

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	$A = \log_{10} \frac{I_0}{I} = \varepsilon c l$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Heat and temperature change	$Q = nC_m \Delta T$
Gibbs energy definition	$G = H - TS$
Gibbs energy and equilibrium constant	$\Delta_r G^\circ = -RT \ln K$
Enthalpy change dependence on temperature (at $\Delta_r C_p = \text{const}$)	$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r C_p (T_2 - T_1)$
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

	Period																Group
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008	2 He 4.003	3 Li 6.94	4 Be 9.01									5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

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.

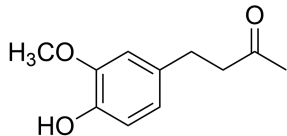
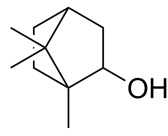
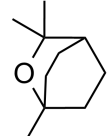
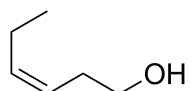
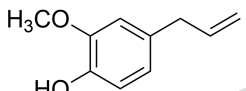
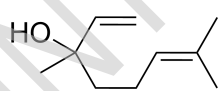
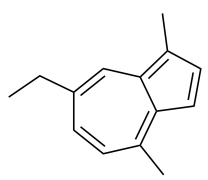
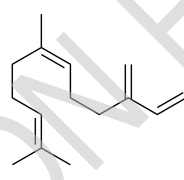
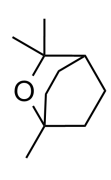
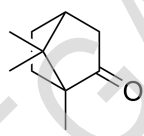
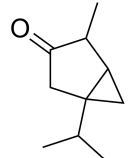
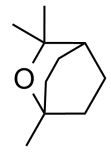
Part 1. The blue elixir

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

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

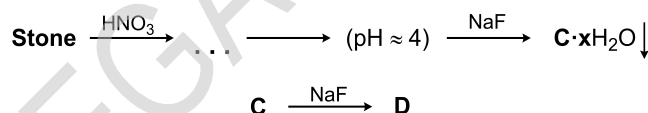
The chemist extracted **W** from the elixir. When **W** was added to an aqueous Fe^{3+} solution, a characteristic colour change was observed. Mass spectrometric analysis of **W** revealed the intensity ratio of $[M]^+ : [M + 1]^+ = 9:1$, where M is the molecular ion. Assume carbon consists exclusively 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

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

4.0 pt

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



1.5 Draw the structures of **E, **F**, and **G**.**

7.0 pt

Then, she analysed the **stone** thermogravimetrically in open air. A 10.00 g sample began to lose mass

Theory



Q1-4

English (Official)

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 |
|------------|--|--------|

DELEGATION PRINT

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

1.1 (3.0 pt)

X:

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

Y:

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

1.2 (4.0 pt)

Z:

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

Theory

1.2 (cont.)

A	B
----------	----------

1.3 (3.0 pt)

$n =$ _____

W:

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

1.4 (4.0 pt)

Q:

C · xH₂O:

D:

1.5 (7.0 pt)

E	F	G
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Theory



A1-5

English (Official)

1.6 (4.0 pt)

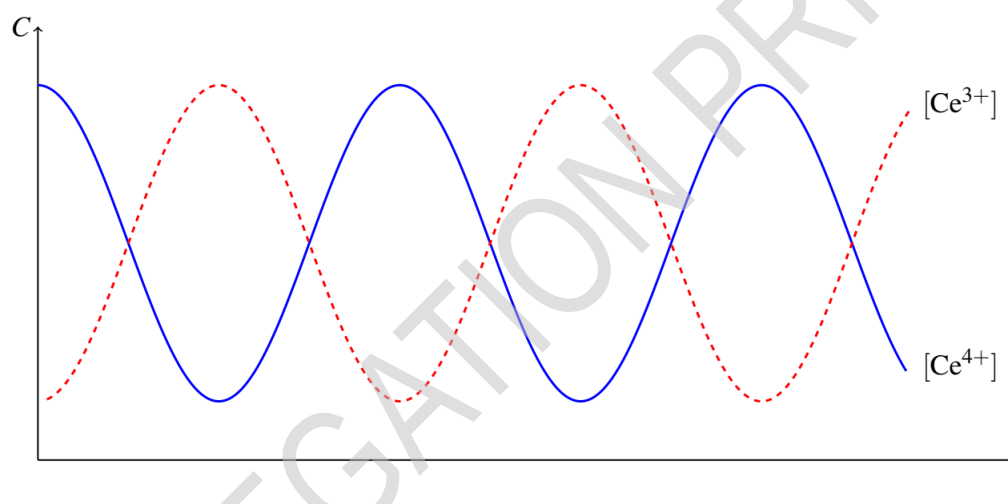
Stone :

H :

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

Theory

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

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

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

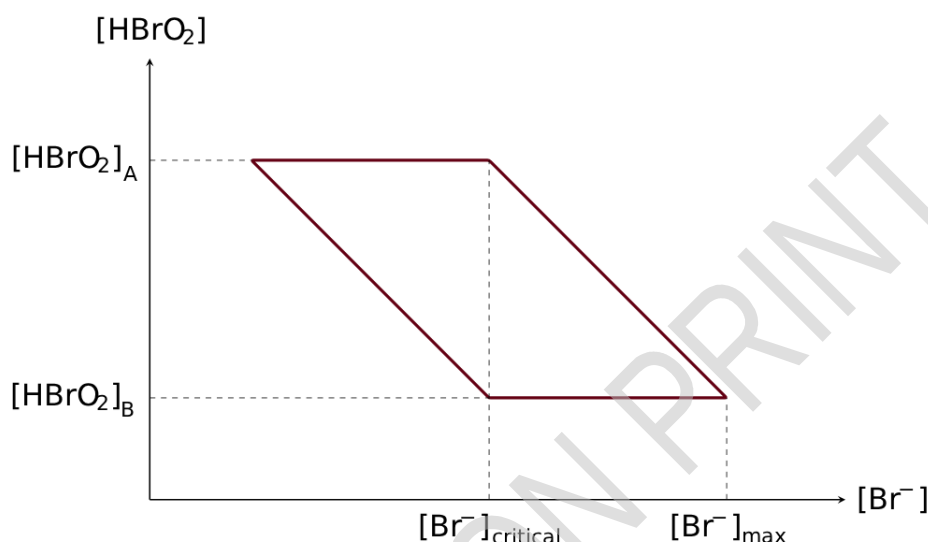
- when **Process A** occurs the solution is yellow and **Process B** practically does not occur;
- when **Process B** occurs the solution is colourless and **Process A** practically does not occur;
- $[\text{BrO}_3^-]_0 = 0.06 \text{ M}$, $[\text{MA}]_0 = 0.1 \text{ M}$, $[\text{H}^+]_0 = 0.8 \text{ M}$, $[\text{Ce}^{4+}]_0 = 0.001 \text{ M}$;
- 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

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

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

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

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

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

- 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

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

2.1 (2.0 pt)

2.2 (11.0 pt)

$[\text{HBrO}_2]_{\text{A}} = \text{_____ M}$

2.2 (cont.)

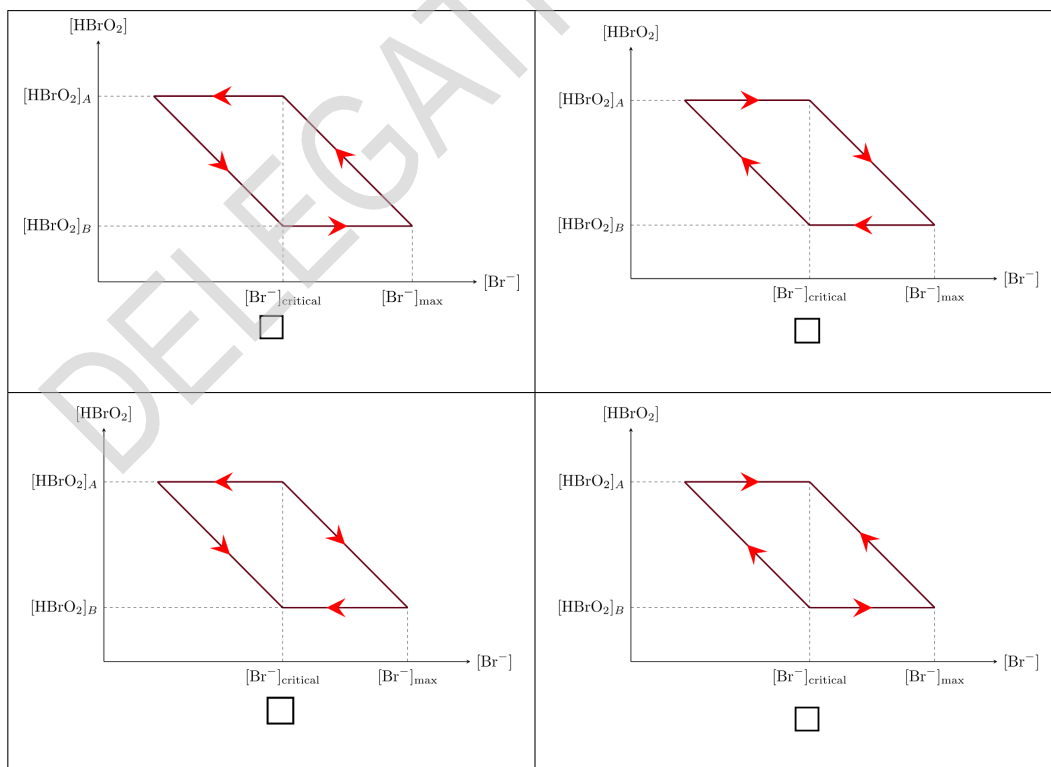
$[\text{HBrO}_2]_{\text{B}} = \text{_____} \text{ M}$

Theory

2.3 (4.0 pt)

$[\text{Br}^-]_{\text{critical}} = \underline{\hspace{2cm}} \text{ M}$

2.4 (2.0 pt)



2.5 (9.0 pt)

