THEORETICAL EXAM

51st — International Chemistry Olympiad France — Paris — 2019

Making science together!

2019-07-26

2018 ANNÉE DE LA CHIMIE de l'école à l'université 2019

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE

MINISTÈRE DE L'ÉDUCATION NATIONALE ET DE LA JEUNESSE

MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR, DE LA RECHERCHE ET DE L'INNOVATION

General instructions

- This theoretical exam booklet contains 60 pages.
- You may begin writing as soon as the Start command is given.
- You have 5 hours to complete the exam.
- All results and answers must be clearly written in pen in their respective designed areas on the exam papers. Answers written outside the answer boxes will not be graded.
- If you need scratch paper, use the backside of the exam sheets. Remember that nothing outside the designed areas will be graded.
- Use only the pen and calculator provided.
- The official English version of the exam booklet is available upon request and serves for clarification only.
- If you need to leave the exam room (to use the toilet or have a snack), wave the corresponding IChO card. An exam supervisor will come to accompany you.
- For multiple-choice questions: if you want to change your answer, fill the answer box completely and then make a new empty answer box next to it.
- The supervisor will announce a 30-minute warning before the Stop command.
- You must stop your work immediately when the Stop command is announced. Failure to stop writing by ½ minute or longer will lead to nullification of your theoretical exam.
- After the Stop command has been given, place your exam booklet back in your exam envelope, then wait at your seat. The exam supervisor will come to seal the envelope in front of you and collect it.

GOOD LUCK!

Table of Contents

This theoretical exam is composed of 9 independent problems, as follows. Their relative weight is indicated in parenthesis.

Physical constants and equations

In these tasks, we assume the activities of all aqueous species to be well approximated by their respective concentration in mol L^{-1}. To further simplify formulas and expressions, the standard concentration $c^\circ = 1$ mol L^{-1} is omitted.

Avogadro's constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J mol^{-1} K^{-1}
Standard pressure:	$p^\circ = 1$ bar $= 10^5$ Pa
Atmospheric pressure:	$P_{atm} = 1$ atm $= 1.013$ bar $= 1.013 \cdot 10^5$ Pa
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.6485 \cdot 10^4$ C mol^{-1}
Watt:	1 W = 1 J s^{-1}
Kilowatt hour:	1 kWh $= 3.6 \cdot 10^6$ J
Planck constant:	$h = 6.6261 \cdot 10^{-34}$ J s
Speed of light in vacuum:	$c = 2.998 \cdot 10^8$ m s^{-1}
Elementary charge:	$e = 1.6022 \cdot 10^{-19}$ C
Electron-volt	1 eV $= 1.6022 \cdot 10^{-19}$ J
Electrical power:	$P = \Delta E \times I$
Power efficiency:	$\eta = P_{obtained}/P_{applied}$
Planck-Einstein relation:	$E = hc/\lambda = h\ \nu$
Ideal gas equation:	$pV = nRT$
Gibbs free energy:	$G = H - TS$
	$\Delta_r G^\circ = -RT \ln K^\circ$
	$\Delta_r G^\circ = -n\ F\ E_{cell}^\circ$
	$\Delta_r G = \Delta_r G^\circ + RT \ln Q$
Reaction quotient Q for a reaction a A(aq) + b B(aq) = c C(aq) + d D(aq):	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Henderson−Hasselbalch equation:	$pH = pK_a + \log\frac{[A^-]}{[AH]}$
Nernst–Peterson equation:	$E = E^o - \frac{RT}{zF}\ln Q$
where Q is the reaction quotient of the reduction half-reaction	at $T = 298$ K, $\frac{RT}{F}\ln 10 \approx 0.059$ V
Beer–Lambert law:	$A = \varepsilon l c$
Rate laws in integrated form:	
- Zero order:	$[A] = [A]_0 - kt$
- First order:	$\ln[A] = \ln[A]_0 - kt$
- Second order:	$1/[A] = 1/[A]_0 + kt$
Half-life for a first order process:	$\frac{\ln 2}{k}$
Number average molar mass M_n:	$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$
Mass average molar mass M_w:	$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$
Polydispersity index I_p:	$I_p = \frac{M_w}{M_n}$

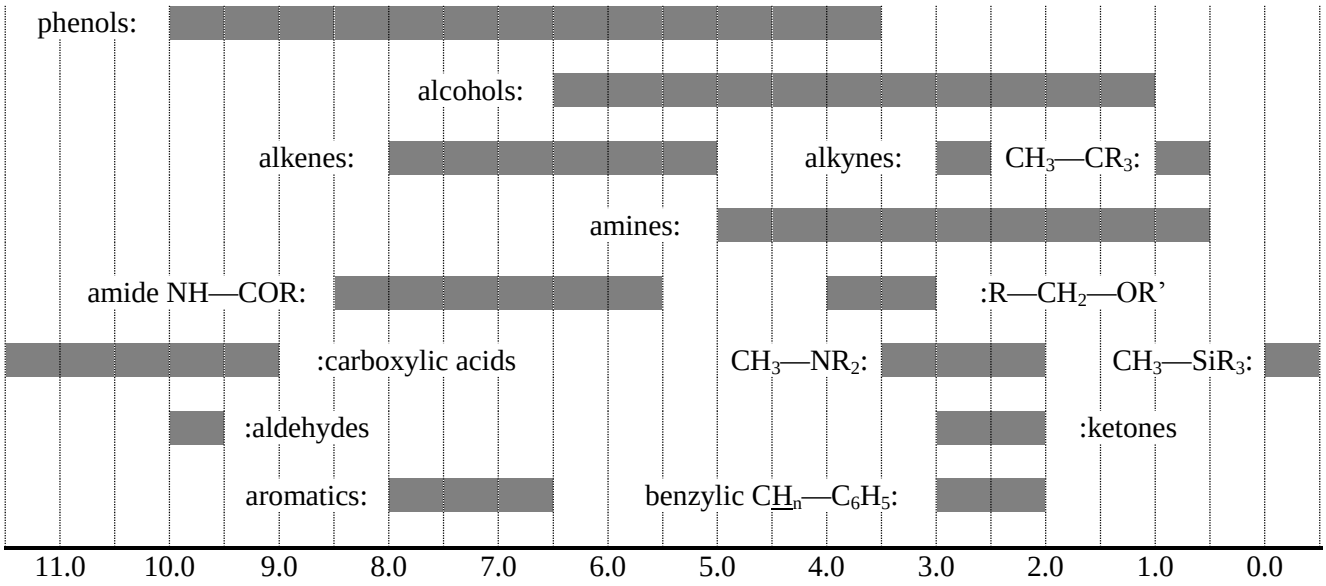
Periodic table

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

^{1}H NMR

Chemical shifts of hydrogen (in ppm / TMS)



H-H coupling constants (in Hz)

Hydrogen type	**$\lvert J_{ab}\rvert$ (Hz)**
$R_2CH_aH_b$	4-20
$R_2H_aC—CR_2H_b$	2-12 if free rotation: 6-8 ax-ax (cyclohexane): 8-12 ax-eq or eq-eq (cyclohexane): 2-5
$R_2H_aC—CR_2—CR_2H_b$	if free rotation: < 0.1 otherwise (rigid): 1-8
$RH_aC=CRH_b$	*cis*: 7-12 *trans*: 12-18
$R_2C=CH_aH_b$	0.5-3
$H_a(CO)—CR_2H_b$	1-3
$RH_aC=CR—CR_2H_b$	0.5-2.5

eq = equatorial, ax = axial

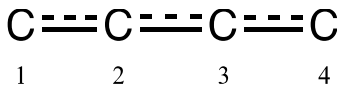
IR spectroscopy table

Vibrational mode	σ (cm^{-1})	Intensity
alcohol O—H (stretching)	3600-3200	strong
carboxylic acid O—H (stretching)	3600-2500	strong
N—H (stretching)	3500-3350	strong
≡C—H (stretching)	3300	strong
=C—H (stretching)	3100-3000	weak
C—H (stretching)	2950-2840	weak
–(CO)—H (stretching)	2900-2800	weak
C≡N (stretching)	2250	strong
C≡C (stretching)	2260-2100	variable
aldehyde C=O (stretching)	1740-1720	strong
anhydride C=O (stretching)	1840-1800; 1780-1740	weak; strong
ester C=O (stretching)	1750-1720	strong
ketone C=O (stretching)	1745-1715	strong
amide C=O (stretching)	1700-1500	strong
alkene C=C (stretching)	1680-1600	weak
aromatic C=C (stretching)	1600-1400	weak
CH_2 (bending)	1480-1440	medium
CH_3 (bending)	1465-1440; 1390-1365	medium
C—O—C (stretching)	1250-1050	strong
C—OH (stretching)	1200-1020	strong
NO_2 (stretching)	1600-1500; 1400-1300	strong

Problem T1 6%	Question	1	2	3	4	5	6	7	8	9	10	11	Total
	Points	3	4	4	2	3	2	2	4.5	2.5	3	3	33
	Score												

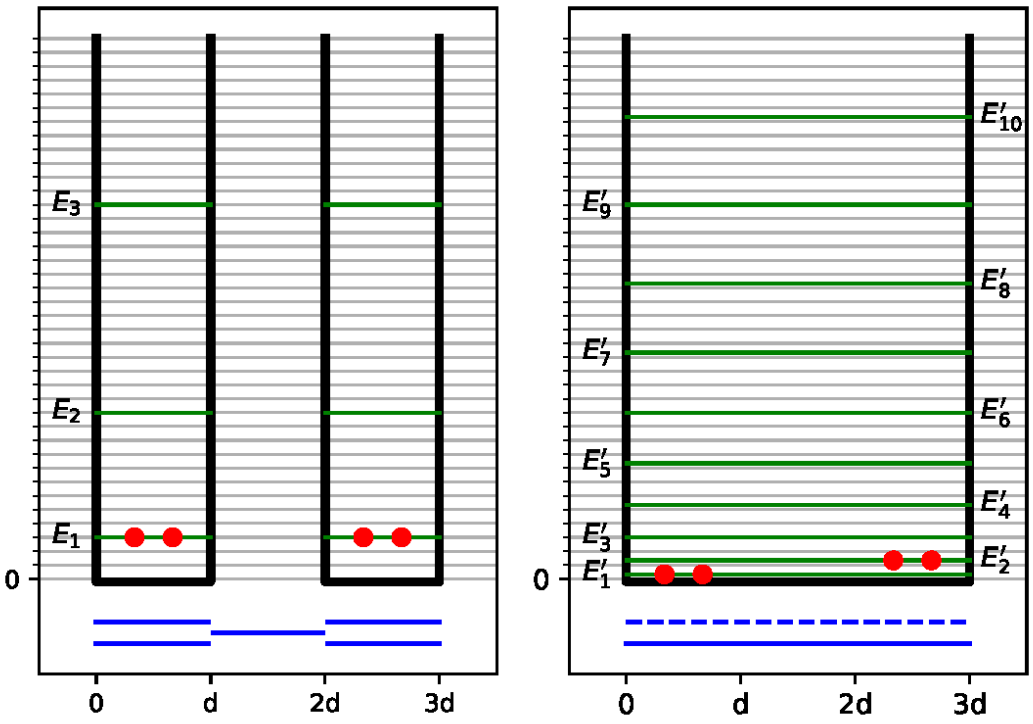
Problem T1: Infinite well and butadiene

The buta-1,3-diene molecule is often written CH_2=CH–CH=CH_2, with alternating single and double bonds. Nevertheless, its chemical reactivity is not consistent with this description and the π electrons are better described by a distribution along the three bonds:



This system can be modeled as a 1D box (*i.e.* infinite well) where the electrons are free. The energy of an electron in an infinite well of length L is: $E_n = \frac{n^2h^2}{8m_eL^2}$, where n is a **non-zero** positive integer.

1. Two different models are studied. **Sketch** at least the three lowest-energy levels E_n **for each model** in the respective diagrams, showing how the relative energy levels differ within and between models.



Model 1 (« localized »): The π electrons are localized on the extremal bonds and evolve in two separate infinite potential wells of length d.

Model 2 (« delocalized »): The π electrons are delocalized on the whole molecule and evolve in a single infinite potential well of length $3d$.

+1 point if the gap between levels increases with increasing energy in model 1
+1 point if the gap between levels increases with increasing energy in model 2
+1 point if the gap of model 1 is larger than the gap of model 2
Total: 3 points

2. **Place** the π electrons for model 1 in the previous diagrams and **express** the total energy of the π system in model 1, as a function of h, m_e and d.

+ 1 point for two electrons for each level
+ 1 point if four electrons in total
+ 1 point if they fill levels by increasing energy

$E(1) = 2 \times 2E_1 = \frac{h^2}{2\,m_e d^2}$ (1 point)

Total: 4 points

3. **Place** the π electrons for model 2 in the previous diagrams and **express** the total energy of the π system in model 2, as a function of h, m_e and d.

+ 1 point for two electrons for each level
+ 1 point if four electrons in total
+ 1 point if they fill levels by increasing energy

$E(2) = 2E_1 + 2E_2 = \frac{5h^2}{36 m_e d^2}$ (1 point)

Total: 4 points

The conjugation energy is the total energy of the actual π system, minus the sum of the energies of ethylene molecules involving the same number of electrons.

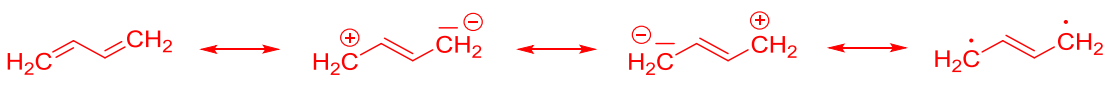
4. **Express** the conjugation energy ΔE_c of butadiene, as a function of h, m_e and d.

$\Delta E_c = E(2) - E(1) = -\frac{13\,h^2}{36\,m_e d^2}$

1 point for the expression $E(2) - E(1)$
1 point for consistent computation
Total: 2 points (only if consistent with Q2 and Q3)

Models 1 and 2 are too simplistic. A new model will be detailed in the following.

5. **Draw** three other resonance structures of butadiene using Lewis notation.



1 point for each acceptable resonance structure (correct charge, number of electrons, etc.).
The non-bonding electron pairs are not required.
Total: 3 points

To take into account the size of carbon atoms, model 2 is now modified into model 3, as follows:

- the new length of the well is L and is located between the abscissa 0 and L;
- the carbon atoms are located at the abscissas $L/8$; $3L/8$; $5L/8$ and $7L/8$.

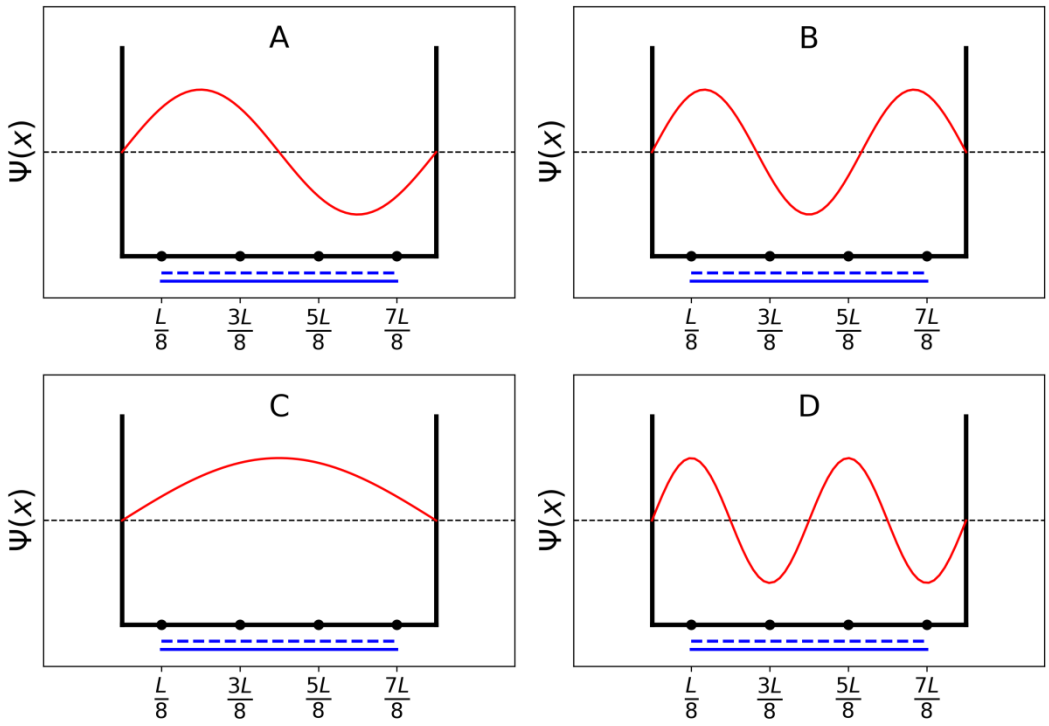
For each level n, the π wavefunction is:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

and the π electron density for a system with N π electrons is:

$$\rho(x) = 2 \sum_{i=1}^{N/2} |\psi_i(x)|^2$$

The four π wavefunctions, which correspond to the molecular orbitals of the π system, are depicted below (**arbitrary order**).



6. **Sort** the energies of the four π wavefunctions (E_A, E_B, E_C and E_D).

E_C < E_A < E_B < E_D

+1 point if E_C is correctly localized

+1 point if the order is correct

Total: 2 points

7. **Give** the labels (A, B, C or D) of the orbitals that are filled with electrons in butadiene.

C and A

1 point for each orbital found correctly

−1 if 3 orbitals given; −2 if 4 orbitals.

Total: 2 points

8. Within model 3, **give** the values of the π wavefunctions ψ_n for occupied levels at positions 0, $L/4$ and $L/2$, for n = 1 and n = 2, as a function of L.

$\psi_1(0) =$ 0 (0.5 point) ; $\psi_1\left(\frac{L}{4}\right) = \sqrt{\frac{1}{L}}$ (1 point) ; $\psi_1\left(\frac{L}{2}\right) = \sqrt{\frac{2}{L}}$ (1 point)

$\psi_2(0) =$ 0 (0.5 point) ; $\psi_2\left(\frac{L}{4}\right) = \sqrt{\frac{2}{L}}$ (1 point) ; $\psi_2\left(\frac{L}{2}\right) =$ 0 (0.5 point)

Total: 4.5 points

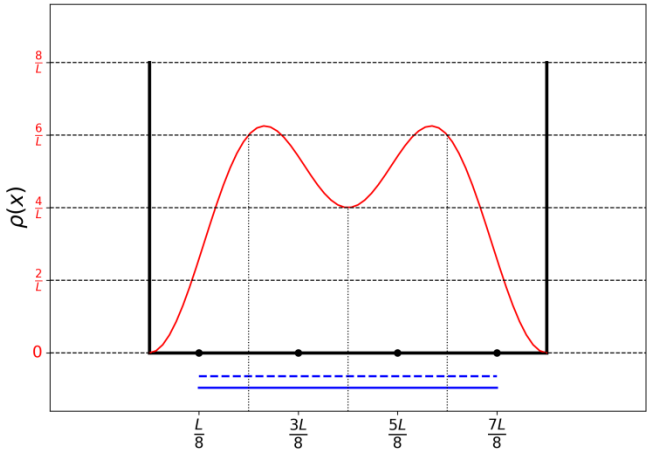
9. Within model 3, **give** the value of the π electron density at positions 0, *L*/4 and *L*/2.

$\rho(0) =$ 0 ; $\rho\left(\frac{L}{4}\right) = \frac{6}{L}$; $\rho\left(\frac{L}{2}\right) = \frac{4}{L}$

0.5 point for the first value, 1 point for each other calculation.

Total: 2.5 points

10. **Draw** the π electron density between 0 and *L*.



1 point if the graph is symmetric
1 point if values at 0, L/4 and L/2 are correctly reported from Q9
1 point if the general trend is correct

Total: 3 points

11. **Sort** the following CC bonds (B1, B2, …, B5) by increasing length, using the symbols = or <:

B1: C1C2 in the butadiene molecule
B2: C2C3 in the butadiene molecule
B3: C3C4 in the butadiene molecule
B4: CC in the ethane molecule
B5: CC in the ethene molecule

B5 < B1 = B3 < B2 < B4

+2×0.5 points for the position of B4 and B5
+1 point for B1 = B3
+1 point for the order between B1/B3 and B2

Total: 3 points

Problem T2 7%	Question	1	2	3	4	5	6	7	8	9	10	Total
	Points	1	4	2	3	3	6	4	1	8	2	34
	Score											

Problem T2: Hydrogen production by water-splitting

Data:

Compound	$H_2(g)$	$H_2O(l)$	$H_2O(g)$	$O_2(g)$
$\Delta_f H°$ (kJ mol^{-1})	0	−285.8	−241.8	0
$S_m°$ (J mol^{-1} K^{-1})	130.6	69.9	188.7	205.2

Molecular hydrogen (H_2) can be used as an alternative to carbon dioxide-emitting fuels. Hence, lowering the cost and the environmental impact of its production is a major challenge. In this field, water-splitting is a promising candidate technology.

1. **Write down** the balanced equation of liquid water splitting reaction using a stoichiometric coefficient of 1 for water.

$H_2O(l) \rightarrow H_2(g) + ½\ O_2(g)$

Total: 1 point

2. Using only the provided thermodynamic data, **justify numerically** whether this reaction is thermodynamically favorable at 298 K.

Calculations:

$\Delta_r H° = 285.8$ kJ mol^{-1} (1 point)

$\Delta_r S° = 163.3$ J K^{-1} mol^{-1} (1 point)

At 298 K, $\Delta_r G° = 237.1$ kJ mol$^{-1} > 0$ (1 point)

Or $K° = \exp(-\Delta_r G°/RT) = 2.75 \times 10^{-42} = 10^{-41.6} << 1$

Reaction thermodynamically favorable?

☐ Yes ☒ No (1 point)

0 point if ☒ No without a numerical justification

Total: 4 points

Water splitting can be performed electrochemically using two electrodes in an acidic water bath, connected by a generator (Fig. 1). Gas bubbles are formed at both electrodes.

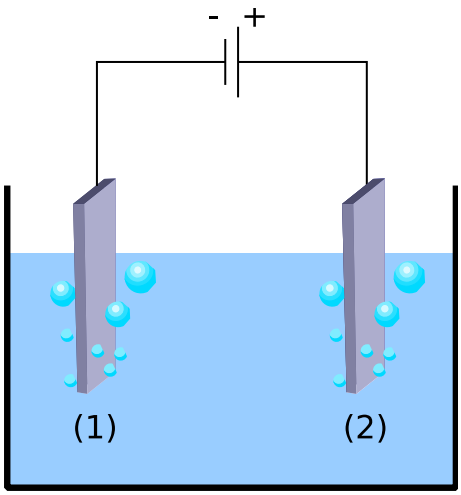


Fig. 1– Water-splitting electrochemical cell.

3. **Write down** the balanced net electrochemical half reactions occurring at each electrode.

On electrode (1): $2H^+ + 2\ e^- \rightarrow H_2$ (1 point)
On electrode (2): $H_2O \rightarrow 2H^+ + ½\ O_2 + 2\ e^-$ (1 point)

Total: 2 points (0 point if not balanced)

4. Using only the provided thermodynamic data (or question 2), **derive** the condition on the applied voltage $\Delta E_{applied}$ between electrodes, compared to value ΔE_{th} (to **determine**), for the process to be thermodynamically favorable at 298 K, when all reactants and products are in their standard state. **Tick** the right condition and **give** the numerical value with 3 decimal places.

Calculation:
$\Delta E_{applied}$ must be $> \Delta E_{th} = \Delta_r G°/2F$
$\Delta E_{th} > \Delta_r G°/2F = 237.1\times10^3/(2 \times 96485)$ (1 point)
The + sign associated to electrolysis is required

☐ $\Delta E_{applied} = \Delta E_{th}$
☒ $\Delta E_{applied} > \Delta E_{th}$, where ΔE_{th} =..1.229.. V
☐ $\Delta E_{applied} < \Delta E_{th}$

(give the result with 3 decimal places)
(1 point for correct symbol, 1 point for numerical value)

Total: 3 points

If you could not calculate ΔE_{th}, the value 1.200 V can be used in the rest of the problem.

Experimentally, a higher voltage is needed to observe water splitting. For a given Pt cathode, the minimum voltage necessary to observe water splitting, ΔE_{min}, depends on the nature of the anode, as displayed in the table below:

Anode	ΔE_{min} (V)
IrO_x	1.6
NiO_x	1.7
CoO_x	1.7
Fe_2O_3	1.9

The difference between ΔE_{min} and ΔE_{th} is responsible for losses in the device.

5. **Give** the expression of the device power efficiency η_{elec} (fraction of the power used for water splitting) as a function of ΔE_{th} and ΔE_{min}. Assuming an identical current value I, **calculate** the water electrolysis power efficiency when a Pt cathode and a Fe_2O_3 anode are used. **Give** the most efficient anode.

$\eta_{elec} = P_{eff}/P_{applied} = \Delta E_{th}/\Delta E_{min}$ (1 point)

Power efficiency when a Pt and a Fe_2O_3 electrodes are used

$\eta_{elec} = 1.229/1.9 = 65\%$ ($\eta_{elec} = 63$ % if used $\Delta E_{th} = 1.200$ V) (1 point)

Most efficient anode: IrO_x (1 point)

Total: 3 points

If you could not calculate η_{elec}, the value $\eta_{elec} = 75\%$ can be used in the rest of the problem.

An alternative to water electrolysis is direct photocatalytic water-splitting. It uses a semiconductor that can be activated by absorbing light.

