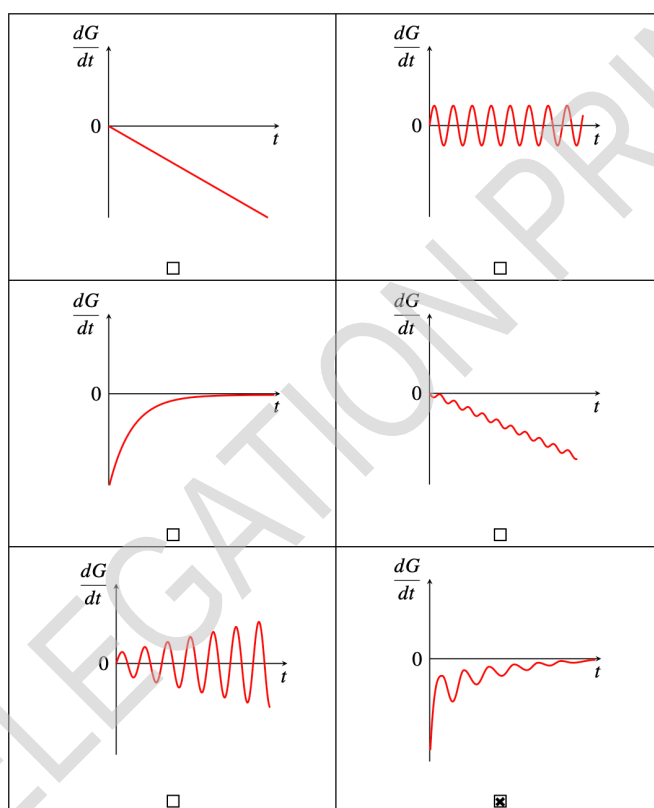
1. "Adding of small amount of Ce^{4+} during **Process A**" will lead to the formation of Br^- in **Process C**, there will be $r_1 < r_4$ and "[c] **Process A** switches to **Process B**".
2. "Adding of small amount of Ag^+ during **Process B**" will lead to precipitation of AgBr , there will be $r_1 > r_4$ and "[d] **Process B** switches to **Process A**".
3. "Adding of small amount of Br^- during **Process B**" will lead to increase in $[\text{Br}^-]_{\text{max}}$ value, accordingly, the time required to reduce $[\text{Br}^-]_{\text{max}}$ to $[\text{Br}^-]_{\text{critical}}$ will be extended, so it will "[b] prolongs **Process B**".
4. "Continuously adding of Br^- " will lead to the concentration of Br^- always being above the $[\text{Br}^-]_{\text{critical}}$ value and **Process B** never switching to **Process A**, so it will "[e] stop oscillations".

For correct answers: 1 point each.

- 2.7 Which graph qualitatively illustrates the rate of change of Gibbs energy ($\frac{dG}{dt}$) of a **closed** system in which an oscillatory reaction occurs? **Tick** the correct box. 3.0 pt

SOLUTION:

In the oscillatory reaction, the Gibbs energy exhibits oscillatory behavior over time, rather than decreasing monotonically as in most typical chemical reactions. In closed systems, the oscillations dampen over time $\rightarrow$ the system eventually reaches equilibrium ($\frac{dG}{dt} = 0$). dG must be less than 0 every time. So, correct answer is last one:



For correct answer: 3 points.

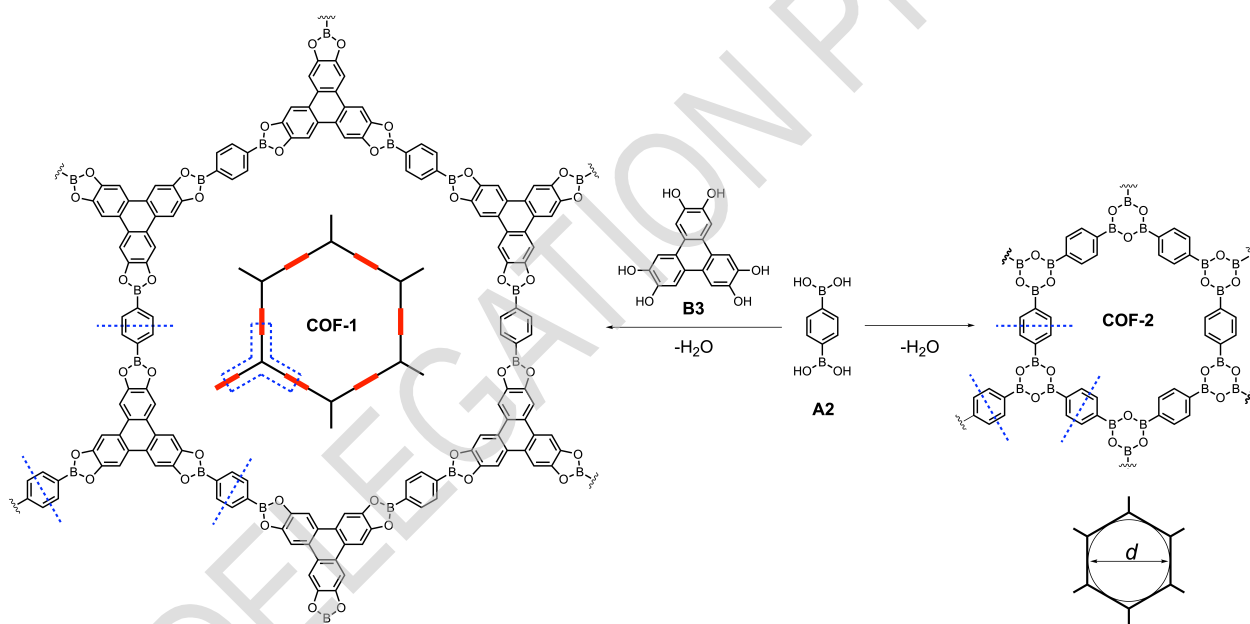
For ticking middle left box which describes $\frac{dG}{dt}$ of a non-oscillatory reaction in a closed system: 1 point.

T3. Into Reticular Chemistry

7%							
3.1	3.2	3.3	3.4	3.5	3.6	3.7	Σ
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

SOLUTION:

The empirical formula of **COF-1** is $C_9H_4BO_2$, its elemental composition is

$$C - \frac{12.01 \cdot 9}{12.01 \cdot 9 + 4 \cdot 1.008 + 10.81 + 32} \cdot 100\% = 69.77\%;$$

C: 69.77%

Empirical formula: $C_9H_4BO_2$

1 pt for empirical formula.

No penalty for $[C_9H_4BO_2]_n$

1 pt for C mass fraction.

no penalty if integer values are used for atomic masses

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

- C-C/C=C (arenes) = 1.39 Å
- C-B = 1.56 Å
- 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.

SOLUTION:

For **COF-2**,

$$a = 2 \cdot B-O + 2 \cdot C-C + 2 \cdot C-B = 8.66$$

$$d = \sqrt{3}a = 15.0$$

$$d = 2r = 15.0$$

$$d = 15.0 \text{ Å}$$

3 pt for correct d

2 pt if only a is given

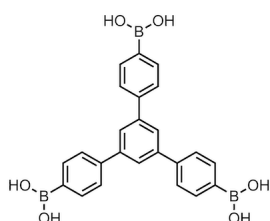
1 pt if only correct formula is given

Theory

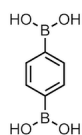
Q3-3

English (Official)

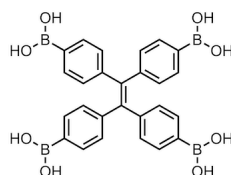
The structures shown below can form 2D and 3D COFs. For this question consider only formation of COFs with boronate esters, imines, and C=C bonds through condensation reactions. **A–D** represent compound classes with different functional groups.



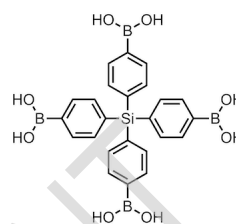
A1



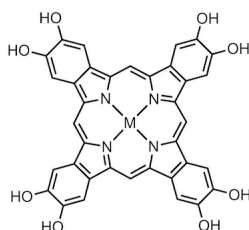
A2



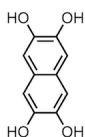
A3



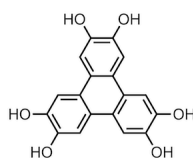
A4



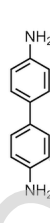
B1



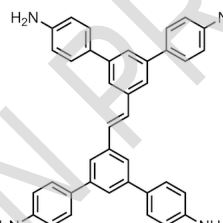
B2



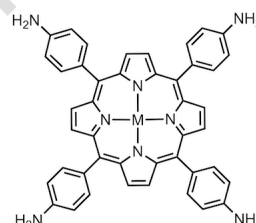
B3



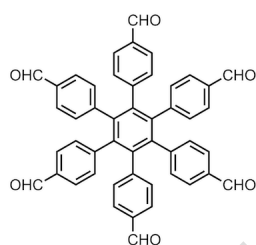
C1



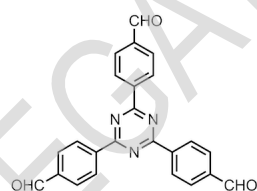
C2



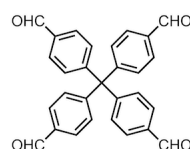
C3



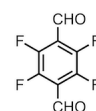
D1



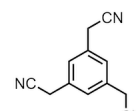
D2



D3



D4



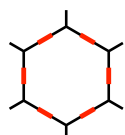
E1



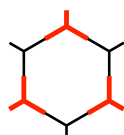
Tetragonal 1



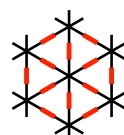
Tetragonal 2



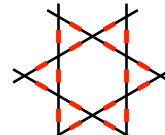
Hexagonal 1



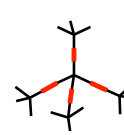
Hexagonal 2



Trigonal



Kagome



Tetrahedral

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	Tetra- hedral
		A2 + B3	E1 + D2		C2 + D4	

SOLUTION:

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetra- hedral
		A2+B3	E1+D2		C2+D4	
C3+D4	XXX	A1+B2	A1+B3	C1+D1	A3+B2	C1+D3
A2+B1	XXX	C1+D2	XXX	XXX	XXX	A4+B2

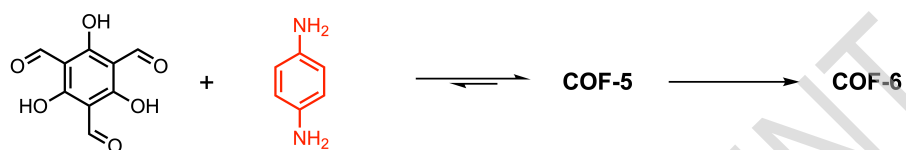
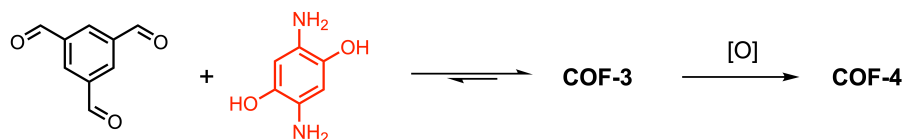
E1 + D4 in *Hexagonal 1* is considered correct
 2 pt for correct combination in correct topology
 1 pt for XXX in correct topology
 -1 pt for incorrect placing of X or combination
 0 pt for acetal from the correct combination only
 0 pt for blank box

Whilst imine-based COFs are easily synthesised, they are also vulnerable to hydrolysis under 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 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.

Theory

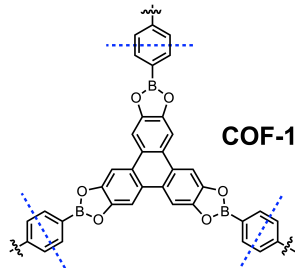
Q3-5

English (Official)

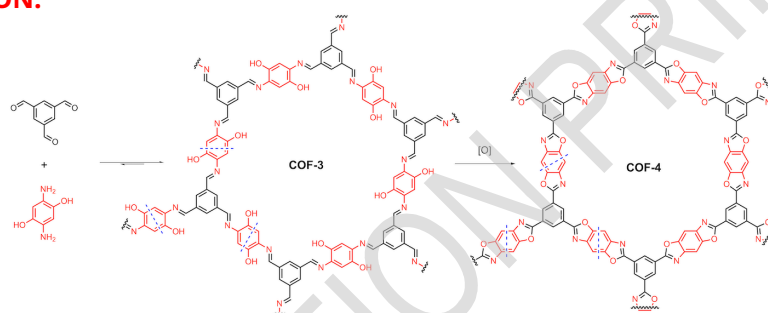


DELEGATION PRINT

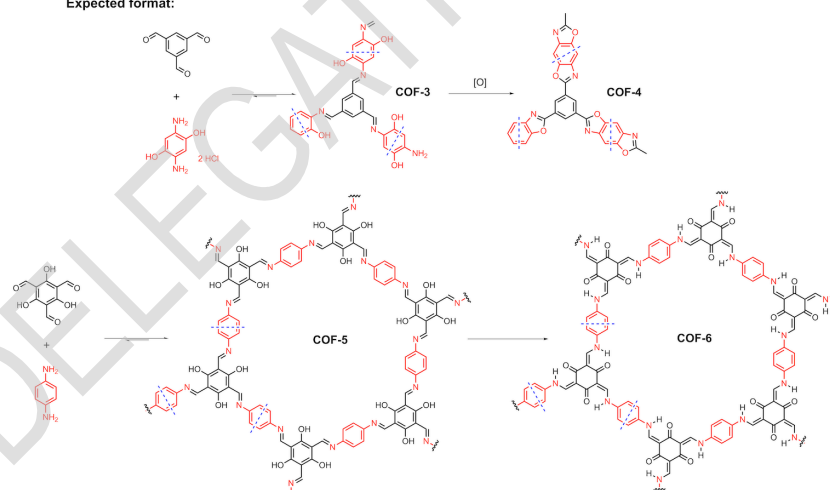
- 3.4 **Draw** the repeat units for **COFs 3-6**. **Indicate** the edges of each repeat unit with a dashed line as shown for **COF-1** below. 12.0 pt



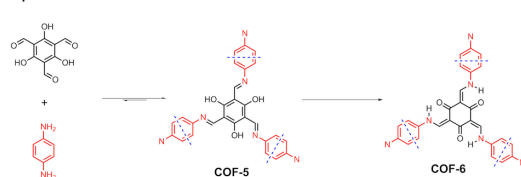
SOLUTION:



Expected format:



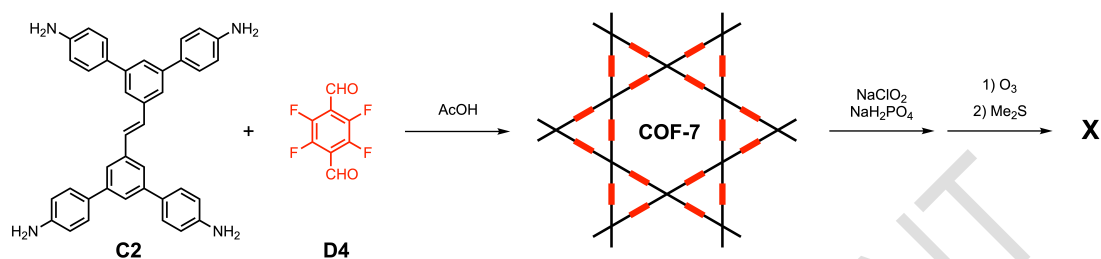
Expected format:



2 pt for each of **COF-3** and **COF-5**. 1 pt for correct structure with wrong defined repeat unit.
4 pt for each of **COF-4** and **COF-6**. 2 pt for correct structure with wrong defined repeat unit.

Theory

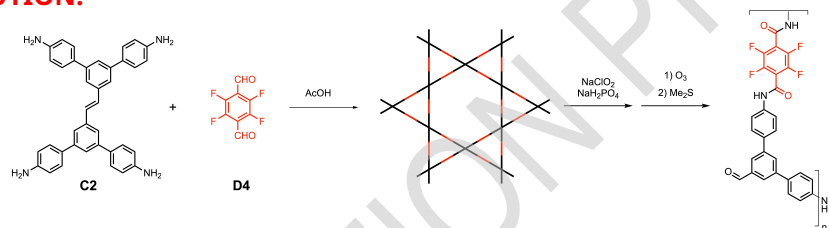
Macrocycle **X** was synthesised by post-synthetic modification of **COF-7** (**C2** + **D4**) followed by degradation.



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

6.0 pt

SOLUTION:



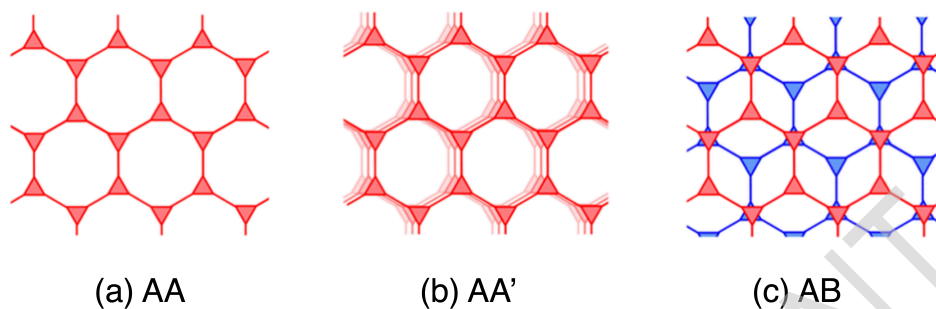
6 pt for repeat unit **X**.

-2 pt for imine product.

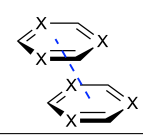
-2 pt if aldehyde is not shown.

-2 pt if fluorines are missing.

