THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Volume 5

51st – 55th IChO
2019 – 2023

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THE COMPETTION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Volume 5

THE COMPETITION PROBLEMS FROM THE 51ST – 55TH IChOs

The authors of the problems were the members of the Scientific Committees of the 51ST - 55TH IChOs, respectively

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Preface

Not less than 362 theoretical and 125 practical problems were set in the competition of the International chemistry olympiad (IChO) during the first fifty years of its existence. They have been published by the IChO International Information Centre (IChO IIC) in Bratislava (Slovakia) in the following four volumes:

- The competition problems from the International Chemistry Olympiads, Volume 1, 1st – 20th IChO, 1968 – 1988 (IChO IIC, Bratislava, 2008), pp. 1 – 405.
- The competition problems from the International Chemistry Olympiads, Volume 2, 21st – 40th IChO, 1989 – 2008 (IChO IIC, Bratislava, 2009), pp. 406 – 1139.
- The competition problems from the International Chemistry Olympiads, Volume 3, 41st – 45th IChO, 2009 – 2013 (IIC IChO, Bratislava, 2013), pp. 1140 – 1424.
- The competition problems from the International Chemistry Olympiads, Volume 4, 46th – 50th IChO, 2014 – 2018 (IIC IChO, Bratislava, 2013), pp. 1425 – 1759.

The present publication (Volume 5) contains theoretical and practical competition problems from the 51st to 55th International Chemistry Olympiads (IChO) organized in the years 2019 — 2023, respectively. The 52nd, 53rd and 54th International Chemistry Olympiads have been influenced by the pandemics and were organized under special conditions. The pandemic situation required a certain change of the regulations, since the members of the Steering Committee and International Jury and in particular the competitors could not attend these IChO personally. Consequently, all the meetings of the Steering Committee as well as those of the International Jury had to be held in an online way and the competition itself had to be organized in a remote way. Moreover, it concerned the theoretical part of the competition only while the practical one had to be eliminated although it represented till now 40 % of the total score in the competition. Therefore, one cannot find any practical competition tasks of the 52nd, 53rd and 54th IChOs in this publication.

As usual, in the elaboration of these collections the editor had to face certain difficulties because the aim was not only to make use of the past recordings but also to give them such a form that they may be used in practice and further chemical education. Some corrections were made in order to unify the form of the problems (numbering of the

tasks in the particular problems, solutions inserted immediately after the text of the each problem, solutions without grading points as they were used in the competition and special graphs used for grading of practical problems).

Nevertheless, the mentioned corrections and changes do not concern the contents and language of the competition problems.

In this publication SI quantities and units are preferred. Only some exceptions have been made when, in an effort to preserve the original text, the quantities and units have been used that are not SI.

Although the numbers of significant figures in the results of some solutions do not obey the criteria generally accepted, they were left without change.

Unfortunately, the authors of the particular competition problems are not known and due to the procedure of creation of the IChO competition problems, it is impossible to assign any author's name to a particular problem. Nevertheless, responsibility for the scientific content and language of the problems lies exclusively with the organizers of the particular International Chemistry Olympiads.

Anton Sirota & Martin Putala, editors

Bratislava, 2026

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51st — International Chemistry Olympiad France — Paris — 2019

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THE FIFTY-FIRST
INTERNATIONAL CHEMISTRY OLYMPIAD
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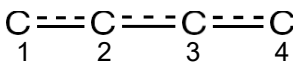
THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

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:

$$E_n = \frac{n^2 h^2}{8 m_e L^2}$$

where n is a non-zero positive integer.

1.1 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.

1.2 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.

1.3 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.

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.

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

Models 1 and 2 are too simplistic. A newä=ú§model will be detailed in the following.

1.5 Draw three other resonance structures of butadiene using Lewis notation.

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 $7L/8$.

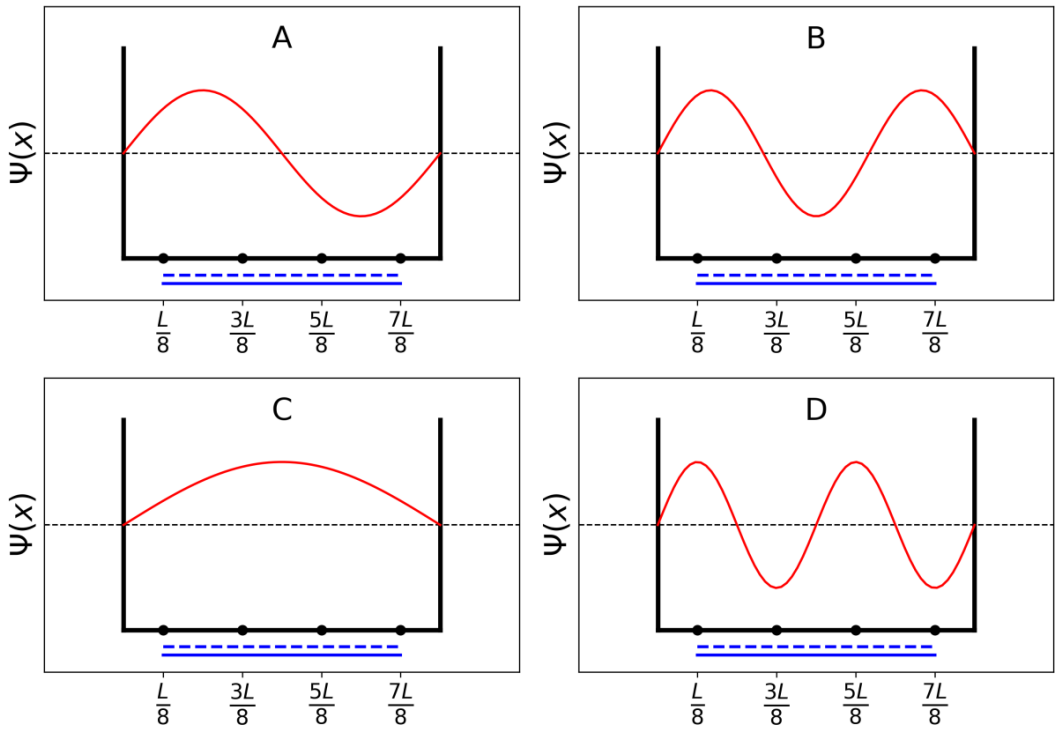
For each level n, the π wavefunction is:

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

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).



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

1.7 Give the labels (A, B, C or D) of the orbitals that are filled with electrons in

butadiene.

1.8 Within model 3, give the values of the $\boldsymbol{\pi}$ 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.

1.9 Within model 3, give the value of the $\boldsymbol{\pi}$ electron density at positions 0, $L/4$ and $L/2$.

1.10 Draw the $\boldsymbol{\pi}$ electron density between 0 and L.

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

B1: C1–C2 in the butadiene molecule

B2: C2–C3 in the butadiene molecule

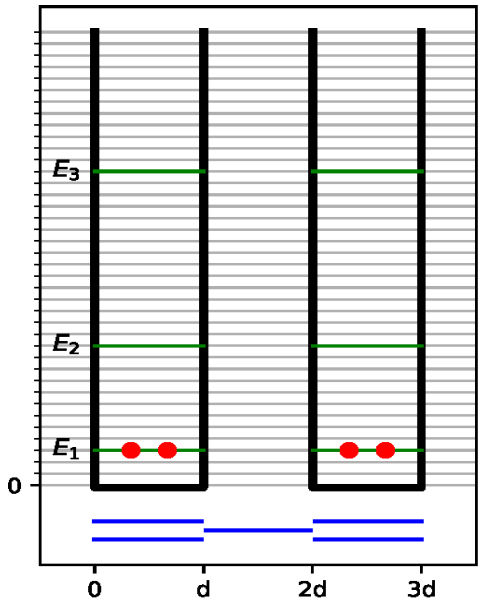
B3: C3–C4 in the butadiene molecule

B4: C–C in the ethane molecule

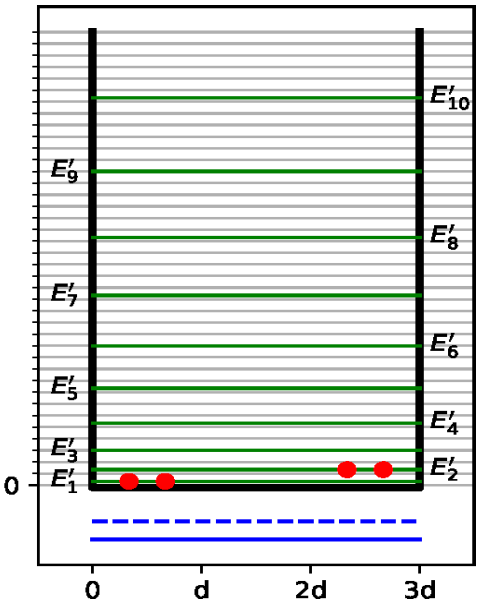
B5: C–C in the ethene molecule

SOLUTION OF THE PROBLEM 1

1.1



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

1.2

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

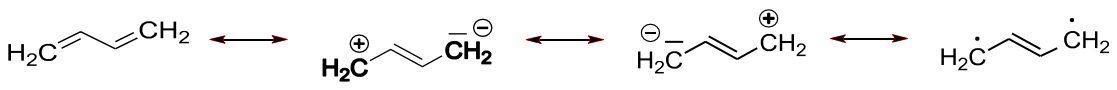
1.3

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

1.4

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

1.5



1.6 $E_C < E_A < E_B < E_D$

1.7 C and A

1.8

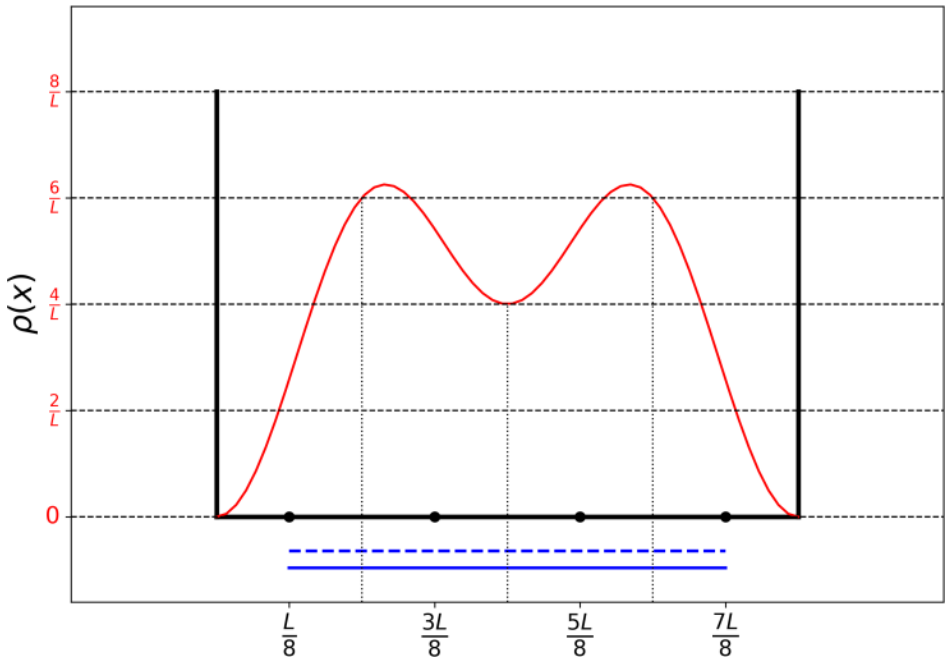
$$\Psi_1(0) = 0 \quad \Psi_1\left(\frac{L}{4}\right) = \sqrt{\frac{1}{L}} \quad \Psi_1\left(\frac{L}{2}\right) = \sqrt{\frac{2}{L}}$$

$$\Psi_2(0) = 0 \quad \Psi_2\left(\frac{L}{4}\right) = \sqrt{\frac{2}{L}} \quad \Psi_2\left(\frac{L}{2}\right) = 0$$

1.9

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

1.10



1.11 B5 < B1 = B3 < B2 < B4

THEORETICAL PROBLEM 2

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.

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

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

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.

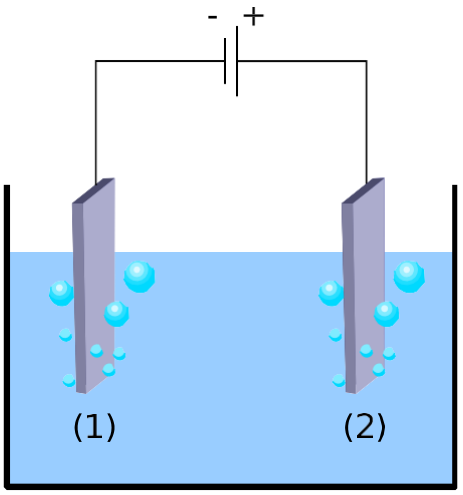


Fig. 1. Water-splitting electrochemical cell.

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

2.4 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.

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.

2.5 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.

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

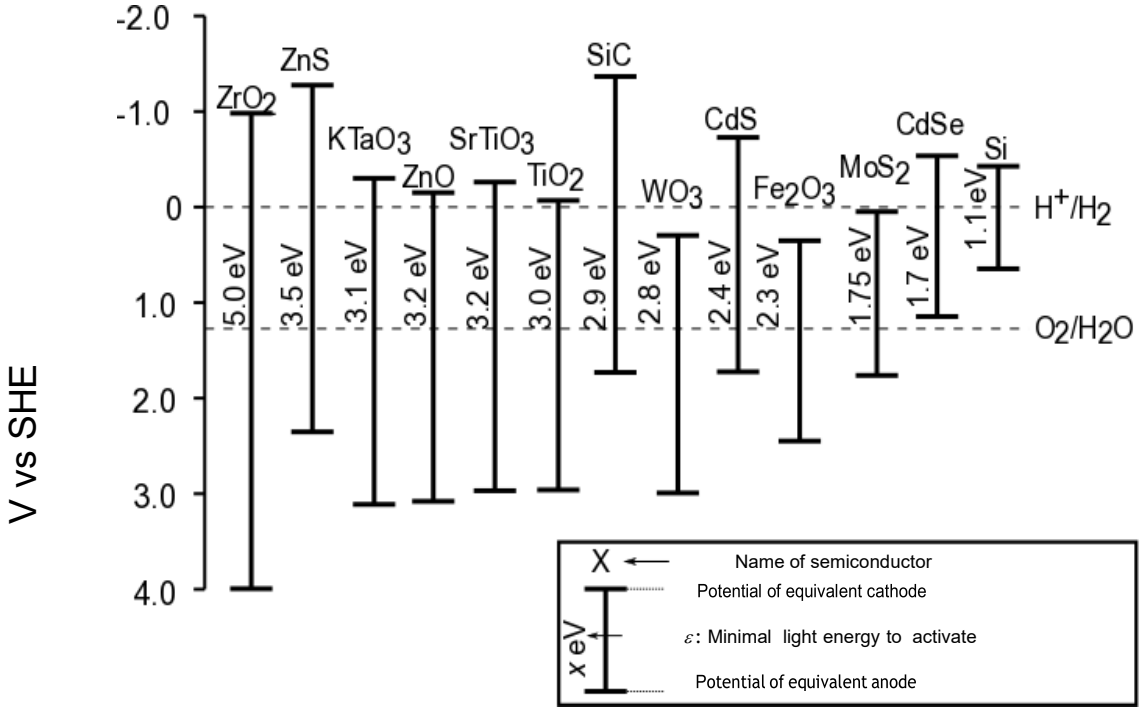


Fig. 2: Activation condition and equivalent electrode potentials of different semiconductors. Dashed lines correspond to water oxidation and reduction potentials. SHE = Standard Hydrogen Electrode

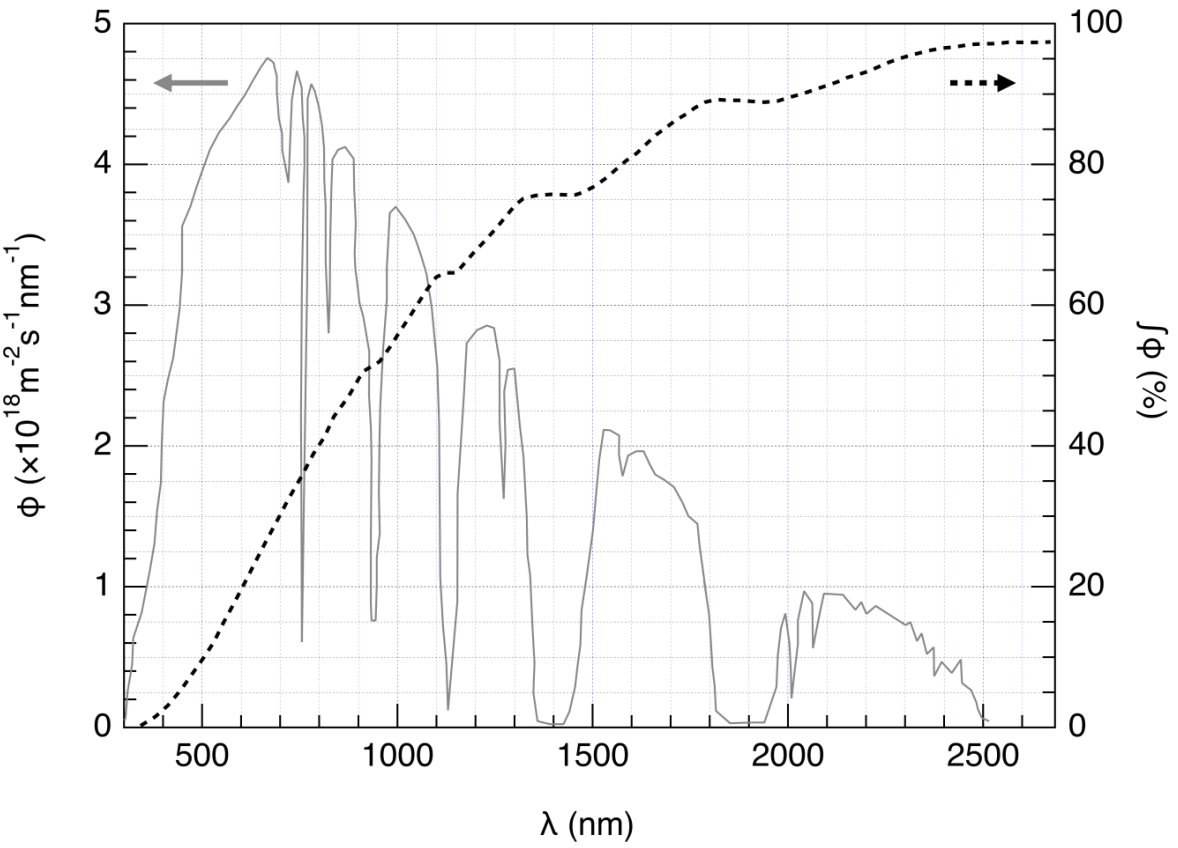


Fig. 3 – Left axis: Spectral distribution of the solar photon flux Φ. The photon flux is the number of photons per unit area per unit time arriving on the semiconductor.
Right axis and dashed line: cumulative photon flux (i.e. fraction of the photon flux with smaller wavelength).

2.6 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.

	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.

2.7 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.

2.8 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.

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.

2.9 Calculate the power efficiency η_{direct} of the conversion.

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 %.

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

SOLUTION OF THE PROBLEM 2

2.1 $H_2O(l) \rightarrow H_2(g) + ½\ O_2\ (g)$

2.2 Calculations:

$\Delta_r H° = 285.8\ kJ\ mol^{-1}$

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

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

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

Reaction thermodynamically favorable?

☐ Yes ☑ No

2.3 On electrode (1): $2\ H^+ + 2\ e^- \rightarrow H_2$

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

2.4 $\Delta E_{applied}$ must be > $E_{th} = \Delta_r G°/2F$

$\Delta E_{th} > \Delta_r G° / 2F = 237.1 \times 10^3 / (2 \times 96485)$

☐ $\Delta E_{applied} = \Delta E_{th}$

☑ $\Delta E_{applied} > \Delta E_{th}$

☐ $\Delta E_{applied} < \Delta E_{th}$

where $\Delta E_{th} = 1.229$ V

2.5 $\eta_{elec} = P_{eff}/P_{applied} = \Delta E_{th}/\Delta E_{min}$

Power efficiency when a Pt and a Fe_2O_3 electrodes are used

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

Most efficient anode: IrO_x

2.6 Explanation / calculation:

$E(J) = hc / \lambda$ so $E(eV) = hc / \lambda e$

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

TiO_2: $\lambda = 1240/3.0 = 413$ nm

CdS: $\lambda = 1240/2.4 = 517$ nm

Si: $\lambda = 1240/1.1 = 1127$ nm

2.7 ☑ ZrO_2 ☑ ZnO ☑ TiO_2 ☐ WO_3

☑ CdS ☐ Fe_2O_3 ☐ CdSe ☐ Si

2.8 Correct answer: CdS

2.9 Calculation:

Energy received from light.

$E = P \times S \times \Delta t = 10^3 \times 3600 \times 16 \times 10^{-6} = 58$ J

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

$n(H_2) \times \Delta_r G° = 3.6$ J

Power efficiency $\eta_{direct} = 3.6 / 58 = 6.2$ %

$\eta_{direct} = 6.2$ %

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

2.10 Calculation:

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

Indirect photocatalysis: $\eta_{indirect} = 0.65 \times 0.20 = 13$ %

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

Indirect photo-electrolysis is the most efficient:

☐ $\eta_{direct} > \eta_{indirect}$

☐ $\eta_{direct} \approx \eta_{indirect}$

☑ $\eta_{direct} < \eta_{indirect}$

THEORETICAL PROBLEM 3

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."

3.1 **Quote A**: Write the balanced chemical equation of AgCl(s) synthesis.

3.2 **Quote B**: Calculate the solubility *s* of AgCl(s) in water at 298 K in mol dm^{-3}.

3.3 **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.

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

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

3.5 Ammonia is added to 0.1 mol of silver chloride in 1 dm^3 of water until the last grain of solid disappears. At this moment, $[NH_3]$ = 1.78 mol dm^{-3}. Determine the stoichiometry of the complex neglecting dilution effects.

3.6 Write the balanced chemical equation corresponding to quote E.

3.7 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.

Part B: The Mohr method

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

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

3.9 Identify the solids.

3.10 Calculate the unknown concentration $c(Cl^-)$ of chloride ions in the sodium chloride solution.

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

3.12 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.

SOLUTION OF THE PROBLEM 3

3.1 $Ag^+(aq) + Cl^-(aq) \leftrightarrows AgCl(s)$

Any balanced equation involving also $NO_3^-(aq)$ or $H_3O^+(aq)$ or $H^+(aq)$ will also be accepted.

3.2 $AgCl(s) = \underset{s}{Ag^+(aq)} + \underset{s}{Cl^-(aq)}$

Thus: $[Ag^+] = [Cl^-] = s$

$K_{s1} = s^2$

$s = \sqrt{K_{s1}} = \sqrt{10^{-pK_{s1}}} = \sqrt{10^{-9.7}}$

$s = 1.41 \times 10^{-5}$

3.3

3.4 $AgCl(s) + n\ NH_3(aq) = [Ag(NH_3)_n]^+(aq) + Cl^-(aq)$

Calculation:

$AgCl(s) = Ag^+(aq) + Cl^-(aq)$ $\quad K_{s1}$

$Ag^+(aq) + n\ NH_3(aq) = [Ag(NH_3)_n]^+(aq)$ $\quad \beta_n$

$AgCl(s) + n\ NH_3(aq) = [Ag(NH_3)_n]^+(aq) + Cl^-(aq)$

$K = K_{s1}\ \beta_n$

$K = 10^{-9.7\ +\ 7.2} = 10^{-2.5}$

$= 3.16 \times 10^{-3}$

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

3.5 Last grain of solid: $[Ag(NH_3)_n^+] = [Cl^-] = 0.1$; $[NH_3] = 1.78$

$$K^o = \frac{[Ag(NH_3)_n^+]\,[Cl^-]}{[NH_3]^n}$$

Thus $n = \dfrac{\log \dfrac{[Ag(NH_3)_n{}^+]\,[Cl^-]}{K^o}}{\log [NH_3]}$

$n = 2$

(If $K = 10^{-3}$ is used, then $n = 4$.)

3.6 $[Ag(NH_3)_2]^+(aq) + 2\ H^+(aq) + Cl^-(aq) = AgCl(s) + 2\ NH_4^+(aq)$

3.7 $O_2(aq) + 2\ H_2O(l) + 4\ e^- = 4\ OH^-(aq)$ (reduction of O_2)

$Ag(s) + Cl^-(aq) = AgCl(s) + e^- = 4\ OH^-$ (oxidation of Ag_2)

- -

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

Calculation:

First possibility:

$K = 10^{\frac{4}{0.06}\left[E^{\circ}(O_2/HO^-) - E^{o}(AgCl/Ag)\right]}$

At the equilibrium all potentials are equal and thus:

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

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

Thus: $E^o(AgCl/Ag) = E^o(Ag^+/Ag) + 0.06 \log K_{s1} = 0.22$ V

$K = 10^{\frac{4}{0.059}(0.75 - 0.22)} = 2.93 \times 10^{35}$

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

Or the second possibility:

$K = (1/K_{s1})^4 \times 10^{\frac{4}{0.06}(0.75 - 0.80)}$

$K = 2.93 \times 10^{35}$

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

3.8 $Ag^+(aq) + Cl^-(aq) = AgCl(s)$

$K^o{}_1 = \dfrac{1}{K_{s1}} = 10^{9.7}$

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

$K^o{}_2 = \dfrac{1}{K_{s2}} = 10^{12}$

3.9 Solid A: AgCl(s)

Solid B: $Ag_2CrO_4(s)$

3.10 At $V_{Ag} = 4.3\ cm^3$, $n_{Ag+,\ added} = n_{Cl^-,\ introduced}$

Thus: $c_{Cl^-} \times 20 = 0.05 \times V_{Ag}$ and $c_{Cl^-} = 0.011\ mol\ dm^{-3}$

3.11 AgCl(s) precipitates as soon as: $K_{s1} = Q_{r,eq} = [Ag^+]\,[Cl^-]$

And $[Cl^-] = c_{Cl} \dfrac{20}{20.5 + V_{Ag}(min)} \approx c_{Cl}$

$$[Ag^+] = \frac{K_{s1}}{[Cl^-]} = \frac{0.05 \times V_{Ag}(min)}{20.5 + V_{Ag}(min)} \approx \frac{0.05 \times V_{Ag}(min)}{20.5} \text{ so } V_{Ag}(min) = \frac{20.5 \times K_{s1}}{0.05 \times [Cl^-]}$$

$V_{Ag}(min) = 8.2 \times 10^{-6}\ cm^3$ with $c_{Cl} = 0.010\ mol\ dm^{-3}$

$V_{Ag}(min) = 7.4 \times 10^{-6}\ cm^3$ with $c_{Cl} = 0.011\ mol\ dm^{-3}$

3.12 Ag_2CrO_4 precipitates as soon as $K_{s2} = [Ag^+]^2[CrO_4^{2-}]$

At this moment:

$$[CrO_4^{2-}] = \frac{7.76 \times 10^{-3} \times 0.5}{20.5 + V_{Ag}} = 1.56 \times 10^{-4}\ mol\ dm^{-3}$$

So: $[Ag^+] = \sqrt{\dfrac{K_{s2}}{[CrO_4^{2-}]}} = 8.00 \times 10^{-5}\ mol\ dm^{-3}$

So: $[Cl^-]_{residual} = \dfrac{K_{s1}}{[Ag^+]}$

$[Cl^-]_{res} = 2.49 \times 10^{-6}\ mol\ dm^{-3}$

CrO_4^{2-} is a good titration endpoint indicator because:

$[Cl^-]_{residual} \ll c$

THEORETICAL PROBLEM 4

From gunpowder to the discovery of iodine

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

4.1 Find the formulas of nitrates **A** and **B** knowing that they are anhydrous salts of alkaline or alkaline-earth metal (M_A and 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 M_A and M_B in the samples is 38.4 w% and 22.4 w%, respectively. Support your answer with calculations.

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 dm^3 at 0 °C and 1 atm (dioxygen can be considered as an ideal gas).

4.2 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.

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

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, the iodine is prepared from the set of reactants (NO_3^-, I^-, H^+) (4) or (IO_3^-, I^-, H^+) (5).

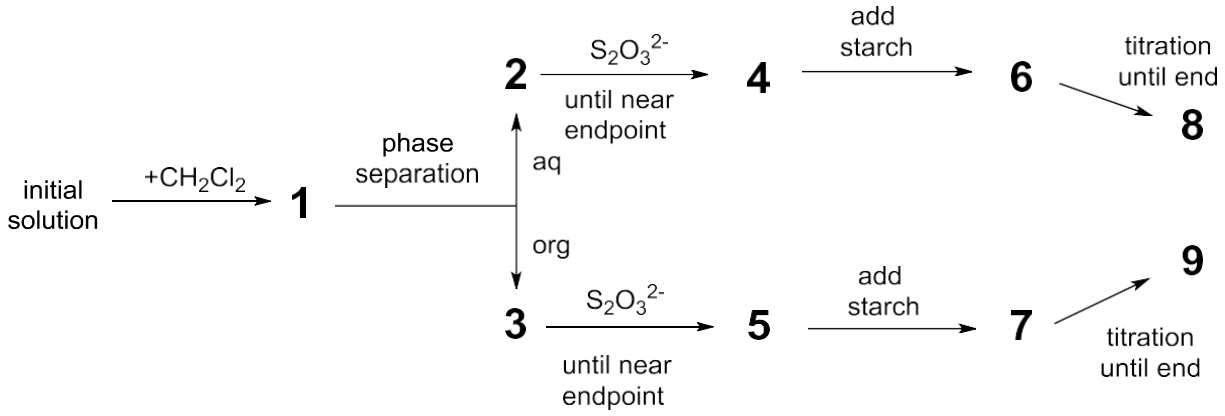
4.4 Write balanced equations for reactions 1 – 5.

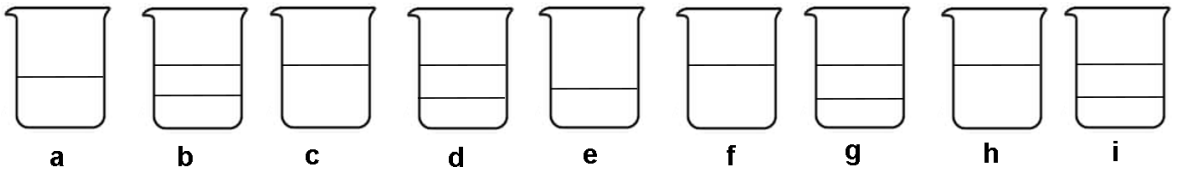
The solubility of iodine is very low in water but significantly increases when iodide ions are added. Together they form ions such as triiodide, I_3^-:

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

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 cm^3 of an aqueous solution of potassium iodide (0.1112 g). Then, 50.0 cm^3 of dichloromethane were added, and the mixture was vigorously shaken until equilibration. After phase separation, each phase was titrated by 16.20 cm^3 (organic phase) and by 8.00 cm^3 (aqueous phase) of the standard aqueous solution of sodium thiosulphate pentahydrate (14.9080 g in 1.000 dm^3 of solution) in the presence of starch. The process is schematically represented below:





a	b	c	d	e	f	g	h	i
Brown	Blue / Pink	Dark blue	Brown / Dark	Dark purple	Colourless	Yellowish / Pink	Yellowish	Colourless / Colourless

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

Stages	Picture
1	
2	
3	
4	
5	
6	
7	
8	
9	

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

4.7 Calculate the mass of iodine used to prepare the initial solution.

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

SOLUTION OF THE PROBLEM 4

4.1 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.

$$w(\mathrm{M}_x) = \frac{M(\mathrm{M}_x)}{M(\mathrm{M}_x\mathrm{NO}_3)}\ 100\ \% \quad \Rightarrow \quad M(\mathrm{M}_x\mathrm{NO}_3) = \frac{M(\mathrm{M}_x)}{w(\mathrm{M}_x)}\ 100\ \% = \frac{M(\mathrm{NO}_3^-)}{100\ -\ w(\mathrm{M}_x)}\ 100\ \%$$

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

In **A**:

$$M(\mathrm{M}_A) = M(\mathrm{M}_A(\mathrm{NO}_3)_m) - m\ M(\mathrm{NO}_3^-) = \frac{62\ m}{1\ -\ 0.384} - 62\ m = 38.65\ m\ \mathrm{g\ mol^{-1}}$$

In **B**:

$$M(\mathrm{M}_B) = M(\mathrm{M}_B(\mathrm{NO}_3)_n) - n\ M(\mathrm{NO}_3^-) = \frac{62\ n}{1\ -\ 0.224} - 62\ n = 17.9\ n\ \mathrm{g\ mol^{-1}}$$

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 M_B in B is between

$$M(\mathrm{M}_B) = M(\mathrm{M}_B(\mathrm{NO}_3)_n) - n\ M(\mathrm{NO}_3^-) = \frac{62\ n}{1\ -\ 0.238} - 62\ n = 19.36\ n\ \ \mathrm{g\ mol^{-1}}$$

And

$$M(\mathrm{M}_B) = M(\mathrm{M}_B(\mathrm{NO}_3)_n) - n\ M(\mathrm{NO}_3^-) = \frac{62\ n}{1\ -\ 0.255} - 62\ n = 21.22\ n\ \ \mathrm{g\ mol^{-1}}$$

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

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

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

4.2 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.

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

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

$2\ KNO_3 = 2\ KNO_2 + O_2$

Now we can calculate the amount of O_2:

$pV = n(O_2)\ RT$

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

[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.

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

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 %.

4.3 We can write the reaction of KNO_3 formation as:

$Ca(NO_3)_2 + K_xX \rightarrow 2\ KNO_3 + CaX_{2/x}(s)$.

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.

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

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

The molar mass of Ca is 40 g mol^{-1}, thus the molar mass of (X^{x-}) × (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).

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

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

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

4.4 1. $2\ HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2\ H_2O$

(any chemically reasonable redox equation involving I_2 will be accepted)

2. $2\ Cu + I_2 \rightarrow 2\ CuI$

3. $2\ I^- + Cl_2 \rightarrow 2\ Cl^- + I_2$

4. $2\ NO_3^- + 6\ I^- + 8\ H^+ \rightarrow 3\ I_2 + 2\ NO + 4\ H_2O$

   or $2\ NO_3^- + 2\ I^- + 4\ H^+ \rightarrow I_2 + 2\ NO_2 + 2\ H_2O$

5. $IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$

4.5

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

4.6 $2\ Na_2S_2O_3 + I_2 = 2\ NaI + Na_2S_4O_6$

$2\ Na_2S_2O_3 + I_3^- = 2\ NaI + I^- + Na_2S_4O_6$

4.7

$$c(Na_2S_2O_3) = \frac{n(Na_2S_2O_3)}{V} = \frac{m(Na_2S_2O_3)}{M(Na_2S_2O_3) \times V} = \frac{14.908}{248.18 \times 1} = 0.060\ \text{mol dm}^{-3}$$

$$m(I_2) = M(I_2)\, n(I_2) = M(I_2) \times \left(\frac{V_1 + V_2}{1000}\right) \times \frac{c(Na_2S_2O_3)}{2} = 254 \times \left(\frac{16.2 + 8.0}{1000}\right) \times \frac{0.06}{2}$$

$m(I_2) = 0.184$ g

4.8 For the organic phase:

$n(Na_2S_2O_3) = c(Na_2S_2O_3)\, V = 0.06 \times 16.20 \times 10^{-3} = 9.72 \times 10^{-4}$ mol

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

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

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

For aqueous phase:

$n(I_2)_{aq} + n(I_3^-)_{aq} = ½\, n(Na_2S_2O_3)_{aq}$

$n(Na_2S_2O_3)_{aq} = c(Na_2S_2O_3).V = 0.06 \times 8.00 \times 10^{-3} = 4.8 \times 10^{-4}$ mol

$n(I_2)_{aq} + n(I_3^-)_{aq} = ½\, c(Na_2S_2O_3)_{aq} . V = ½\, 0.06 \times 8.00 \times 10^{-3} = 2.4 \times 10^{-4}$ mol

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

We can calculate the initial amount of substance of KI. This amount is equal to the total amount of substance of iodide and triiodide in the aqueous solution:

$$n(I^-)_{aq} + n(I_3^-)_{aq} = n(KI) = \frac{m}{M} = \frac{0.1112 \text{ g}}{166 \text{ g mol}^{-1}} = 6.7 \times 10^{-4} \text{ mol}$$

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

The equilibrium constant is:

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

THEORETICAL PROBLEM 5

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.

5.1 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}).

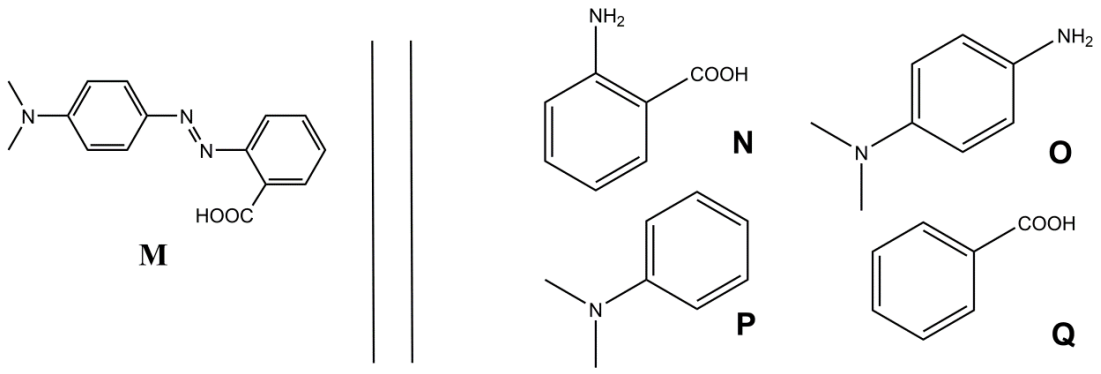


Fig. 1. Possible reactants for the synthesis of M.

5.2 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.

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.

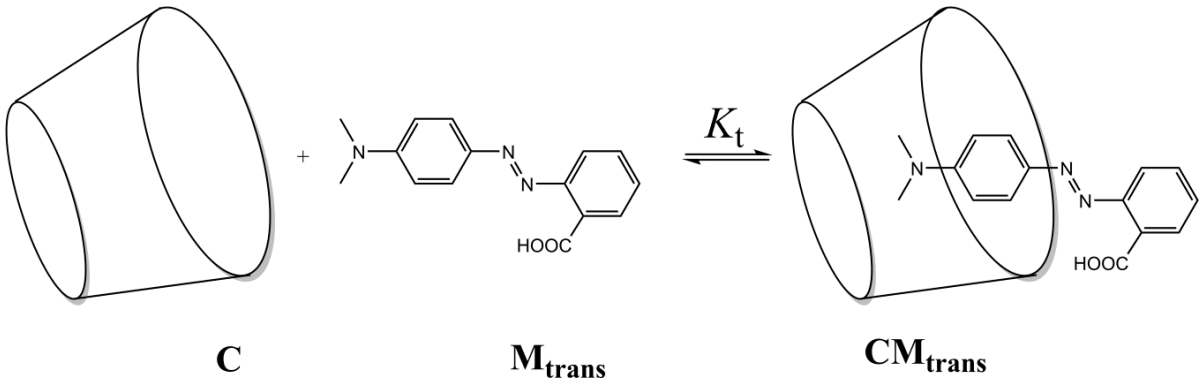


Fig. 2 – Formation of the CM_{trans} inclusion complex.

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.

5.3 Demonstrate that $\Delta A = \alpha\,[\mathbf{CM_{trans}}]$ and express α in terms of known constant(s).

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

5.5 Demonstrate that in case when C is in a large excess with respect to $\mathbf{M_{trans}}$, (*i.e.* $[\mathbf{C}]_o \gg [\mathbf{M_{trans}}]_o$),

$$\Delta A = \alpha \frac{\beta[C]_o}{1 + K_t[C]_o}$$

and express β in terms of constant(s) and initial concentration(s).

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

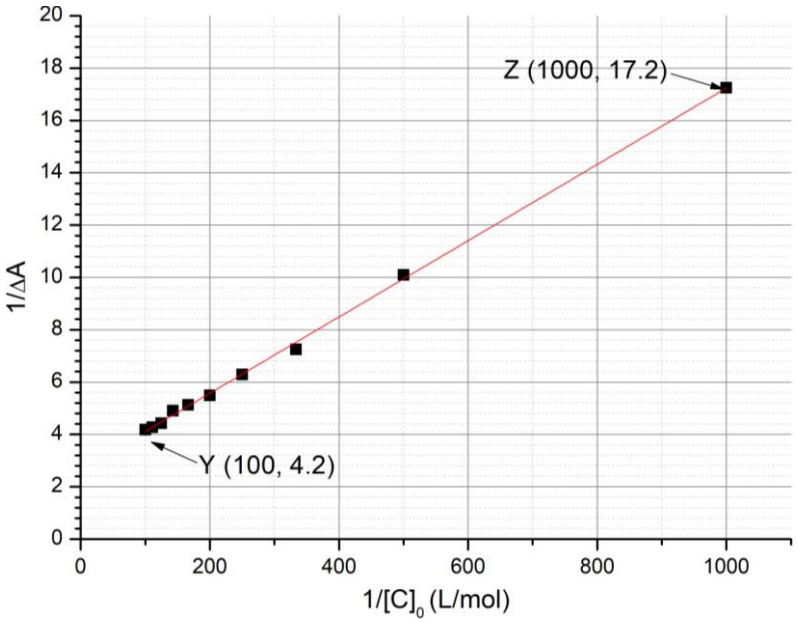


Fig. 3 – Evolution of $1/\Delta A$ as a function of $1/[C]_0$.