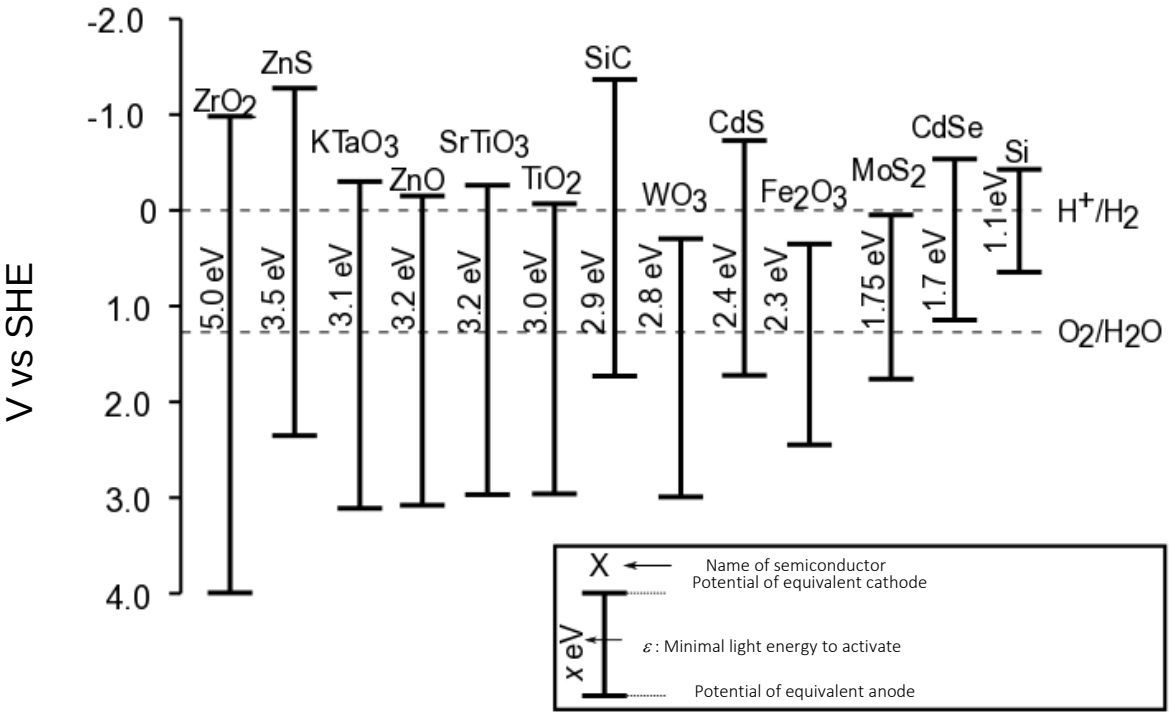


Fig. 2 – Activation condition and equivalent electrode potentials of different semiconductors. Dashed lines correspond to water oxidation and reduction potentials. SHE = Standard Hydrogen Electrode

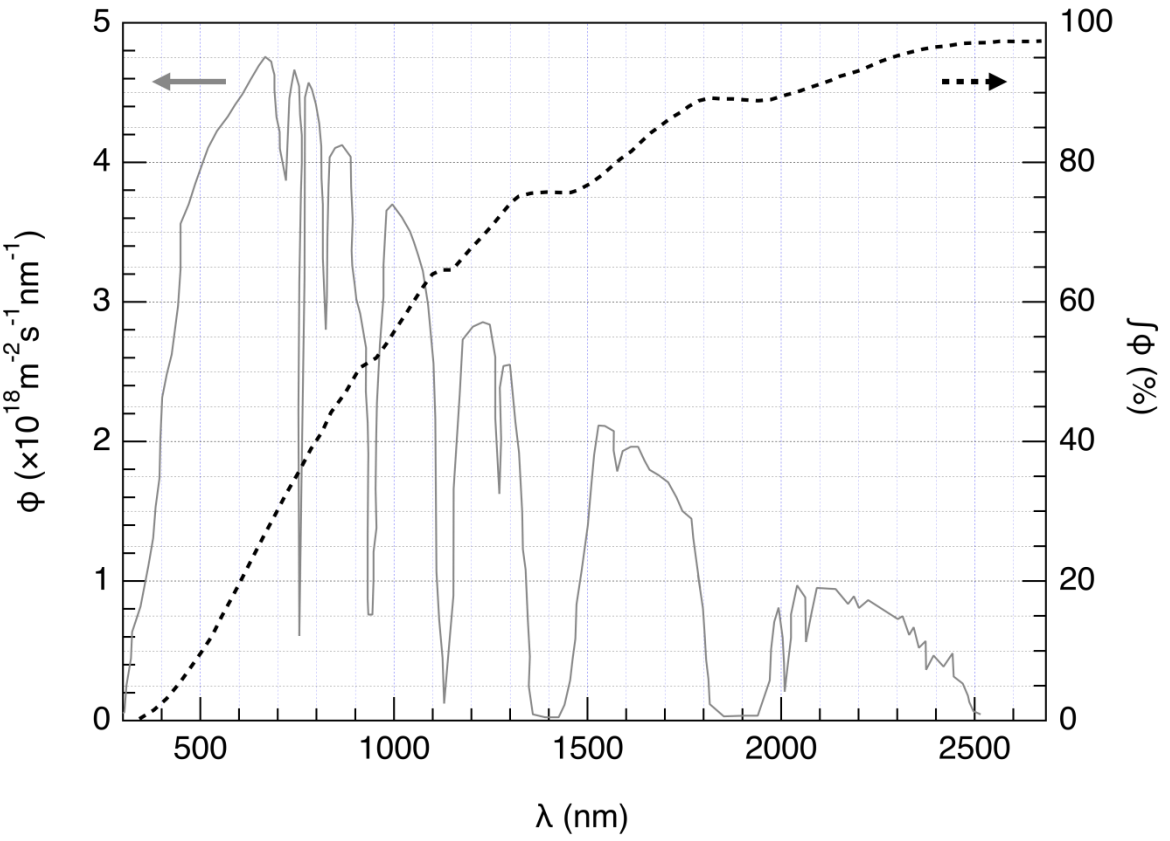


Fig. 3 – Left axis: Spectral distribution of the solar photon flux ϕ. The photon flux is the number of photons per unit area per unit time arriving on the semiconductor. Right axis and dashed line: cumulative photon flux (i.e. fraction of the photon flux with smaller wavelength).

6. **Estimate** the fraction of the solar photon flux that can activate the following semiconductors: TiO_2, CdS, Si. **State** explicitly the equations and units used for the computation.

Explanation / calculation:

E(J) = hc / λ so E(eV) = hc / λe

$\lambda = (hc/e)(1/E) = 1.240 \cdot 10^{-6}/E$ (m) $\lambda = 1240/E$ (nm)

TiO_2 $\lambda = 1240/3.0 = 413$ nm (1 point)

CdS $\lambda = 1240/2.4 = 517$ nm (1 point)

Si $\lambda = 1240/1.1 = 1127$ nm (1 point)

Graphical determination of % according to the λ values. (1 point for each value)

Total: 6 points

	Approximate fraction
TiO_2	1%
CdS	15%
Si	65%

The activation of the semi-conductor results in a modification of the surface potentials, so that it can be seen as two electrodes of different potentials.

7. Using the data in Fig 2, **choose** the semiconductor(s) in the following list that, once activated, can play both roles of anode and cathode for water-splitting reaction.

☒ ZrO_2	☒ ZnO	☒ TiO_2	☐ WO_3
☒ CdS	☐ Fe_2O_3	☐ CdSe	☐ Si

(1 point for each correct answer, −1 point for each error. No negative points in total.)

Total: 4 points

8. **Give** the semiconductor that, used as both cathode and anode, is expected to be the most efficient for water splitting upon a given solar shining.

CdS

Total: 1 point

The evolution of H_2 and O_2 when a semiconductor is irradiated by simulated solar light at T = 25 °C at p_{atm} was recently studied. Using an incident power light of P = 1.0 kW m^{-2} and a photoelectrode with a S = 16 mm^2 surface, the production of V = 0.37 cm^3 of H_2(g) was measured after Δt = 1 hour of reaction.

9. **Calculate** the power efficiency η_{direct} of the conversion.

Calculation:

Energy received from light.
$E = P \times S \times \Delta t = 10^3 \times 3600 \times 16 \times 10^{-6} = 58$ J (2 points)

Energy contained in H_2
$n(H_2) = pV/RT = 1.013 \times 10^5 \times 0.37 \times 10^{-6}/(8.314 \times 298) = 15$ µmol (2 points)
$n(H_2) \times \Delta_r G° = 3.6$ J (2 points)

Power efficiency $\eta_{direct} = 3.6/58 = 6.2$ % (2 points)

η_{direct} = 6.2 %

Total: 8 points

If you could not calculate η_{direct}, the value η_{direct} = 10% can be used in the rest of the problem.

Two modes of converting solar energy to hydrogen can thus be compared: direct photocatalysis, and indirect photo-electrolysis combining a photovoltaic panel with an electrolyzer. The efficiency of photovoltaic panels on the market is around η_{panels} = 20%.

10. **Compare** the power efficiencies of the two modes, η_{direct} and $\eta_{indirect}$, using Fe_2O_3 and Pt electrodes for the electrolysis.

Calculation:

Direct photocatalysis: $\eta_{direct} = 6.2\ \%$

Indirect photocatalysis:

$\eta_{indirect} = 0.65 \times 0.20 = 13\ \%$ (1 point)

(if calculated with the given values: $0.75 \times 0.20 = 12\ \%$)

Indirect photo-electrolysis is the most efficient:

☐ $\eta_{direct} > \eta_{indirect}$ ☐ $\eta_{direct} \approx \eta_{indirect}$ ☒ $\eta_{direct} < \eta_{indirect}$ (1 point)

(0.5 point if the data to conclude are not specified)

Total: 2 points

Problem T3 5%	Question	1	2	3	4	5	6	7	8	9	10	11	12	Total
	Points	1	3	3	3	4	2	7	2	2	3	4	6	40
	Score													

Problem T3: About silver chloride

Data at 298 K:

pK_{s1}(AgCl) = 9.7 ; pK_{s2}(Ag_2CrO_4) = 12
Formation constant of the complex $[Ag(NH_3)_n]^+$: $\beta_n = 10^{7.2}$
Potentials against the standard hydrogen electrode:
Standard potential of $Ag^+/Ag(s)$: $E°(Ag^+/Ag(s)) = 0.80$ V
Apparent potential of $O_2(aq)/HO^-(aq)$ (in seawater): $E'(O_2(aq)/HO^-(aq)) = 0.75$ V

Part A: Quotes from a chemistry lesson by Louis Joseph Gay-Lussac

The following quotes from a chemistry lesson by Louis Joseph Gay-Lussac (French chemist and physicist, 1778–1850) deal with some properties of silver chloride.

Quote A: "I will now talk about silver chloride, a milk-white solid. It is easily obtained by pouring hydrochloric acid into an aqueous solution of silver nitrate."
Quote B: "This salt has no taste since it is insoluble."
Quote C: "This compound is completely insoluble in alcohol and even in acids, except in concentrated hydrochloric acid which dissolves it readily."
Quote D: "On the other hand, silver chloride is highly soluble in aqueous solution of ammonia."
Quote E: "Then, we can make silver chloride appear again by adding an acid which reacts with ammonia."
Quote F: "If you take a bowl made of silver to evaporate salty seawater, you will get impure sodium chloride, mixed with a milk-white solid."

1. **Quote A: <u>Write</u>** the balanced chemical equation of AgCl(s) synthesis.

$Ag^+(aq) + Cl^-(aq) = AgCl(s)$ (1 point)
Any balanced equation involving also $NO_3^-(aq)$ or $H_3O^+(aq)$ or $H^+(aq)$ will also be accepted.

0 point if the equation isn't balanced.
Total: 1 point

2. **Quote B**: **<u>Calculate</u>** the solubility s of AgCl(s) in water at 298 K in mol L^{-1}.

Calculation:

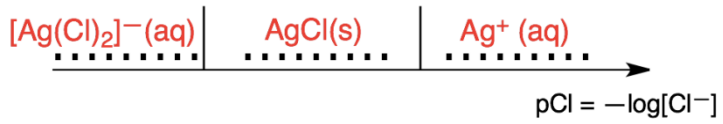
$AgCl(s) = Ag^+(aq) + Cl^-(aq)$
/ 0 0
/ s s
So $[Ag^+] = [Cl^-] = s$ (1 point)
$K_{s1} = s^2$ (1 point)
so $s = \sqrt{K_{s1}} = \sqrt{10^{-pK_{s1}}} = \sqrt{10^{-9.7}}$

$s =$ $1.41\ 10^{-5}$ mol L^{-1} (1 point)

s = $1.0\ 10^{-5}$ mol L^{-1} will be accepted

Total: 3 points

3. **Quote C**: In a highly concentrated solution of chloride ions, a well-defined complex of stoichiometry 1:2 is formed. On the following qualitative axis (with pCl increasing from left to right), **place** in each domain the silver-containing species that is predominant (or exists, for solids). pCl values at frontiers are not expected.



1 point for each domain correctly attributed
0 point if the same domain is given more than once

Total: 3 points

Quote D: When ammonia is added to silver chloride, a well-defined complex of stoichiometry n is formed.

4. **Write** the balanced equation corresponding to the synthesis of the complex $[Ag(NH_3)_n]^+$ from silver chloride and **calculate** the corresponding equilibrium constant.

Equation:
$AgCl(s) + n\ NH_3(aq) = [Ag(NH_3)_n]^+(aq) + Cl^-(aq)$ (1 point)
Calculation:
$AgCl(s) = Ag^+(aq) + Cl^-(aq)$ K_{s1}
$Ag^+(aq) + n\ NH_3(aq) = [Ag(NH_3)_n]^+(aq)$ β_n
$AgCl(s) + n\ NH_3(aq) = [Ag(NH_3)_n]^+(aq) + Cl^-(aq)$

$K = K_{s1}\beta_n$ (1 point)

$K = 10^{-9.7 + 7.2} = 10^{-2.5}$ (1 point)
$= 3.16 \cdot 10^{-3}$

Total: 3 points

If you could not calculate K, the following value can be used in the rest of the problem: $K = 10^{-3}$

5. Ammonia is added to 0.1 mol of silver chloride in 1 L of water until the last grain of solid disappears. At this moment, $[NH_3]$ = 1.78 mol L^{-1}. **Determine** the stoichiometry of the complex neglecting dilution effects.

Calculation:
Last grain of solid: $[Ag(NH_3)_n^+] = [Cl^-] = 0.1$ mol L^{-1} ; $[NH_3] = 1.78$ mol L^{-1} (1 point)
$K^\circ = \frac{[Ag(NH_3)_n^+][Cl^-]}{[NH_3]^n}$ (1 point)

so $n = \frac{\log(\frac{[Ag(NH_3)_n^+][Cl^-]}{K^\circ})}{\log([NH_3])}$ (1 point)

$n = 2$ (If $K = 10^{-3}$ is used, $n = 4$ is found.) (1 point)

Total: 4 points

6. **Write** the balanced chemical equation corresponding to **quote E**.

$[Ag(NH_3)_2]^+(aq) + 2\ H^+(aq) + Cl^-(aq) = AgCl(s) + 2\ NH_4^+(aq)$

2 points for the balanced equation (H^+ or H_3O^+ must appear as a reactant)

0 point if the equation is not balanced.

Total: 2 points

7. Assuming that seawater is slightly basic and rich in dioxygen, and that silver metal can reduce dioxygen in such conditions, **write** a balanced chemical equation corresponding to the formation of the solid mentioned in **quote F.** A stoichiometric coefficient of 1 will be chosen for dioxygen. **Calculate** its equilibrium constant at 298 K.

Equation:

$O_2(aq) + 2\ H_2O(l) + 4\ e^- = 4\ OH^-(aq)$ (reduction of O_2)

$Ag(s) + Cl^-(aq) = AgCl(s) + e^-$ (oxidation of Ag)

$4Ag(s) + 4Cl^-(aq) + O_2(aq) + 2\ H_2O(l) = 4AgCl(s) + 4\ OH^-$

(3 points: if correct equation)

without 1 for the stoichiometry for O_2: –1 point

without AgCl precipation: –1 point

Calculation:

First possibility:

$K = 10^{\frac{4}{0.06}[E'(O_2/HO^-) - E^\circ(AgCl/Ag)]}$ (1 point)

At the equilibrium, all potentials are equal, so:

$E_{eq}(AgCl/Ag) = E_{eq}(Ag^+/Ag)$ (1 point)

$E^\circ(AgCl/Ag) + 0.06 \log(1/[Cl^-]) = E^\circ(Ag^+/Ag) + 0.06 \log [Ag^+]$

so: $E^\circ(AgCl/Ag) = E^\circ(Ag^+/Ag) + 0.06 \log K_{S1} = 0.22$ V (1 point)

$K = 10^{\frac{4}{0.06}[0.75 - 0.22]} = 2.93 \times 10^{35}$ (1 point)

If $\frac{RT \ln 10}{F} = 0.059$ *is used then* $K = 10^{\frac{4}{0.059}[0.75 - 0.22]} = 2.57 \times 10^{35}$

OR

Second possibility: $K = (1/K_{s1})^4 \times 10^{\frac{4}{0.06}[0.75 - 0.80]}$ (3 points)

$K = 2.93 \times 10^{35}$ (1 point)

If $\frac{RT \ln 10}{F} = 0.059$ *is used then* $K = 2.57 \times 10^{35}$

without AgCl precipitation: 1 point for the determination of the constant

Total: 7 points

Part B: The Mohr method

The Mohr method is based on the colorimetric titration of Cl^- by Ag^+ in the presence of potassium chromate ($2K^+$, CrO_4^{2-}). Three drops (~ 0.5 mL) of a K_2CrO_4 solution at about $7.76 \cdot 10^{-3}$ mol L^{-1} are added to V_0 = 20.00 mL of a sodium chloride solution of unknown concentration C_{Cl}. This solution is then titrated by silver nitrate (Ag^+, NO_3^-) at C_{Ag} = 0.050 mol L^{-1}, which immediately leads to the formation of solid **A**. A red precipitate (solid **B**) appears at V_{Ag} = 4.30 mL.

8. **Write** the balanced equations of the two reactions occurring during the experiment. **Calculate** the corresponding equilibrium constants.

$Ag^+(aq) + Cl^-(aq) = AgCl(s)$ (0.5 point)

$K°_1 = \frac{1}{K_{S1}} = 10^{9.7}$ (0.5 point)

$2\ Ag^+(aq) + CrO_4^{2-}(aq) = Ag_2CrO_4(s)$ (0.5 point)

$K°_2 = \frac{1}{K_{S2}} = 10^{12}$ (0.5 point)

Total: 2 points

9. **Identify** the solids.

Solid **A**: $AgCl(s)$ (1 point)

Solid **B**: $Ag_2CrO_4(s)$ (1 point)

Total: 2 points

10. **Calculate** the unknown concentration C_{Cl} of chloride ions in the sodium chloride solution.

Calculations:

At V_{Ag} = 4.3 mL, $n_{Ag+,added} = n_{Cl-,introduced}$ (1 point)

so $C_{Cl} \times 20 = 0.05 \times V_{Ag}$ (1 point)

C_{Cl} = 0.011 mol L^{-1} (1 point)

Total: 3 points

If you could not calculate C_{Cl}, the value C_{Cl} = 0.010 mol L^{-1} can be used in the rest of the problem.

11. **Calculate** the minimal volume $V_{Ag}(min)$ for which AgCl(s) precipitates.

Calculation:

$AgCl_{(s)}$ precipitates as soon as: $K_{s1} = Q_{r,éq} = [Ag^+][Cl^-]$ (1 point)

And $[Cl^-] = C_{Cl} \times \frac{20}{20.5+V_{Ag}(min)} \approx C_{Cl}$ (1 point)

$[Ag^+] = \frac{K_{S1}}{[Cl^-]} = \frac{0.05 \times V_{Ag}(min)}{20.5+V_{Ag}(min)} \approx \frac{0{,}05 \times V_{Ag}(min)}{20.5}$ so $V_{Ag}(min) = \frac{20.5 \times K_{S1}}{0.05 \times [Cl^-]}$ (1 point)

$V_{Ag}(min) = 8.2 \cdot 10^{-6}$ mL with C_{Cl} = 0.010 mol L^{-1}

($V_{Ag}(min) = 8.4 \cdot 10^{-6}$ mL if no approximation $[Cl^-] \approx C_{Cl}$)

$V_{Ag}(min) = 7.4 \cdot 10^{-6}$ mL with $C_{Cl} = 0.011$ mol $^{-1}$
($V_{Ag}(min) = 7.6 \cdot 10^{-6}$ mL if no approximation $[Cl^-] \approx C_{Cl}$)

(1 point)

Total: 4 points

12. **Calculate** the residual concentration $[Cl^-]_{res}$ of chloride ions when silver chromate begins to precipitate. **Justify** why CrO_4^{2-} is a good titration endpoint indicator by comparing two values.

Calculation:

$Ag_2CrO_{4(s)}$ precipitates as soon as: $K_{s2} = Q_{r,éq} = [Ag^+]^2[CrO_4^{2-}]$ (1 point)

At this moment: $[CrO_4^{2-}] = \frac{7.76 \times 10^{-3} \times 0.5}{20.5 + V_{Ag}} = 1.56 \cdot 10^{-4}$ mol L^{-1} (1 point)

So: $[Ag^+] = \sqrt{\frac{K_{s2}}{[CrO_4^{2-}]}} = 8.00 \cdot 10^{-5}$ mol L^{-1} (1 point)

So: $[Cl^-]_{residual} = \frac{K_{s1}}{[Ag^+]}$ (1 point)

$[Cl^-]_{res} = 2.49 \cdot 10^{-6}$ mol L^{-1} (1 point)

CrO_4^{2-} is a good titration endpoint indicator because:
$[Cl^-]_{residual} << C$ (1 point)

Total: 6 points

Problem T4 7%	Question	1	2	3	4	5	6	7	8	Total
	Points	6	9	8	5	6	2	2	12	50
	Score									

Problem T4: From gunpowder to the discovery of iodine

In the 19th century, the French entrepreneur B. Courtois specialized in the production of nitrate **A** ($\mathbf{M_A}(NO_3)_m$), used for gunpowder. Initially imported from Asia, **A** was later produced from nitrate **B** ($\mathbf{M_B}(NO_3)_n$) using exchange reaction with compound **C**, obtained from algae.

1. **Find** the formulas of nitrates **A** and **B** knowing that they are anhydrous salts of alkaline or alkaline-earth metal ($\mathbf{M_A}$ and $\mathbf{M_B}$). One of the nitrates contains no more than 1 w% of non-metallic impurities while the other contains 9 ± 3 w% of impurities. The content of metals $\mathbf{M_A}$ and $\mathbf{M_B}$ in the samples is 38.4 w% and 22.4 w% respectively. **Support** your answer with calculations.

We do not know which nitrate **A** or **B** correspond to each amount of impurities, thus we have to check both options. Let's try to apply the condition that there is less than 1% of impurity for both nitrates and check if we find a correct metal in one of both cases. 1% is such a low quantity that it can be neglected.

$$w(\mathrm{M_X}) = \frac{M(\mathrm{M_X})}{M(\mathrm{M_X NO_3})} \cdot 100\% \Rightarrow M(\mathrm{M_X NO_3}) = \frac{M(\mathrm{M_X})}{w(\mathrm{M_X})} \cdot 100\% = \frac{M(\mathrm{NO_3^-})}{100 - w(\mathrm{M_X})} \cdot 100\%$$

(2 points)

Thus, the mass fraction of $\mathbf{M_A}$ in **A** is 38.4% and $\mathbf{M_B}$ in **B** is 22.4%:
In **A**:

$$M(\mathrm{M_A}) = M(\mathrm{M_A}(\mathrm{NO_3})_m) - m \cdot M(NO_3^-) = \frac{62m}{1 - 0.384} - 62m = 38.65m \text{ g mol}^{-1}$$

In **B**:

$$M(\mathrm{M_B}) = M(\mathrm{M_B}(\mathrm{NO_3})_n) - n \cdot M(NO_3^-) = \frac{62n}{1 - 0.224} - 62n = 17.9n \text{ g mol}^{-1}$$

(2 points)

For the second nitrate we cannot find the correct metal while for the **A**, the metal ($\mathbf{M_A}$) is potassium (n = 1).

Thus, for nitrate **B** we have 6 to 12% of impurities, which means that we have 88 to 94% of nitrate. We need to recheck the range of atomic mass of M_B as we have two possible candidates Na and Ca.
The mass fraction of $\mathbf{M_B}$ in **B** is between 0.224/0.94 = 0.238 and 0.224/0.88 = 0.255.
Thus the molar mass of $\mathbf{M_B}$ in **B** is between

$$M(\mathrm{M_B}) = M(\mathrm{M_B}(\mathrm{NO_3})_n) - n \cdot M(NO_3^-) = \frac{62n}{1 - 0.238} - 62n = 19.36n \text{ g mol}^{-1}$$

And

$$M(\mathrm{M_B}) = M(\mathrm{M_B(NO_3)_}n) - n \cdot M(NO_3^-) = \frac{62n}{1-0.255} - 62n = 21.22n \text{ g mol}^{-1}$$

Finally we find **B**: $Ca(NO_3)_2$ (2 points)

$\mathbf{M_A}$: K and $\mathbf{M_B}$: Ca

A: KNO_3 and **B**: $Ca(NO_3)_2$

Total: 6 points (3 points for each correct compound).

To obtain **A**, 262.2 g of solid compound **C** were added to the solution containing 442.8 g of **B**. **B** is known to be in excess. As a result, 190.0 g of white precipitate **D** were formed and removed by filtration. The filtrate was evaporated, and the obtained solid mixture **E** was heated until the mass of the sample (containing only nitrites, NO_2^-) was constant. The only gaseous product was dioxygen: 60.48 L at 0 °C at 1 atm (dioxygen can be considered as an ideal gas).

2. **Calculate** the composition (in w%) of mixture **E** considering that it contained only compounds **A** and **B** and no other impurities, and that **C** was taken in pure anhydrous state.

We have the following reaction: $Ca(NO_3)_2$ + **C** → KNO_3 + **D**(s)

As $Ca(NO_3)_2$ is in excess thus **C** is the limiting reactant. All compound **C** was consumed and **D** was precipitated, thus the mixture **E** represents a mixture of $Ca(NO_3)_2$ in excess and KNO_3 which was formed. Using the mass conservation law, we can calculate the mass of the mix **E**:

m(nitrates) = *m*(**A**) + *m*(**B**) – *m*(**D**) = 442.8 + 262.2 – 190 = 515.0 g (2 points)

The reactions of the decomposition of both nitrates can be written:

$Ca(NO_3)_2 = Ca(NO_2)_2 + O_2$

$2KNO_3 = 2KNO_2 + O_2$

(1 point for each equilibrated reaction,
–0.5 point per reaction if the coefficients are wrong)

Now we can calculate the amount of O_2:

$$PV = n(\mathrm{O_2}) \cdot RT$$

$$\Rightarrow n(\mathrm{O_2}) = \frac{PV}{RT} = \frac{101.325 \times 60.48}{8.314 \times 273.15} = 2.70 \text{ mol}$$

(2 points)

[It is not necessary to calculate the amount of O_2, which is the same as the initial amount of $Ca(NO_3)_2$.]

Now we can write the following equation for the numbers of moles, assuming that the mass of **A** is *x* g and the mass of **B** is (515 – *x*) g.

$$\frac{x}{2 \times 101} + \frac{515 - x}{164} = 2.70 \Rightarrow x = 383.8 \text{ g}$$ (2 points)

So the mass of **A** (KNO_3) is 383.8 g and the mass of **B** is 131.2 g ($Ca(NO_3)_2$).

And thus the w% of **A** is 74.5% and w% of **B** is 25.5%. (1 point)

w% of **A**: 74.5 and of **B**: 25.5

Total: 9 points

3. **Determine** the formulas of compounds **C** and **D** and **write** the balanced reaction equation between **B** and **C**.

We can write the reaction of KNO_3 formation as:
$Ca(NO_3)_2 + K_xX \rightarrow 2KNO_3 + CaX_{2/x}(s)$.
Our aim is to find the anion X^{x-} by calculating its molar mass.
If $n(KNO_3) = 383.8/101 = 3.8$ mol, the amount $n(CaX_{2/x}) = 1.9$ mol.

(2 points)

And knowing its mass which is 190 g, we obtain the molar mass of $CaX_{2/x}$:

$$M(\mathrm{CaX}) = \frac{m}{n} = \frac{190}{1.9} = 100\ g\ mol^{-1}$$

The molar mass of Ca is 40 g mol^{-1}, thus the molar mass of $X^{x-} \times x/2$ is 60 g mol^{-1} and it corresponds to CO_3^{2-} (first we consider that X is a pure element and then we consider that it is binary and contains oxygen).

(2 points)

C: K_2CO_3 and **D:** $CaCO_3$

(2 points)

Reaction between **B** and **C**:

$Ca(NO_3)_2 + K_2CO_3 \rightarrow 2KNO_3 + CaCO_3(s)$ (2 points)

Total: 8 points

In 1811, when working with algae ashes, Courtois observed that copper vessels were worn out faster than usual. While he was studying this phenomenon, his cat entered the laboratory and spilled the solution of concentrated sulfuric acid on the dry algae ashes: violet vapors instantly came out of the vessel (**1**, sulfuric acid is the oxidizing agent): iodine (I_2) had just been discovered! Iodine was the cause of the copper corrosion **(2)**. However, because of the medicinal applications of iodine, Courtois opened a new manufacture to produce it by reaction of algae with chlorine (**3**).
Nowadays, iodine is prepared from the set of reactants (NO_3^-, I^-, H^+) (**4**) or (IO_3^-, I^-, H^+) (**5**).

4. **Write** balanced equations for reactions **1–5**.