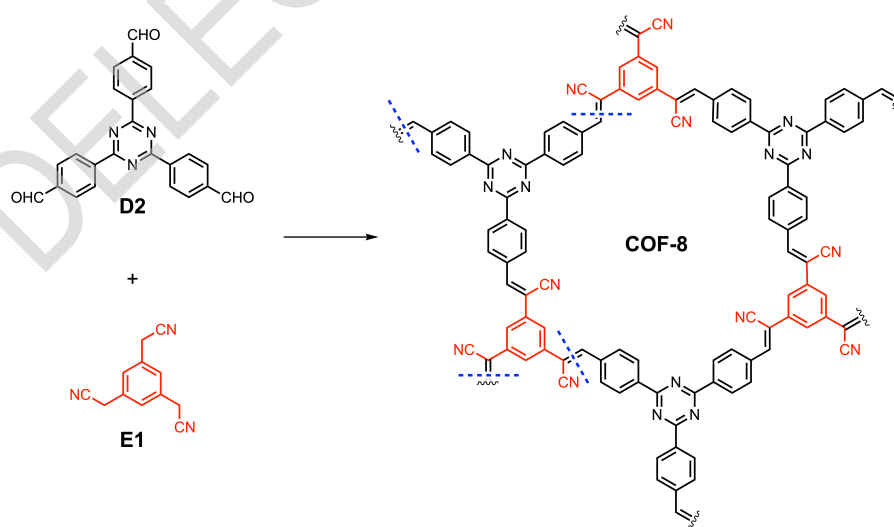
π - π interactions result in different stacking modes of COF layers, some of which are shown below.



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

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

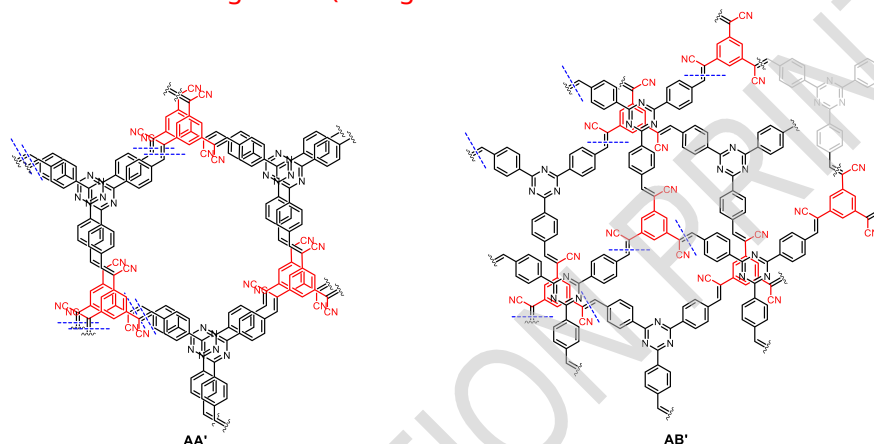
COF-8, synthesised from (**E1** + **D2**), is notable for its remarkable stability. The **AA'** slightly shifted mode of a **COF-8** bilayer has a π - π stacking interaction energy of $-67.1 \text{ kJ mol}^{-1}$ between two layers of one repeat unit.



- 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**

SOLUTION:

COF-8 represents hexagonal 2 topology. Each repeat unit contain 4 benzene and 1 triazine rings. For **AA** and **AA'** stacking modes there will be 4 b-b and 1 t-t interactions. For **AB** each repeat unit will have 1 b-t interactions as shown below for **AB'** arrangement (hexagons is redrawn to show all interactions).



Thus, calculations will be as follows:

	Interaction number			Interaction energy, kJ mol ⁻¹			Total energy, kJ mol ⁻¹
	b-b	b-t	t-t	b-b	b-t	t-t	
AA	4	0	1	-7.9	-49.8	-6.7	-38.3
AA'	4	0	1	-12.6	-55.6	-16.7	-67.1
AB	0	1	0	-7.9	-49.8	-6.7	-49.8
AB'	0	1	0	-12.6	-55.6	-16.7	-55.6

$$AA : 4 \cdot (-7.9) + 1 \cdot (-6.7) = -38.3 \text{ kJ mol}^{-1}$$

$$AB : 1 \cdot (-49.8) = -49.8 \text{ kJ mol}^{-1}$$

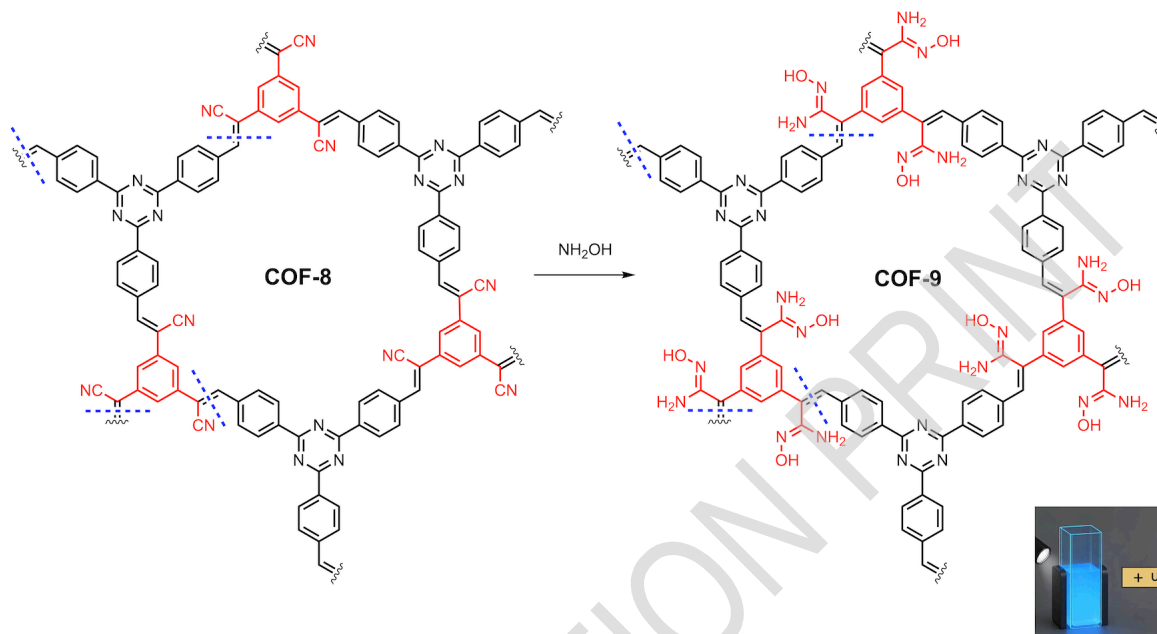
$$AB' : 1 \cdot (-55.6) = -55.6 \text{ kJ mol}^{-1}$$

(**AB'**) interlayer stacking mode energy matches slipped benzene-triazine π - π stacking.

4 pt for each correct total energy in **AA**, **AB**, **AB'**

COF-9, obtained from **COF-8**, adsorbs UO_2^{2+} ions and loses its fluorescence. In an experiment, a suspension of 5.000 mg **COF-9** in 19.90 mg dm⁻³ UO_2^{2+} solution (200.0 mL) was filtered after equilibrium was

reached. The final concentration of UO_2^{2+} was 9.225 mg dm^{-3} .



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

SOLUTION:

$$q_e = \frac{C_0 - C_e}{m \cdot L}$$

$$q_e = \frac{19.90 \text{ mg dm}^{-3} - 9.225 \text{ mg dm}^{-3}}{5.000 \cdot 10^{-3} \text{ g}} \cdot 200.0 \cdot 10^{-3} \text{ dm}^3 = 427.0 \text{ mg g}^{-1}$$

Since one repeating unit ($\text{C}_{36}\text{H}_{27}\text{N}_9\text{O}_3$) represents one pore, the molar ratio of the **COF-9** pore to UO_2^{2+} :

$$\frac{1.000 \text{ g}}{633.67 \text{ g}} : \frac{427.0 \cdot 10^{-3} \text{ g}}{270.03 \text{ g}} = 1 : 1$$

COF-9 pore : $\text{UO}_2^{2+} = 1:1$

2 pt for q_e .

3 pt for correct molar ratio between pore and uranium.

1 pt if only correct molar mass of repeating unit is given.

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	Σ
2	3	3	2	2	2	2	2	4	22

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

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

SOLUTION:

Using the average atomic mass of uranium from the Periodic Table as 238.03 a.u., and isotope masses as 235.04 a.u. for ^{235}U and 238.05 a.u. for ^{238}U , we can calculate the atomic abundance, x , of ^{235}U .

Equation:

$$238.03 = x \times 235.04 + (1 - x) \times 238.05 \quad (1)$$

$$238.03 = 235.04x + 238.05 - 238.05x$$

$$238.03 - 238.05 = x(235.04 - 238.05)$$

$$-0.02 = x(-3.01)$$

$$x = \frac{-0.02}{-3.01} = 0.00664 = 0.66\%$$

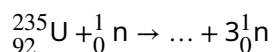
The atomic abundance of ^{235}U in natural uranium is approximately 0.66%, which is a slightly lower estimate compared to the commonly accepted value of about 0.72%, influenced by rounding and exact values used.

The atomic abundance of ^{235}U is 0.66%

2 points total: 1 point for equation (1);

1 point for the correct answer.

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



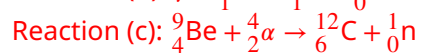
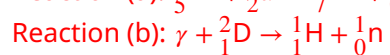
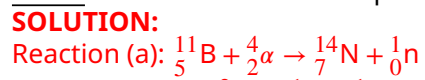
Neutrons that induce the chain reaction are produced by several ways:

- Reaction of ${}^{11}\text{B}$ with α -particles inside the reactor core
- Interaction of γ rays with ${}^2\text{D}$ nuclei present in the reactor coolant water
- Reaction of ${}^9\text{Be}$ with α -particles produced in an externally installed neutron source.

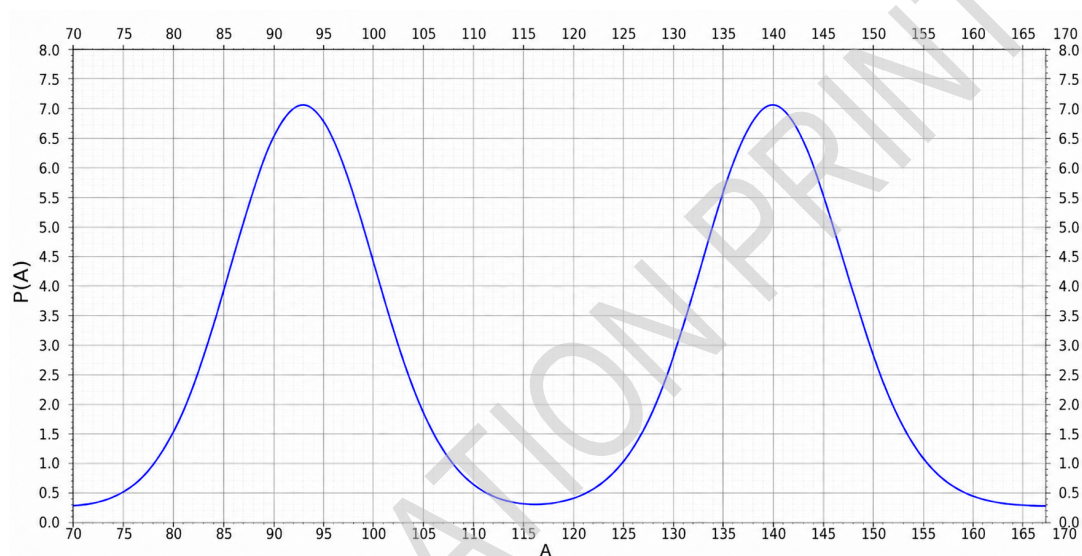
4.2 Write the nuclear reaction equations for (a), (b), and (c).

3.0 pt

SOLUTION:



3 points total: 1 point for each full and correct equation.



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

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

SOLUTION:

Let us presume that total atomic mass of elements in the fission products is $\sum A = 235 + 1 - 3 = 233$. There are two maxima on the graph at $A = 93$ and $A = 140$, which sum up to 233. Thus, there are only two fission products beside neutrons considered in the question. To find the atomic numbers we use conservation of charge and come to equation: $x + y = 92$ with x and y denoting atomic numbers of elements. These elements are in the same group, the intervals between them may be 2, 8, 18, 32, and 50. Let's solve the equation for those parameters:

$$x + (x + a) = 92 \text{ where } a = 2, 8, 18, 32, 50$$

$$x = 45, y = 47 \text{ (Rh, Ag, } a = 2\text{)}$$

$$x = 42, y = 50 \text{ (Mo, Sn, } a = 8\text{)}$$

$$x = 37, y = 55 \text{ (Rb, Cs, } a = 18\text{)}$$

$$x = 30, y = 62 \text{ (Zn, Sm, } a = 32\text{)}$$

$$x = 21, y = 71 \text{ (Sc, Lu, } a = 50\text{)}$$

Technically, Sc-Lu pair might do it, but there is no evidence for such high mass number isotope of scandium ($A = 93$), so the only reasonable answer is Rb and Cs.



3 points total:

0.6 point for each correct atomic mass of two elements (1.2 points). If the student provides the sum of the atomic masses of two elements they will also be given 1.2 points.

0.6 point for each correct element (1.2 points).

0.6 point for nuclear fission reaction equation.

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

SOLUTION:

$$\Delta E = 8.45 \times 233 - 7.59 \times 235 = 185.20 \text{ MeV}$$

Released energy: 185.2 MeV

2 points for the correct answer and relevant calculations; 1 point may be given for the right formula but the wrong answer.

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:

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

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

SOLUTION:

$$n_c = \frac{\ln\left(\frac{E_{\text{initial}}}{E_{\text{final}}}\right)}{\xi} = 19.97 \approx 20$$

2 points for the correct answer 20.

1 point may be given for the right formula but the wrong answer.

In 1966, the *Urtabulak* gas field suffered an uncontrolled natural gas well blowout, releasing enormous volumes of burning methane.

- 4.6** **Calculate** $\Delta_r H_{298}^\circ$ (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

SOLUTION:

Balanced reaction: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

$$\Delta_r H_{298}^\circ = [\Delta_f H^\circ(\text{CO}_2) + 2\Delta_f H^\circ(\text{H}_2\text{O})] - [\Delta_f H^\circ(\text{CH}_4) + 2\Delta_f H^\circ(\text{O}_2)]$$

$$\Delta_r H_{298}^\circ = [(-393.5 + 2(-241.8)) - (-74.8 + 0)] \text{ kJ mol}^{-1} = -802.3 \text{ kJ mol}^{-1}$$

Molar enthalpy of methane combustion at 298 K, $\Delta_r H_{298}^\circ = -802.3 \text{ kJ mol}^{-1}$

2 points for the correct answer; 1 point if the answer is incorrect but the calculation of difference in enthalpies of products and reagents exists.

$\Delta_f H_{298}^\circ(\text{CH}_4)$	-74.8 kJ mol ⁻¹
$\Delta_f H_{298}^\circ(\text{H}_2\text{O, gas})$	-241.8 kJ mol ⁻¹
$\Delta_f H_{298}^\circ(\text{CO}_2)$	-393.5 kJ mol ⁻¹
$C_P(\text{CH}_4)$	35 J mol ⁻¹ K ⁻¹
$C_P(\text{H}_2\text{O, gas})$	34 J mol ⁻¹ K ⁻¹
$C_P(\text{O}_2)$	29 J mol ⁻¹ K ⁻¹
$C_P(\text{CO}_2)$	37 J mol ⁻¹ K ⁻¹

If you did not get an answer for 4.6, use $\Delta_r H_{298}^\circ = -750 \text{ kJ mol}^{-1}$ for further calculations.

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

SOLUTION:

Assume constant heat capacities.

$$\Delta H(T) = \Delta H(298 \text{ K}) + \Delta C_p(T - 298 \text{ K})$$

$$\Delta C_p = [C_p(\text{CO}_2) + 2C_p(\text{H}_2\text{O})] - [C_p(\text{CH}_4) + 2C_p(\text{O}_2)]$$

$$\Delta C_p = [37 + 2(34)] - [35 + 2(29)] = 12 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r H_{2000}^\circ = -802.3 \text{ kJ mol}^{-1} + \frac{(12 \text{ J mol}^{-1} \text{ K}^{-1})(1702 \text{ K})}{1000} = -781.876 \text{ kJ mol}^{-1}$$

$$\Delta_r H_{2000}^\circ = -781.9 \text{ kJ mol}^{-1}$$

For a given value of $\Delta_r H_{298}^\circ = -750 \text{ kJ/mol}$ alternative answer will be:

$$\Delta_r H_{2000}^\circ = -781.9 \text{ kJ mol}^{-1}$$

$$\Delta_r H_{2000}^\circ = -750 \text{ kJ mol}^{-1} + \frac{(12 \text{ J mol}^{-1} \text{ K}^{-1})(1702 \text{ K})}{1000} = -729.576 \text{ kJ mol}^{-1}$$

$$\Delta_r H_{2000}^\circ = -729.6 \text{ kJ mol}^{-1}$$

2 points total:

1 point for the correct heat capacity change calculation.

1 point for the correct enthalpy calculation at 2000 K.

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

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

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

SOLUTION:

Using the flow as a gas volume measured at 1 atm and 298 K:

$$n = \frac{PV}{RT} = \frac{101325 \text{ Pa} \times 2.2 \times 10^5 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 9.00 \times 10^6 \text{ mol day}^{-1}$$

$$\text{Total combustion energy released daily} = 7.04 \times 10^{12} \text{ J day}^{-1}$$

$$\text{For provided } \Delta_r H_{2000}^\circ = -700 \text{ kJ mol}^{-1} \text{ the answer} = 6.30 \times 10^{12} \text{ J day}^{-1}$$

2 points for the correct answer.

1 point if the answer is incorrect but the relevant calculation exists.

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}U isotope, and 33% of the ^{235}U underwent fission. 4.0 pt

If you did not get an answer for 4.4, use $\Delta E = 200 \text{ MeV}$.