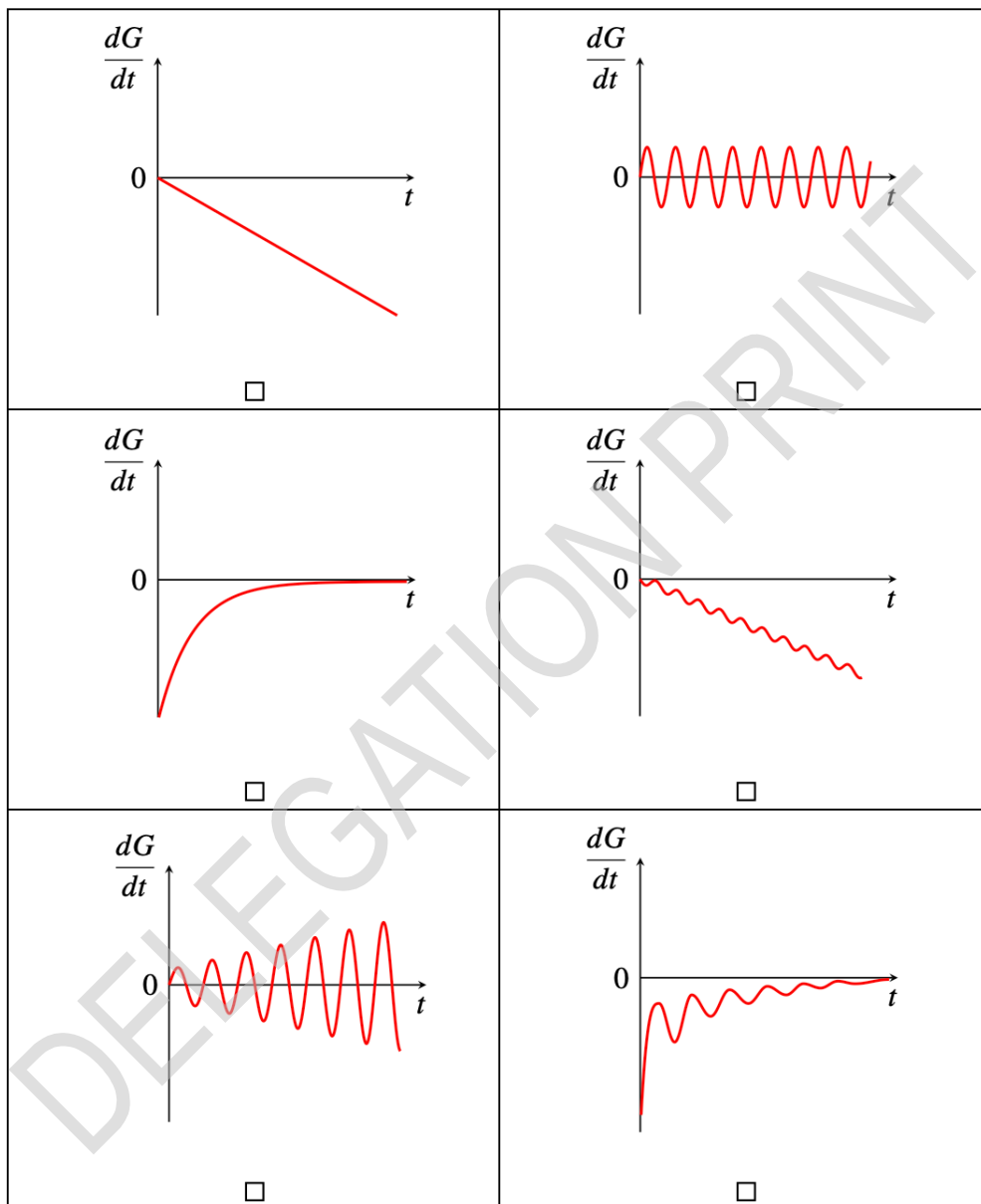
DELEGATION PRINT

$\tau =$ _____ s

2.6 (4.0 pt)

	a	b	c	d	e
1.	☐	☐	☐	☐	☐
2.	☐	☐	☐	☐	☐
3.	☐	☐	☐	☐	☐
4.	☐	☐	☐	☐	☐

2.7 (3.0 pt)

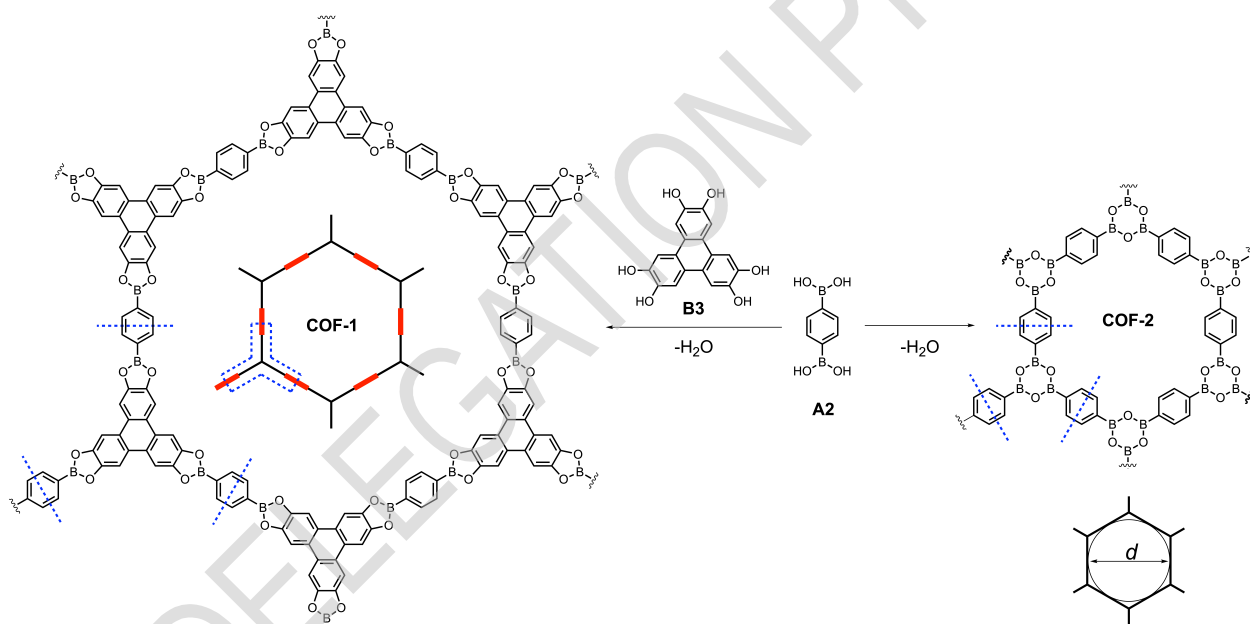


T3. Into Reticular Chemistry

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

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

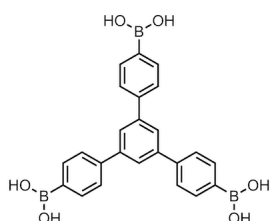
- C-C/C=C (arenes) = 1.39 Å
- C-B = 1.56 Å
- B-O = 1.38 Å
- Note, the diameter of a circle, d , inscribed inside a hexagon, is given by $d = \sqrt{3}a$, where a is the side length of the hexagon.
- Neglect the width of the linkers.

Theory

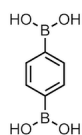
Q3-3

English (Official)

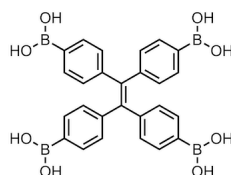
The structures shown below can form 2D and 3D COFs. For this question consider only formation of COFs with boronate esters, imines, and C=C bonds through condensation reactions. **A–D** represent compound classes with different functional groups.



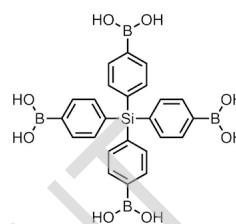
A1



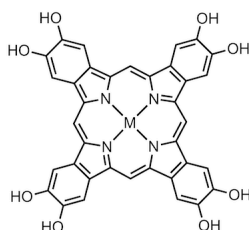
A2



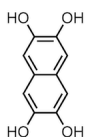
A3



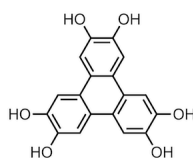
A4



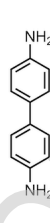
B1



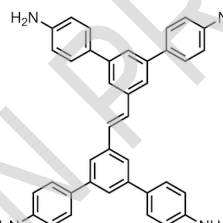
B2



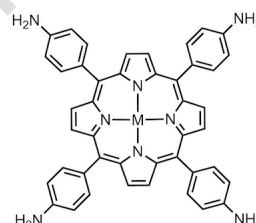
B3



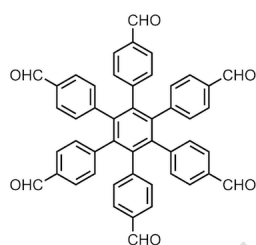
C1



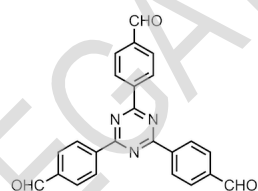
C2



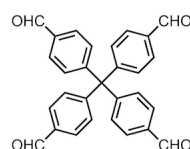
C3



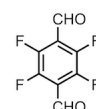
D1



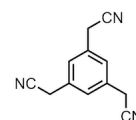
D2



D3



D4



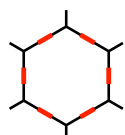
E1



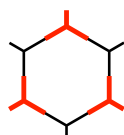
Tetragonal 1



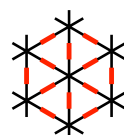
Tetragonal 2



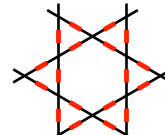
Hexagonal 1



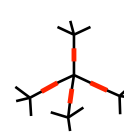
Hexagonal 2



Trigonal



Kagome



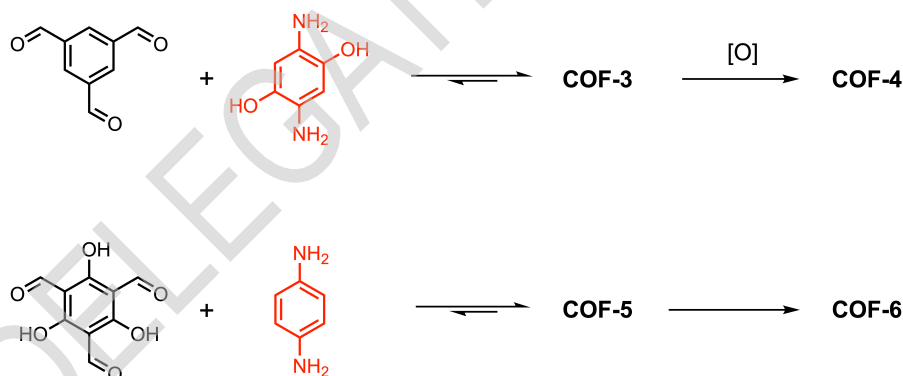
Tetrahedral

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

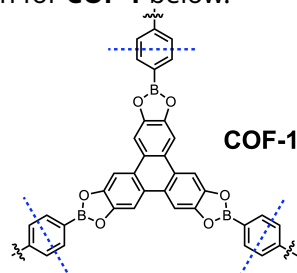
- 3.3** **Fill all the table** cells with either new examples of monomer combinations that give the topologies shown above or with "XXX" if you are certain that no additional combinations satisfy that topology. Both the combinations and the "XXX" entries will be graded. Incorrect answers (both combinations 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	

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.

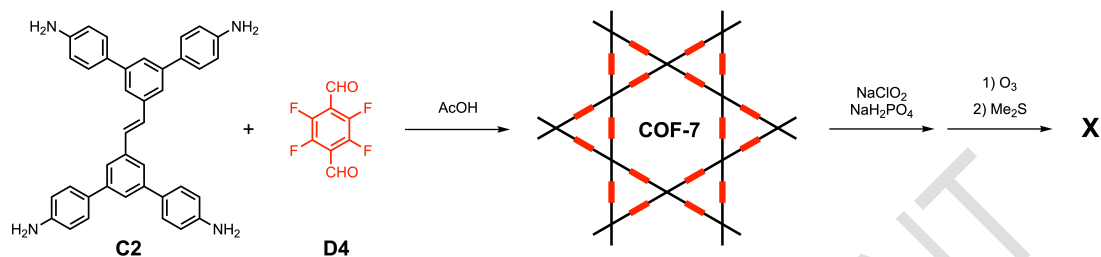


- 3.4** **Draw** the repeat units for **COFs 3-6**. **Indicate** the edges of each repeat unit with a dashed line as shown for **COF-1** below. 12.0 pt



Theory

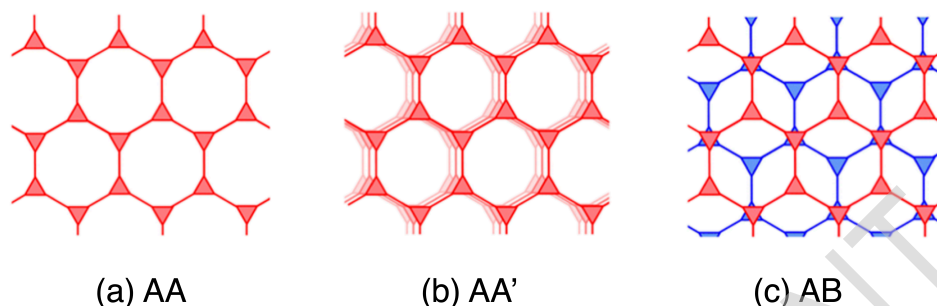
Macrocycle **X** was synthesised by post-synthetic modification of **COF-7** (**C2** + **D4**) followed by degradation.