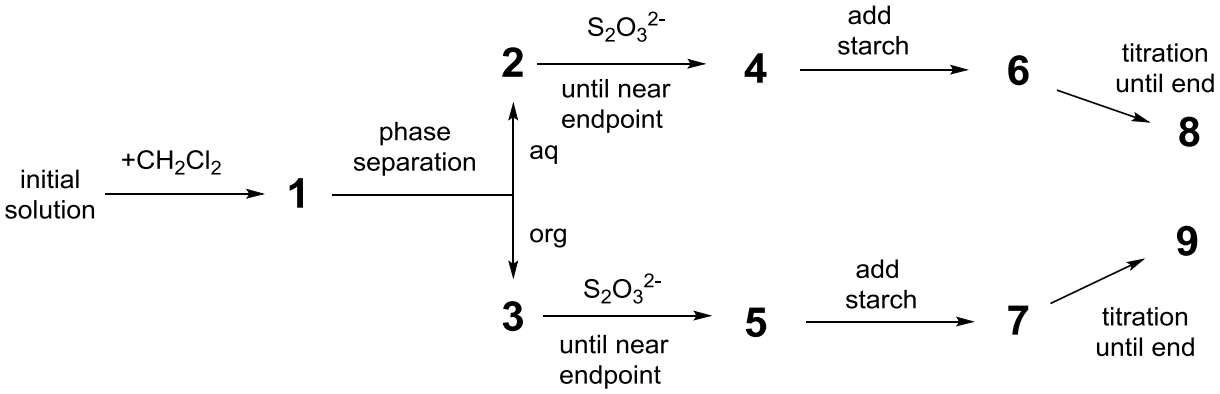
1 $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$ (any chemically reasonable redox equation involving I_2 will be accepted)	(1 point)
2 $2Cu + I_2 \rightarrow 2CuI$	(1 point)
3 $2I^- + Cl_2 \rightarrow 2Cl^- + I_2$	(1 point)
4 $2NO_3^- + 6I^- + 8H^+ \rightarrow 3I_2 + 2NO + 4H_2O$ or $2NO_3^- + 2I^- + 4H^+ \rightarrow I_2 + 2NO_2 + 2H_2O$	(1 point)
5 $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$	(1 point)
Total: 5 points	

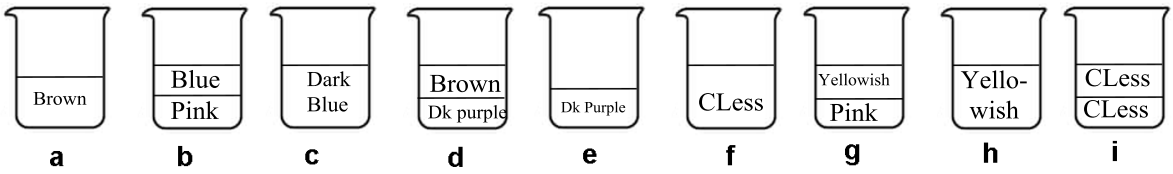
The solubility of iodine is very low in water but significantly increases when iodide ions are added. Together they form ions such as triiodide, I_3^-:

$$I^-(aq) + I_2(aq) = I_3^-(aq) \qquad \textbf{(6)}$$

Equilibrium (**6**) can be studied through the extraction of I_2 with dichloromethane. Indeed, I^- and I_3^- do not dissolve in organic solvents but I_2 does and, when extracted, it is 15 times more concentrated in dichloromethane than in water.

The following experiment was performed. To prepare the initial solution, a few crystals of solid iodine were dissolved in 50.0 mL of an aqueous solution of potassium iodide (0.1112 g). Then, 50.0 mL of dichloromethane were added, and the mixture was vigorously shaken until equilibration. After phase separation, each phase was titrated by 16.20 mL (organic phase) and by 8.00 mL (aqueous phase) of the standard aqueous solution of sodium thiosulphate pentahydrate (14.9080 g in 1.000 L of solution) in the presence of starch. The process is schematically represented below:





CLess = coulourless Dk = dark

5. **Find** the correspondence between the stages on the scheme (**1**–**9**) and the schematic pictures representing them (**a**–**i**).

Stages	Picture
1	d
2	a
3	e
4	h
5	g
6	c
7	b
8	f
9	i

Total: 6 points

(1 point for **1**, **4** and **5**; 0.5 point for the others)

6. **Write** balanced equations for the two possible chemical reactions in the aqueous phase during the titration involving iodine species and sodium thiosulphate.

$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$ (1 point)
$2Na_2S_2O_3 + I_3^- = 2NaI + I^- + Na_2S_4O_6$ (1 point)

Total: 2 points

7. **Calculate** the mass of iodine used to prepare the initial solution.

$$C_M(Na_2S_2O_3) = \frac{n(Na_2S_2O_3)}{V} = \frac{m(Na_2S_2O_3)}{M(Na_2S_2O_3)\cdot V} = \frac{14.908}{248.18\times 1} = 0.060 \text{ mol L}^{-1}$$

The concentration of $Na_2S_2O_3$ solution is then 0.060 mol L^{-1}. (1 point)

$$m(I_2) = M(I_2)\cdot n(I_2) = M(I_2)\cdot\left(\frac{V_1+V_2}{1000}\right)\cdot\frac{C_M(Na_2S_2O_3)}{2} = 254\cdot\left(\frac{16.2+8.0}{1000}\right)\cdot\frac{0.06}{2} = 0.184 \text{ g}$$

(0.5 point)

$m(I_2) =$ 0.184 g (0.5 point)

Total: 2 points

8. **Calculate** the equilibrium constant $K°$ for equilibrium of reaction (**6**).

For the organic phase:

$n(Na_2S_2O_3) = C_M(Na_2S_2O_3)\cdot V = 0.06\times 16.20\cdot 10^{-3} = 9.72\cdot 10^{-4}$ mol (1 point)

Now we can calculate the amount of iodine in aqueous solution using the extraction constant:

$$K_{ex} = \frac{[I_2]_{org}}{[I_2]_{aq}} = \frac{\frac{n(I_2)_{org}}{V_{org}}}{\frac{n(I_2)_{aq}}{V_{aq}}} = \frac{n(I_2)_{org}}{n(I_2)_{aq}} = 15$$

$$\Rightarrow n(I_2)_{aq} = \frac{n(I_2)_{org}}{15} = \frac{0.5\cdot n(Na_2S_2O_3)_{org}}{15} = \frac{0.5\times 9.72\cdot 10^{-4}}{15} = 3.24\cdot 10^{-5} \text{ mol}$$

(2 points)

For aqueous phase:

$n(I_2)_{aq} + n(I_3^-)_{aq} = \frac{1}{2}n(Na_2S_2O_3)_{aq}$ (1 point)

$n(Na_2S_2O_3)_{aq} = C_M(Na_2S_2O_3)\cdot V = 0.06\cdot 8.00\cdot 10^{-3} = 4.8\cdot 10^{-4} mol$ (1 point)

$n(I_2)_{aq} + n(I_3^-)_{aq} = \frac{1}{2}C_M(Na_2S_2O_3)_{aq}\cdot V = \frac{1}{2}\cdot 0.06\cdot 8.00\cdot 10^{-3} = 2.4\cdot 10^{-4} mol$ (1 point)

$n(I_3^-)_{aq} = \left[n(I_2)_{aq} + n(I_3^-)_{aq}\right] - n(I_2)_{aq} = 2.4\cdot 10^{-4} - 3.24\cdot 10^{-5} = 2.08\cdot 10^{-4} mol$ (1 point)

We can calculate the initial number of moles of KI, this amount is equal to the total number of moles of iodide and triiodide in aqueous solution:

$$n(I^-)_{aq} + n(I_3^-)_{aq} = n(KI) = \frac{m}{M} = \frac{0.1112g}{166g/mol} = 6.7 \cdot 10^{-4} mol$$

(1 point)

$$n(I^-)_{aq} = n(KI) - n(I_3^-)_{aq} = 6.7 \cdot 10^{-4} - 2.08 \cdot 10^{-4} = 4.62 \cdot 10^{-4} mol$$

(2 points)

The equilibrium constant is:

$$K_{eq} = \frac{[I_3^-]}{[I^-] \cdot [I_2]} = \frac{2.08 \cdot 10^{-4} / 0.05}{4.62 \cdot 10^{-4} / 0.05 \cdot 3.24 \cdot 10^{-5} / 0.05} = 695$$

$K°$ = 695
(2 points)

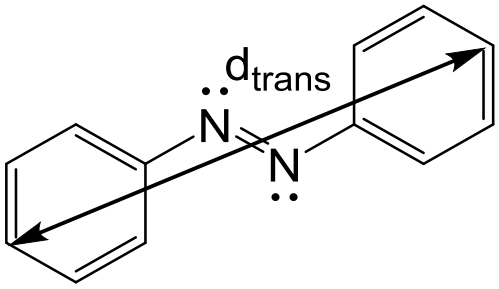
Total: 12 points

Problem T5 8%	Question	1	2	3	4	5	6	7	8	9	10	11	12	Total
	Points	3	4	4	2	5	5	4	3	5	2	2	2	41
	Score													

Problem T5: Azobenzene – β-cyclodextrin complexes for the formation of nanomachines

Nanomachines are molecular assemblies that enable the transformation of an energy source into a nano-movement for applications such as drug delivery. Numerous nanomachines make use of the isomerization of azo compounds (R–N=N−R') upon irradiation.

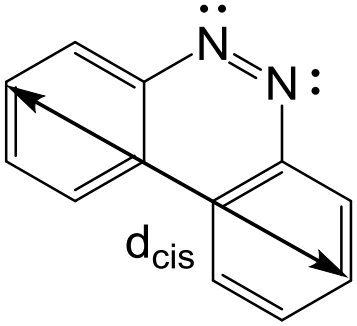
1. **Draw** the stereoisomers of azobenzene (H_5C_6–N=N–C_6H_5) and **draw** a line between the two carbon atoms that are the furthest apart. **Compare** these two distances (d_{trans} and d_{cis}).



(0.5 point: correct *trans* formula) (Ph, C_6H_5 also accepted, 150° > CNN angles > 100°, correct NCC angles)

(0.5 point: correct *trans* distance scheme) (Ph should be developed to show all C atoms, the arrows should represent exactly the distance between the two extreme C4 and C4' carbon atoms. No approximation.)

trans



(0.5: point correct *cis* formula) (Ph, C_6H_5 also accepted, 150° > CNN angles > 100°, correct NCC angles)

(0.5 point: correct *cis* distance scheme) (Ph should be developed to show all C atoms, the arrows should represent exactly the distance between the two extreme carbons (C3-C3' or C4-C4' depending on the drawing, not C3-C4'). No approximation.)

cis

Comparison: d_{trans} > d_{cis} (1 point)

Total: 3 points

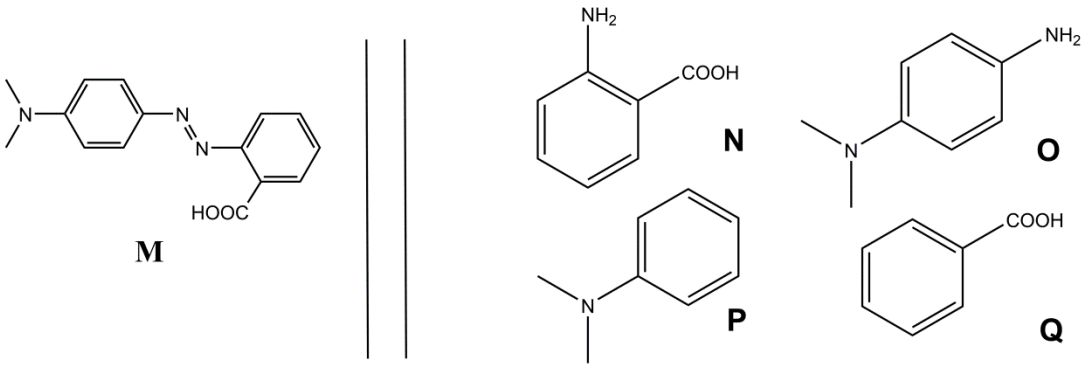


*Fig. 1 – Possible reactants for the synthesis of **M**.*

2. **M** can be synthesized in two steps from simple reactants (Fig. 1). **Choose** among the suggested reactants (**N** to **Q**) the ones that can provide **M** with very high regioselectivity. Sodium nitrite ($NaNO_2$) in cold aqueous hydrochloric acid is used as reagent for the first step of the synthesis.

Reactants: **N** and **P** **Total: 4 points** (1 point for **O** + **Q**)

Determination of the association constant K_t

β-cyclodextrin (C, Fig. 2) is a cyclic heptamer of glucose, which can form inclusion complexes with azo compounds. In tasks 3 to 6, we will determine by spectroscopy the association constant K_t, corresponding to the formation of the inclusion complex CM_{trans} as depicted in Fig. 2.

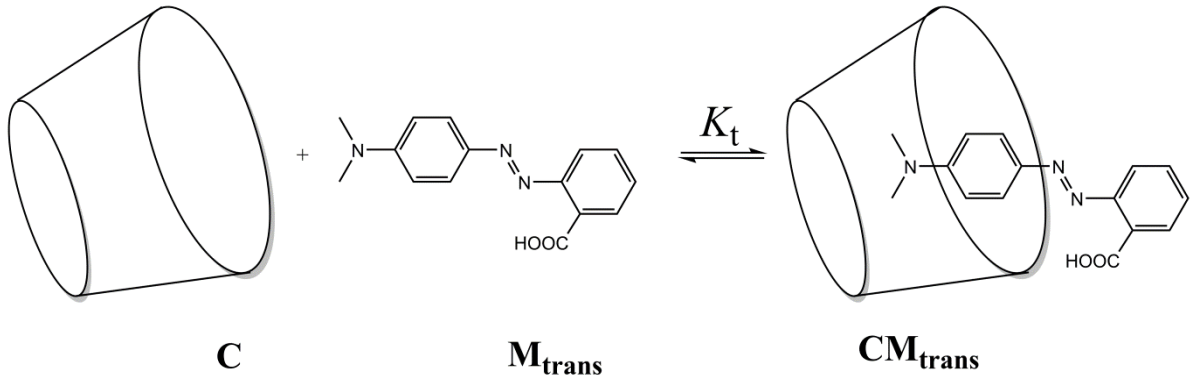


*Fig. 2 – Formation of the **CM**$_{trans}$ inclusion complex.*

Several solutions are prepared by mixing **C** and $\mathbf{M}_{trans}$ in different proportions to reach initial concentrations $[\mathbf{C}]_0$ and $[\mathbf{M}_{trans}]_0$. While $[\mathbf{M}_{trans}]_0$ is identical for all solutions, $[\mathbf{C}]_0$ varies. We follow, at a fixed wavelength, the evolution of the difference in absorbance ΔA between the absorbance of each solution and the pure $\mathbf{M}_{trans}$ solution. We note the molar absorption coefficients of $\mathbf{CM}_{trans}$ and $\mathbf{M}_{trans}$, $\varepsilon_{CMtrans}$ and ε_{Mtrans}, respectively. L is the path length of the beam through the sample. The absorbance of **C** (ε_C) is negligible.

3. **Demonstrate** that $\Delta A = \alpha \cdot [\mathbf{CM}_{trans}]$ and **express** α in terms of known constant(s).

Demonstration:

$\Delta A = A(\mathbf{CM_{trans}}) + A(\mathbf{M_{trans}}) - A(\text{pure } \mathbf{M}_{\text{trans}} \text{ solutions})$: (1 point: definition ΔA)

$\Delta A = \varepsilon_{CMtrans}.L.[\mathbf{CM_{trans}}] + \varepsilon_{Mtrans}.L.[\mathbf{M_{trans}}] - \varepsilon_{Mtrans}.L.[\mathbf{M_{trans}}]_0$ (1 point: Beer Lambert)

As $[\mathbf{M_{trans}}]_0 = [\mathbf{CM_{trans}}] + [\mathbf{M_{trans}}]$ (1 point : mass balance)

$\Delta A = \varepsilon_{CMtrans}.L.[\mathbf{CM_{trans}}] + \varepsilon_{Mtrans}.L.([\mathbf{M_{trans}}]_0 - [\mathbf{CM_{trans}}]) - \varepsilon_{Mtrans}.L.[\mathbf{M_{trans}}]_0$

$= (\varepsilon_{CMtrans} - \varepsilon_{Mtrans}).L.[\mathbf{CM_{trans}}]$

$$\alpha = L\,(\varepsilon_{CMtrans} - \varepsilon_{Mtrans})$$ (1 point)

Total: 4 points

4. **Demonstrate** that, when **C** is in large excess with respect to $\mathbf{M}_{\text{trans}}$ (*i.e.* $[\mathbf{C}]_0 >> [\mathbf{M_{trans}}]_0$), the concentration of **C** may be considered as constant, $[\mathbf{C}] \simeq [\mathbf{C}]_0$.

Demonstrations:

$[\mathbf{C}] = [\mathbf{C}]_0 - [\mathbf{CM_{trans}}]$ (1 point)

$[\mathbf{CM_{trans}}] < [\mathbf{M_{trans}}]_0$, $<< [\mathbf{C}]_0$, so $[\mathbf{C}] \simeq [\mathbf{C}]_0$ (1 point)

Total: 2 points

5. **Demonstrate** that, when **C** is in large excess with respect to $\mathbf{M}_{\text{trans}}$ (*i.e.* $[\mathbf{C}]_0 >> [\mathbf{M_{trans}}]_0$), $\Delta A = \alpha \cdot \frac{\beta \cdot [\mathbf{C}]_0}{1 + K_t \cdot [\mathbf{C}]_0}$ and **express** β in terms of constant(s) and initial concentration(s).

Demonstration:

$K_t = \frac{[\mathbf{CMtrans}]}{[\mathbf{Mtrans}].[\mathbf{C}]}$ (Or $K_t = \frac{[\mathbf{CMtrans}].c^\circ}{[\mathbf{Mtrans}].[\mathbf{C}]}$) (1.5 point: K_t)

$[\mathbf{M_{trans}}]_0 = [\mathbf{CM_{trans}}] + [\mathbf{M_{trans}}]$ (0.5 point: mass balance)

So $[\mathbf{M_{trans}}]_0 = [\mathbf{CM_{trans}}](1 + \frac{1}{K_t \cdot [C]})$

So $[\mathbf{CM_{trans}}] = [\mathbf{M_{trans}}]_0 \frac{K_t \cdot [C]}{1 + K_t \cdot [C]}$

As $[\mathbf{C}] \simeq [\mathbf{C}]_0$, $[\mathbf{CM_{trans}}] = [\mathbf{M_{trans}}]_0 \frac{K_t \cdot [C]_0}{1 + K_t \cdot [C]_0}$

$\Delta A = \alpha\,[\mathbf{M_{trans}}]_0 \frac{K_t \cdot [C]_0}{1 + K_t \cdot [C]_0}$

$$\beta = K_t\,[\mathbf{M_{trans}}]_0$$ (3 points)

Total: 5 points

6. **Determine** K_t using the following experimental curve (Fig. 3).

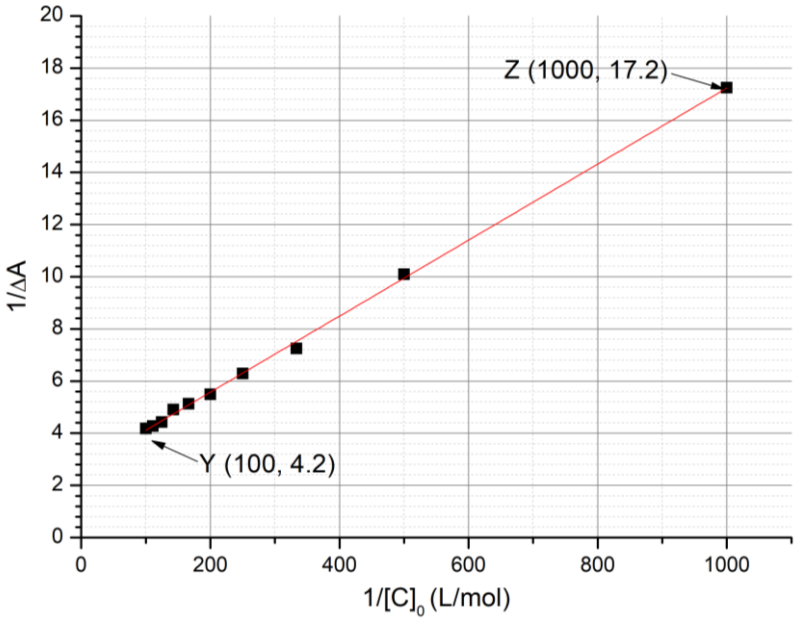


Fig. 3 – Evolution of 1/ΔA as a function of 1/[C]$_0$.

Calculations:

$\frac{1}{\Delta A} = \frac{1}{a\,\beta}\left(\frac{1}{[C]_0} + K_t\right)$ (1 point)

$K_t = \frac{intercept}{slope}$ (1 point)

Using either the graph or linear regression on calculator, we determine the equation

$\frac{1}{\Delta A} = 0.0144\left(\frac{1}{[C]_0}\right) + 2.76$ (1 point: 0.5 slope + 0.5 intercept, within 10%)

(within ± 10% for slope and intercept, no unit needed).

Slope = $\frac{yZ-yY}{xZ-xY}$; intercept = $\frac{xZ.yZ-xZ.yY}{xZ-xY}$;

So $\frac{\text{intercept}}{\text{slope}} = \frac{xZ.yY-xY.yZ}{yZ-yY}$

$K_t = \frac{1000\times4.2-100\times17.2}{17.2-4.2}$

K_t = 191 (2 points if within 10%, 1 point if within 20%)

Total: 5 points

Determination of the association constant K_c

In tasks 7 to 9, we will determine by kinetic studies the association constant K_c, corresponding to the formation of the inclusion complex with $\mathbf{M}_{cis}$, $\mathbf{CM}_{cis}$. A sample containing only $\mathbf{M}_{trans}$ is irradiated, thus producing a known amount of $\mathbf{M}_{cis}$, $[\mathbf{M}_{cis}]_0$. $\mathbf{M}_{cis}$ (free or within the inclusion complex) then thermally isomerizes into $\mathbf{M}_{trans}$. In the absence of **C**, the isomerization follows a first order kinetics with a rate constant k_1. All complexation equilibria are faster than the isomerization processes. The kinetic scheme corresponding to this experiment is provided in Fig. 4.

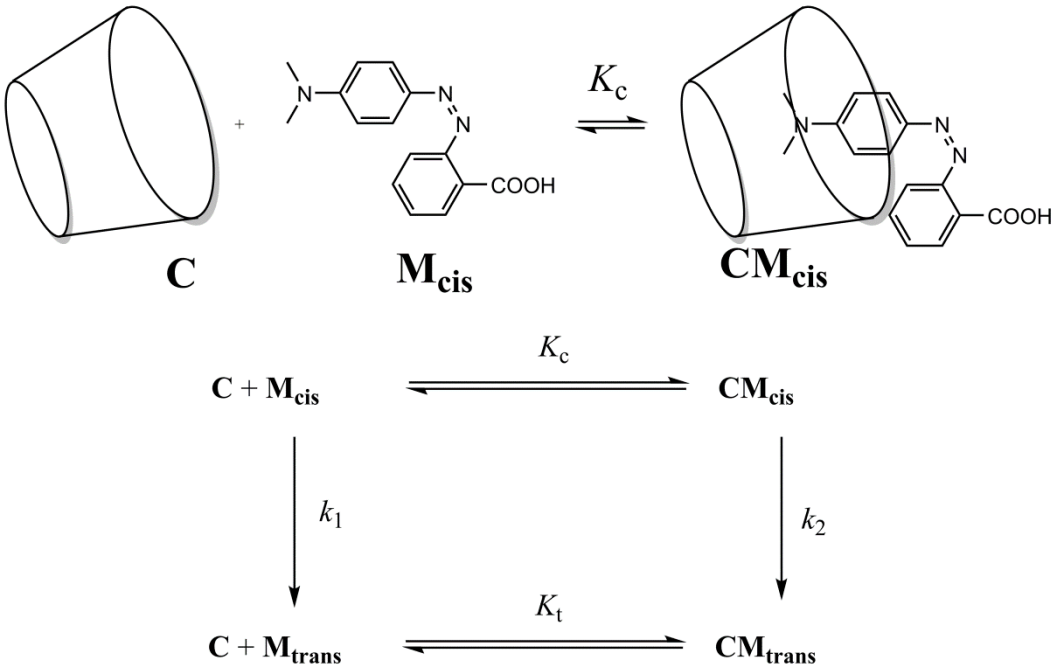


*Fig. 4 – Kinetic scheme for the isomerization of $\boldsymbol{M}_{cis}$ in the presence of **C**.*

The rate of disappearance r for the total amount of $\mathbf{M}_{cis}$ (free and complexed) is defined as

$$r = k_1[\mathbf{M}_{cis}] + k_2[\mathbf{CM}_{cis}]$$

Experimentally, r follows an apparent first order kinetic law with an apparent rate constant k_{obs}:

$$r = k_{obs}([\mathbf{M}_{cis}] + [\mathbf{CM}_{cis}])$$

7. **Demonstrate** that $k_{obs} = \frac{\gamma+\delta\cdot k_2[\mathbf{C}]}{1+K_c[\mathbf{C}]}$ and **express** γ and δ in terms of known constant(s).

Demonstration:

$k_{obs}([\mathbf{M}_{cis}]+ [\mathbf{CM}_{cis}]) = k_1[\mathbf{M}_{cis}] + k_2 [\mathbf{CM}_{cis}]$ (0.5 point)

and $K_c = \frac{[\mathbf{CMcis}]}{[\mathbf{Mcis}].[\mathbf{C}]}$ (1.5 point: K_c)

so $[\mathbf{CM}_{cis}] = K_c [\mathbf{C}] [\mathbf{M}_{cis}]$

So $k_{obs}([\mathbf{M}_{cis}]+ K_c [\mathbf{C}] [\mathbf{M}_{cis}]) = k_1[\mathbf{M}_{cis}] + k_2 K_c [\mathbf{C}] [\mathbf{M}_{cis}]$,
Which can be written as:

$$k_{obs} = \frac{k_1 + K_c \cdot k_2[\mathbf{C}]}{1 + K_c[\mathbf{C}]}$$

$\gamma = k_1$ (1 point) and $\delta = K_c$ (1 point)

Total: 4 points

8. **Choose** in which condition(s) the half-life $t_{1/2}$ corresponding to k_{obs} can be expressed as $t_{1/2} = \frac{\ln 2}{\gamma}(1 + K_c[\mathbf{C}]_0)$ given that $[\mathbf{C}]_0 >> [\mathbf{M}_{cis}]_0$. Mathematically **justify** your answer.

- ☒ Very slow isomerization of $\mathbf{M}_{cis}$ within cyclodextrin (2 points)
- ☐ Very slow isomerization of free $\mathbf{M}_{cis}$
- ☐ $\mathbf{CM}_{cis}$ very stable
- ☐ $\mathbf{CM}_{trans}$ very stable

0 for any other answer, or multiple answers.

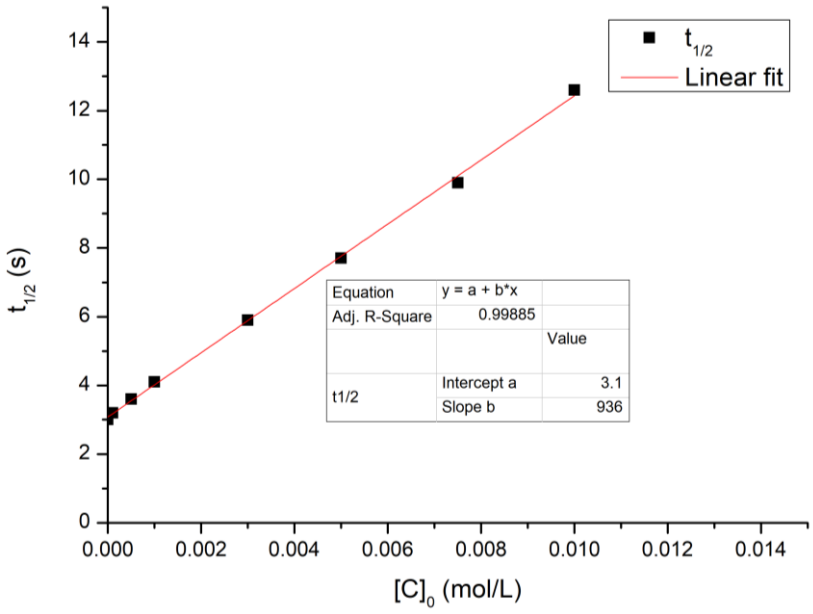
Demonstration:

We need $k_{obs} \simeq \frac{\gamma}{1+K_c[C]}$, so $\gamma \gg k_2\,[\mathbf{C}]_0$, so $k_2 \simeq 0$: slow isomerization (1 point)

Total: 3 points

9. Assuming the condition(s) in task 8 satisfied, **determine** K_c by a linear regression using the data below. You may use a calculator or plot a graph.