SOLUTION:

Explosion energy $E = 30.0 \times 10^3 \text{ ton} \times 4.184 \text{ GJ ton}^{-1} = 1.2552 \times 10^{14} \text{ J}$

Using energy per fission from **4.4**:

$$185.2 \text{ MeV} \times 1.602 \times 10^{-13} \text{ J MeV}^{-1} = 2.967 \times 10^{-11} \text{ J}$$

$$TN = \frac{E}{E_{\text{fission}}} = \frac{1.2552 \times 10^{14}}{2.967 \times 10^{-11}} = 4.23 \times 10^{24} \text{ fissions}$$

$$n(^{235}\text{U}) = \frac{N}{N_A} = \frac{4.27 \times 10^{24}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 7.03 \text{ mol}$$

$$m = 7.03 \text{ mol} \times 235.04 \text{ g mol}^{-1} = 1.65 \times 10^3 \text{ g} = 1.65 \text{ kg}$$

Accounting that enriched uranium contains 90% of ^{235}U isotope and only 33% is undergoing decay process:

$$\frac{1.67}{0.9 \times 0.33} = 5.56 \text{ kg}$$

$$TN = 4.23 \times 10^{24} \text{ fissions}$$

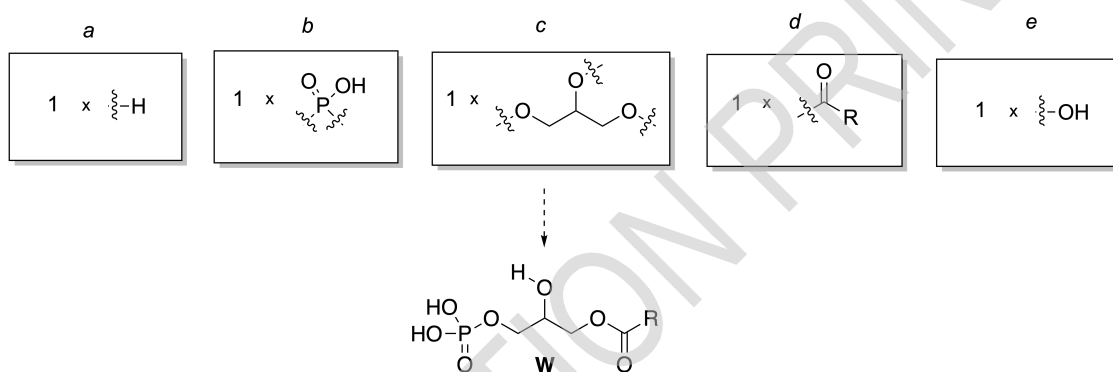
$$m = 5.56 \text{ kg}$$

4 points total: 2 points for the correct number of fissions; 1 point if the answer is incorrect but the relevant calculation exists. 2 points for the correct mass of enriched uranium; 1 point if the answer is incorrect but the relevant calculation exists.

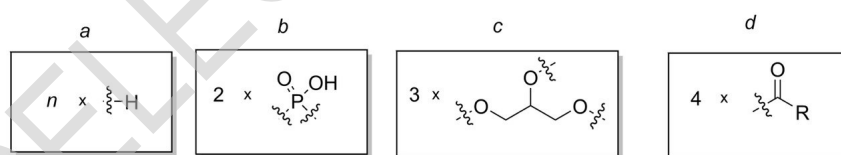
T5. Cardiolipins

6%						
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.

SOLUTION:

Each bond involves two atoms, so the total number of atoms with broken bonds (indicated by the wavy line on the fragments of the molecule) must be an even number. For fragments with a known number of repeats in the **PL1** molecule, the total number of atoms with broken bonds is 17 ($2 \cdot 2 + 3 \cdot 3 + 4$). Thus the total number of hydrogen atoms with broken bonds must be an odd number. Therefore, n is an odd number.

(a)	(b)	(c)
	X	

Correct answer: 1 point.

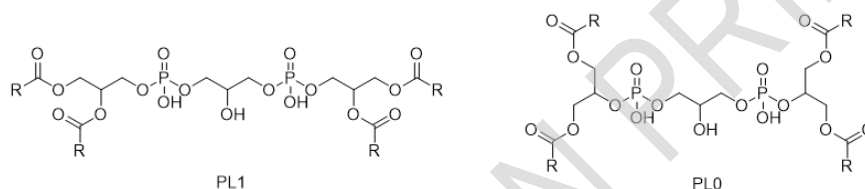
Some cardiolipins are chiral molecules, even if they contain four identical fatty acid residues, as in the case of **PL1**. One enantiomer of **PL1** is found in prokaryotes and eukaryotes, and the other only in archaea. All other diastereomers of **PL1** are achiral molecules, since they have a plane 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 ($pK_{a2} \gg pK_{a1}$) due to the special, stable structure of monoanion **Y**.

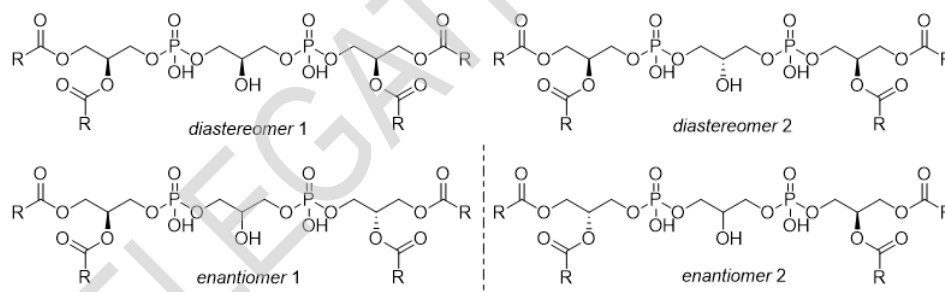
- 5.2** **Draw** the structure of one enantiomer of **PL1**. **Draw** the structure of **Y** in a way that shows the stabilisation that explains the difference between pK_{a1} and pK_{a2} . Use the abbreviation R for the fatty acid residues. 6.0 pt

SOLUTION:

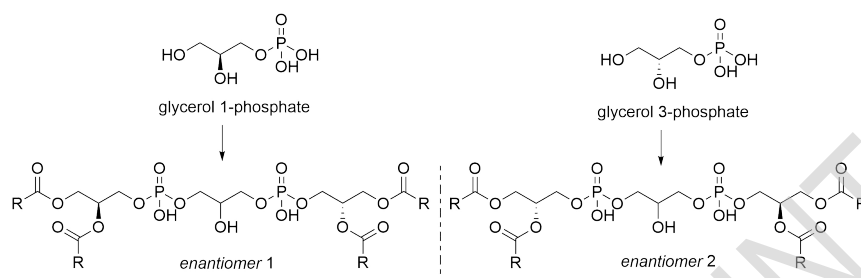
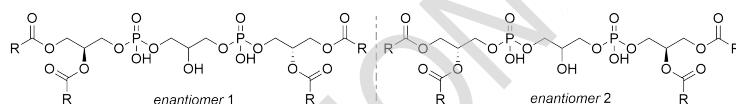
To obtain the diastereomer of **PL1** with a plane of symmetry, we must construct a symmetric structure from the given fragments. Glycerol backbones can only be linked through phosphate groups since there is no peroxide bond present. The number of glycerol moieties suggests that one glycerol occupies the central position with the remaining fragments arranged around it to achieve an overall plane of symmetry. The number of *a* fragments in **PL1** is $n = 3 \cdot 3 - 2 \cdot 2 - 4 = 1$. So, **PL1** has $d_2c - b - c(a) - b - cd_2$ skeleton. Two options, presented below, can have a plane of symmetry:



The **PL0** structure is achiral, so it cannot be **PL1**. All possible stereoisomers of **PL1** are as follows:

SOLUTION:

Enantiomer 2 is found in prokaryotes and eukaryotes. These organisms use glycerol 3-phosphate for cardiolipin synthesis, while archaea use glycerol 1-phosphate for this purposes and synthesise *enantiomer 1*:

SOLUTION:**PL1**

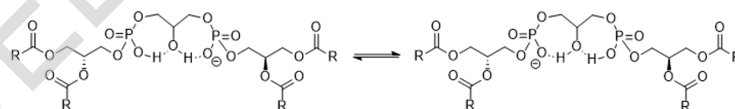
For drawing of enantiomer 1 or 2 as **PL1**: 4 points.

For drawing the correct structure of **PL1** with wrong or missing stereochemistry: 3 points.

For drawing achiral **PLO** structure: 2 points.

Any other structure that uses exactly $1 \times a$, $2 \times b$, $3 \times c$, $4 \times d$ and contains no peroxide bond: 1 point.

Intramolecular hydrogen bond between the phosphoric acid residue and the alcohol group significantly reduces the pK_{a2} value.



For any correct tautomer of **Y**: 2 points.

For a tautomer of **Y** (not shown above) with a hydrogen bond between the two phosphate groups: 1 point

Correctly drawn structures with incorrect **PL1** structure are also accepted.

For structures containing hydrogen bond between phosphoric acid residues and esters 0 point, because they are possible for each phosphoric acid residue even in molecular form and don't make difference between pK_{a1} and pK_{a2} .

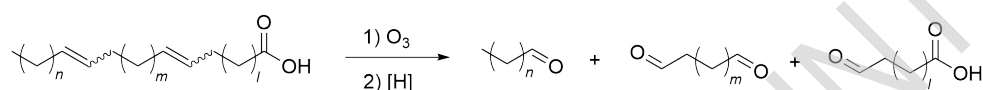
A series of experiments was conducted to identify the fatty acid (RCOOH) in **PL1** found predominantly in mammalian hearts. During reductive ozonolysis, RCOOH forms three different organic products in equimolar amounts.

- 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 α -d fragments from 5.1.*

SOLUTION:

Correct scheme of reductive ozonolysis of RCOOH is as follows:



So, $N_{C=C} = 2$.

If we take R as C_xH_y , then:

$$y = (2x+1) \cdot N_{C=C} \cdot 2 = 2x-3. \text{ (eq.3.1)}$$

Then the formula for calculating the number of bonds in **PL1** can be written as follows:

$$0.5 \cdot 1 + 5 \cdot 2 + 11.5 \cdot 3 + 4 \cdot (3 + 2x + 0.5y) = 255,$$

$$4x + y = 99. \text{ (eq.3.2)}$$

Combining eq.3.1 and eq.3.2:

$$4x + y = 4x + 2x - 3 = 6x - 3 = 99 \Rightarrow x = 17, y = 31.$$



For correct eq.3.2: 2 points.

For correct number of double bonds: 1 point.

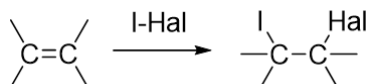
For correct formula of $C_{17}H_{31}COOH$: 1 point.

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

SOLUTION:

During determination of the iodine number, the following reaction takes place:



The iodine number of RCOOH and the iodine mass fraction in the adduct are described as follows:

$$181.0 = \frac{N_{\text{C}=\text{C}} \times 253.8}{M_{\text{RCOOH}}} \times 100 \Rightarrow \frac{M_{\text{RCOOH}}}{N_{\text{C}=\text{C}}} = 140.2$$

$$0.3657 = \frac{N_{\text{C}=\text{C}} \times 126.9}{M_{\text{RCOOH}} + N_{\text{C}=\text{C}} \times (126.9 + A_{\text{Hal}})} \Rightarrow A_{\text{Hal}} = 79.9 \text{ g mol}^{-1}$$

So, **X** is iodine monobromide, IBr.

If **X** was molecular iodine (I₂), then:

$$\omega_{\text{I}} = \frac{N_{\text{C}=\text{C}} \times 253.8}{M_{\text{RCOOH}} + N_{\text{C}=\text{C}} \times 253.8} = 0.6441$$

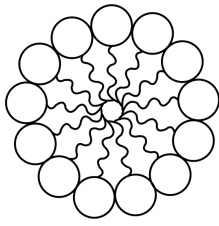
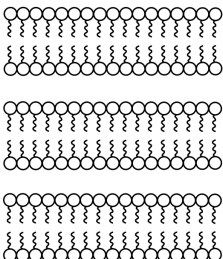
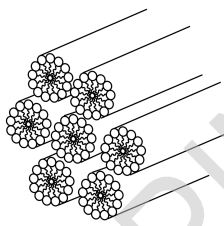
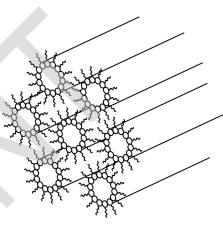
which is incorrect.

For correct formula of **X**: 1 point.

For correct calculations: 1 point.

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.

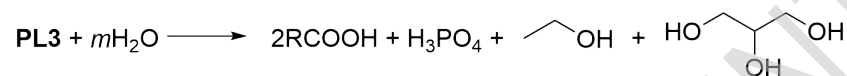
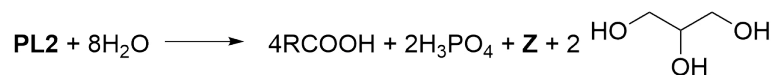
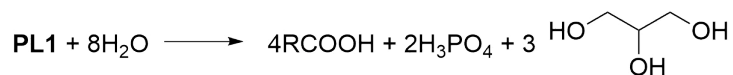
			
(a) micellar	(b) lamellar	(c) hexagonal	(d) inverse hexagonal

SOLUTION:

PL1 has 4 acyl chains but only 2 phosphate head groups, so its tail volume is already large relative to the head group — which is why the dianion is lamellar, not micellar/hexagonal. Protonating both acidic groups shrinks the head group further (loss of charge and its water shell), tipping the balance even more toward the tails. Starting from lamellar, this shift leads to the inverse hexagonal phase. Correct answer is (d).

Only for correct answer: 2 point.

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

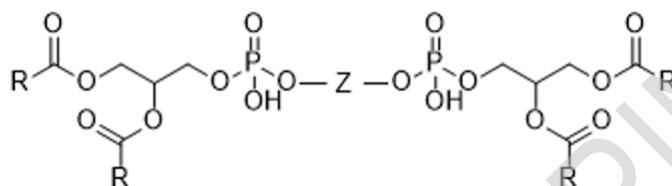


- The non-ionised form of **PL2** contains 254 σ and π bonds between atoms in total. It is a chiral and a more symmetrical molecule than **PL1**,
- **Z** contains C, H, and O only, and it doesn't react with H_2 in the presence of a catalyst,
- Phospholipid **PL3** is a charged molecule at physiological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

SOLUTION:

The hydrolysis of **PL1** proceeds through breaking of 8 ester bonds, which requires 8 water molecules. So, **PL2** also contains all these ester bonds and has the same skeleton with **PL1** and the residue of molecule **Z** needs to be located in the centre of **PL2** due to its symmetry:

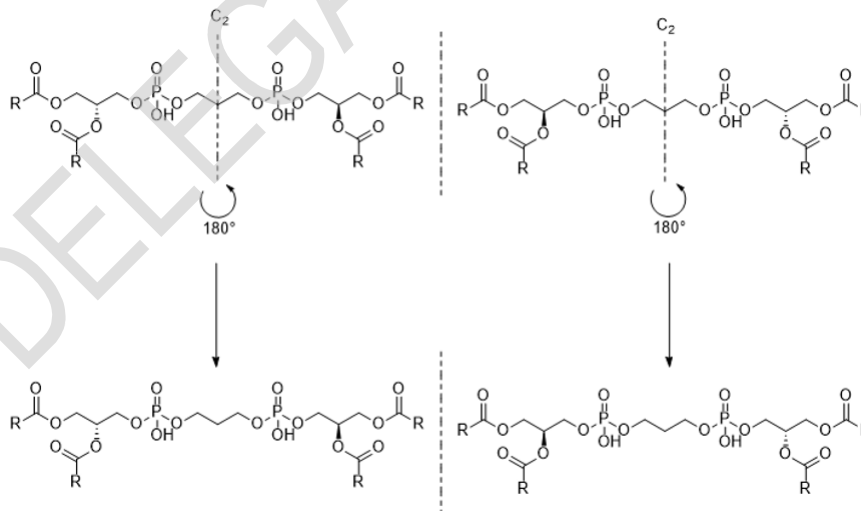


In the case of **Z** reducing the number of covalent bonds, leads to decreasing numbers of C, H or O atoms:

- removing each C atom decreases the number of covalent bonds by 3;
- removing a pair of H atoms forms a C=C or C=O double bond, which reacts with H_2 in presence of catalyst;
- removing each O atom decreases the number of covalent bonds by 1.

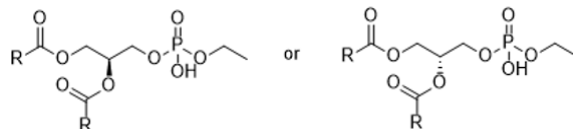
Thus, **Z** is propane-1,3-diol: it contains only C, H, and O; does not react with H_2 in the presence of a catalyst; has one fewer covalent bond; and is more symmetrical than glycerol.

Note that replacing OH with H makes the **PL2** molecule more symmetrical – a C_2 rotation axis appears:



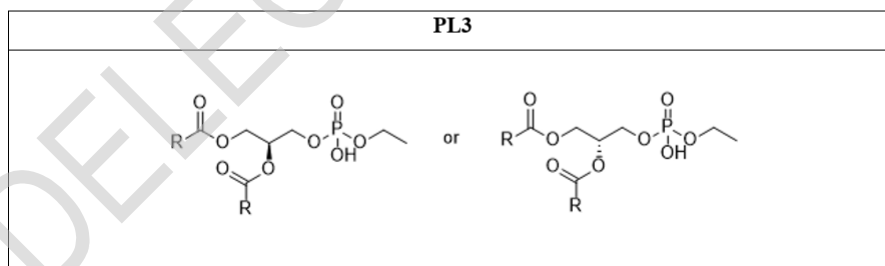
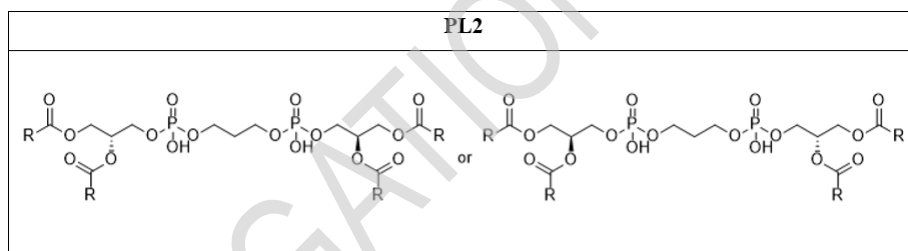
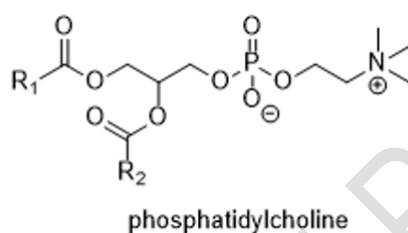
This diastereomer of these enantiomers isn't chiral due to its symmetry plane. **PL3** needs to be synthesised from the same precursors and via the same metabolic pathways as **PL1**. So, it can be one of the following enantiomers:

SOLUTION:



The right structure is typical of prokaryotes and eukaryotes, while the left one is possible for archaea. **PL3** demonstrates the structure of phosphatidic acid derivatives such as phosphatidylcholine.