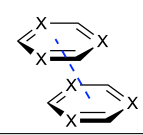
3.5 Draw the smallest repeat unit of macrocycle **X**.

6.0 pt

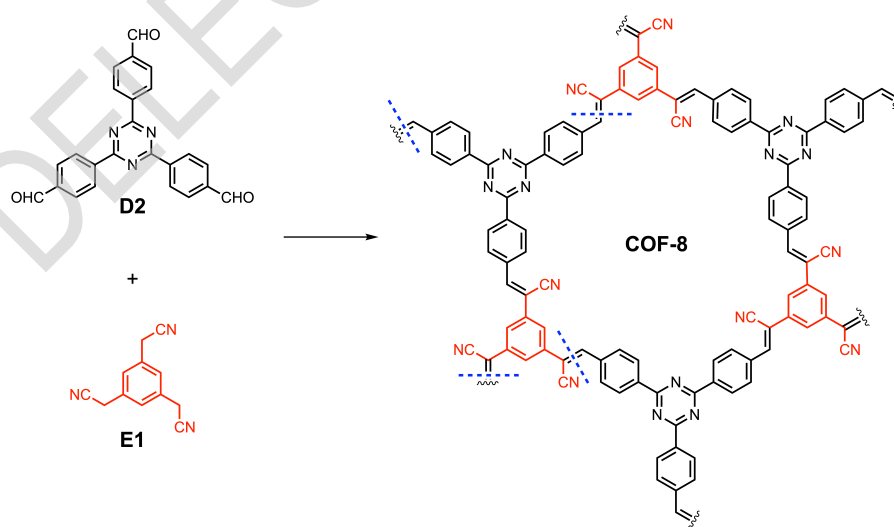
π - π interactions result in different stacking modes of COF layers, some of which are shown below.



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

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

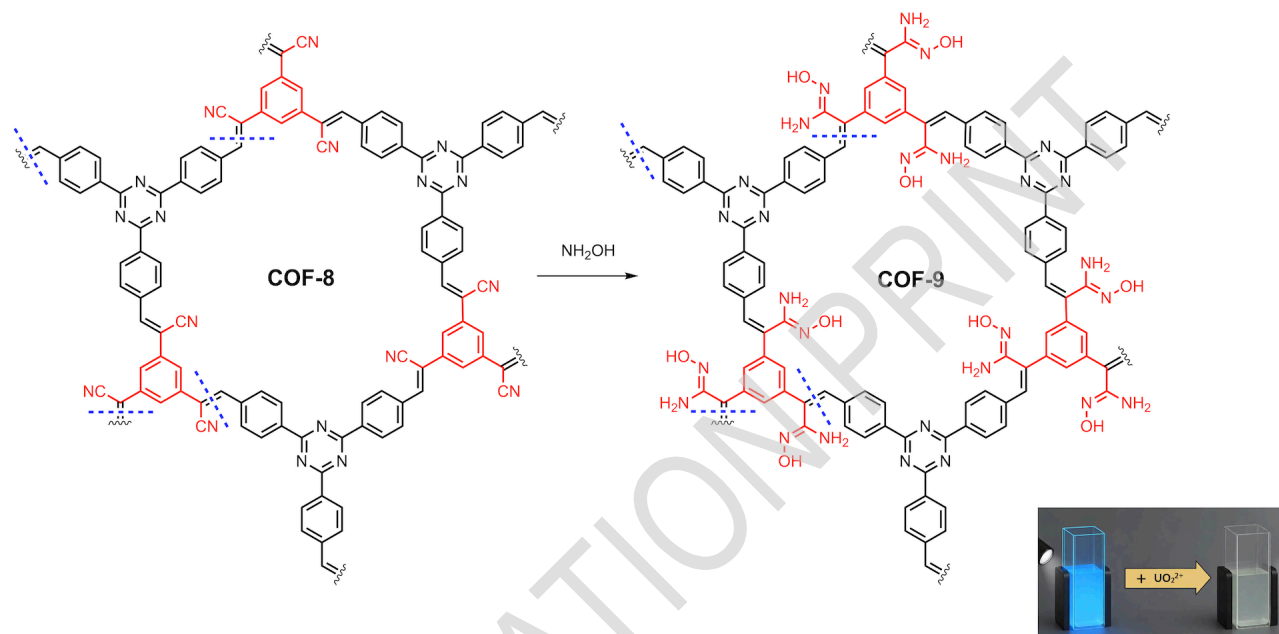
COF-8, synthesised from (**E1** + **D2**), is notable for its remarkable stability. The **AA'** slightly shifted mode of a **COF-8** bilayer has a π - π stacking interaction energy of $-67.1 \text{ kJ mol}^{-1}$ between two layers of one repeat unit.



- 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

Theory

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.

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

3.1 (2.0 pt)

COF-1: _____

C: _____ %

3.2 (3.0 pt)

d = _____ Å

Theory

3.3 (23.0 pt)

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetrahe- dral
		A2 + B3	E1 + D2		C2 + D4	

3.4 (12.0 pt)

COF-3	COF-4
COF-5	COF-6

3.5 (6.0 pt)

3.6 (12.0 pt)

$E, \text{kJ mol}^{-1}$	AA	AA'	AB	AB'
		-67.1		

3.7 (5.0 pt)

$q_e =$ _____ mg g^{-1}

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

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

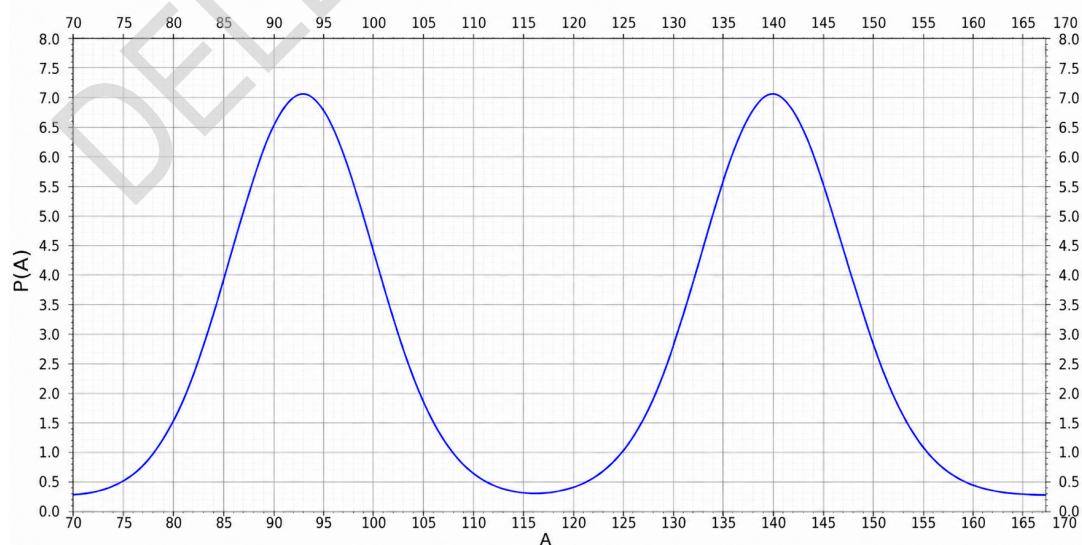
The main reaction occurring in nuclear power plants is the reaction where ^{235}U absorbs a neutron and undergoes fission, releasing energy and producing three additional neutrons, thus sustaining a chain reaction.



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

- Reaction of ^{11}B with α -particles inside the reactor core
- Interaction of γ rays with ^2D nuclei present in the reactor coolant water
- Reaction of ^9Be 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



Theory

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

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

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

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

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

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

Theory

Q4-3

English (Official)

- 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

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

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 $\Delta E = 200 \text{ MeV}$.

T4. The nuclear past of Uzbekistan

6% of total									
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

4.1 (2.0 pt) ^{235}U : _____%**4.2** (3.0 pt)

(a) :

(b) :

(c) :

4.3 (3.0 pt)

Theory



A4-2

English (Official)

4.4 (2.0 pt)

ΔE : _____ MeV

4.5 (2.0 pt)

n_c : _____

4.6 (2.0 pt)

$\Delta_r H_{298} =$ _____ kJ mol^{-1}

Theory

4.7 (2.0 pt)

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

4.8 (2.0 pt)

$$E = \text{_____} \text{ J day}^{-1}$$

Theory

4.9 (4.0 pt)

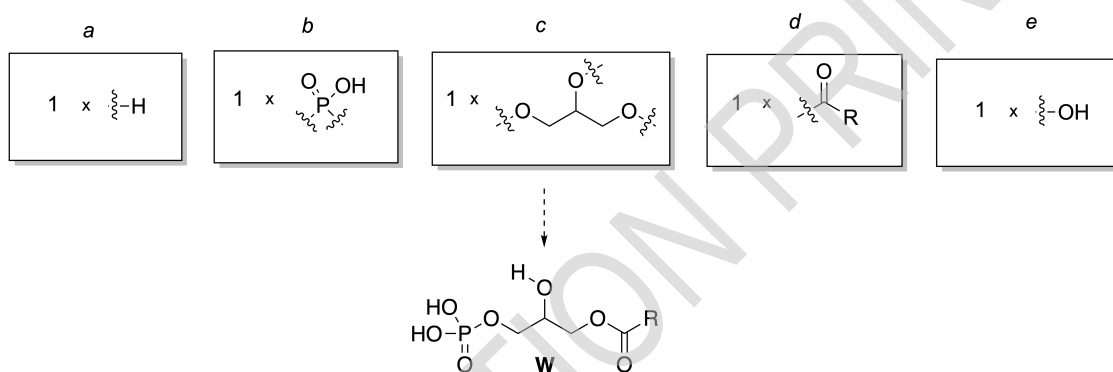
$TN =$ _____

$m =$ _____ kg

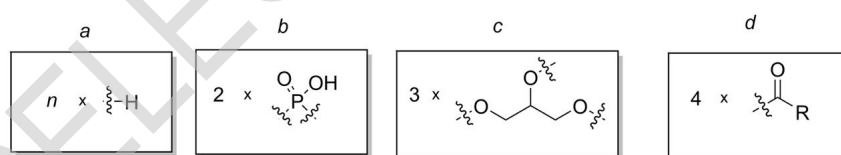
T5. Cardiolipins

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.