$[\mathbf{C}]_0$ (mol L^{-1})	$t_{1/2}$ (s)	$[\mathbf{C}]_0$ (mol L^{-1})	$t_{1/2}$ (s)
0	3.0	$3.0\cdot10^{-3}$	5.9
$1.0\cdot10^{-4}$	3.2	$5.0\cdot10^{-3}$	7.7
$5.0\cdot10^{-4}$	3.6	$7.5\cdot10^{-3}$	9.9
$1.0\cdot10^{-3}$	4.1	$1.0\cdot10^{-2}$	12.6



Equation of the linear regression:

Using a graphical representation or linear regression on the calculator one can determine:

$t_{1/2} = \frac{ln2}{\gamma}(1 + K_c[\boldsymbol{C}]_0) = 3.1 + 936\,[\mathbf{C}]_0$ (2 points : 1 slope + 1 intercept within 20%)

$K_c = \frac{slope}{intercept}$ (1 point)

$K_c =$ 302 (2 points)

Total: 5 points

Formation of nanomachines

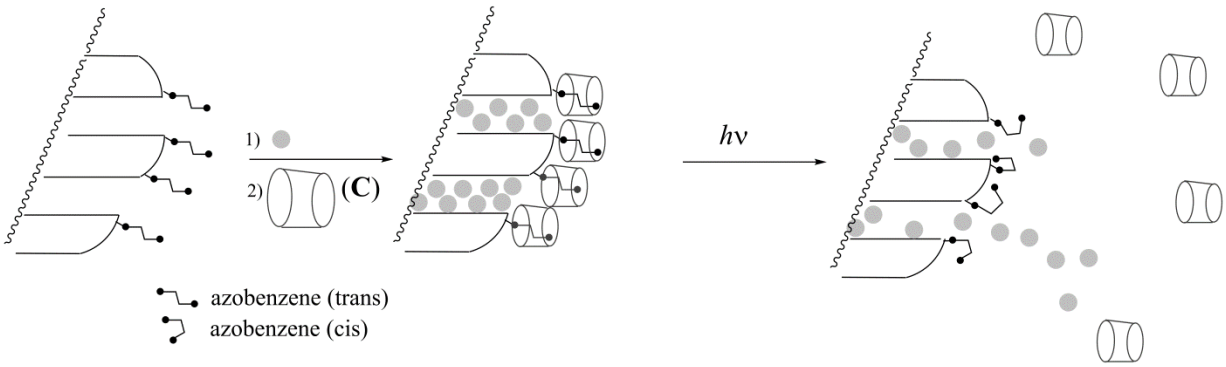


Fig. 5 – Cleavage of an azobenzene–cyclodextrin inclusion complex induced by a light-triggered isomerization, which allows delivery of a dye (grey circles).

Another azobenzene compound (for which $K_c << K_t$), initially in the *trans* form, is covalently grafted on silica (Fig. 5). The silica pores are filled with a dye (rhodamine B, grey circles in Fig. 5). Upon addition of **C**, an inclusion complex is formed, which blocks the pores and prevents the release of the dye.

10. **Choose** the most appropriate condition (one choice only) so that the pores are initially blocked in the presence of **C**, and the dye can be released upon irradiation.

☐ $K_t >> 1$	(1 point)
☒ $K_t >> 1$ and $K_c << 1$	(2 points)
☐ $K_t / K_c << 1$	(0 point)
☐ $K_t >> 1$ and $K_c >> 1$	(0 point)
☐ $K_c << 1$	(1 point)

0 point if multiple answers except for ☒ $K_c << 1$ AND ☒ $K_t >> 1$: 1 point

Total: 2 points

This azobenzene-silica powder loaded with a dye is placed in the corner of a cuvette (Fig. 6) so that the powder cannot move into solution. The powder is irradiated at a wavelength λ_1 to trigger the release of the dye from the pores (Fig. 5). To monitor this release by absorbance spectroscopy we measure the absorbance of the solution at wavelength λ_2.

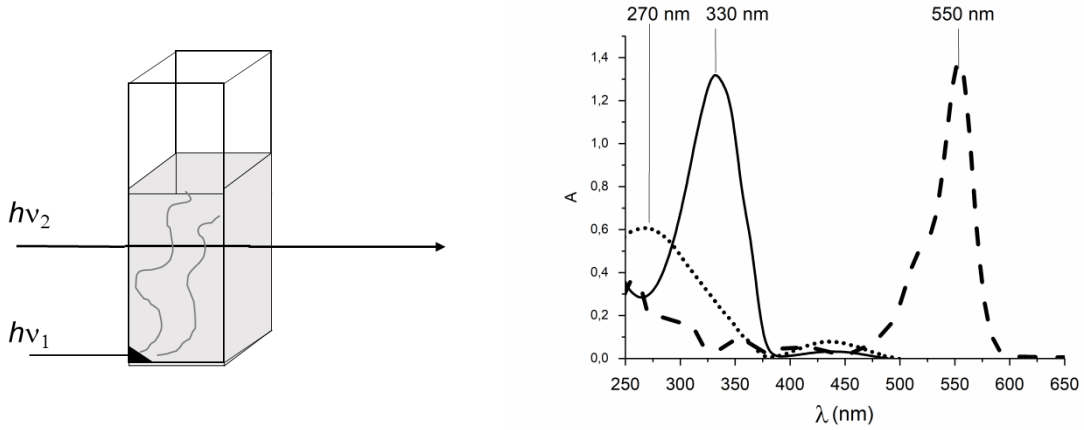


Fig. 6 – Left: experimental setup used to monitor the release of the dye; right: absorption spectra of trans-azobenzene (full line), cis-azobenzene (dotted line) and rhodamine B (dashed line).

11. **Determine** λ_1.

λ_1 = 330 nm (*trans* azobenzene is irradiated to form the *cis* compound which dissociates)

Total: 2 points

12. **Determine** λ_2.

λ_2 = 550 nm (the release of the dye into solution is monitored)
Total: 2 points

Problem T6 8%	Question	1	2	3	4	5	6	7	8	9	Total
	Points	4	4	5	3	10	2	9	6	5	48
	Score										

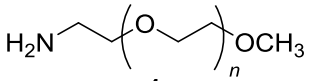
General remarks:

1. For an incorrectly carried out calculation, 0.5 points are subtracted.
2. Unless stated otherwise, – 0.5 point for minor mistakes, including wrong valency, missing carbon or hydrogen atom on a heteroatom or wrong/missing charge.

Problem T6: Characterization of a block-copolymer

Block-copolymers, obtained by linking different polymers (blocks), have unique properties, such as the ability to self-assemble. In this problem, the synthesis and characterization of such macromolecules are studied.

Study of the first block



1

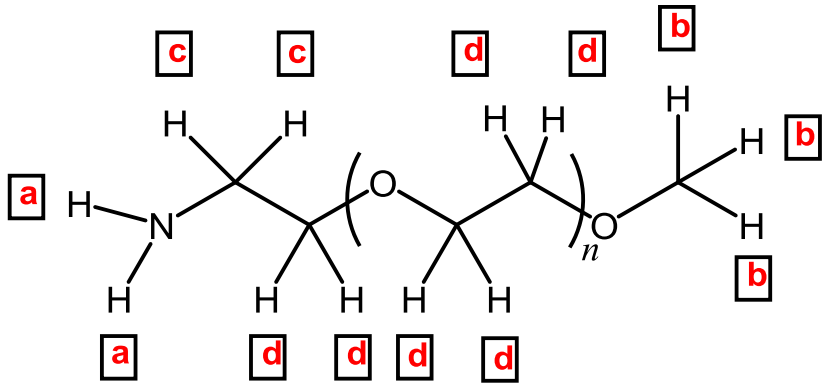
In this first part, we will study the water soluble homopolymer **1** (α-methoxy-ω-aminopolyethyleneglycol).

The ^{1}H NMR spectrum of **1** (DMSO-d_6, 60 °C, 500 MHz) includes the following signals:

Index	δ (ppm)	Peak Area
a	2.7*	0.6
b	3.3	0.9
c	3.4	0.6
d	~ 3.5	133.7

*Table 1, *in the presence of D_2O, the signal at 2.7 ppm disappears.*

1. **Match** the ^{1}H NMR signals (a, b, c, d) from Table 1 with each of the corresponding protons.



Total: 4 points

–1 point for each misassigned or unassigned group of equivalent protons, irrespective of the exact number of misassigned/unassigned protons for a group.
0 point for three or more misassigned or unassigned groups

2. **Express** the average degree of polymerization n as a function of the area A_{OC2H4} of the NMR peak of the repeating unit and the area A_{OCH3} of the NMR peak of the methyl end group. **Calculate** n.

$n = (A_{OC2H4}/4)/(A_{OCH3}/3)$ $A_{OC2H4} = A_d – 0.6$ (3 points)
1.5 if any proportionality relation

$n = \frac{133.1 \cdot 3}{0.9 \cdot 4} = 111$ (1 point)

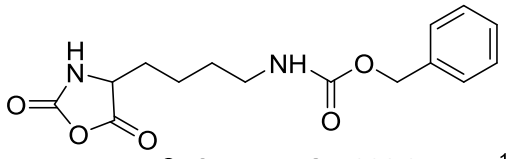
$n = 111$

Total: 4 points

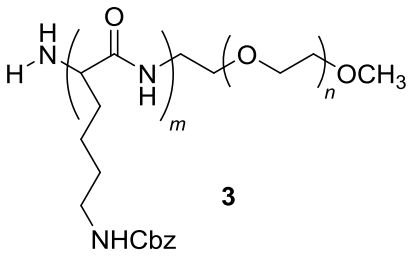
If you could not calculate n, the value n = 100 can be used in the rest of the problem.

Study of a diblock-copolymer

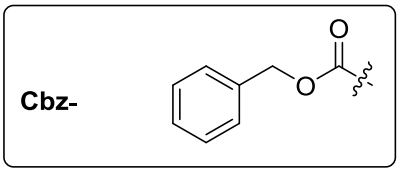
The synthesis of the second block of the copolymer is performed through the reaction of **1** with **2** (ε-(benzyloxycarbonyl)-lysine *N*-carboxyanhydride). This yields the block-copolymer **3**.



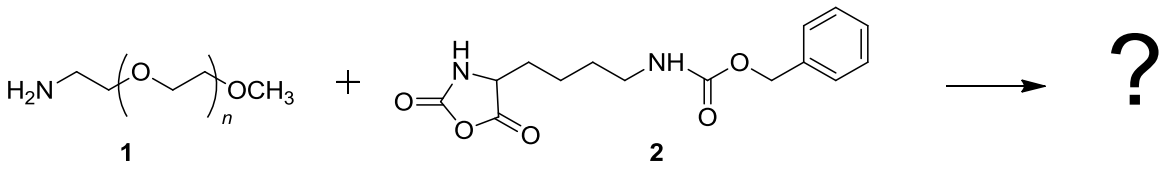
2: $C_{15}H_{18}N_2O_5$, 306.3 g mol^{-1}



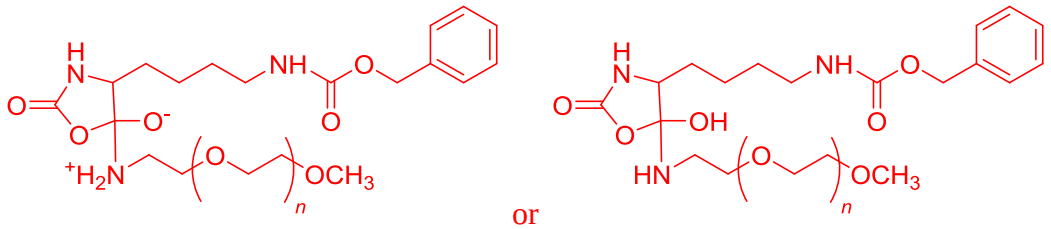
3



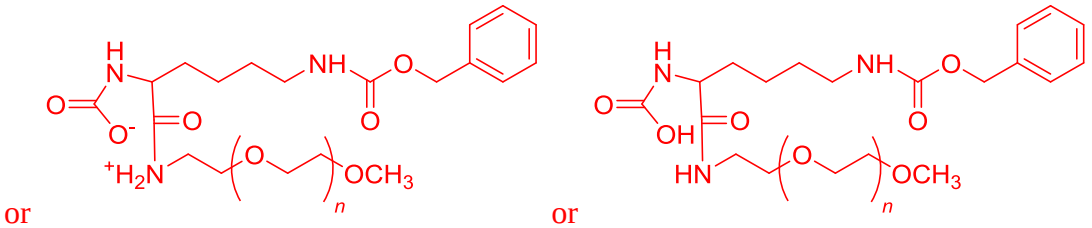
3. **Draw** the reaction intermediate that is formed in the first step of the addition of **1** to **2**. The second step of the mechanism leads to the formation of a gas molecule, **G**. **Draw** its structure.



1 + **2** → ?



or

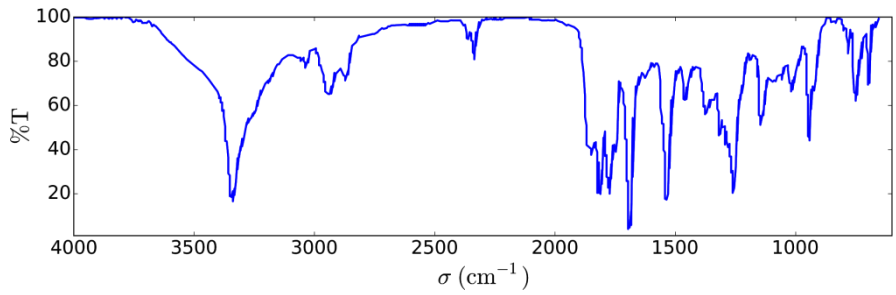


(4 points:
2 points for an intermediate resulting from a nucleophilic attack drawn towards one of the two carbonyl groups at the *N*-carboxy anhydride moiety)
(2 points for choosing the OCOCH carbon, consistent with the final structure)

X: CO_2 (1 point)

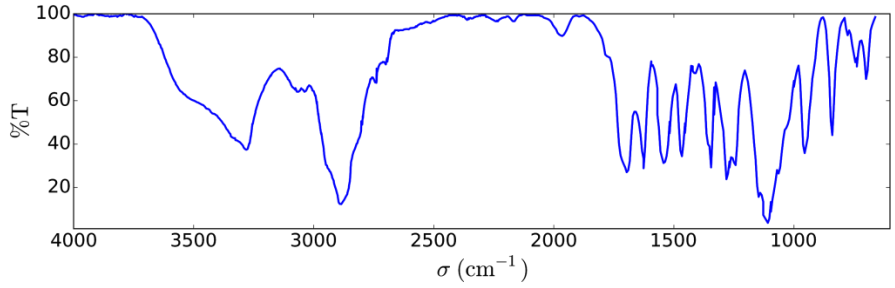
Total: 5 points

4. Infrared (IR) measurements are performed to characterize the compounds. **Match** the three IR spectra with compounds **1**, **2** and **3**.



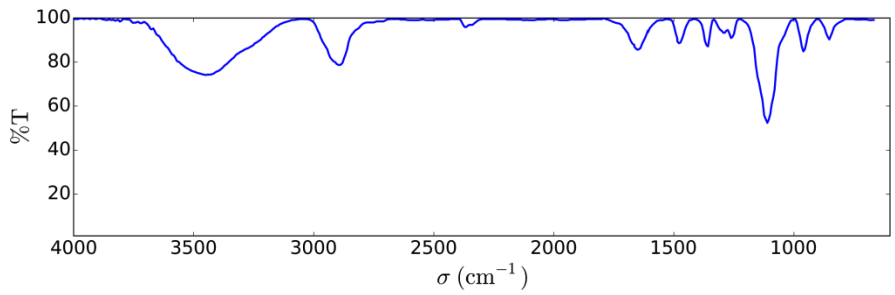
Compound:

☐ 1 ☒ 2 ☐ 3



Compound:

☐ 1 ☐ 2 ☒ 3



Compound:

☒ 1 ☐ 2 ☐ 3

(1 point per correct answer)
selecting at least twice the same compound number leads to 0 point for the question

Total: 3 points

5. The ^{1}H NMR spectrum of copolymer **3** (in DMSO-d_6, at 60 °C, 500 MHz) is reported in Fig. 1. Using some or all of the NMR signals, the areas of which are reported in Table 2, **calculate** its number average molar mass M_n, considering n from question 2. For your calculations, **draw** a circle around the group(s) of atoms you used and **give** their corresponding symbol(s) (α,β …).

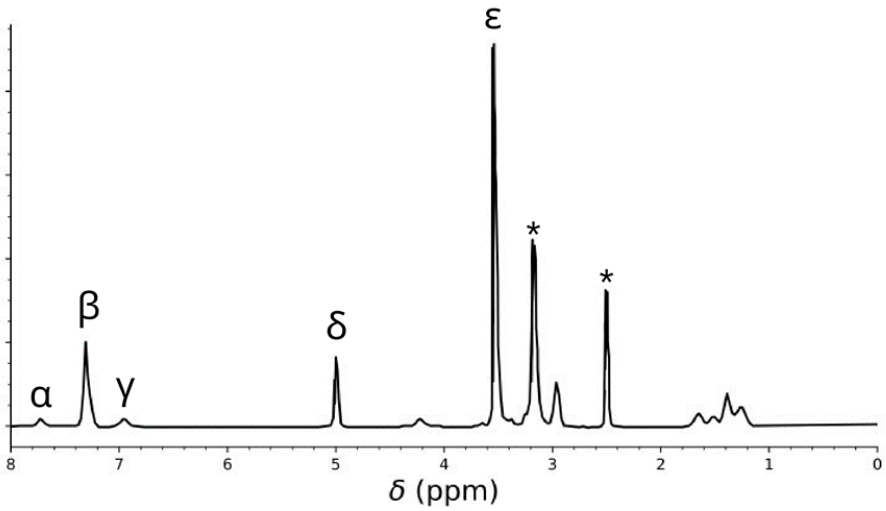
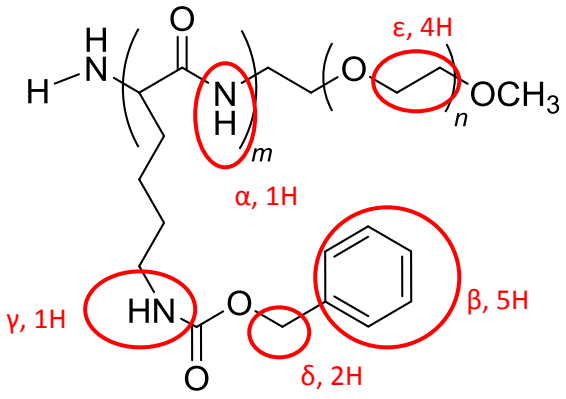


*Fig. 1 – signals marked with * correspond to the solvent and water.*

Table 2

Peak	Area
α	22.4
ß	119
γ	23.8
δ	47.6
ε	622



(3 points for the choice and identification of ε (1 point) and at least one of the signals α, β, γ or δ (2 points))

N.B.: attributing the carbamate signal to an amide and *vice versa* will also be accepted and given full mark

Calculations for *n*:

n is the same as in question 2, which allows to calculate the conversion factor χ between the relative number of protons in the molecule and the area of the NMR peak (peak that has the same chemical shift as signal d in question 1).

$n = 111$, $A_\varepsilon = 622$, → $\chi = 622/(4\times111) = 1.4$ ($\chi = 1.6$ for $n = 100$)

(2 points, 0 if the conversion factor (or equivalent) is assumed to be 1 or if conversion factors from question 1 are used)

Calculation of *m*:

For example: $m = A_\beta/5\chi = 17$ (for $n = 111$), $m = 14.9$ (for $n = 100$)

(3 points)

Calculation of M_n:

Number average molar mass, using $m = 17$, $n = 111$:
$M_n = 111 \times 44 + 262 \times 17 + 1 + 31 + 43 = 9.41$ kg mol^{-1}

$M_n = 9.41$ kg mol^{-1}
Provide your answer with two decimal places.
(2 points)
–1 point if the ending groups are not taken into account (then 0.075 kg mol^{-1} will be missing)
–0.5 point if incomplete ending groups

Total: 10 points

This reaction of **1** with **2** yielded the copolymers **3a** after 20 h, **3b** after 25 h and **3c** after 30 h of reaction at 40 °C. Results of size-exclusion chromatography (SEC) experiments are presented in Fig. 2.

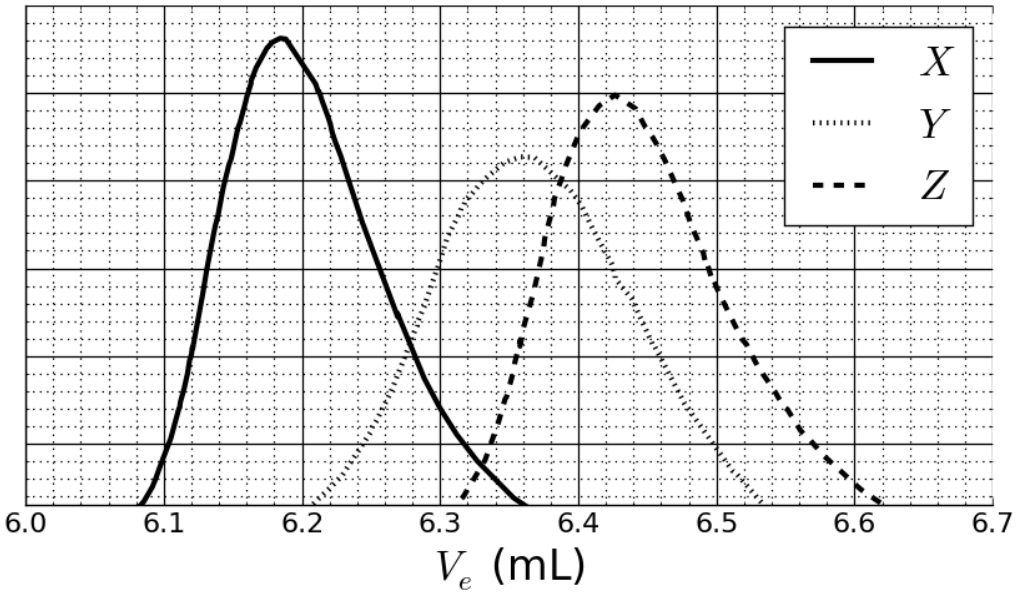


*Fig. 2 – SEC chromatograms of **3a**, **3b** and **3c** as a function of the elution volume, V_e.*

6. **Match** the signals in Fig. 2 with the copolymers **3a**, **3b** and **3c**.

3a:	☐ *X*	☐ *Y*	☒ *Z*
3b:	☐ *X*	☒ *Y*	☐ *Z*
3c:	☒ *X*	☐ *Y*	☐ *Z*

Total: 2 points if everything is correct.
0 point for any other answer

In order to calibrate the chromatogram, a mixture of standard polymers of known masses (3, 30, 130, 700 and 7000 kg mol^{-1}) has been studied (Fig. 3).
The log value of the molar mass is a linear function of the elution volume, V_e.

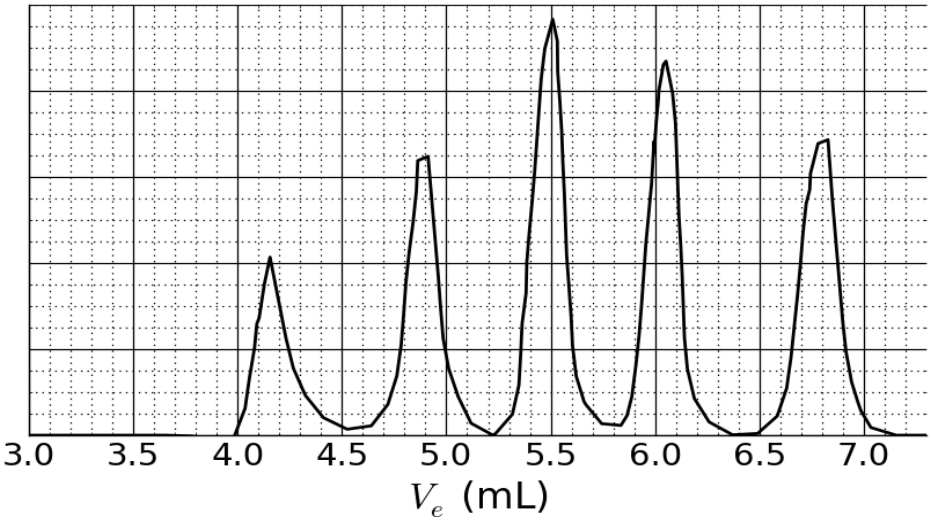


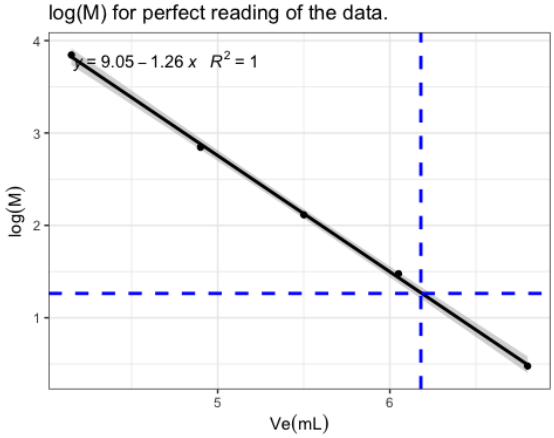
Fig. 3 – SEC chromatogram of the mixture of standards.

7. Based on the SEC curves in Fig. 2 and 3, **determine** V_e of the polymer that corresponds to curve *X* and use it to **estimate** the degree of polymerization *m* of its second block. **Detail** your calculation; you may use a calculator or plot a graph.

V_e = mL

The elution volume $V_e(\boldsymbol{X})$ has a peak at 6.18 mL (1 point for correct reading +/– 0.01 mL)

Determination of a function such as log *M* or ln *M* = *a* × V_e (mL) + *b* either graphically or numerically.



log(*M*)= 9.05 – 1.26 × V_e (mL) or ln(*M*) = 9.05 – 1.26 × V_e (mL)

In case of a mistake in the relation between the standard masses and the elution volumes, such a graph could also be obtained and the answers derived from it will also be taken into account. (4 points)

−1 point if wrong function but good choice of values

−1 point if a linear function of type log(*M*) = *a*·V_e is used

−1 is the sign of the slope is not consistent with Q6

Calculation of the molar mass, $M_n(\boldsymbol{X})$:

The use of the calibration allows to determine the value of $M_n(\boldsymbol{X})$:

log $M_n(\boldsymbol{X})$ = – 1.26 × 6.18 + 9.05 so M_n = 18.3 kg mol^{-1} (1 point)

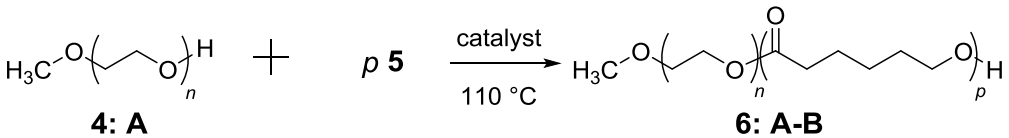
Calculation of *m* from the molar mass:

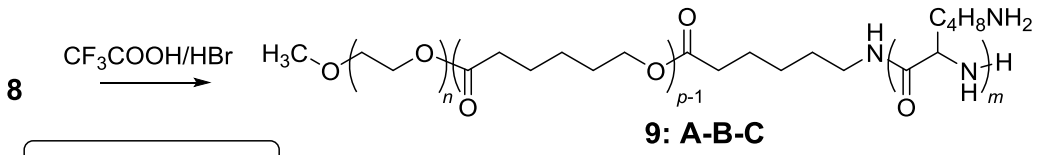
$m = (M_n(\boldsymbol{X}) - M(\mathbf{1}))/262 = (M_n(\boldsymbol{X}) - 44\,n - 75)/262$ (75 g mol^{-1} correspond to the end groups)
or, for instance:
$m = [18330 - 100 \times 44 - 75]/262 = 52$ (for $n = 100$)
$m = [18330 - 111 \times 44 - 75]/262 = 51$ (for $n = 111$)
$m = 51$ (3 points)

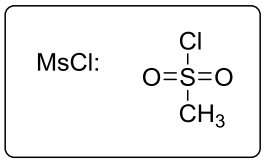
Total: 9 points

Triblock copolymer synthesis

For biological applications, involving the formation of micelles, a triblock copolymer **9** can be synthesized through the introduction of a middle block, **B**, using monomer **5**.