SOLUTION:



For correct structure of **PL2** with correct stereochemistry: 2 points.

For correct structure of **PL2** with incorrect stereochemistry: 1 point.

For the structure of **PL2** with a keto group in the central position: 1 point.

For correct structure of **PL3** without any stereochemistry: 1 point.

For structure of **PL3** with monoethyl phosphate in central position: 1 point

Correctly drawn structures corresponding to **PL1** in answer to 5.2 are also accepted.

T6. Carbon Nanorings

7%							
6.1	6.2	6.3	6.4	6.5	6.6	6.7	Σ
10	11	2	12	24	20	4	83

In 2019, C_{18} , the first example of a new class of carbon allotropes called cyclo[n]carbons (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. C_{13} has triplet ($^3C_{13}$, spin $S = 1$), and singlet ($^1C_{13}$, 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 C_{18} , C_{16} , $^3C_{13}$, and $^1C_{13}$. 10.0 pt

Fill in all blanks.

SOLUTION:

Number of Rings	C_{18}	C_{16}	$^3C_{13}$	$^1C_{13}$
A	2	0	0	1
AA	0	2	0	1

For C_{18} and C_{16} : 2 pts each.

If both A and AA correct: 2 pts

If one correct, one blank: 1 pt

If one correct, one wrong: 0 pt

Both wrong: 0 pt

For triplet C_{13} and singlet C_{13} : 3 pts each

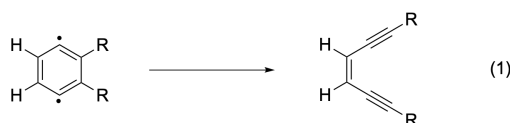
If both A and AA correct: 3 pts

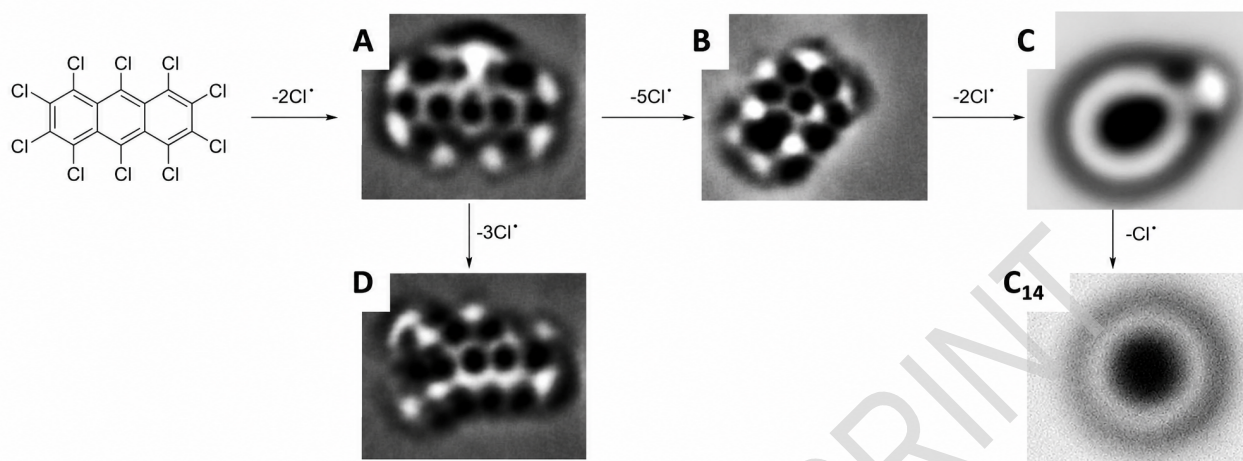
If one correct, one blank: 2 pt

If one correct, one wrong: 1 pt

Both wrong: 0 pt

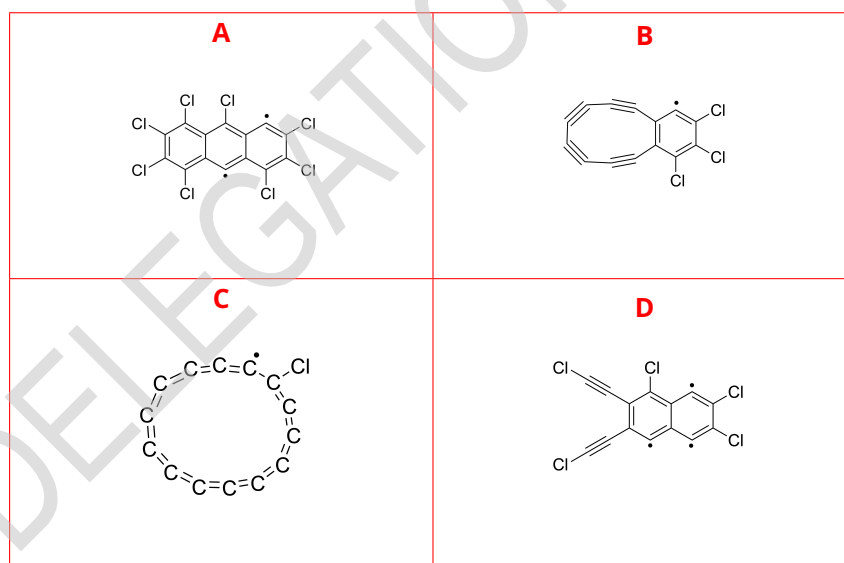
Later, cyclo[n]carbons C_{10} , C_{12} , C_{14} , C_{20} , and C_{26} were generated by a combination of dehalogenation and retro-Bergman (1) reactions on a surface. AFM images taken during the synthesis of C_{14} are shown below:





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

SOLUTION:



A is given to the students.

B is worth 4 points. 1 pt awarded to incorrect structure with 3 Cl. 1 pt awarded to incorrect structures with 2 alkynes in 1,5-relationship, indicating understanding of retro-Bergman. -1 pt if radicals missing or incorrect.

C is worth 3 points. Full points also given to alternating single and triple bonds. 1 pt awarded to incorrect structure with 1 Cl. -1 pt if radicals missing or incorrect.

D is worth 4 points. 1 pt awarded to incorrect structure with 5 Cl. 1 pt awarded to incorrect structures with two alkynes in 1,5-relationship, indicating understanding of retro-Bergman. -1 pt if radicals missing or incorrect.

- 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 / kJ mol^{-1}
C-F	467
C-Cl	346
C-Br	290
C-I	228

SOLUTION:

First, we need to convert eV to kJ mol^{-1} :

$$E_{\text{given}}[\text{kJ mol}^{-1}] = 2.5 \times (1.602 \times 10^{-19} \times 6.022 \times 10^{23}) / 1000 \text{ kJ mol}^{-1} \quad (1)$$

$$E_{\text{given}} = 2.5 \cdot 96.485 \text{ kJ mol}^{-1} = 241.2 \text{ kJ mol}^{-1} \quad (2)$$

The only candidate with $BDE \leq E_{\text{given}}$ is the C-I bond.

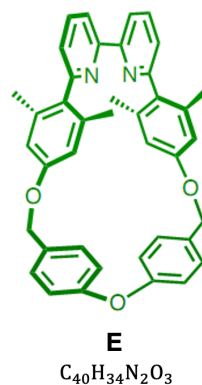
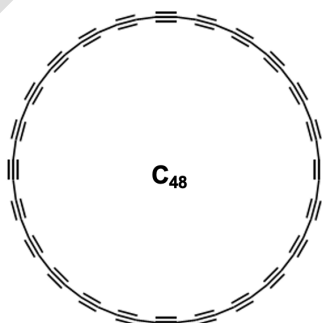
X = I

1 point for unit transformation, 1 point for correct halogen choice.

(2 pts awarded if I is chosen with no working)

0 pts for other halogens or more than one halogen chosen.

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



- 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

SOLUTION:

Molecular weight of **E** is 590 ($C_{40}H_{34}N_2O_3$). Molecular weight of C_{48} is 576. The first signal is given and corresponds to $[E+H]^+$. The catenane with one molecule of **E** would yield signal m/z 1161 which does not match with given signals. Hence we should consider the probability of di- and tri-catenation as well as dication and trication formation (question clearly states positive mode):

m/z	$+1H^+$	$+2H^+$	$+3H^+$
$C_{48}E$	1167	584	389.7
$C_{48}E_2$	1757	879	586.3
$C_{48}E_3$	2347	1174	783

Therefore, 783 and 1174 peaks correspond to tri-catenane $[C_{48}E_3 + 3H]^{3+}$ and $[C_{48}E_3 + 2H]^{2+}$ ions. Peak at 879 corresponds to dicatenane dication $[C_{48}E_2 + 2H]^{2+}$.

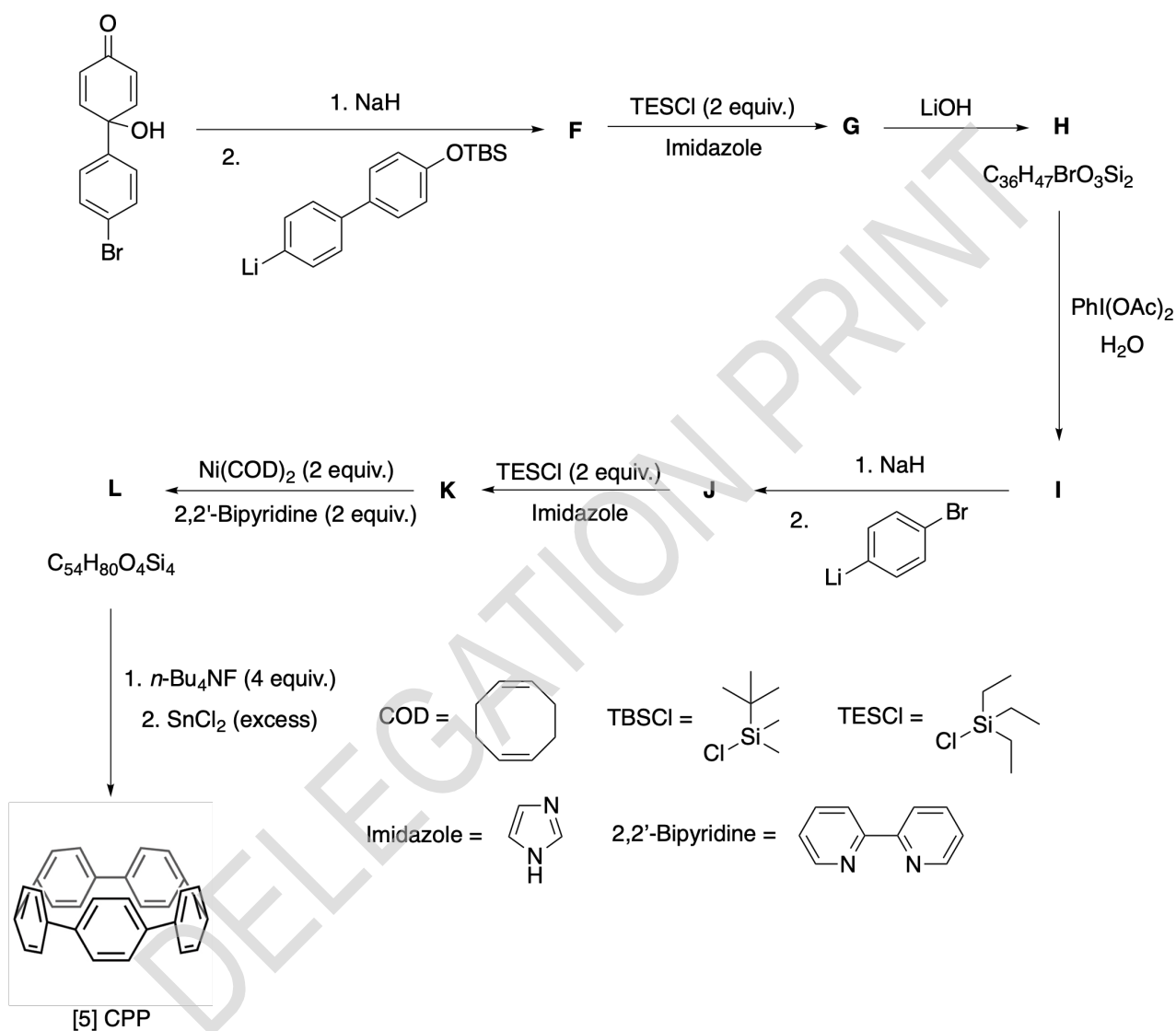
m/z	591	783	879	1174
	$[E + H]^+$	$[C_{48}E_3 + 3H]^{3+}$	$[C_{48}E_2 + 2H]^{2+}$	$[C_{48}E_3 + 2H]^{2+}$

4 points for each correct ionic species.

No partial credit as other answers will not have correct m/z ratios.

Theory

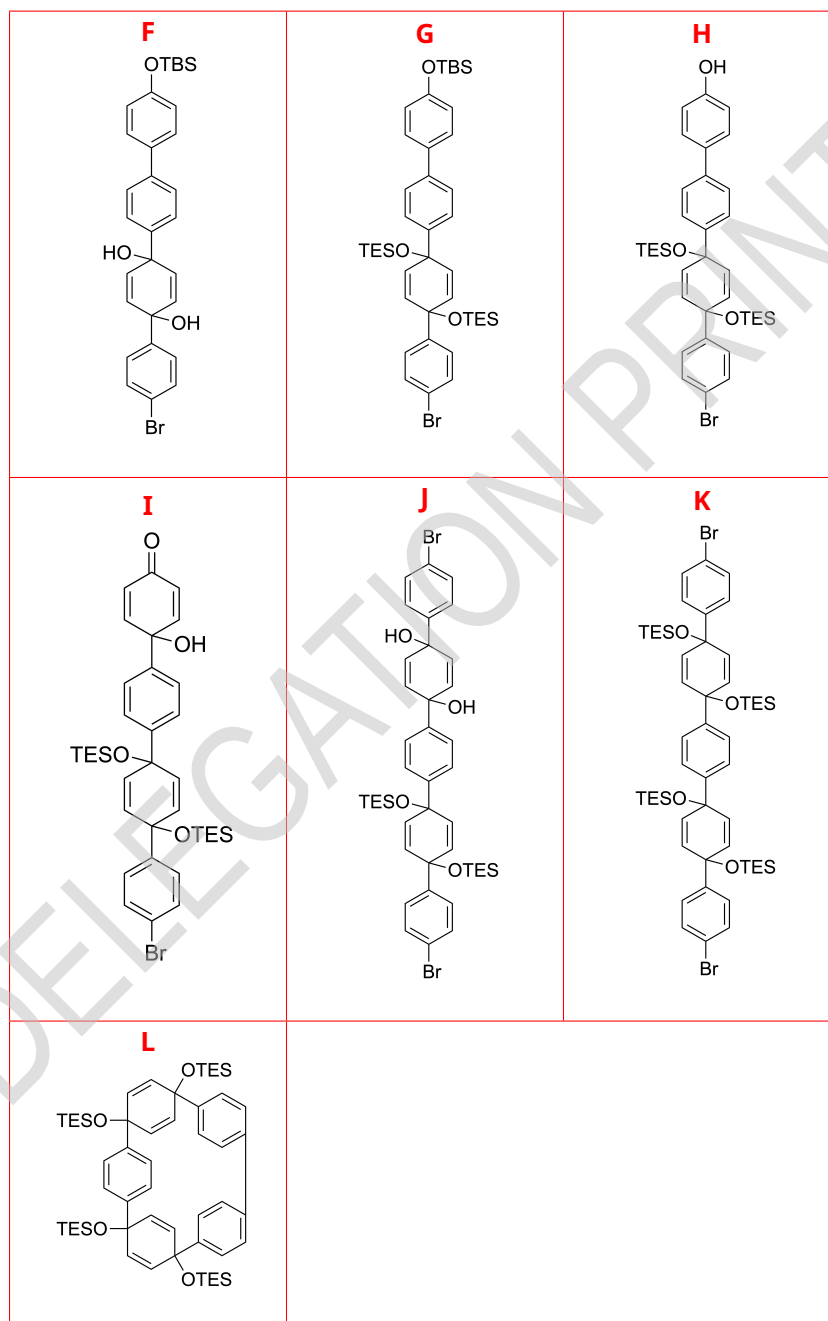
Cycloparaphenylene (CPP) is another cyclic, highly-strained molecule commonly called a carbon nanohoop. The synthesis of the smallest known member, [5]CPP, is shown below, where $\text{PhI}(\text{OAc})_2$ acts as a two electron oxidant.



(equiv. = Equivalent, excess = Excess)

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

24.0 pt

SOLUTION:

RUBRICS:

F: 4 pts

G: 3 pts

H: 3 pts

I: 4 pts

J: 3 pts

K: 3 pts

L: 4 pts

Error carry forward can be awarded if the desired reactivity is shown and the chemistry is sensible.