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.

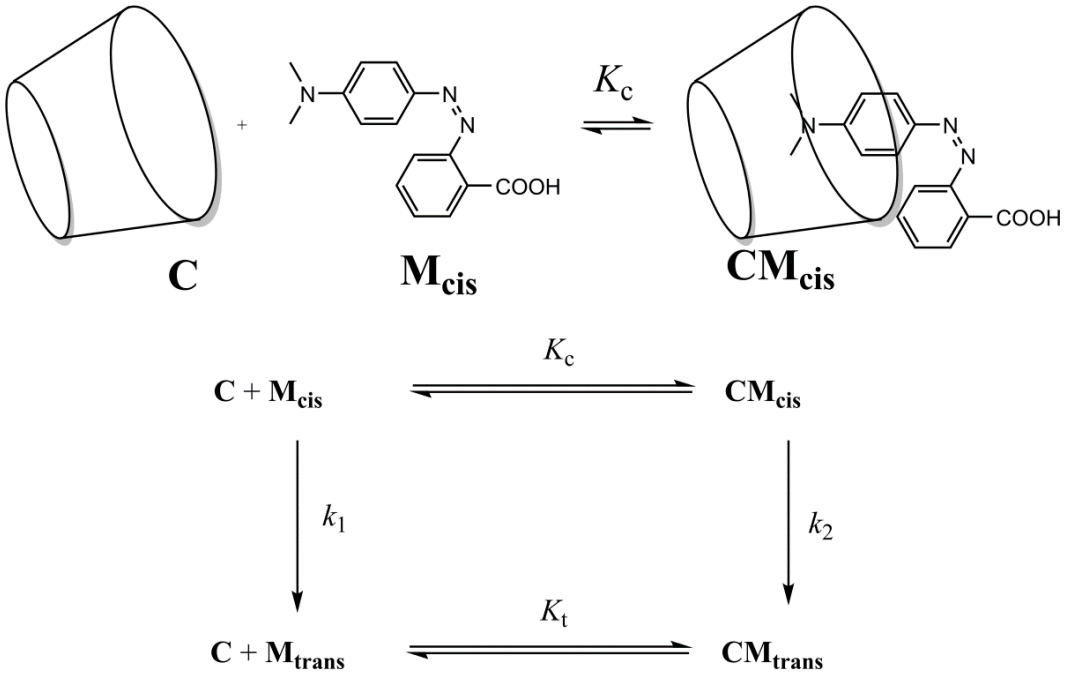


Fig. 4 – Kinetic scheme for the isomerization of M_{cis} in the presence of **C**.

The rate of disappearance r for the total amount of M_{cis} (free and complexed) is defined as

$$r = k_1[\mathbf{M_{cis}}] + k_2[\mathbf{C\ M_{cis}}]$$

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

$$r = k_{obs}([\mathbf{M_{cis}}] + [\mathbf{CM_{cis}}])$$

5.7 Demonstrate that

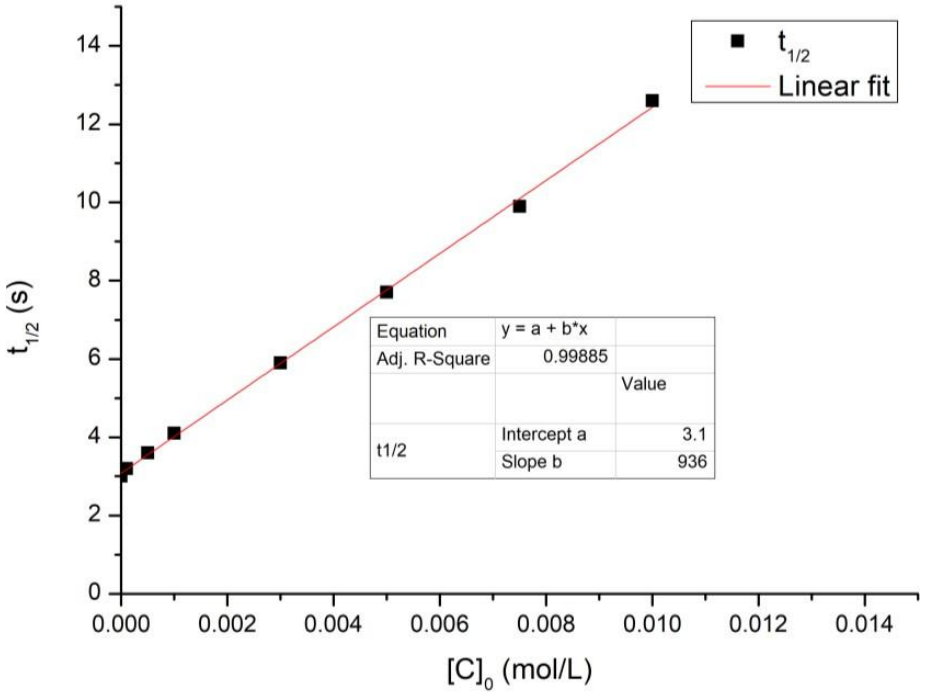
$$k_{obs} = \frac{\gamma + \delta\, k_2[C]}{1 + K_c[C]}$$

and express γ and δ in terms of known constant(s).

5.8 Choose in which condition(s) the half-life $t_{1/2}$ corresponding to k_{obs} can be expressed as $t_{½} = \ln(2 / \gamma)(1 + K_c[\mathbf{C}]_o)$ given that $[\mathbf{C}]_o >> [\mathbf{M_{cis}}]_0$. Mathematically justify your answer.

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

$[C]_0$ (mol dm^{-3})	$t_{1/2}$ (s)	$[C]_0$ (mol dm^{-3})	$t_{1/2}$ (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



Formation of nanomachines

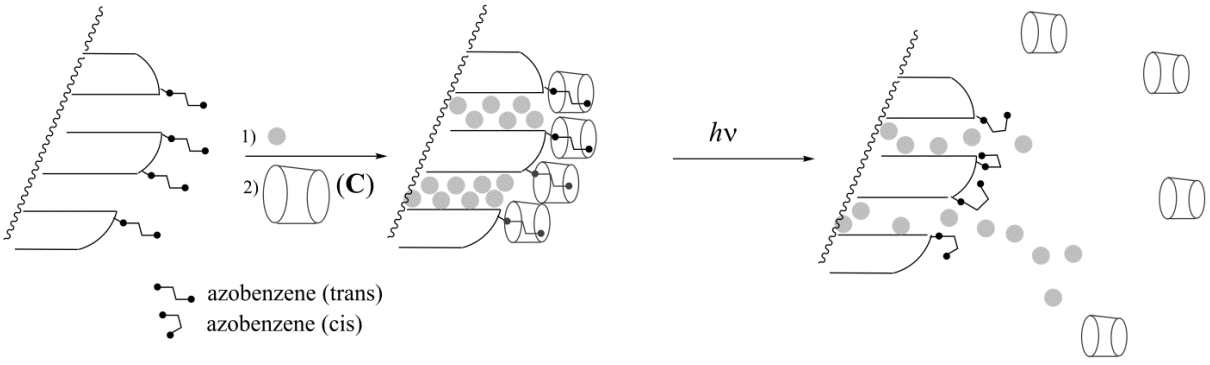


Fig. 5 – Cleavage of an azobenzene–cyclodextrin inclusion complex induced by a light-triggered isomerization, which allows delivery of a dye (grey circles).

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.

5.10 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. 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.

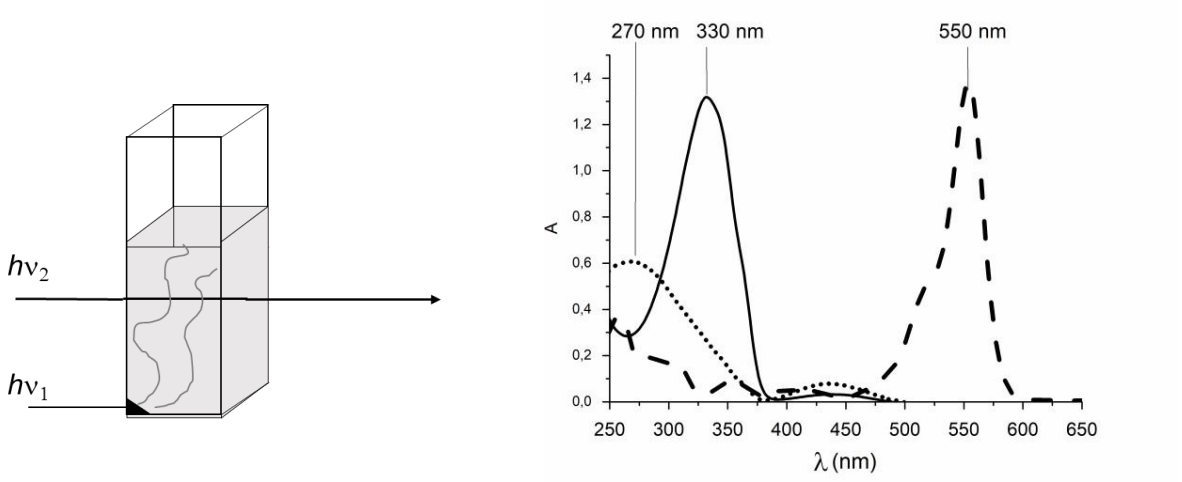


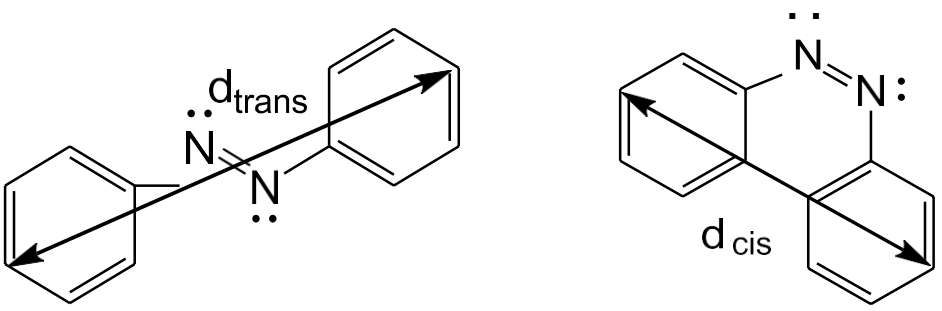
Fig. 6 – Left: experimental setup used to monitor the release of the dye;
right: absorption spectra of trans-azobenzene (full line), cis-azobenzene (dotted line) and rhodamine B (dashed line).

5.11 Determine λ_1.

5.12 Determine λ_2.

SOLUTION OF THE PROBLEM 5

5.1



..

trans cis

$d_{trans} > d_{cis}$

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

5.2 Reactants: N and P

5.3 Demonstration:

$\Delta A = A(\mathbf{C\ M_{trans}}) + A(\mathbf{M_{trans}}) - A(\text{pure } \mathbf{M_{trans}} \text{ solutions})$:

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

As $[\mathbf{M_{trans}}]_0 = [\mathbf{C\ M_{trans}}] + [\mathbf{M_{trans}}]$

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

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

$\alpha = L\ (\varepsilon_{\mathbf{CMtrans}} - \varepsilon_{\mathbf{Mtrans}})$

5.4 $[\mathbf{C}] = [\mathbf{C}]_0 - [\mathbf{C\ M_{trans}}]$

$[\mathbf{CM_{trans}}] < [\mathbf{M_{trans}}]_0$, << $[\mathbf{C}]_0$, thus $[\mathbf{C}] \simeq [\mathbf{C}]_0$

5.5

$$K_t = \frac{[\mathbf{C}\ M_{trans}]}{[M_{trans}]\,[\mathbf{C}]} \quad \text{or} \quad K_1 = \frac{[\mathbf{C}\ M_{trans}]\,c_0}{[M_{trans}]\,[\mathbf{C}]}$$

$[\mathbf{M_{trans}}]_0 = [\mathbf{C\ M_{trans}}] + [\mathbf{M_{trans}}]$

$$\text{So } [\mathbf{M}_{trans}]_o = [\mathbf{CM}_{trans}]\left(1 + \frac{1}{K_t\,[C]}\right)$$

$$\text{So } [\mathbf{CM}_{trans}] = [\mathbf{M}_{trans}]_o \frac{K_t\,[C]_o}{1 + K_t[C]_o}$$

$$As\,[\mathbf{C}] \cong [\mathbf{C}]_o\,, \quad [\mathbf{CM_{trans}}] = [\mathbf{M}_{trans}]_o \frac{K_t\,[C]_o}{1 + K_t[C]_o}$$

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

$$\beta = K_1\,[\mathbf{M_{trans}}]_o$$

5.6

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

$$K_t = \frac{intercept}{slope}$$

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

$$\frac{1}{\Delta A} = 0.0144\left(\frac{1}{[C]_o}\right) + 2.76$$

(within $\pm$ 10 % for slope and intercept, no unit needed)

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

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

$$K_t = \frac{1000 \times 4.2 - 100 \times 17.2}{17.2 - 4.2} = 191$$

5.7

$$k_{obs}\left([\mathbf{M}_{\text{cis}}]\right) + [\mathbf{CM}_{\text{cis}}]\ ) = k_1\,[\mathbf{M}_{\text{cis}}] + k_2[\mathbf{CM}_{\text{cis}}]$$

$$\text{and } K_c \frac{[\mathbf{CM}_{\text{cis}}]}{[\mathbf{M}_{\text{cis}}]\,[\mathbf{C}]}$$

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

$$\text{Thus } k_{obs}\left([\mathbf{M}_{\text{cis}}]\right) + K_c\,[\mathbf{C}]\,[\mathbf{M}_{\text{cis}}] = k_1\,[\mathbf{M}_{\text{cis}}] + k_2 K_c[\mathbf{C}]\,[\mathbf{M}_{\text{cis}}]$$

which can be written as:

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

$\gamma = k_1$ and $\delta = K_c$

5.8 Correct: ☑ Very slow isomerization of M_{cis} within cyclodextrin.

Demonstration:

We need

$k_{obs} \cong \frac{\gamma}{1 + K_c[C]}$ so $\gamma \gg k_2[C]_o$ and thus $k_2 \cong 0$: slow isomerization

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

$$t_{½} = \frac{\ln 2}{\gamma}(1 + K_c[\mathbf{C}]_o) = 3.1 + 936\,[\mathbf{C}]_o$$

$$K_c = \frac{slope}{intercept}$$

$K_c = 302$

5.10 Answer: ☑ $K_1 \gg 1$ and $K_c \ll 1$

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

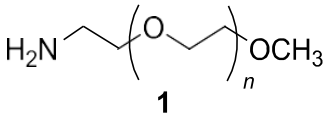
5.12 λ_2 = 550 nm (the release of the dye into solution is monitored)

THEORETICAL PROBLEM 6

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



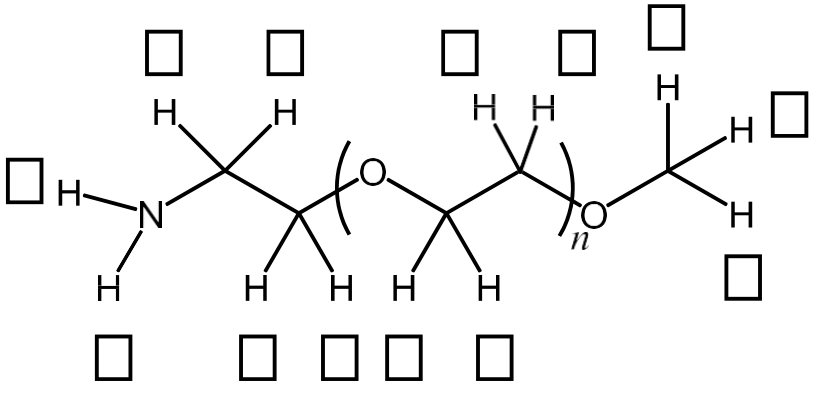
1

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.*

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

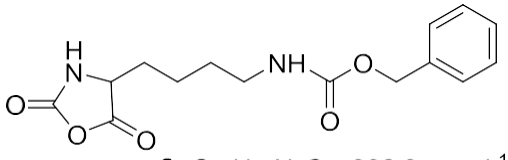


6.2 Express the average degree of polymerization *n* as a function of the area A_{OC2H4} of the NMR peak of the repeating unit and the area A_{OCH3} of the NMR peak of the methyl end group. Calculate *n*.

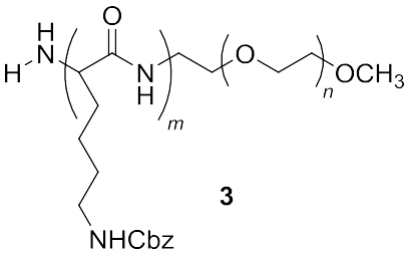
Study of a diblock-copolymer

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

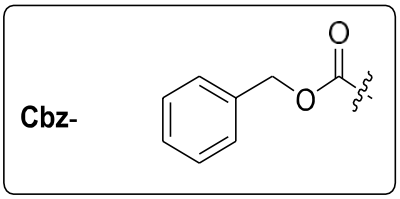
This yields the block-copolymer 3.



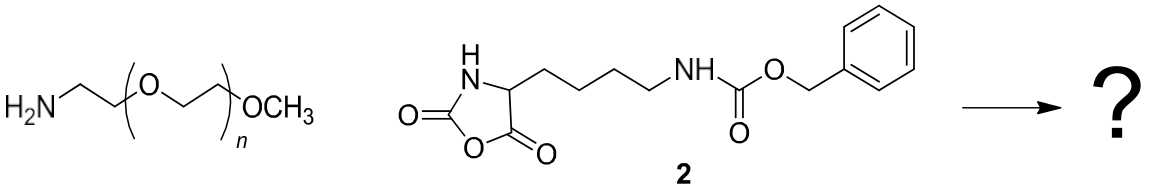
2: $C_{15}H_{18}N_2O_5$, 306.3 g mol^{-1}



3

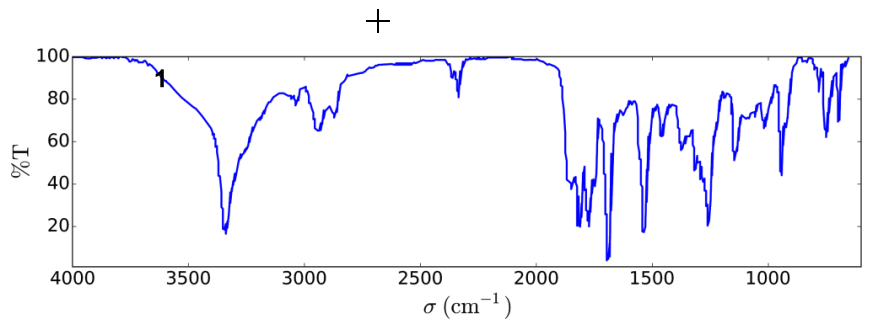


6.3 Draw the reaction intermediate that is formed in the first step of the addition of 1 to 2. The second step of the mechanism leads to the formation of a gas molecule, **G**. Draw its structure.



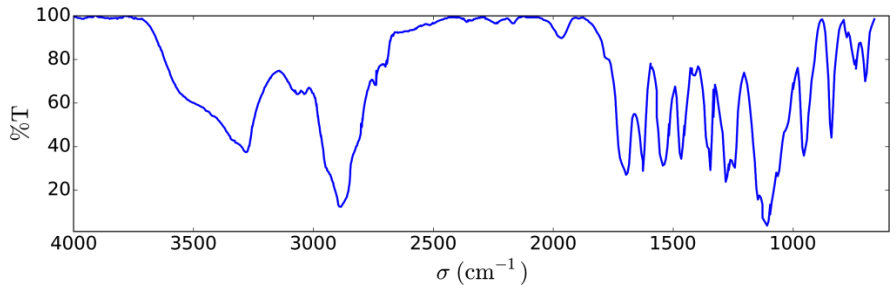
1 **2**

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



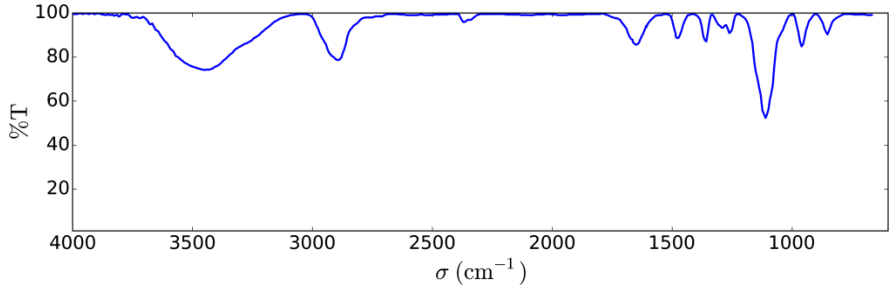
Compound

☐ 1 ☐ 2 ☐ 3



Compound

☐ 1 ☐ 2 ☐ 3



Compound

☐ 1 ☐ 2 ☐ 3

6.5 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 …).

Table 2

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

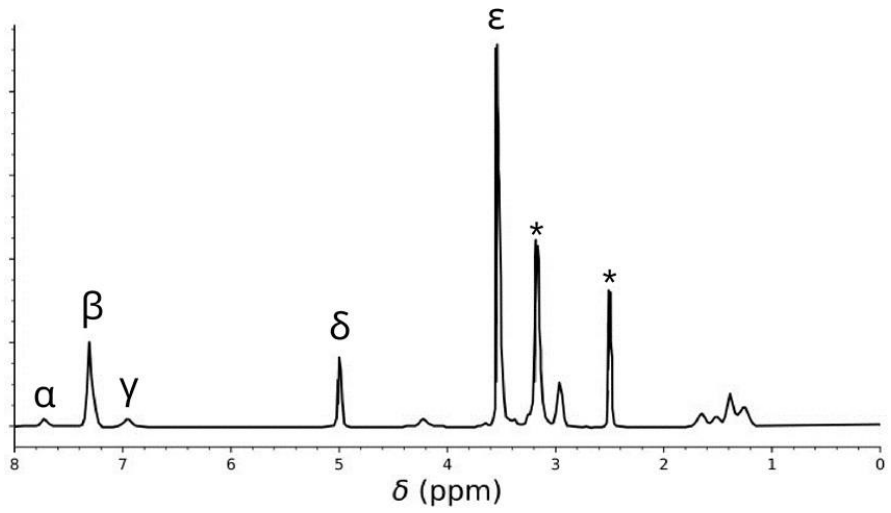


Fig. 1 – signals marked with * correspond to the solvent and water.

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.

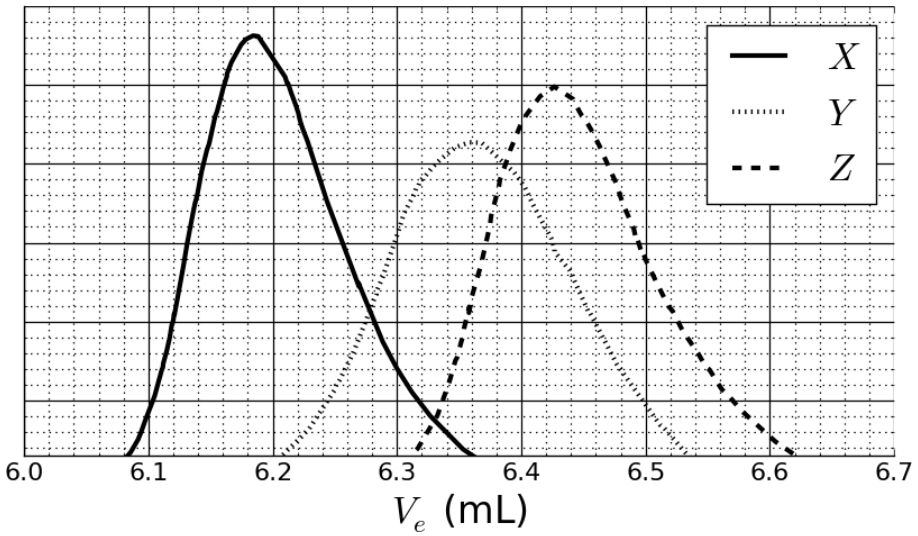


Fig. 2 – SEC chromatograms of 3a, 3b and 3c as a function of the elution volume, V_e.

6.6 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

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.

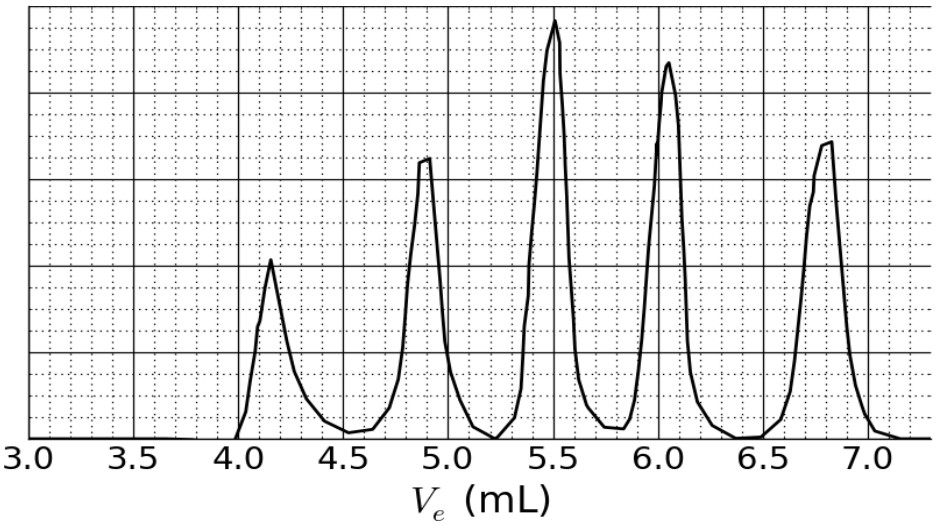
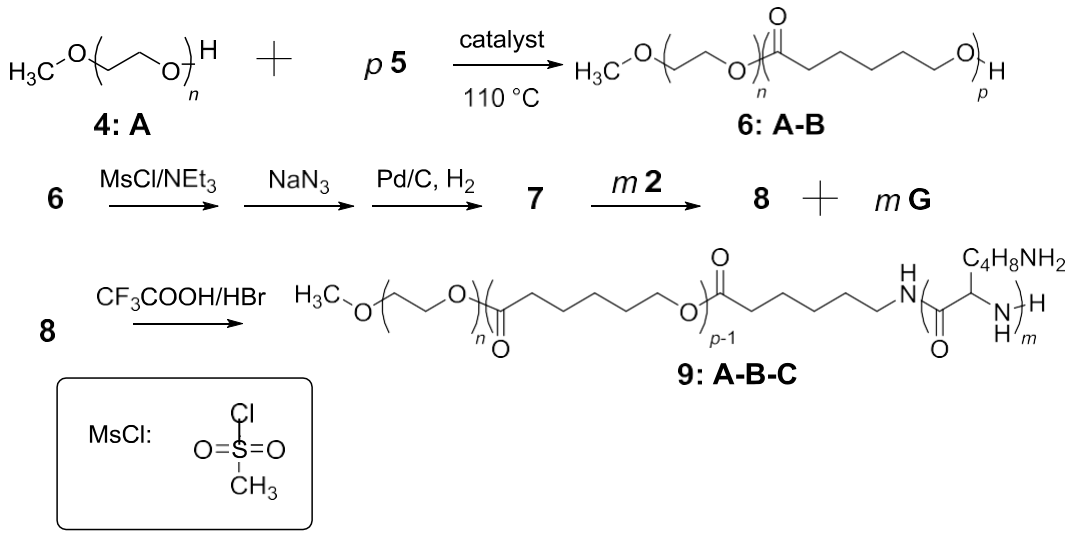


Fig. 3 – SEC chromatogram of the mixture of standards.

6.7 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.

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.

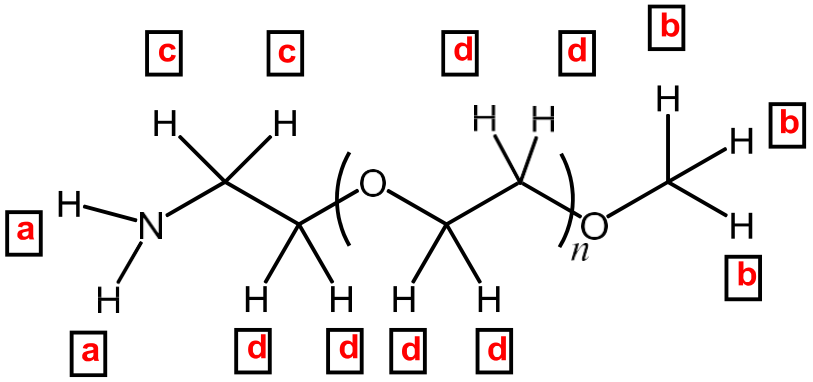


6.8 Draw the structures of 5, 7 and 8.

6.9 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.

SOLUTION OF THE PROBLEM 6

6.1



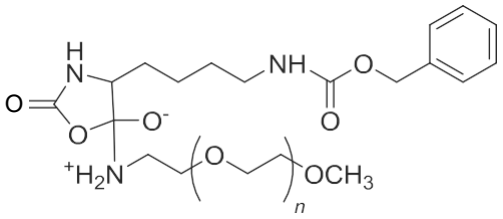
6.2

$n = (A_{OC2H4} / 4) / (A_{OCH3} / 3)$ $A_{OC2H4} = A_d - 0.6$

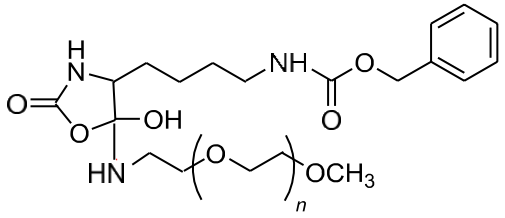
$$n = \frac{133.1 \times 3}{0.9 \times 4} = 111$$

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

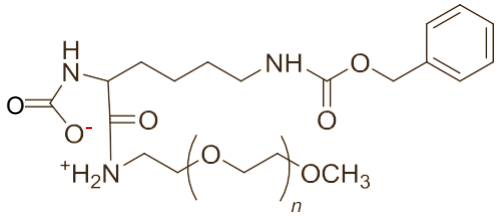
6.3



or



or



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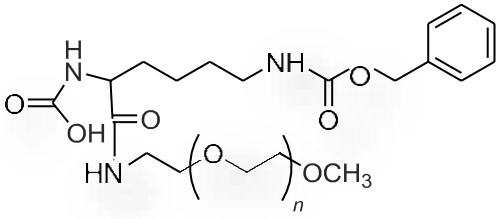


X = CO_2

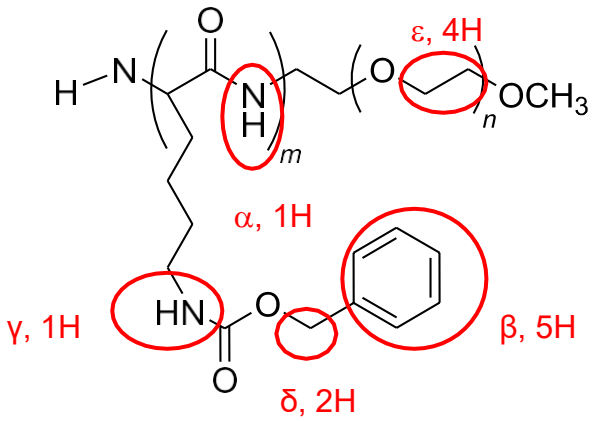
6.4

3a: ☐ X ☑ Y ☐ Z

3b: ☐ X ☐ Y ☑ Z

3c: ☑ X ☐ Y ☐ Z

6.5



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).

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

Calculation of *m*:

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

Calculation of M_n:

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}

6.6

3a: ☐ X ☐ Y ☑ Z

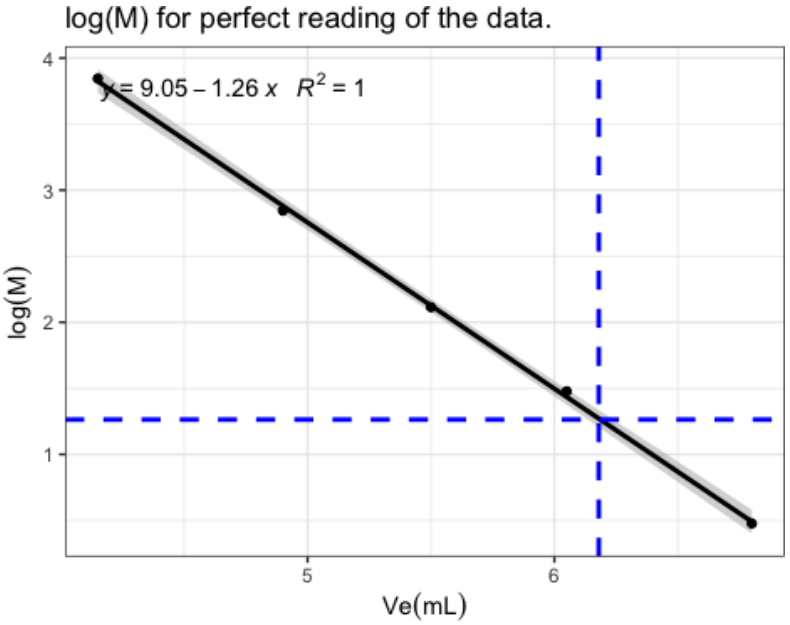
3b: ☐ X ☑ Y ☐ Z

3c: ☑ X ☐ Y ☐ Z

6.7 $V_e =$ cm^3

The elution volume $V_e(X)$ has a peak at 6.18 cm^3

Determination of a function such as log M or ln $M = a \times V_e$ (cm^3) + b either graphically or numerically.



log(M)= 9.05 – 1.26 × V_e (cm^3) or ln(M) = 9.05 – 1.26 × V_e (cm^3)

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.

Calculation of the molar mass, $M_n(X)$:

The use of the calibration allows to determine the value of $M_n(X)$:

log $M_n(X)$ = – 1.26 × 6.18 + 9.05

M_n = 18.3 kg mol^{-1}

Calculation of m from the molar mass:

m = ($M_n(X)$ – $M(1)$) / 262 = ($M_n(X)$ – 44 n – 75) / 262 (75 g mol^{-1} correspond to the end groups) or, for instance:

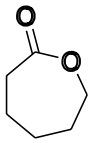
m = [18330 – 100 × 44 – 75] / 262 = 52 (for n = 100)

m = [18330 – 111 × 44 – 75] / 262 = 51 (for n = 111)

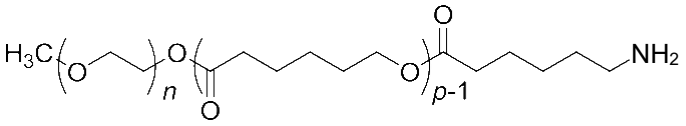
m = 51

6.8

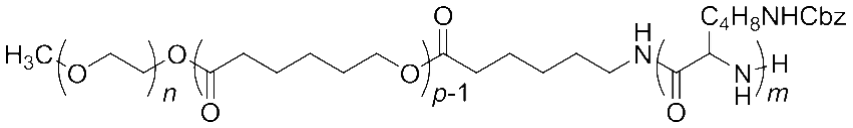
5 (no other products than **6** : A-B are obtained)



7 (a gas is formed in the final step)



8

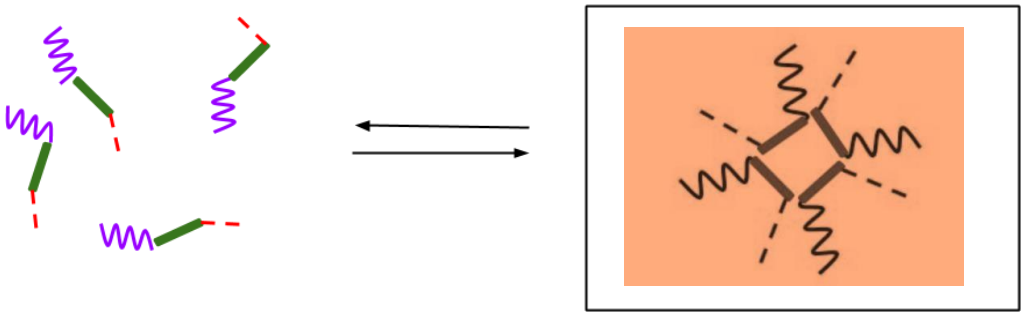


6.9

A: ☐ hydrophobic ☑ hydrophilic

B: ☑ hydrophobic ☐ hydrophilic

C: ☐ hydrophobic ☑ hydrophilic



THEORETICAL PROBLEM 7

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).

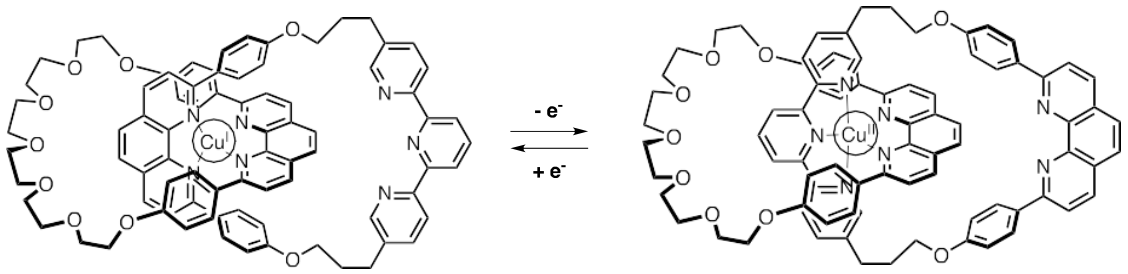
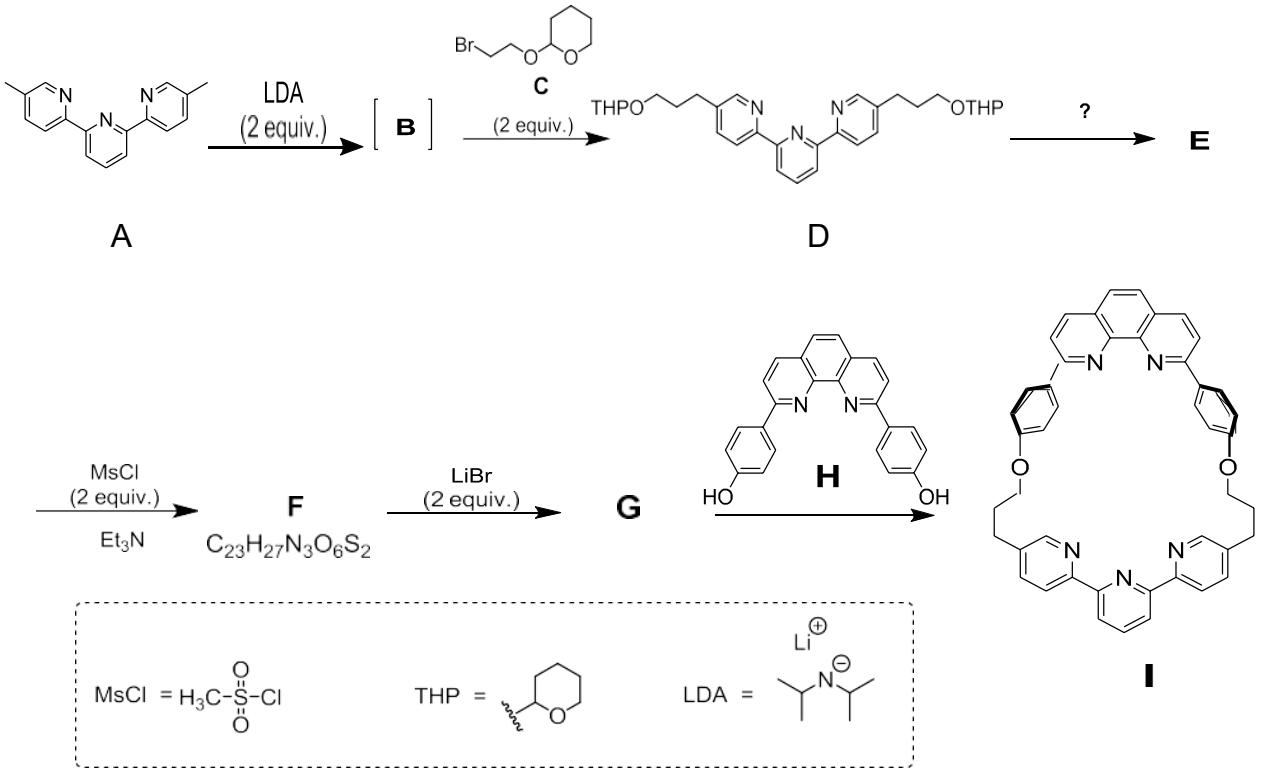


Fig. 1 – Multi-stability of a ring in a [2]catenane.