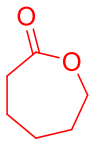






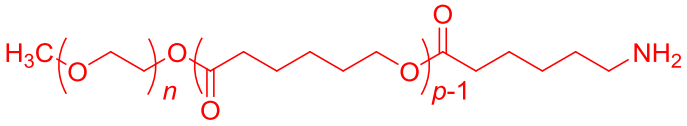
8. **Draw** the structures of **5**, **7** and **8**.

5 (no other products than **6:A-B** are obtained)



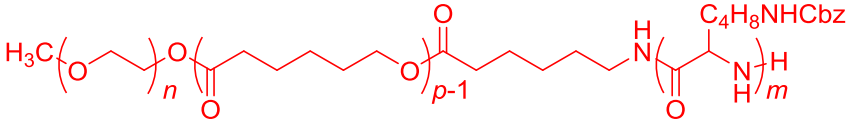
(2 points)
linear acid instead of the caprolactone: 0 point

7 (a gas is formed in the final step)



(2 points)

8



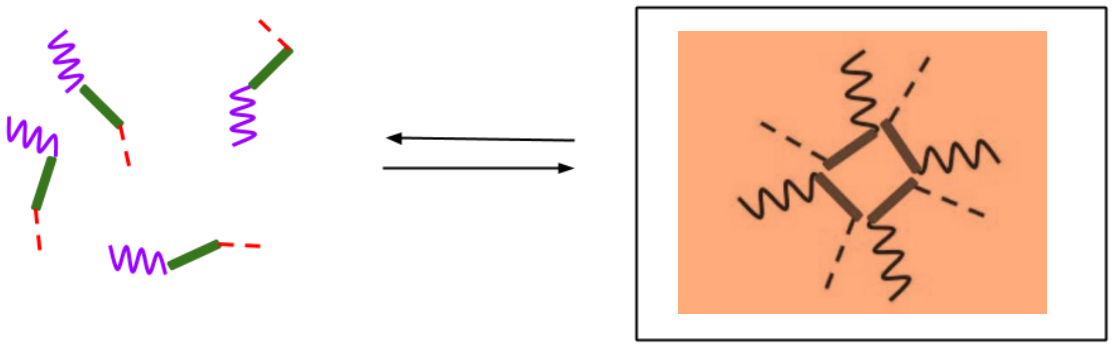
(2 points)

Total: 6 points

9. Amphiphilic block copolymers, such as **9: A-B-C**, can be used for medical applications, as they self-assemble into micelles in water (pH = 7), which can be used as drug carriers. **Assign** each block of the copolymer to a property. **Draw** a scheme of the micelle with only 4 polymer chains.

A:	☐ hydrophobic	☒ hydrophilic
B:	☒ hydrophobic	☐ hydrophilic
C:	☐ hydrophobic	☒ hydrophilic

(3 points)



(2 points for correct micelle assembly, in accordance with the predicted property)
Hydrophile/hydrophobe/hydrophile case: 1 point if a sheet-like structure instead of a micelle

Total: 5 points

Problem T7 6%	Question	1	2	3	4	5	6	7	8	9	10	11	Total
	Points	4	12	2	2	2	5	5	8	4	5	5	54
	Score												

Problem T7: Ring motion in a [2]catenane

In 2016, the Nobel Prize in Chemistry was awarded to J.-P. Sauvage, Sir J. F. Stoddart and B. L. Feringa *"for the design and synthesis of molecular machines"*. An example of these is [2]catenane, a molecule consisting of two interlocked rings. In this system, one macrocycle contains a single phenanthroline (bidentate) ligand and the second contains two ligands: a phenanthroline and a terpyridine (tridentate) ligand. A copper ion is coordinated by one ligand from each macrocycle. Depending on the oxidation state of the copper (+I or +II), two configurations are obtained (Fig. 1).

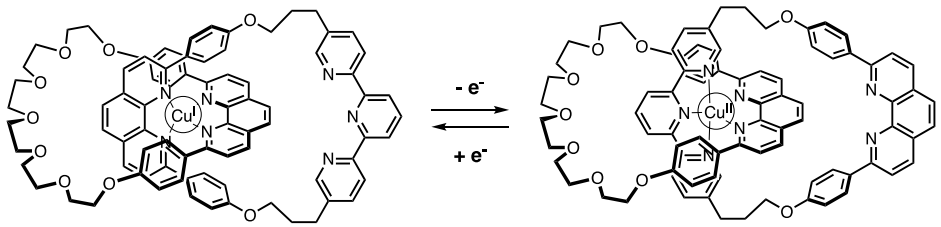
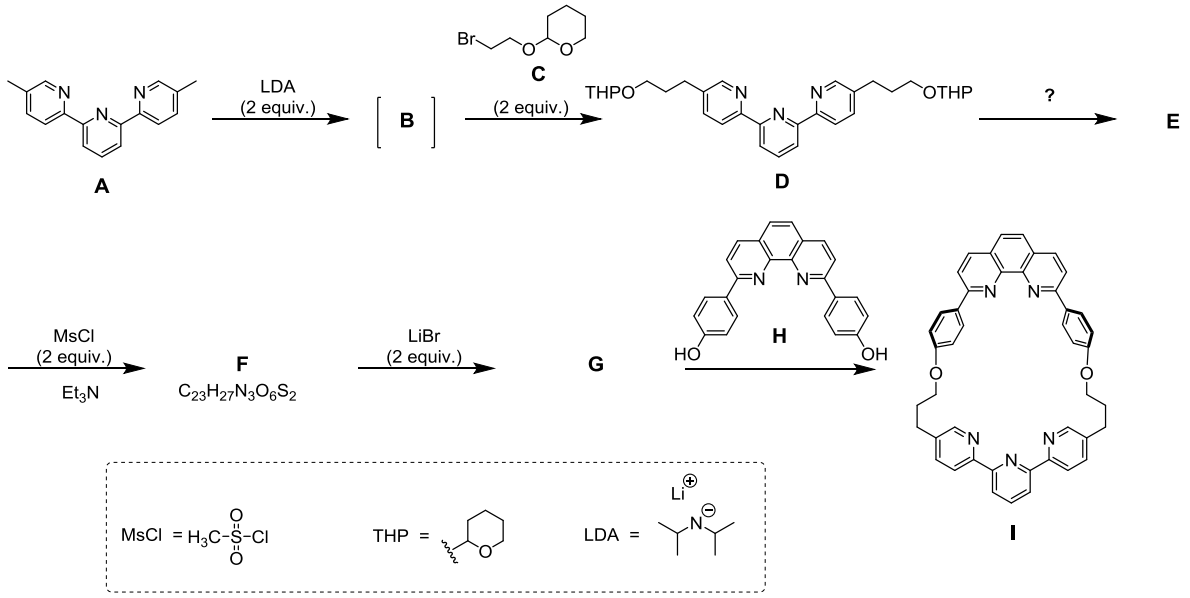


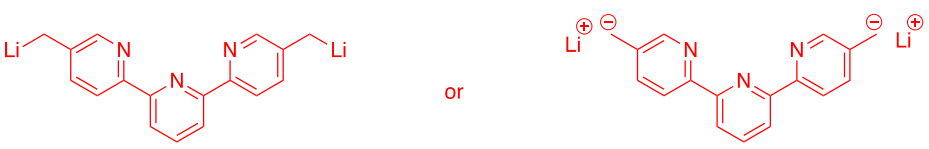
Fig. 1 – Multi-stability of a ring in a [2]catenane.

The synthesis of the macrocycle is the following:



1. **Draw** the structure of **B**.

B



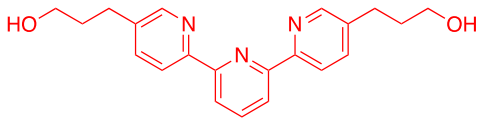
4 points

2 points for mono deprotonated species
−1 point if a + charge appears instead of the − charge
−2 points for minor errors (wrong number of carbon atoms in alkyl chains,…)
−1 point for missing double bond in pyridine ring

Total: 4 points

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

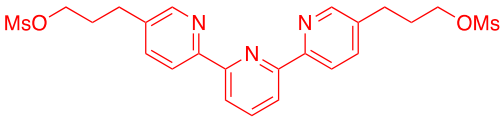
E



4 points

2 points for monodeprotected compound
−2 points for minor errors

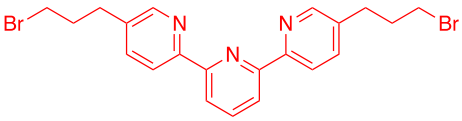
F



4 points

0 point if not correct molecular formula
−2 points for minor errors

G



4 points

2 points for monosubstituted compound
−2 points for minor errors

Total: 12 points

3. Out of the following the reaction conditions, **choose** which one(s) can produce **E** from **D**:

☒ H^+, H_2O (2 points)
☐ OH^-, H_2O
☐ $NaBH_4$, CH_3OH
☐ H_2, Pd/C, THF

−1 point for each incorrect answer. The total score in question 3 may not be negative.

Total: 2 points

4. In the synthetic strategy, MsCl is used to obtain:

☒ a leaving group (2 points)
☐ a protecting group

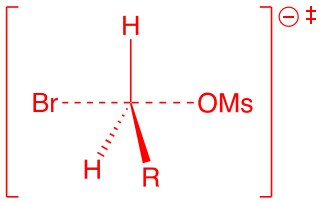
☐ a deactivating group
☐ a directing group
0 point for any other or multiple answers
Total: 2 points

5. **G** is obtained by the reaction between **F** and LiBr in acetone. This reaction is:

☐ electrophilic aromatic substitution
☐ nucleophilic aromatic substitution
☐ S_N1
☒ S_N2 (2 points)
0 point for any other or multiple answers
Total: 2 points

6. **Draw** the transition state of the rate-determining step of the reaction **F** → **G**, showing the 3D geometry. Depict only one reaction center. The main carbon chain can be represented as an R group.

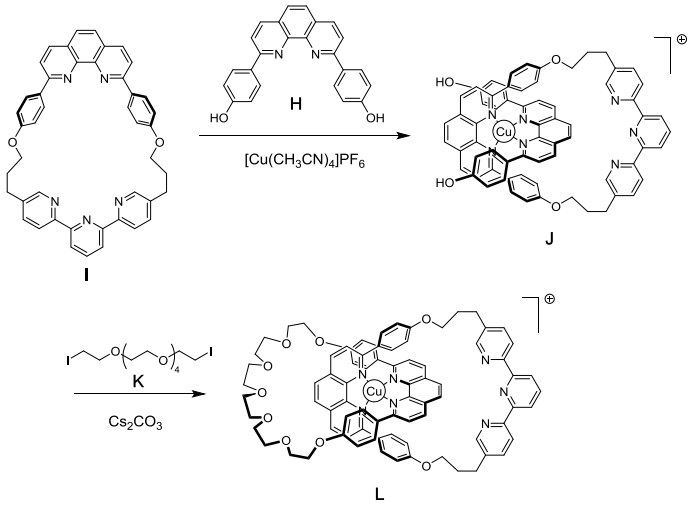
Transition state:



0 point if wrong geometry or disposition of the groups
−1 point for the absence of a global (−1) charge or of two partial (δ^-) charges
−1 point if no dashed bonds for Br—C and MsO—C
−2 points if R = RCH_2 (*ie* R includes the stereogenic carbon atom)
The total score in question 6 may not be negative.

Total: 5 points

The synthesis of [2]catenane **L** uses the template effect of a copper complex:



7. **Write** the full electronic configuration of Cu(0) in its ground state. Give the oxidation state of Cu in complex **J** and write the electronic configuration of Cu in the free ion corresponding to **J**.

Electronic configuration of Cu(0):

$[Ar]4s^1 3d^{10}$ or $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ (2 points)
1 point for $[Ar]4s^2 3d^9$
1 point for $4s^1 3d^{10}$
1 point if both $[Ar]4s^2 3d^9$ and $[Ar]4s^1 3d^{10}$ configurations are given.

Oxidation state of Cu in **J**:
+1 or + I (1 point)
Cu^+ notation also accepted

Electronic configuration of Cu in **J**:
$[Ar]3d^{10}$ or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (2 points)
2 points for other electronic configurations, if in agreement with the oxidation state
1 point for $[Ar]4s^1 3d^9$ if $[Ar]4s^2 3d^9$ was given as electronic configuration of Cu(0)
1 point for $3d^{10}$ but 2 points if [Ar] is already missing in the electronic configuration of Cu(0)

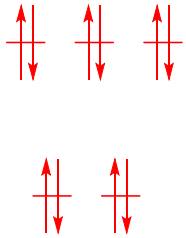
Total: 5 points

8. **Select** the geometry of the copper ion in **L**. Assuming an ideal geometry of the ligands around the copper center, **draw** the electronic levels of the d orbitals subject to the crystal field. **Fill** the orbital diagram. **Give** the maximum value of the spin (*S*) for this complex.

The geometry of Cu in **L** is:
☐ Octahedral
☒ Tetrahedral
☐ Square planar
☐ Trigonal bipyramid

(2 points)

Splitting and filling of d orbitals:



(4 points)

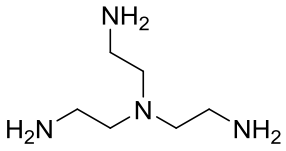
3 points for orbital splitting
1 point for electron filling

S = 0 (2 points)

Total: 8 points

9. Out of the following compounds, **choose** the one(s) that can remove the copper ion in **L** to obtain the free [2]catenane:

☐ CH_3CN
☐ NH_4PF_6
☒ KCN
☒ tren



tren

2 points for each correct answer
−1 point if CH_3CN is selected
−1 point if NH_4Cl is selected
The total score in question 10 may not be negative.

Total: 4 points

In [2]catenane **L**, the copper ion can exist in two oxidation states (+I) or (+II), and each of them exhibits a different coordination sphere (tetra- or penta-coordinated, respectively).

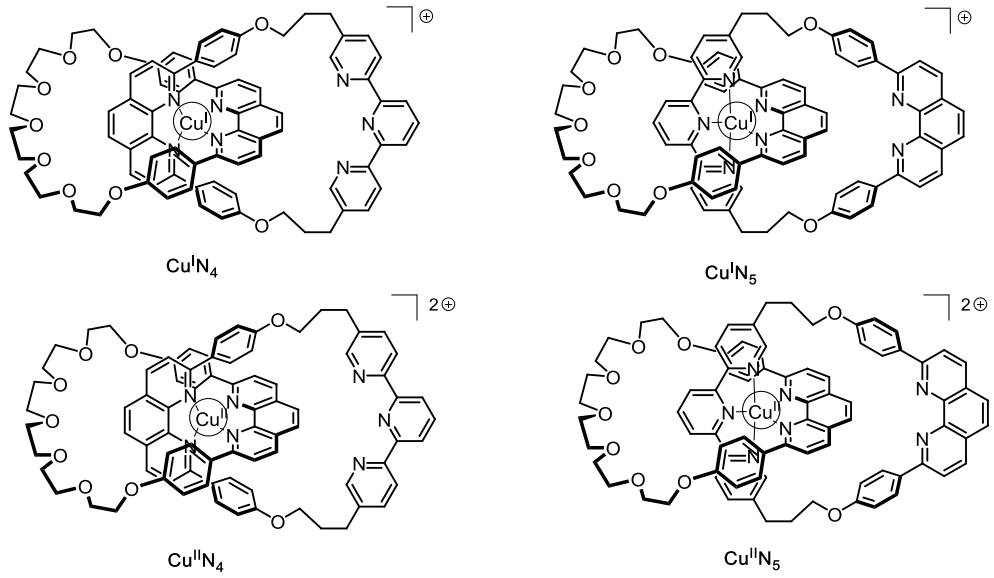


*Fig. 2 – [2]catenane **L** states*

The stability of Cu(I) complexes can be inferred by comparing their electronic structures to that of a noble gas.

10. **Fill** in the blanks with a number or a tick:

The $Cu^{I}N_4$ complex has 18 electrons in the coordination sphere of the metal.

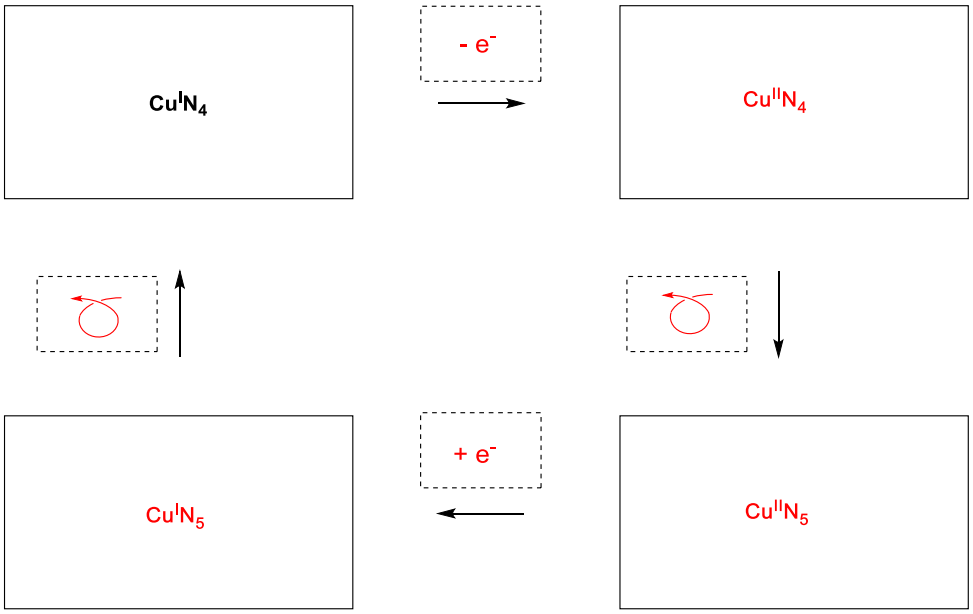
The $Cu^{I}N_5$ complex has 20 electrons in the coordination sphere of the metal.

The $Cu^{I}N_4$ complex is ☑ more / ☐ less stable than the $Cu^{I}N_5$ complex.

2 points for each correct number of valence electrons
1 point for correct more / less choice

Total: 5 points

11. **Fill** in the solid boxes with the designation of the involved complexes in Fig. 2 and **complete** the sequence to achieve electrochemical control of the system using the following notation for the dashed boxes: ↺ (rotation) ; + e^- ; – e^-.



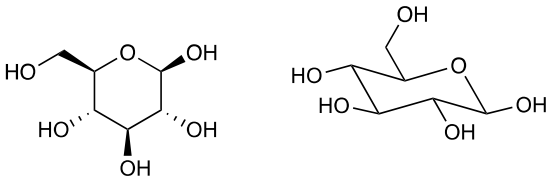
1 point for each correct assignment of complexes
0.5 point for each correct assignment on the arrows

Total: 5 points

Problem T8 6%	Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Total
	Points	2	6	2	2	11	2	4	3	4	2	6	8	2	6	4	64
	Score																

Problem T8: Identification and synthesis of inositols

In this problem, we define "3D structure" and "perspective formula" as indicated for β-glucose in the following figure.

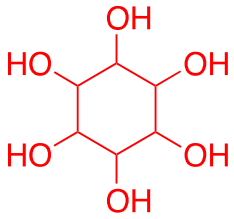


3D structure perspective formula

Inositols are cyclohexane-1,2,3,4,5,6-hexols. Some of these 6-membered carbocycles, in particular *myo*-inositol, are involved in a number of biological processes.

Structure of *myo*-inositol

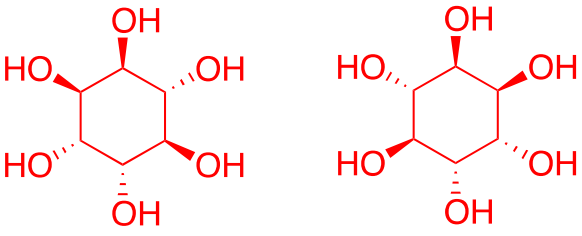
1. **Draw** the structural formula of inositols, without stereochemical details.



Total: 2 points for the correct structure

This family of molecules contains 9 different stereoisomers, including enantiomers.

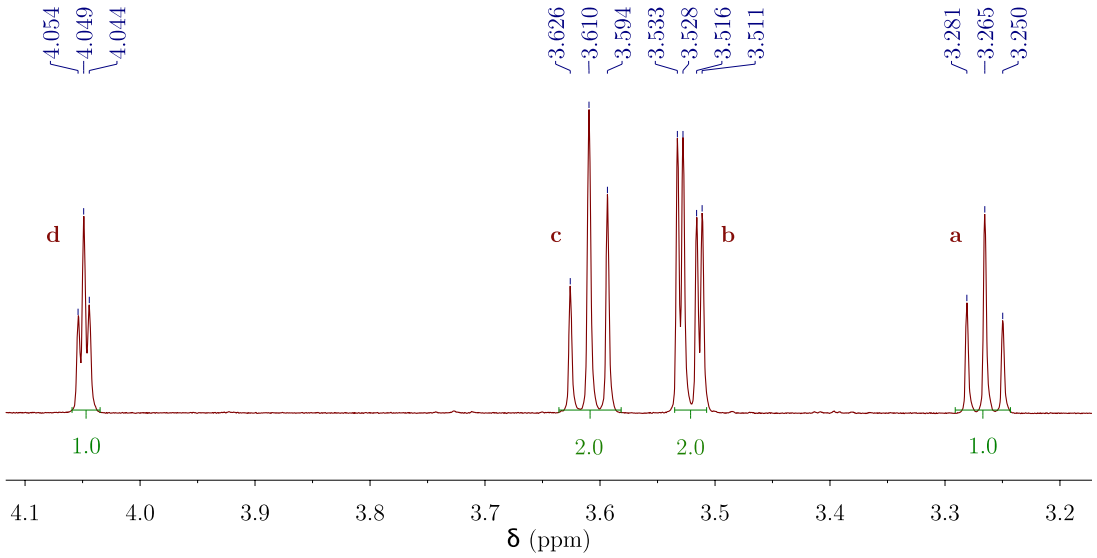
2. **Draw** all 3D structures of the stereoisomers that are optically active.



Total: 6 points if both enantiomers are given
3 points if only one enantiomer with the correct stereochemistry is given
3 points if the two correct perspective formulas are given
–2 points for each other stereoisomer

The total score in question 2 may not be negative

The structure of a specific inositol, called *myo*-inositol, is studied here. Only one of its chair conformers is predominant and its structure can be deduced from its ^{1}H NMR spectrum. The spectrum below was obtained at 600 MHz in D_2O. No other signal from that compound was observed in the spectrum. The integration is indicated on the spectrum below each signal.



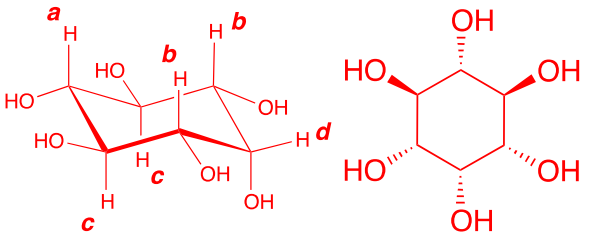
3. **Give** the molecular formula of the predominant compound derived from *myo*-inositol in this sample that is consistent with the number of protons observed in the ^{1}H NMR spectrum.

$C_6H_6O_6D_6$
Total: 2 points (1 point if wrong structure containing D)

4. Based on the number and integrations of the proton signals, **give** the number of symmetry plane(s) that exist(s) in this molecule.

1
Total: 2 points

5. **Complete** the following perspective drawing of the most stable conformation of *myo*-inositol. Then **label** each hydrogen with the corresponding letter (**a**, **b**, **c** or **d**) according to the NMR spectrum above. Proton **a** must be on carbon **a** on the following representation. **Draw** its 3D structure.

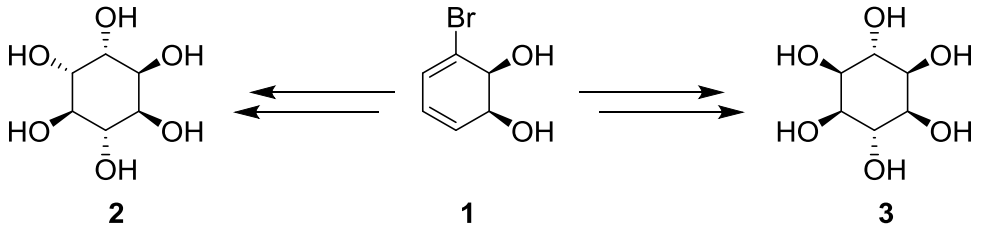


Total: 11 points
3 points if the correct perspective drawing of the most stable conformer is given
1 point if the stereoisomer is correct but it is not the most stable conformer
1 point if the all-equatorial isomer is depicted

6 points for the correct attribution of the chemical shifts
3 points if the attribution is correct but with H non depicted
2 points for the correct 3D structure

Synthesis of inositols

For medicinal applications, it is useful to synthesize some inositol phosphates on a large scale. We will study the synthesis of inositol **2** from bromodiol **1**.



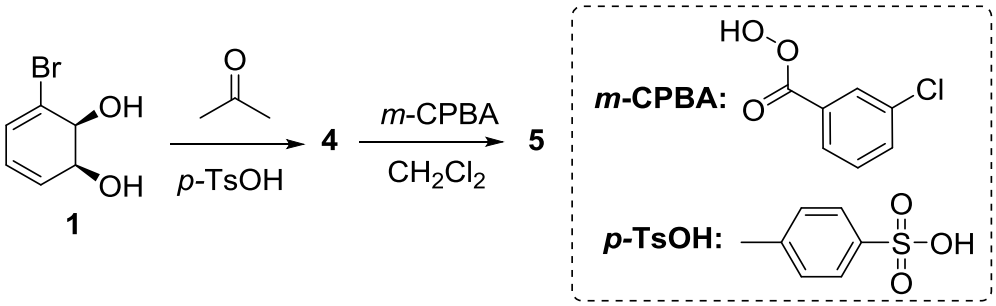
6. **Choose** the correct structural relationship(s) between **2** and **3**.