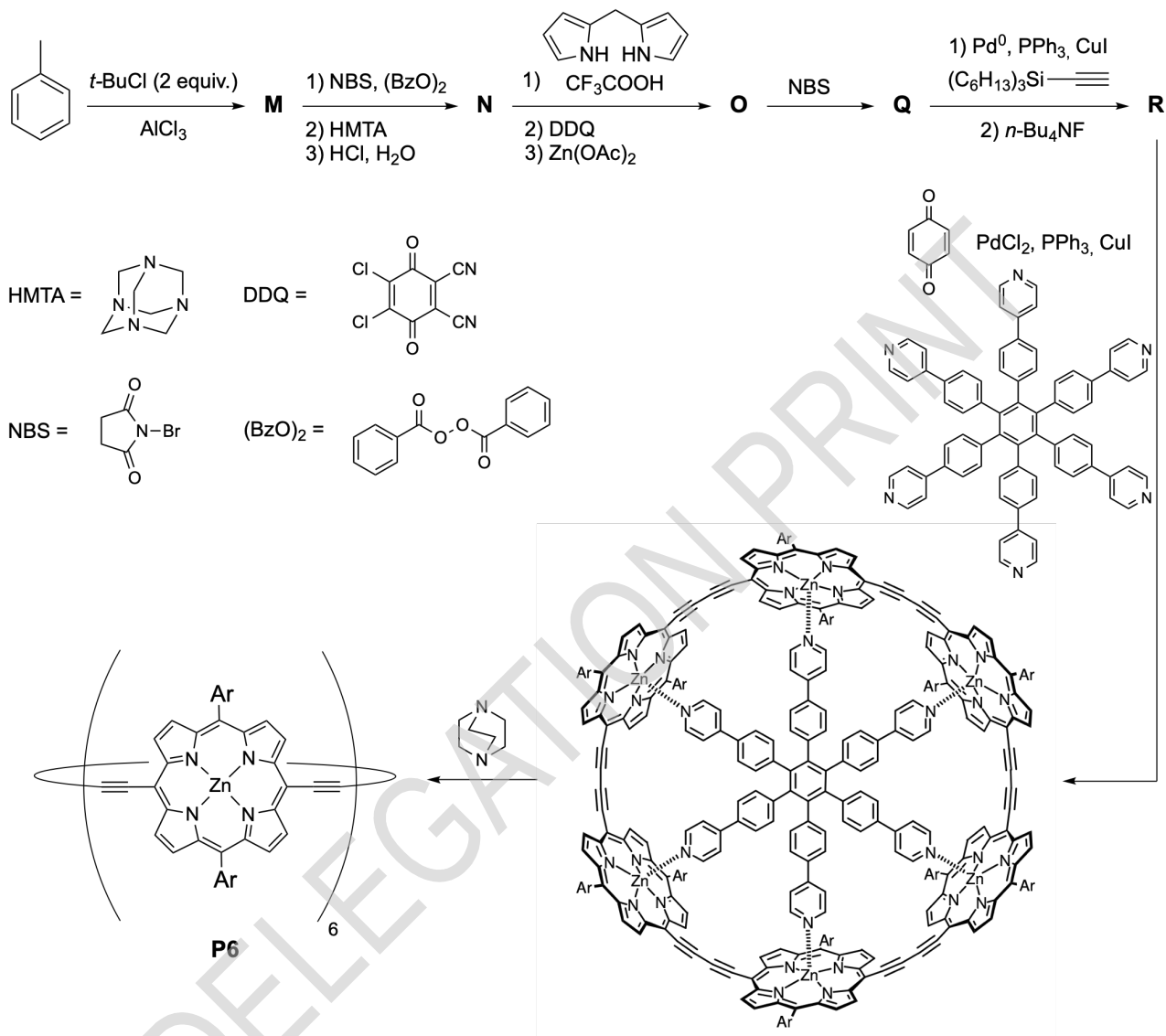
-1 pt for each mistake in a part of the molecule not undergoing reaction.

For **F** and **J**, the di-anion of the product or salts (OLi/ONa) will be accepted for full credit.

For **H**, the mono-anion of the product or salt (OLi) will be accepted for full credit.

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.

Theory



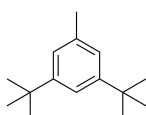
(equiv. = Equivalent)

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

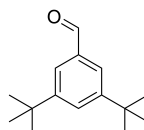
20.0 pt

SOLUTION:

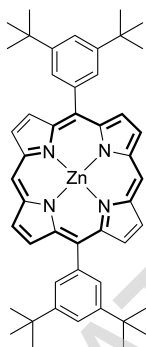
M



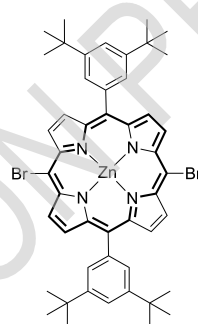
N



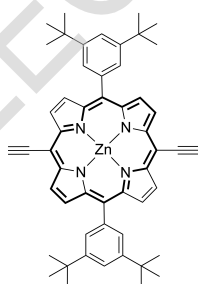
O



Q



R



RUBRICS:

M: 4 pts

Substitution pattern should be determined with information on four types of proton.

1 pt for any structure with one *t*-Bu group.3 pt for structure with *t*-Bu added at both *ortho* positions, 1 pt for any other structure with two *t*-Bu groups.**N:** 4 pts

4 pts if amine is given instead of the aldehyde (Delepine reaction). Does not affect the grading of the rest of the parts.

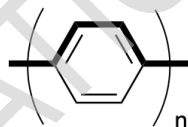
1 pt if Br instead of aldehyde.

O: 4 pts**Q:** 4 pts**R:** 4 pts

- 1 pt if double bonds in porphyrin drawn incorrectly, this penalty will be applied at most once.

- 2 pt if Zn is missing, this penalty will be applied at most once.

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.

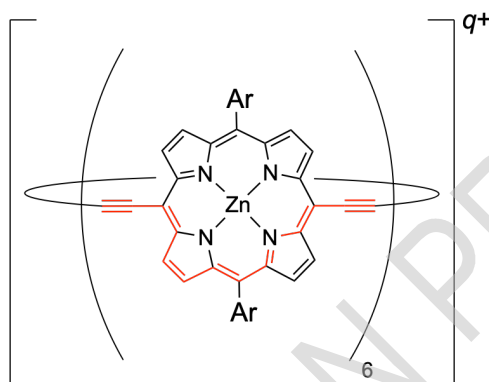


When **P6** is oxidised, it can exhibit global aromaticity and global anti-aromaticity.

- 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

SOLUTION:

We should count electrons around the abbreviated structure of **P6** as shown below:



The total number of π -electrons is $14 \times 6 = 84$ in the ground state.
To achieve global aromaticity by Hückel's rule, we need $4n + 2$ π -electrons.
The minimum number of π -electrons that need to be lost is two electrons and the total number of π -electrons is 82.

$n(e)$	2
$n(t)$	82

4 pts for fully correct.

2 pts if total number of electrons is wrong but it satisfies Hückel's $4n + 2$ rule.

No partial points for the loss of two electrons.

T7. Nitrogen Fixation

7%							
7.1	7.2	7.3	7.4	7.5	7.6	7.7	Σ
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.

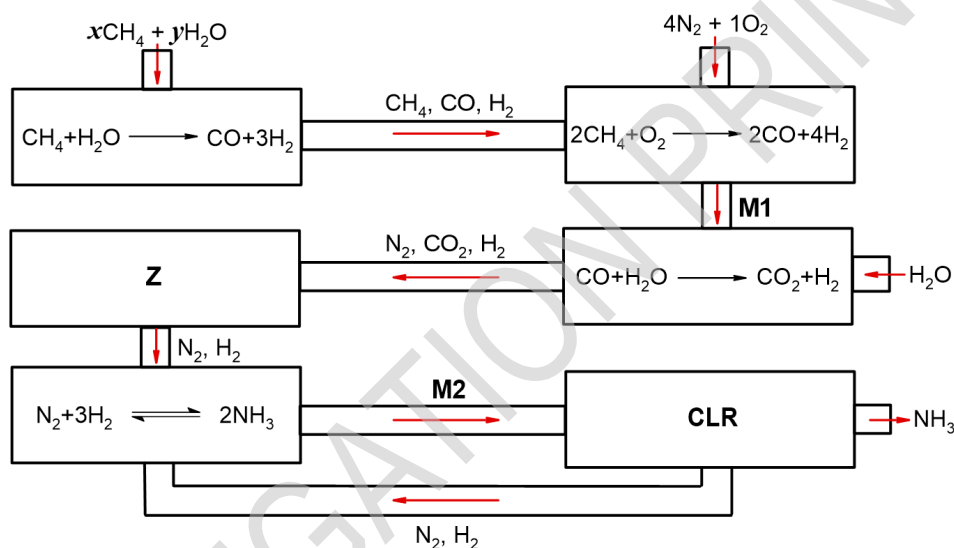


Fig. 1. M1 - Mixture 1, M2 - Mixture 2, Z – CO_2 scrubber, CLR - cooler

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

Theory

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

SOLUTION:

	CH ₄	H ₂ O	CO	O ₂	H ₂	N ₂	NH ₃	CO ₂
M1			✓		✓	✓		
M2					✓	✓	✓	

$x > y$	$x = y$	$x < y$
✓		

For composition of **M1**: 1 pt

For two correct ticks: 0.5 pt; If only one correct tick given: 0.25 pt

-0.25 pt penalty for each incorrect tick, but not below 0 pt.

For composition of **M2**: 1 pt; For two correct ticks: 0.5 pt; If only one correct tick given: 0.25 pt

-0.25 pt penalty for each incorrect tick, but not below 0 pt.

For relationship: 1 pt.

An ammonia production complex with a capacity of 660,000 tons per year was commissioned at the Navoiyazot 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 *Navoiyazot* operates according to the **Fig. 1**. 8.0 pt

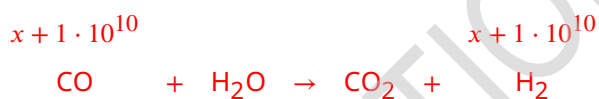
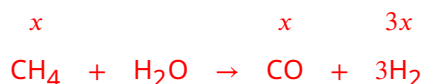
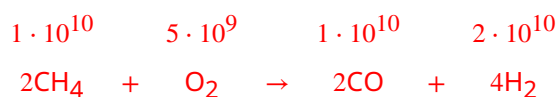
SOLUTION:

$$n(\text{NH}_3) = \frac{6.6 \cdot 10^{11}}{17} = 3.88 \cdot 10^{10} \text{ mol}$$

$$n(\text{N}_2, \text{init.}) = \frac{3.88 \cdot 10^{10}}{2 \cdot 0.97} = 2 \cdot 10^{10} \text{ mol}$$

$$n(\text{H}_2, \text{init.}) = 3 \cdot 2 \cdot 10^{10} = 6 \cdot 10^{10} \text{ mol}$$

$$n(\text{O}_2) = 2 \cdot 10^{10} \cdot \frac{1}{4} = 5 \cdot 10^9 \text{ mol}$$



$$6 \cdot 10^{10} = 2 \cdot 10^{10} + 3x + x + 1 \cdot 10^{10}$$

$$x = 7.5 \cdot 10^9$$

$$m(\text{CH}_4) = (7.5 \cdot 10^9 + 1 \cdot 10^{10}) \cdot 0.016 \cdot 10^{-3} = 280,000 \text{ tons}$$

$$m(\text{CH}_4) = 280,000 \text{ tons}$$

For $n(\text{NH}_3)$: 0.5 pt, for $n(\text{N}_2, \text{init.})$: 0.5 pt, for $n(\text{H}_2, \text{init.})$: 0.5 pt, for $n(\text{O}_2, \text{init.})$: 0.5 pt, for correct equation to calculate $n(\text{CH}_4)$: 3 pt, for $n(\text{CH}_4)$ from equation: 1 pt, for $m(\text{CH}_4)$: 2 pt.

Theory

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 $\text{N}_2 : \text{H}_2 = 1 : 3$ 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.

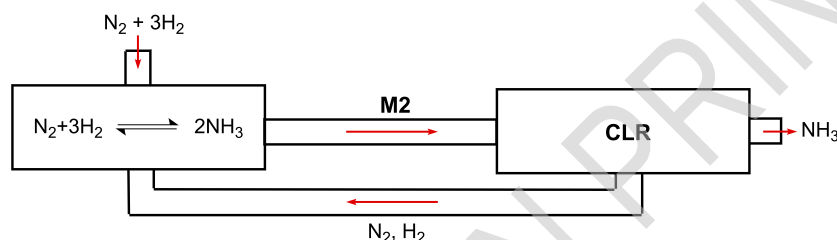


Fig. 2. M2. – Mixture 2, **CLR** - cooler.

- 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.* 15.0 pt

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

SOLUTION:

Each time, along with the unreacted gases, a stoichiometric mixture of N_2 and H_2 is added to the synthesis reactor. Let's define f_n as the number of moles of N_2 , which are present in the reactor after the reaction and before adding the next portion. For moles of N_2 , the following recurrence relation is obtained:

$$f_n = \left(\frac{n_0}{4} + f_{n-1}\right)(1 - \eta), \quad f_1 = (1 - \eta)\frac{n_0}{4} \quad (2 \text{ pt each})$$

Applying the relation and using $n_0 = 4$, we obtain:

$$f_2 = (1 + f_1)(1 - \eta) = (1 - \eta) + (1 - \eta)^2$$

$$f_3 = (1 + f_2)(1 - \eta) = (1 - \eta) + (1 - \eta)^2 + (1 - \eta)^3$$

$$f_4 = (1 + f_3)(1 - \eta) = (1 - \eta) + (1 - \eta)^2 + (1 - \eta)^3 + (1 - \eta)^4$$

...

$$f_n = (1 - \eta) + (1 - \eta)^2 + (1 - \eta)^3 + (1 - \eta)^4 + \dots + (1 - \eta)^n = \sum_{i=1}^n (1 - \eta)^i \quad (2 \text{ pt})$$

$$= (1 - \eta) \frac{1 - (1 - \eta)^n}{1 - (1 - \eta)} = \left(\frac{1}{\eta} - 1\right) (1 - (1 - \eta)^n) \quad (2 \text{ pt})$$

a) After using the numerical values, we can easily calculate

$$f_n = 5.6662 \quad (2 \text{ pt})$$

If student calculated the answer by calculating every single f_n and got the final answer correctly, full marks for the answer are given, but 0 for the equations.

For any other reasonable solution, giving the correct answer, full mark will be given.

b) Over n cycles, n moles of nitrogen have entered the system:

$$1 - \eta_{final} = \frac{\left(\frac{1}{\eta} - 1\right) (1 - (1 - \eta)^n)}{n} \quad (3 \text{ pt})$$

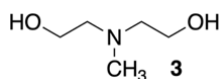
When $\eta = 0.15$ and $\eta_{final} = 0.97$, the exact answer is $n = 188.9$, so the required number of cycles is 189 (2 pt).

Note: this equation can be easily converted to a linear one by mentioning that $(1 - (1 - \eta)^n) \approx 1$, which is practically true after $n = 30$. For any other reasonable solution, giving the correct answer, full marks will be given.

$$n = \underline{\quad 189 \quad}$$

Total: 15 pt

An aqueous solution of **3** is being used to remove CO_2 from the mixture.



Theory

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

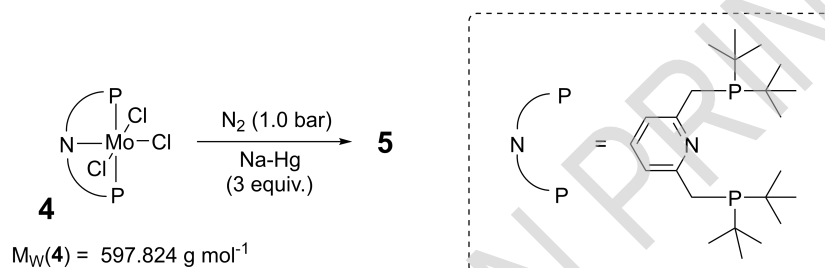
SOLUTION:



3 pt

Any other reasonable reactions will be credited partially.

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 cm³ of N₂ at 273.15 K and 1.0 bar. 6.0 pt

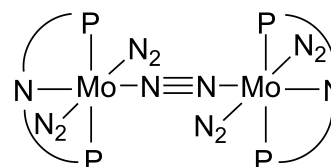
SOLUTION:

$$n(\text{N}_2) = \frac{PV}{RT} = \frac{100 \times 0.09497}{8.314 \times 273.15} = 4.182 \times 10^{-3} \text{ mol}$$

$$n(\mathbf{4}) = \frac{1.00 \text{ g}}{597.824 \text{ g mol}^{-1}} = 1.673 \times 10^{-3} \text{ mol}$$

$$\frac{n(\text{N}_2)}{n(\mathbf{4})} = \frac{4.182 \times 10^{-3}}{1.673 \times 10^{-3}} = 2.5$$

Thus, one molecule of the complex absorbs 2.5 moles of nitrogen, which means that two molecules of the complex absorb 5 molecules of nitrogen.

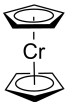
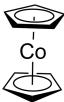
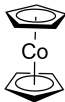
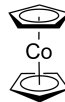
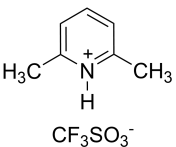
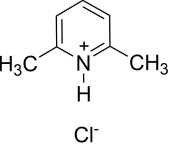
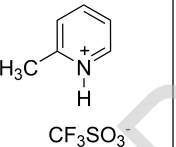
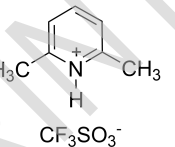


For calculating the ratio of nitrogen and complex: 3 pt, for correct structure (stereochemistry is not marked): 3 pt, for any other structures, fitting the ratio: 1 pt

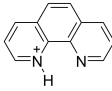
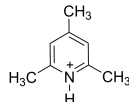
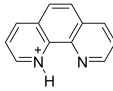
If student found CORRECT structure but did not show calculations, full marks will be given.

The effect of different reductants and additives on the yield of NH₃ was examined. The different Red and Ad combinations, their respective E° and pK_a , together with the resulting NH₃ yield are presented below.