The synthesis of the macrocycle is the following:



7.1 Draw the structure of **B**.

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

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

- ☐ H^+, H_2O
- ☐ OH^-, H_2O
- ☐ $NaBH_4$, CH_3OH
- ☐ H_2, Pd/C, THF

Tick the relevant box.

7.4 In the synthetic strategy, MsCl is used to obtain:

- ☐ a leaving group
- ☐ a protecting group
- ☐ a deactivated group
- ☐ a directing group

Tick the relevant box.

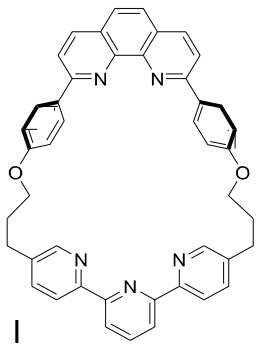
7.5 **G** is obtained by the reaction between **F** and LiBr in acetone. This reaction is:

- ☐ electrophilic aromatic substitution,
- ☐ nucleophilic aromatic substitution,
- ☐ S_N1
- ☐ S_N2

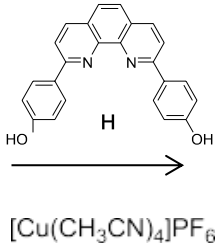
Tick the relevant boxes.

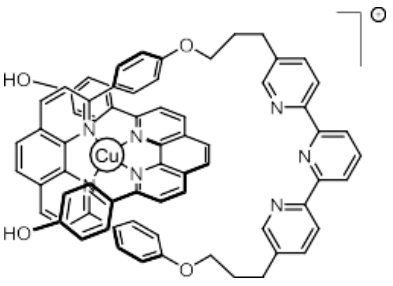
7.6 Draw the transition state of the rate-determining step of the reaction **F** → **G**, showing the 3D geometry. Depict only one reaction center. The main carbon chain can be represented as an R group.

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

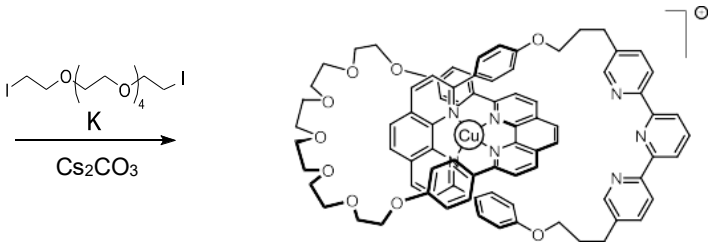


I





J



L

7.7 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**.

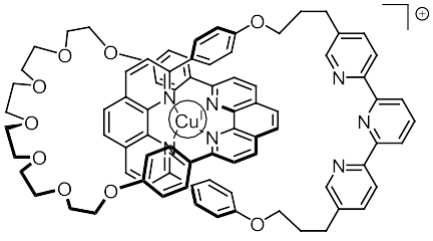
7.8 Select the geometry of the copper ion in **L**. Assuming an ideal geometry of the ligands around the copper center, draw the electronic levels of the d-orbitals in accord with the crystal field theory. Fill the orbital diagram. Give the maximum value of the spin (*S*) for this complex. The geometry of the Cu in **L** is:

- ☐ octahedral,
- ☐ tetrahedral,
- ☐ square planar,
- ☐ trigonal bipyramidal.

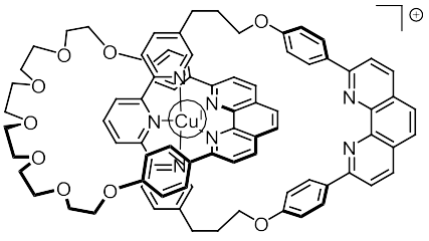
7.9 Out of the following compounds, choose the one(s) that can remove the copper ion in **L** to obtain the free [2]catenane (tick relevant boxes):

- ☐ CH_3CN
- ☐ NH_4PF_6
- ☐ KCN
- ☐ tren

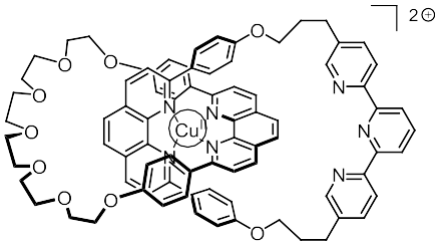
In [2]catenane L, the copper ion can exist in two oxidation states (+I) or (+II), and each of them exhibits a different coordination sphere (tetra- or penta-coordinated, respectively).



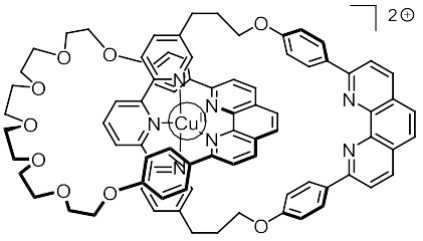
$Cu^{I}N_4$



$Cu^{I}N_5$



$Cu^{II}N_4$



$Cu^{II}N_5$

Fig. 2 – [2] catenate L states

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

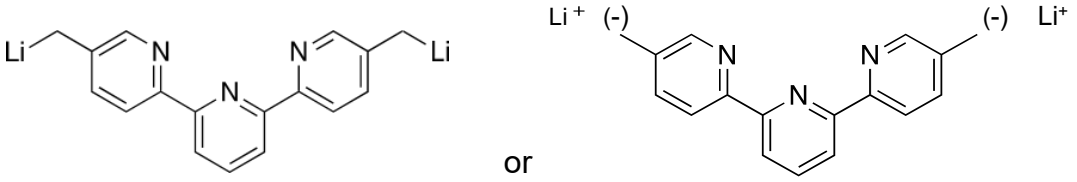
7.10 Fill in the blanks with a number or a tick:

- The $Cu^{I}N_4$ complex has ☐ (number) electrons in the coordination sphere of the metal.
- The $Cu^{I}N_5$ complex has ☐ (number) electrons in the coordination sphere of the metal.
- The $Cu^{I}N_4$ complex is (tick):
  - ☐ more stable than the $Cu^{I}N_5$ complex or
  - ☐ less stable than the $Cu^{I}N_5$ complex.

7.11 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^-.

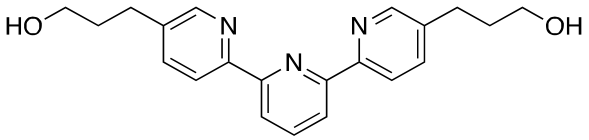
SOLUTION OF THE PROBLEM 7

7.1 The structure of **B**:

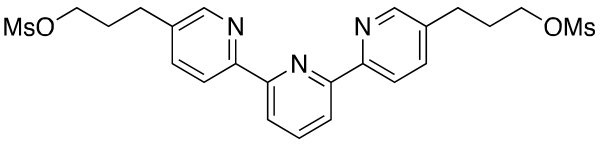


7.2 The structures of **E**, **F** and **G**:

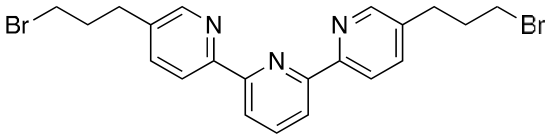
E



F



G



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

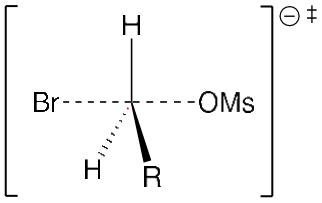
- ☑ H^+, H_2O
- ☐ OH^-, H_2O
- ☐ $NaBH_4$, CH_3OH
- ☐ H_2, Pd/C, THF

7.4 In the synthetic strategy, MsCl is used to obtain:

☑ a leaving group

7.5 ☑ S_N2

7.6 Transition state:



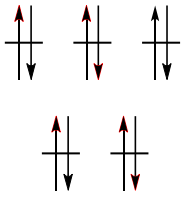
7.7

Electronic configuration of Cu^0: $[Ar]4s^13d^{10}$ or $1s^22s^22p^63s^23p^64s^13d^{10}$
Oxidation state of Cu in J: +1 or + I Cu^+ notation also accepted
Electronic configuration of Cu in J: $[Ar]3d^{10}$ or $1s^22s^22p^63s^23p^63d^{10}$

7.8 The geometry of Cu in **L** is:

☑ Tetrahedral

Splitting and filling of d orbitals:

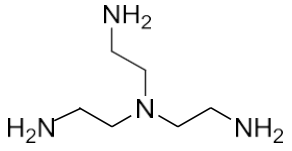


S = 0

7.9 The following compounds can remove the copper ion in L to obtain the free [2]catenane:

☑ KCN

☑ tren



tren

7.10 Fill in the blanks with a number or a tick:

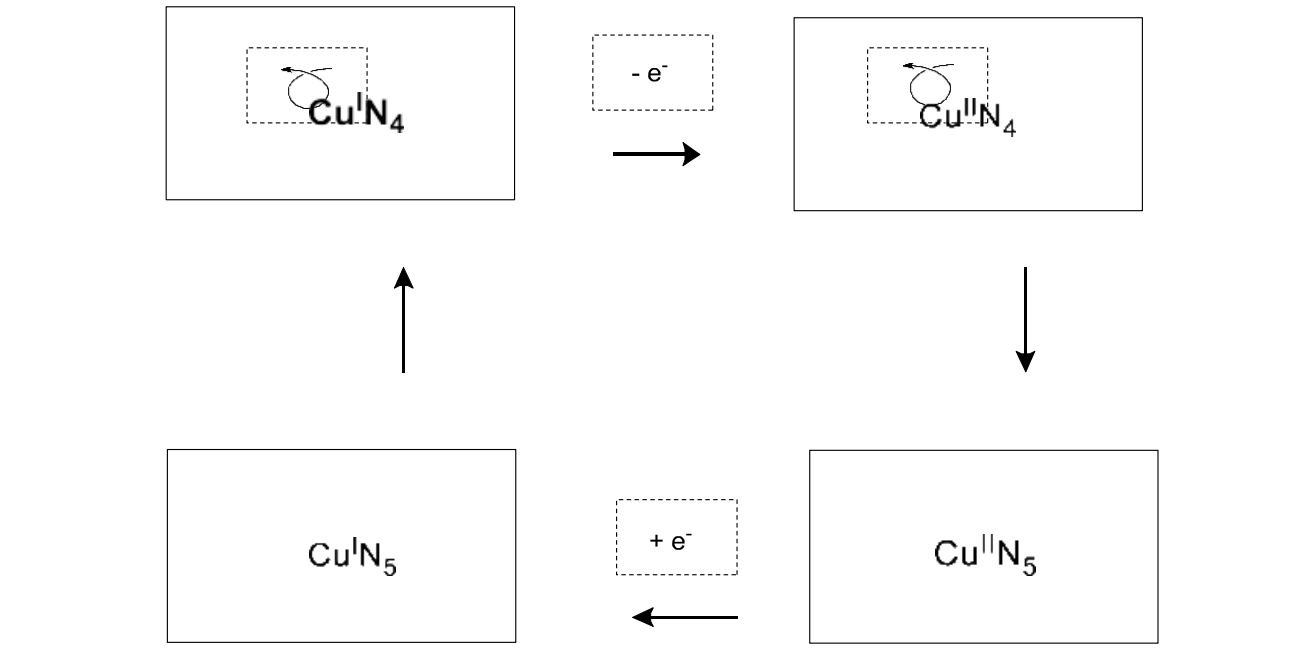
The $Cu^{I}N_4$ complex has **18** electrons in the coordination sphere of the metal.

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

The $Cu^{I}N_4$ complex is

☑ more stable than the $Cu^{I}N_5$ complex.

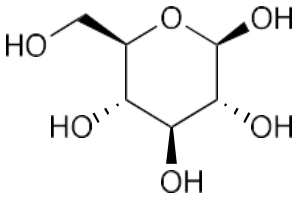
7.11



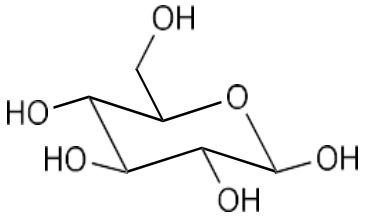
THEORETICAL PROBLEM 8

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

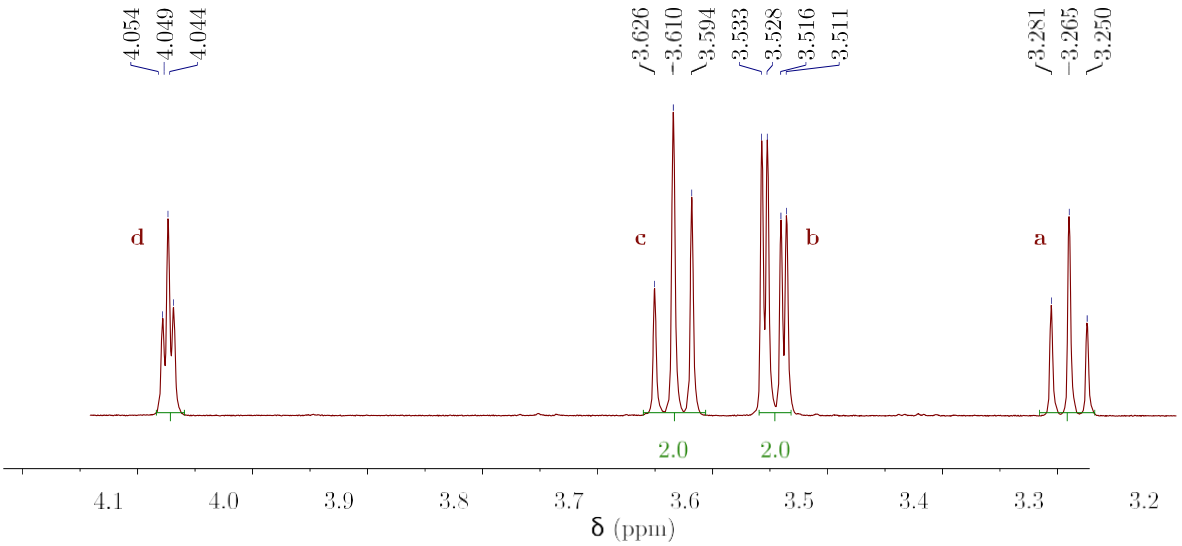
8.1 Draw the structural formula of inositols, without stereochemical details.

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

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

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 (next page) 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.

8.3 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.

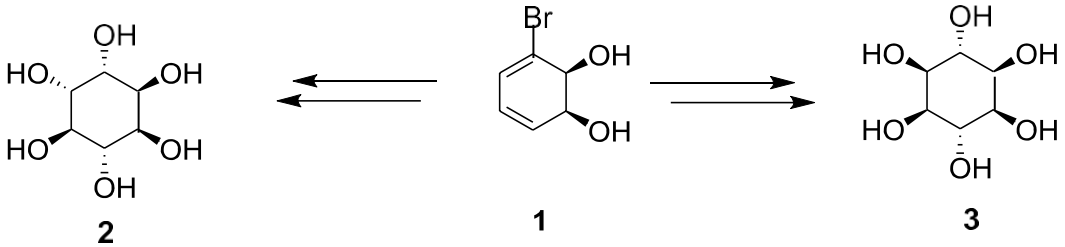


8.4 Based on the number and integrations of the proton signals, give the number of symmetry plane(s) that exist(s) in this molecule.

8.5 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.

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.

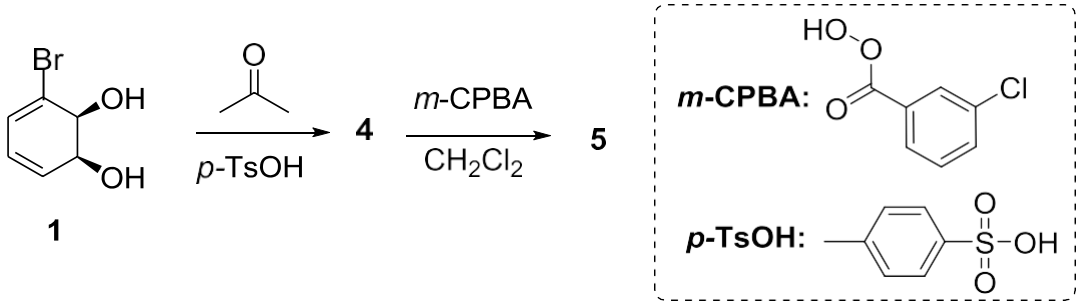


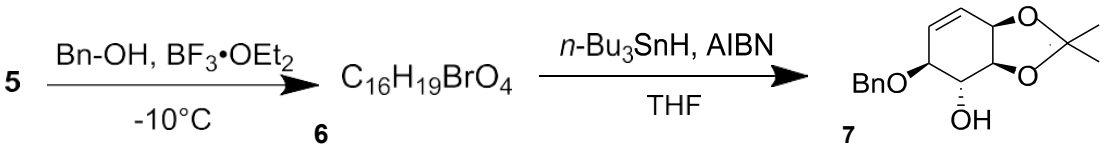
2 **1** **3**

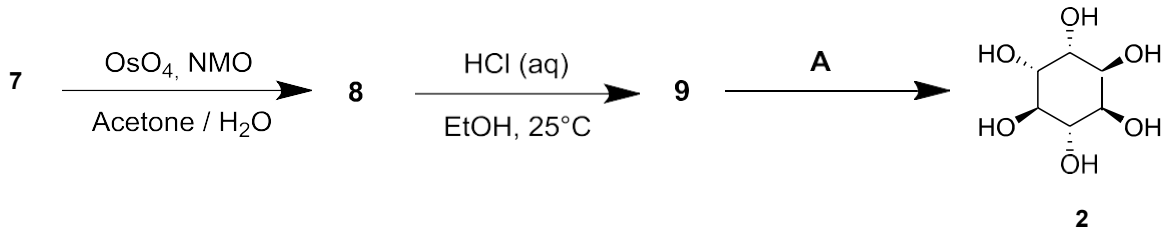
8.6 Choose the correct structural relationship(s) between **2** and **3**. Tick relevant boxes.

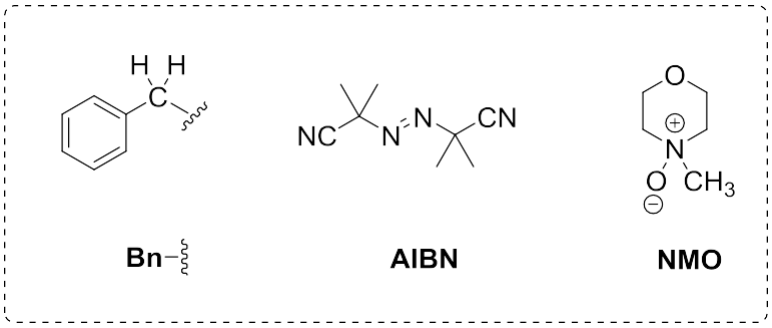
- ☐ enantiomers
- ☐ epimers
- ☐ diastereomers
- ☐ atropoisomers

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









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

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

8.9 Draw the 3D structure of the major diastereoisomer **5**.

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

8.11 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'**.

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

8.13 Select the right set(s) of conditions **A** to obtain **2**. Tick relevant boxes.

- ☐ H_2, Pd/C
- ☐ K_2CO_3, HF
- ☐ HCOOH, H_2O
- ☐ $BF_3.OEt_2$

8.14 If the bromine is not present in compound **1**, in addition to **2**, another stereoisomer would be obtained. Considering that 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** (tick relevant boxes).

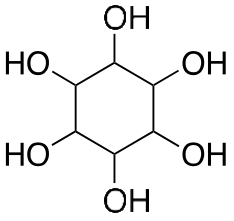
- ☐ enantiomers
- ☐ epimers
- ☐ diastereoisomers
- ☐ atropoisomers

8.15 During the synthesis of 2 from 1 choose the removal step(s) of <u>protecting or directing</u> groups.

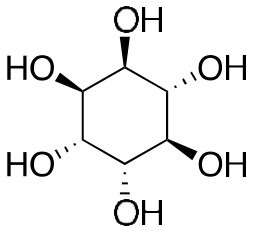
- ☐ **1** → **4**
- ☐ **4** → **5**
- ☐ **5** → **6**
- ☐ **6** → **7**
- ☐ **7** → **8**
- ☐ **8** → **9**
- ☐ **9** → **2**

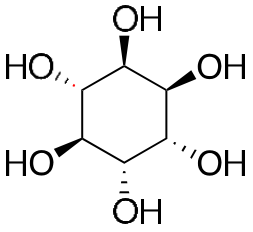
SOLUTION OF THE PROBLEM 8

8.1



8.2

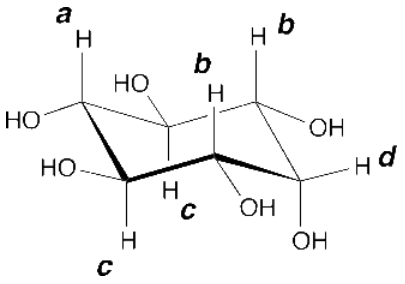


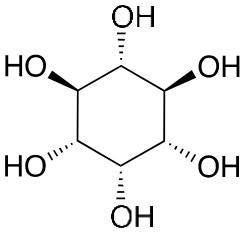


8.3 $C_6H_6O_6D_6$

8.4 The correct answer: 1

8.5

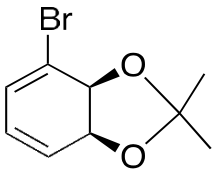




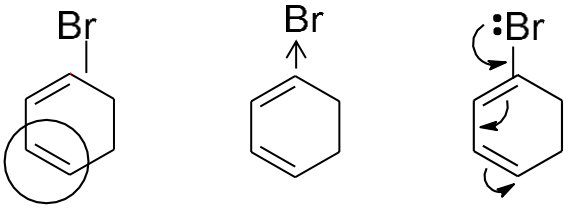
8.6 Correct: ☑ epimers

☑ diastereomers

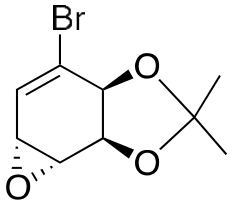
8.7



8.8

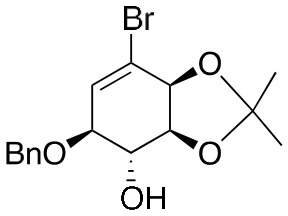
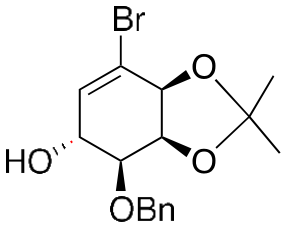


8.9



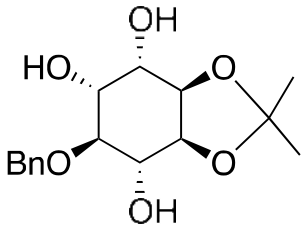
8.10 The correct answer: 2.

8.11

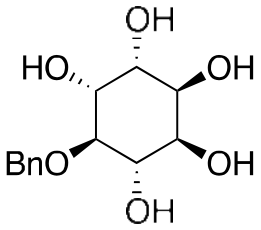
6: 	**6'**: 

8.12

8:

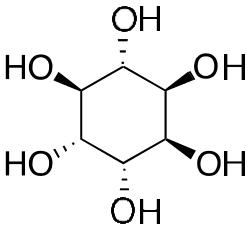


9:



8.13 Correct: ☑ H_2, Pd/C

8.14



The correct answer: ☑ enantiomers

8.15 ☑ 6 → 7

☑ 8 → 9

☑ 9 → 2

THEORETICAL PROBLEM 9

Synthesis of levobupivacaine

Part I.

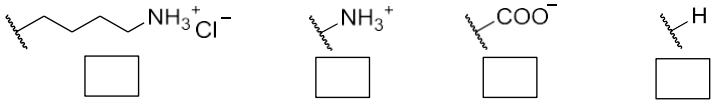
The local anesthetic bupivacaine (marketed as Marcaine) is on the World Health Organization List of Essential Medicines. Although the drug is currently used as a racemic mixture, it was demonstrated that one enantiomer of bupivacaine, levobupivacaine, is less cardiotoxic and, therefore, safer than the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

L-Lysine hydrochloride

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

Configuration: ☐ R ☐ S

Priority 1 > 2 > 3 > 4:



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

☐ Natural L-amino acids are levorotatory.

☐ Natural L-amino acids can be levorotatory or dextrorotatory.

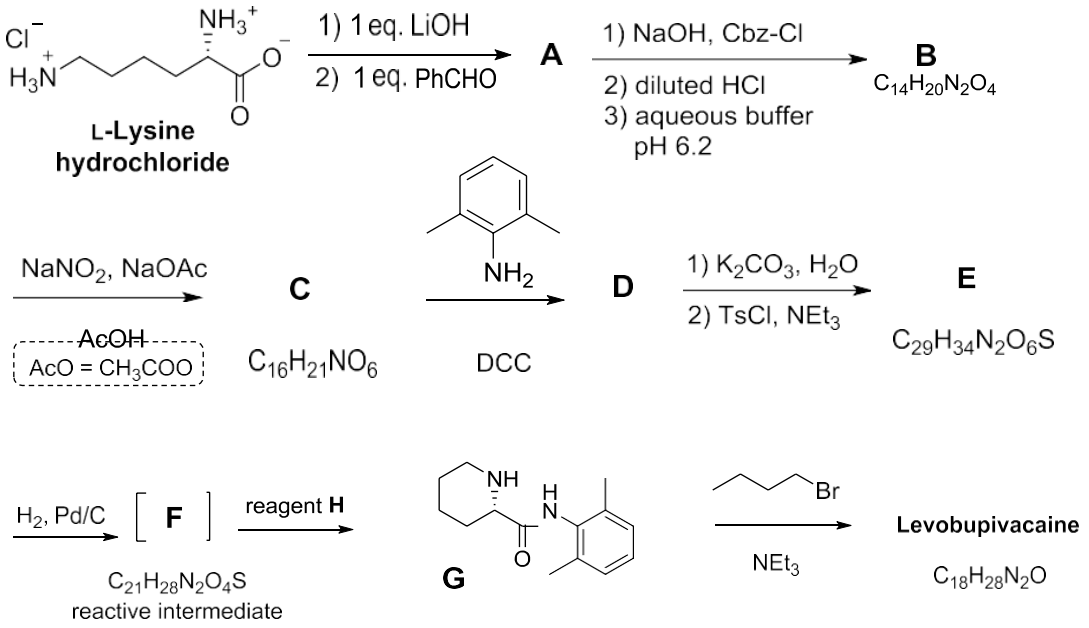
☐ All natural L-amino acids are (*S*).

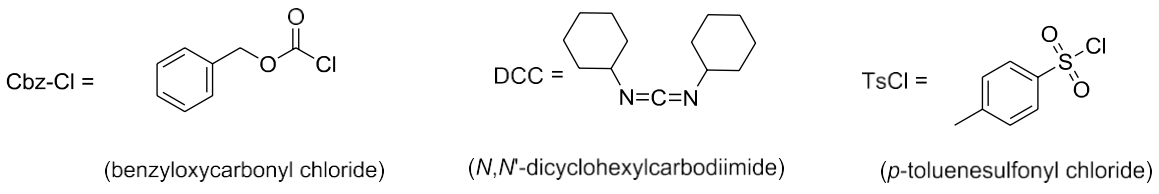
☐ All natural L-amino acids are (*R*).

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.

9.3 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.

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.

9.4 Draw the structure of compound A, including the appropriate stereochemistry.

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

- ☐ an enantioselective reaction
- ☐ an enantiospecific reaction
- ☐ a regioselective reaction

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

9.7 What is the role of DCC in the transformation **C** → **D**? Tick relevant boxes.

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

9.8 TsCl is used in the synthesis to enable (tick relevant boxes):

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

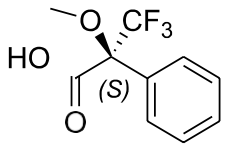
9.9 Mark all possible reagents which could be used as reagent H:

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

9.10 Draw the structure of levobupivacaine, including the appropriate stereochemistry.

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 amide using Mosher's acid (see the structure of the (*S*) isomer below).



(S)-Mosher's acid

9.11 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.

9.12 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)? Tick relevant boxes.

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

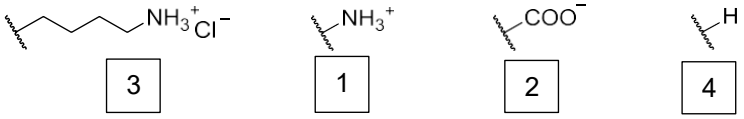
9.13 Choose the method(s) which can be used to quantitatively determine the enantiomeric purity of lysine after its derivatization with (*S*)-Mosher's acid. Tick the relevant boxes:

- ☐ NMR spectroscopy
- ☐ Liquid chromatography
- ☐ NMR spectroscopy
- ☐ Liquid chromatography

SOLUTION OF THE PROBLEM 9

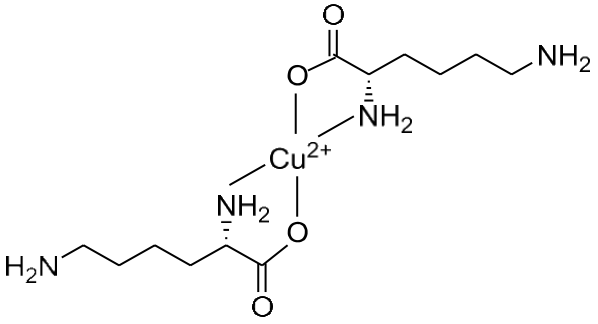
9.1 Configuration: ☐ *R* ☑ *S*

Priority 3 > 1 > 2 > 4:

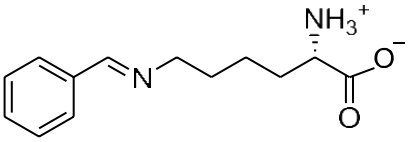


9.2 The correct answer: ☑ Natural L-amino acids can be levorotatory or dextrorotatory.

9.3 Complex:

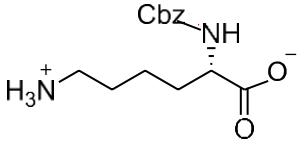
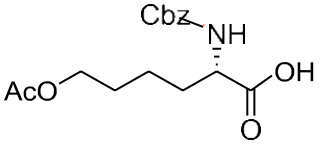


9.4

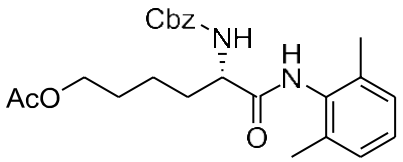


9.5 ☑ a regioselective reaction

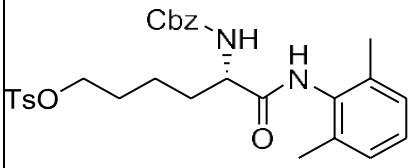
9.6 Draw the structures of compounds B–F, including the appropriate stereochemistry.

B $C_{14}H_{20}N_2O_4$ 	**C** $C_{16}H_{21}NO_6$ 

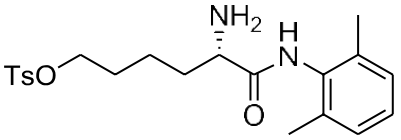
D



E $C_{29}H_{34}N_2O_6S$



F $C_{21}H_{28}N_2O_4S$



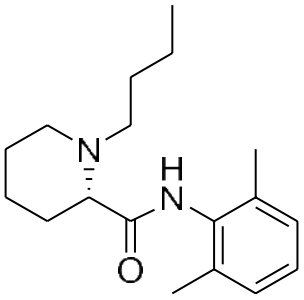
9.7 Correct: ☑ Activating agent for the amide bond formation.

9.8 Correct: ☑ Nucleophilic substitution of a hydroxy group.

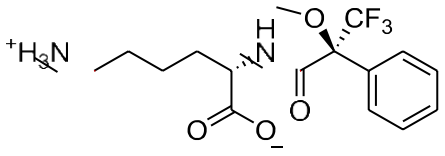
9.9 Correct: ☑ K_2CO_3

☑ diluted NaOH

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



9.11



9.12 Correct: ☑ Two diastereoisomers.

9.13 Correct: ☑ NMR spectroscopy.

☑ Liquid chromatography.

The original page:

PRACTICAL

EXAM

51st — International Chemistry Olympiad France — Paris — 2019

Making science together!

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

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MINISTÈRE DE L'ÉDUCATION NATIONALE ET DE LA JEUNESSE

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

2019-07-24

The experimental problems - introduction

The practical part of the 51st IChO competition contained three experimental problems which were expected to be solved in laboratories. The solving of the problems required some equipment which was common for all three experiments. Moreover some other equipment was necessary which was required when the particular problems were solved.

Chemicals for all problems:

- Deionized water
- Ethanol in a wash bottle
- Sample of white wine, 300 cm^3, in amber plastic bottle

Equipment for all problems:

- Pipette filler bulb	1
- Safety goggles	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:

- UV lamp for TLC visualization	2 per lab
- Colorimeter	5 per lab
- Gloves All sizes (S, M, L, XL) available	
- Ice bucket	1 per lab

PRACTICAL PROBLEM 1

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.

The task is to perform:

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

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

Chemicals

- 4-nitrobenzaldehyde, 1.51 g in amber glass vial
- Eluent A, 20 cm^3 in glass vial
- Eluent B, 20 cm^3 in glass vial
- Oxone® (potassium peroxomonosulfate salt), 7.87 g in plastic bottle
- Sample of 4-nitrobenzaldehyde for TLC

Equipment

- Laboratory stand with:
  - Clamp holder with small clamp 2
  - Clamp holder with large clamp 1
- Erlenmeyer flask with ground joint, 100 cm^3 1
- Erlenmeyer flask with ground joint, 50 cm^3 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 cm^3 1
- Beaker, 150 cm^3 2
- Plastic powder funnel 1
- Disposable plastic pipette 2
- Amber glass vial for TLC sample, 1.5 cm^3, with stopper, labelled C and R 2
- Pre-weighed amber glass vial, 10 cm^3, with stopper 1
- Magnetic stirring bar retriever 1

_____

Procedure:

I. Oxidation of 4-nitrobenzaldehyde

1. Mix 20 cm^3 of water and 5 cm^3 of ethanol.
2. Insert the magnetic bar in the 100 cm^3 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 and 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 ,ark on the heater corresponds to the necessary power to get a gentle reflux.

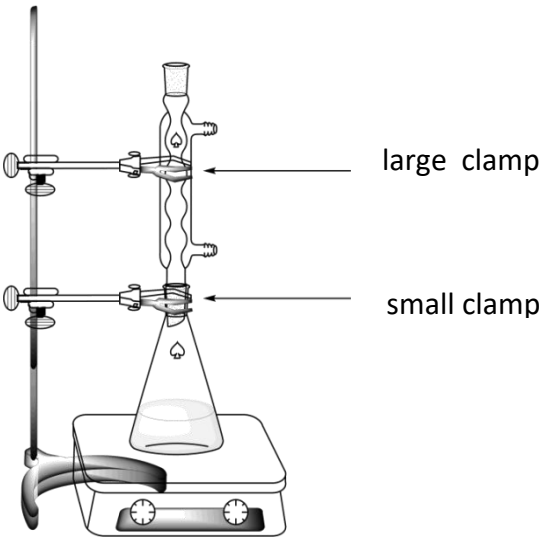


Figure 1. Setup for heating the reaction mixture under reflux

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 mixture filled with an ice-water mixture. Let it standing 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.

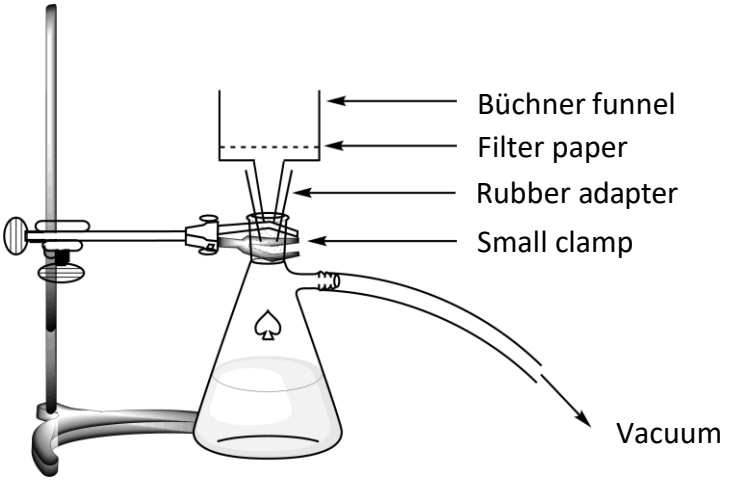


Figure 2. Setup for the vacuum filtration

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 cm^3).
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 cm^3 amber glass vial, labeled C. Close the vial and save it for part III.
11. Transfer all of the remaining solid into the 50 cm^3 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 cm^3 of water with 21 cm^3 of ethanol.
2. Perform the recrystallization of the crude product contained in the 50 cm^3 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). Add the solvent by the top of 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 cm^3 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.

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 cm^3 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.

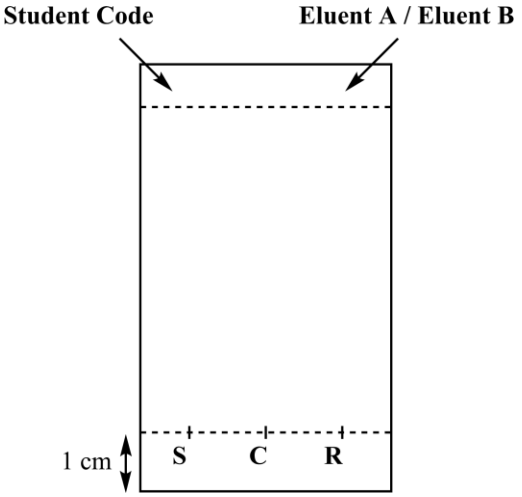
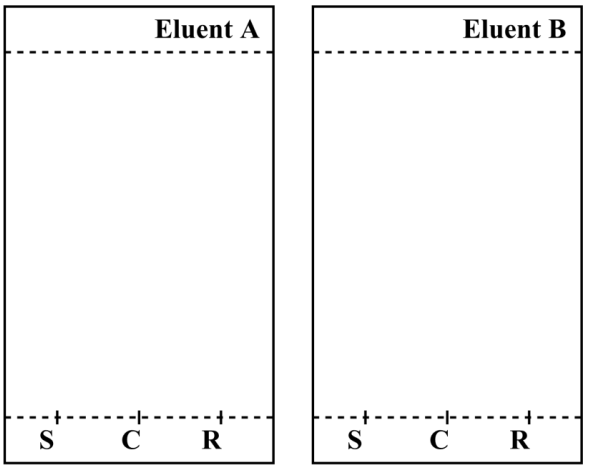


Figure 3. TLC plate preparation

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.



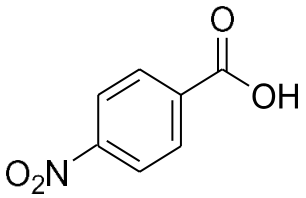
At the end of the examination, your lab supervisor will pick up the following items:

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

IV. Tasks

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

   The correct answer is as follows:



2. Based on your results on the TLC analysis, answer the following questions (tick the relevant boxes).

a) Which eluent is better to follow the reaction progress?

A ☐ or B ☐

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

True ☐ False ☐

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

True ☐ False ☐

PRACTICAL PROBLEM 2

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.

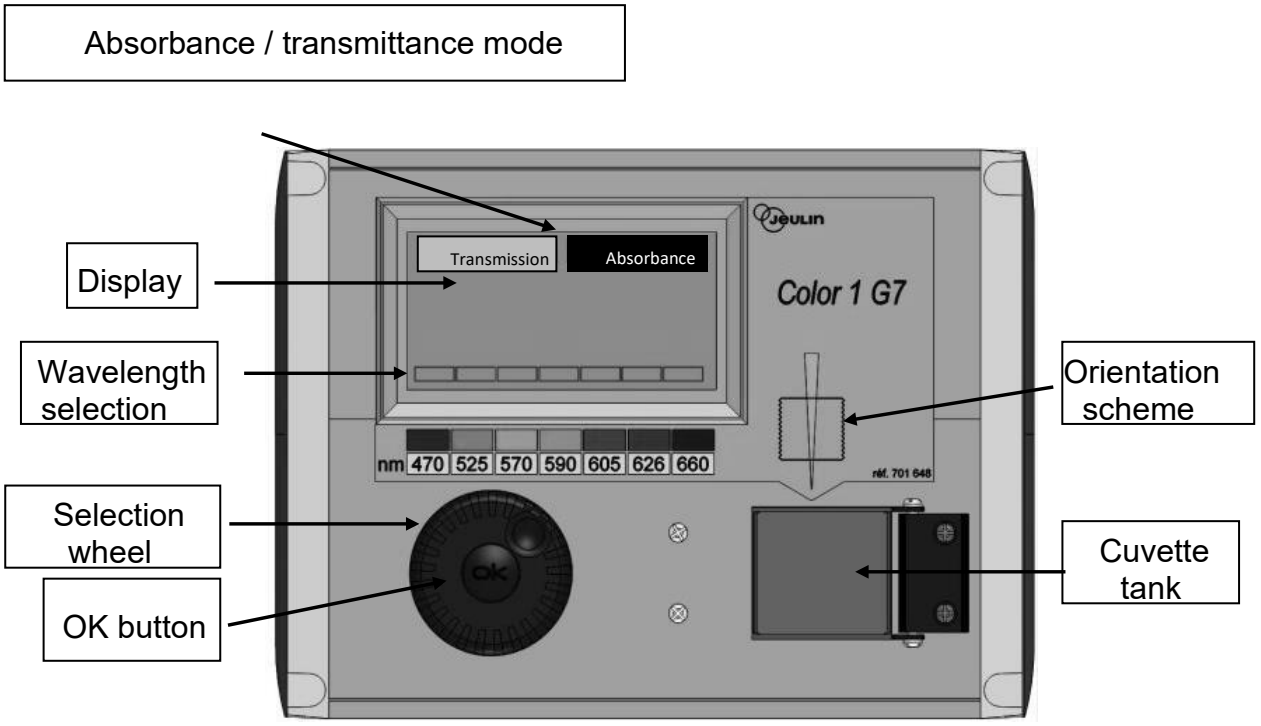
Given the very low concentration of iron species, a colored complex of iron(III) with thiocyanate SCN^- as a ligand is used to quantify the iron amount, through spectrophotometric measurements.