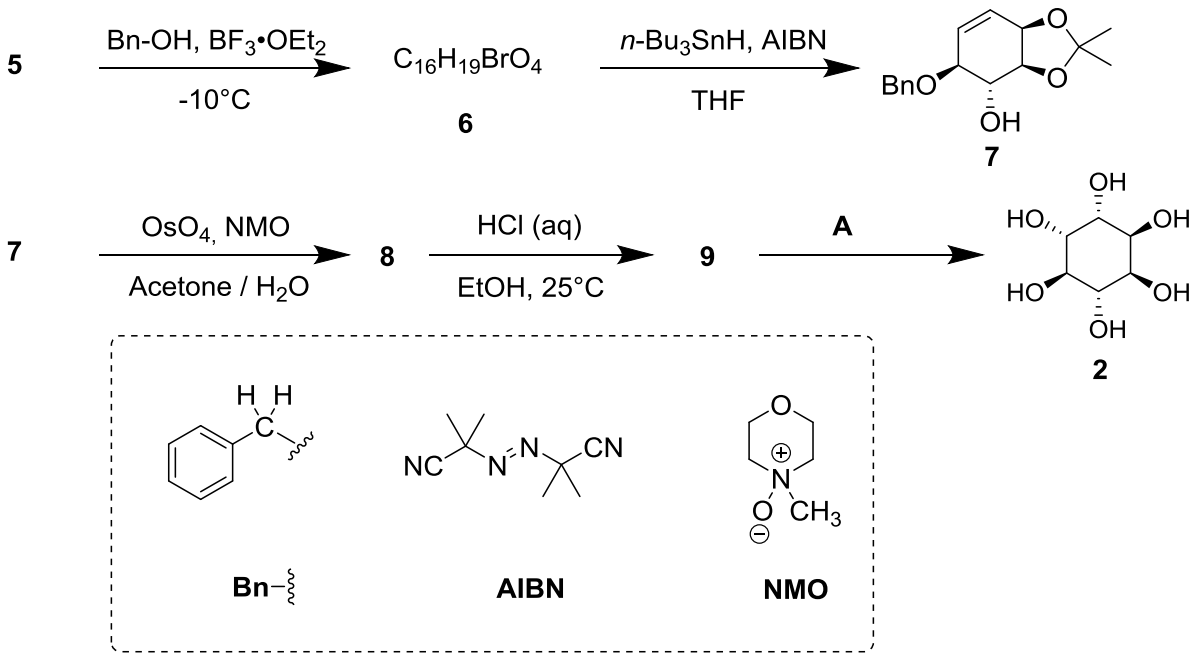
- ☐ enantiomers
- ☒ epimers
- ☒ diastereomers
- ☐ atropoisomers

Total: 2 points

–1 point per incorrect answer given

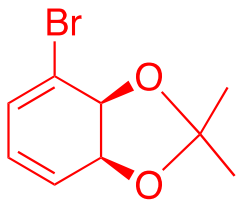
Inositol **2** can be obtained from compound **1** in 7 steps.





7. **Draw** the 3D structure of **4**.

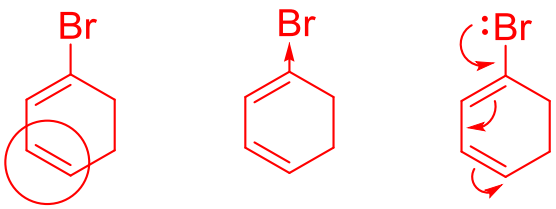
4



Total: 4 points

2 points if the structure is drawn correctly without or with an incorrect stereochemistry
1 point if the structure of the protected diol is correct but the rest of the molecule is not

8. The reaction leading to **5** occurs on the double bond with the highest electron density. Consider below the structure of 1-bromo-1,3-cyclohexadiene, which is a substructure of **4**. **Circle** the double bond with the highest electron density. **Represent** all the electronic effects due to the bromine.

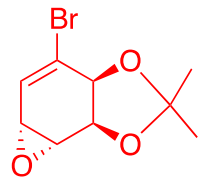


Total: 3 points

1 point if the double bond is correctly selected
1 point if –I is correctly represented (arrow or delta charges)
1 point if +M is correctly represented

9. **Draw** the 3D structure of the major diastereomer **5**.

5



Total: 4 points

2 points if the structure is drawn correctly without or with an incorrect stereochemistry
2 points if a bromonium bridge additional to the epoxide is depicted
1 point if the structure is drawn with an incorrect regioselectivity but with the correct stereochemistry
0.5 point if the structure is drawn with an incorrect regioselectivity and an incorrect stereoselectivity

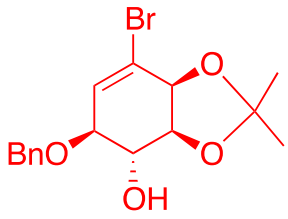
10. **Give** the total number of stereoisomers of **5** possibly obtained by this synthesis, starting from enantiopure compound **1**.

2

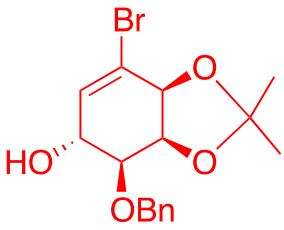
Total: 2 points

11. For the step **5** → **6**, another product with the same molecular formula, denoted **6'**, can be produced. **Draw** the 3D structures of **6** and **6'**.

6



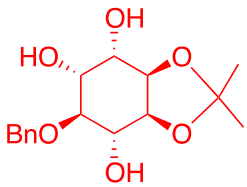
6'



Total: 6 points for both molecules
1 point for each structure drawn correctly without or with an incorrect stereochemistry

12. **Draw** the 3D structures of major diastereomers **8** and **9**.

8



9

Total: 8 points for both molecules

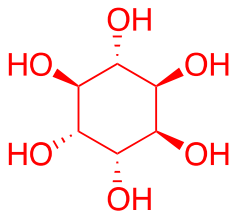
2 points for each structure drawn correctly without or with an incorrect stereochemistry
For **9**: 2 points if Bn is also deprotected, 0 point if only Bn is deprotected

13. **Select** the right set(s) of conditions **A** to obtain **2**.

☒ H_2, Pd/C
☐ K_2CO_3, HF
☐ HCOOH, H_2O
☐ $BF_3 \cdot OEt_2$

Total: 2 points
–1 point for each incorrect answer given

14. If the bromine is not present in compound **1**, in addition to **2**, another stereoisomer would be obtained. Considering that the stereoselectivity of the reactions that take place in the synthesis remains unchanged and that the following steps involve the same number of equivalents as for **2**, **draw** the 3D structure of this stereoisomer and **give** its relationship with **2**.



4 points
2 points if the structure is drawn correctly with an incorrect stereochemistry for the dihydroxylation
2 points if the structure is drawn correctly with an incorrect stereochemistry for the addition of BnOH
3 points if Bn is still present

☒ enantiomers
☐ epimers
☐ diastereoisomers
☐ atropoisomers

2 points if the answer is consistent with the previous structure
–1 point for each incorrect answer

Total: 6 points

15. During the synthesis of **2** from **1, choose** the removal step(s) of protecting or directing groups.

☐ **1 → 4**
☐ **4 → 5**
☐ **5 → 6**
☒ **6 → 7**
☐ **7 → 8**
☒ **8 → 9**
☒ **9 → 2**

Total: 4 points if all correct steps are given
–1 point if 6 → 7 is missing
–2 points if 8 → 9 or 9→2 is missing or if another step is chosen

Problem T9 7%	Question	1	2	3	4	5	6	7	8	9	10	11	12	13	Total
	Points	2	2	4	3	2	17	1	1	2	4	2	2	2	44
	Score														

Problem T9: Synthesis of levobupivacaine

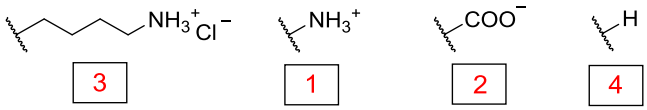
Part I.

The local anesthetic bupivacaine (marketed as Marcaine) is on the World Health Organization List of Essential Medicines. Although the drug is currently used as a racemic mixture, it was demonstrated that one enantiomer of bupivacaine, levobupivacaine, is less cardiotoxic and, therefore, safer than the racemate. Levobupivacaine can be synthesized from the natural amino acid L-lysine.

L-Lysine hydrochloride

Note on grading: unless stated otherwise, –1 point for minor mistakes, including wrong valency, missing hydrogen atom on a heteroatom or wrong/missing charge.

1. **Assign** the absolute configuration of the stereogenic center in L-lysine hydrochloryde and **justify** your answer by classifying the substituents in order of their priority.

Configuration:	Priority 1 > 2 > 3 > 4:
☐ *R* ☒ *S*	

2 points for both correct answers, no partial points.

Total: 2 points

2. The prefix L in L-lysine refers to relative configuration. **Choose** all correct statements:

☐ All natural L-amino acids are levorotatory.
☒ Natural L-amino acids can be levorotatory or dextrorotatory.
☐ All natural L-amino acids are (*S*).
☐ All natural L-amino acids are (*R*).

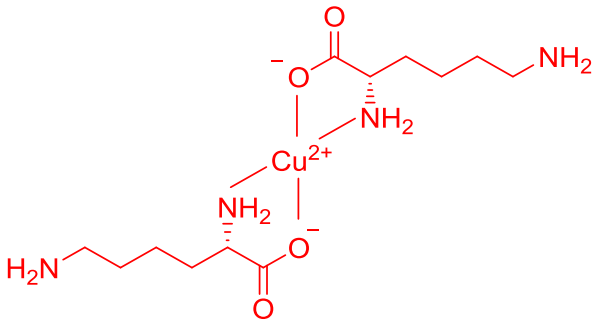
2 points for the correct answer. 0 points if any incorrect answer.

Total: 2 points

Often, we want only one of the amino groups in L-lysine to react. A Cu^{2+} salt with excess aqueous hydroxide can selectively mask the reactivity of one of the amino groups. After the complex is formed, only the non-complexed NH_2 group is available to react.

3. Considering that L-lysine acts as a bidentate ligand and that two L-lysines coordinate to one Cu^{2+} ion in the presence of aqueous hydroxide, **draw** the structure of the intermediate complex.

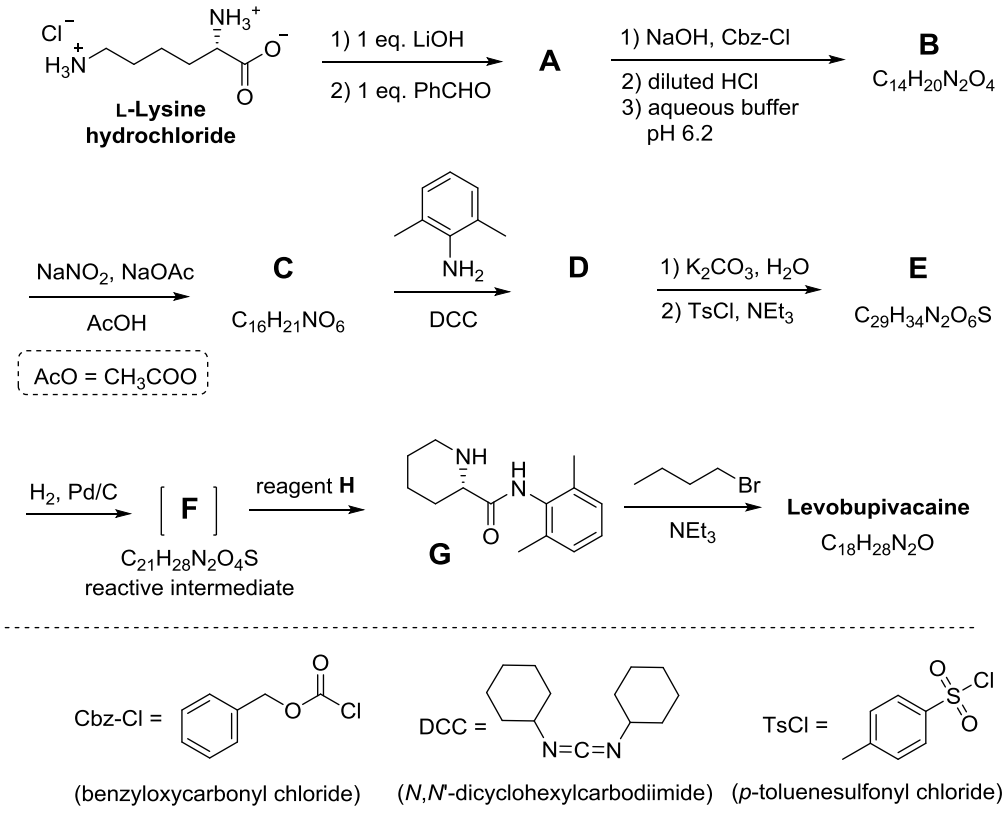
Complex



4 points (both planar (*cis* and *trans*) and tetrahedral structures accepted).
−1 point if one or both ε-NH_3^+ instead of ε-NH_2.
−2 points if one or both α-NH_3^+ instead of α-NH_2.
−2 points if ε-NH_2 group is coordinated together with the carboxylate.
−2 points if COOH instead of COO^- in case of Cu^{2+} (basic conditions)
−1 point if COO^- and Cu^0
−1 point if COO (uncharged) and Cu^{2+}
0 point if both NH_2 coordinated
−2 points if not neutral
One or two molecules of water may be coordinated
One or two HO^- may be coordinated if the overall charge is correct
0 points if the ligand is not bidentate or if only one or more than two molecules of L-lysine are coordinated.

Total: 4 points

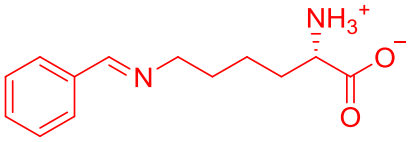
Fortunately, in the synthesis of levobupivacaine shown below, the same amino group reacts even without Cu^{2+} salt.



From this point on, you can use the abbreviations proposed in the scheme above.

4. **Draw** the structure of compound **A**, including the appropriate stereochemistry.

A



3 points for the correct structure (both *E* and *Z* isomers accepted).
−1 point if stereochemistry is wrong or missing.
−1 point if the overall charge is not zero.
−1 point if hemiaminal instead of imine.
−1 point if two equivalents of LiOH were used.
−2 points if α-amino group was transformed into imine.
0 point if both amino groups were transformed into imines.
Full score if ε coordinated in Q3 and α protected in Q4

Total: 3 points

5. Transformation of L-lysine into **A** is (**choose** proper answer(s)):

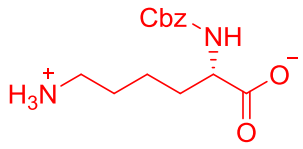
☐ an enantioselective reaction.
☐ an enantiospecific reaction.
☒ a regioselective reaction.

2 points.
0 point if any incorrect answer.

Total: 2 points

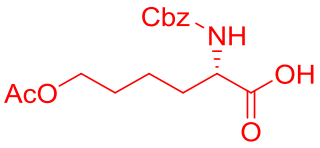
6. **Draw** the structures of compounds **B**–**F**, including the appropriate stereochemistry.

B $C_{14}H_{20}N_2O_4$

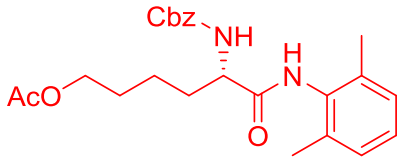
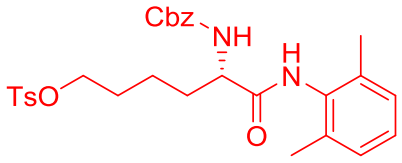
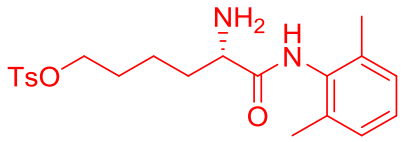


3 points
No penalty if ε-Cbz protected lysine starting from α-imine.
−1 point if stereochemistry is wrong or missing, unless already penalized in the previous structure.
−1 point if overall charge is not neutral.
0 point if ε NH_2 protected from ε imine.
0 point if α NH_2 protected from α imine.

C $C_{16}H_{21}NO_6$



4 points
No penalty if correct transformation of α-amino group starting from ε-Cbz protected lysine.
−1 point if stereochemistry is wrong or missing, unless already penalized in the previous structure.
−2 points if alcohol instead of acetate.

D  3 points −1 point if stereochemistry is wrong or missing, unless already penalized in the previous structure. 0 point if Cbz is cleaved in this step. 0 point if Ac is cleaved in this step, unless no Ac in the previous structure.	**E** $C_{29}H_{34}N_2O_6S$  3 points −1 point if stereochemistry is wrong or missing, unless already penalized in the previous structure. 0 point if Cbz is cleaved in this step. 0 point if Ac is cleaved in this step, unless no Ac in the previous structure.
F $C_{21}H_{28}N_2O_4S$  4 points −1 point if stereochemistry is wrong or missing, unless no Ac in the previous structure. 0 point if Ts is cleaved.	**Total: 17 points**

7. What is the role of DCC in the transformation **C** → **D**?

- ☐ Protecting group for the amino group.
- ☐ Protecting group for the hydroxy group.
- ☒ Activating agent for the amide bond formation.

Total: 1 point

8. TsCl is used in the synthesis to enable:

- ☐ Nucleophilic substitution of an amino group.
- ☐ Electrophilic substitution of an amino group.
- ☒ Nucleophilic substitution of a hydroxy group.
- ☐ Electrophilic substitution of a hydroxy group.

Total: 1 point

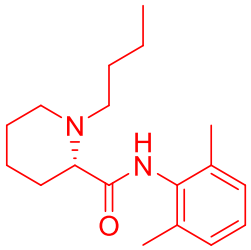
9. **Mark** all possible reagents which could be used as reagent **H**:

☐ diluted HCl	☐ Zn/HCl
☒ K_2CO_3	☐ H_2SO_4
☐ diluted $KMnO_4$	☒ diluted NaOH
☐ $SOCl_2$	☐ PCl_5

1 point for each correct answer.
−1 point for each incorrect answer.
The total score in question 9 may not be negative.
Total: 2 points

10. **Draw** the structure of levobupivacaine, including the appropriate stereochemistry.

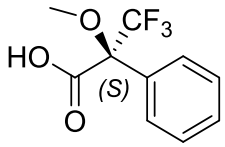
Levobupivacaine $C_{18}H_{28}N_2O$



4 points
−1 point if stereochemistry is wrong or missing
−2 points if amide is alkylated instead of amine
Total: 4 points

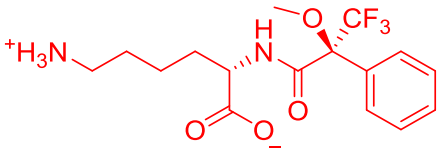
Part II.

The synthesis of levobupivacaine requires the use of enantiomerically pure L-lysine. A common method to confirm the enantiomeric purity of aminoacids is their transformation into amides using Mosher's acid (see the structure of the (*S*) isomer below).



(S)-Mosher's acid

11. **Draw** the structure of the amide formed when the α-amino group of L-lysine is derivatized with (*S*)-Mosher's acid. Clearly show the stereochemistry of each chiral center.



2 points (neutral as well as zwitterionic forms accepted)
−1 point for each stereogenic center if stereochemistry is wrong or missing.
−1 point if total charge is not neutral.
No penalty if ε NH_2 instead of α NH_2.
Total: 2 points

12. **How many products** will be formed from racemic lysine and (*S*)-Mosher's acid (consider that only the α-amino group of lysine is derivatized)?

- ☒ Two diastereoisomers.
- ☐ Four diastereoisomers.
- ☐ A racemic mixture of two enantiomers.
- ☐ Four compounds: two enantiomers and two diastereoisomers.

Total: 2 points

13. **Choose** the method(s) which can be used to quantitatively determine the enantiomeric purity of lysine after its derivatization with (*S*)-Mosher's acid:

- ☒ NMR spectroscopy.
- ☒ Liquid chromatography.
- ☐ Mass spectrometry.
- ☐ UV-vis spectroscopy.

1 point for each correct answer.
−1 point for each incorrect answer.
The total score in question 13 may not be negative.

Total: 2 points

XXX_1

PRACTICAL EXAM

51st — International Chemistry Olympiad
France — Paris — 2019

Making science together!

2019-07-24

2018 ANNÉE DE LA CHIMIE de l'école à l'université 2019

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE

MINISTÈRE DE L'ÉDUCATION NATIONALE ET DE LA JEUNESSE

MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR, DE LA RECHERCHE ET DE L'INNOVATION

General instructions

- This practical booklet contains 27 pages.
- Before the start of the practical exam, the **Read** command is given. You will have 15 minutes to read the exam booklet. You may only **read** during this time; d**o not write nor use the calculator.**
- You may begin working as soon as the **Start** command is given. You will then have **5 hours** to complete the exam.
- You may work on the tasks in any order, but **starting with problem P1 is advised**.
- All results and answers must be clearly written **in pen in their respective designed areas** on the exam papers. Answers written outside the answer boxes will not be graded.
- If you need scratch paper, use the backside of the exam sheets. Remember that **nothing outside the designed areas will be graded**.
- The official English version of the exam booklet is available upon request and serves for clarification only.
- If you need to leave the laboratory (to use the restroom or have a drink or snack), raise the appropriate card. A lab assistant will come to accompany you.
- Shelves above the benches are not to be used during the task for the purpose of equality.
- You must **follow the safety rules** given in the IChO regulations. If you break the safety rules, you will receive only one warning from the lab assistant. Any safety rule violation after the first warning will result in your dismissal from the laboratory and the nullification of your practical examination.
- Chemicals and labware, unless otherwise noticed, will be refilled or replaced without penalty only for the first incident. Each further incident will result in the deduction of 1 point from your 40 practical exam points.
- The lab supervisor will announce a 30 minutes warning before the **Stop** command.
- You must stop your work immediately when the **Stop** command is announced. Failure to stop working or writing by one minute or longer will lead to nullification of your practical exam.
- After the **Stop** command has been given, the lab supervisor will come to sign your answer sheet.
- After both the supervisor and you sign, place this exam booklet in the envelope and submit it for grading together with your product and thin-layer chromatography (TLC) plates.

Lab rules and safety

- You must wear a lab coat and keep it buttoned up. Footwear must completely cover the foot and the heel.
- Always wear safety glasses or prescription glasses when working in the lab. Do not wear contact lenses.
- Do not eat or drink in the lab. Chewing gums are not allowed.
- Work only in the designated area. Keep your work area and the common work areas tidy.
- No unauthorized experiments are allowed. No modification of the experiments is allowed.
- Do not pipette with your mouth. Always use a pipette filler bulb.
- Clean up spills and broken glassware immediately from both the bench and the floor.
- All waste must be properly discarded to prevent contamination or injury. Water solutions are eligible for sink disposal. Organic waste must be disposed of in the marked capped container.

Physical constants and equations

In these tasks, we assume the activities of all aqueous species to be well approximated by their respective concentration in mol L^{-1}. To further simplify formulae and expressions, the standard concentration $c^\circ = 1$ mol L^{-1} is omitted.

Avogadro's constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J mol^{-1} K^{-1}
Standard pressure:	$p^\circ = 1$ bar $= 10^5$ Pa
Atmospheric pressure:	$P_{atm} = 1$ atm $= 1.013$ bar $= 1.013 \cdot 10^5$ Pa
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.649 \cdot 10^4$ C mol^{-1}
Watt:	1 W = 1 J s^{-1}
Kilowatt hour:	1 kWh $= 3.6 \cdot 10^6$ J
Planck constant:	$h = 6.626 \cdot 10^{-34}$ J s
Speed of light in vacuum:	$c = 2.998 \cdot 10^8$ m s^{-1}
Elementary charge:	$e = 1.6022 \cdot 10^{-19}$ C
Electrical power:	$P = \Delta E \times I$
Power efficiency:	$\eta = P_{obtained}/P_{applied}$
Planck-Einstein relation:	$E = hc/\lambda$
Ideal gas equation:	$pV = nRT$
Gibbs free energy:	$G = H - TS$
	$\Delta_r G^\circ = -RT \ln K^\circ$
	$\Delta_r G^\circ = -n F E_{cell}^\circ$
	$\Delta_r G = \Delta_r G^\circ + RT \ln Q$
Reaction quotient Q for a reaction a A(aq) + b B(aq) = c C(aq) + d D(aq):	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Henderson−Hasselbalch equation:	$pH = pK_a + \log\frac{[A^-]}{[AH]}$
Nernst–Peterson equation:	$E = E^o - \frac{RT}{zF}\ln Q$
where Q is the reaction quotient of the reduction half-reaction	at $T = 298$ K, $\frac{RT}{F}\ln 10 \approx 0.059$ V
Beer–Lambert law:	$A = \varepsilon l c$

Rate laws in integrated form:

- Zero order:	$[A] = [A]_0 - kt$
- First order:	$\ln[A] = \ln[A]_0 - kt$
- Second order:	$1/[A] = 1/[A]_0 + kt$
Half-life for a first order process:	$t_{1/2} = \ln 2/k$
Number average molar mass M_n:	$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$
Mass average molar mass M_w:	$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$
Polydispersity index I_p:	$I_p = \frac{M_w}{M_n}$

Note

The unit of molar concentration is either "M" or "mol L^{-1}":

1 M = 1 mol L^{-1} 1 mM = 10^{-3} mol L^{-1} 1 µM = 10^{-6} mol L^{-1}

Periodic table

1												13	14	15	16	17	18
1 H 1.008	2																2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Definition of GHS statements

The GHS hazard statements (H-phrases) associated with the materials used are indicated in the problems. Their meanings are as follows.

Physical hazards

H225 Highly flammable liquid and vapor.
H226 Flammable liquid and vapor.
H228 Flammable solid.
H271 May cause fire or explosion; strong oxidizer.
H272 May intensify fire; oxidizer.
H290 May be corrosive to metals.

Health hazards

H301 Toxic if swallowed.
H302 Harmful if swallowed.
H304 May be fatal if swallowed and enters airways.
H311 Toxic in contact with skin.
H312 Harmful in contact with skin.
H314 Causes severe skin burns and eye damage.
H315 Causes skin irritation.
H317 May cause an allergic skin reaction.
H318 Causes serious eye damage.
H319 Causes serious eye irritation.
H331 Toxic if inhaled.
H332 Harmful if inhaled.
H333 May be harmful if inhaled.
H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335 May cause respiratory irritation.
H336 May cause drowsiness or dizziness.
H351 Suspected of causing cancer.
H361 Suspected of damaging fertility or the unborn child.
H371 May cause damage to organs.
H372 Causes damage to organs through prolonged or repeated exposure.
H373 May cause damage to organs through prolonged or repeated exposure.

Environmental hazards

H400 Very toxic to aquatic life.
H402 Harmful to aquatic life.
H410 Very toxic to aquatic life with long-lasting effects.
H411 Toxic to aquatic life with long-lasting effects.
H412 Harmful to aquatic life with long-lasting effects.