Theory

#	1	2	3	4
Red				
E° (V)	-0.88	-1.15	-1.15	-1.15
Ad				
pK_a	14.4	14.4	13.9	14.4
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

#	A	B	C	D	
Red					
E° (V)	-0.09	-1.10	-1.10	-1.10	
Ad	 CF_3SO_3^-	 CF_3SO_3^-	 CF_3SO_3^-	 CF_3SO_3^-	
pK_a	13.7	15.0	13.7	10.6	

SOLUTION:**B>C>D>A=0****A = 0:** NiCp₂ at -0.09 V is below the reductant threshold, so no NH₃ is produced.**B>C:** B benefits from a slightly higher pK_a : stronger acids favour hydrogen evolution. It can be seen from the table as well (**3 vs 4**). (2 pt)**C>D:** Switching from OTf⁻ to Cl⁻ causes a large suppression because of the stronger coordination. This is shown in the table (**2 vs 3**). (2 pt)**D>A:** D gives small non-zero yield — Cl⁻ suppresses heavily but the strong reductant and good pK_a sustain some catalytic turnover (**2**), when **A** gives zero. (2 pt)

Total: 6 pt

Nitrogen fixation can also be achieved via binary nitrides (compounds containing N³⁻). Such nitrides **7**, **8**, **9** were obtained from pure elements. When they are heated together with SiO₂, red crystals of a stable compound **10** are formed as the single product. The minimal possible formula, describing the structure of compound **10** is Q_αR_βS₂T[Si₁₂N₂₄]. In addition:

- Mass fractions of nitrogen are $w(\text{N})_7 = 9.16\%$, $w(\text{N})_8 = 18.90\%$, $w(\text{N})_9 = 39.94\%$
- Q** and **R** are metal cations in their highest oxidation state.
- S** is a monoatomic anion.
- T** is an anion with tetrahedral configuration.
- For the quantitative formation of **10**, the mass ratio **7** : **8** : **9** : SiO₂ = 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

SOLUTION:

For binary nitride Z_3N_n (we can suggest nitrogen as trivalent for the start):

$$w(N) = \frac{14.007 \times n(N)}{14.007 \times n(N) + M(Z) \times 3}, \text{ so } M(Z) = \frac{14.007}{3} \left(\frac{1}{w(N)} - 1 \right) \times n$$

For analysing mass fraction data let's create a table:

n	$M(Z_7)$	$M(Z_8)$	$M(Z_9)$
1	46.30	20.03	7.02
2	92.61	40.07 (Ca_3N_2)	14.04
3	138.909 (LaN)	60.105	21.063
4	185.21	80.14	28.08 (Si_3N_4)
5	231.52	100.18	35.11
6	277.82	120.21	42.13
7	324.12	140.24	49.15
8	370.42	160.28	56.19

After calculations and the use of the common chemical sense we get only 3 possibilities: **7** = LaN , **8** = Ca_3N_2 , **9** = Si_3N_4 . Now let's convert mass ratios to molar ones:

$$n(\text{LaN}) : n(\text{Ca}_3\text{N}_2) : n(\text{Si}_3\text{N}_4) : n(\text{SiO}_2)$$

$$\frac{5.09}{138.91+14.01} : \frac{2.96}{40.07 \cdot 3 + 14.01 \cdot 2} : \frac{3.27}{28.08 \cdot 3 + 14.01 \cdot 4} : \frac{1}{28.08 + 16.00 \cdot 2} = 10 : 6 : 7 : 5$$

So, the reaction of formation of **10** looks like:



Thus, the formula of **10** should be $\text{La}_{10}\text{Ca}_{18}\text{Si}_{26}\text{N}_{50}\text{O}_{10}$. **T** should have a tetrahedral configuration, which is really unlikely for both nitrogen and oxygen, so anion **T** should have the formula SiX_4^{n-} (X might be different). As we need to have two identical monoatomic anions, which cannot be obtained from one atom of nitrogen, **T** = $\text{SiO}_3\text{N}^{5-}$, **S** = O^{2-} . So, the final answer is **10** = $\text{La}_5\text{Ca}_9(\text{O})_2(\text{NSiO}_3)[\text{Si}_{12}\text{N}_{24}]$.

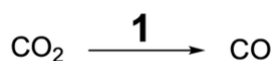
for **7, 8, 9**: 3 pt each (for **9** = Li_3N 1 pt);

for **10**: 4 pt if both **S** and **T** are emphasised, 2 pt for empirical formula.

T8. Recycling of Carbon Dioxide

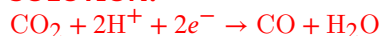
7%										
8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10	Σ
2	16	2	29	5	10	2	4	12	2	84

Removing CO₂ gas from the atmosphere is key to combat climate change. One promising solution is the photocatalytic reduction of CO₂ to CO using molecular catalyst **1**.



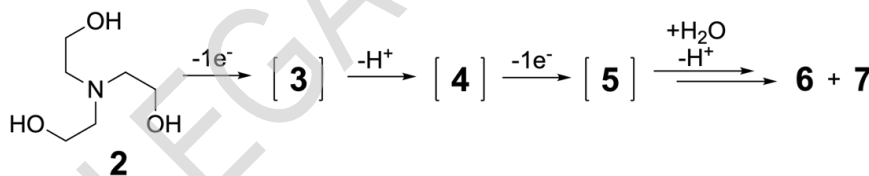
8.1 Write the half equation for the reduction of CO₂ to CO in an acidic medium. 2.0 pt

SOLUTION:



2 points for a fully correct reaction equation.

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



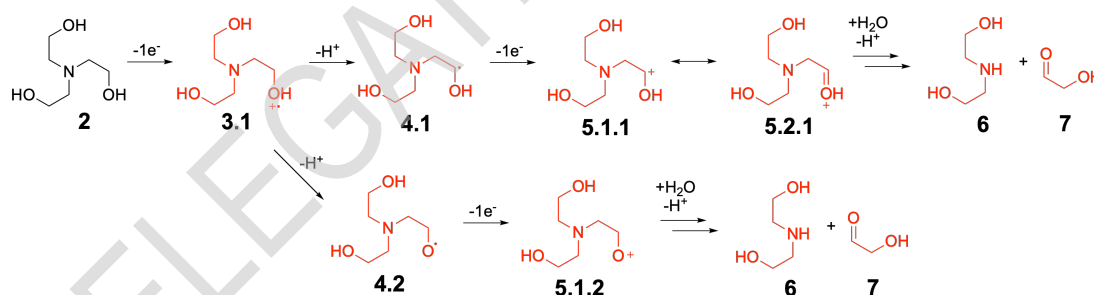
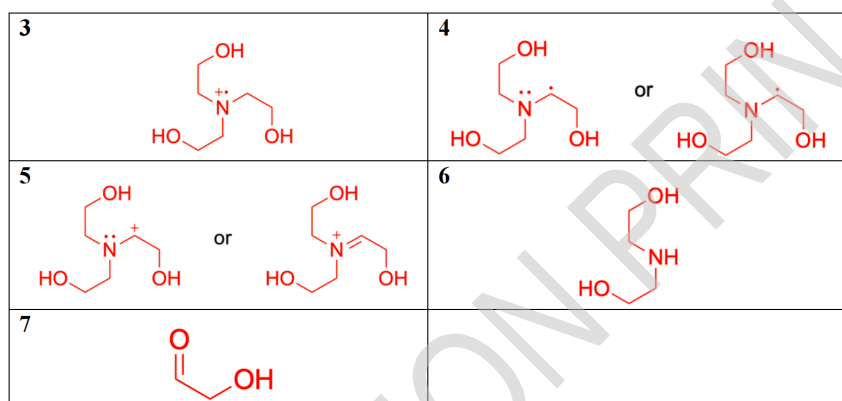
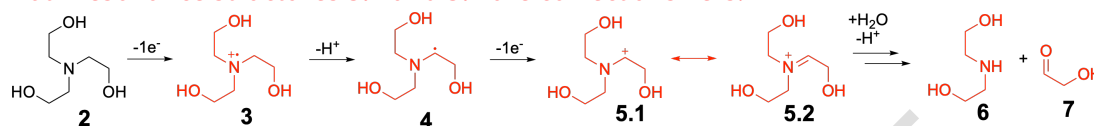
Species **3**, **4**, and **5** are short-lived ionic and radical intermediates. **7** yields a silver mirror with the [Ag(NH₃)₂]OH test.

8.2 Draw the structures of 3-7.

16.0 pt

SOLUTION:

Both resonance structures 5.1 and 5.2 are correct answers.

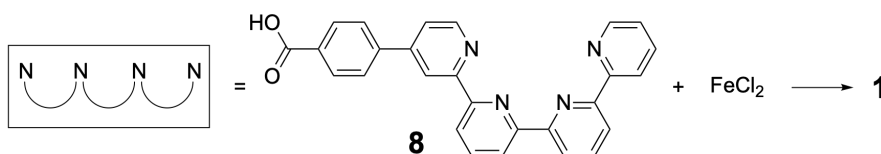


4 points for each correctly drawn structure of 3, 4, and 5.1 or 5.2.

2 points for each correctly drawn structure of 6 and 7.

Half of the marks will be given for the alternative reasonable structures, as shown above.

Catalyst 1 can be synthesised with the following reaction.

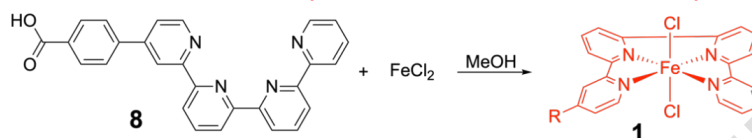


8.3 **Tick** the correct geometry for the structure of **1**.

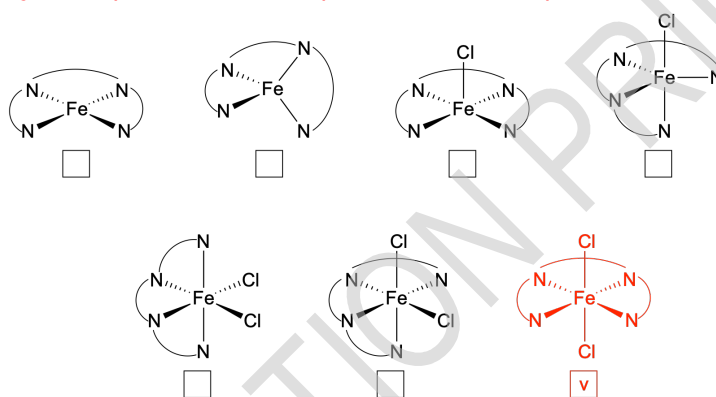
2.0 pt

SOLUTION:

The pyridine donor groups are planar in ligand **8**, thus, the final configuration of ligand **8** should also be in one plane around the metal in complex **1**.



There is only one option that corresponds to this complex.



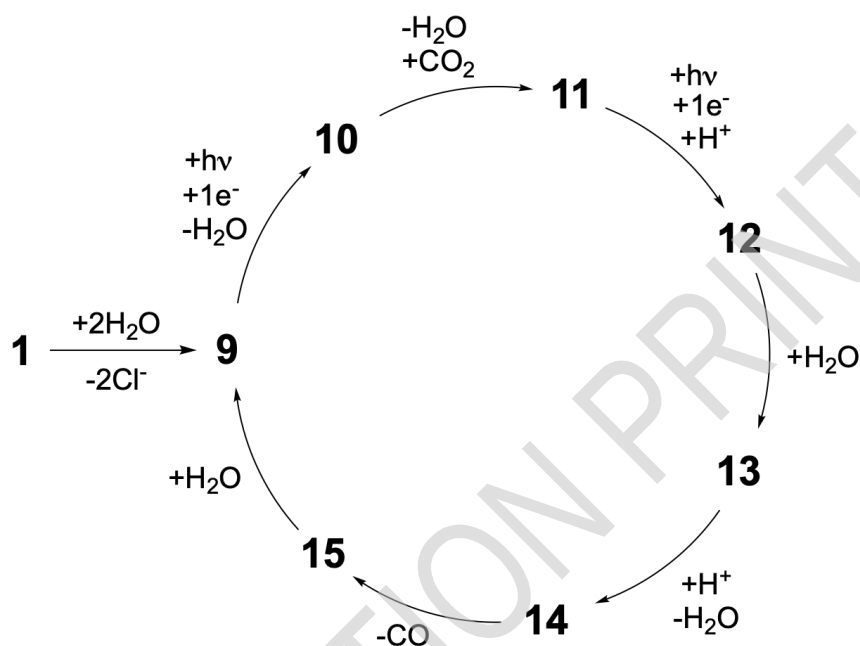
2 points for the only correct answer.

Theory

Q8-4

English (Official)

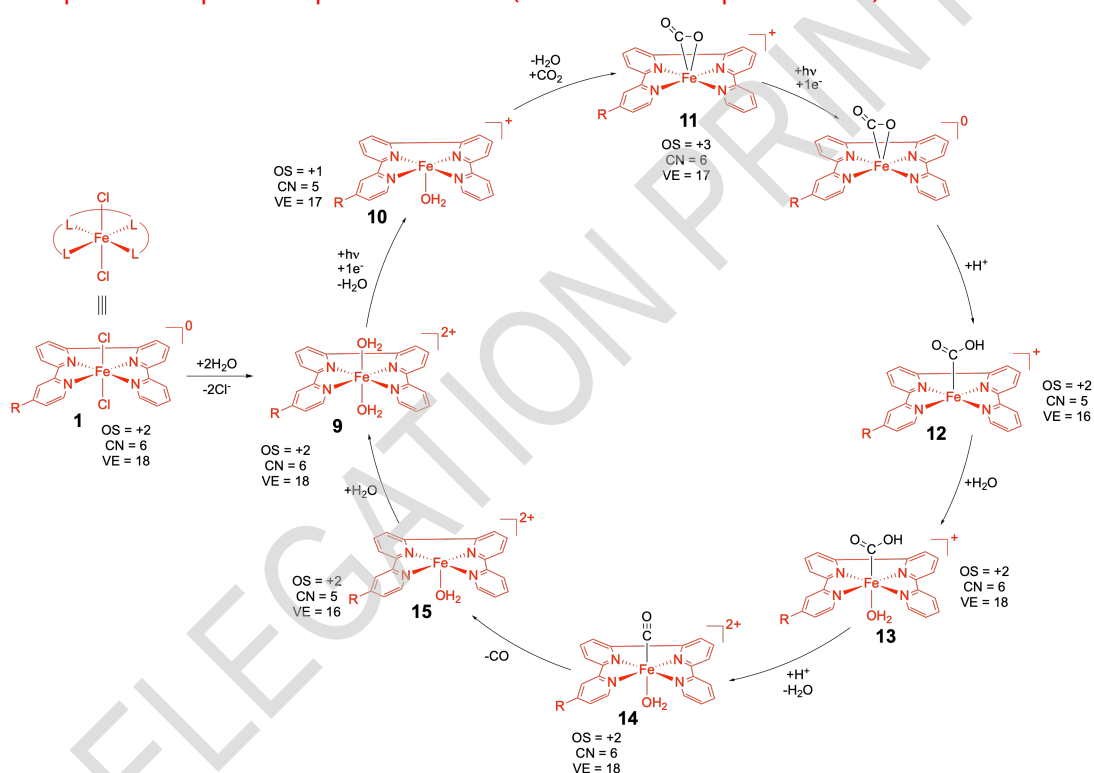
When **1** is loaded on crystalline carbon nitride (C_3N_4) support material, it can reduce CO_2 via the following mechanism.



- 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.

SOLUTION:

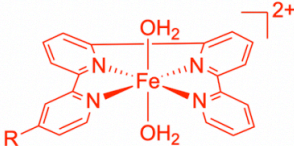
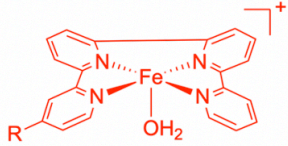
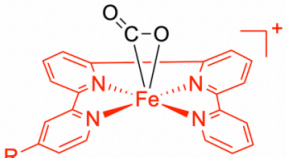
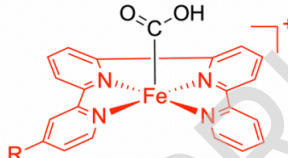
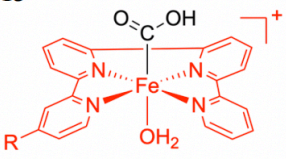
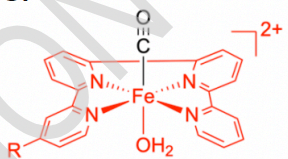
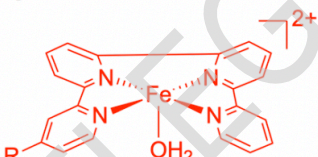
The catalytic cycle is presented below. In this part of the task, the arrangement of ligand **8** is not graded as long as it corresponds to the one around the metal complex in the previous part of the task (to avoid double punishment).



For each correct OS, CN, and VE: 0.5 points.

For each correctly drawn structure of **9-15**: 3 points.

-0.5 points for each structure (**9-15**) in which the total charge is not correct.

9  OS = +2 CN = 6 VE = 18 Z = +2	10  OS = +1 CN = 5 VE = 17 Z = +1
11  OS = +3 CN = 6 VE = 17 Z = +1	12  OS = +2 CN = 5 VE = 16 Z = +1
13  OS = +2 CN = 6 VE = 18 Z = +1	14  OS = +2 CN = 6 VE = 18 Z = +2
15  OS = +2 CN = 5 VE = 16 Z = +2	

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

SOLUTION:

In 1 nm^2 there is $\frac{1}{17.8 \times 10^{18}} = 5.618 \times 10^{-20} \text{ g C}_3\text{N}_4$. The catalytic loading formula is $\frac{m_{\text{cat}}}{m_{\text{cat}} + m_{\text{C}_3\text{N}_4}} \times 100\% = 3.8\%$. If we find m_{cat} from here it will be $m_{\text{cat}} = 2.219 \times 10^{-21} \text{ g}$.

The molar mass of catalyst is $557.21 \text{ g mol}^{-1} \rightarrow N = \frac{2.219 \times 10^{-21}}{557.21} \times 6.02 \times 10^{23} = 2.4$.

3 points for using the specific surface area of $17.8 \text{ m}^2 \text{ g}^{-1}$ for the $\text{C}_3\text{N}_4/\mathbf{1}$ mixture and, calculating N_{cat} as 2.3.

5 points for the correct N_{cat} value.

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

The formula for calculating the quantum yield is given below:

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

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

SOLUTION:

$$\frac{m_{\mathbf{1},\text{cat}}}{m_{\mathbf{1},\text{cat}} + 0.01} \times 100\% = 3.8\% \rightarrow m_{\text{cat}} = 3.95 \times 10^{-4} \text{ g}.$$

$$n = \frac{3.95 \times 10^{-4}}{557.21} = 7.089 \times 10^{-7} \text{ mol}.$$

$$r_{\text{CO}} = \frac{7.089 \times 10^{-7} \times 8 \times 6.02 \times 10^{23}}{3600} = 9.48 \times 10^{14} \text{ s}^{-1}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = 5.1 \times 10^{-19} \text{ J}$$

$$r_{\text{photon}} = \frac{50 \times 10^{-3}}{5.1 \times 10^{-19}} = 9.8 \times 10^{16} \text{ s}^{-1}$$

$$\varphi = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \cdot 100\% = \frac{r_{\text{CO}} \cdot 2}{r_{\text{photon}}} \cdot 100\% \quad (\text{eq.8.6.1})$$

$$\varphi = \frac{9.48 \times 10^{14} \times 2}{9.8 \times 10^{16}} \cdot 100\% = 1.94\%$$

2 points for r_{CO} value.