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.

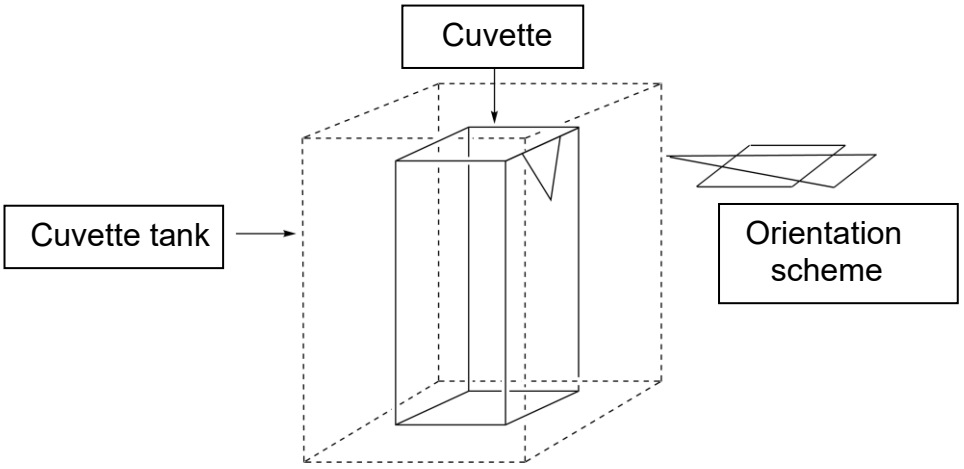
WARNING

- 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.



Chemicals

- Potassium thiocyanate solution, c = 1 mol dm^{-3}, 20 cm^3 in a plastic bottle
- Potassium thiocyanate solution, c = 0.00200 mol dm^{-3}, 60 cm^3 in a plastic bottle
- Perchloric acid solution, c = 1 mol dm^{-3}, 10 cm^3 in a plastic bottle
- Iron(III) solution, c = 0.00200 mol dm^{-3}, 80 cm^3 in a plastic bottle
- Iron(III) solution, c = 0.000200 mol dm^{-3}, 80 cm^3 in a plastic bottle
- Hydrogen peroxide solution, 0.3 %, 3 cm^3 in amber glass bottle

Equipment

Volumetric pipette, 10 cm^3	1
Graduated pipette, 10 cm^3	3
Graduated pipette, 5 cm^3	3
Test tube stand	1
Test tube	15
Test tube stopper	7
Colorimeter cuvette, 1.0 cm	2
Beaker, 100 cm^3	2
Disposable plastic pipette	15

_____

I. Determination of the iron content in the wine

In this part, you will need the iron(III) solution (c = 0.000200 mol dm^{-3}) and the potassium thiocyanate solution (c = 1.00 mol dm^{-3}).

Procedure

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

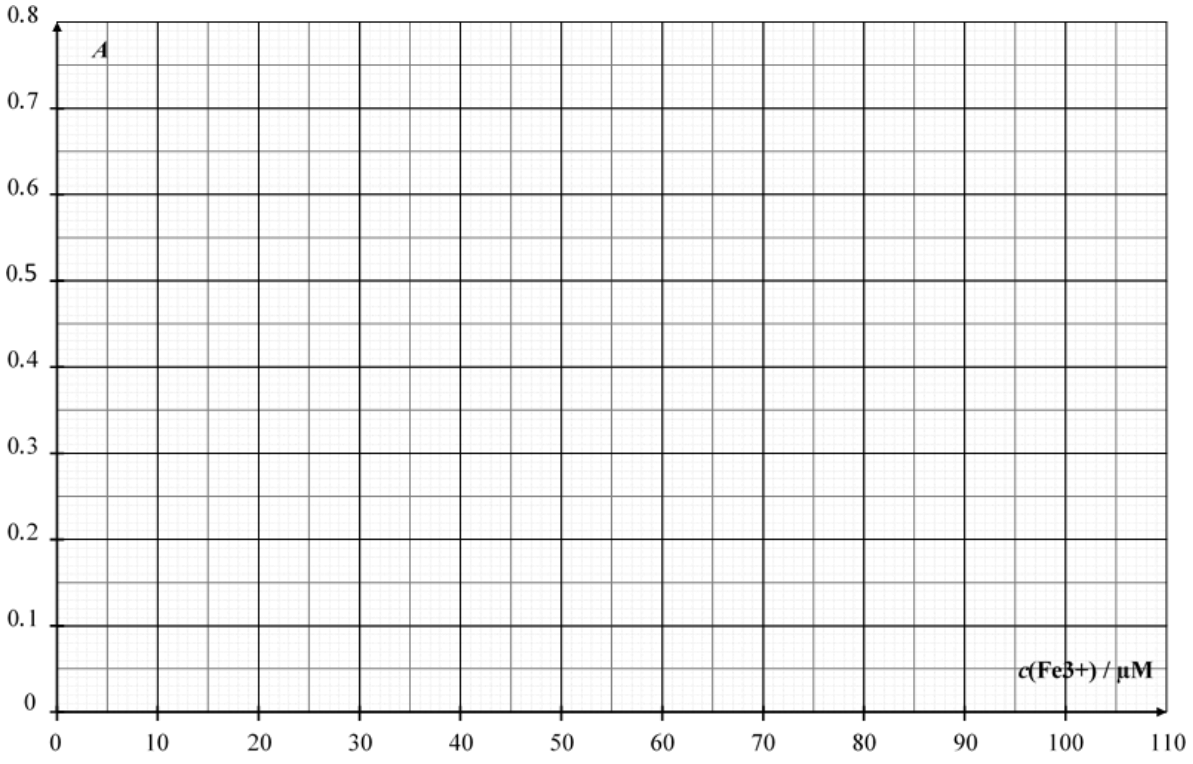
Tube #	1	2	3	4	5	6
iron(III) solution (c = 0.000200 mol dm^{-3})	1.0 cm^3	2.0 cm^3	4.0 cm^3	6.0 cm^3	---	---
perchloric acid solution (c = 1.00 mol dm^{-3})	1.0 cm^3	1.0 cm^3	1.0 cm^3	1.0 cm^3	1.0 cm^3	1.0 cm^3
Wine	---	---	---	---	10.0 cm^3	10.0 cm^3
Hydrogen peroxide solution	---	---	---	---	0.5 cm^3	0.5 cm^3
Deionized water	9.5 cm^3	8.5 cm^3	6.5 cm^3	4.5 cm^3	---	1.0 cm^3

2. Stopper the tubes and homogenize.
3. Add 1.0 cm^3 of potassium thiocyanate solution (c = 1 mol dm^{-3}) 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.
6. Set the wavelength at 470 nm. Use deionized water for the blank.
7. 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 $c(Fe^{3+})$ / μmol dm^{-3}	16	32	64	96	---	---
Colorimeter code						

Tasks:

P2.1 Plot the absorbance A of the solutions in the tubes 1 to 4 as a function of the analytical concentration of Fe^{3+}. Use the millimeter paper attached below.



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				

P2.2 Using the previous plot and the data you have chosen, draw the calibration straight line on the previous plot and determine the analytical concentration (in μmol.dm^{-3}) of Fe^{3+} in tube 5.

P2.3 Calculate the mass concentration, in mg per liter, of iron in the studied white wine.

II. Determination of the complex stoichiometry

In this part, you will need the iron(III) solution (c = 0.00200 mol dm^{-3}) and the potassium thiocyanate solution (c = 0.00200 mol dm^{-3}).

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:

- 80 cm^3 of iron(III) solution (already acidified) with c = 0.00200 mol dm^{-3}.
- 80 cm^3 of potassium thiocyanate solution with c = 0.00200 mol dm^{-3}.

You also have test tubes (with stoppers that you can wash and dry), graduated pettes, 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.

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

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

x) M = mol dm^{-3}

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).
4. Set the wavelength at 470 nm. Use deionized water for the blank.
5. Record the absorbance of each tube at this wavelength. Report the results in the previous table.

Tasks

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

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

a = _____ b = _____

PRACTICAL PROBLEM 3

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 withchemicals in wine such as acetaldehyde, pigments, sugars, etc. forming products P. The total concentration of sulfur dioxide is the sum of the concentrations 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 dm^{-3} for red wine and 150 mg dm^{-3} for white or rosé.

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

Chemicals

- iodine solution, c = 0.01 mol dm^{-3}, 200 cm^3 in brown plastic bottle
- sodium thiosulfate solution, c = 0.03 mol dm^{-3}, 200 cm^3 in plastic bottle
- sodium hydroxide solution, c = 1 mol dm^{-3}, 55 cm^3 in a plastic bottle
- sulfuric acid solution, c = 2.5 mol dm^{-3}, 80 cm^3 in a plastic bottle
- potassium iodide solution, c = 0.5 mol dm^{-3}, 25 cm^3 in a plastic bottle
- potassium iodate, *ca* 100 mg (exact mass is written on the label), in a glass vial
- starch solution, 25 cm^3 in a plastic bottle

Equipment

Laboratory stand with burette clamps	1
Clamp holder with small clamp	2
Clamp holder with large clamp	1

Burette, 25 cm^3	1
Glass transfer funnel	1
Erlenmeyer flask, 100 cm^3	3
Erlenmeyer flask, 250 cm^3	3
Beaker, 150 cm^3	1
Beaker, 100 cm^3	2
Volumetric flask, 100 cm^3, with stopper	1
Volumetric pipette, 50 cm^3	1
Volumetric pipette, 25 cm^3	1
Volumetric pipette, 20 cm^3	1
Graduated cylinder, 25 cm^3	1
Graduated cylinder, 10 cm^3	1
Graduated cylinder, 5 cm^3	1
Disposable plastic pipette	3
Parafilm	20 sheets

Procedure

I. <u>Standardization of the sodium thiosulfate solution</u>

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 cm^3 volumetric flask, using the whole sample of solid potassium iodate and deionized water. This solution is called S.
3. In a 100 cm^3 Erlenmeyer flask, add:
   - 20 cm^3 of solution S with a volumetric pipette;
   - 5 cm^3 of the potassium iodide solution (c = 0.5 mol dm^{-3}), using a 5 cm^3 graduated cylinder;
   - 10 cm^3 of the sulfuric acid solution (c = 2.5 mol dm^{-3}) with a 10 cm^3 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.

6. 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.

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

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

Analysis N°	V_1 / cm^3
1	
2	
3	
Reported value V_1 / cm^3	

II. Standardization of the iodine solution

1. Transfer with a volumetric pipette 25 cm^3 of the iodine solution (labeled I_2) into a 100 cm^3 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 / cm^3
1	
2	
3	

Reported value V_2 / cm^3	

III. Determination of total sulfur dioxide

1. With a volumetric pipette, transfer 50 cm^3 of wine into a 250 cm^3 Erlenmeyer flask.
2. Add 12 cm^3 of the sodium hydroxide solution (c = 1 mol dm^{-3}) with a 25 cm^3 graduated cylinder. Cover the flask with Parafilm, swirl the content then let it stand for at least 20 minutes.
3. Add 5 cm^3 of the sulfuric acid solution (2.5 mol dm^{-3}), and *ca* 2 cm^3 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 / cm^3
1	
2	
3	
Reported value V_3 / cm^3	

Tasks

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

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

3.3 Calculate the concentration of the iodine solution.

3.4 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-}.

3.5 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}.

SOLUTION OF TASKS

3.1 $IO_3^-(aq) + 5\ I^-(aq) + 6\ H^+(aq) = 3\ I_2(aq) + 3\ H_2O(l)$ or

$IO_3^-(aq) + 5\ I^-(aq) + 6\ H_3O^+(aq) = 3\ I_2(aq) + 9\ H_2O(l)$ or

$IO_3^-(aq) + 8\ I^-(aq) + 6\ H^+(aq) = 3\ I_3^- + 3\ H_2O$ or

$IO_3^-(aq) + 8\ I^-(aq) + 6\ H_3O^+ = 3\ I_3^-(aq) + 9\ H_2O(l)$

and

$I_3^-(aq) + 2\ S_2O_3^{2-}(aq) = 3\ I^-(aq) + S_4O_6^{2-}(aq)$ or

$I_2(aq) + 2\ S_2O_3^{2-}(aq) = 2\ I^-(aq) + S_4O_6^{2-}(aq)$

3.2 - 3.3

The concentrations of sodium thiosulfate and iodine solutions can be calculated using the relations between the particular quantities of the compounds in the above equations.

3.4 The equation of the reaction between iodine I_2 and sulfur dioxide SO_2 assuming that sulfur dioxide is oxidized to sulfate ions:

$SO_2(aq) + 2\ H_2O(l) + I_3^-(aq) = SO_4^{2-}(aq) + 4\ H^+(aq) + 3\ I^-(aq)$

or

$SO_2(aq) + 2\ H_2O(l) + I_2(aq) = SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ I^-(aq)$

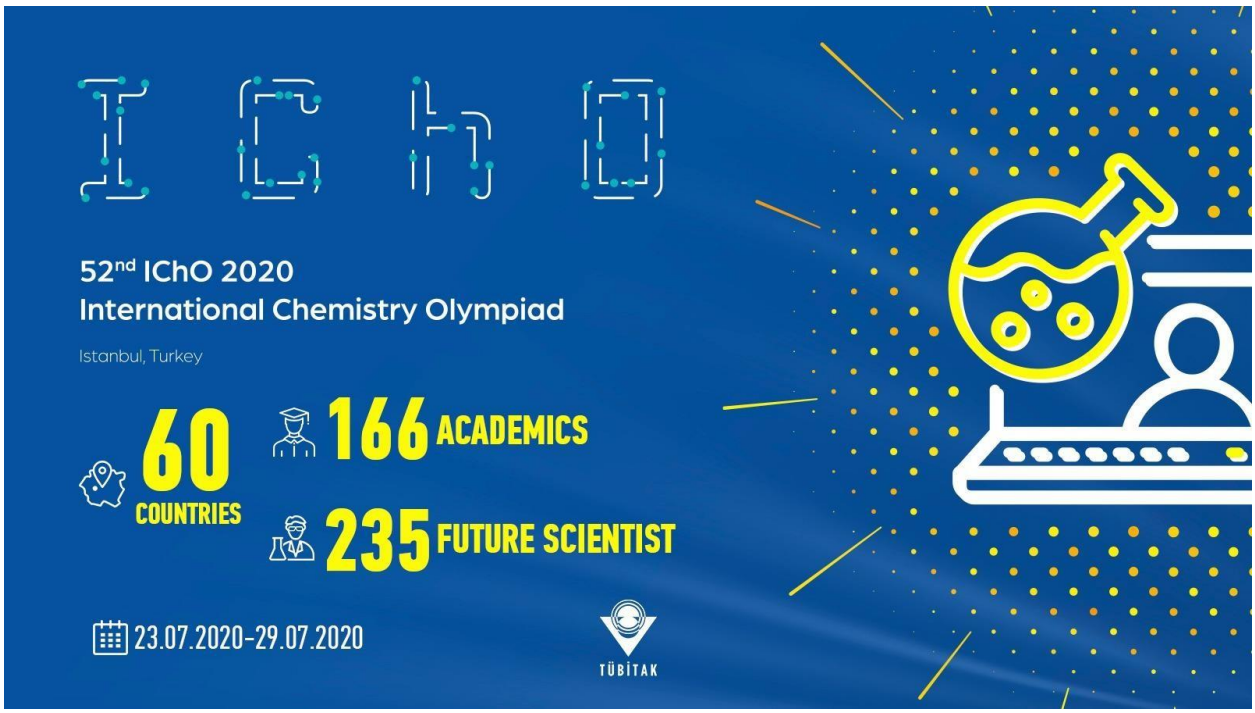
3.5 The mass concentration of sulfur dioxide thiosulfate and iodine solutions can be calculated using the relations between the particular quantities of the compounds given in the above equations.

52nd

International Chemistry Olympiad

9 theoretical problems

The original front page:



52nd IChO 2020

International Chemistry Olympiad

Istanbul, Turkey

CHEMISTRY FOR A BETTER TOMORROW

TÜBİTAK

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Physical Constants and Equations

Avogadro's number, $N_A = 6.0221 \times 10^{23} \text{mol}^{-1}$
Boltzmann constant, $k_B = 1.3807 \times 10^{-23}\ \text{JK}^{-1}$
Universal gas constant, $R = 8.3145\ \text{JK}^{-1}\text{mol}^{-1} = 0.08205\ \text{atm L K}^{-1}\text{mol}^{-1}$
Speed of light, $c = 2.9979 \times 10^{8} \text{ms}^{-1}$
Planck's constant, $\text{h} = 6.6261 \times 10^{-34}\ \text{J s}$
Faraday's constant, $F = 9.6485 \times 10^{4}\ \text{C mol}^{-1}$
Mass of electron, $m_e = 9.1093 \times 10^{-31}\ \text{kg}$
Standard pressure, $P = 1\ \text{bar} = 1 \times 10^{5}\ \text{Pa}$
Atmospheric pressure, $P_{atm} = 1.01325 \times 10^{5}\ \text{Pa} = 760\ \text{mmHg} = 760\ \text{torr}$

Zero of the Celsius scale, $273.15\ \mathrm{K}$

1 picometer (pm) = 1×10^{-12} m; $1\text{Å} = 1 \times 10^{-10}\ m$; 1 nanometer (nm) = 1×10^{-9} m

$1\ \mathrm{eV} = 1.6 \times 10^{-19}\ \mathrm{J}$

$1\ \mathrm{cal} = 4.184\ J$

$1\ \mathrm{amu} = 1.6605 \times 10^{-27}\ \mathrm{kg}$

Charge of an electron: $1.6 \times 10^{-19}\ \mathrm{C}$

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U + PV$

Gibbs free energy: $G = H - TS$

$\Delta G = \Delta G^0 + RTlnQ$

$\Delta_r \boldsymbol{G^0} = -RTlnK = -nFE^0_{cell}$

Entropy change:

$\Delta S = \frac{q_{rev}}{T}$, where q_{rev} is heat for the reversible process

$\Delta S = nRln\frac{V_2}{V_1}$ (for isothermal expansion of an ideal gas)

Nernst equation: $E = E^0 + \frac{RT}{nF}\ln\frac{C_{oxidation}}{C_{reduction}}$

Energy of a photon: $E = \frac{hc}{\lambda}$

Integrated rate law

Zeroth-order: $[A] = [A]_0 - kt$

First-order: $\ln[A] = \ln[A]_0 - kt$

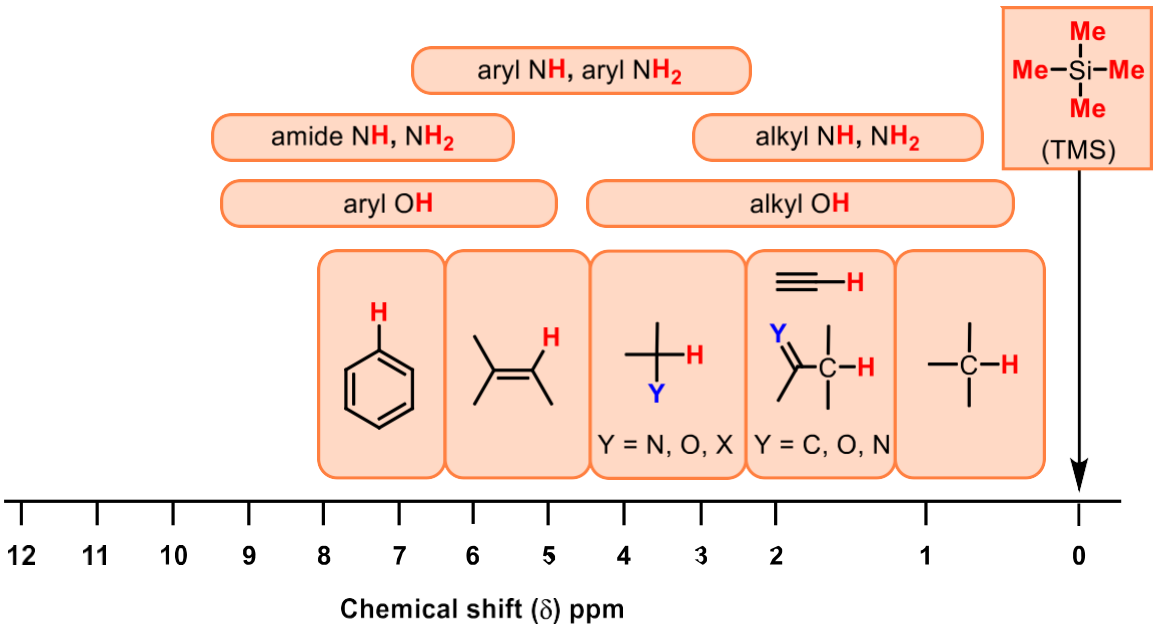
Second order: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Arrhenius equation: $k = A\,e^{-E_a/RT}$

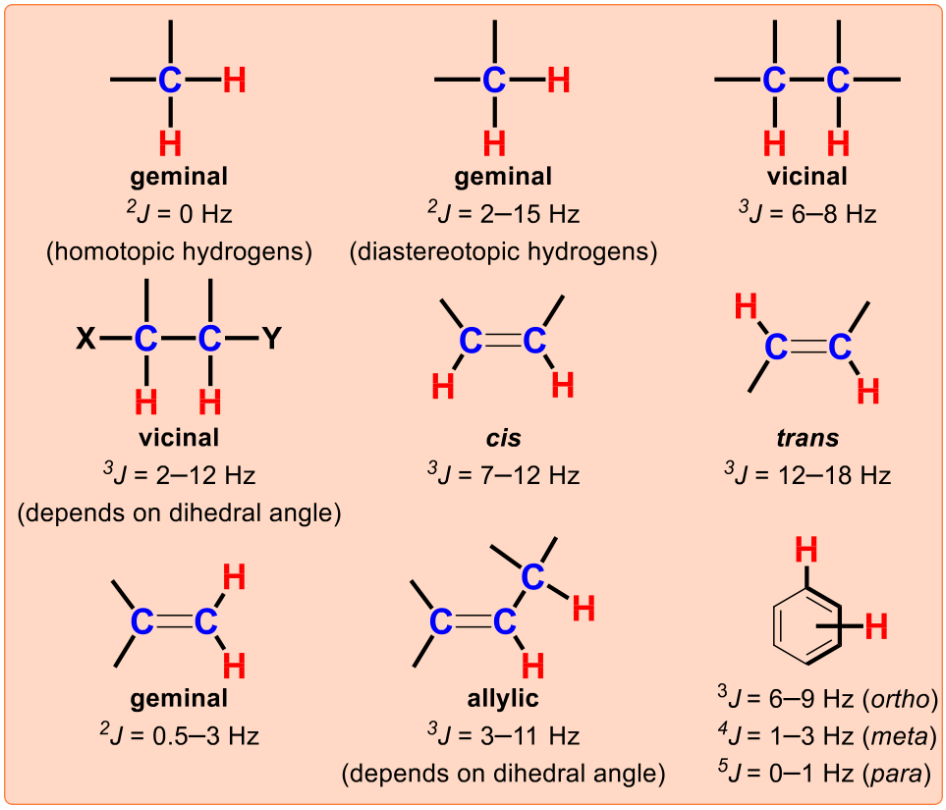
Equation of linear calibration curve: $y = mx + n$

Lambert–Beer equation: $A = \varepsilon lc$

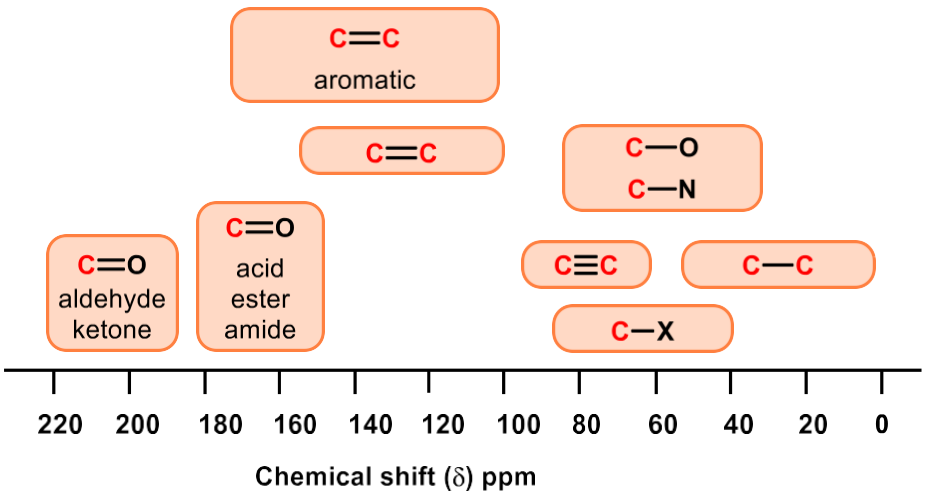
^{1}H-NMR Chemical Shifts



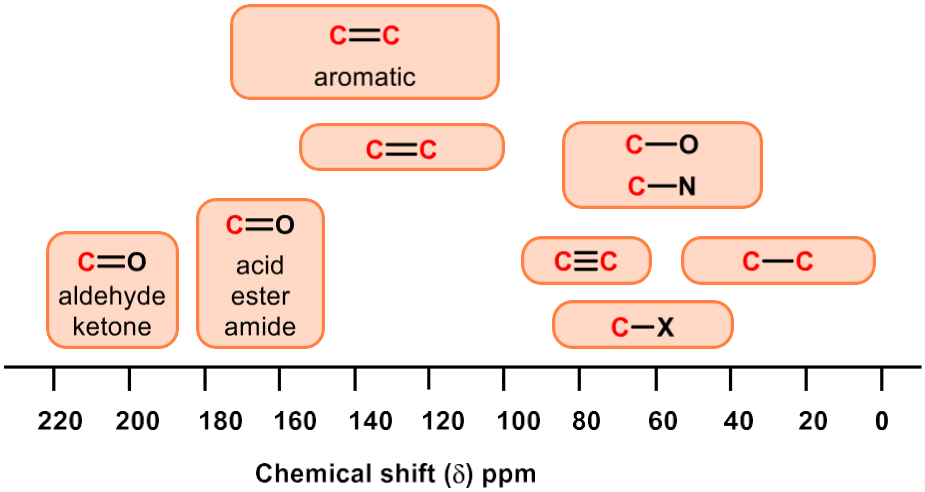
Typical Coupling Constants



^{13}C-NMR Chemical Shifts



^{13}C-NMR Chemical Shifts



IR Absorption Frequency Table

Functional Group	Type of Vibration	Absorption Frequency Region (cm^{-1})	Intensity
Alcohol			
O–H	(stretch, H-bonded)	3600–3200	strong, broad
	(stretch, free)	3700–3500	strong, sharp
C–O	(stretch)	1150–1050	strong
Alkane			
C–H	stretch	3000–2850	strong
	bending	1480–1350	variable
Alkene			
=C–H	stretch	3100–3010	medium
	bending	1000–675	strong
C=C	stretch	1680–1620	variable
Alkyl Halide			
C–F	stretch	1400–1000	strong
C–Cl	stretch	800–600	strong
C–Br	stretch	600–500	strong
C–I	stretch	500	strong
Alkyne			
C–H	stretch	3300	strong, sharp
C≡C	stretch	2260–2100	variable, not present in symmetrical alkynes
Amine			
N–H	stretch	3500–3300	medium (primary amines have two bands; secondary amines have one band, often very weak)

C–N	stretch	1360–1080	medium-weak
N–H	bending	1600	medium
Aromatic			
C–H	stretch	3100–3000	medium
C=C	stretch	1600–1400	medium-weak, multiple bands
Carbonyl			
C=O	stretch	1820–1670	strong
Acid			
C=O	stretch	1725–1700	strong
O–H	stretch	3300–2500	strong, very broad
C–O	stretch	1320–1210	strong
Aldehyde			
C=O	stretch	1740–1720	strong
C–H	stretch	2850–2820 & 2750–2720	medium, two peaks
Amide			
C=O	stretch	1690–1640	strong
N–H	stretch	3500–3100	unsubstituted have two bands
	bending	1640–1550	
Anhydride			
C=O	stretch	1830–1800 &1775–1740	two bands
Ester			
C=O	stretch	1750–1735	strong
C–O	stretch	1300–1000	two bands or more
Ketone			
acyclic	stretch	1725–1705	strong
cyclic	stretch	3-membered - 1850	strong
	stretch	4-membered - 1780	strong
	stretch	5-membered - 1745	strong
	stretch	6-membered - 1715	strong
	stretch	7-membered - 1705	strong
α,β – unsaturated	stretch	1685–1665	strong
conjugation moves absorptions to lower wavenumbers			
aryl ketone	stretch	1700–1680	strong
Ether			
C–O	stretch	1300–1000 (1150–1070)	strong
Nitrile			
C≡N	stretch	2260–2210	medium
Nitro			
O–N–O	stretch	1560–1515 & 1385–1345	strong, two bands

Contents

THE FIFTY-SECOND INTERNATIONAL CHEMISTRY OLYMPIAD

23 – 29 JULY 2020, ISTANBUL, TURKEY

THEORETICAL PROBLEMS

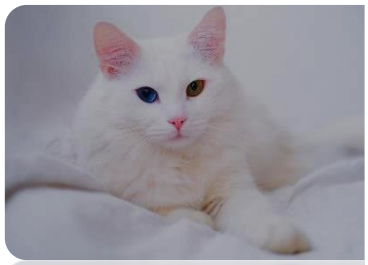
THEORETICAL PROBLEM 1

Two Beauties of Turkey: the Van Cat and the Ankara Cat

The most beautiful of cats, the Van cat is a pure breed living only in Lake Van basin. Another endemic cat breed is the Ankara cat. They are called Angora cats. Their most important feature is their two different eye colors.

Van cat

Ankara cat



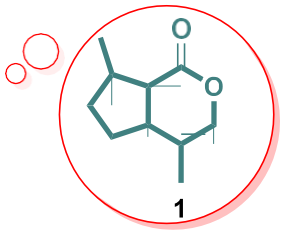
Nepeta cataria (catnip)

Just like people, cats can sometimes be stressed and angry. Just as people are made happy by melatonin, the stress of cats can be reduced and they can be made happy thanks to a natural product. Nepetalactone is an organic compound isolated from the plant catnip (*Nepeta cataria*), which acts as a cat attractant. Nepetalactone is a ten-carbon bicyclic mono- terpenoid compound derived from isoprene with two fused rings: a

cyclopentane and a lactone.

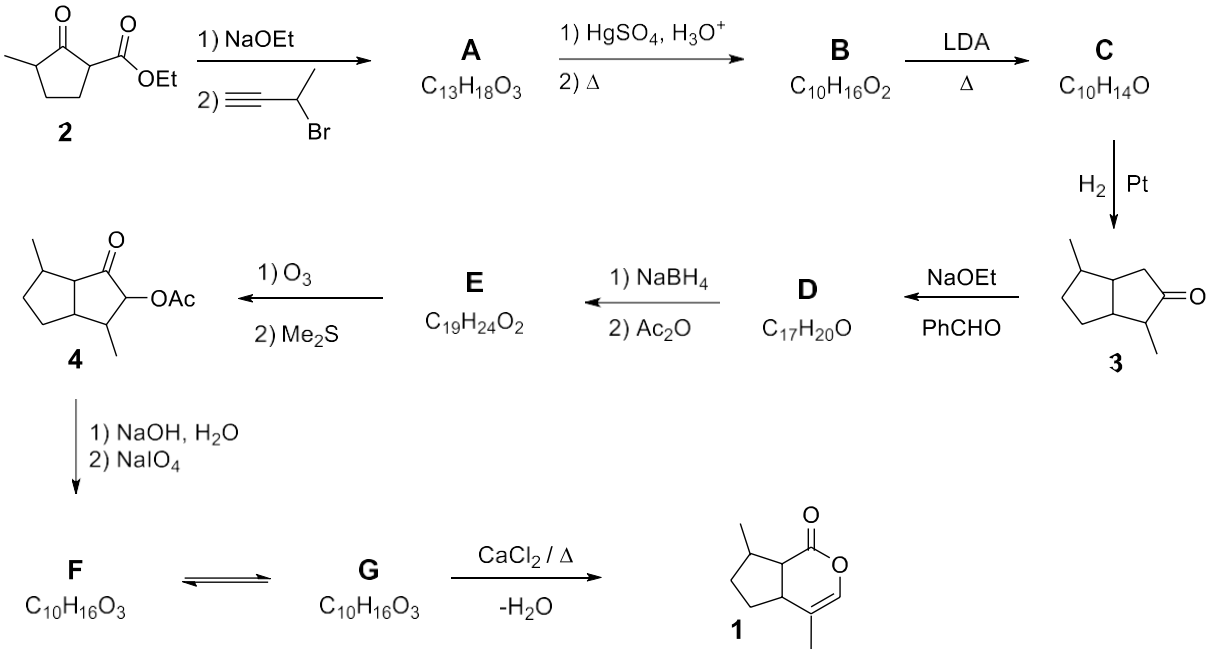
Cat eCat eating catnip in the garden

Cat's dream



Nepetalactone

Total synthesis of nepetalactone:

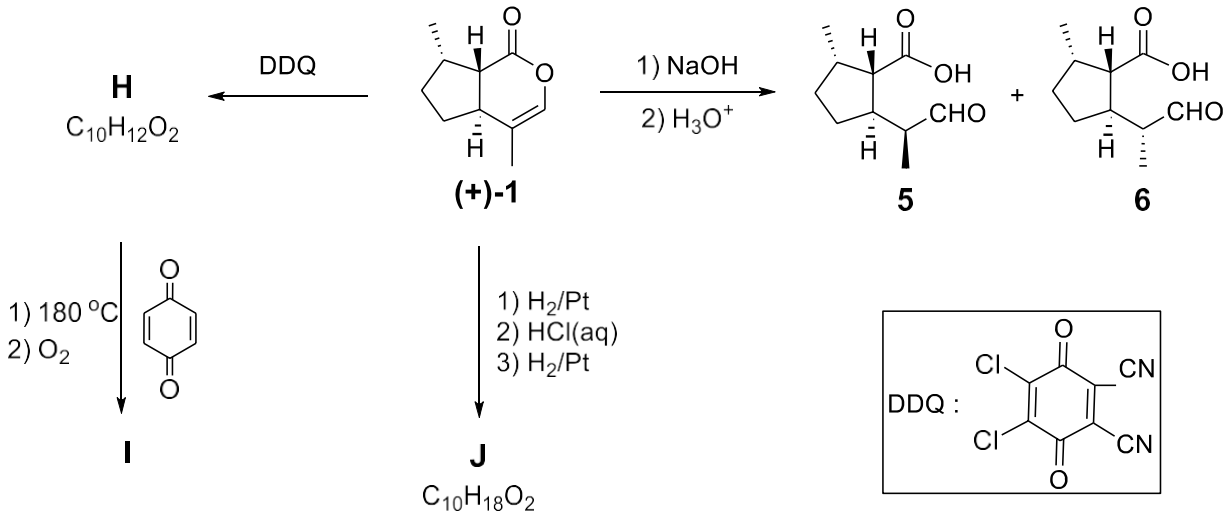


1.1 The above scheme describes the total synthesis of nepetalactone. Draw structures of **A**–**G**, without stereochemical details.

Hints:

- Compound **A** has strong and sharp band at 3300 cm^{-1} in the IR spectrum.
- **A**, **B,** and **F** are monocyclic, while **C**, **D**, **E**, and **G** are bicyclic compounds.
- **F** has one doublet at ~ 9.8 ppm in the ^{1}H-NMR spectrum.

Reactions of nepetalactone:



The above scheme includes a few reactions of one of the enantiopure nepetalactone **1** isomers. Three of the reaction products (**5**, **6**, and **J**) are used as insect repellents in industry.

1.2 For the relationship between **5** and **6**, which of the following is/are true? Tick the box next to the correct answer(s) on your answer sheets.

☐	Enantiomers
☐	Diastereomers
☐	Identical
☐	Stereoisomers

Reaction of **1** with DDQ gives highly conjugated compound **H**. Also, thermal reaction of compound **H** with *p*-quinone gives **I** with molar mass of 226.28 g/mol.

1.3 Draw the structures of **H**, **I**, and **J** indicating stereochemistry.

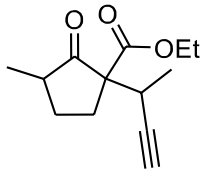
Hints:

- During the formation of **I**, sequential pericyclic reactions and an oxidation reaction (due to the presence of O_2) take place, and a well-known gas forms during the reaction.
- **J** has a strong and very broad band between 3300 and 2500 cm^{-1} in the IR spectrum.

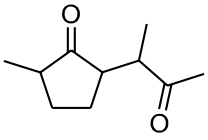
SOLUTION OF THE PROBLEM 1

1.1 The structures of **A** – **G** without stereochemical details (see the total synthesis of nepetalactone):

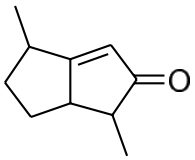
A



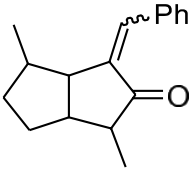
B



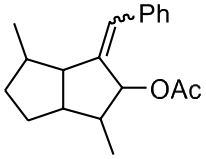
C



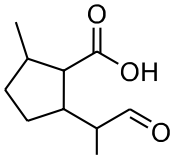
D



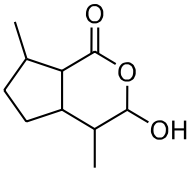
E



F



G



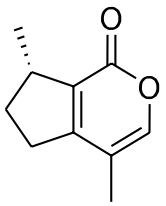
1.2 The correct answers are:

☑ Diastereomers

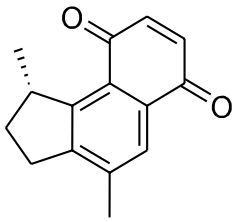
☑ Stereoisomers

1.3 The structures of **H**, **I**, and **J (**indicating stereochemistry):

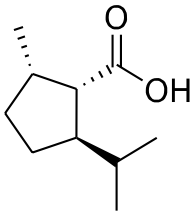
H



I



J

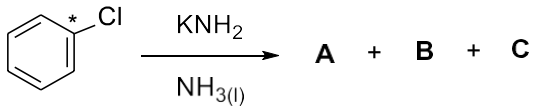


THEORETICAL PROBLEM 2

A tale of a reactive intermediate

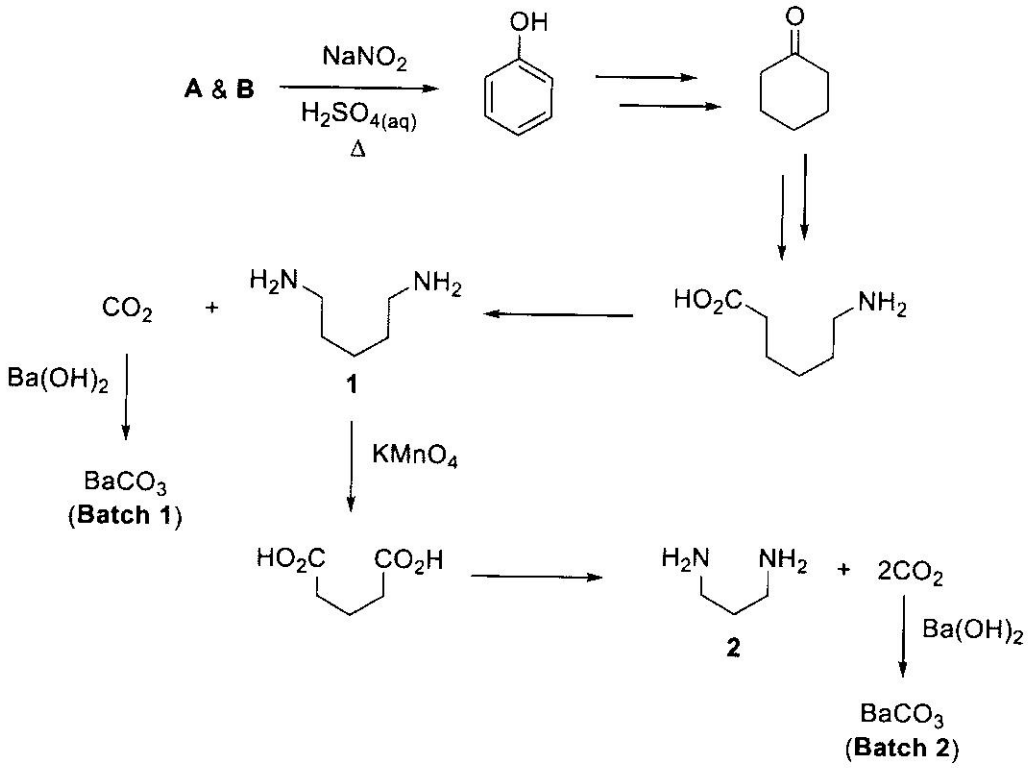
Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.