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

DELEGATION PRINT

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

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

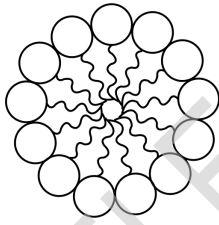
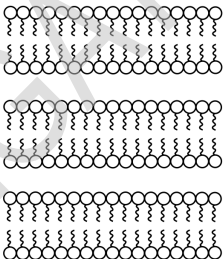
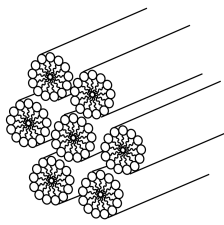
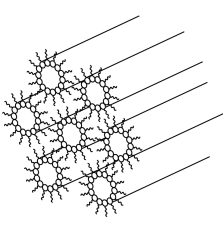
*If you were unable to find the structural formula of **PL1**, you can use a-d fragments from 5.1.*

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

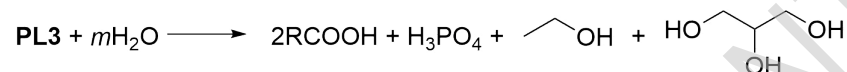
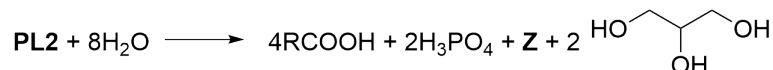
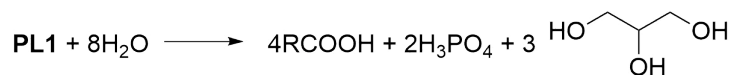
- 5.4** **Determine** the molecular formula of **X**. **Support** your answer with calculations. 2.0 pt

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

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

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

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. 3.0 pt
Show stereochemistry where appropriate.

T5. Cardiolipins

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

5.1 (1.0 pt)

(a)	(b)	(c)

5.2 (6.0 pt)

PL1

Y

Theory

5.3 (4.0 pt)

$N_{C=C} =$

RCOOH : _____

5.4 (2.0 pt)

X:

5.5 (2.0 pt)

(a)	(b)	(c)	(d)

5.6 (3.0 pt)

PL2

PL3

DELEGATION PRINT

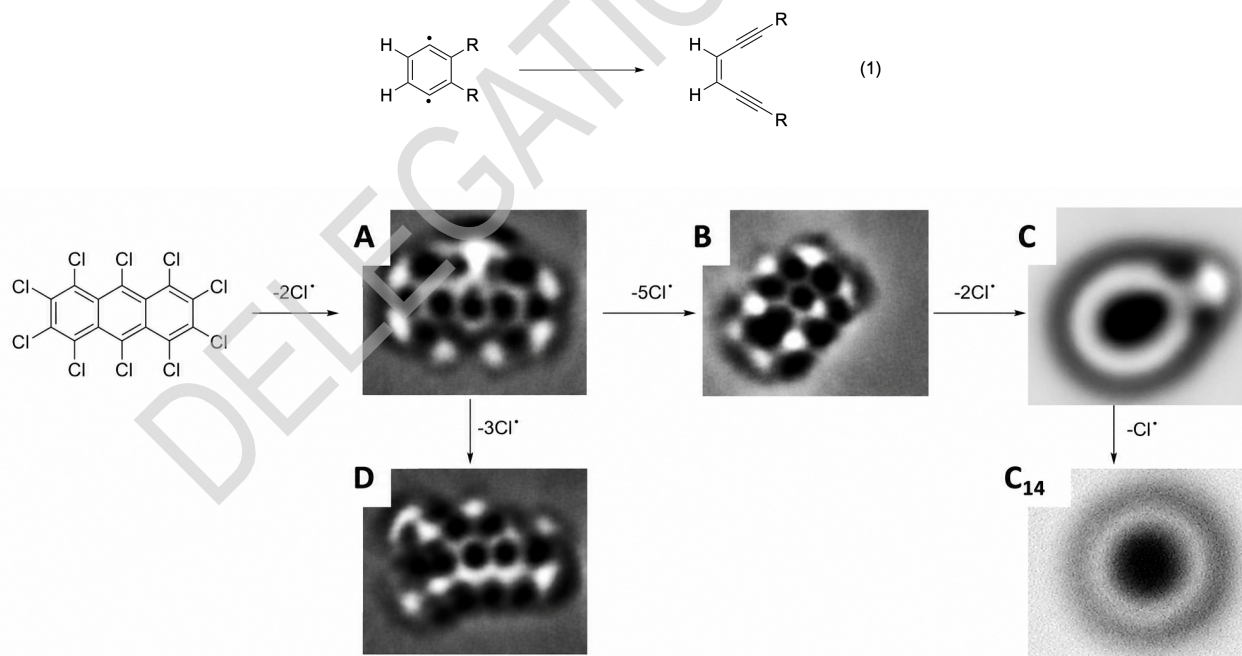
T6. Carbon Nanorings

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 $^1C_{13}$. **Fill in all blanks.** 10.0 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:

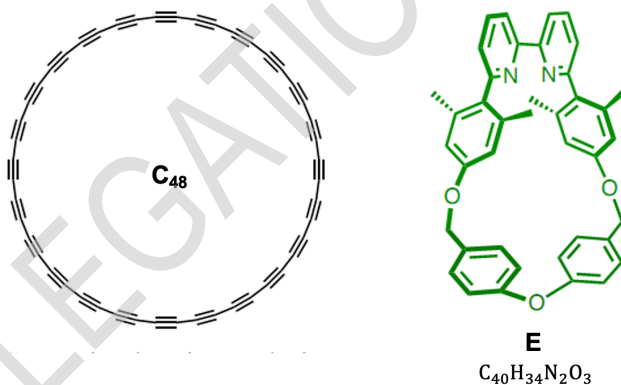


- 6.2** Draw structures **B-D**. Note they may contain one or more unpaired electrons. The structure of **A** is given as an example. 11.0 pt

- 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

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.



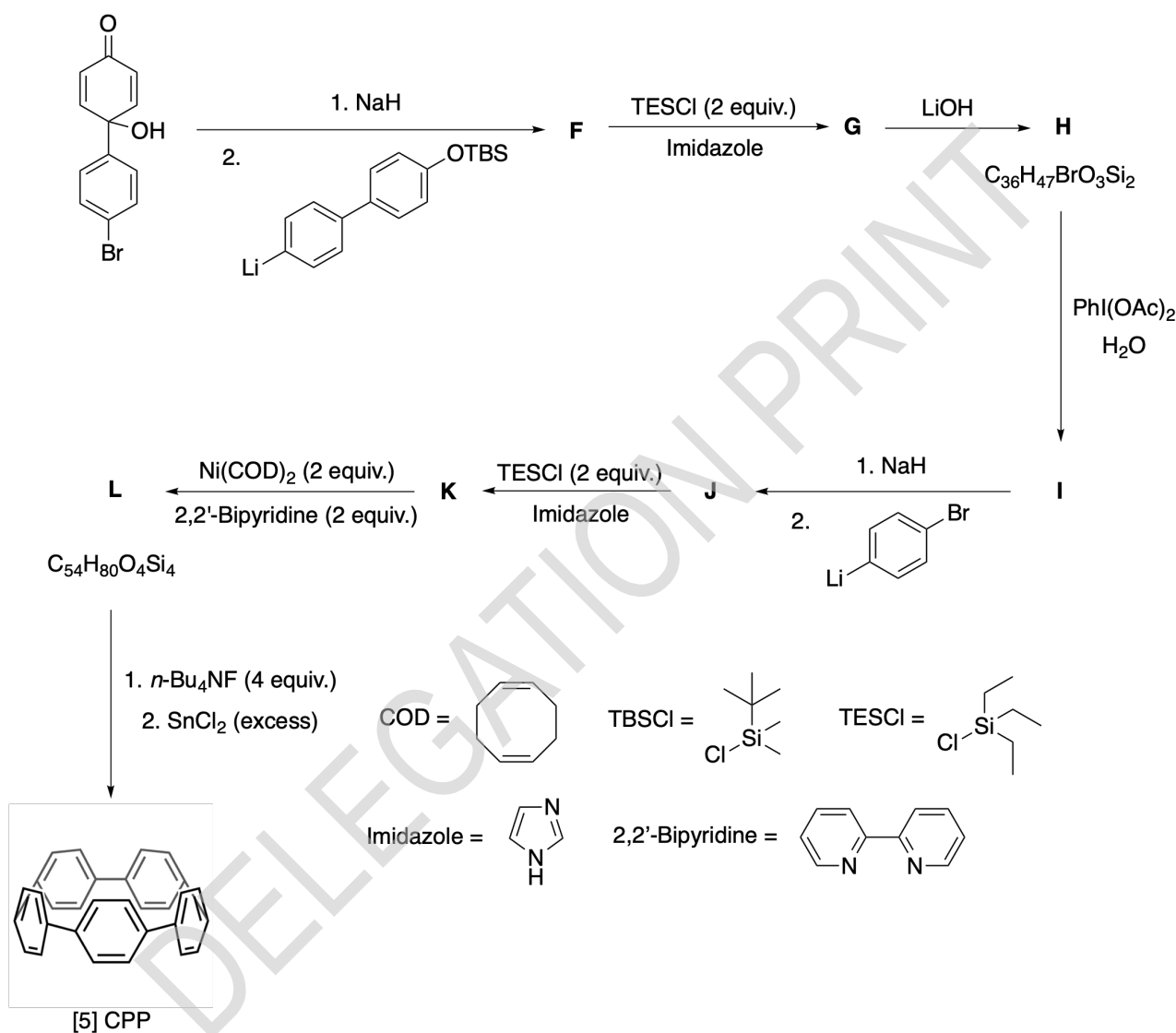
- 6.4** In the mass spectrum obtained, four intense peaks were observed m/z : 591, 783, 879, and 1174. **Suggest** the identity of these ions. **Use** integer atomic masses and **assume** no fragmentation happened. The ion corresponding to $m/z = 591$ is given as an example. 12.0 pt

Theory

Q6-3

English (Official)

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.



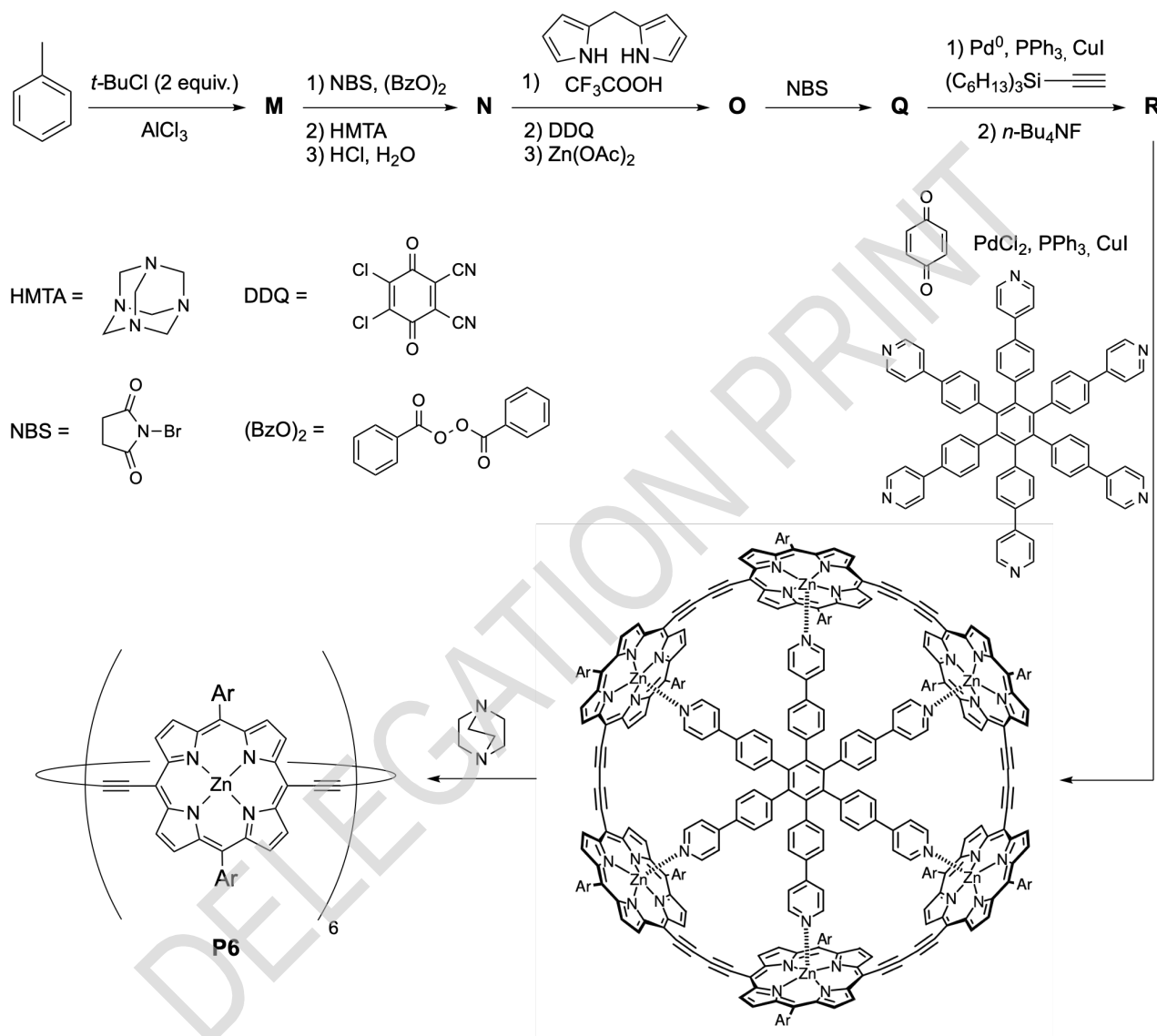
(equiv. = Equivalent, excess = Excess)