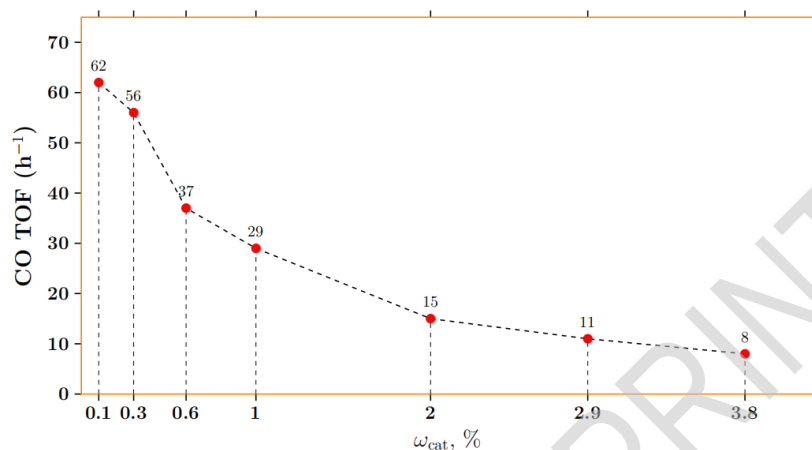
2 point for E_{photon} value.

2 point for the correct photon flux r_{photon} .

2 points for eq.8.6.1.

2 point for the correct φ value.

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



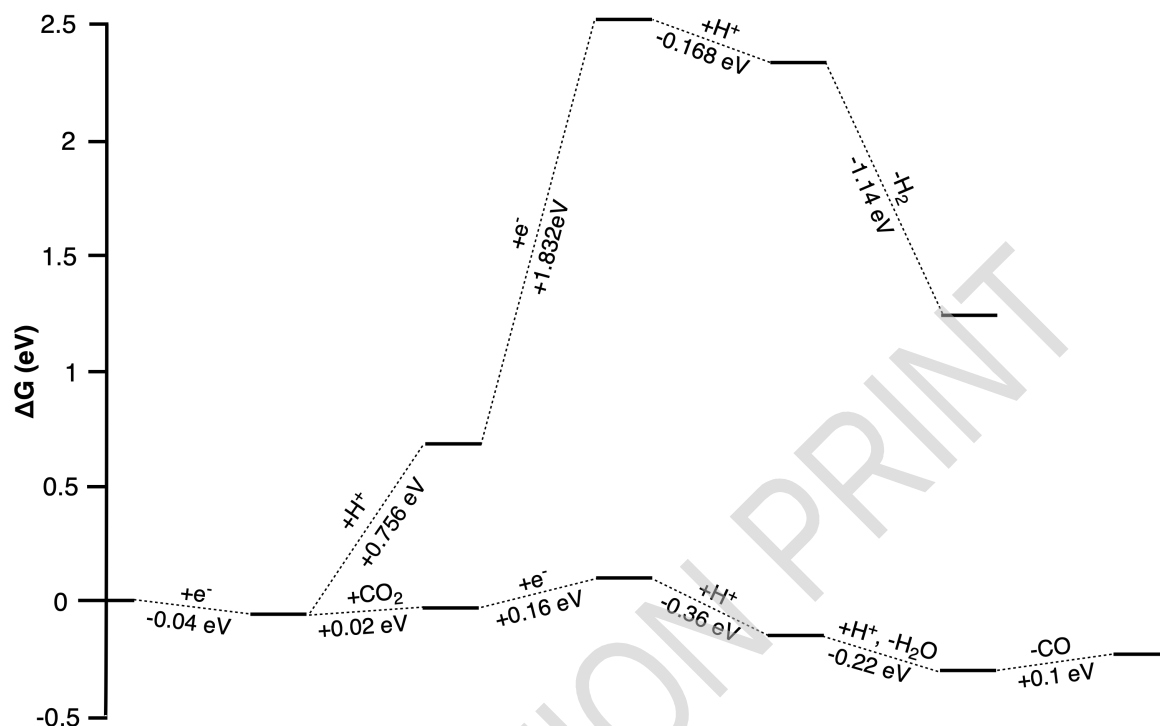
8.7 How does the overall rate of CO formation per gram of C_3N_4 loaded with **1** 2.0 pt change with increasing ω_{cat} ? Tick the correct box.

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

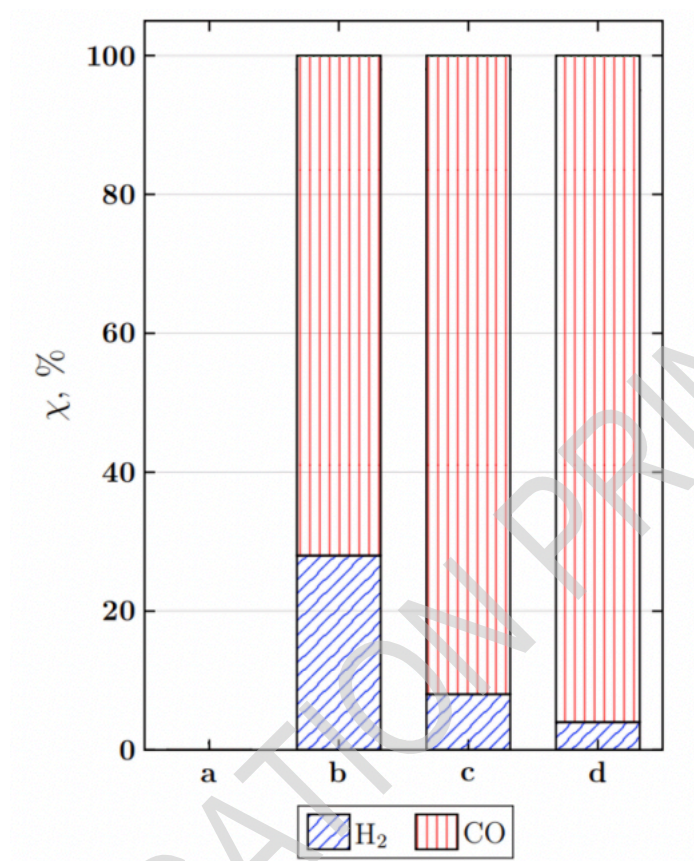
SOLUTION:

a	b	c
x		

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 H₂ and CO produced during the reduction of CO₂ 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

SOLUTION:

	N	R	G	B
a	×			
b				×
c			×	
d		×		

1 point for each correct tick

-1 point for each incorrect tick

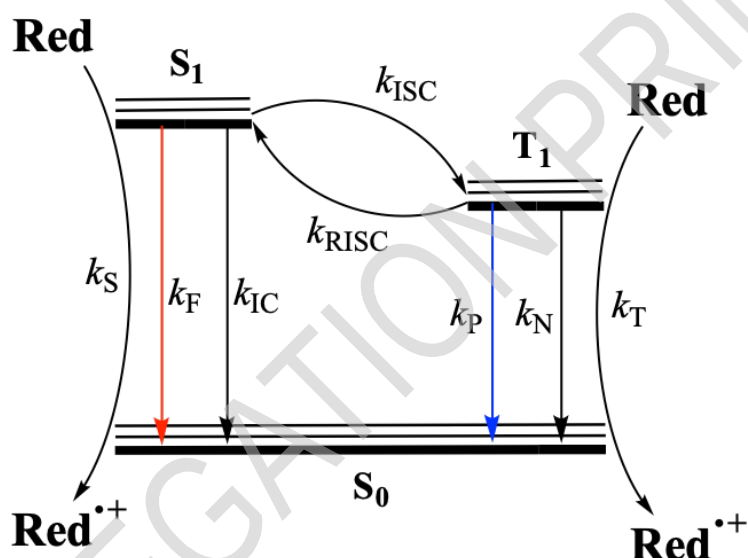
The overall score for this part will not be negative.

Theory

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 $\text{PS}^{\bullet-}$, which donates electrons to CO_2 through the Mn(I)-containing complex.



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



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

- 8.9 Calculate** the percentage of quenching, η_q , (in %) of **S₁** and **T₁** states, when [Red] = 0.1 M. Note: here $k_F \gg k_{ISC}$. 12.0 pt

SOLUTION:

The decay process of the S₁ excited state can be represented by the following equation:

$$-\frac{d[S_1]}{dt} = (k_F + k_{IC} + k_{ISC}) \times [S_1] \approx (k_F + k_{IC}) \times [S_1] \quad (\text{eq.8.10.1})$$

According to the formula for the lifetime of the reagent in a 1st order reaction

$$\Rightarrow \tau_0 = \frac{1}{k_F + k_{IC}}$$

The decay process of the T₁ excited state can be represented by the following equation:

$$-\frac{d[T_1]}{dt} = (k_P + k_N + k_{ISC}) \times [T_1] \Rightarrow \tau_0 = \frac{1}{k_P + k_N + k_{ISC}} \quad (\text{eq.8.10.2})$$

In the presence of the Red, S₁ is reductively quenched by Red, and the fraction of quenched molecules is as follows:

$$\eta_q = \frac{k_S[S_1][Red]}{(k_F + k_{IC})[S_1] + k_S[S_1][Red]} = \frac{k_S\tau_0[Red]}{1 + k_S\tau_0[Red]} \quad (\text{eq.8.10.3})$$

$$\eta_q = \frac{2.7 \times 10^9 \times 2.9 \times 10^{-9} \times 0.1}{1 + 2.7 \times 10^9 \times 2.9 \times 10^{-9} \times 0.1} = 0.44 \text{ (or 44\%)}$$

In the presence of the Red, T₁ is reductively quenched by it and fraction of quenched molecules as follows:

$$\eta_q = \frac{k_T[T_1][Red]}{(k_P + k_N + k_{ISC})[T_1] + k_T[T_1][Red]} = \frac{k_T\tau_0[Red]}{1 + k_T\tau_0[Red]} \quad (\text{eq.8.10.4})$$

$$\eta_q = \frac{1.5 \times 10^8 \times 84 \times 10^{-6} \times 0.1}{1 + 1.5 \times 10^8 \times 84 \times 10^{-6} \times 0.1} = 0.999 \text{ (or 99.9\%)}$$

2 points for each correctly derived equations 8.10.1-8.10.4.

2 points for each correct η_q value.

- 8.10 How** do the emission lifetimes of **S₁** and **T₁** states change when [Red] increases? 2.0 pt
Tick the correct box.

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

SOLUTION:

After quenching of the PS, the following equation is derived:

$$-\frac{d[S_1]}{dt} = (k_F + k_{IC} + k_S \times [Red]) \times [S_1] \Rightarrow \tau = \frac{1}{k_F + k_{IC} + k_S \times [Red]}$$

As the concentration of [Red] increases, τ decreases accordingly.

a	b	c
	×	

T9. Cyclodextrin Chemistry

7%									
9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9	Σ
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.

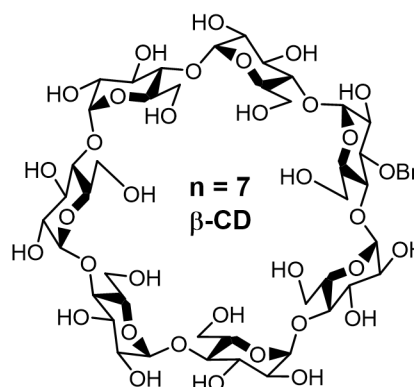
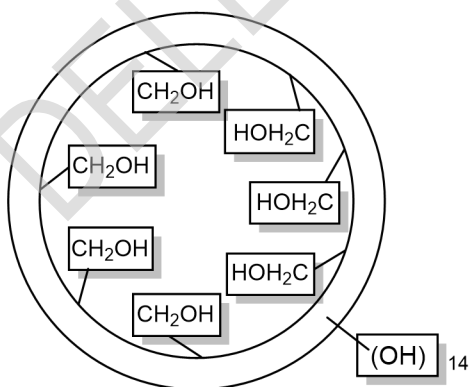
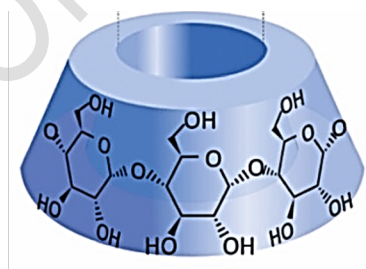
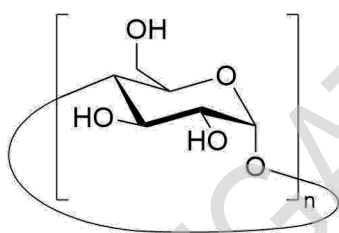
9.1 Calculate the molar mass of β -CD. Assume $M_w(\text{glucose}) = 180.16 \text{ g mol}^{-1}$. 2.0 pt

SOLUTION:

$$M_w(\beta - \text{Cyclodextrin}) = 180.16 \cdot 7 - 18.016 \cdot 7 = 1135.01 \text{ g/mol}$$

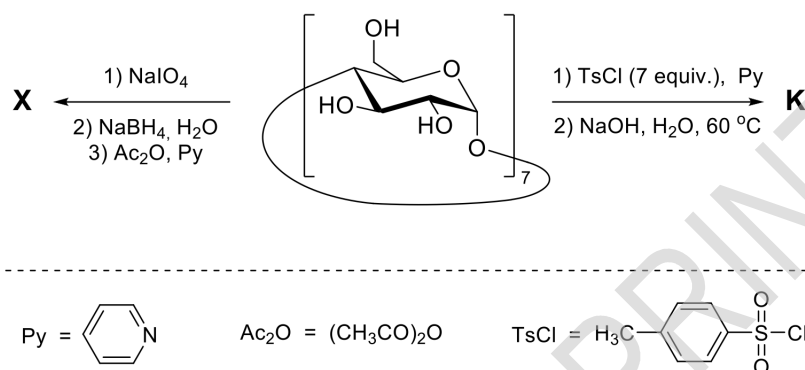
Mw: β -CD = 1135.01 g/mol

2 points



Theory

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.

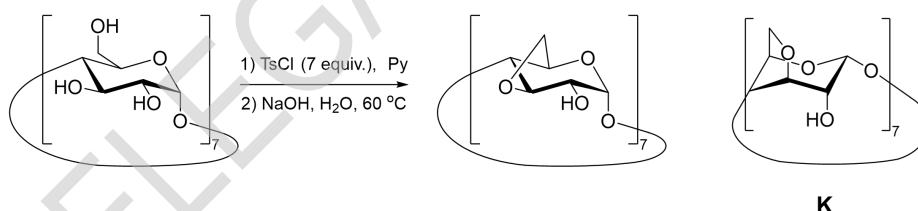


equiv.= equivalent

- 9.2** Tick the favorable chair conformation and draw the structure of **K** by completing the CD template. Show stereochemistry unambiguously. 6.0 pt

SOLUTION:

Since in this reaction we observe the formation of new ring on glucopyranose unit, the bridging atoms should be at axial positions. Therefore, the second conformation will be favoured.

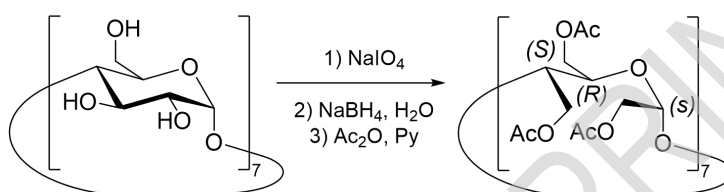


6 points for correct structure, -2 points for incorrect conformation, -1 point for each incorrect substituent/stereocentre, 0 if no new ring is formed.