In one such experiment, chlorobenzene, whose carbon at position 1 was labeled with radioactive ^{14}C, was reacted with KNH_2 in liquid NH_3 to give nearly equal amounts of isotopic isomers **A** and **B** along with the inorganic salt **C**. This reaction proceeds via the formation of aryne intermediate **D**.



2.1 Draw the structure of **A**, **B** and **D**, and provide the formula of **C**. Indicate the position(s) of ^{14}C-labeled carbon(s) with an asterisk (*) whenever applicable."

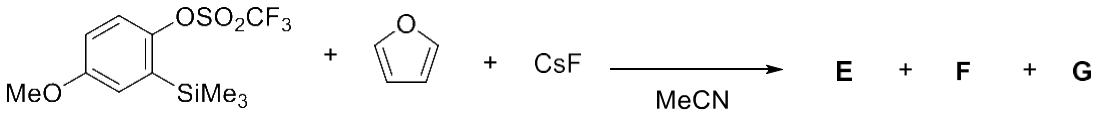
Analysis of the ^{14}C-labeled product(s) was achieved via degradation experiments (the ^{14}C- labeled carbons are not shown on the structures). Radioactivities of the intermediates and final products were examined.



2.2 Tick the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only **A**:	Considering only **B**:
☐ Compound **1**	☐ Compound **1**
☐ $BaCO_3$ (Batch **1**)	☐ $BaCO_3$ (Batch **1**)
☐ Compound **2**	☐ Compound **2**
☐ $BaCO_3$ (Batch **2**)	☐ $BaCO_3$ (Batch **2**)

With the aim of facilitating aryne formation, Kobayashi and co-workers developed a fluoride- induced aryne generation protocol. Using this method, benzene derivative **3** is reacted with furan (**4**) in the presence of CsF, resulting in the formation of **E**, **F**, and **G**.



3 **4**

- Combustion analysis of **E** revealed the following atom content: 75.8 % carbon, 5.8 % hydrogen, and 18.4% oxygen.
- **E** does not have a proton that is exchangeable with D_2O in ^{1}H-NMR spectroscopy.
- **F** is an ionic compound.

2.3 Determine the structures of **E**, **F**, and **G** (without stereochemical details).

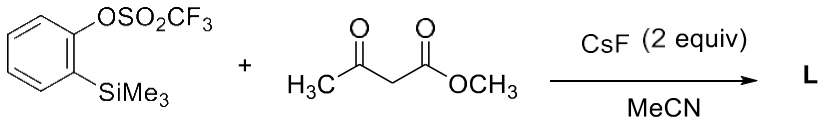
In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerization or [2+2+2]-type cyclotrimerization reactions under suitable conditions. The aryne derivative that is obtained when **3** is treated with one equivalent of CsF in MeCN can give, in principle, four different dimerization and trimerization products (**H** – **K**).

- **H** has two planes of symmetry.
- **I** is expected to exhibit 21 signals in its ^{13}C-NMR spectrum.
- **I** and **J** both exhibit an *m/z* value of 318.1 in their mass spectra.

2.4 Determine the structures of **H** – **K**.

When **5** is reacted with β-ketoester **6** in the presence of 2 equivalents of CsF at 80 °C, **L** is obtained as the major product. The ^{1}H-NMR and ^{13}C-NMR data for **L**, in $CDCl_3$, are as follows:

- ^{1}H-NMR: δ 7.79 (dd, J = 7.6, 1.5 Hz, 1H), 7.47–7.33 (m, 2H), 7.25–7.20 (m, 1H), 3.91 (s, 2H), 3.66 (s, 3H), 2.56 (s, 3H) ppm.
- ^{13}C-NMR: δ 201.3, 172.0, 137.1, 134.4, 132.8, 132.1, 130.1, 127.5, 51.9, 40.2, 28.8 ppm.



5 **6**

2.5 Determine the structure of **L**.

2.6 In the reaction shown in task **2.5**, which of the following statement(s) describe(s) the function of CsF?

- The pK_a values of HF and β-ketoester **6** in dimethyl sulfoxide (DMSO) are about 15 and 14, respectively.

☐ F^- hydrolyzes the trifluoromethanesulfonate (O_3SCF_3) group of **5**

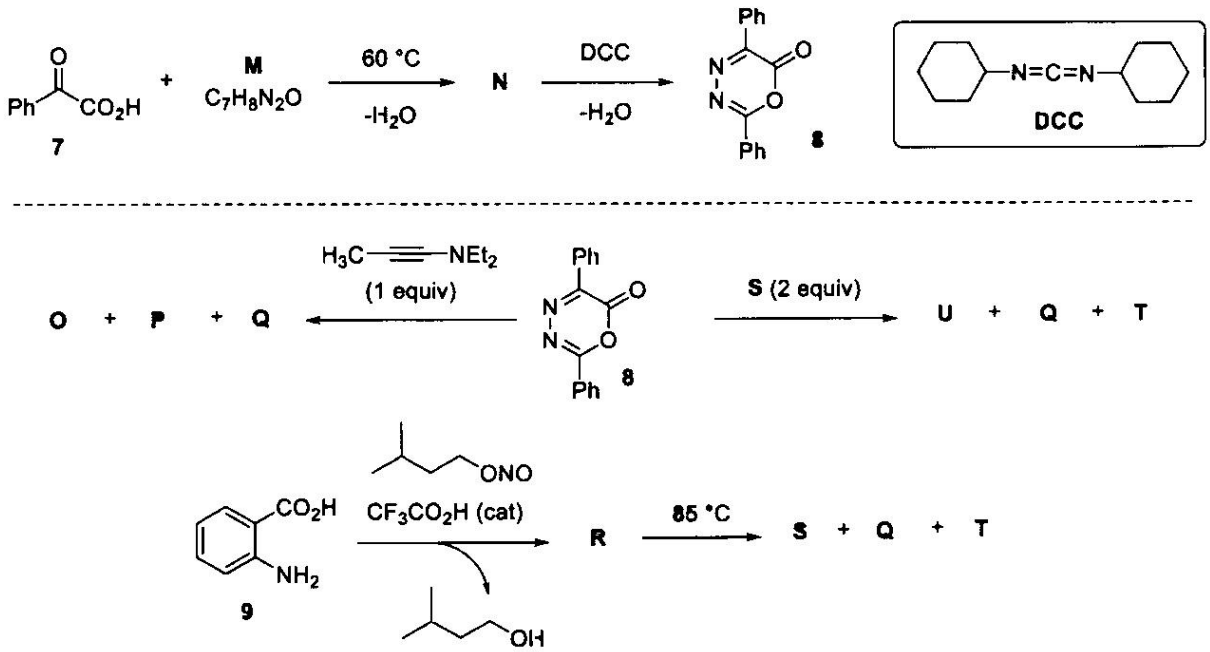
☐ F^- attacks the $-SiMe_3$ group of **5**.

☐ F^- acts as a base to deprotonate **6**.

☐ F^- acts as a nucleophile and attacks the ester group of **6**.

Diazapyrone derivative **8** was shown to be a useful reactant for the construction of a variety of cyclic frameworks. Its preparation from phenylglyoxylic acid (**7**) and its use in two different reactions are described below.

- **Q** and **T** are gases under ambient conditions.
- **O** and **P** are constitutional isomers.
- **Q** does not have any signals in its IR spectrum.
- Heating 1 mol of **R** at 85 °C generates 1 mol of reactive intermediate **S**.
- Reaction of **8** with two equivalents of **S** gives **U**, **Q**, and **T**.



Note:

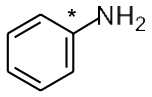
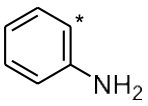
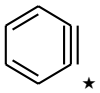
equiv = equivalent

cat = catalyst

2.7 Determine the structures of **M** – **U**.

SOLUTION OF THE PROBLEM 2

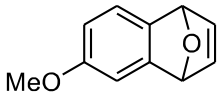
2.1 The structures of **A** – **D** are as follows. The position(s) of ^{14}C-labeled carbon(s) are indicated with an asterisk (*).

A 	**B** 
C KCl or 	**D** 

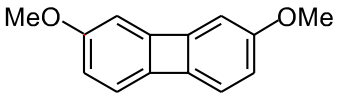
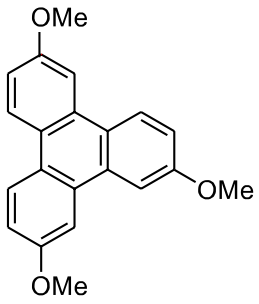
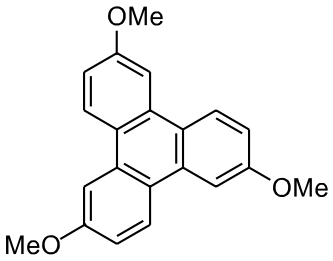
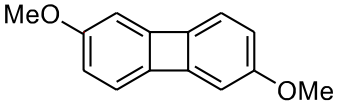
2.2 Tick the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only **A:**	Considering only **B**:
☐ Compound 1	☑ Compound **1**
☑ $BaCO_3$ (Batch **1**)	☐ $BaCO_3$ (Batch **1**)
☐ Compound **2**	☐ Compound **2**
☐ $BaCO_3$ (Batch **2**)	☑ $BaCO_3$ (Batch **2**)

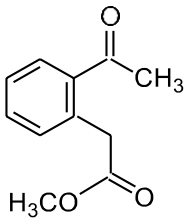
2.3 The structures of **E**, **F**, and **G** (without stereochemical details):

E	**F**
	CsO_3SCF_3 or $Cs^+CF_3SO_3^-$ or CsOTf
G	
$(CH_3)_3SiF$ or Me_3SiF	

2.4 The structures of **H** – **K**.

H	**I**
	
J	**K**
	

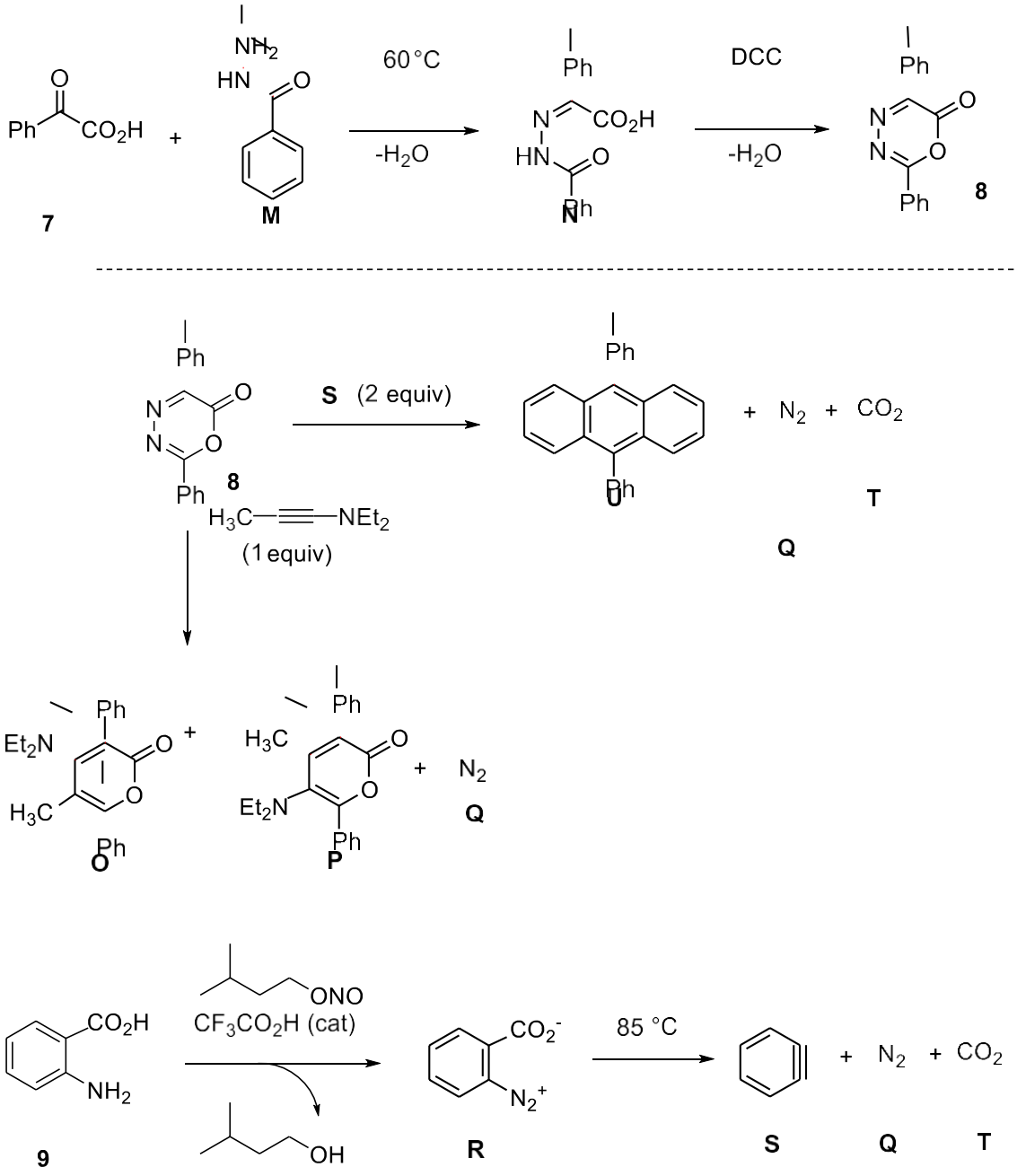
2.5 The structure of **L:**



2.6 In the reaction shown in task **2.5**, the following statement(s) in the answer sheet describe(s) the function of CsF:

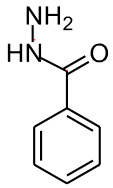
☑ F^- attacks the $-SiMe_3$ group of **5**.

☑ F^- acts as a base to deprotonate **6**.

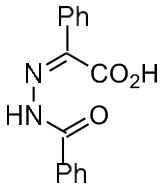


2.7 The structures of **M** – **U**.

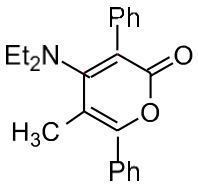
M



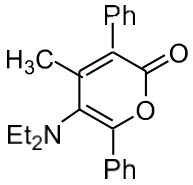
N



O and **P**



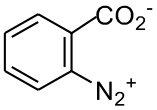
and



Q

N_2

R

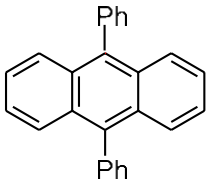


S

T

CO_2

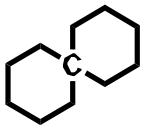
U



THEORETICAL PROBLEM 3

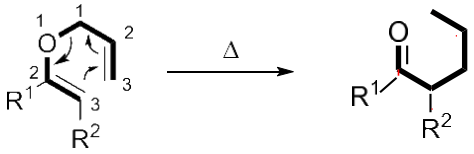
(±)-Coerulescine

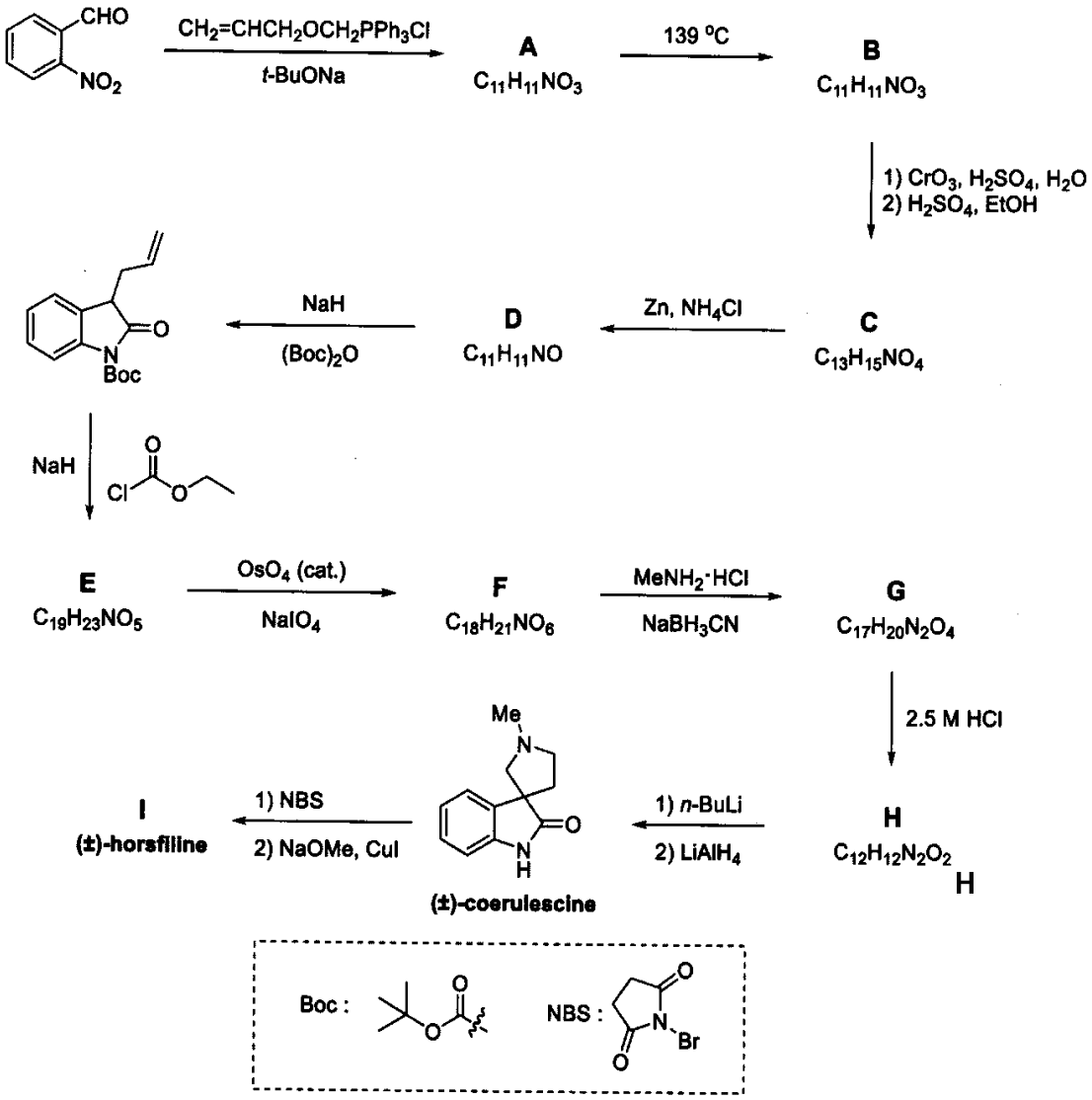
A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom) as carbon atom with bold in figure below. The spiro[pyrrolidin-3,3′- oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds. Coerulescine (**1**) and horsfiline are the simplest prototype members of this subfamily that can be synthesized by the route shown below.



Claisen rearrangement, which is a [3,3]-sigmatropic rearrangement, is a powerful carbon– carbon bond-forming reaction in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound as shown in the Scheme below. When compound **A** is heated, it undergoes Claisen rearrangement to give carbonyl compound **B**.

For this entire task, your answers can be given without any stereochemical details.





3.1 Draw the structures of **A** and **B**.

- **A** is an inseparable mixture of *cis/trans* isomers.
- **B** has IR absorption at 1726 cm^{-1}.

3.2 Draw structures for **C**, **D**, **E**, and **F**.

- **D**–**F** have a bicyclic structure.

3.3 Choose the correct order of steps for the transformation of **F** to **G**.

☐ Imine formation, then reduction, then amidation

☐ Amidation, then imine formation, then reduction

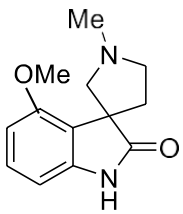
☐ Reduction, then amidation, then imine formation

3.4 Draw the structures for **G** and **H** (both spiro compounds).

3.5 Draw the structure of the intermediate produced by treatment with *n*-BuLi in the step **H** → coerulescine (1).

Coerulescine (1), on treatment with *N*-bromosuccinimide (NBS), gives the bromo derivative, which upon heating with sodium methoxide in the presence of cuprous iodide gives **horsfiline** (**I**) in 60% yield.

3.6 Choose the correct structure for compound **I** consistent with the following selected ^{1}H-NMR data: δ 7.05 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.4 Hz, 1H) ppm. Tick the relevant box.



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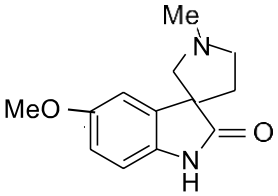

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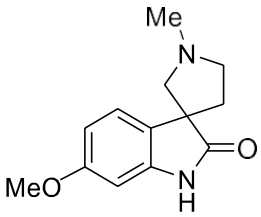

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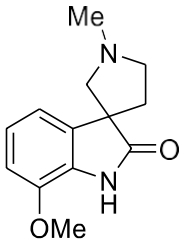

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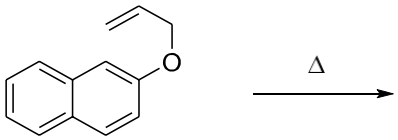
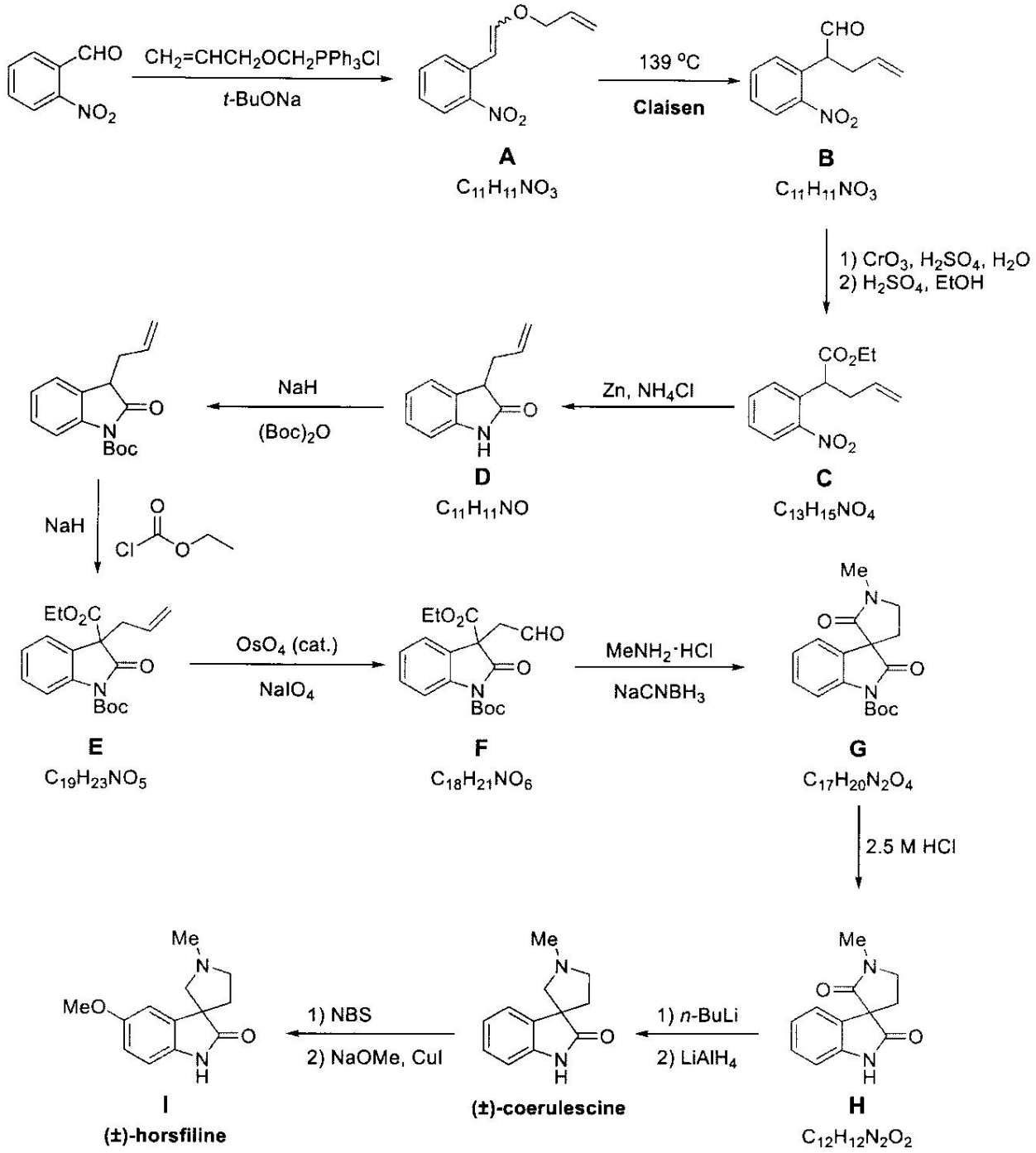
3.7 When the allyl ether of 2-naphthol is heated a sigmatropic rearrangement is initiated. Write the structure of major product isolated from this reaction.

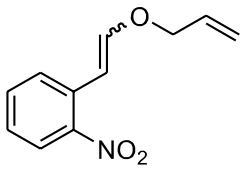
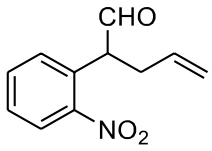


SOLUTION OF THE PROBLEM 3

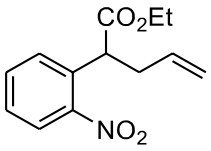
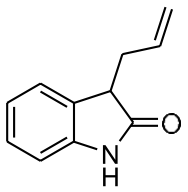
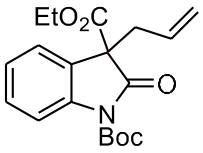
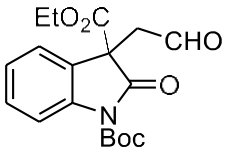
Reaction scheme:



3.1 The structures of **A** and **B** are as follows:

A	B
	

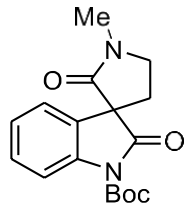
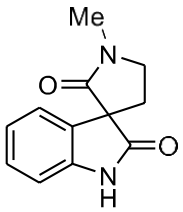
3.2 The structures of **C**, **D**, **E** and **F**:

C	D
	
E	**F**
	

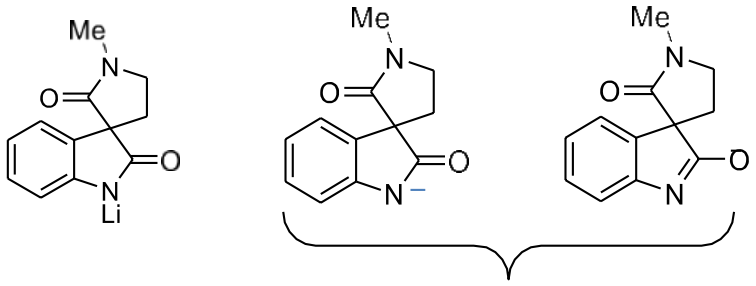
3.3 The correct reaction order for the transformation of **F** to **G:**

☑ Imine formation, then reduction, then amidation.

3.4 The structures of **G** and **H**:

G	H
	

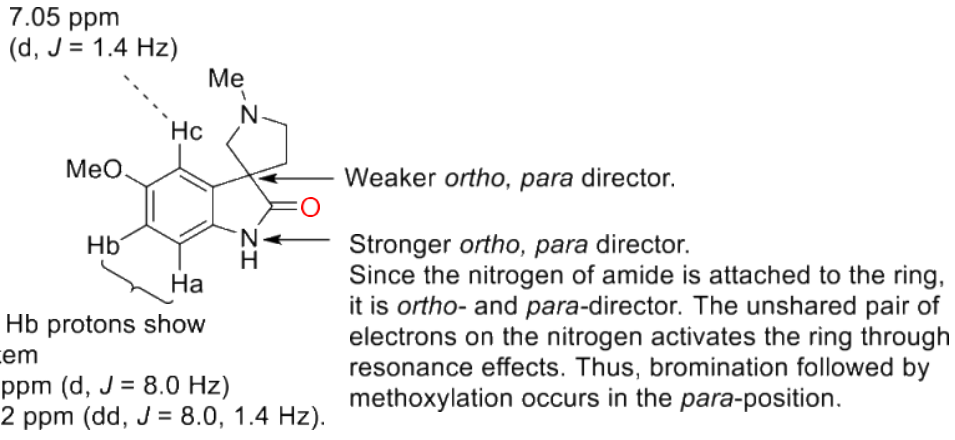
3.5 The structure of the intermediate for the reaction with *n*-BuLi in the step **H** → **coerulescine**.



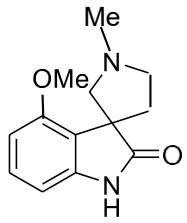
acceptable

Regioselective reduction of carbonyl group can be achieved via lithiation of free NH.

3.6 The correct structure for compound **I** consistent with the following selected ^{1}H-NMR data: δ 7.05 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.4 Hz, 1H) ppm is as follows:



NMR data are compatible with this structure,
but not compatible with the possible *ortho*-substitute product.



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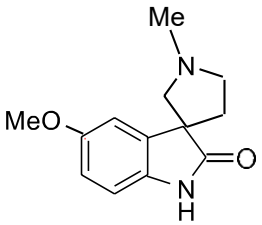

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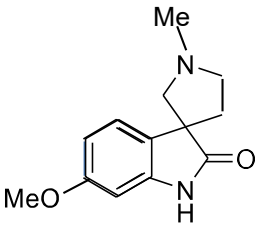

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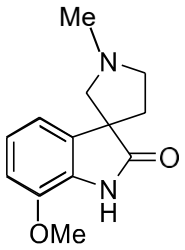

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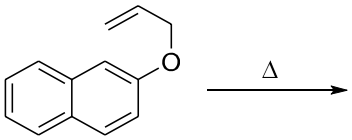
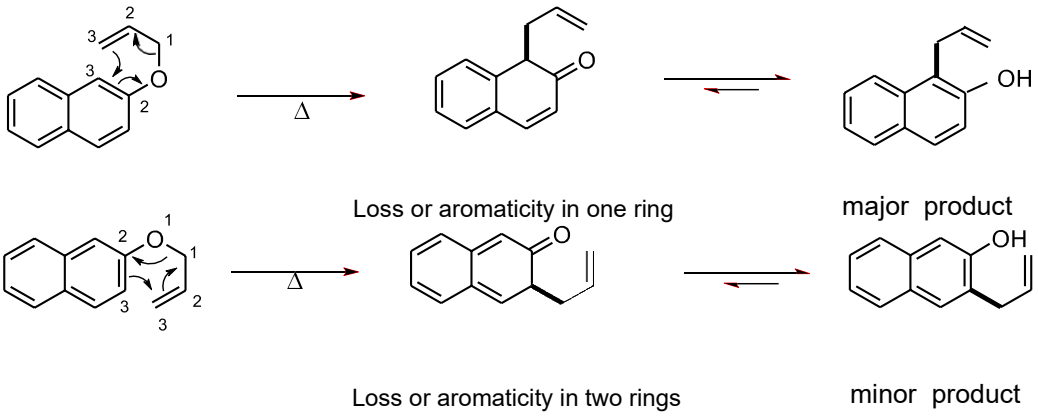
3.7 When the allyl ether of 2-naphthol is heated a sigmatropic rearrangement is initiated. The structure of major product isolated from this reaction:



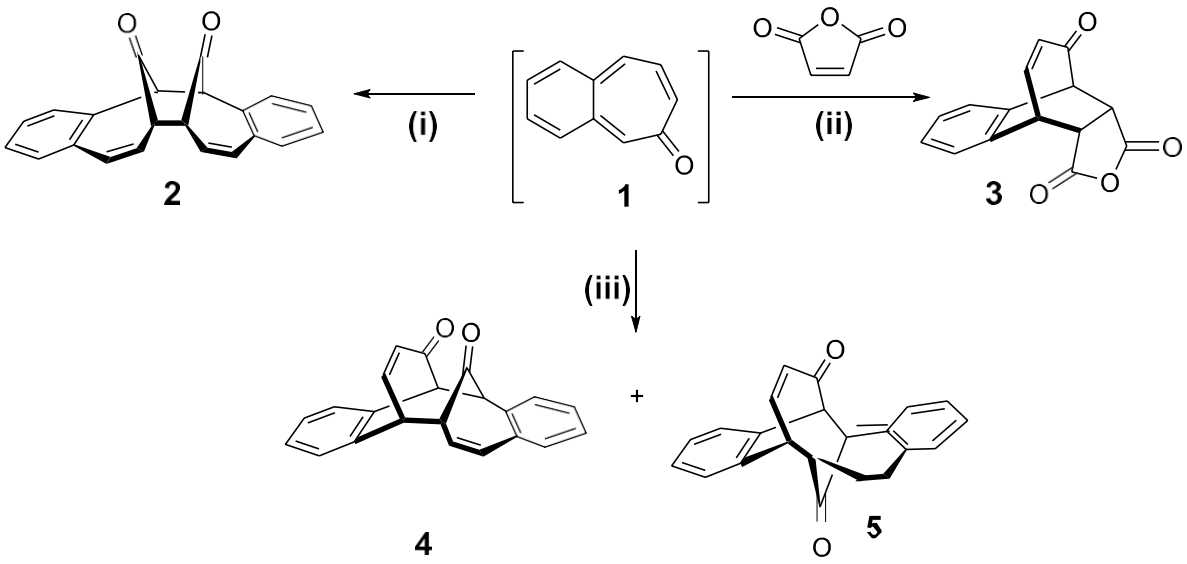
The correct structure:



THEORETICAL PROBLEM 4

Symmetry Does Matter

There are numerous reactions in organic chemistry that proceed through cyclic transition states and these are classified as pericyclic reactions. Woodward–Hoffmann rules, developed by Robert B. Woodward and Roald Hoffmann, are used to rationalize stereochemical aspects and the activation energy of pericyclic reactions.



Woodward–Hoffmann rules				
	Electrocyclic reactions		**Cycloadditions**	
Number of electrons	Thermal (Δ)	Photochemical (hν)	Thermal (Δ)	Photochemical (hν)
$4n$ (n = 1, 2, ..)	Conrotatory (con)	Disrotatory	Disfavored	Favored
$4n+2$ (n = 1, 2, ..)	Disrotatory (dis)	Conrotatory	Favored	Disfavored

4.1 Fill in the table for reactions (**i**)–(**iii**) or products **2**–**5**:

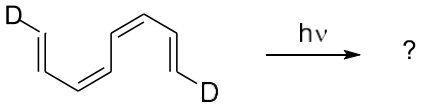
Reaction	Product	[? + ?] cycloaddition	Δ or hν
i	**2**		
ii	**3**		
iii	**4**		
	5		

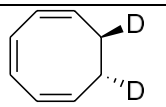
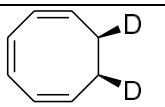
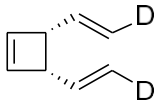
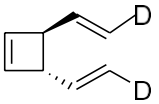
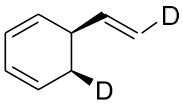
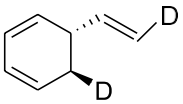
There are three possible benzotropone isomers. Although two of the benzotropone isomers were isolated, 3,4-benzotropone (**1**) has not been isolated. Its instability is attributed to the *o*- quinoidal structure of **1** because it has no sextet electron system in the

benzene ring.

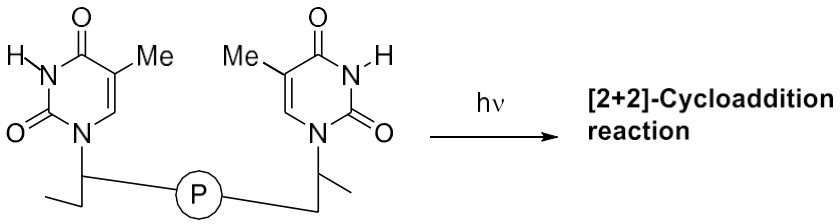
4.2 Draw the structures of stable benzotropone isomers **A** (with 6 signals in its ^{13}C-NMR) and **B** (with 11 signals in its ^{13}C-NMR).

4.3 When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) of three different ring sizes can form according to the Woodward–Hoffmann rules. Tick the correct answer in each row.



☐		☐	
☐		☐	
☐		☐	

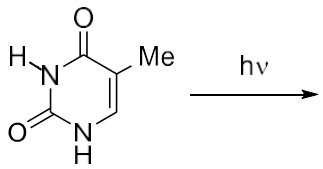
Prof. Dr. Aziz Sancar



The Nobel Prize in Chemistry 2015 was awarded jointly to the Turkish scientist Aziz Sancar, Swedish scientist Tomas Lindahl, and American scientist Paul Modrich for their “mechanistic studies of DNA repair”. Pyrimidine bases found in DNA may undergo a photochemical **[2+2]-cycloaddition reaction** (see figure above) with UV light that reaches a person’s skin, causing damage to DNA, which may ultimately lead to skin cancer. The research by Professor Aziz Sancar focused on the DNA repair mechanism for this type of damage.

Thymine (**T**) is one of the nucleobases that can undergo such a photochemical

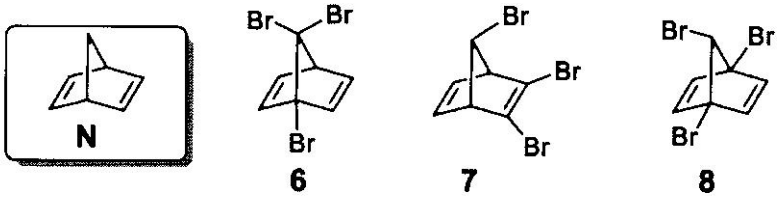
reaction with UV light. Let us assume that we have a solution of free thymine that was subjected to UV irradiation.



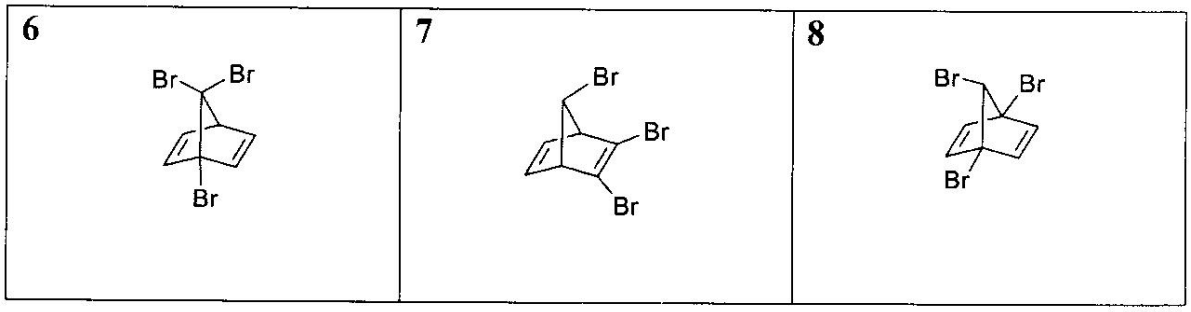
T

4.4 Considering stereochemistry, draw the structures of all possible products of this reaction between two free thymine (**T**) molecules. Circle the compound(s) which is/are chiral. A drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction.

A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral (meso) isomers. Three of these isomers (**6, 7** and **8**) are given below.



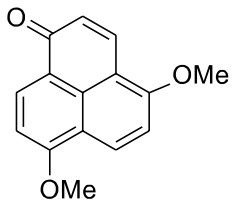
4.5 How many signals do you expect from the ^{13}C-NMR spectra of **6**, **7**, and **8**? Fill in the following boxes.



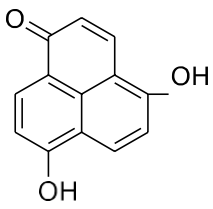
4.6 Draw structures of the remaining achiral (meso) tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to **6** – **8** over the given figures in the boxes.

C	D	E
		

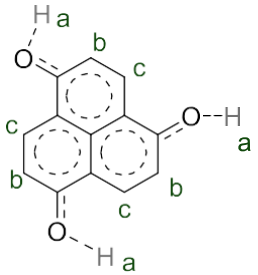
The NMR spectrum of ether **9** is complex. Two MeO– groups are different as are all the hydrogen atoms on the rings. However, diphenol **10** has a very simple NMR spectrum and there are only three types of protons (marked as a, b, and c). A reasonable average structure responsible for all resonance structures and its symmetry is shown as **11**.