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

24.0 pt

Theory

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



(equiv. = Equivalent)

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

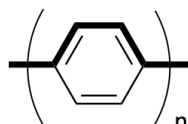
20.0 pt

Theory

Q6-5

English (Official)

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, <u>find</u> the minimum number of electrons, $n(e)$, from P6 that should be removed to achieve global aromaticity. <u>Write</u> the total number of π electrons, $n(t)$, in the global aromatic system. | 4.0 pt |
|------------|--|--------|

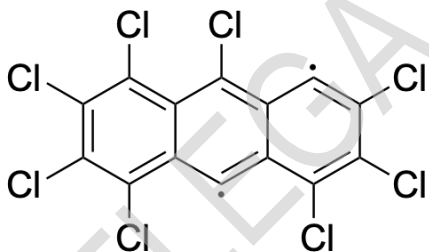
T6. Carbon Nanorings

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

6.1 (10.0 pt)

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

6.2 (11.0 pt)

 A	B
C	D

6.3 (2.0 pt)

X = _____

6.4 (12.0 pt)

<i>m/z</i>	591	783	879	1174
	[E + H] ⁺			

6.5 (24.0 pt)

F	G
H	I

DELEGATION PRINT

6.5 (cont.)

J	K
L	

Theory

6.6 (20.0 pt)

M	N
O	Q

DELEGATION PRINT

6.6 (cont.)**6.7 (4.0 pt)**

$n(e)$	
$n(t)$	

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.

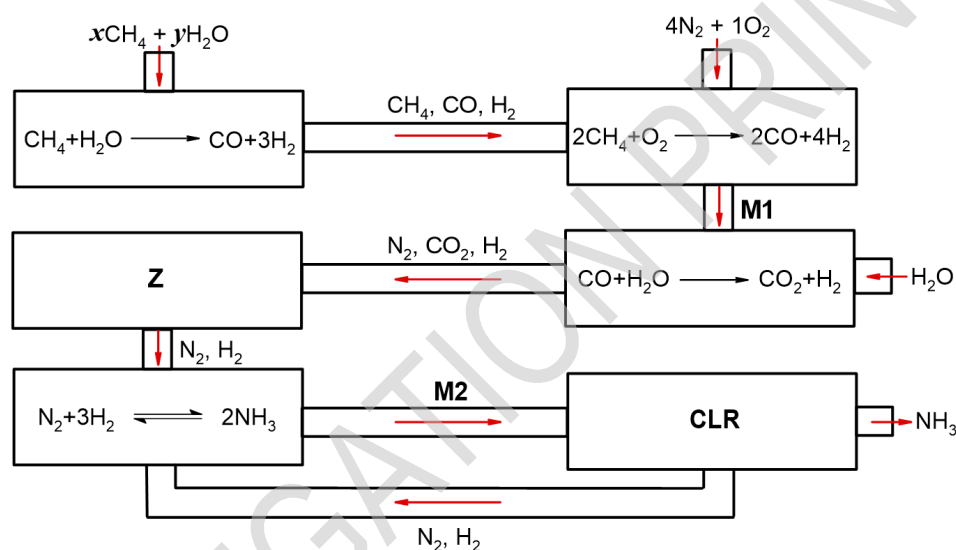


Fig. 1. **M1** - Mixture 1, **M2** - Mixture 2, **Z** – CO₂ scrubber, **CLR** - cooler

In the following calculations, assume that all reactions in **Fig. 1**, except NH₃ formation, are quantitative.

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

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

- 7.2** Calculate the mass of CH₄ (tons) required annually to produce 660,000 tons of ammonia, if the *Navoiazot* operates according to the **Fig. 1**. 8.0 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.

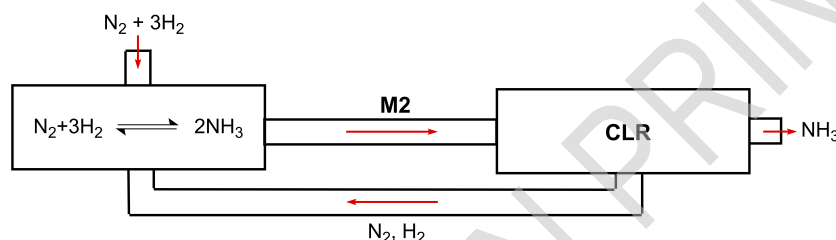
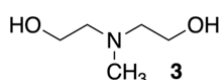


Fig. 2. M2. – Mixture 2, CLR - cooler.

- 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%.

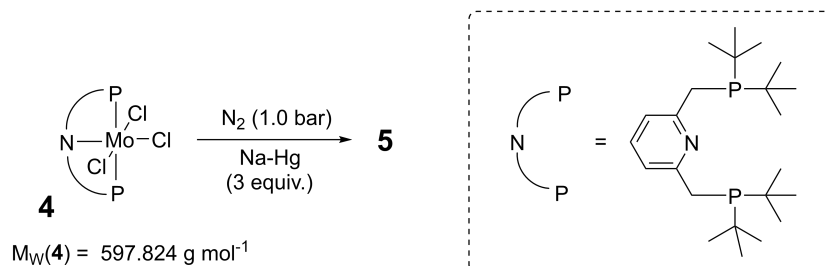
An aqueous solution of **3** is being used to remove CO_2 from the mixture.



- 7.4** **Write** the equation for this reaction.

3.0 pt

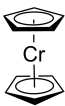
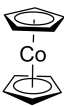
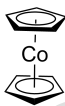
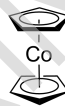
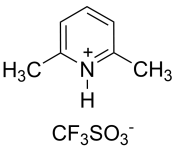
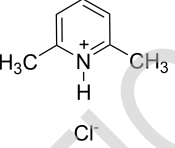
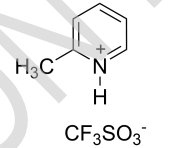
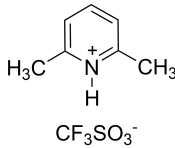
Complex **5** is obtained through the fixation of the molecular nitrogen according to the scheme below.



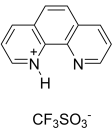
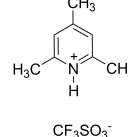
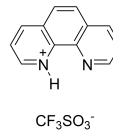
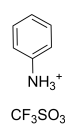
Theory

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 cm^3 of N_2 at 273.15 K and 1.0 bar. 6.0 pt

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

#	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				
pK_a	13.7	15.0	13.7	10.6

Theory

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

1. Mass fractions of nitrogen are $w(\text{N})_7 = 9.16\%$, $w(\text{N})_8 = 18.90\%$, $w(\text{N})_9 = 39.94\%$
2. **Q** and **R** are metal cations in their highest oxidation state.
3. **S** is a monoatomic anion.
4. **T** is an anion with tetrahedral configuration.
5. For the quantitative formation of **10**, the mass ratio **7** : **8** : **9** : $\text{SiO}_2 = 5.09 : 2.96 : 3.27 : 1.00$.

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

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

7.1 (3.0 pt)

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

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

Theory



A7-2

English (Official)

7.2 (8.0 pt)

$m(\text{CH}_4) = \underline{\hspace{2cm}}$

DELEGATION PRINT

Theory



A7-3

English (Official)

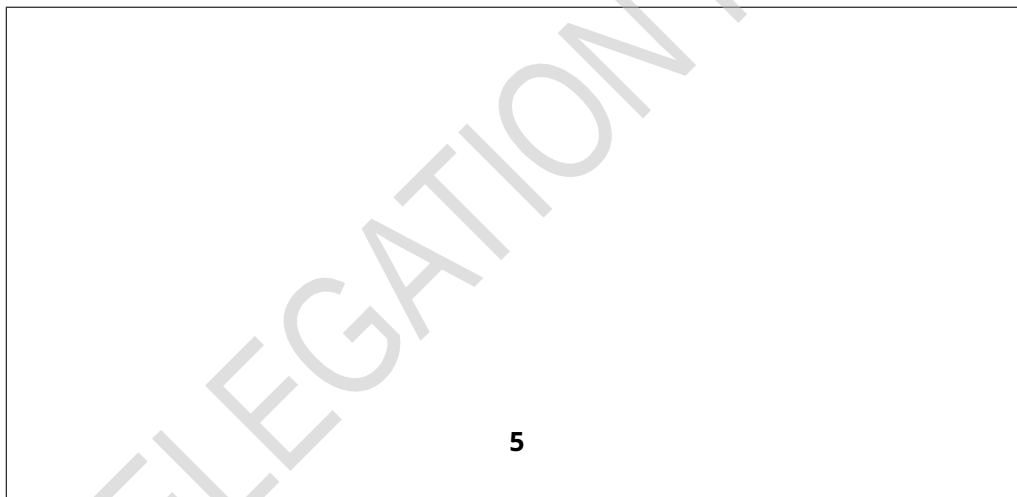
7.3 (15.0 pt)

$f_n =$ _____

$n =$ _____

7.4 (3.0 pt)

7.5 (6.0 pt)



7.6 (6.0 pt)

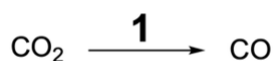
7.7 (13.0 pt)

7: _____ 8: _____ 9: _____ 10: _____

T8. Recycling of Carbon Dioxide

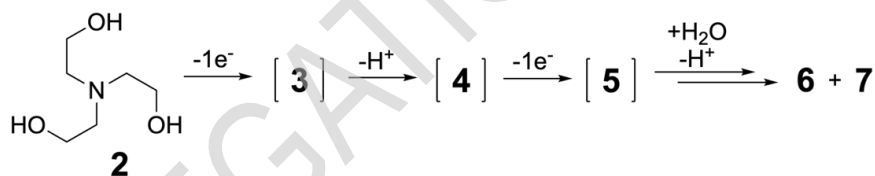
7%										
8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10	Σ
2	16	2	29	5	10	2	4	12	2	84

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

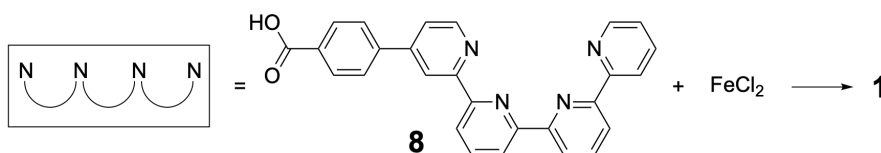
The conjugate oxidation reaction occurs with sacrificial reductant **2** in aqueous solution with the following mechanism:



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

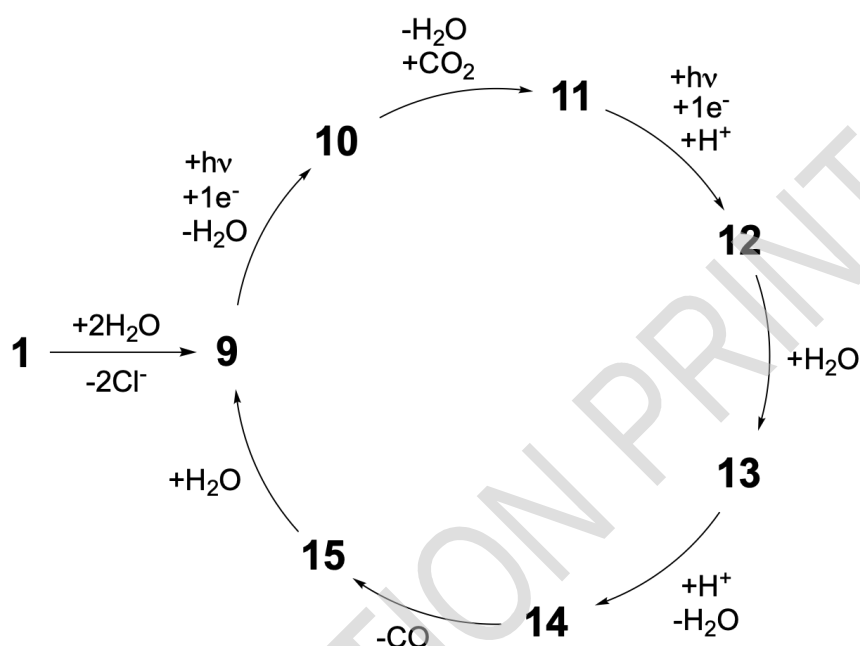
8.2 Draw the structures of **3-7**. 16.0 pt

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



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

When **1** is loaded on crystalline carbon nitride (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. 29.0 pt

- 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

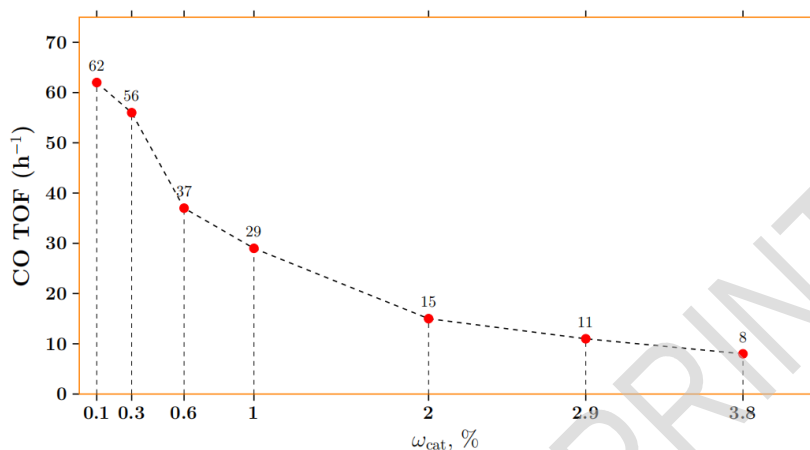
The Turnover Frequency of a catalyst (TOF) is the number of product molecules formed per active catalyst molecule per hour. Under LED illumination ($\lambda = 390 \text{ nm}$) with power of 50 mW , there was a TOF of 8 h^{-1} for 10 mg of C_3N_4 , loaded with **1** with $\omega_{\text{cat}} = 3.8\%$

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

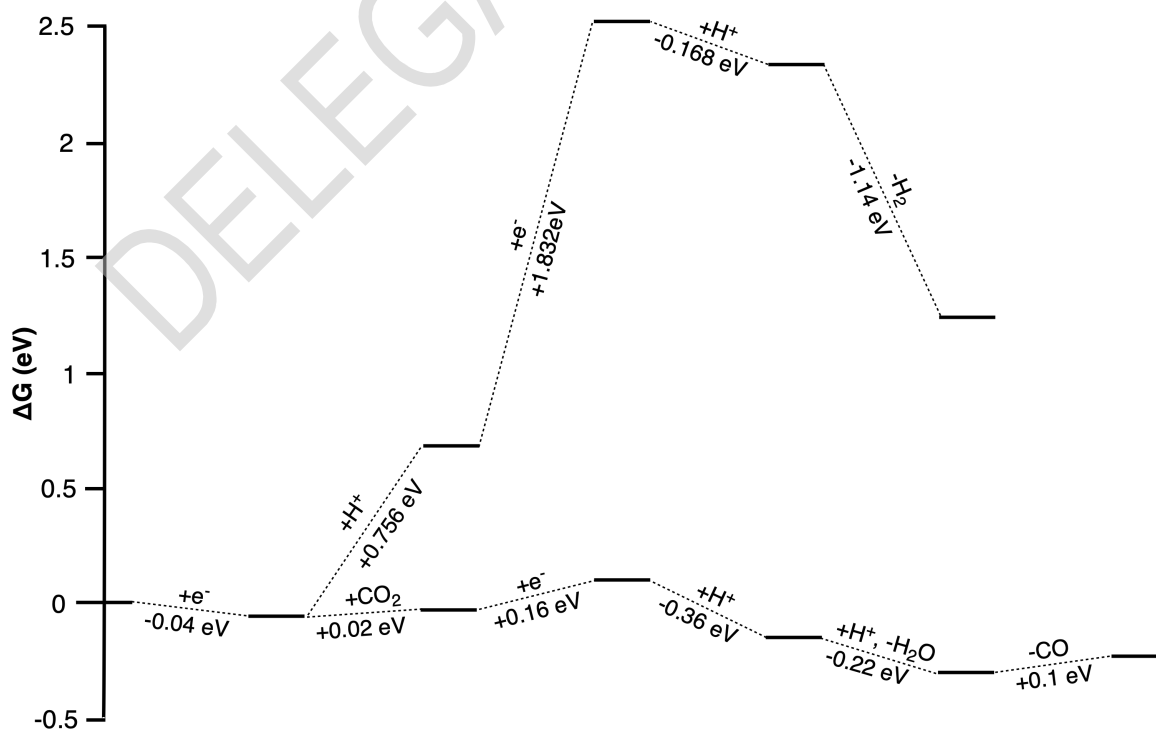
The diagram below shows the change in the TOF of CO as ω_{cat} is varied.



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.

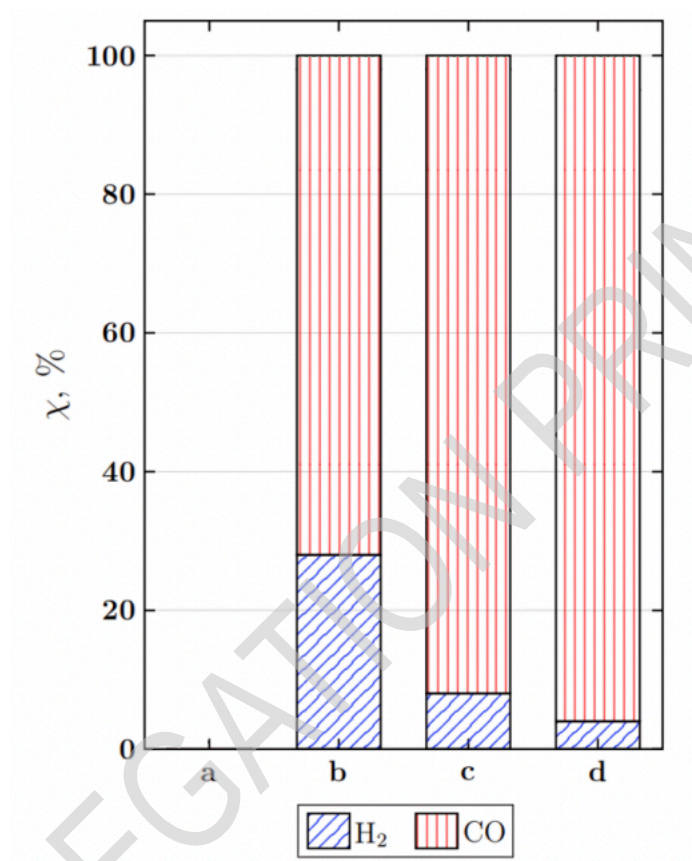
- a) increases
b) decreases
c) doesn't change

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.



Theory

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



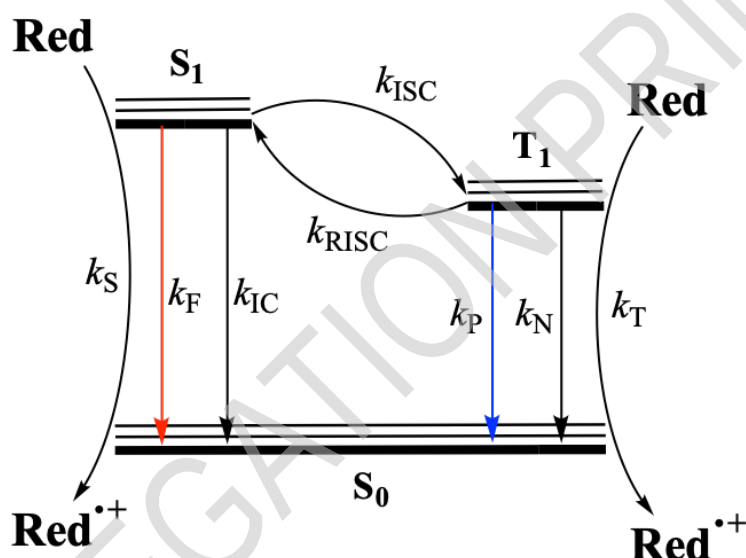
- 8.8** Tick which of the four conditions, mentioned above, corresponds to **a**, **b**, **c** and **d** in the diagram. 4.0 pt

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 S_1 and T_1 states, when $[\text{Red}] = 0.1 \text{ M}$. Note: here $k_F \gg k_{ISC}$. 12.0 pt

8.10 How do the emission lifetimes of S_1 and T_1 states change when $[\text{Red}]$ increases? 2.0 pt
Tick the correct box.