Chemicals

For all problems

Chemicals	Labeled as	GHS hazard statements
Deionized water in: - Wash bottle (bench) - Plastic bottle (bench) - Plastic canister (hood)	**Deionized Water**	Not hazardous
Ethanol, in a wash bottle	**Ethanol**	H225, H319
Sample of white wine, 300 mL in amber plastic bottle	**Wine sample**	H225, H319

For problem P1

Chemicals	Labeled as	GHS hazard statements
4-nitrobenzaldehyde, 1.51 g in amber glass vial	**4-nitrobenzaldehyde**	H317, H319
Eluent A, 20 mL in glass vial	**Eluent A**	H225, H290, H304, H314, H319, H336, H410
Eluent B, 20 mL in glass vial	**Eluent B**	H225, H290, H304, H314, H319, H336, H410
Oxone® (potassium peroxomonosulfate salt), 7.87 g in plastic bottle	**Oxone®**	H314
Sample of 4-nitrobenzaldehyde for TLC	**TLC standard**	H317, H319

For problem P2

Chemicals	Labeled as	GHS hazard statements
1 M potassium thiocyanate solution, 20 mL in plastic bottle	**KSCN 1 M**	H302+H312+H332, H412
0.00200 M potassium thiocyanate solution, 60 mL in plastic bottle	**KSCN 0.00200 M**	Not hazardous
1 M perchloric acid solution, 10 mL in plastic bottle	**$HClO_4$**	H290, H315, H319
0.00200 M iron(III) solution, 80 mL in plastic bottle	**Fe(III) 0.00200 M**	Not hazardous
0.000200 M iron(III) solution, 80 mL in plastic bottle	**Fe(III) 0.000200 M**	Not hazardous
0.3% hydrogen peroxide solution, 3 mL in amber glass bottle	**H_2O_2**	Not hazardous

For problem P3

Chemicals	Labeled as	GHS hazard statements
0.01 M iodine solution, 200 mL in brown plastic bottle	**I_2**	H372
0.03 M sodium thiosulfate solution, 200 mL in plastic bottle	**$Na_2S_2O_3$**	Not hazardous
1 M NaOH solution, 55 mL in plastic bottle	**NaOH**	H290, H314
2.5 M sulfuric acid solution, 80 mL in plastic bottle	**H_2SO_4**	H290, H315, H319
0.5 M potassium iodide solution, 25 mL in plastic bottle	**KI**	H372
Potassium iodate, *ca* 100 mg (exact mass written on the label), in glass vial	**KIO_3**	H272, H315, H319, H335
Starch solution, 25 mL in plastic bottle	**Starch**	Not hazardous

Equipment
For all problems

Personal equipment	Quantity
Pipette filler bulb	1
Safety goggles	1
1 L plastic bottle for organic waste, labeled "**Organic waste**"	1
Paper towels	15 sheets
Precision wipers	30 sheets
Spatula (large)	1
Spatula (small)	1
Stopwatch	1
Pencil	1
Eraser	1
Black pen	1
Felt-tip pen for glassware	1
Ruler	1

Shared equipment	Quantity
UV lamp for TLC visualization	2 per lab
Colorimeter	5 per lab
Gloves	All sizes (S, M, L, XL) available upon request to a lab assistant
Ice bucket	1 per lab

For problem P1

Personal equipment	Quantity
Laboratory stand with: - Clamp holder with small clamp - Clamp holder with large clamp	1 2 1
Erlenmeyer flask with ground joint, 100 mL	1
Erlenmeyer flask with ground joint, 50 mL	1
Reflux condenser	1
Hotplate stirrer	1
Crystallizing dish	1
Magnetic stirring bar	1
Suction flask	1
Büchner funnel with rubber adapter	1
Zipped bag with 3 pieces of filter paper	1
Petri dish	1
TLC elution chamber, labeled "**TLC elution chamber**"	1
Zipped bag with 3 TLC plates (with fluorescence indicator), labeled with Student Code	1
TLC graduated spotters (in the Petri dish)	4
Plastic tweezers	1
Glass rod	1
Graduated cylinder, 25 mL	1
Beaker, 150 mL	2
Plastic powder funnel	1
Disposable plastic pipette	2

Amber glass vial, for TLC sample, 1.5 mL, with stopper, labeled **C** and **R**	2
Pre-weighed amber glass vial, 10 mL, with stopper, labeled with **Student Code**	1
Magnetic stirring bar retriever	1

For problem P2

Personal equipment	Quantity
Volumetric pipette, 10 mL	1
Graduated pipette, 10 mL	3
Graduated pipette, 5 mL	3
Test tube stand	1
Test tube	15
Test tube stopper	7
Colorimeter cuvette, path length 1.0 cm	2
Beaker, 100 mL	2
Disposable plastic pipette	15

For problem P3

Personal equipment	Quantity
Laboratory stand with burette clamp	1
Burette, 25 mL	1
Glass transfer funnel	1
Erlenmeyer flask, 100 mL	3
Erlenmeyer flask, 250 mL	3
Beaker, 150 mL	1
Beaker, 100 mL	2
Volumetric flask, 100 mL, with stopper	1
Volumetric pipette, 50 mL	1
Volumetric pipette, 25 mL	1
Volumetric pipette, 20 mL	1
Graduated cylinder, 25 mL	1
Graduated cylinder, 10 mL	1
Graduated cylinder, 5 mL	1
Disposable plastic pipette	3
Parafilm	20 sheets

Problem P1 13% of total	Question	Yield	Purity	TLC	P1.1	P1.2	Total
	Points	12	12	8	2	3	37
	Score						

Problem P1. Greening the oxidation of nitrobenzaldehyde

For the last decades, chemists have tried to replace harmful reagents in oxidation processes in order to reduce hazardous waste treatment. In this problem, potassium peroxomonosulfate has been chosen as oxidizing agent, because it only produces non-toxic and non-polluting sulfate salts. It is provided here as Oxone®. Furthermore, the reaction itself is performed in a mixture of water and ethanol, which are classified as green solvents.

Your task is to perform the oxidation of 4-nitrobenzaldehyde, to recrystallize the product, to compare TLC eluents and to check the purity of the product using TLC.

Note: Ethanol waste and eluent must be disposed of in the "Organic waste" bottle.

Procedure

I. Oxidation of 4-nitrobenzaldehyde

1. **Mix** 20 mL of water and 5 mL of ethanol.

2. **Insert** the magnetic bar in the 100 mL **ground-joint** Erlenmeyer flask.

3. **Transfer** the pre-weighed 1.51 g of 4-nitrobenzaldehyde into the Erlenmeyer flask. **Add** all of the water/ethanol mixture prepared previously. **Clamp** the Erlenmeyer flask to the stand. **Start stirring** the mixture, then **add** the pre-weighed 7.87 g of Oxone®.

4. **Attach** the reflux condenser by loosening the large clamp and adjusting the ground joints (see Figure 1). **Raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate.

5. **Heat** the reaction mixture with a gentle reflux (*ca* 1 drop refluxing per second) for 45 minutes. The mark on the heater corresponds to the necessary power to get a gentle reflux.

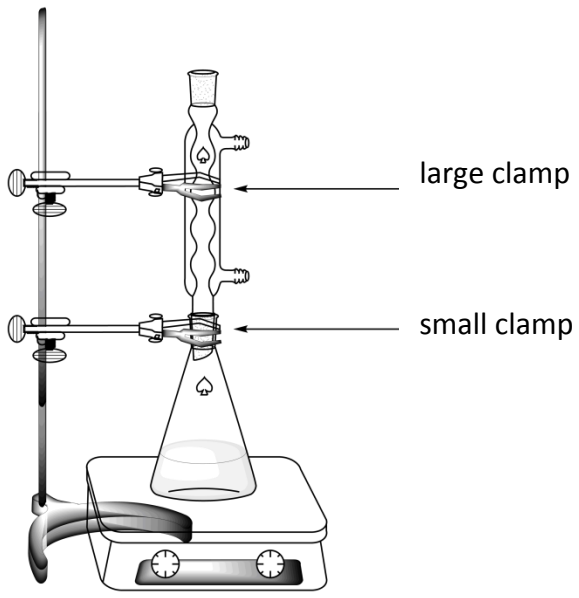


Figure 1. Setup for heating the reaction mixture under reflux

6. Then **turn off** the heating on the hotplate stirrer. **Remove** the hot plate and **let** the reaction mixture cool down for 10 minutes. **Place** it afterwards in the crystallizing dish filled with an ice-water mixture. **Let** it stand for another 10 minutes.

7. **Set up** a vacuum filtration apparatus (see Figure 2) using a Büchner funnel, a filter paper and a suction flask, that is secured to the laboratory stand with a small clamp. **Raise** your HELP card. A lab assistant will come and show how to connect the suction flask to the vacuum source.

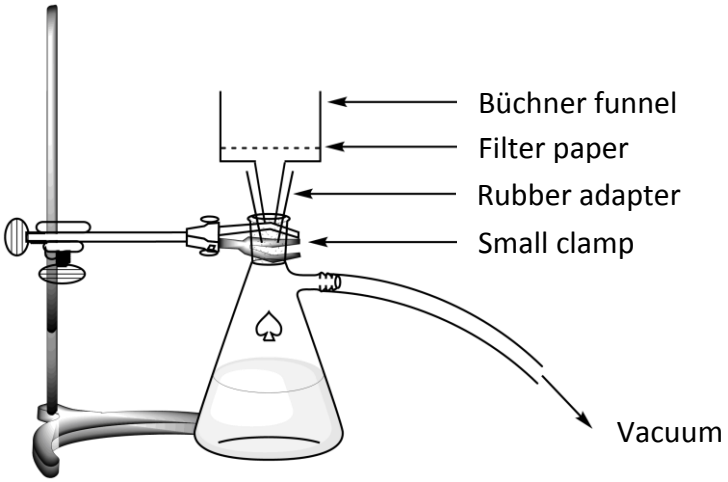


Figure 2. Setup for the vacuum filtration

8. **Wet** the filter paper with water and **ensure** that it covers all the holes of the Büchner funnel.

9. **Pour** the suspension of the crude product into the Büchner funnel and **apply** vacuum. **Wash** the solid thoroughly with deionized water (at least 4×20 mL).

10. **Let** air suck through the precipitate for 5 minutes to pre-dry the product. **Disconnect** the vacuum source. **Use** the small spatula to transfer one tip of spatula of the product in the 1.5 mL amber glass vial, **labeled C**. **Close** the vial and **save** it for part III.

11. **Transfer** all of the remaining solid into the 50 mL ground-joint Erlenmeyer flask.

12. **Discard** the filtrate in the "Organic waste" bottle and **wash** both the suction flask and the Büchner funnel with ethanol and water. **Use** the "Organic waste" bottle to dispose of ethanol waste.

II. Recrystallization of the product

1. **Mix** 9 mL of water and 21 mL of ethanol.

2. **Perform** the recrystallization of the crude product contained in the 50 mL ground-joint Erlenmeyer flask with the appropriate amount of this water/ethanol mixture, using the same setup as for the reflux heating (see Figure 1). **Raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate. **Add** the solvent by the top of the condenser, if needed.

3. Once the product has crystallized, **use** the same procedure as described previously (I.7 to I.10) to collect the solid. **Use** the small spatula to transfer one tip of spatula of the recrystallized product in the 1.5 mL amber glass vial, **labeled R**. **Close** the vial and **save** it for part III.

4. **Transfer** the purified solid in the pre-weighed vial labeled with your Student Code. **Close** the vial.

5. **Discard** the filtrate in the "Organic waste" bottle and **raise** your HELP card. A lab assistant will come to turn off the water of the condenser.

III. TLC analysis

1. **Prepare the elution chamber. Load** the elution chamber with *ca* 0.5 cm in height of eluent A. Cover it with a Petri dish. **Wait** for the eluent to saturate the atmosphere in the elution chamber.

2. **Prepare your samples**. You are provided a sample of 4-nitrobenzaldehyde in an amber glass vial labeled **TLC standard** (referred as **S** on the TLC). You have also kept a small sample of your crude product (vial **C**) and your recrystallized product (vial **R**) in two other amber glass vials. **Add** *ca* 1 mL of ethanol in each of the vials in order to dissolve the samples.

3. **Prepare your TLC plate**. Use a pencil to **draw** carefully the start line (1 cm above the bottom of the plate) and **mark** the positions in order to spot the 3 samples. **Label** them **S** (Starting material), **C** (Crude product) and **R** (Recrystallized product), as described in Figure 3. On the top left of the plate, **write** your **Student Code**. On the top right of the plate, **write** the eluent you use (first **Eluent A**, then **Eluent B**). **Spot** the three samples on the plate, using capillary spotters.

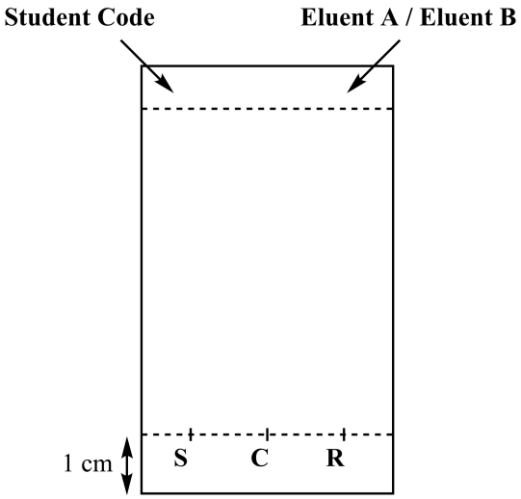


Figure 3. TLC plate preparation

4. **Perform the TLC analysis**. Using tweezers, **insert** the TLC plate into the elution chamber and **cover** it with the Petri dish. **Let** the eluent **reach** approximately 1 cm below the top of the plate. Using tweezers, **remove** the plate, mark the eluent front with a pencil and let the plate air-dry.

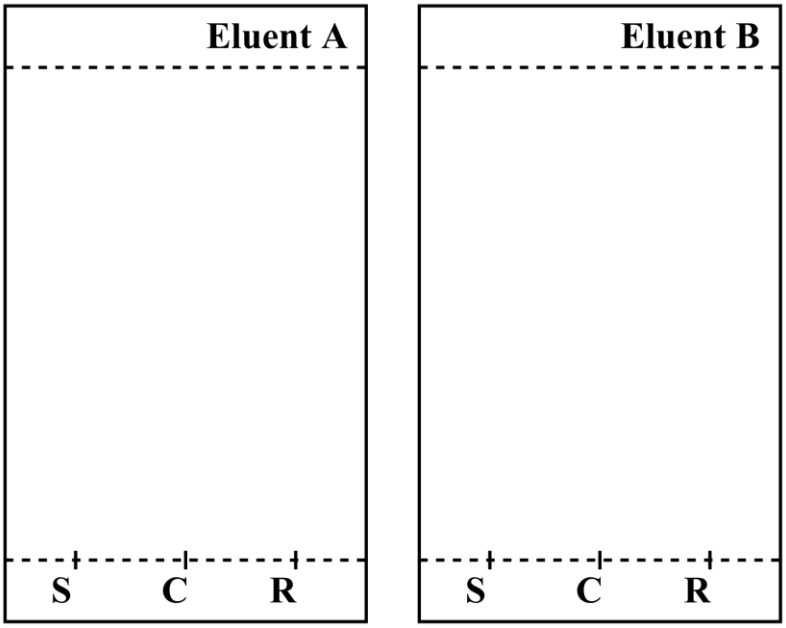
5. **Visualize the TLC plate**. **Place** the TLC plate under the UV lamp kept on the common bench. With a pencil, **circle** all the visible spots.

6. **Discard the eluent into the "Organic waste" bottle**.

7. **Repeat** steps 1, 3, 4, 5, and 6 with eluent B.

8. **Place** your plates in the zipped bag with your Student Code.

Results of your TLC analysis (**complete** the schemes with your results). You may use these drawings to make a scheme of your TLC plates that may help you answer the following questions. The scheme will not be graded.



At the end of the examination, your lab supervisor will pick up the following items:

- Glass vial labeled with your **Student Code** containing your recrystallized product;
- TLC plates A and B in zipped bag labeled with your **Student Code**.

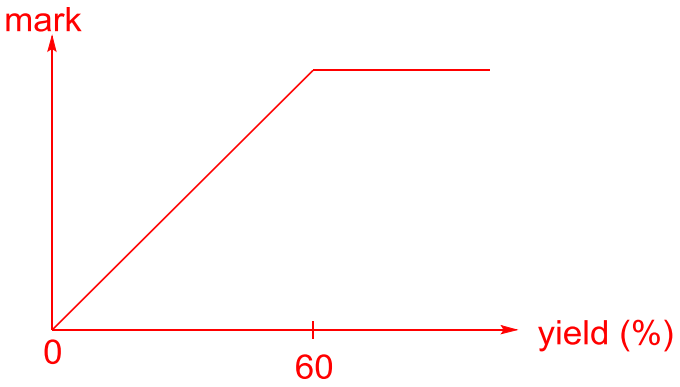
Submitted items	
Recrystallized product	□
TLC plate A	□
TLC plate B	□

Signatures

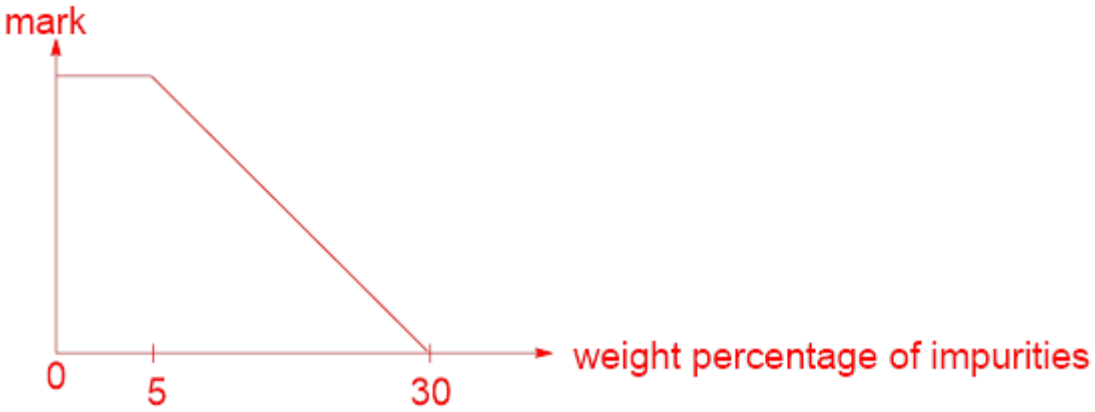
Student _____ Lab Supervisor _____

Grading of the product:

- 12 points for the effective yield of 4-nitrobenzoic acid



- 12 points for the purity (based on NMR and conductivity measurements)



If the student failed to transfer the solid in the vial during the exam, he-she has been asked to do it after the end of the exam. 1 point penalty.

12+12 points

Grading of the TLC:

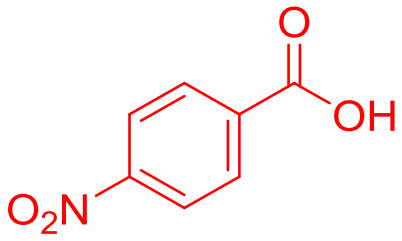
For each TLC:
- The plate is eluted: 1 point
- The start line, the eluent front and the ticks for the deposit are present: 1 point
- All the visible spots are circled: 1 point

For the good eluent only:
- The elution has been performed successfully (spots separated, straight elution; TLC forgotten, …): 2 points

8 points

Questions

1. **Propose** a structure for the final organic product from the reaction of 4-nitrobenzaldehyde and Oxone®.



2 points
1 point if potassium carboxylate
2 points

2. Based on your results on the TLC analysis, **answer** the following questions.

- Which eluent is better to follow the reaction progress?

□ **A** □ **B**

- The crude product (C) contains traces of 4-nitrobenzaldehyde.

□ **True** □ **False**

- The recrystallized product (R) contains traces of 4-nitrobenzaldehyde.

□ **True** □ **False**

1 point for each question, in agreement with the TLC plates submitted
3 points

Problem P2 14% of total	Question	Calibration	Iron determination	P2.1	P2.2	P2.3	Stoichiometry determination	P2.4	P2.5	Total
	Points	10	6	3	4	3	9	3	2	40
	Score									

Problem P2. The iron age of wine

Iron is an element which can naturally be found in wine. When its concentration exceeds 10 to 15 mg per liter, iron(II) oxidation into iron(III) may lead to quality loss, through the formation of precipitates. It is therefore necessary to assess the iron content of the wine during its production.

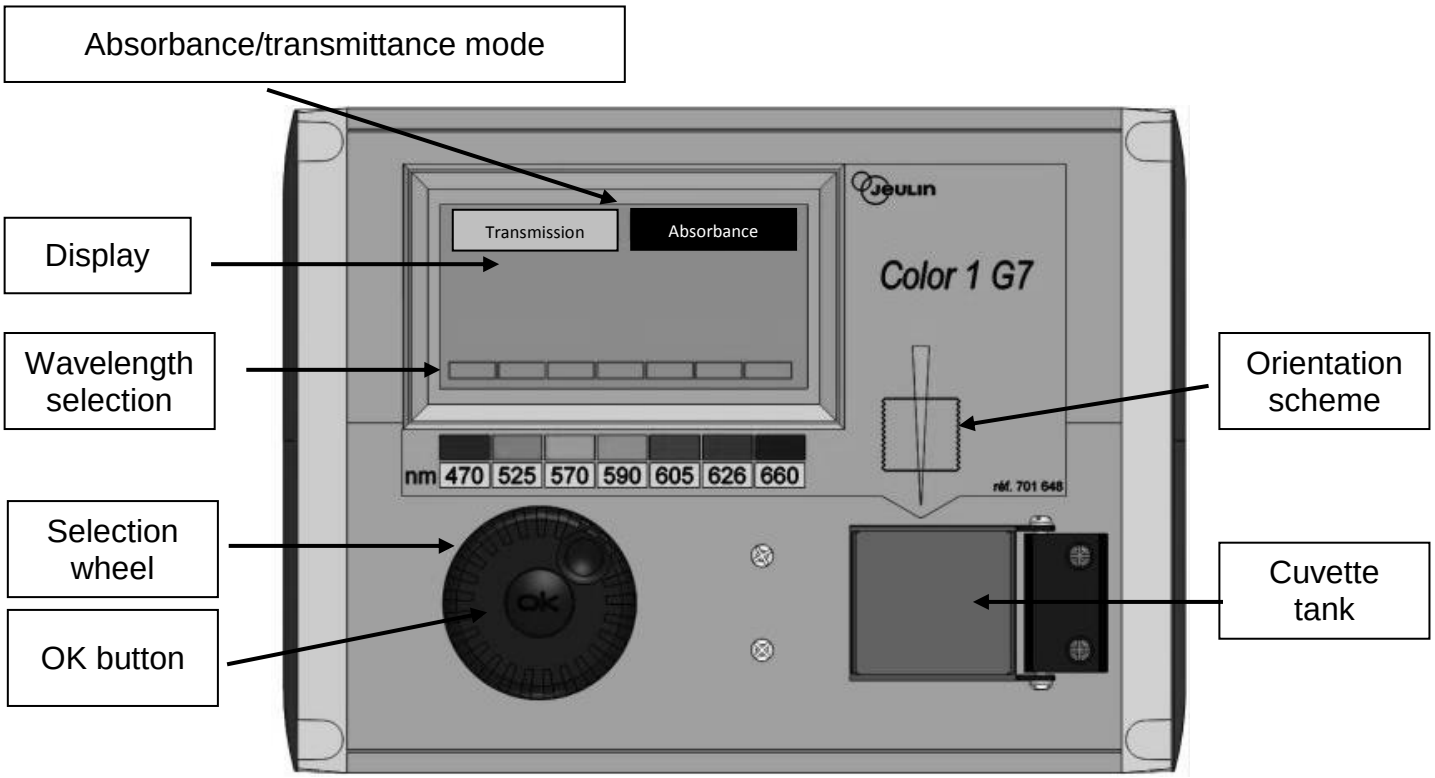
Given the very low concentration of iron species, a colored complex of iron(III) with thiocyanate SCN^- as a ligand is used to quantify the iron amount, through spectrophotometric measurements.

Your task is to determine the total iron concentration of the white wine provided, using spectrophotometry, and to determine the stoichiometry of the thiocyanate – iron(III) complex.

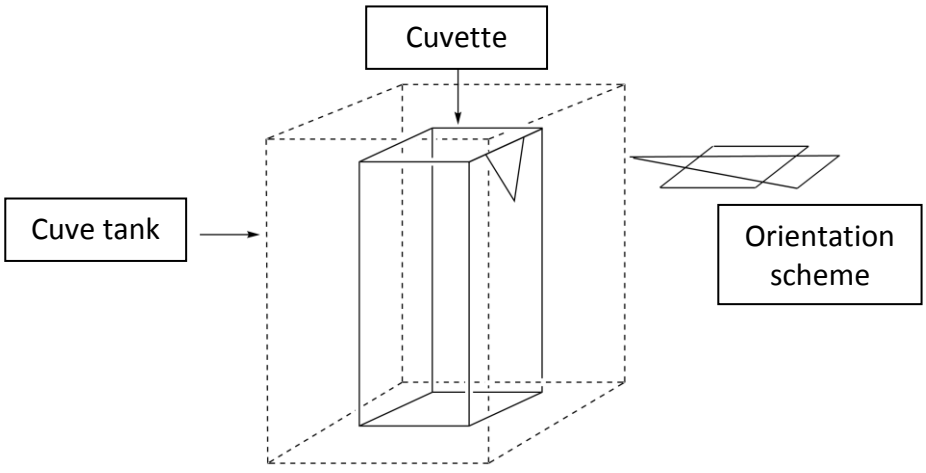
WARNING

- In this task, you are provided with two iron(III) solutions and two potassium thiocyanate solutions of different concentrations. Be very careful not to confuse them.
- Once the solutions are ready for spectrophotometric measurements, record the absorbance no later than one hour after the addition of thiocyanate.
- When you need a colorimeter, raise your HELP card. A lab assistant will give you a colorimeter labeled. You will have the exclusive use of this colorimeter for up to 15 minutes. The lab assistant will take it back as soon as you have finished or when the 15 minutes are over. If no colorimeter is available at the precise moment, you will be added to a waiting-list.
- Instructions for the colorimeter are presented on the following page.
- You can call for the colorimeter only three times for this problem.

Instructions for the use of the colorimeter



- Plug in the colorimeter.
- Check that "Absorbance" is highlighted. If not, turn the selection wheel until a dashed line appears around "Absorbance" and then press the OK button.
- Turn the selection wheel until a dashed line appears around the desired wavelength (470 nm). Press the OK button.
- Place the cuvette with *ca* 3 cm in height of the blank solution in the tank. Be careful to choose the correct orientation (look at the orientation scheme on the colorimeter, the beam is in the direction of the yellow arrow, see figure below), and to push the cuvette down until the final position. Close the lid.
- Turn the selection wheel until a dashed line appears around "Absorbance" and then press the OK button. Using the selection wheel, highlight "Calibration" and press the OK button.
- Wait until the display reads 0.00 (or –0.00).
- Place the cuvette with *ca* 3 cm in height of the analyzed solution in the tank. Close the lid.
- Read the absorbance value.



I. Determination of the iron content in the wine

In this part, you will need the 0.000200 M iron(III) solution and the 1 M potassium thiocyanate solution.

Procedure

1. **Prepare** 6 tubes by adding to each tube the required volumes of the provided solutions, as described in the table below.

Tube #	**1**	**2**	**3**	**4**	**5**	**6**
0.000200 M iron(III) solution	1.0 mL	2.0 mL	4.0 mL	6.0 mL		
1 M perchloric acid solution	1.0 mL	1.0 mL	1.0 mL	1.0 mL	1.0 mL	1.0 mL
Wine					10.0 mL	10.0 mL
Hydrogen peroxide solution					0.5 mL	0.5 mL
Deionized water	9.5 mL	8.5 mL	6.5 mL	4.5 mL		1.0 mL

2. **Stopper** the tubes and **homogenize**.

3. **Add** 1.0 mL of 1 M potassium thiocyanate solution in tubes **1**, **2** **3**, **4** and **5**. Do **not** add in tube **6**. **Stopper** and **homogenize**.

4. When all the tubes are ready, **raise** your HELP card to get a colorimeter from a lab assistant.

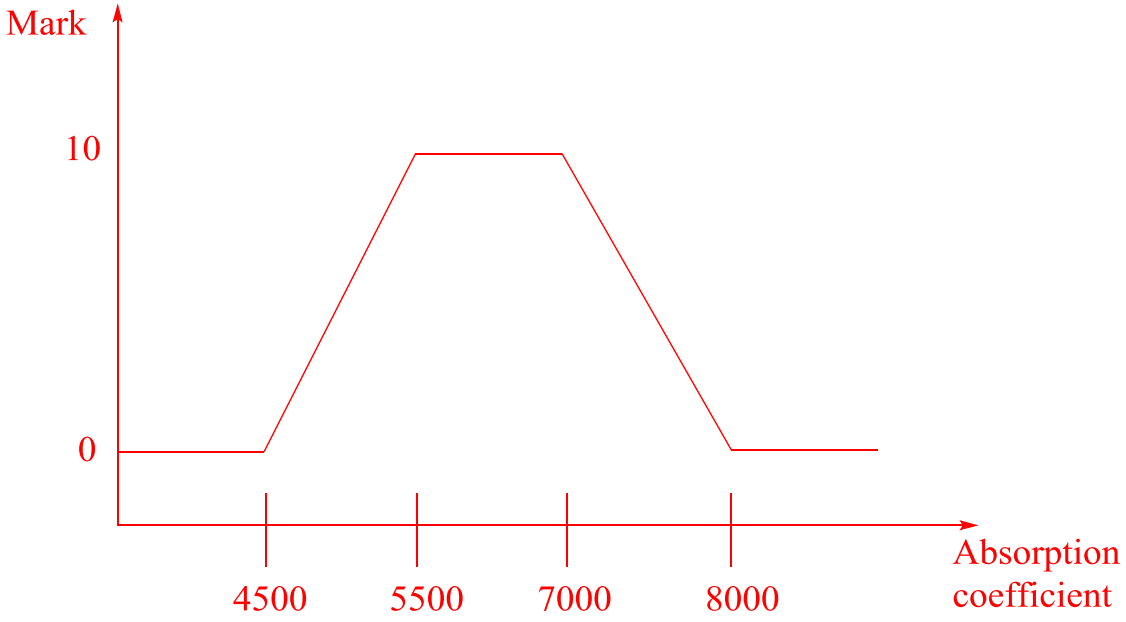
5. **Prepare** the colorimeter using the procedure described previously (see page 16). **Set** the wavelength at 470 nm. **Use** deionized water for the blank.