9

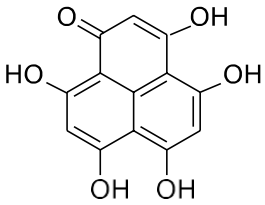


10

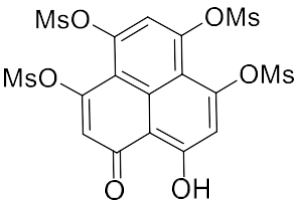


11

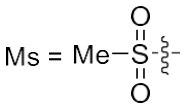
4.7 How many signals do you expect from the ^{13}C- and ^{1}H-NMR spectra of **12** and **13**?



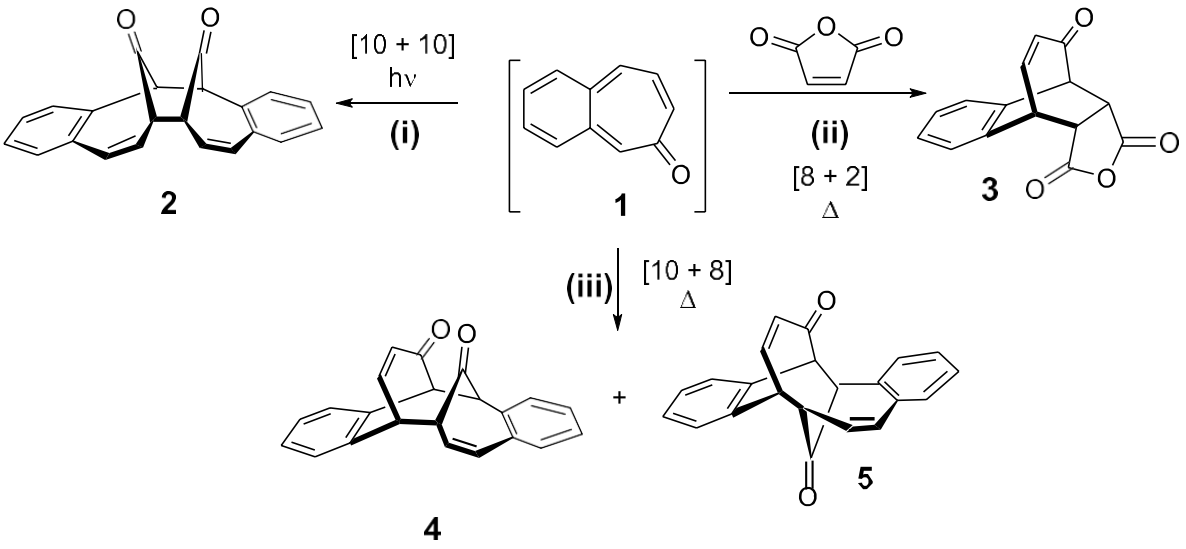
12



13



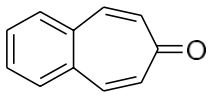
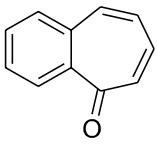
SOLUTION OF THE PROBLEM 4



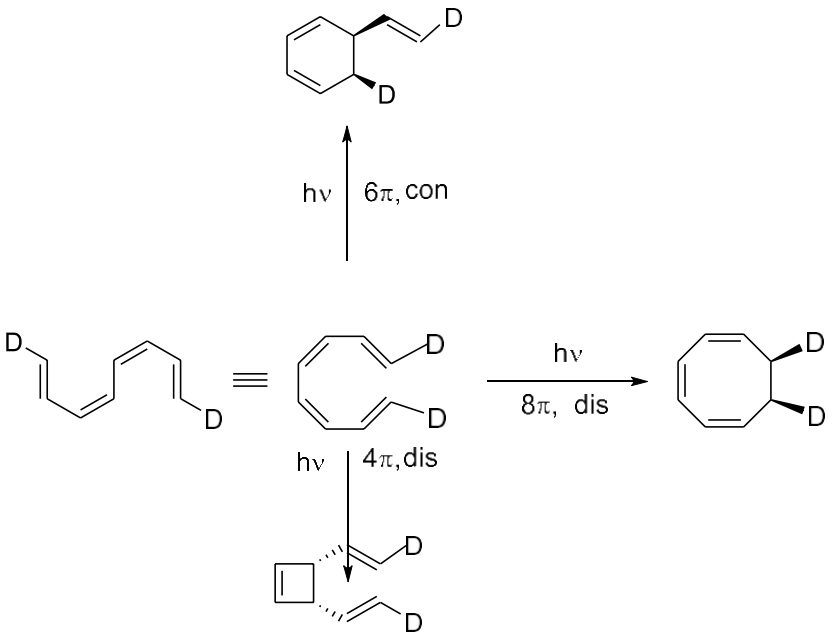
4.1 Fill **i**n the table for reactions (**i**)–(**iii**) or products **2**–**5**:

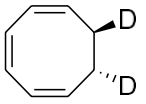
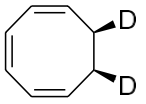
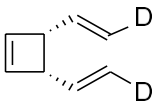
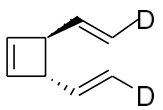
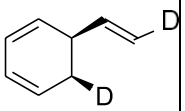
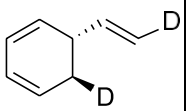
Reaction	Product	[? + ?] cycloaddition	Δ or hν
i	**2**	[10 + 10]; ([6 + 6] is also acceptable)	hν
ii	**3**	**[8** + 2]; ([4 + 2] is also acceptable).	Δ
iii	**4**	[10 + 8]; ([6 + 4] is also acceptable).	Δ
	5	[10 + 8]; ([6 + 4] is also acceptable).	Δ

4.2 Draw the structures of stable benzotropone isomers **A** (with 6 signals in its ^{13}C-NMR) and **B** (with 11 signals in its ^{13}C-NMR).

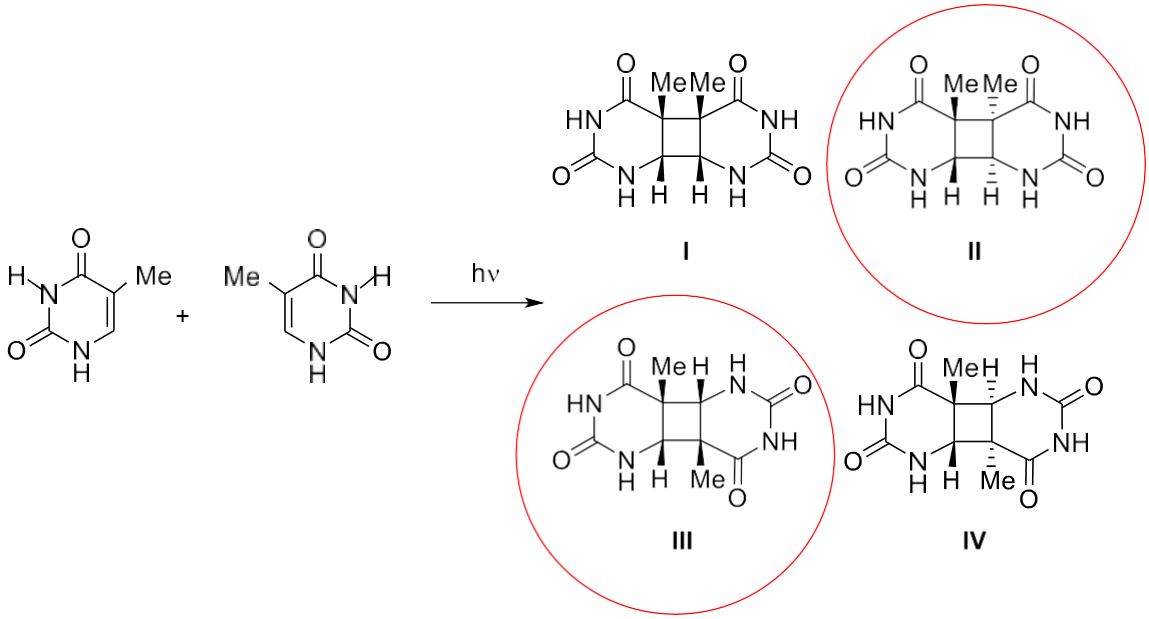
A	B
	

4.3 When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) can form according to the Woodward–Hoffmann rules. Tick the correct answer(s).

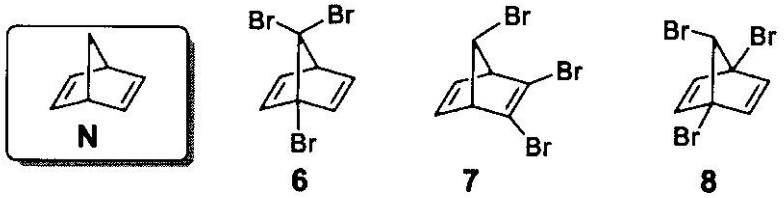


☐		☑	
☑		☐	
☑		☐	

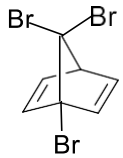
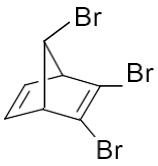
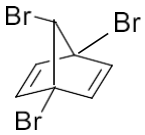
4.4



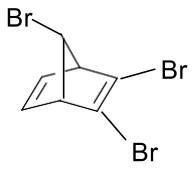
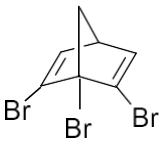
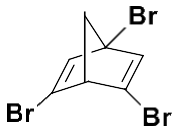
A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral (meso) isomers. Three of these isomers (**6, 7** and **8**) are given below.



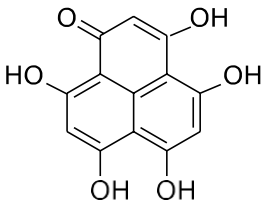
4.5 The numbers of signals expected from the ^{13}C-NMR spectra of **6**, **7**, and **8** are given in the following boxes:

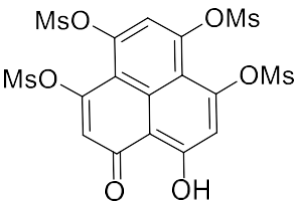
6	**7**	**8**
		
5 signals in ^{13}C-NMR	4 signals in ^{13}C-NMR	4 signals in ^{13}C-NMR

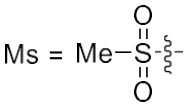
4.6 The open structures of the remaining achiral (meso) tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) are given in the following boxes:

C	D	E
		

4.7 The number of signals that are expected in the ^{13}C- and ^{1}H-NMR spectra of **12** and **13:**







12	**13**
4 signals in ^{13}C-NMR	10 signals in ^{13}C-NMR
2 signals in ^{1}H-NMR	5 signals in ^{1}H-NMR

THEORETICAL PROBLEM 5

Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision

Mevlana (Rumi) was a great mystic and Sufi poet who lived out his days in Konya in the 13th century. The indirect relevance of Konya to chemistry is that the city provides 65% of the country's carrot production, from which one of the essential vitamins (vitamin A) is obtained.

Carrot is an important source of β-carotene, which gives the vegetable its orange color. This molecule is a red-orange pigment naturally found in plants and fruits and is a provitamin A carotenoid. It is converted to vitamin A, which is essential for normal growth and development, the immune system, and vision function.

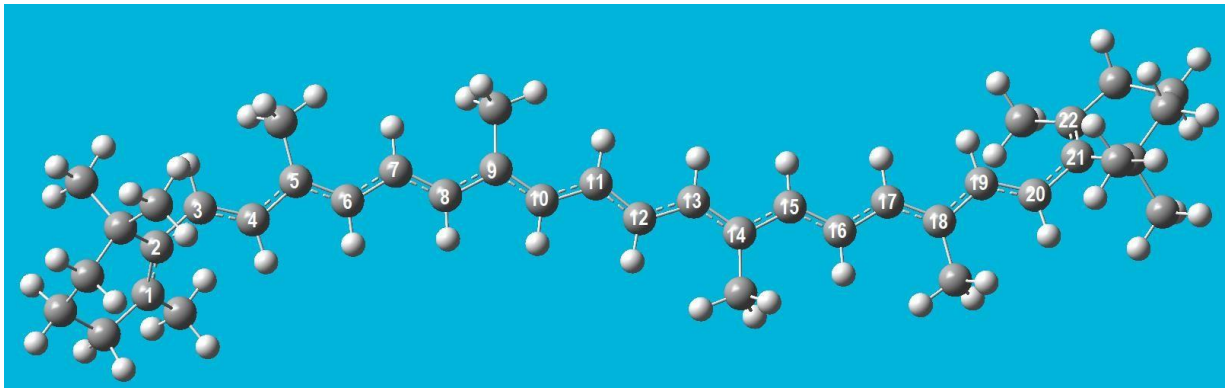


Figure 1. Ball and stick representation of the structure of β-carotene. The gray and white spheres represent the carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π-segment of the molecule.

β-Carotene has an extended polyene chain of 22 carbon atoms. It is a conjugated π-system, having alternating single and double bonds. Its experimental maximum absorption wavelength (λ_{max}) is 455 nm. We assume that all the bonds between C_1 and C_{22} are conjugated bonds. There are 22 π-electrons in the molecule (Figure 1).

To a crude approximation, the electrons in the C-$2p_z$ orbitals, which are perpendicular to the molecular plane, are assumed to move along the entire molecule, without interacting with each other. They are like independent particles confined in a molecule moving along the x-axis in one dimension. These characteristics of π-electrons make them eligible for being treated by the simplest model called the **particle in one-dimensional box** model.

The wave function and the energies of the quantized levels for an electron moving in a one- dimensional box with infinite potential walls are given as follows:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

here n is the quantum number, n = 1,2,3,4,….∞, and L is the box length.

$$E_n = \frac{n^2 h^2}{8 m_e L^2}$$

In two dimension system, within the framework of independent particle approximation, the wavefunction is expressed as a product of one-dimensional wavefunctions, and the energy is expressed as a sum of one-dimensional energies. The energy levels of the two dimensional rectangular box is given as follows:

$$E_{n_x n_y} = \left[\frac{n_x{}^2}{L_x{}^2} + \frac{n_y{}^2}{L_y{}^2}\right]\left\{\frac{h^2}{8 m_e}\right\}$$

L_y e x

where n_x, n_y are the quantum numbers and they are positive integers. L_x, L_y are the dimensions of the box in the 2D model. They are positive numbers.

5.1 The β-carotene molecule is orange in color because:

i) It absorbs in the visible region of the electromagnetic spectrum.

ii) HOMO → LUMO transition occurs by absorption of IR photon.

iii) The spacing between the 22nd and the 23rd energy levels is equal to the energy of the IR photon at the orange wavelength.

iv) It absorbs green/blue light and it transmits red/yellow color.

v) It absorbs in the UV-VIS region since the molecule has no net dipole moment.

Choose which pair of the above sentences is correct?

The pairs of sentences are as follows:

☐ a) i and ii ☐ b) i and iii ☐ c) i and iv ☐ d) i and v

☐ e) ii and iii ☐ f) ii and iv ☐ g) ii and v ☐ h) iii and iv

☐ j) iii and v ☐ k) iv and v

Although it is highly unrealistic, let us assume that the conjugated segment of the molecule is linear and treated with the particle in a one-dimensional box model as shown in figure 2. In this case, the length of the box can be approximated as $L = 1.40 \times n_C$ (in Å), where n_C is the number of carbon atoms in the conjugated segment.

Use this information to answer the questions 5.2–5.6.

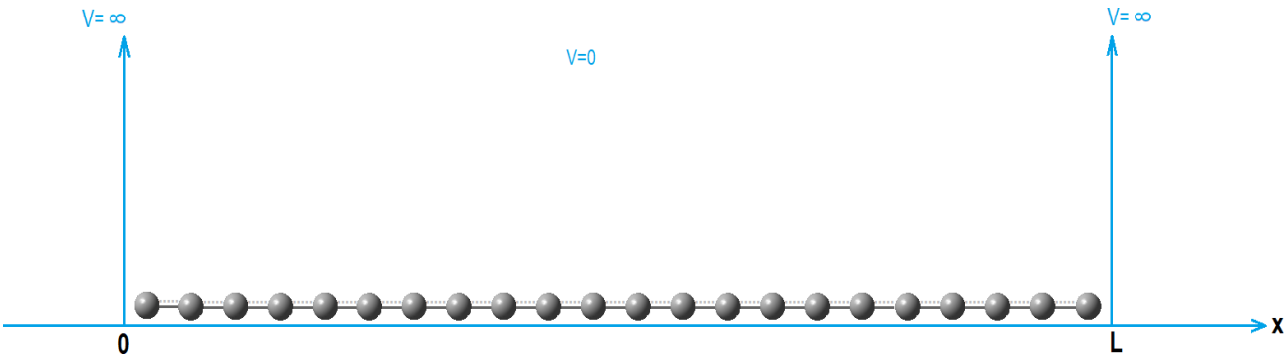


Figure 2. Schematic representation of the conjugated line segment made up carbon atoms of β-carotene in a one-dimensional box of length L.

5.2 Calculate the energies (in J) of the lowest two energy levels.

5.3 Draw the wavefunctions of the lowest two energy levels with proper labelling the x-axis.

5.4 Sketch the energy level diagram up to $n = 4$ showing the relative spacing.

5.5 What is the total π-energy (in J) of the molecule?

5.6 Calculate the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.

Use the particle in a two-dimensional box model to answer questions 5.7 – 5.8.

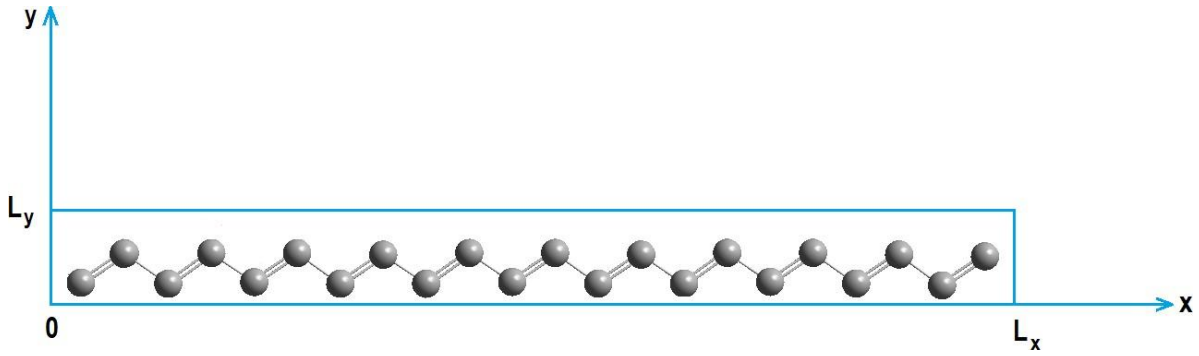


Figure 3. Schematic representation of the conjugated carbon atoms of β-carotene in a two-dimensional box.

Assume that the conjugated segment is made up of conjugated bonds that are all-trans to each other. The motion of the π-electrons is studied in the two-dimensional rectangular box with the dimensions L_x = 26.0 Å, L_y = 3.0 Å (Figure 3).

5.7 Calculate the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these energy levels occurs.

5.8 What should be the L_x value (in Å) in order for the molecule to absorb light at the experimental λ_{max}=455 nm if L_y is kept constant at 3.0 Å. (Assume that the quantum numbers for homo and lumo are the same as in the question 5.7.)

SOLUTION OF THE PROBLEM 5

5.1 The correct answer: ☑ **c)** i and iv.

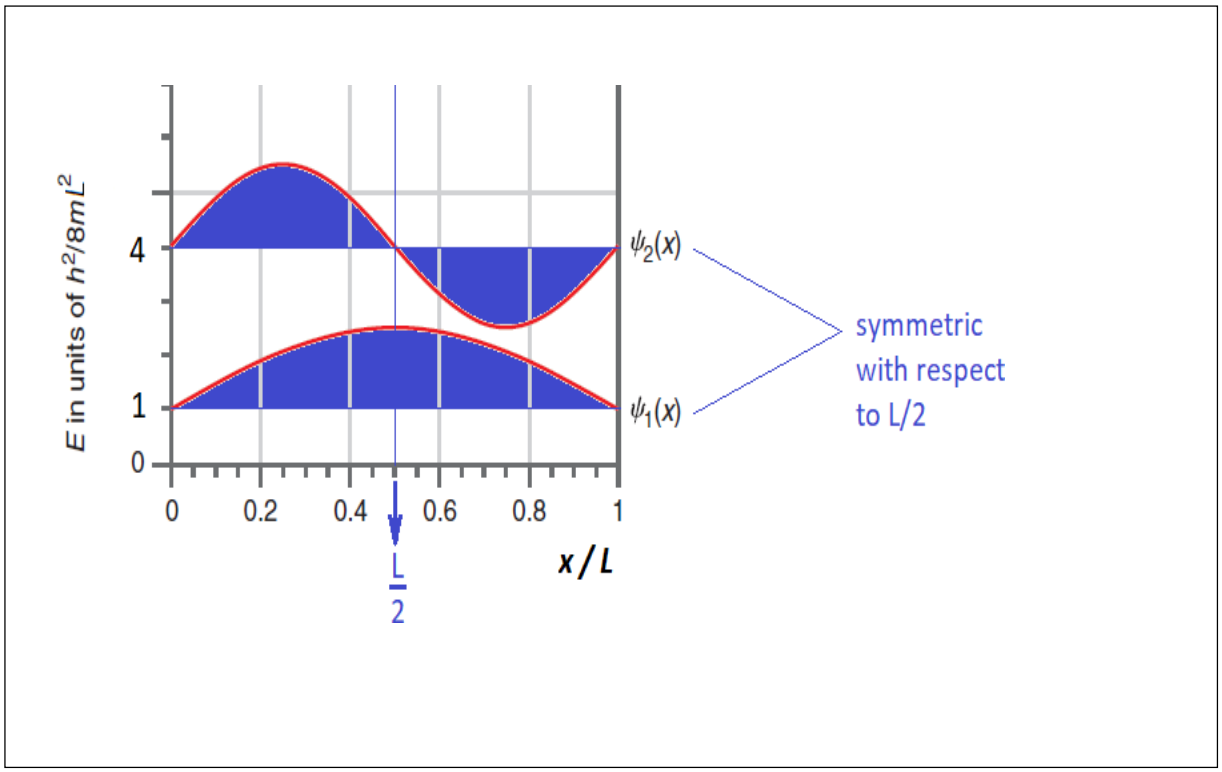
5.2 Calculation:

$L = 1.40 \times 22 = 30.8$ Å

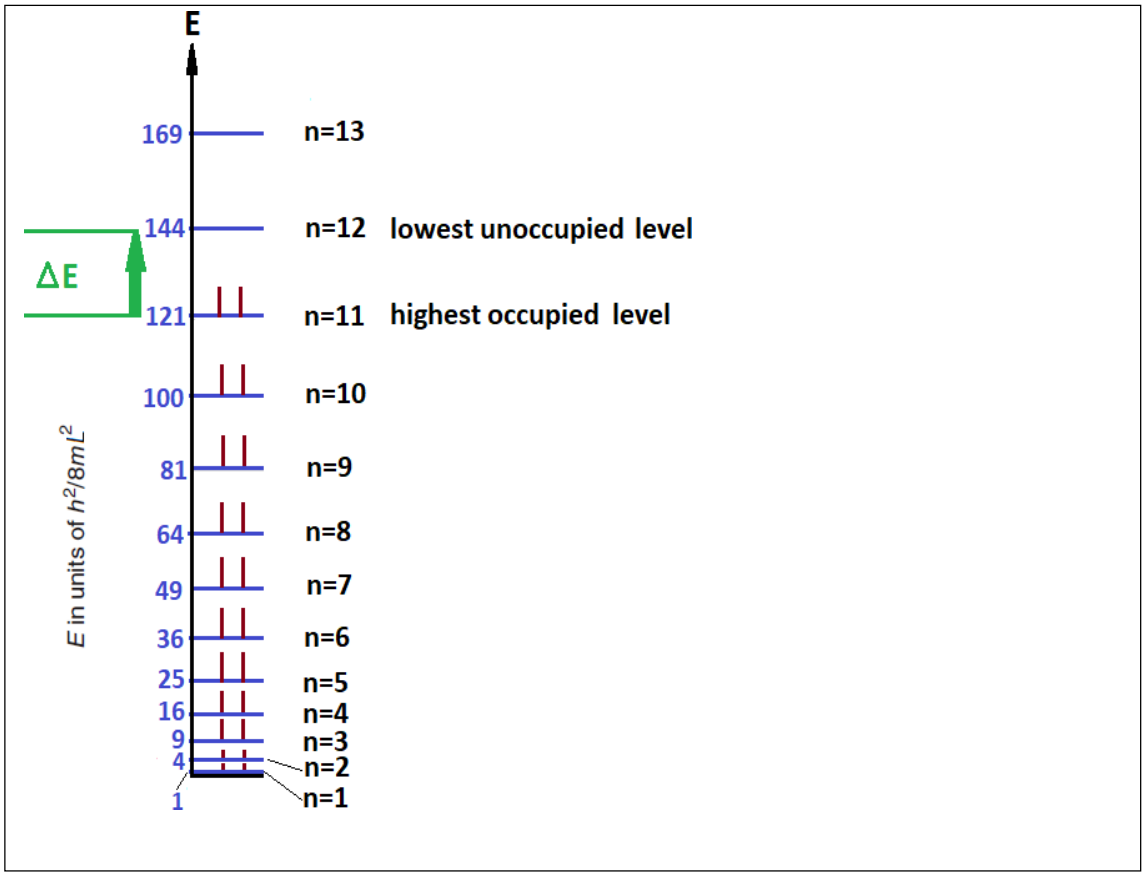
$$E_n = \frac{n^2 h^2}{8 m_e L^2} = n^2 (6.351 \times 10^{-21})\ \text{J}$$

$E_1 = 6.351 \times 10^{-21}$ J $\quad E_2 = 2.540 \times 10^{-20}$ J

5.3 The wavefunction of the lowest two energy levels with proper labelling the x-axis:



5.4 The energy level diagram up to $n = 4$ showing the relative spacing is shown on the next page.



5.5 Calculation of the total π-energy (in J) of the molecule:

$$E_{\pi(total)} = 2\sum_{i=1}^{o.l.} E_1 \quad (o.\,l. = occupied\ levels)$$

E_π (total) = 2 × (E_1+E_2+E_3+E_4+E_5+E_6+E_7+E_8+E_9+E_{10}+E_{11}) = 6.427 × 10^{-18} J

5.6 Calculation the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs:

The quantum numbers for the highest occupied and lowest unoccupied energy levels are 11 and 12, respedtively.

$$\Delta E = E_{12} - E_{11} = E_n = \frac{12^2\,h^2}{8\,m_e L^2} - \frac{11^2\,h^2}{8\,m_e L^2} = \frac{23\,h^2}{8\,m_e L^2} = \frac{hc}{\lambda} \quad \text{then}$$

$$\lambda = \frac{8\,m_e c\,L^2}{23\,h} = 1360 \text{ nm}$$

5.7 Calculation of the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these

energy levels occurs:

$$E_{n_x n_y} = \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]\left\{\frac{h^2}{8\,m_e}\right\} = \left[\frac{n_x^2}{26^2} + \frac{n_y^2}{3^2}\right] 6.025\times10^{-18}\ \text{J},$$

where L_x and L_y should be in Å

The quantum numbers and the energies of the highest occupied and the lowest unoccupied energy levels are:

$n_x = 11$, $n_y = 1$ and $n_x = 12$, $n_y = 1$

$$E_{11,1} = \left[\frac{11^2}{26^2} + \frac{1^2}{3^2}\right] 6.025\times10^{-18}\ \text{J} = 17.48\times10^{-19}\ \text{J}$$

$$E_{12,1} = \left[\frac{12^2}{26^2} + \frac{1^2}{3^2}\right] 6.025\times10^{-18}\ \text{J} = 19.53\times10^{-19}\ \text{J}$$

The transition wavelength is:

$\Delta E = E_{12,1} - E_{11,1} = (19.53 - 17.48)\times10^{-19}\ \text{J} = 2.050\times10^{-19}\ \text{J}$

$\Delta E = E_{photon} = (hc)/\lambda$ and $\lambda = (hc)/\Delta E = 9.69\times10^{-7}\ \text{m}$ $\lambda = 969\ \text{nm}$

5.8 Calculation:

$$\Delta E = \left[\frac{12^2}{L_x^2} + \frac{1^2}{L_y^2} - \frac{11^2}{L_x^2} - \frac{1^2}{L_y^2}\right]\left\{\frac{h^2}{8\,m_e}\right\} = \left[\frac{23}{L_x^2}\right] 6.025\times10^{-18}\ \text{J} = \frac{1.386\times10^{-18}}{L_x^2}\quad (L_x \text{ is in Å})$$

$$\Delta E = E_{photon} = \frac{hc}{\lambda} \rightarrow \frac{1.386\times10^{-18}}{L_x^2} = \frac{6.626\times10^{-34}\times2.998\times10^{8}}{455\times10^{-9}}$$

$L_x = 1.782\times10^{-9}$ m **$L_x = 17.82$ Å**

THEORETICAL PROBLEM 6

Thermodynamics through an Interstellar Journey

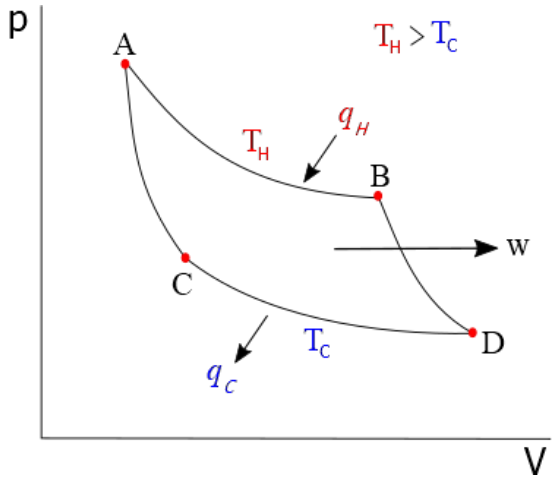
Part 1

In a hypothetical universe, an unknown amount of diborane participates in the following reaction:

$$B_2H_6(g) + 6\ H_2O(l) \rightarrow 2\ H_3BO_3(s) + 6\ H_2O(g)$$

Assume that in this hypothetical universe, $H_3BO_3(s)$ obtained from this reaction was completely sublimed at 300 K. The necessary energy for sublimation was obtained through work released by **one cycle** of an ideal heat engine in which one mole of monoatomic perfect gas flows through the cycle described in the pressure (p) – volume (V) diagram below:

- A→B; isothermal reversible expansion receiving 250 J by heat transfer (q_H) at a temperature of 1000 K (T_H) from a hot source.
- B→D; reversible adiabatic expansion.
- D→C; isothermal reversible compression at a temperature of 300 K (T_C) releasing some amount of heat (q_C) to a cold sink.
- C→A; reversible adiabatic compression.



After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

$$\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C}$$

The efficiency of the cycle can be found by work released by cycle (w) divided by heat absorbed by cycle (q_H).

You are provided with the change in enthalpies of the following reactions at 300 K.

(1) $B_2H_6(g) + 6\ Cl_2 \rightarrow 2\ BCl_3(g) + 6\ HCl(g)$ $\Delta_rH(1) = -1326$ kJ mol^{-1}

(2) $BCl_3(g) + 3\ H_2O(l) \rightarrow H_3BO_3(g) + 3\ HCl(g)$ $\Delta_rH(2) = -112.5$ kJ mol^{-1}

(3) $B_2H_6(g) + 6\ H_2O(l) \rightarrow 2\ H_3BO_3(s) + 6\ H_2(g)$ $\Delta_rH(3) = -493.4$ kJ mol^{-1}

(4) $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightarrow HCl(g)$ $\Delta_rH(4) = -92.3$ kJ mol^{-1}

6.1 Calculate the molar enthalpy of sublimation (in kJ mol^{-1}) for H_3BO_3 at 300 K.

6.2 Calculate the Δ_rU (internal energy) in terms of kJ mol^{-1} at 300 K for the reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).

6.3 Calculate the amount of overall work produced by a heat engine ($|w|$) in terms of J and the amount of overall heat released to the cold sink ($|q_C|$) in terms of J.

6.4 Calculate the efficiency of the heat engine described above.

6.5 Calculate the entropy change (ΔS) for A→B and D→C processes in the heat engine in terms of J K^{-1}.

6.6 Calculate the Gibbs energy change (ΔG) in terms of J for A→B and D→C processes in the heat engine.

6.7 Calculate the ratio of pressure at point A to the pressure at point B in the cycle (standard pressure: 1 bar).

6.8 Calculate the amount of $H_2(g)$ (in moles) produced according to the reaction given at the beginning of the task for one cycle of the engine.

Part 2

Interstellar journeys can be done by using diborane as rocket fuel. Combustion of diborane is shown below:

$$B_2H_6\,(g) + 3\ O_2\,(g) \rightarrow B_2O_3\,(s) + 3\ H_2O\,(g)$$

Combustion of diborane is experimented in a closed container (100 dm^3) at different temperatures and the equilibrium amounts were recorded.

Temperature	**8930 K**	**9005 K**
B_2H_6(g)	0.38 mol	0.49 mol
H_2O(g)	0.20 mol	0.20 mol

Partial pressure of O_2(g) was stabilized to 1 bar and kept constant at all conditions. Assume that in this hypothetical universe; $\Delta_r S°$ and $\Delta_r H°$ are independent of temperature, the standard molar entropy ($S°$) of B_2O_3(s) does not change with pressure, all the gas species behave as an ideal gas, and all species remain in the same phase, without any further decomposition before or after reaction, at all temperatures then:

6.9 Calculate K_p (pressure based equilibrium constant) at 8930 K and 9005 K.

6.10 Calculate $\Delta_r G°$ of the reaction in terms of kJ mol^{-1} at 8930 K and 9005 K. (If you failed to find K_p, please use K_p (8930 K) = 2, K_p (9005 K) = 0.5.)

6.11 Calculate $\Delta_r G°$ (in terms of kJ mol^{-1}), $\Delta_r H°$ (in terms of kJ mol^{-1}), and $\Delta_r S°$ (in terms of J mol^{-1} K^{-1}) of the combustion reaction at 298 K. (If you failed to find K_p, please use K_p(8930 K) = 2, K_p(9005 K) = 0.5)

6.12 Tick the correct answer in the table by determining whether combustion reactions are favored or not at given temperature T below under standard pressure (1 bar).

Temperature	Favored	Unfavored
298 K	☐	☐
8930 K	☐	☐
9005 K	☐	☐
9100 K	☐	☐

6.13 Calculate the $\Delta_f H$ (kJ mol^{-1}) and $S°$(kJ mol^{-1} K^{-1}) of H_2O(g) using the values given in the table below. ($\Delta_f H$ = enthalpy of formation, $S°$ = standard entropy)
(If you fail to find $\Delta_r H°$ and $\Delta_r S°$ of the combustion, please use $\Delta H°$ = 1000 kJ mol^{-1}, $\Delta S°$= 150 J K^{-1} mol^{-1})

Compound	ΔH_f (298 K)	S° (298 K)
B_2H_6 (g)	36.40 kJ mol^{-1}	0.23 kJ mol^{-1} K^{-1}
O_2 (g)	0.00 kJ mol^{-1}	0.16 kJ mol^{-1} K^{-1}
B_2O_3 (s)	–1273 kJ mol^{-1}	0.05 kJ mol^{-1} K^{-1}

SOLUTION OF THE PROBLEM 6

6.1 Calculation:

Hess rule:

$\Delta H(3) - 2\times\Delta H(2) + 12\times\Delta H(4) - \Delta H(1) = -2 \times \Delta H_{sub}(H_3BO_3)$

$\Delta H_{sub}(H_3BO_3) = 25$ kJ mol^{-1}

6.2 Calculation:

$\Delta U = \Delta H - \Delta(PV) = \Delta H - (\Delta n_{gas})\, RT$

$RT = 8.3145$ J mol^{-1}K^{-1} $\times$ 300 K = 2.494 kJ mol^{-1}

$\Delta U = \Delta H - (\Delta n_{gas}) \times 2.494$ kJ mol^{-1}

$\Delta U(2) = -112.5$ kJ $-$ (3 mol) $\times$ 2.494 kJ mol^{-1} = $-$ 120 kJ

$\Delta U(4) = -92.3$ kJ $-$ (0) $\times$ 2.494 kJ mol^{-1} = -92.3 kJ

6.3 Calculation:

$$\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C} \rightarrow \frac{250\text{ J}}{q_C} = \frac{1000\text{ K}}{300\text{ K}} \rightarrow |q_C| = 75\text{ J}$$

$|w| = q_H - |q_C| = 250$ J $-$ 75 J = 175 J

6.4 Calculation:

$$efficiency = \frac{|w|}{|q_H|} = \frac{175\text{ J}}{250\text{ J}} = 0.70$$

6.5 Calculation:

$$\Delta S = \frac{dq_{reversible}}{T}$$

For A → B

$\Delta S_{\mathbf{A}\rightarrow\mathbf{B}} = 250$ J / 1000 K = 0.25 J K^{-1}

For D → C

$\Delta S_{\mathbf{A}\rightarrow\mathbf{B}} = -75$ J / 300 K = $-$ 0.25 J K^{-1}

6.6 Calculation:

$\Delta G = \Delta H - T\,\Delta S$, for isothermal processes $\Delta H = 0$, then $\Delta G = \mathbf{-}\, \boldsymbol{T}\, \Delta S$

$\Delta G_{\mathbf{A}\rightarrow\mathbf{B}} = -0.25$ J K^{-1} $\times$ 1000 K = $-$ 250 J

$\Delta G_{\mathbf{D}\rightarrow\mathbf{C}} = -(-0.25$ J K$^{-1}) \times 300$ K = 75 J

6.7 Calculation:

$$\Delta S = \frac{dq_{reversible}}{T} = nR \ln \frac{V_B}{V_A}$$

$0.25\ J\ K^{-1} = 1\ mol \times 8.314\ J\ mol^{-1}K^{-1} \ln(V_B / V_A)$

$\ln(V_B / V_A) = 0.03007 \rightarrow (V_B / V_A) = 1.03$

$$\frac{V_B}{V_A} = \frac{p_A}{p_B} \Rightarrow \frac{p_A}{p_B} = 1.03$$

6.8 Calculation:

($0.175\ kJ / 25\ kJ\ mol^{-1}) = 7\times10^{-3}$ mol of H_3BO_3 is sublimated

$(7\times10^{-3}) \times 3 = 21 \times 10^{-3}$ mol H_2 is generated

6.9 Calculation:

$$pV = nRT \Rightarrow p = \frac{nRT}{V} \Rightarrow p = \frac{n \times 0.08205\ L\ atm\ mol^{-1}\ K^{-1} \times T}{100\ L}$$

At 8930 K:

For $B_2H_6(g)$:

$$p_{B_2H_6} = \frac{0.38\ mol \times 0.08205\ L\ atm\ mol^{-1}\ K^{-1} \times 8930\ K}{100\ L} = 2.784\ atm \Rightarrow 2.821\ bar$$

For $H_2O(g)$:

$$p_{H_2O} = \frac{0.20\ mol \times 0.08205\ L\ atm\ mol^{-1}\ K^{-1} \times 8930\ K}{100\ L} = 1.465\ atm \Rightarrow 1.484\ bar$$

At 9005 K:

For $B_2H_6(g)$:

$$p_{B_2H_6} = \frac{0.49\ mol \times 0.08205\ L\ atm\ mol^{-1}\ K^{-1} \times 9005\ K}{100\ L} = 3.618\ atm \Rightarrow 3.666\ bar$$

For $H_2O(g)$:

$$p_{H_2O} = \frac{0.20\ mol \times 0.08205\ L\ atm\ mol^{-1}\ K^{-1} \times 9005\ K}{100\ L} = 1.478\ atm \Rightarrow 1.498\ bar$$

$$K_p\ at\ 8930\ K = \frac{\left(p_{H_2O(g)}\right)^3}{\left(p_{O_2(g)}\right)^3 \times p_{B_2H_6(g)}} = \frac{(1.484)^3}{1^3 \times 2.821} = 1.159$$

$$K_p\ at\ 9005\ K = \frac{\left(p_{H_2O(g)}\right)^3}{\left(p_{O_2(g)}\right)^3 \times p_{B_2H_6(g)}} = \frac{(1.498)^3}{1^3 \times 3.666} = 0.917$$

6.10 Calculation:

$\Delta G^o = -RT\,lnK_p$

ΔG^o at 8930 K = $-8.3145\ J\ mol^{-1}\ K^{-1} \times 8930\ K \times \ln 1.159 = -10.956\ kJ\ mol^{-1}$

ΔG^o at 9005 K = $-8.3145\ J\ mol^{-1}\ K^{-1} \times 9005\ K \times \ln 0.917 = 6.488\ kJ\ mol^{-1}$

6.11 Calculation:

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\Delta G^o(8930\ K) = -10956\ J\ mol^{-1} = \Delta H^o - 8930\ K \times \Delta S^o$

$\Delta G^o(9005\ K) = -6488\ J\ mol^{-1} = \Delta H^o - 9005\ K \times \Delta S^o$

$\Delta S^o = -249.1\ J\ mol^{-1}\ K^{-1}$

$\Delta H^o = -2237.1\ kJ\ mol^{-1}$

$\Delta G^o(298\ K)$ = $-2237.1\ kJ\ mol^{-1} - 298\ K \times (-0.2491\ kJ\ mol^{-1}\ K^{-1})$ =

= **$-2162.9\ kJ\ mol^{-1}$**

6.12 Correct answers:

Temperature	Favored	Unfavored
298 K	☑	☐
8930 K	☑	☐
9005 K	☐	☑
9100 K	☐	☑

6.13 Calculation:

$B_2H_6(g) + 3\ O_2(g) \rightarrow B_2O_3(s) + 3\ H_2O(g)$

$\Delta H^o = [\Delta_f H(B_2O_3(s)) + 3 \times \Delta_f H(H_2O(g))] - [\Delta_f H(B_2H_6(g)) + 3 \times \Delta_f H(O_2(g))]$

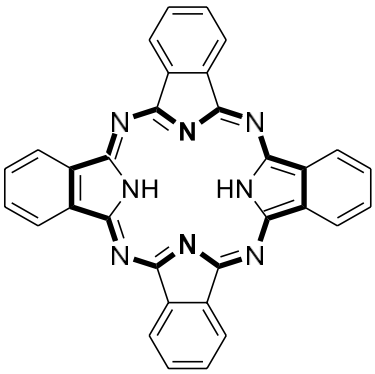
$\Delta S^o = [S^o(B_2O_3(s) + 3 \times S^o(H_2O(g))] - [S^o(B_2H_6(g)) + 3 \times S^o(O_2(g))]$

ΔH_f ($H_2O(g)$) = $-309.2\ kJ\ mol^{-1}$

S^o ($H_2O(g)$) = $0.137\ kJ\ mol^{-1}\ K^{-1}$

THEORETICAL PROBLEM 7

Phthalocyanines



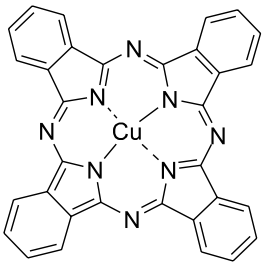
1

Emeritus Professor Özer Bekaroğlu

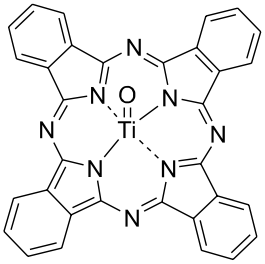
The term phthalocyanine (Pc) takes its origin from the Greek “naphtha”, which means rock oil, and “cyanine”, which means dark blue. Turkish scientist Özer Bekaroğlu can be regarded as the pioneer of Pc chemistry in Turkey.