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

T8. Recycling of Carbon Dioxide

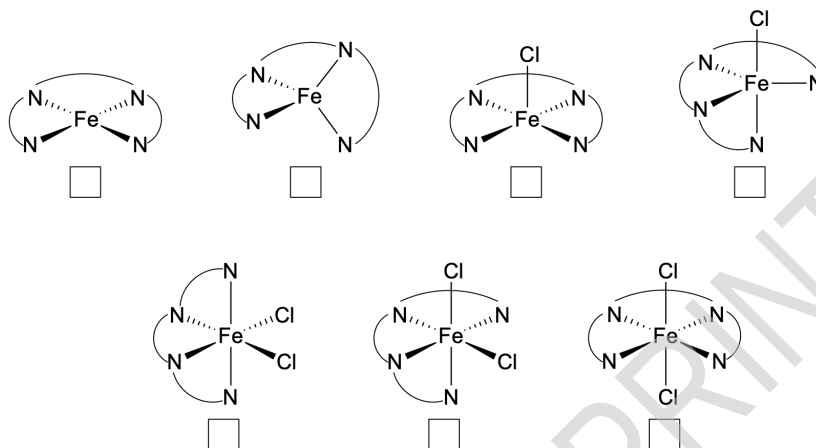
7%										
8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10	Σ
2	16	2	29	5	10	2	4	12	2	84

8.1 (2.0 pt)

8.2 (16.0 pt)

3	4
5	6
7	

8.3 (2.0 pt)



8.4 (29.0 pt)

9

 $Z = \underline{\hspace{2cm}}$ $OS = \underline{\hspace{2cm}} \quad CN = \underline{\hspace{2cm}} \quad VE = \underline{\hspace{2cm}}$

10

 $Z = \underline{\hspace{2cm}}$ $OS = \underline{\hspace{2cm}} \quad CN = \underline{\hspace{2cm}} \quad VE = \underline{\hspace{2cm}}$

11

 $Z = \underline{\hspace{2cm}}$ $OS = +3 \quad CN = 6 \quad VE = \underline{\hspace{2cm}}$

12

 $Z = \underline{\hspace{2cm}}$ $OS = \underline{\hspace{2cm}} \quad CN = 5 \quad VE = \underline{\hspace{2cm}}$

8.4 (cont.)

13

 $Z = \underline{\hspace{2cm}}$ $OS = +2 \quad CN = \underline{\hspace{2cm}} \quad VE = \underline{\hspace{2cm}}$

14

 $Z = \underline{\hspace{2cm}}$ $OS = \underline{\hspace{2cm}} \quad CN = \underline{\hspace{2cm}} \quad VE = \underline{\hspace{2cm}}$

15

 $Z = \underline{\hspace{2cm}}$ $OS = \underline{\hspace{2cm}} \quad CN = \underline{\hspace{2cm}} \quad VE = 16$

8.5 (5.0 pt)

$N_{cat} =$ _____

8.6 (10.0 pt)

$\varphi =$ _____ %

8.7 (2.0 pt)

a	b	c
☐	☐	☐

8.8 (4.0 pt)

	N	R	G	B
a	☐	☐	☐	☐
b	☐	☐	☐	☐
c	☐	☐	☐	☐
d	☐	☐	☐	☐

8.9 (12.0 pt)

$$\eta_q(S_1) = \text{_____} \%$$

$$\eta_q(T_1) = \text{_____} \%$$

8.10 (2.0 pt)

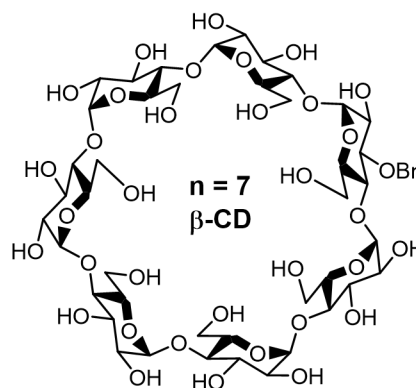
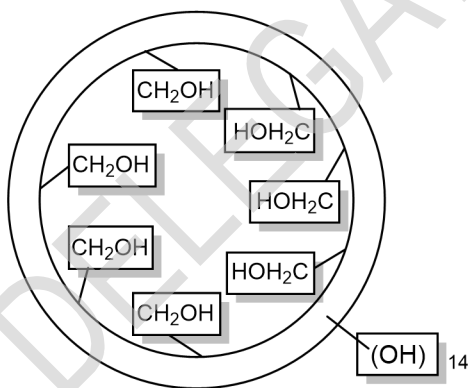
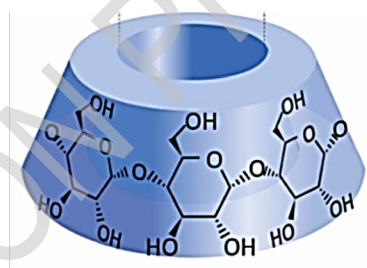
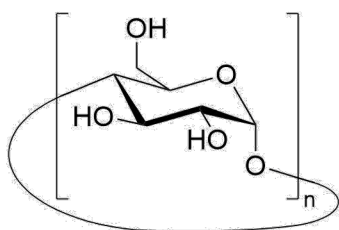
a	b	c
☐	☐	☐

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

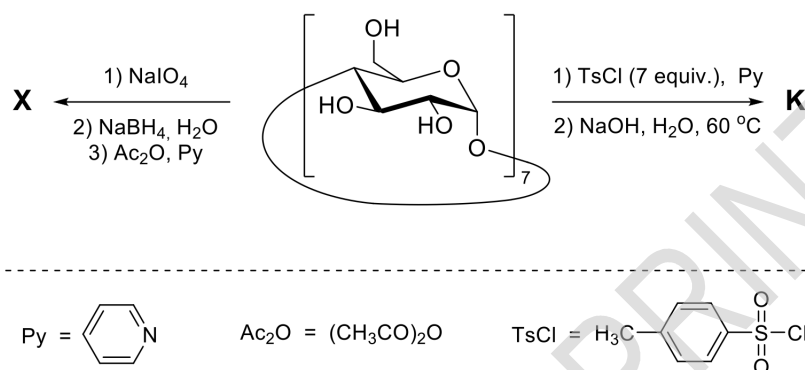
Cyclodextrins (CD) are a family of cyclic oligosaccharides, consisting of glucose subunits joined by α -1,4-glycosidic bonds. The three most common cyclodextrins (α -, β -, γ -cyclodextrin) contain 6, 7, and 8 α -D-glucopyranoside units, respectively.

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



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.

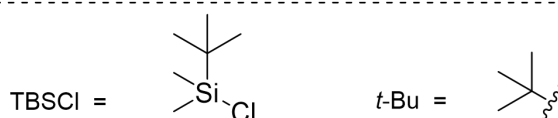
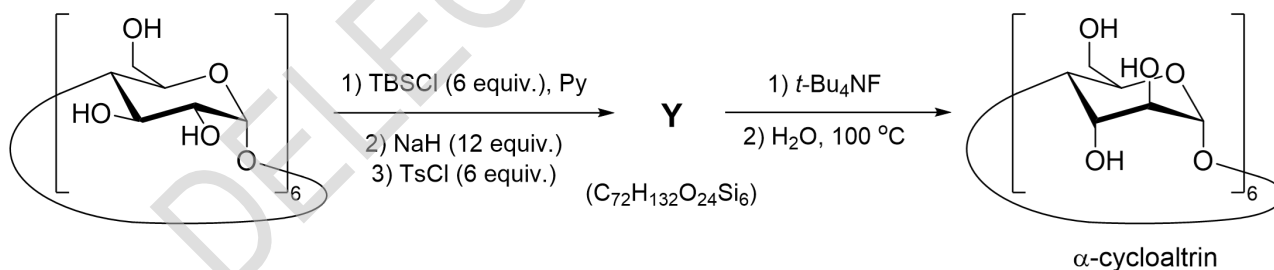


equiv. = equivalent

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

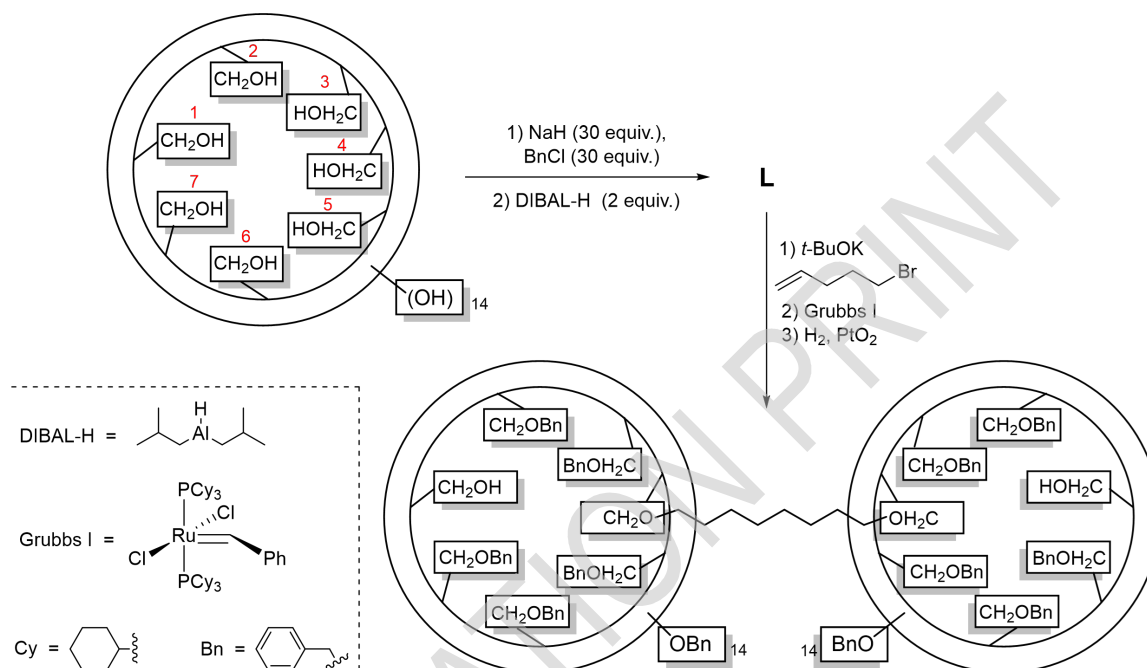
9.3 Determine the ring size, *rs*, of macrocycle **X**. Give the number of stereocentres, *sc*, in **X**. 8.0 pt

α-Cycloaltrin, a synthetic analogue of α-CD, was synthesised as follows.



9.4 Draw the structure of **Y** with stereochemistry by completing the CD template. 3.0 pt

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

9.6 Determine the number of isomers of the β -CD dimer that can form during the synthesis by Sinay *et al.*

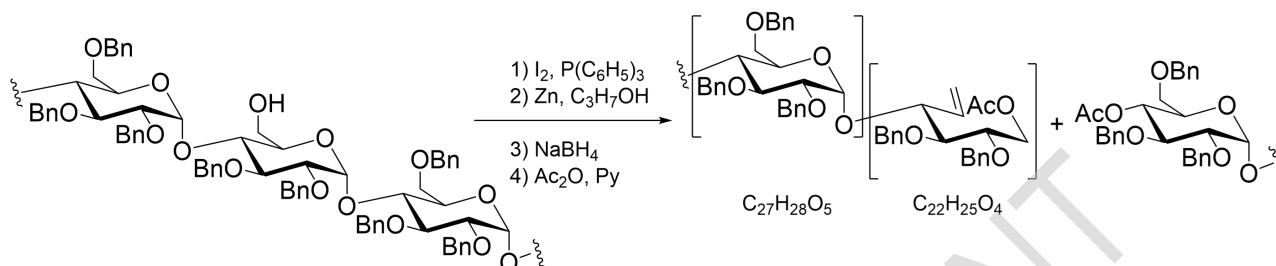
4.0 pt

Theory

Q9-4

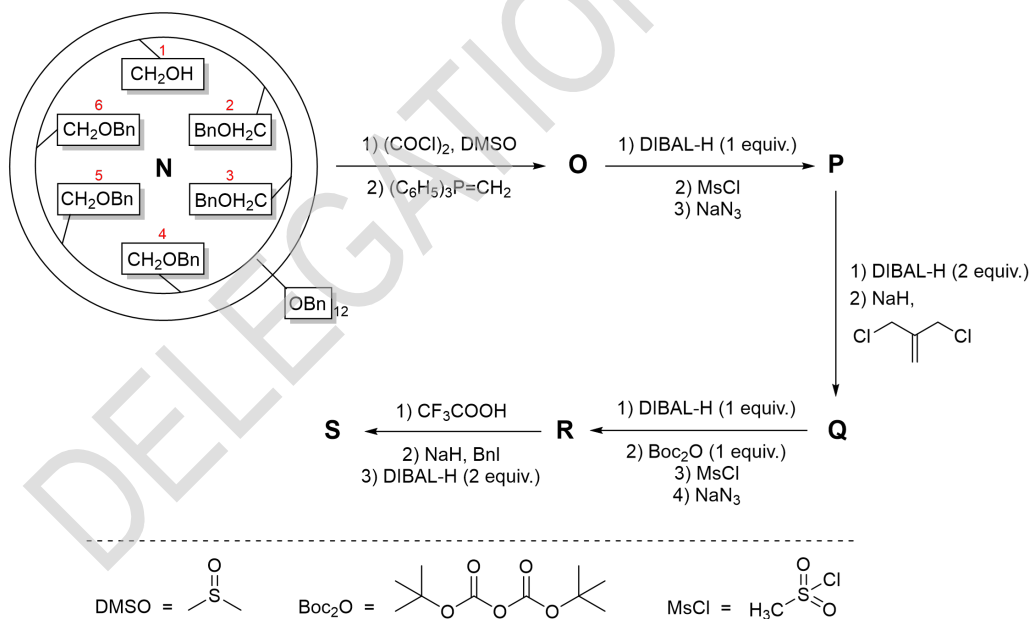
English (Official)

To confirm the positions of debenzoylation, **L** was subjected to the “hexo-5-enose degradation” reaction, as shown below. The products were then analysed by mass spectrometry.