6. **Record** the absorbance of each tube (**1** to **6**) at this wavelength. **Report** the results in the following table. **Raise** your HELP card to return the colorimeter.

Tube #	**1**	**2**	**3**	**4**	**5**	**6**
Absorbance (at 470 nm)						
Analytical concentration of Fe^{3+} in the tube $c(Fe^{3+})$ / µM	16	32	64	96		
Colorimeter code						

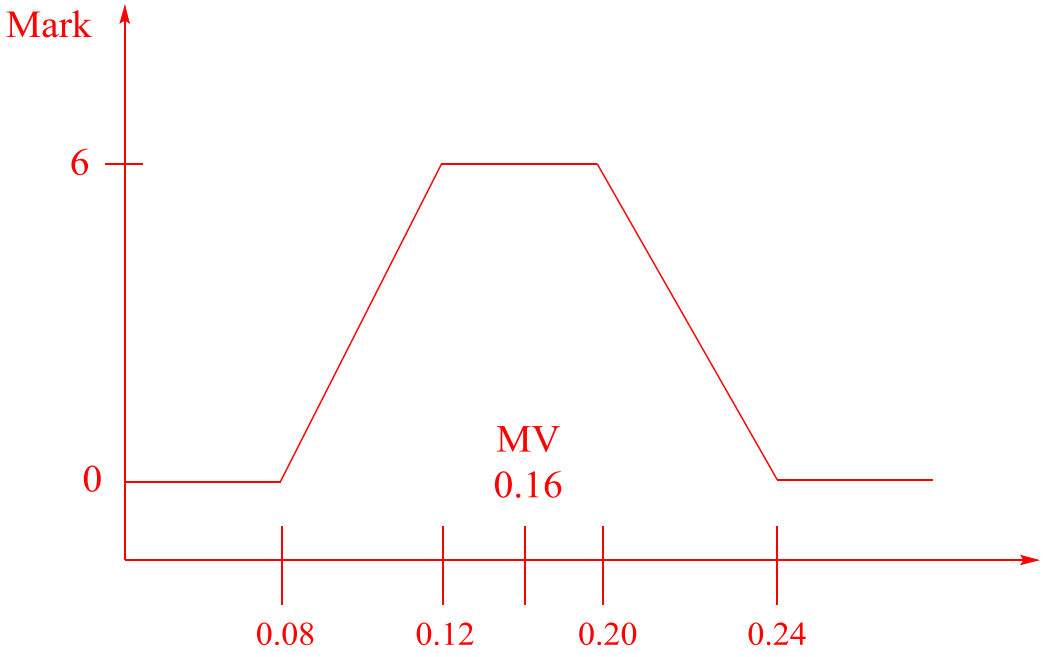
Grading scheme

- 10 points for absorption coefficient value, based on the values ticked in the table



10 points

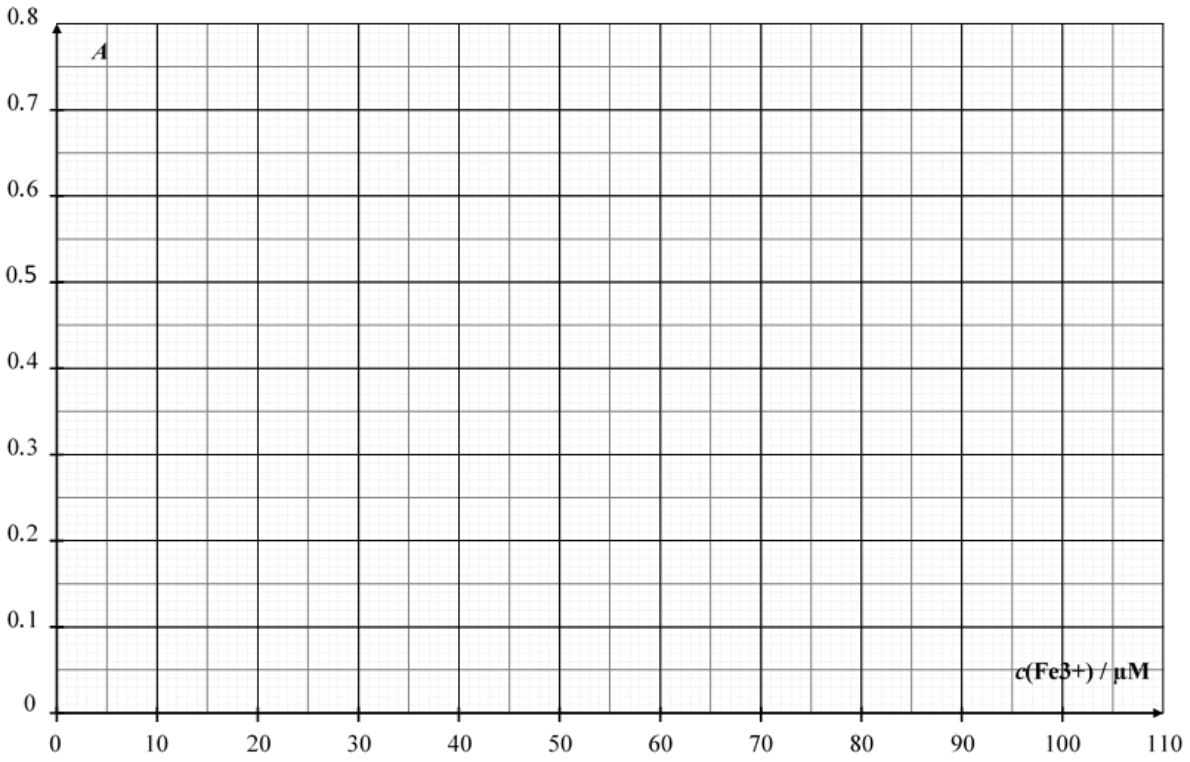
- 6 points for the value of A_5-A_6



6 points

Questions

1. **Plot** the absorbance *A* of tubes **1** to **4** as a function of the analytical concentration of Fe^{3+} in the tube.



Grading scheme:

- 3 points for the right position of the points on the plot

3 points

- In the following, check the boxes of the data you will consider for your calibration curve.

Tube #	**1**	**2**	**3**	**4**
Absorbance values used for the calibration curve				

2. Using the previous plot and the data you have chosen, **draw** the calibration straight line on the previous plot **determine** the analytical concentration (in µmol L^{-1}) of Fe^{3+} in tube **5**.

Calibration curve drawn: 1 point
Use of A5-A6: 2 points (1 point if use of A5)
Good reading of the value of the concentration on the plot: 1 point
4 points

$$c(Fe^{3+})_{TUBE\ 5} = \underline{\qquad\qquad} \ \mu mol\ L^{-1}$$

If you could not calculate $c(Fe^{3+})$, the value $c(Fe^{3+}) = 50\ \mu mol\ L^{-1}$ can be used in the rest of the problem.

3. **Calculate** the mass concentration, in mg per liter, of iron in the studied white wine.

1 point for the dilution factor
1 point for the relation between mass concentration and molar concentration
1 point for numerical value (with the correct unit)
3 points

c_m(iron) = _____ mg L^{-1}

II. Determination of the complex stoichiometry

In this part, you will need the 0.00200 M iron(III) solution and the 0.00200 M potassium thiocyanate solution.

Procedure

In part I of this problem, we use the color of the iron(III)-thiocyanate complex to determine the concentration of iron in the sample of wine. Part II of this problem aims at investigating the stoichiometry of the $[Fe_a(SCN)_b]^{(3a-b)+}$ complex (coordination of water is not shown), where *a* and *b* are integers no greater than 3.

You are provided with the following aqueous solutions for this part:

- 0.00200 M iron(III) solution (already acidified) (80 mL)
- 0.00200 M potassium thiocyanate solution (80 mL)

You also have test tubes (with stoppers that you can wash and dry), graduated pipettes, a spectrophotometer cuvette, a colorimeter (upon request), and any other labware on your bench that you think useful.

1. **Fill** the first three lines of the following table with volume values that will allow you to determine the stoichiometry of the complex, by spectrophotometric measurements. *You don't have to fill all the columns.* **Calculate** the molar fraction of iron(III) in each tube, using the following formula.

$$x(\mathrm{Fe^{3+}}) = \frac{V_{\mathrm{Fe(III)}}}{V_{\mathrm{Fe(III)}} + V_{\mathrm{SCN^-}}}$$

Tube #	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Volume of 0.00200 M iron(III) solution $V_{Fe(III)}$ / mL									
Volume of 0.00200 M potassium thiocyanate solution V_{SCN-} / mL									
Molar fraction in iron(III) $x(Fe^{3+})$									
Absorbance (at 470 nm)									
Colorimeter code									

2. **Prepare** the tubes. When all the tubes are ready, **raise** your HELP card to get a colorimeter from a lab assistant.

3. **Prepare** the colorimeter using the procedure described previously (see page 16). **Set** the wavelength at 470 nm. **Use** deionized water for the blank.

4. **Record** the absorbance of each tube at this wavelength. **Report** the results in the previous table.

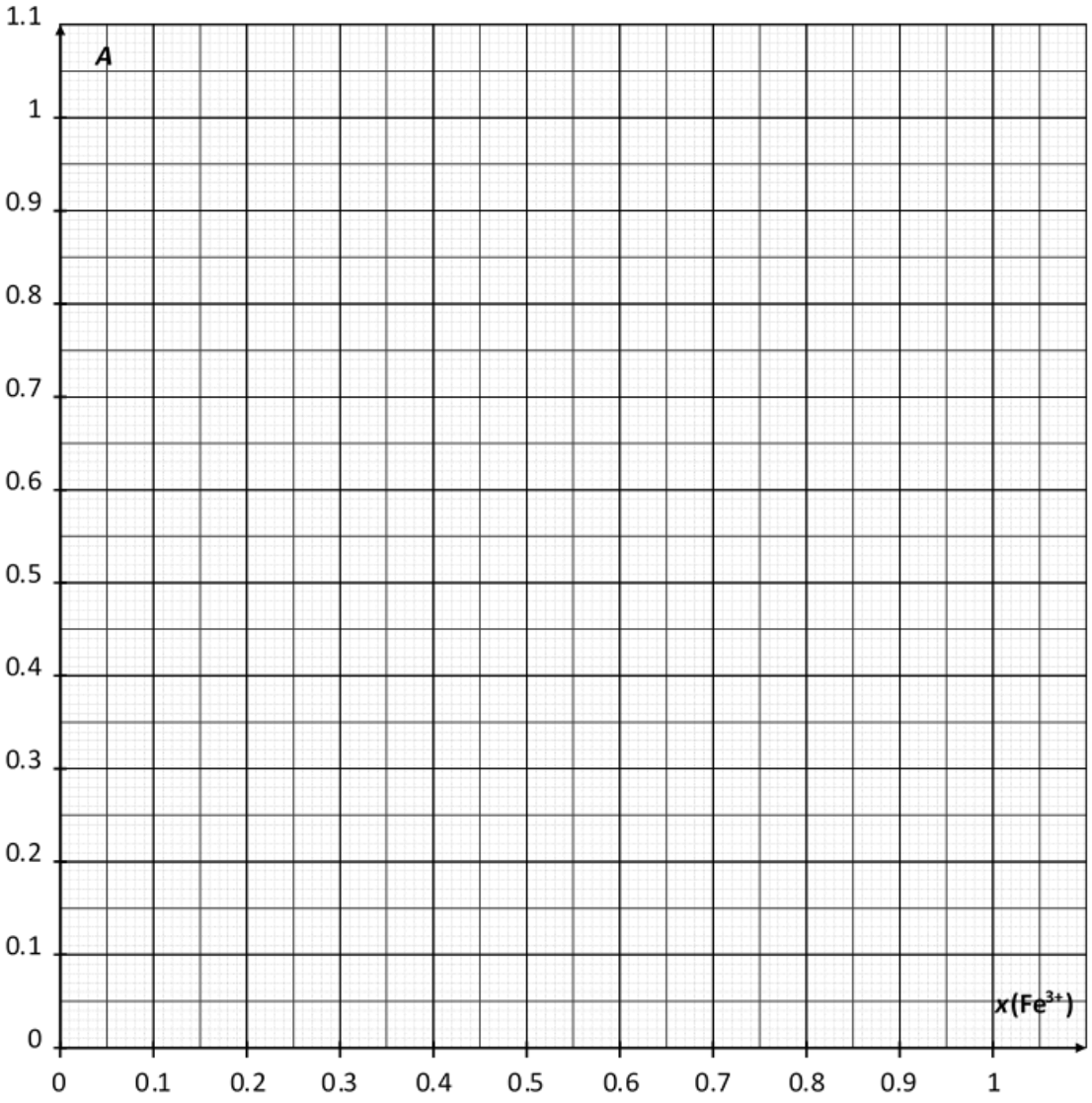
Grading scheme:

- 4 points if at least 2 points in $x(Fe^{3+})$ in]0;0,5] and at least 2 points in [0,5;1[
- 2 points if $x(Fe^{3+})$ in agreement with the volumes
- 3 points for the agreement of the absorbance values with the expected values

9 points

Questions

4. **Plot** the absorbance *A* of the tubes as a function of the molar fraction of iron(III) $x(Fe^{3+})$.



3 points if the points are placed the correct way on the plot.

3 points

5. Based on the results of the experiments you carried out, **determine** the stoichiometry of the complex $[(Fe)_a(SCN)_b]^{(3a-b)+}$.

2 points if the values are in agreement with the plot and/or the data

2 points

a = _____ ***b*** = _____

Problem P3 13% of total	Question	Titration I	Titration II	Titration III	P3.1	P3.2	P3.3	P3.4	P3.5	Total
	Points	10	10	8	4	4	2	2	2	42
	Score									

Problem P3. Wine for keeping

Sulfur dioxide, SO_2, is used as a preservative in wine. When SO_2 is added to wine, it can react with water leading to bisulfite ions, HSO_3^-, and protons, H^+. Bisulfite can also be converted to sulfite, SO_3^{2-}, by the loss of a second proton.

$$SO_2 + H_2O = H^+ + HSO_3^-$$
$$HSO_3^- = H^+ + SO_3^{2-}$$

These three different forms of sulfur dioxide in water can react with chemicals in wine such as acetaldehyde, pigments, sugars, etc. forming products P. The total concentration of sulfur dioxide is the sum of the concentration of the "free" forms (SO_2, HSO_3^- and SO_3^{2-}) and P.

The preservative concentration is regulated because sulfites and sulfur dioxide can be harmful to some people. In the EU, the maximum total sulfur dioxide content is set at 100 mg L^{-1} for red wine and 150 mg L^{-1} for white or rosé.

Your task is to determine the total sulfur dioxide concentration of the provided white wine by iodometric titration.

Procedure

I. Standardization of the sodium thiosulfate solution

1. You are given a sample of *ca* 100 mg of pure potassium iodate KIO_3. The exact mass is written on the label of the vial. **Report** it in the table below.

2. **Prepare** 100 mL of potassium iodate solution in the 100 mL volumetric flask, using the whole sample of solid potassium iodate and deionized water. This solution is called **S**.

3. In a 100 mL Erlenmeyer flask, **add**:
- 20 mL of solution **S** with a volumetric pipette;
- 5 mL of the potassium iodide solution (0.5 M), using a 5 mL graduated cylinder;
- 10 mL of the sulfuric acid solution (2.5 M) with a 10 mL graduated cylinder.

4. **Swirl** the Erlenmeyer flask, **cover** it with Parafilm and **keep** it in the cupboard for at least five minutes.

5. **Fill** the burette with the provided thiosulfate solution using a beaker. **Titrate** the content of the Erlenmeyer flask with constant swirling. When the liquid turns pale yellow, **add** ten drops of the starch solution and **keep titrating** until the solution becomes colorless. **Record** the titration volume V_1.

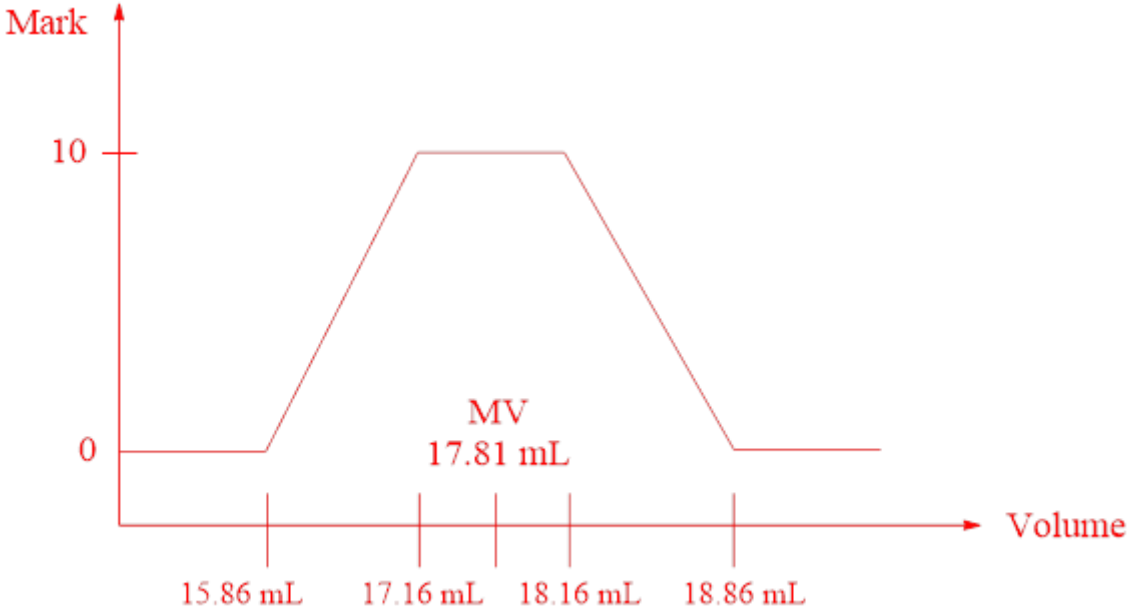
6. **Repeat** the procedure (steps 3-5) as needed.

Mass of potassium iodate (report the value on the label)	

Analysis n°	**V_1 / mL**
1	
2	
3	
Reported value V_1 / mL	

Grading scheme:

Master value corrected for 100 mg



1 point penalty if KIO_3 mass is not reported or reported incorrectly
2 points penalty if the reported value is missing
10 points

II. Standardization of the iodine solution

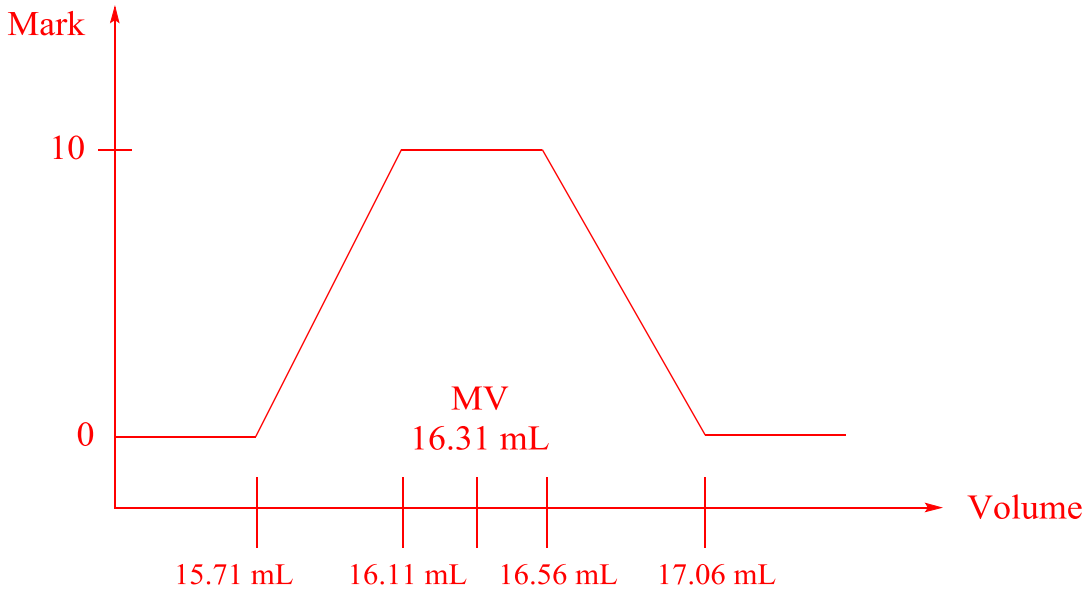
1. With a volumetric pipette, **transfer** 25 mL of the iodine solution labeled $\mathbf{I_2}$ into a 100 mL Erlenmeyer flask.

2. **Titrate** the content of the Erlenmeyer flask with the sodium thiosulfate solution. When the liquid turns pale yellow, **add** ten drops of the starch solution and **keep titrating** until the solution becomes colorless. **Record** the titration volume V_2.

3. **Repeat** the procedure (steps 1-2) as needed.

Analysis n°	**V_2 / mL**
1	
2	
3	
Reported value V_2 / mL	

Grading scheme:



2 points penalty if the reported value is missing

10 points

III. Determination of total sulfur dioxide

1. With a volumetric pipette, **transfer** 50 mL of wine into a 250 mL Erlenmeyer flask.

2. **Add** 12 mL of the sodium hydroxide solution (1 M), with a 25 mL graduated cylinder. **Cover** the flask with Parafilm, **swirl** the content then let it stand for at least 20 minutes.

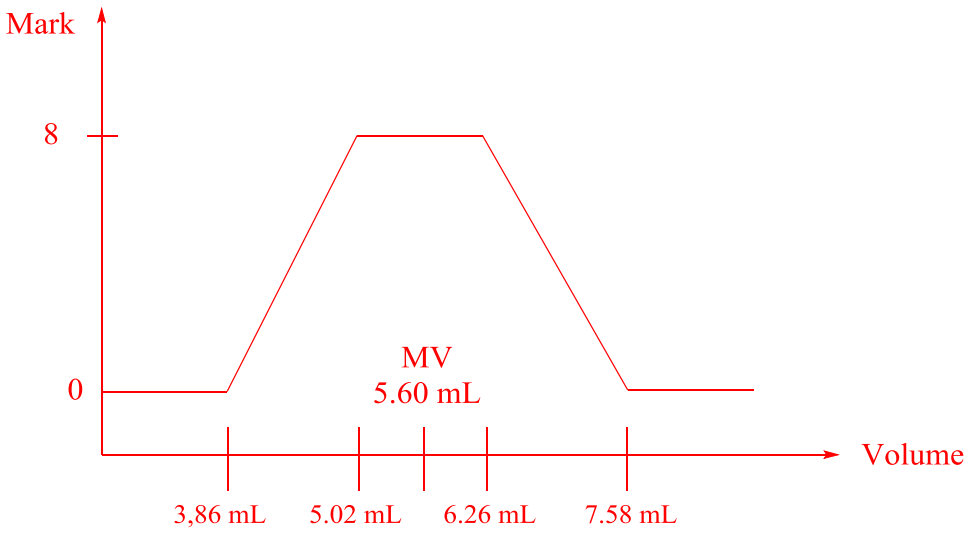
3. **Add** 5 mL of the sulfuric acid solution (2.5 M), and *ca* 2 mL of starch solution using a graduated disposable plastic pipette.

4. **Titrate** the content of the Erlenmeyer flask with the iodine solution in the burette, until a dark color appears and persists for at least 15 seconds. **Record** the titration volume V_3.

5. **Repeat** the procedure (steps 1-4) as needed.

Analysis n°	**V_3 / mL**
1	
2	
3	
Reported value V_3 / mL	

Grading scheme:



2 points penalty if the reported value is missing

8 points

Questions

1. **Write down** the balanced equations of all the reactions occurring during the standardization of the sodium thiosulfate solution.

(1) or or or	$IO_{3\,(aq)}^{-} + 5I_{(aq)}^{-} + 6H_{(aq)}^{+} = 3I_{2\,(aq)} + 3H_2O_{(l)}$ $IO_{3\,(aq)}^{-} + 5I_{(aq)}^{-} + 6H_3O_{(aq)}^{+} = 3I_{2\,(aq)} + 9H_2O_{(l)}$ $IO_{3\,(aq)}^{-} + 8I_{(aq)}^{-} + 6H_{(aq)}^{+} = 3I_{3\,(aq)}^{-} + 3H_2O_{(l)}$ $IO_{3\,(aq)}^{-} + 8I_{(aq)}^{-} + 6H_3O_{(aq)}^{+} = 3I_{3\,(aq)}^{-} + 9H_2O_{(l)}$	2 point
(2) or	$I_{3\,(aq)}^{-} + 2S_2O_{3\,(aq)}^{2-} = 3I_{(aq)}^{-} + S_4O_{6\,(aq)}^{2-}$ $I_{2\,(aq)} + 2S_2O_{3\,(aq)}^{2-} = 2I_{(aq)}^{-} + S_4O_{6\,(aq)}^{2-}$	2 point
Any equation that is not balanced will get 0 mark If the equations are merged as one, 2 points 4 points		

2. **Calculate** the molar concentration of the sodium thiosulfate solution. The molar mass of potassium iodate is $M(KIO_3)$ = 214.0 g mol^{-1}.

4 points in total

Partial marks given:
- 1 point if the relations between the amounts of substance are given.
- 0.5 point for each amount of substance (iodate, iodine or thiosulfate) correctly calculated
- −1 point if the concentration is given in the wrong unit
- 2.5 points if the dilution by 5 has been forgotten

4 points

$c(S_2O_3^{2-})$ = _____ mol L^{-1}

If you could not calculate $c(S_2O_3^{2-})$, the value $c(S_2O_3^{2-}) = 0.0500$ mol L^{-1} can be used in the rest of the problem.

3. **Calculate** the molar concentration of the iodine solution.

2 points in total
1 point if the relation between the amounts of substance is given
−0.5 point if the result is given in the wrong unit
2 points

$c(I_2)$ = _____ mol L^{-1}

If you could not calculate $c(I_2)$, the value $c(I_2)$ = 0.00700 mol L^{-1} can be used in the rest of the problem.

4. **Write down** the equation of the reaction between iodine I_2 and sulfur dioxide SO_2, assuming that sulfur dioxide is oxidized into sulfate ions SO_4^{2-}.

$SO_{2(aq)} + 2H_2O_{(l)} + I^-_{3\,(aq)} = SO^{2-}_{4\,(aq)} + 4H^+_{(aq)} + 3I^-_{(aq)}$ or: $SO_{2(aq)} + 2H_2O_{(l)} + I_{2(aq)} = SO^{2-}_{4\,(aq)} + 4H^+_{(aq)} + 2I^-_{(aq)}$	2 points
1 point only if the reaction is written in basic medium 2 points	

5. **Calculate** the mass concentration, in mg per liter, of total sulfur dioxide in the wine. The molar mass of sulfur dioxide is $M(SO_2)$ = 64.1 g mol^{-1}.

2 points in total
1 point if the relation between the amount of substance is given
−0.5 point if the result is given in the wrong unit
2 points

$c_m(SO_2)$ = _____ mg L^{-1}

PENALTIES

Incident #	Student signature	Lab supervisor signature
1 (no penalty)		
2		
3		
4		
5		