Metal-free phthalocyanine (**1**, H_2Pc) is a large planar macrocyclic compound with the formula $(C_8H_4N_2)_4H_2$.

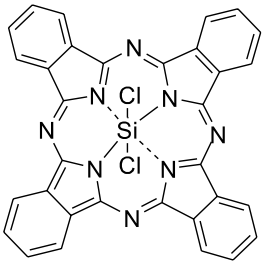
7.1 How many π-electrons are there in the bold region of the H_2Pc molecule in compound **1** shown above?



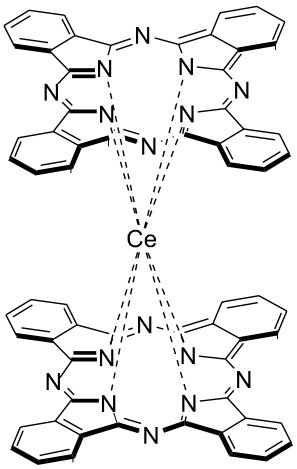
CuPc
2



TiOPc
3



$SiCl_2Pc$
4



$Ce(Pc)_2$
5

Pcs containing one or two metal ions are called metallo-phthalocyanines (MPcs) and they exhibit different geometries as given above.

7.2 Complete the table in your answer sheet by determining the coordination number of central ions in **2**–**5**.

Central ion	**Copper ion**	**Titanium ion**	**Silicon ion**	**Cerium ion**
Coordination number				

7.3 Complete the table in your answer sheet by determining the oxidation number of each metal (Cu, Ti, and Ce) in **2**, **3**, and **5**.

Metal in compounds	**2**	**3**	**5**
Oxidation number			

7.4 Complete the table in your answer sheet by determining the geometry of compounds **2**–**5**.

Geometry	**Compound**
Octahedral	
Square prism	
Square pyramidal	
Square planar	

7.5 Complete the table in your answer sheet by determining the magnetic property of compounds **2**–**5**.

- Use the letter "**p**" for paramagnetic property and letter "**d**" for a diamagnetic property.

Compound	**Magnetic property**
2	
3	
4	
5	

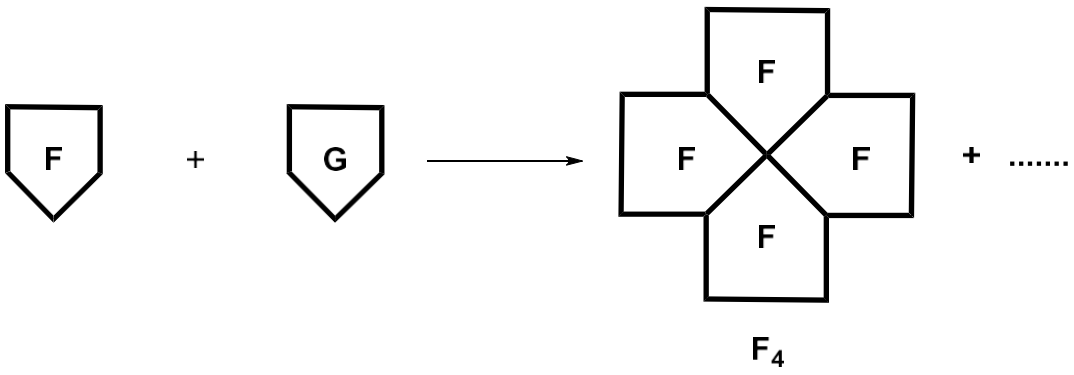
7.6 Write the ground-state electron configuration of the silicon (Si) ion in the compound 4 and find all the quantum numbers for the 2p electrons in its ground state.

Electron configuration:				
Quantum numbers for 2p electrons:	***n***	***l***	m_l	m_s

Metal-free phthalocyanine (**1**, H_2Pc) is commonly formed through the cyclotetramerization of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, which can be prepared by the statistical cyclization of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

7.7 Draw the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers label as *cis*- or *trans*-.

- **F** and **G** represent two different symmetrical phthalonitriles.
- One of the products is $\mathbf{F_4}$ as given below.
- Draw other products similar to the format of $\mathbf{F_4}$.



$\mathbf{F_4}$

Pcs are used as photosensitizers in the photodynamic therapy (PDT) of cancer due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitizer**, light, and oxygen. None of these is individually toxic, but together they initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen ($^1O_2$) that can destroy cancer cells.

$$(\text{multiplicity})\ {}^{1}\mathbf{O_2}$$

- The multiplicity of an energy level is defined as $2S+1$
- If the two spins are parallel (↑↑), $S = 1$, and if the two spins are antiparallel (↑↓), $S = 0$.

7.8 Draw the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1O_2$) and calculate bond order.

- There are no unpaired electrons in that state!

7.9 If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, calculate the energy (in kJ/mol) needed for this transition process.

_____

SOLUTION OF THE PROBLEM 7

7.1 The number of π-electrons in an H_2Pc: **18 π-electrons**

7.2

Central ion	Copper ion	Titanium ion	Silicon ion	Cerium ion
Coordination number	4	5	6	8

7.3

Metal in compounds	2	3	5
Oxidation number	+2	+4	+4

7.4 Complete the table in your answer sheet by determining the geometry of compounds **2** – **5**.

Geometry	**Compound**
Octahedral	4
Square prism	5
Square pyramidal	3
Square planar	2

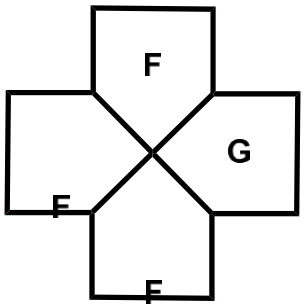
7.5 Complete the table in your answer sheet by determining the magnetic property of compounds **2**–**5**.

Compound	**Magnetic property**
2	p
3	d
4	d
5	d

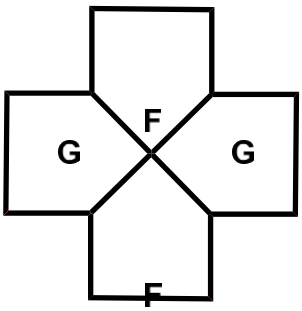
7.6 Write the ground-state electron configuration of the silicon (Si) ion in the compound and find all the quantum numbers for the 3p electrons in its ground state.

Electron configuration: Si^{4+}: [He] $2s^2 2p^6$				
	n	***l***	m_l	M_s
Quantum numbers for 2p electrons:	2	1	+1	+1/2
	2	1	0	+1/2
	2	1	-1	+1/2
	2	1	+1	-1/2
	2	1	0	-1/2
	2	1	-1	-1/2

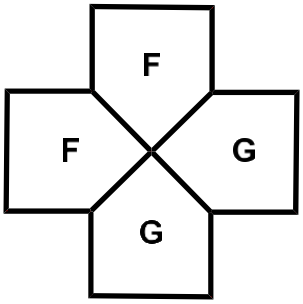
7.7 The possible products that may occur in the statistical cyclization method by using **F** and **G:**



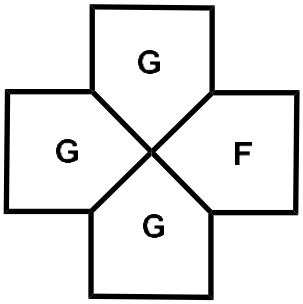
F_3G



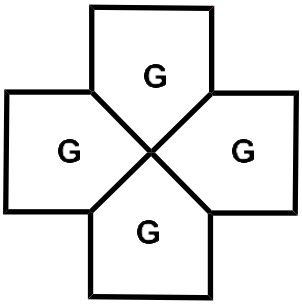
***trans*-F_2G_2**



***cis*-F_2G_2**



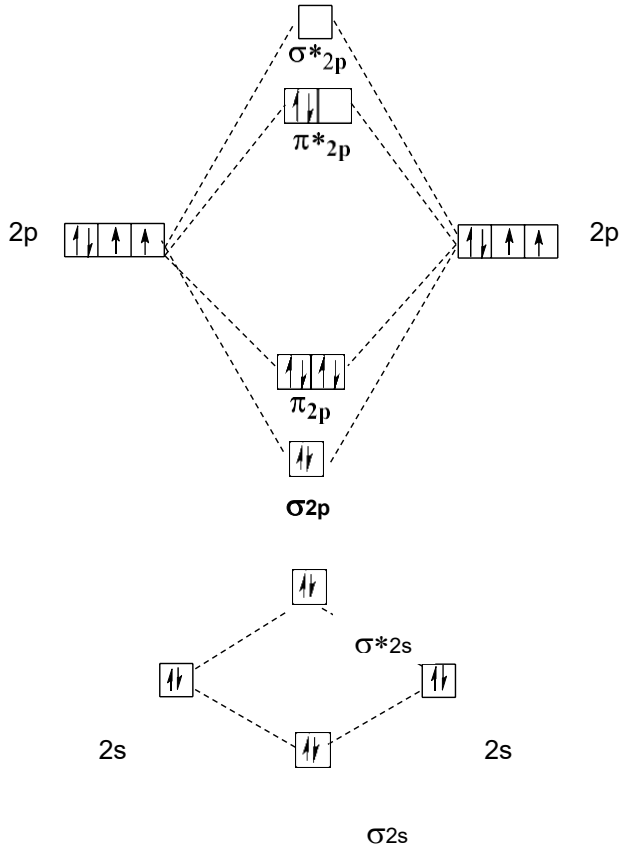
G_3F



G_4

7.8 **Draw** the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1O_2$) and calculate bond order.

MO diagram:



Bond order: (8 – 4) / 2 = 2

7.9 1 nm = 1×10^{-9} m and 1270 nm = 1.270×10^{-6} m

$E = (h \times c) \div \lambda$

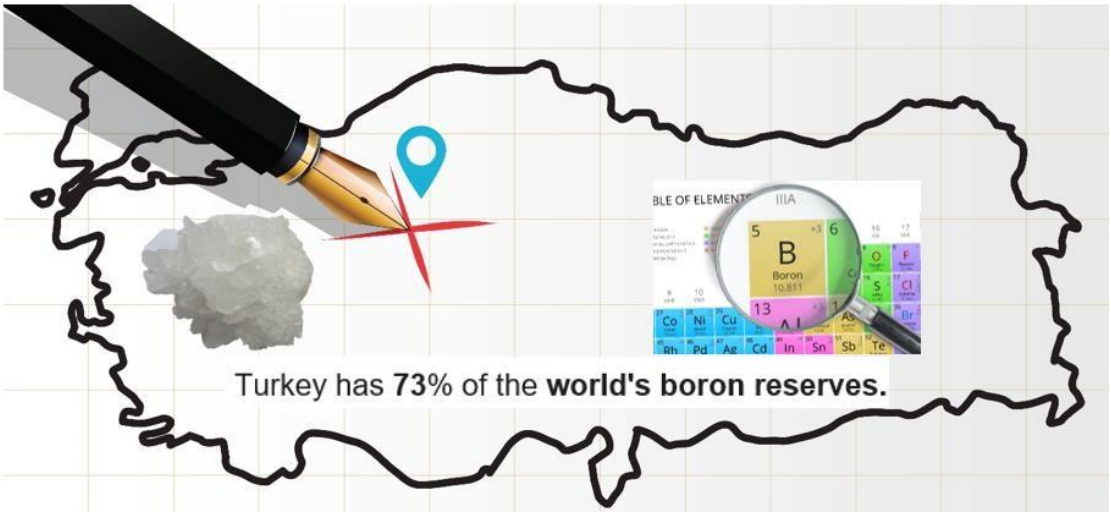
$E = (6.6261\times10^{-34}\ \text{J s})\ (2.9979\times10^{8}\ \text{m s}^{-1}) \div 1270\times10^{-6}\ \text{m} = 1.564\times10^{-19}$ J or 1.564×10^{-22} kJ

For 1 mol (when E is multiplied by Avogadro´s constant):

$E = (1.564\times10^{-22}\ \text{kJ}) \times (6.0221\times10^{23}\ \text{mol}^{-1}) = 94.19\ \text{kJ mol}^{-1}$

THEORETICAL PROBLEM 8

Boron Compounds and Hydrogen Storage



Sodium borohydride ($NaBH_4$) and ammonia borane (BNH_6) are the most studied chemical hydrogen storage materials. In this question, you will explore the chemistry of boron and the use of boron compounds as hydrogen storage materials.

Borax ($Na_2B_4O_7 \cdot n\ H_2O$) is a boron mineral that is produced by ETI Mining Company in Turkey. $NaBH_4$ can be synthesized by the reduction of anhydrous borax with metallic sodium under high-pressure hydrogen gas in the presence of silicon dioxide (silica) at 700 °C, namely the Bayer process. In this process, all hydrogen is stored in $NaBH_4$. On the other hand, it has been shown that ammonia borane (BNH_6) can be synthesized by the reaction of $NaBH_4$ and ammonium sulfate in dry tetrahydrofuran (THF) at 40 °C

(**Hint:** BNH_6 synthesis must be conducted in a well-ventilated fume-hood because flammable gas is generated as one of the by-products). While $NaBH_4$ is an ionic compound, ammonia borane is a Lewis acid–base adduct.

8.1 Write a balanced chemical equation for the synthesis of $NaBH_4$ from anhydrous borax.

8.2 Write a balanced chemical equation for the synthesis of ammonia borane from $NaBH_4$.

8.3 Draw the molecular geometry of the BH_4^- and BNH_6 molecule.

8.4 Calculate the hydrogen content of $NaBH_4$ and BNH_6 as a percentage by mass wt%.

The hydrogen stored in both compounds can be released via hydrolysis reactions in the presence of a suitable catalyst at room temperature. Upon the hydrolysis reactions, 4 and 3 moles of H_2 gas are released from the hydrolysis of 1 mole of $NaBH_4$ and BNH_6, respectively, along with metaborate anion including B-O bonds.

8.5 Write the balanced chemical equations for the hydrolysis of $NaBH_4$ and BNH_6.

One of the simplest stable borates is diboron trioxide (B_2O_3). Higher borates such as $B_3O_6^{3-}$ having cyclic structures containing B-O-bonds can be formed. Since B_2O_3 is an acidic compound, it is easily reacted with water to produce boric acid (H_3BO_3). On the other hand, the high temperature and high-pressure reaction of B_2O_3 with ammonia yields two-dimensional boron nitride, which consists of planar graphite-like sheets of alternating B and N atoms.

8.6 Write the balanced chemical equations for the synthesis of boric acid and boron nitride.

8.7 Draw the molecular structures of the $B_3O_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet.
Hint: Show at least 10 boron atoms in the boron nitride structure.

Furthermore, B-H compounds, called boranes, are an important class of boron compounds. The simplest stable borane is diborane (B_2H_6) and many of the higher boranes can be prepared by the pyrolysis of diborane. Diborane can be synthesized via metathesis of a boron halide and a hydride source.

8.8 Write a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$.
Hint: Both products are boron compounds.

8.9 Draw the molecular geometry of the diborane molecule. Hint: there is no B-B bond in the structure.

BH_3 (borane) is an unstable and highly reactive molecule. Therefore, it is not possible to isolate it as BH_3 under ordinary conditions. However, it can be stabilized via its reaction with carbon monoxide to yield borane carbonyl (BH_3-CO) compound, which is an adduct of borane. The preparation of BH_3CO plays an important role in exploring the chemistry of boranes as it indicates the likely existence of the borane molecule.

8.10 Sketch the Lewis dot structure of BH_3–CO molecule by showing the formal charges.

8.11 Which of the statements given in your answer sheet is observed in the C–O bond of a CO molecule upon the bond formation between BH_3 and CO? Tick the correct box.

- ☐ It gets longer because there will be π-back donation from BH_3 to CO.
- ☐ It gets longer because CO donates π-bonding electrons to BH_3.
- ☐ No or slight change on it because CO donates its mainly non-bonding electrons to BH_3.
- ☐ It gets shorter because CO donates π^* anti-bonding electrons to BH_3.

Borazine with the molecular formula $B_3N_3H_6$ consists of single and double bonded cyclic B–N units and hydrogen atoms attached to these atoms and is isostructural to benzene. Borazine can be synthesized by using a two-step procedure including the synthesis of symmetrically trisubstituted chlorine derivatives of borazine ($B_3N_3H_3Cl_3$) from the reaction of ammonium chloride and boron trichloride, and then reduction of $B_3N_3H_3Cl_3$ with $LiBH_4$ in THF.

8.12 Write the balanced chemical equations for the two-step synthesis of borazine starting from ammonium chloride in THF (tetrahydrofuran). Hint: THF stabilizes one of the products by forming a Lewis acid-base adduct.

8.13 Draw the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.

Catalysts are substances that accelerate the rate of reactions by allowing them to proceed in a lower energy pathway. The catalytic activity of the catalysts is generally determined by the turnover frequency (TOF), which is calculated by dividing the molar amount of the product to the mole of active catalyst and the time (TOF = mole product / (mole catalyst x time)). A typical hydrolysis of BNH_6 was carried out in 10.0 cm^3 of water by using 100.0 mmole BNH_6 and 5.0 mg of CuPt/C catalyst (CuPt alloy nanoparticles supported on carbon black containing 8.2 wt% Pt atoms). The volume of hydrogen gas generated in 5 minutes was 67.25 cm^3.

8.14 Assuming that the catalytic reaction is performed under standard conditions (1 atm and 273.15 K), **calculate** the TOF (min^{-1}) of the CuPt/C catalyst **in terms of only Pt atoms** in the hydrolysis of BNH_6 by considering the volume of the hydrogen gas generated.

As a result of detailed crystal analysis of a synthesized Cu_xPt_y alloy nanoparticles

(the subscripts indicate molar percentages of the atoms in the alloy structure), it was determined that the face centered cubic (fcc) unit cell was formed by Pt atoms and the Pt atoms on the face of the fcc unit cell are supposed to be replaced with Cu atoms to form Cu_xPt_y displacement alloy nanoparticles. According to this information, answer the following questions.

8.15 Determine the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y.

8.16 Sketch the shape of the described crystal unit cell of Cu_xPt_y alloy nanoparticles by showing the position of all atoms on the unit cell.

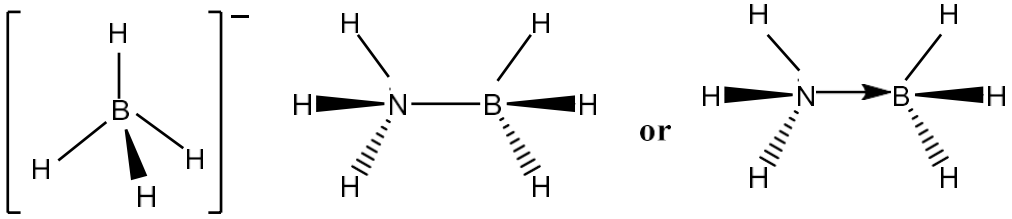
8.17 Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has a fcc unit cell with an edge length of 380 pm, but the Cu and Pt atoms are randomly distributed in the atomic positions. Calculate the density of this alloy in g/cm^3.

SOLUTION OF THE PROBLEM 8

8.1 $Na_2B_4O_7 + 16\ Na + 8\ H_2 + 7\ SiO_2 \rightarrow 4\ NaBH_4 + 7\ NaSiO_3$

8.2 $2\ NaBH_4 + (NH_4)_2SO_4 \rightarrow 2\ BNH_6 + 2\ H_2 + Na_2SO_4$

8.3



8.4

$$\text{Mass \% H in } NaBH_4 = \frac{4 \times A_r(H)}{M_r(NaBH_4)} \times 100 = \frac{4.032}{37.83} = 10.65$$

$$\text{Mass \% H in } BNH_6) = \frac{6 \times A_r(H)}{M_r(BNH_6)} \times 100 = \frac{6.048}{30.87} = 19.59$$

8.5 $NaBH_4 + 2\ H_2O \rightarrow NaBO_2 + 4\ H_2$

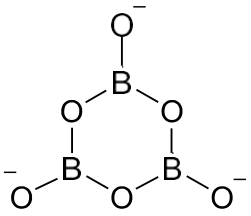
$BNH_6 + 2\ H_2O \rightarrow NH_4BO_2 + 3\ H_2$

8.6

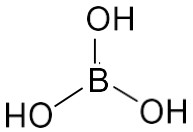
$B_2O_3 + 3\ H_2O \rightarrow 2\ H_3BO_3$

$B_2O_3 + 2\ NH_3 \xrightarrow{high\ T\ /\ high\ p} 2\ BN + 3\ H_2O$

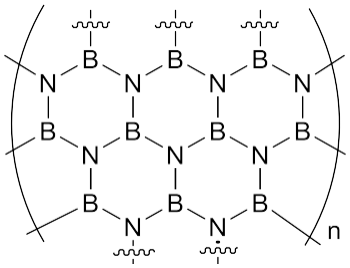
8.7



$B_3O_6^{3-}$



boric acid

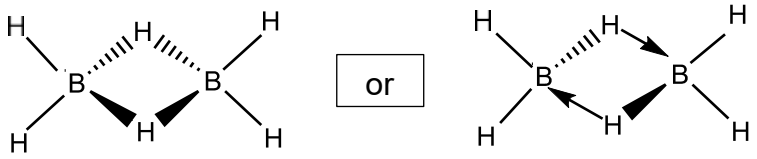


boron nitride

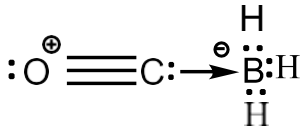
8.8 The synthesis of diborane from the reaction of BF_3 and $LiBH_4$:

$3\ LIBH_4 + 4\ BF_3 \rightarrow 2\ B_2H_6 + 3\ LiBF_4$

8.9



8.10



8.11 The correct answer:

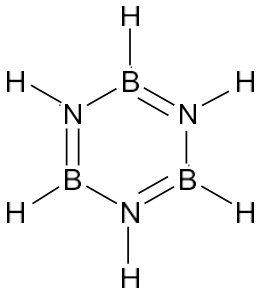
☑ No or slight change on it because CO donates its mainly non-bonding electrons to BH_3.

8.12 The chemical equations required:

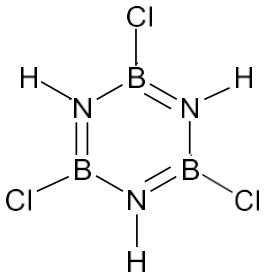
$3\ NH_4Cl\ +\ 3\ BCl_3\ \rightarrow\ B_3N_3H_3Cl_3\ +\ 9\ HCl$

in THF: $B_3N_3H_3Cl_3\ +\ 3\ LiBH_4\ \rightarrow\ B_3N_3H_6\ +\ 3\ LiCl\ +\ 3\ THF{\cdot}BH_3$

8.13 The molecular structures of borazine and its symmetrically trisubstituted chlorine derivative:



$B_3N_3H_6$



$B_3N_3H_3Cl_3$

8.14 Assuming the catalytic reaction is performed under standard conditions, calculate the TOF of the CuPt/C catalyst in terms of only Pt atoms in the hydrolysis of BNH_6 by considering the volume of the hydrogen gas generated.

$$n(H_2)_{generated} = \frac{67.25\ cm^3}{22.41\ cm^3} = 3\times10^{-3}\ mol$$

$$n(Pt) = \frac{\frac{0.005\ \times 8.2}{100}}{195.1} = 2.1\times10^{-6}\ mol$$

$$TOF = \frac{3 \times 10^{-3} \text{ mol } H_2}{2.1 \times 10^{-6} \text{ mol Pt} \times 5.0 \text{ min}} = 286 \text{ min}^{-1}$$

8.15 **In a regular *fcc* unit cell**:

Corners = (8×1) / 8 = 1 Pt atom

Faces = (6×1) / 2 = 3 Pt atoms

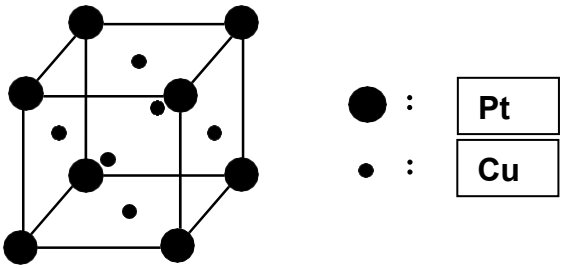
After the replacement of surface Pt atoms with Cu atoms:

Corners = (8×1) / 8 = 1 Pt atom

Faces = (6×1) / 2 = 3 Cu atoms

***Alloy composition*: Cu_3Pt**

8.16



8.17 Actual unit cell composition: $Cu_{2.66}Pt_{1.33}$

$V = a^3$

a = 380 pm = 3.80×10^{-8} cm

$V = (3.80 \times 10^{-8} \text{ cm})^3 = 54.87 \times 10^{-24} \text{ cm}^3$

$$d = \frac{m}{V} = \frac{[2.66 \times A_r(\text{Cu}) + 1.33 \times A_r(\text{Pt})] / N_A}{54.87 \times 10^{-24} \text{ cm}^3}$$

$$= \frac{[(2.66 \times 63.54) + (1.33 \times 195.1)] / 6.02 \times 10^{23}}{54.87 \times 10^{-24}} = 12.97 \text{ g cm}^{-3}$$

THEORETICAL PROBLEM 9

Quantification of heavy metals ions

For the quantitative analysis of heavy metal ions in a factory's wastewater pool, the following steps have been applied by an analyzer at 298 K:

Step 1) 10 cm^3 samples of each were obtained from five different regions in a wastewater pool, mixed in a 100-cm^3 beaker, and then stirred for 5 minutes using a magnetic stirrer.

Step 2) 10 cm^3 of sample solution was taken from the 100-cm^3 beaker and 142 mg of Na_2SO_4 was added while stirring, followed by transfer to a three-electrode cell as seen in Figure 1a. In this electrochemical cell, Pt wire, Ag/AgCl (KCl, c = 3 mol dm^{-3}), and Pt foil served as the working, reference, and counter electrodes, respectively.

Step 3) These electrodes were connected to a potentiostat and a constant potential of –0.50 V vs. Ag/AgCl was applied for 14 minutes as seen in Figure 1b (horizontal line). It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

(a) **(b)**

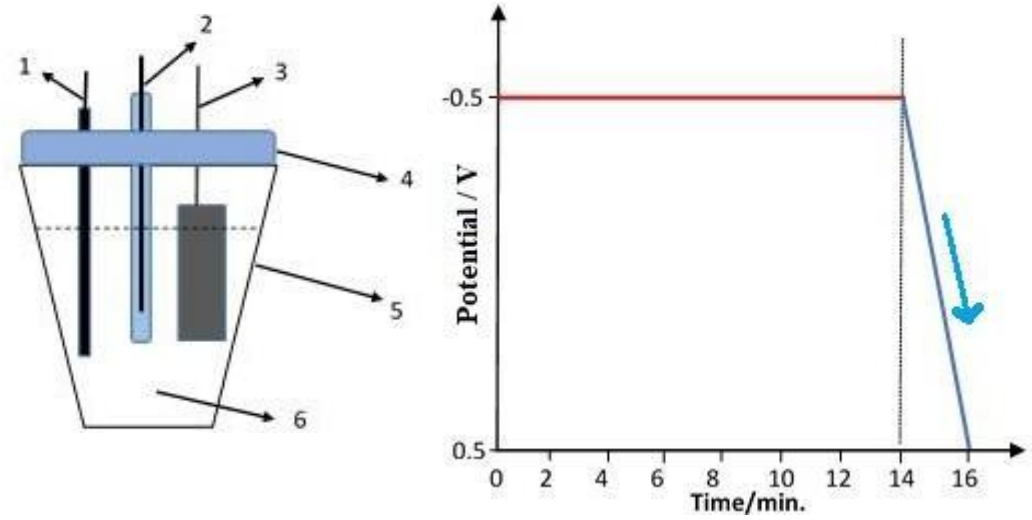


Figure 1.

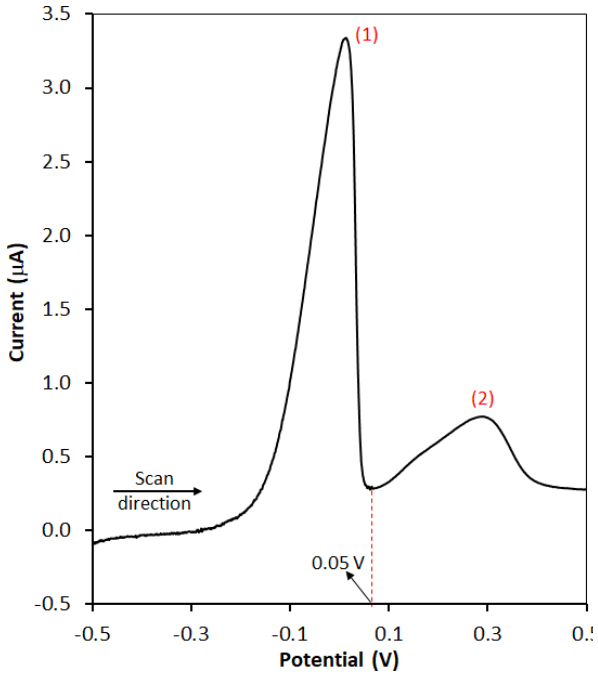
(a) Electrochemical cell design: 1) working electrode (Pt wire), 2) reference electrode (Ag/AgCl, KCl solution, c = 3 mol dm^{-3}), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10 cm^3 of sample solution.

(b) Potential change of working electrode as a function of time. y-axis: potential/V vs Ag/AgCl, x-axis: time/min.

Step 4) The electrodes were rinsed with distilled water, placed into another electrochemical cell including 10 cm^3 of H_2SO_4 solution (c = 0.1 mol dm^{-3}), and potential was scanned between –0.50 and +0.50 V as seen in Figure 1b (downward sloping line in 2 min.).

Current *vs.* potential data for this step are presented in Figure 2a, which is like an excellent view of *Mount Ararat* (*Ağrı Dağı*), the highest mountain in Turkey (Figure 2b).

(a)



(b)

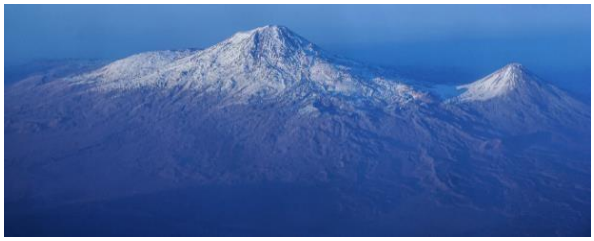


Figure 2.

(a) **S**can of the working electrode as a function of current in H_2SO_4 solution (after keeping it constant at a potential of –0.50 V in 10 cm^3 of wastewater sample as seen in Figure 1b (horizontal line). y-axis: Potential current/μA, x-axis: potential/V *vs* Ag/AgCl.

b) A view of *Great and Little Ararat* peaks.

Step 5) Another 10 cm^3 of the sample solution prepared in step 1 was taken and the processes explained in steps 2 and 3 were applied in that order. The electrodes

were rinsed with distilled water and placed into 10 cm^3 of H_2SO_4 solution (c = 0.1 mol dm^{-3}). Then the potential of the working electrode was kept constant at +0.05 V for 14 minutes. It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

Step 6) After step 5 was performed, the solution in the electrochemical cell was placed in a suitable oven to evaporate at 150 °C until dry solid was obtained.

Step 7) 5 cm^3 of ethylenediaminetetraacetic acid (EDTA, H_4Y) (Figure 3) solution was added to the solid obtained in *step 6* and it was shaken to dissolve. It is known that 1 cm^3 of EDTA solution is equivalent to 3.85 mg/cm^3 $BaCO_3$. Then, pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard $Ni(NO_3)_2$ solution (c = 0.0010 mol dm^{-3} and it was observed that 95.60 cm^3 of $Ni(NO_3)_2$ solution was consumed up to the endpoint.

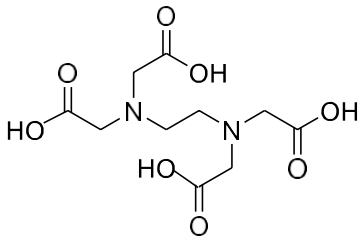


Figure 3. Chemical structure of EDTA (H_4Y).

- In water saturated with H_2S, equilibrium concentration of [H_2S] is 0.1 mol dm^{-3}.
- $K_{sp}(NiS) = 4.0 \times 10^{-20}$; $K_{sp}(CuS) = 1.0 \times 10^{-36}$
- $K_{a1}(H_2S) = 9.6 \times 10^{-8}$; $K_{a2}(H_2S) = 1.3 \times 10^{-14}$

Reaction	E^o / V (at 298 K)
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	– 0.83
$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$	– 0.24
$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$	0.00
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+ 0.34
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.80
$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O\ (l)$	+ 1.23

9.1 Which of the following can be considered for peak 1 and peak 2 in Figure 2a, respectively?

Tick the correct box of the answer sheet.electrochemical oxidation of Cu

9.2 Which of the statements is expected, if the potential is applied as –1.2 V instead of –0.5 V at the first step (horizontal line) in Figure 1b? Tick the correct box on the answer sheet.

9.3 Calculate the scan rate of data presented in Figure 2a as mV/s at 298 K.

The potential of the following cell is measured as 0.437 V.

The cell: Pt, H_2 (0.92 bar) | HCl (c = 1.50 mol dm^{-3}), AgCl(sat) | Ag

9.4 Calculate the standard electrode potential value (V) of half-cell of at 298 K.

Note: You must show all works.

9.5 Which of the statements is the main purpose of step 5 in this analysis? Tick the correct box on the answer sheet.

9.6 Write net ionic equations for the complexation and the back titration reaction of step 7 on the answer sheet.

9.7 Calculate the mass concentration of Ni^{2+} in mg/L in the waste water of the factory.

Note: You must show all works.

9.8 Calculate the minimum pH value for starting the precipitation of Ni^{2+} ions in the solution obtained in step 5 by passing H_2S gas into the solution until saturation. If you cannot solve question **9.7**, use mass concentration of the Ni^{2+} in the sample equal to 20 mg dm^{-3} for this question.

Note: You must show all works.

Electrochemical oxidation of Ni / Peak 2: Electrochemical oxidation of Cu

SOLUTION OF THE PROBLEM 9

9.1 The correct answer is as follows:

☑ Peak 1: electrochemical oxidation of Ni / Peak 2: electrochemical oxidation of Cu.

9.2 The correct answer:

☑ Hydrogen evolution

9.3 Calculation:

The scan rate can be calculated using the slope of figure 1b (downward sloping line).

Scan rate = 1000 mV / 120 s = 8.33 mV/s.

9.4 Calculation:

$E_{cell} = E_{right} - E_{left}$

Half-reactions:

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

$H^+(aq) + 2\,e^- \rightarrow H_2(g)$

$$E_{cell} = (E^o_{AgCl/Ag} - 0.0592 \log [Cl^-]) - (E^o_{H^+/H_2} - \frac{0.0592}{2} \log \frac{p_{H_2}}{[H^+]^2})$$

$$0.437 = (E^o_{AgCl/Ag} - 0.0592 \log 1.5 \times 10^{-2}) - (0.00 - \frac{0.0592}{2} \log \frac{0.92}{(1.5 \times 10^{-2})^2}$$

$E^o_{AgCl\,/\,Ag} = 0.22$ V

9.5 The correct answer is as follows:

▫ Electrochemical stripping of Ni from Cu–Ni-modified Pt wire to the solution.

9.6 Complexation: $Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$ or $Ni^{2+}(aq) + HY^{3-}(aq) \rightarrow NiHY^-(aq)$

Back titration: $Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$ or $Ni^{2+}(aq) + HY^{3-}(aq) \rightarrow NiHY^-(aq)$

9.7 Calculations proposed by the authors:

5 pieces of 10 cm^3 samples were collected and the total sample volume is 50 cm^3

from which 10 cm^3 were taken for the analysis.

EDTA titration: 3.85 mg $BaCO_3$ / cm^3 EDTA

$Ba^{2+}(aq) + Y^{4-}(aq) \rightarrow BaY^{2-}(aq)$

$$c(\text{EDTA}) = \frac{\frac{3.85\ \text{g BaCO}_3}{1.97\ \text{g BaCO}_3}}{\frac{1\ \text{mmol BaCO}_3}{1\ \text{cm}^3\ \text{EDTA}}} \times \frac{1\ \text{mmol EDTA}}{1\ \text{mmol BaCO}_3} = 0.01954\ \text{mol dm}^{-3}$$

$Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$

$$m(\text{Ni}^{2+}) = \left[\left(\frac{0.01954\ \text{mmol EDTA}}{1\ \text{cm}^3\ \text{EDTA}} \times 5.00\ \text{cm}^3\ \text{EDTA}\right) - \left(\frac{0.0010\ \text{mmol Ni}^{2+}}{1\ \text{cm}^3\ \text{Ni}^{2+}} \times 95.60\ \text{cm}^3\ \text{Ni}^{2+} \times \frac{1\ \text{mmol EDTA}}{1\ \text{mmol Ni}^{2+}}\right)\right] \times \frac{1\ \text{mmol Ni}^{2+}}{1\ \text{mmol EDTA}} = 0.0021\ \text{mmol Ni}^{2+}$$

$$c(\text{Ni}^{2+}) = \frac{\left(0.0021\ \text{mmol Ni}^{2+} \times \frac{58.7\ \text{mg Ni}^{2+}}{1\ \text{mmol Ni}^{2+}}\right)\frac{50\ \text{cm}^3}{10\ \text{cm}^3}}{0.05\ \text{dm}^3\ \text{sample}} = 12.33\ \text{mg dm}^{-3}$$

Zadajte rovnicu.