9.3 **Determine** the ring size, rs , of macrocycle **X**. **Give** the number of stereocentres, sc , in **X**. 8.0 pt

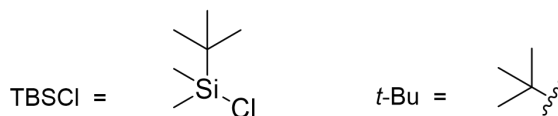
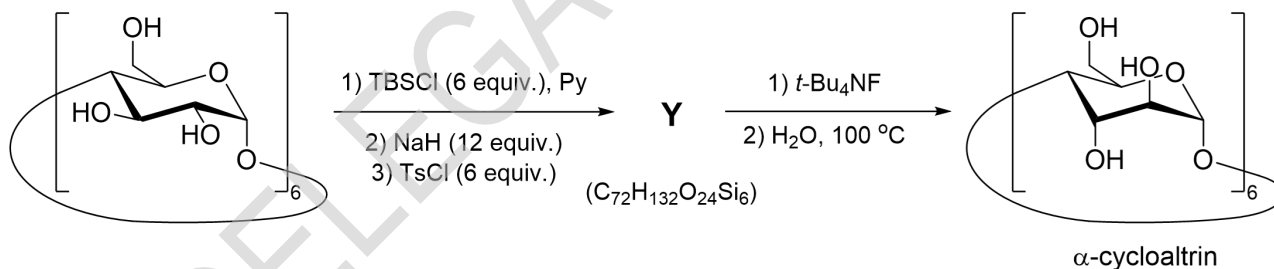
SOLUTION:

Cleavage of the diol results in reduction of the number of asymmetric atoms in the glucopyranose unit down to three, one of which (the acetal) is pseudo-chiral. Overall, the macrocycle becomes achiral since it consists of *meso*-butanetetrol/glycolaldehyde acetal units. The number of atoms in the macrocyclic ring for each repeat unit is five.

 rs : 35 sc : 21

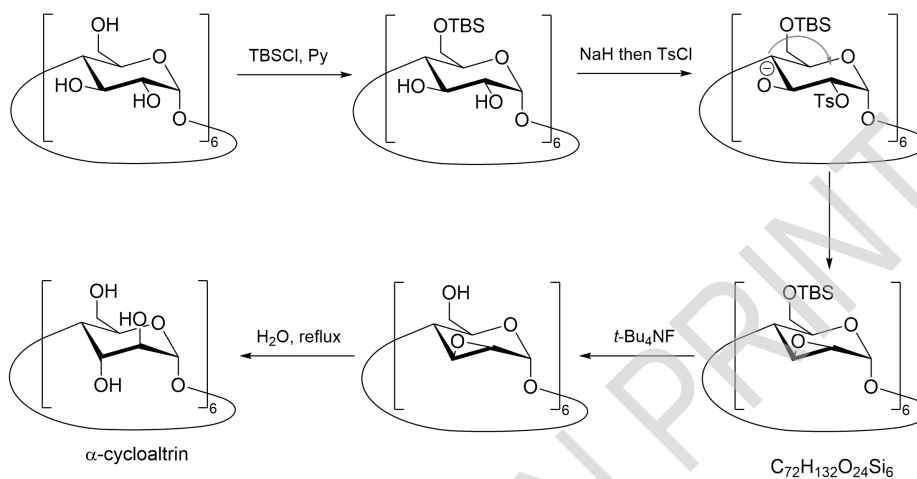
rs – 4 points; sc – 4 points; 4 points if $sc = 14$; 2 points if $sc = 3$ or 2;

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

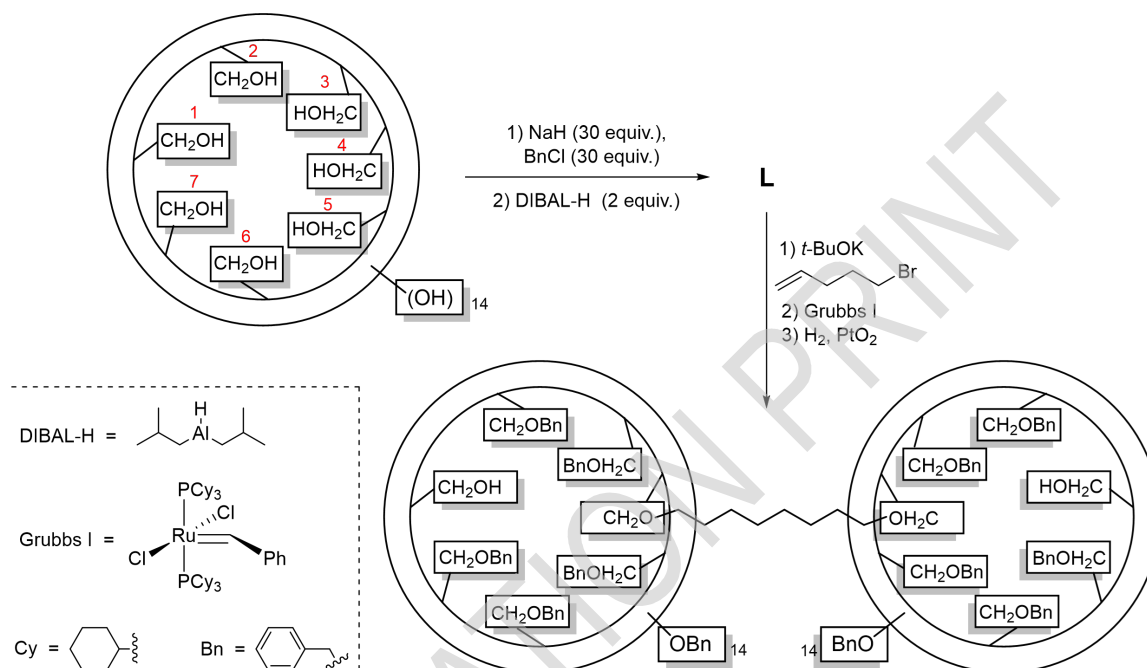
SOLUTION:



Correct structure 3 points. Epoxide with opposite configuration is also accepted; -1 point for any missing or incorrect substituent.

Theory

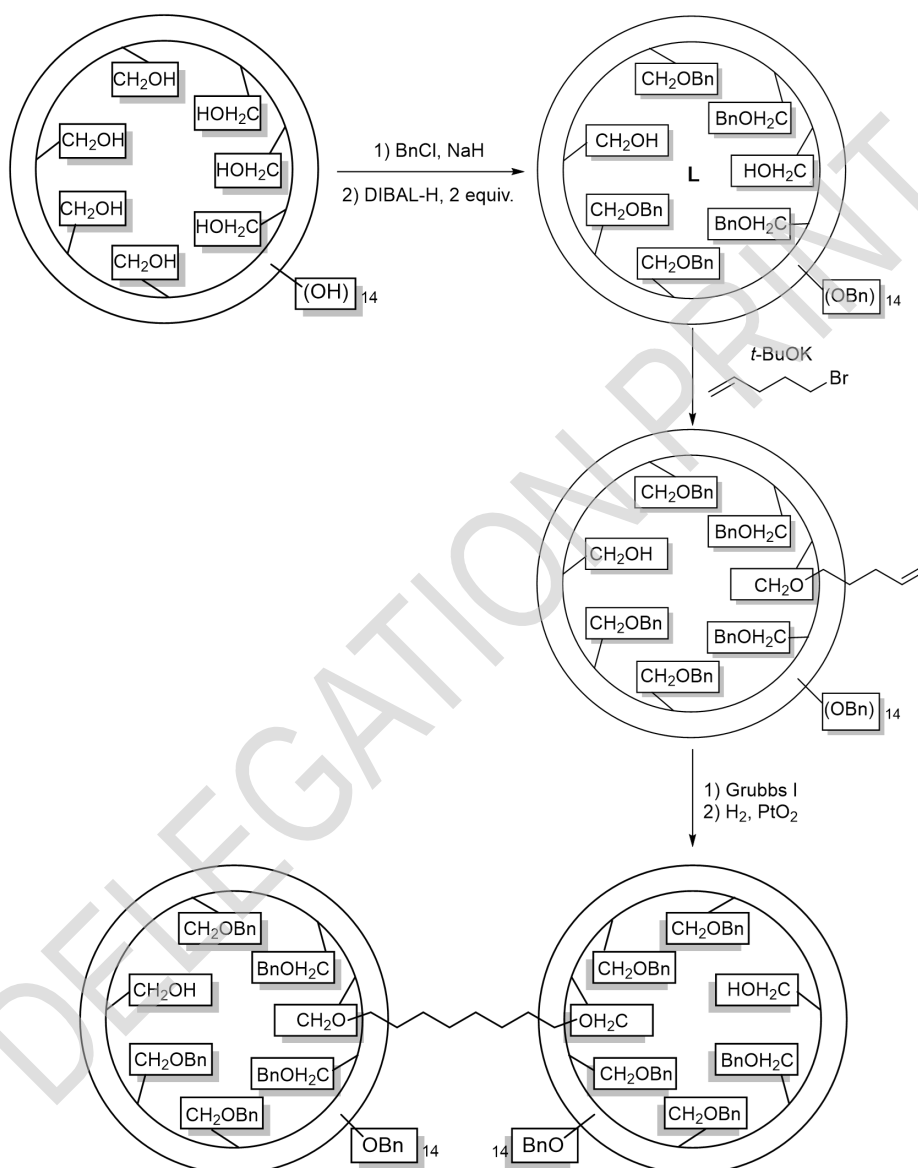
In 2000, Sinay *et al.* demonstrated that a single protic group (NH and OH) at unit 1 directs the **next** reductive debenzoylation of a primary OH group to unit 4 in the macrocyclic ring (or to unit 3 if the unit 4 position is not available). This allowed the synthesis of the following β -CD dimer as 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

SOLUTION:



Correct structure 2 points.

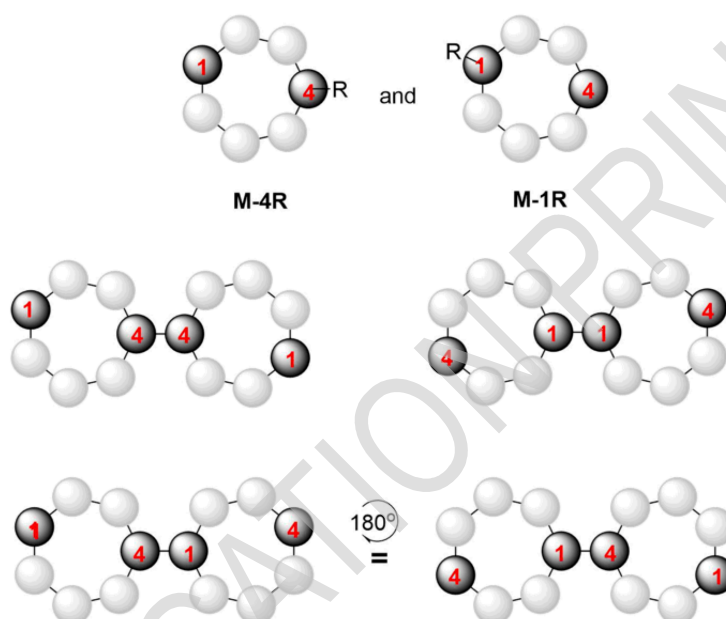
-1 p for each incorrect substituent

0 p if 2 or more incorrect substituents

- 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

SOLUTION:

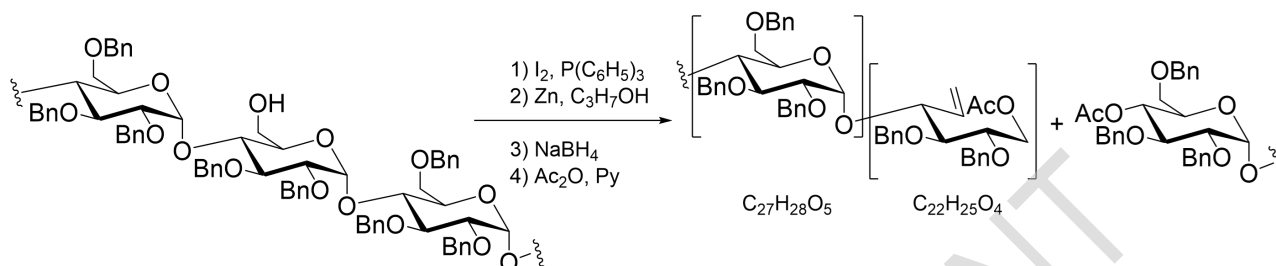
Due to β -CD consisting of seven units and being chiral, two regioisomers are formed in the alkylation reaction (**M-4R**, **M-1R**). Therefore, the dimer would have **three** isomers with following connections: 4-4, 1-1, 1-4. (Note 4-1 = 1-4)



Correct number of isomers 4 points.

Theory

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

SOLUTION:

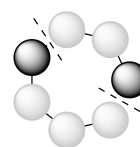
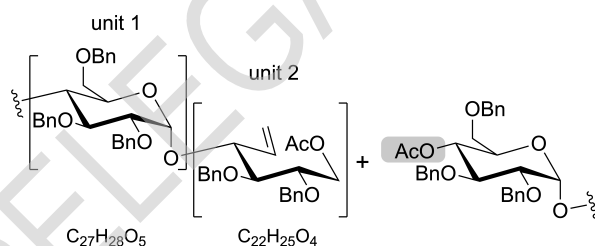
Since we know the chemical formula for the units, we can calculate molecular weights of the two products. Each product should have one unit 2 (black sphere) and 2-3 unit 1s (white sphere). Additionally, we should add $C_2H_3O_2$, which corresponds to the mass of the OAc group. Therefore:

$$M_1 : 2C_{27}H_{28}O_5 + C_{22}H_{25}O_4 + C_2H_3O_2 = C_{78}H_{84}O_{16}$$

$$[M_1 + Na]^+ = 1299$$

$$M_2 : 3C_{27}H_{28}O_5 + C_{22}H_{25}O_4 + C_2H_3O_2 = C_{105}H_{112}O_{21}$$

$$[M_2 + Na]^+ = 1731$$



$$[M_1 + Na]^+ = \underline{1299}$$

$$[M_2 + Na]^+ = \underline{1731}$$

Each correct answer 3 points, total – 6 points

m/z without Na^+ 1p each

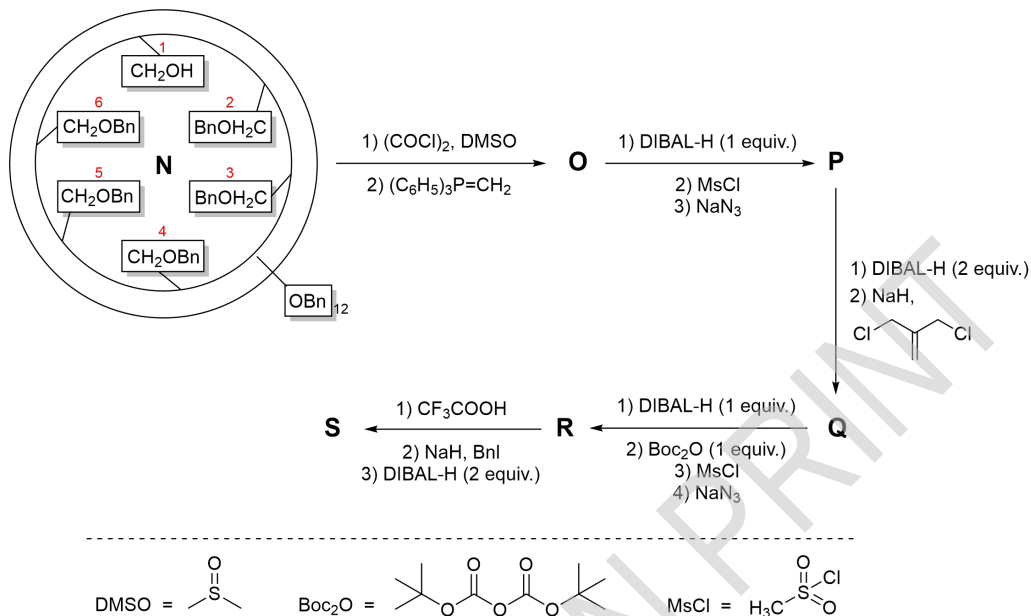
m/z without $C_2H_2O_2$ 1p each

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**:

Theory

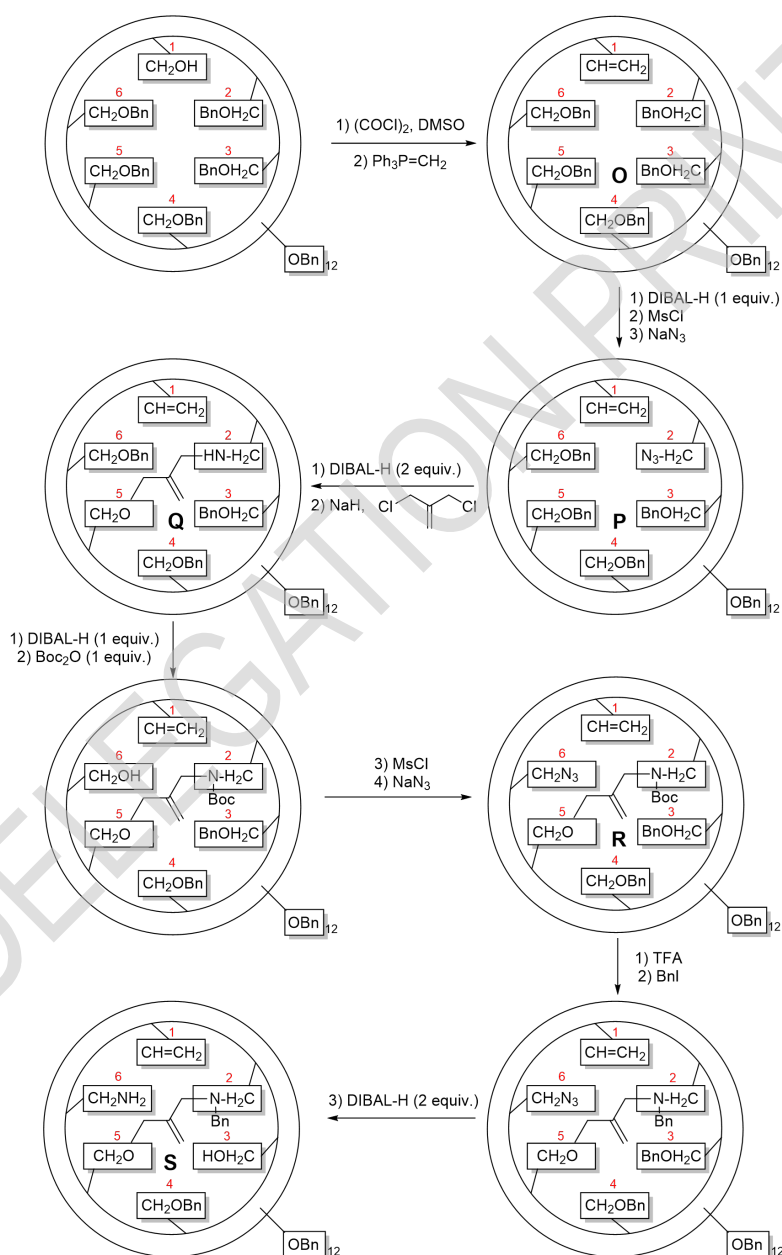
Q9-9

English (Official)



- 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**

SOLUTION:

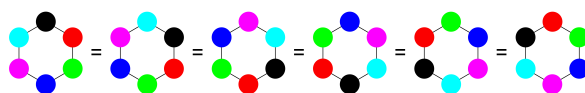


O - 2 points, **P-S** - 4 points, total 18 points. -1 point for incorrect or missing substituents for each structure. Mistakes carried over will be ignored if following structures fit the functional group direction logic.

- 9.9 **Determine** the number of all possible arrangements of the functional groups on a hexadifferentiated α -CD (**assume** only the CH_2OH groups have been modified). 4.0 pt

SOLUTION:

If we have 6 linear positions for 6 coloured balls, the total number of arrangements will be $6! = 720$. But in α -CD, positions are in a circle, which makes all arrangements below equal. The correct answer $6!/6 = 120$.



Correct answer 4 points; if the answer 720 or 60– 2 points, if answer 320 - 1 point. All other answers - 0.