- 9.7 Calculate** the m/z value for the two $[M + Na]^+$ peaks that were observed for the degradation products from **L**. **Use** integer values of atomic mass. 6.0 pt

Later, Sollogoub *et al.* applied the ability of alkenes to direct the debenzoylation to the “ortho”-glucopyranose unit for the synthesis of hexadifferentiated α -CD **S**:



- 9.8 Draw** the structures of **O-S** on the α -CD templates. **Fill in** all the boxes. You may draw structures outside the boxes if appropriate. **Assume** 1,2-unit modification happens **clockwise**, while 1,3-unit modification happens **counterclockwise**. Protic groups have stronger directing effects than alkenes. 18.0 pt

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

DELEGATION PRINT

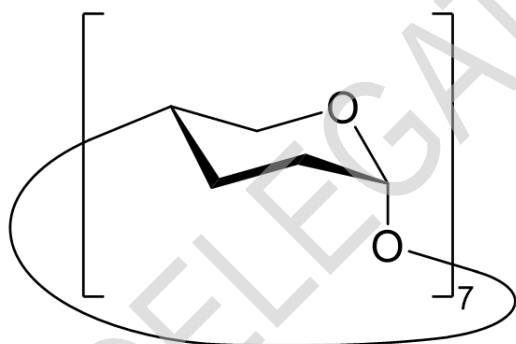
T9 Cyclodextrin Chemistry

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

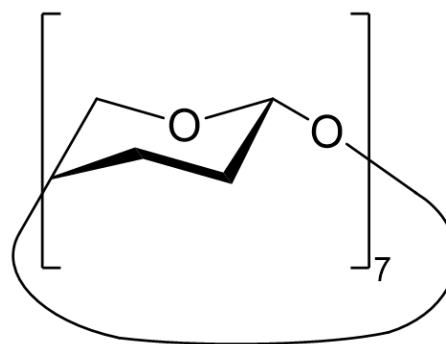
9.1 (2.0 pt)

 $M_w : \beta\text{-CD} = \underline{\hspace{2cm}}$

9.2 (6.0 pt)



□



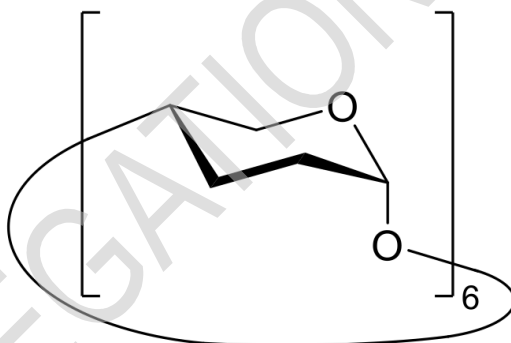
□

9.3 (8.0 pt)

rs: _____

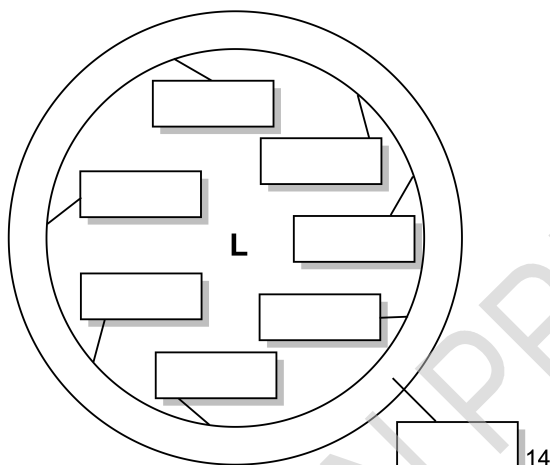
sc: _____

9.4 (3.0 pt)



Y – $\text{C}_{72}\text{H}_{132}\text{O}_{24}\text{Si}_6$

9.5 (2.0 pt)



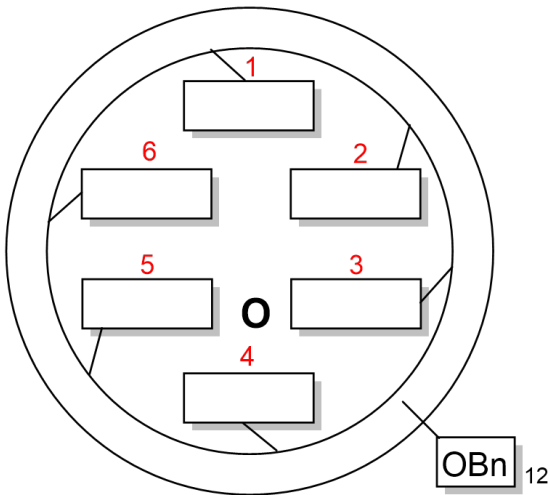
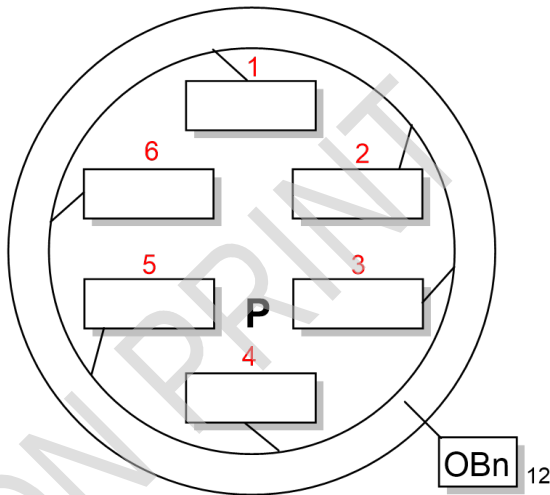
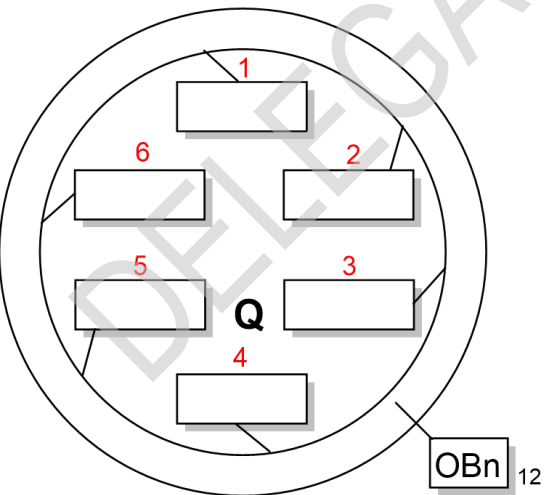
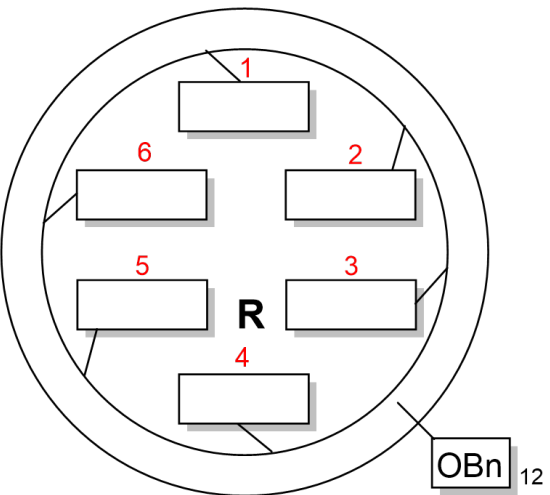
9.6 (4.0 pt)

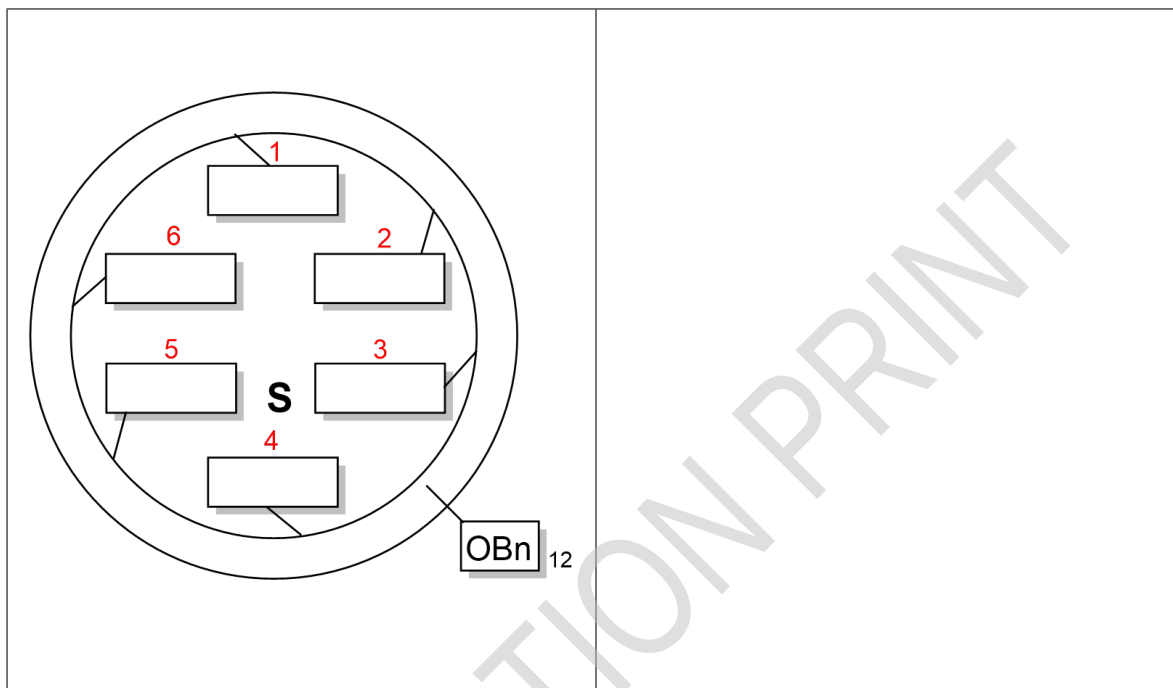
9.7 (6.0 pt)

$[M_1 + Na]^+$: _____

$[M_2 + Na]^+$: _____

9.8 (18.0 pt)

9.8 (cont.)**9.9 (4.0 pt)**