9.8 Calculation as suggested by the author(s):

$$c(\text{Ni}^{2+}) = \frac{0.0021\ \text{mmol Ni}^{2+}}{10\ \text{cm}^3\ \text{sample}} = 2.1 \times 10^{-4}\ \text{mol dm}^{-3}$$

or

$$c(\text{Ni}^{2+}) = \frac{\frac{0.01233\ \text{g Ni}^{2+}}{58.7\ \text{g mol}^{-1}}}{1\ \text{dm}^3\ \text{sample}} = 2.1 \times 10^{-4}\ \text{mol dm}^{-3}$$

$NiS \leftrightarrows Ni^{2+}(aq) + S^{2-}(aq)$

$4.0 \times 10^{-20} = 2.1 \times 10^{-4} \times [S^{2-}]$

$[S^{2-}] = 1.905 \times 10^{-16}$

$$H_2S + H_2O \rightleftarrows HS^- + H_3O^+ \qquad K_{a1} = 9.6 \times 10^{-8} = \frac{[HS^-][H_3O^+]}{[H_2S]}$$

$$HS^- + H_2O \rightleftarrows S^{2-} + H_3O^+ \qquad K_{a2} = 1.3 \times 10^{-14} = \frac{[S^{2-}][H_3O^+]}{[HS^-]}$$

$0.1 = [H_2S] + [HS^-] + [S^{2-}]$

$[H_2S] \gg [HS^-] + [S^{2-}]$ and $[H_2S] = 0.1$

$$K_{a1} \times K_{a2} = 1.25 \times 10^{-21} = \frac{[S^{2-}]\,[H_3O^+]^2}{[H_2S]}$$

$$1.25 \times 10^{-21} = \frac{1.905 \times 10^{-16}\,[H_3O^+]^2}{0.1}$$

$[H_3O^+] = 8.1 \times 10^{-4}$

pH = 3.09

53rd

International Chemistry Olympiad

9 theoretical problems

The original front page:

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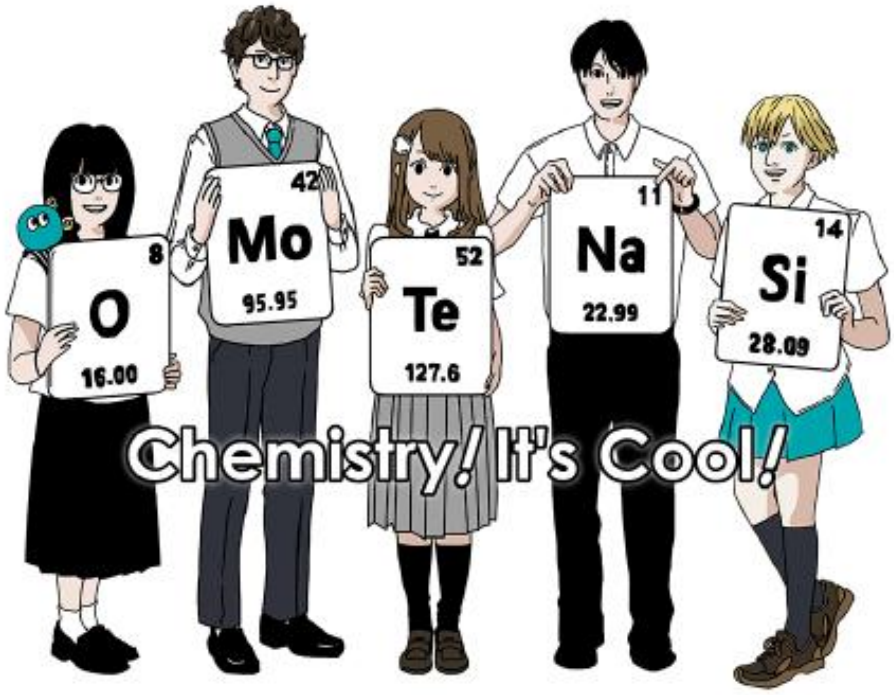
English (Official)

International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July – 2nd August, 2021
https://www.icho2021.org



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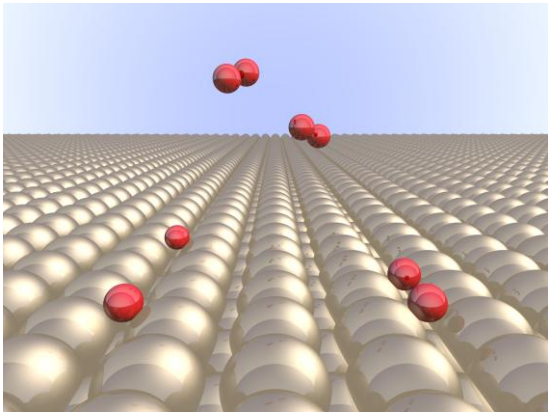
Theoretical problems

THE FIFTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
25 JULY – 2 AUGUST 2021, Japan

THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

Hydrogen at a Metal Surface



Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

PART A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $H_2(g) \rightarrow 2H(ad)$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (H_2) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of H_2 is represented by two variables: the interatomic distance, *d*, and the height relative to the surface metal atom, *z.* It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the

potential energy in units of kJ per mole of H_2. The solid line spacing is 20 kJ mol^{-1}, the dashed line spacing is 100 kJ mol^{-1}, and the spacing between solid and dashed lines is 80 kJ mol^{-1}. The zero-point vibration energy is ignored.

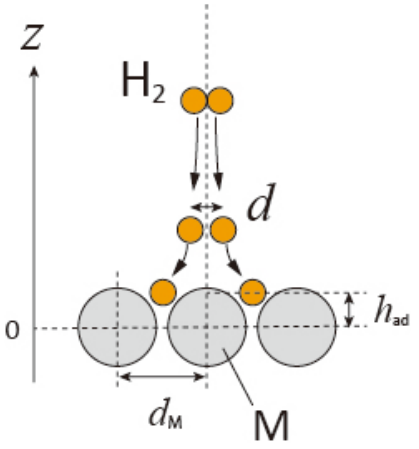


Fig.1 Definition of variables. Drawing is not in scale.

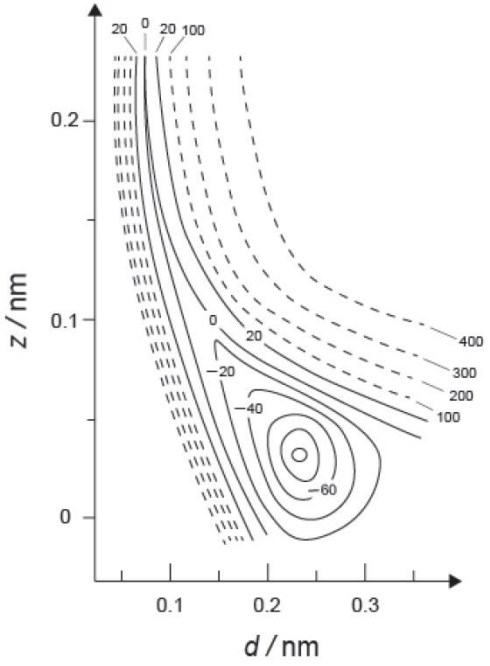


Fig.2

1.1 For each of the following items (i)–(iii), select the closest value from A–G.

(i) The interatomic distance for a gaseous H_2 molecule

(ii) The interatomic distance between metal atoms (d_M in Fig. 1)

(iii) The distance of adsorbed H atoms from the surface (h_{AD} in Fig. 1)

A. 0.03 nm	B. 0.07 nm	C. 0.11 nm	D. 0.15 nm
E. 0.19 nm	F. 0.23 nm	G. 0.27 nm	

1.2 For each of the following items (i)–(ii), select the closest value from A–H.

(i) the energy required for the dissociation of gaseous H_2 to gaseous H [$H_2(g) \rightarrow 2H(g)$]

(ii) the energy released during the adsorption of a gaseous H_2 [$H_2(g) \rightarrow 2H(ad)$]

A. 20 kJ mol^{-1}	B. 40 kJ mol^{-1}	C. 60 kJ mol^{-1}	D. 100 kJ mol^{-1}
E. 150 kJ mol^{-1}	F. 200 kJ mol^{-1}	G. 300 kJ mol^{-1}	H. 400 kJ mol^{-1}

PART B

The adsorbed hydrogen atoms are then either absorbed into the bulk, or recombine and desorb back into the gas phase, as shown in the reactions (1a) and (1b). H(ab) represents a hydrogen atom absorbed in the bulk.

$$H_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2H(ad) \quad (1a)$$

$$H(ad) \xrightarrow{k_3} H(ab) \quad (1b)$$

The reaction rates per surface site for adsorption, desorption, and absorption are r_1[s^{-1}], r_2[s^{-1}] and r_3[s^{-1}], respectively. They are expressed as:

$$r_1 = k_1 P_{H_2} (1-\theta)^2 \quad (2)$$

$$r_2 = k_2 \theta^2 \quad (3)$$

$$r_3 = k_3 \theta \quad (4)$$

where k_1 [s^{-1} Pa^{-1}], k_2 [s^{-1}] and k_3 [s^{-1}] are the reaction rate constants and P_{H_2} is the pressure of H_2. Among the sites available on the surface, θ ($0 \leq \theta \leq 1$) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption ($r_1, r_2 \gg r_3$) and that θ remains constant.

1.3 r_3 can be expressed as:

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{H_2} C}}} \quad (5)$$

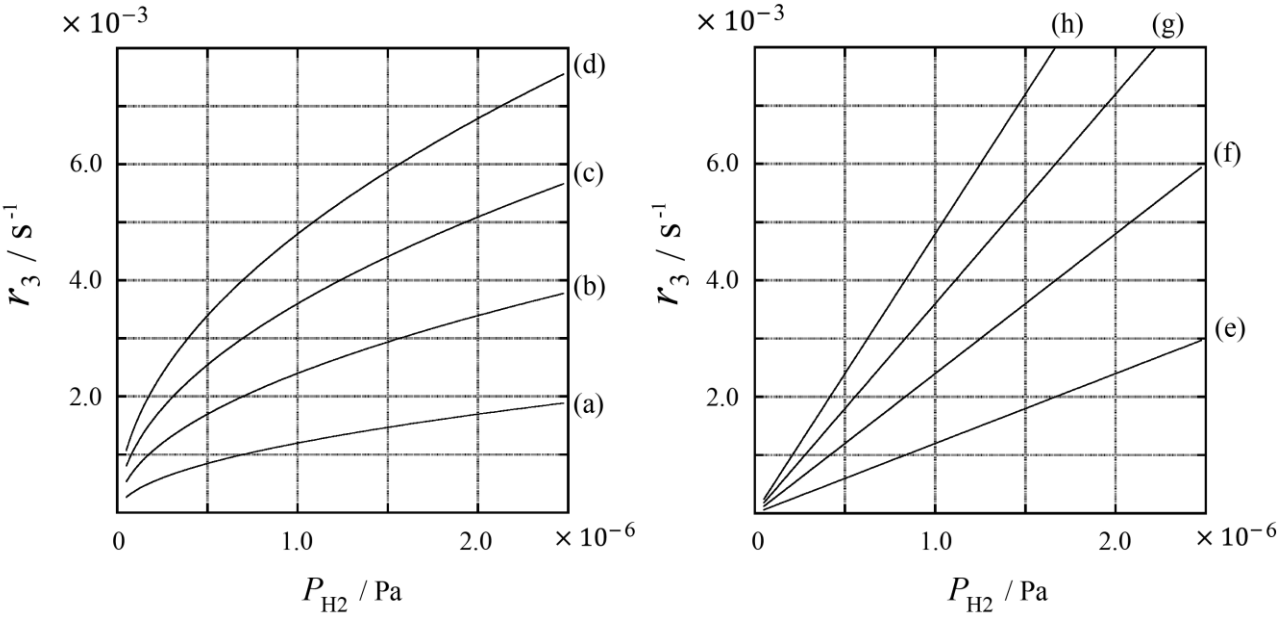
Express C using k_1 and k_2.

A metal sample with a surface area of S = 1.0 × 10^{-3} m^2 was placed in a container (1L = 1.0 × 10^{-3} m^3) with H_2 (P_{H_2} = 1.0 × 10^2 Pa). The density of hydrogen-atom adsorption sites on the surface was N = 1.3 × 10^{18} m^{-2}. The surface temperature was kept at T = 400 K. As the reaction (1) proceeded, P_{H_2} decreased at a constant rate of v = 4.0 × 10^{-4} Pa s^{-1}. Assume that H_2 is an ideal gas and that the volume of the metal sample is negligible.

1.4 Calculate the amount of H atoms in moles absorbed per unit area of the surface per unit time, A [mol s^{-1} m^{-2}].

1.5 At T = 400 K, C equals 1.0 × 10^2 Pa^{-1}. Calculate the value of k_3 at 400 K. If you did not obtain the answer to **1.4**, use A = 3.6 × 10^{-7} mol s^{-1} m^{-2}.

1.6 At a different T, C = 2.5 × 10^3 Pa^{-1} and k_3 = 4.8 × 10^{-2} s^{-1} are given. For r_3 as a function of P_{H_2} at this temperature, select the correct plot from (a)–(h).



SOLUTION OF THE PROBLEM 2

1.1 (i) B (ii) F (iii) A

1.2 (i) H (ii) D

1.3 From r_1, $r_2 \gg r_3$ and $r_1 = r_2 + r_3$,

$r_1 = r_2$.

Then $k_1 P_{H_2} (1-\theta)^2 = k_2 \theta^2$ (1')

Solve for θ:

$$\theta = \frac{1}{1 + \sqrt{\frac{k_2}{P_{H_2} k_1}}}$$ (2')

From $r_3 = k_3\theta$:

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{k_2}{P_{H_2} k_1}}}$$

Thus, $C = \frac{k_1}{k_2}$.

1.4 The change in the amount of hydrogen atoms per unit time in the gas phase is $A \times S$. Thus,

$$A \times S = \frac{2vV}{RT}$$ (1')

$= 2 \times 4.0 \times 10^{-4} \times \frac{1.0 \times 10^{-3}}{8.31 \times 400} = 2.4 \times 10^{-10}$ mol s^{-1}

Therefore,

$A = 2.4 \times 10^{-7}$ mol s^{-1} m^{-2}

1.5 The relationship between r_3 and A is:

$A = r_3 \times \frac{N}{N_A}$

Thus,

$r_3 = A \times \frac{N_A}{N} = 1.1 \times 10^{-1}$ s^{-1} (1')

Solution 1:

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{k_2}{P_{H_2} k_1}}} = \frac{k_3}{1 + \sqrt{\frac{1}{10000}}} = \frac{k_3}{1.01}$$ (2')

Thus, k_3 = 1.01 × r_3 = 1.1 × 10^{-1} s^{-1}

Solution 2:

Under the condition $P_{H_2}C \gg 1$, it follows that:

$$r_3 = \frac{k_3}{1+\sqrt{\frac{k_2}{P_{H_2}k_1}}} \approx \frac{k_3}{1} = k_3 \text{ (3')}$$

Thus, k_3 = r_3 = 1.1 × 10^{-1} s^{-1}

(1.7 × 10^{-1} s^{-1} with A = 3.6 × 10^{-7} mol s^{-1} m^{-2})

1.6 The figures show the region in which $P_{H_2}C \ll 1$. Therefore,

$$r_3 = \frac{k_3}{1+\sqrt{\frac{1}{P_{H_2}C}}} \text{ (1')}$$

$$\approx \frac{k_3}{\sqrt{\frac{1}{P_{H_2}C}}} = k_3\sqrt{P_{H_2}C} = 2.4\sqrt{P_{H_2}}$$

Thus, (b).

THEORETICAL PROBLEM 2

Isotope Time Capsule

Molecular entities that differ only in isotopic composition, such as CH_4 and CH_3D, are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

Assume that all of the substances shown in this Question are in a gas phase.

Let us consider the following equilibrium:

$$^{12}C^{16}O_2 + {}^{12}C^{18}O_2 \rightleftharpoons 2\,{}^{12}C^{16}O^{18}O \qquad K = \frac{[{}^{12}C^{16}O^{18}O]^2}{[{}^{12}C^{16}O_2][{}^{12}C^{18}O_2]} \qquad (1)$$

The entropy, S, increases with increasing the number of possible microscopic states of a system, W:

$$S = k_B \ln W \qquad (2)$$

W = 1 for $^{12}C^{16}O_2$ and $^{12}C^{18}O_2$. In contrast, W = 2 for a $^{12}C^{16}O^{18}O$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}C^{16}O^{18}O$ molecules, $W = 2^2 = 4$.

2.1 The enthalpy change, ΔH, of eq. 3 is positive regardless of the temperature.

$$H_2 + DI \rightleftharpoons HD + HI \qquad (3)$$

Calculate the equilibrium constants, K, for eq. 3 at very low (think of $T \rightarrow 0$) and very high (think of $T \rightarrow +\infty$) temperatures. Assume that the reaction remains unchanged at these temperatures and that ΔH converges to a

constant value for high temperatures.

The Δ*H* of the following process can be explained by molecular vibrations.

$$2HD \rightleftharpoons H_2 + D_2 \qquad K = \frac{[H_2][D_2]}{[HD]^2} \tag{4}$$

At T = 0 K, the vibrational energy of a diatomic molecule whose vibration frequency is ν [s^{-1}] is expressed as:

$$E = \frac{1}{2}h\nu \tag{5}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{6}$$

Wherein k is the force constant and μ the reduced mass, which is expressed in terms of the mass of the two atoms in the diatomic molecule, m_1 and m_2, according to:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7}$$

2.2 The vibration of H_2 is at 4161.0 cm^{-1} when reported as a wavenumber. Calculate the ΔH of the following equation at T = 0 K in units of J mol^{-1}.

$$2HD \rightarrow H_2 + D_2 \tag{8}$$

Assume that:

- only the vibrational energy contributes to the ΔH.
- the k values for H_2, HD, and D_2 are identical.
- the mass of H to be 1 Da and the mass of D to be 2 Da.

The molar ratio of H_2, HD, and D_2 depends on the temperature in a system in equilibrium. Here, Δ_{D_2} is defined as the change of the molar ratio of D_2.

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 \tag{9}$$

Here, R_{D_2} refers to $\frac{[D_2]}{[H_2]}$ in the sample and $R^*_{D_2}$ to $\frac{[D_2]}{[H_2]}$ at $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

2.3 Calculate Δ_{D_2} with natural D abundance when the isotopic exchange is in

equilibrium at the temperature where K in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, respectively.

In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO_2 molecules with molecular weights of 44 and 47, which are described as CO_2[44] and CO_2[47] below. The quantity Δ_{47} is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \tag{10}$$

R_{47} refers to $\frac{[CO_2[47]]}{[CO_2[44]]}$ in the sample and R_{47}^* to $\frac{[CO_2[47]]}{[CO_2[44]]}$ at $T \rightarrow +\infty$. The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

	^{12}C	^{13}O
natural abundance	0.988888	0.011112

	^{16}O	^{17}O	^{18}O
natural abundance	0.997621	0.0003790	0. 0020000

The temperature dependence of Δ_{47} is determined as follows, where T is given as the absolute temperature in units of K:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4} \tag{11}$$

2.4 The Δ_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-5}. **Estimate** the temperature using this R_{47}. This temperature is interpreted as the air temperature during the era in which the plankton lived. Consider only the most common isotopologue of CO_2[47] for the calculation.

SOLUTION OF THE PROBLEM 2

2.1

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \rightarrow \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$
$$\left(K = \exp\left[-\frac{\Delta H^\circ}{RT}\right] \exp\left[\frac{\Delta S^\circ}{R}\right]\right)$$

$T \rightarrow 0$: As $\Delta H^\circ > 0$, ln K converges to $-\infty$ and therefore $K = 0$.

$T \rightarrow +\infty$: ln $K \rightarrow \frac{\Delta S^\circ}{R}$

Given that ΔS° per 1 mole is $N_A k_B \ln W = R \ln 2$, $K = 2$.

2.2

$\mu_{H_2} = 1/2$ Da, $\mu_{HD} = 2/3$ Da, $\mu_{D_2} = 1$ Da.
Using $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, $\frac{\nu_{HD}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}}$ and $\frac{\nu_{D_2}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}}$ are obtained.

The frequency of the H_2 vibration is 4161.0 cm^{-1} in units of wavenumbers. Therefore, the frequencies of the molecular vibration for HD and D_2 are calculated to be 3603.5 cm^{-1} and 2942.3 cm^{-1}, respectively.
The difference of the zero-point energies of eq. 4 is calculated to be (4161.0 + 2942.3)/2 − 3603.5 = − 51.9 cm^{-1}.
$E = N_A h\nu = N_A hc\tilde{\nu}$ ($\tilde{\nu}$: frequency in wavenumbers), and therefore
$E = \Delta H^\circ$ = − 621 J mol^{-1}.

2.3 Let the sum of the concentrations of H_2, HD, and D_2 be C.

Solution 1:

$T \rightarrow +\infty$ (K = 1/4):

$[H_2]_0 = (1 - 1.5576 \times 10^{-4})^2\, C = 9.9969 \times 10^{-1}\, C$

$[D_2]_0 = (1.5576 \times 10^{-4})^2\, C = 2.4261 \times 10^{-8}\, C$

K = 0.300:

Let the amount of change in the molar ratio be x.

$$\frac{[H_2][D_2]}{[HD]^2} = \frac{\left(\frac{[H_2]_0}{C} + x\right)\left(\frac{[D_2]_0}{C} + x\right)}{\left(\frac{[HD]_0}{C} - 2x\right)^2} = K$$

Solve the equation for x when K = 0.300:

$$(1-4K)x^2+\left(\frac{[H_2]_0}{C}+\frac{[D_2]_0}{C}+4K\frac{[HD]_0}{C}\right)x+\left(\frac{[H_2]_0[D_2]_0}{C^2}-K\frac{[HD]_0^2}{C^2}\right)=0,$$

x = 4.8504 × 10^{-9}.

From this value, we obtain $[H_2]$ = 9.9969 × $10^{-1}C$ and $[D_2]$ = 2.9112 × $10^{-8}C$.

$$\Delta_{D_2}=\frac{R_{D_2}}{R^*_{D_2}}-1=\frac{\frac{2.9112\times10^{-8}}{9.9969\times10^{-1}}}{\frac{2.4261\times10^{-8}}{9.9969\times10^{-1}}}-1=0.200$$

Solution 2:

By using an appropriate approximation, we can obtain the answer without calculating the concentration of each species.

Let the increase of $[D_2]$ be δ.

$$K=\frac{[H_2][D_2]}{[HD]^2}=\frac{([H_2]_0+\delta)([D_2]_0+\delta)}{([HD]_0-2\delta)^2}\simeq\frac{[H_2]_0([D_2]_0+\delta)}{[HD]_0^2}=\frac{[H_2]_0[D_2]}{[HD]_0^2}$$

$$\Delta_{D_2}=\frac{R_{D_2}}{R^*_{D_2}}-1=\frac{\frac{[D_2]}{[H_2]}}{\frac{[D_2]_0}{[H_2]_0}}-1\simeq\frac{[D_2]}{[D_2]_0}-1=\frac{\frac{[H_2]_0[D_2]}{[HD]_0^2}}{\frac{[H_2]_0[D_2]_0}{[HD]_0^2}}-1\simeq\frac{0.300}{0.250}-1=0.200$$

2.4 The most common isotopologue of CO_2[47] is $^{13}C^{16}O^{18}O$.

The molar ratio of $^{13}C^{16}O^{18}O$ in the case where all the isotopes are distributed randomly is:

0.011112×0.002000×0.997621 × 2 [O is distinguishable] = 4.43423 × 10^{-5}

The molar ratio of $^{12}C^{16}O2$ (CO_2[44]) in the case where all the isotopes are distributed randomly is:

0.988888 × 0.9976212 = 9.84188 × 10^{-1}

$$R^*_{47}=\frac{4.43423\times10^{-5}}{9.84188\times10^{-1}}=4.50547\times10^{-5}$$

Δ_{47} = 7.06 × 10^{-4}

T = 296 K.

THEORETICAL PROBLEM 3

Lambert–Beer Law?

In this problem, ignore the absorption of the cell and the solvent. The temperatures of all solutions and gases are kept constant at 25 °C.

PART A

An aqueous solution **X** was prepared using HA and NaA. The concentrations [A^-], [HA], and [H^+] in solution **X** are 1.00×10^{-2} mol L^{-1}, 1.00×10^{-3} mol L^{-1}, and 1.00×10^{-4} mol L^{-1}, respectively, which are correlated via the following acid-base equilibrium:

$$HA \rightleftharpoons A^- + H^+ \qquad K = \frac{[A^-][H^+]}{[HA]} \tag{1}$$

The optical path length is l in Part A. Ignore the density change upon dilution. Assume that no chemical reactions other than eq 1 occur.

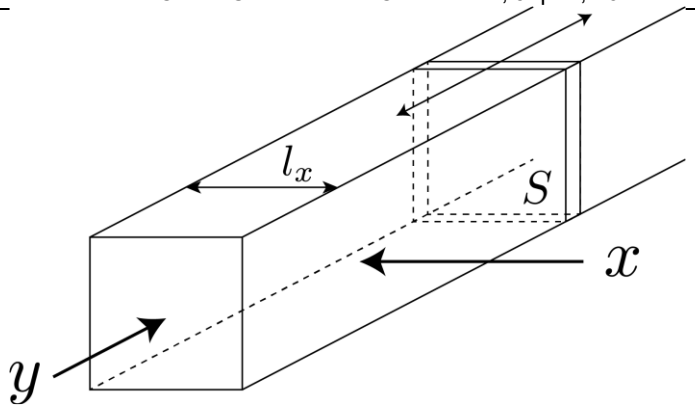
3.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. Determine the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-} represent the absorption coefficients of HA and of A^-, respectively, at λ_1.

PART B

Let us consider the following equilibrium in the gas phase:

$$D \rightleftharpoons 2M \tag{2}$$

Pure gas D is filled into a cuboid container that has a transparent movable wall with a cross-section of S (see the figure below) at a pressure P, and equilibrium is established while the total pressure is kept at P. The absorbance of the gas is $A = \varepsilon(n/V)l$, where ε, n, V, and l are the absorption coefficient, amount of the gas in moles, volume of the gas, and optical path length, respectively. Assume that all components of the gas mixture behave as ideal gases.



Use the following definitions if necessary.

	Initial state		After equilibrium	
	D	M	D	M
Partial pressure	P	0	p_{D}	p_{M}
Amount in moles	n_0	0	n_{D}	n_{M}
Volume	V_0		V	

3.2 The absorbance of the gas at λ_{B1} measured from direction x ($l = l_x$) was A_{B1} both at the initial state and after the equilibrium. Determine the ratio $\varepsilon_D/\varepsilon_M$ at λ_{B1}, where ε_D and ε_M represent the absorption coefficients of D and of M, respectively.

3.3 The absorbance of the gas at λ_{B2} measured from direction y was A_{B2} both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). Determine the ratio $\varepsilon_D/\varepsilon_M$ at λ_{B2}.

SOLUTION OF THE PROBLEM 3

3.1

$$K = \frac{[A^-][H^+]}{[HA]} = \frac{(1.00 \times 10^{-2})(1.00 \times 10^{-4})}{1.00 \times 10^{-3}} = 1.00 \times 10^{-3} \text{ mol L}^{-1}$$

Concentration before the dilution:

$[HA] = 1.00 \times 10^{-3}$ mol L^{-1}

$[A^-] = 1.00 \times 10^{-2}$ mol L^{-1}

$[H^+] = 1.00 \times 10^{-4}$ mol L^{-1}

Concentrations just after the dilution (nominal initial concentrations before the equilibrium):

$[HA] = 5.00 \times 10^{-4}$ mol L^{-1}

$[A^-] = 5.00 \times 10^{-3}$ mol L^{-1}

$$[H^+] = \frac{1.00 \times 10^{-4} + 3.16 \times 10^{-3}}{2} = 1.63 \times 10^{-3} \text{ mol L}^{-1}$$

(pH = 2.500 → $[H^+] = 3.16 \times 10^{-3}$ mol L^{-1})

Equilibrium after the dilution:

$$\frac{[A^-][H^+]}{[HA]} = \frac{(5.00 \times 10^{-3} - x)(1.63 \times 10^{-3} - x)}{5.00 \times 10^{-4} + x} = 1.00 \times 10^{-3} \text{ mol L}^{-1}$$

Solve the equation for x: $x = 1.19 \times 10^{-3}$ mol L^{-1}

→ $[A^-] = 3.81 \times 10^{-3}$ mol L^{-1}, $[HA] = 1.69 \times 10^{-3}$ mol L^{-1}.

Therefore,

$1.00 \times 10^{-2}\, \varepsilon_{A^-} + 1.00 \times 10^{-3}\, \varepsilon_{HA} = 3.81 \times 10^{-3}\, \varepsilon_{A^-} + 1.69 \times 10^{-3}\, \varepsilon_{HA}$

By solving this equation: $\varepsilon_{HA}/\varepsilon_{A^-} = 9.0$

3.2 Solution 1:

The absorbance at the initial state is:

$$A_{B1} = \frac{\varepsilon_D n_0}{V_0} l_x$$

The absorbance after equilibrium is:

$$A_{B1} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V} l_x$$

From the ideal gas law, the following relationship is obtained:

$$\frac{n_0}{V_0} = \frac{P}{RT} = \frac{n_\mathrm{D} + n_\mathrm{M}}{V} \text{ (*1)}$$

From these equations, the following relationship is obtained:

$$A_{\mathrm{B1}} = \frac{\varepsilon_\mathrm{D} n_0}{V_0} l_x = \frac{\varepsilon_\mathrm{D}(n_\mathrm{D} + n_\mathrm{M})}{V} l_x = \frac{\varepsilon_\mathrm{D} n_\mathrm{D} + \varepsilon_\mathrm{M} n_\mathrm{M}}{V} l_x$$
$$\rightarrow \varepsilon_\mathrm{D} n_\mathrm{M} = \varepsilon_\mathrm{M} n_\mathrm{M}$$
$$\rightarrow 0 = (\varepsilon_\mathrm{M} - \varepsilon_\mathrm{D}) n_\mathrm{M}$$

As $n_\mathrm{M} > 0$ after the equilibrium, $\varepsilon_\mathrm{D} = \varepsilon_\mathrm{M}$ holds at λ_{B1}.

Solution 2:

Using the ideal gas law, the absorbance at the initial state is expressed as:

$$A_{\mathrm{B1}} = \frac{\varepsilon_\mathrm{D} n_0}{V_0} l_x = \varepsilon_\mathrm{D} \frac{P}{RT} l_x \text{ (*2)}$$

The absorbance after equilibrium is:

$$A_{\mathrm{B1}} = \frac{\varepsilon_\mathrm{D} n_\mathrm{D} + \varepsilon_\mathrm{M} n_\mathrm{M}}{V} l_x = \frac{\varepsilon_\mathrm{D} p_\mathrm{D} + \varepsilon_\mathrm{M} p_\mathrm{M}}{RT} l_x \text{ (*3)}$$

From these equations, the following relationship is obtained:

$$A_{\mathrm{B1}} = \varepsilon_\mathrm{D} \frac{P}{RT} l_x = \frac{\varepsilon_\mathrm{D} p_\mathrm{D} + \varepsilon_\mathrm{M} p_\mathrm{M}}{RT} l_x$$

Using tuhe fact that $p_\mathrm{D} = P - p_\mathrm{M}$,

$$\varepsilon_\mathrm{D} P = \varepsilon_\mathrm{D}(P - p_\mathrm{M}) + \varepsilon_\mathrm{M} p_\mathrm{M} = \varepsilon_\mathrm{D} P + (\varepsilon_\mathrm{M} - \varepsilon_\mathrm{D}) p_\mathrm{M}$$
$$\rightarrow 0 = (\varepsilon_\mathrm{M} - \varepsilon_\mathrm{D}) p_\mathrm{M}$$

As $p_\mathrm{M} > 0$ after the equilibrium, $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M} = 1$ holds at λ_{B1}.

3.3 Solution 1:

The absorbance at the initial state is:

$$A_{\mathrm{B2}} = \frac{\varepsilon_\mathrm{D} n_0}{V_0} l_{y0}$$

The absorbance after equilibrium is:

$$A_{\mathrm{B2}} = \frac{\varepsilon_\mathrm{D} n_\mathrm{D} + \varepsilon_\mathrm{M} n_\mathrm{M}}{V} l_y$$

Using the fact that:

$$l_y = l_{y0} \frac{V}{V_0}$$

The absorbance after equilibrium is expressed as follows:

$$A_{B2} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V} l_y = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V_0} l_{y0}$$

From these equations, the following relationship is obtained:

$$A_{B2} = \frac{\varepsilon_D n_0}{V_0} l_{y0} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V_0} l_{y0}$$

Using the fact that:

$n_M = 2(n_0 - n_D)$ (*4)

The following relationship is obtained:

$\varepsilon_D n_0 = \varepsilon_D n_D + 2\varepsilon_M(n_0 - n_D) = 2\varepsilon_M n_0 + (\varepsilon_D - 2\varepsilon_M) n_D$

$\rightarrow (\varepsilon_D - 2\varepsilon_M) n_0 = (\varepsilon_D - 2\varepsilon_M) n_D$

As $n_0 > n_D$ after the equilibrium, $\varepsilon_D = 2\varepsilon_M$ holds at λ_{B2}.

Solution 2:

Using the fact that $V_0 = l_{y0}S$, the absorbance at the initial state is expressed as:

$$A_{B2} = \frac{\varepsilon_D n_0}{V_0} l_{y0} = \varepsilon_D \frac{n_0}{S}$$

Using the fact that $V = l_y S$, the absorbance after equilibrium is expressed as:

$$A_{B2} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V} l_y = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{S}$$

From these equations, the following relationship is obtained:

$$A_{B2} = \varepsilon_D \frac{n_0}{S} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{S}$$

Using the fact that:

$n_M = 2(n_0 - n_D)$ (*4)

The following relationship is obtained:

$\varepsilon_D n_0 = \varepsilon_D n_D + 2\varepsilon_M(n_0 - n_D) = 2\varepsilon_M n_0 + (\varepsilon_D - 2\varepsilon_M) n_D$

$\rightarrow (\varepsilon_D - 2\varepsilon_M) n_0 = (\varepsilon_D - 2\varepsilon_M) n_D$

As $n_0 > n_D$ after the equilibrium, $\varepsilon_D/\varepsilon_M = 2$ holds at λ_{B2}.

THEORETICAL PROBLEM 4

The Redox Chemistry of Zinc

Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

PART A

The dissolution equilibrium of zinc hydroxide $Zn(OH)_2(s)$ at 25 °C and the relevant equilibrium constants are given in eq. 1–4.

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = 1.74 \times 10^{-17} \tag{1}$$

$$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq) \qquad K_1 = 2.62 \times 10^{-6} \tag{2}$$

$$Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq) \qquad K_2 = 6.47 \times 10^{-2} \tag{3}$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14} \tag{4}$$

The solubility, S, of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

$$S = [Zn^{2+}(aq)] + [Zn(OH)_2(aq)] + [Zn(OH)_4^{2-}(aq)] \tag{5}$$

4.1 When the equilibria in eq. 1–4 are established, calculate the pH range in which $[Zn(OH)_2(aq)]$ is the greatest among $[Zn^{2+}(aq)]$, $[Zn(OH)_2(aq)]$ and $[Zn(OH)_4^{2-}(aq)]$.

4.2 A saturated aqueous solution of $Zn(OH)_2(s)$ with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. Calculate the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.

PART B

Next, the recovered zinc hydroxide is heated to obtain zinc oxide according to the reaction below:

$$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(l) \quad (6)$$

The zinc oxide is then reduced to metallic zinc by reaction with hydrogen:

$$ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g) \quad (7)$$

4.3 In order for reaction (7) to proceed at a hydrogen pressure kept at 1 bar, it is necessary to reduce the partial pressure of the generated water vapor. Calculate the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 °C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are $\Delta G_{ZnO}(300°C) = -2.90 \times 10^2$ kJ mol^{-1} and $\Delta G_{H_2O}(300°C) = -2.20 \times 10^2$ kJ mol^{-1}, respectively.

Metallic zinc is used as a negative electrode (anode) material for metal-air batteries. The electrode consists of Zn and ZnO. It uses the following redox reaction to generate electricity with the electromotive force (e.m.f.) at 25 °C and pressure of 1 bar, $E°$.

$$Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s) \qquad E° = 1.65\,V \quad (8)$$

4.4 A zinc–air battery was discharged at 20 mA for 24 hours. Calculate the change in mass of the negative electrode (anode) of the battery.

Mt. Fuji

4.5 Consider the change of e.m.f. of a zinc–air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are −38 °C (February) and 3776 m, respectively. The atmospheric pressure is represented by

$$P\,[\mathrm{bar}] = 1.013 \times \left(1 - \frac{0.0065h}{T + 0.0065h + 273.15}\right)^{5.257} \qquad (9)$$

at altitude h [m] and temperature T [°C]. The molar ratio of oxygen in the atmosphere is 21%. The Gibbs energy change of reaction (8) is $\Delta G_{\mathrm{ZnO}}(-38°\mathrm{C}) = -3.26 \times 10^2$ kJ mol^{-1} at −38 °C and 1 bar.

4.6 Calculate the Gibbs energy change for reaction (6) at 25 °C. Note that the standard reduction potentials, $E°(\mathrm{Zn^{2+}/Zn})$ and $E°(\mathrm{O_2/H_2O})$ at 25 °C and 1 bar are given as (10) and (11), respectively.

$$\mathrm{Zn^{2+} + 2e^- \rightarrow Zn} \qquad E°(\mathrm{Zn^{2+}/Zn}) = -0.77\,\mathrm{V} \qquad (10)$$

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \qquad E°(\mathrm{O_2/H_2O}) = 1.23\,\mathrm{V} \qquad (11)$$

SOLUTION OF THE PROBLEM 4

4.1 Solution 1:

From $[Zn(OH)_2(aq)] > [Zn^{2+}]$:

$$\frac{K_{sp}}{[OH^-]^2} < K_1 \text{ (1')}$$

Solve this for $[OH^-]$:

pH > 8.4

$[Zn(OH)_2(aq)] > [Zn(OH)_4^{2-}]$:

$K_1 > K_2[OH^-]^2$ (2')

Solve this for $[OH^-]$:

pH < 11.8

Thus,

8.4 < pH < 11.8

Solution 2:

From (1):

$\log [Zn^{2+}][OH^-]^2 = \log K_{sp}$

$\log [Zn^{2+}] = \log K_{sp} - 2 \log [OH^-]$

From (2'):

$\log [Zn(OH)_2(aq)] = \log K_1$

$[Zn(OH)_2(aq)] > [Zn^{2+}]$:

$\log K_{sp} - 2 \log [OH^-] < \log K_1$ (1')

$\log K_{sp} - 2 (pH - 14) < \log K_1$

From (3'):

$\log ([Zn(OH)_4^{2-}]/[OH^-]^2) = \log K_2$

$\log [Zn(OH)_4^{2-}] = 2 \log[OH^-] + \log K_2$

$[Zn(OH)_2(aq)] > \log [Zn(OH)_4^{2-}]$

$\log K_1 > 2 \log [OH^-] + \log K_2$ (2')

$\log K_1 > 2 (pH - 14) + \log K_2$

Thus,

8.4 < pH < 11.8

4.2 For pH = 12.00:

log [$Zn(OH)_4^{2-}$] = −29.19 + 2 pH = −5.19

log [$Zn(OH)_2(aq)$] = −5.58

log [Zn^{2+}] = 11.24 − 2 pH = −12.76

Thus, S = 9.0865 × 10^{-6} mol L^{-1} (1')

For pH = 7.00:

log [$Zn(OH)_4^{2-}$] = −29.19 + 2 pH = −15.19

log [$Zn(OH)_2(aq)$] = −5.58

log [Zn^{2+}] = 11.24 − 2 pH = −2.76

Thus,

S = 1.7404 × 10^{-3} mol L^{-1} (2')

The percentage of zinc precipitated is:

$$\frac{1.7404 \times 10^{-3} - 9.0865 \times 10^{-6}}{1.7404 \times 10^{-3}} = 0.9948 = 99.5\%$$

4.3 Zn + ½ O_2 → ZnO, ΔG_{ZnO}(300°C) = −2.90 × 10^2 kJ mol^{-1}

H_2 + ½ O_2 → H_2O, ΔG_{H2O}(300°C) = −2.20 × 10^2 kJ mol^{-1}

Thus,

ZnO + H_2 → Zn + H_2O, ΔG = ΔG_{H2O}(300°C) − ΔG_{ZnO}(300°C) (1')

= 7.0 × 10^1 kJ mol^{-1}

$$\ln K = \ln \frac{p_{H_2O}}{p_{H_2}} = -\frac{\Delta G}{RT}$$ (2')

From T = 573.15 K,

p_{H2O} = 4.14 × 10^{-7} bar = 4.1 × 10^{-7} bar

4.4 The reaction Zn → ZnO occurs at the negative electrode and consumes 2 mol electrons per mol Zn oxidized.

Thus, the weight change is:

$$W = \frac{0.02 \times 24 \times 60 \times 60 \times 16}{2F}$$ (1')

$$= 0.14\,\text{g}$$

4.5 **Solution 1:**

From (9), the air pressure at 3776 m and T = −38 °C is

P = 0.6011 bar (1')

From the oxygen content of 21% , the partial pressure of oxygen is:

P_{O2} = 0.126 bar

From the Nernst equation (T = −38 °C):

$$E(-38\,^\circ\mathrm{C}) - E^\circ(-38\,^\circ\mathrm{C}) = -\frac{RT}{2F}\ln\frac{1}{\sqrt{P_{O_2}}} = -0.01048\,\mathrm{V} = -0.01\,\mathrm{V}\ (2')$$

$$E^\circ(-38\,^\circ\mathrm{C}) = -\frac{\Delta G^\circ(-38\,^\circ\mathrm{C})}{2F} = \frac{326000}{2F} = 1.6894\,\mathrm{V} = 1.69\,\mathrm{V}\ (3')$$

From (2') and (3'):

E(−38 °C) = 1.68 V

Solution 2:

From (9), the air pressure at 3776 m and T = −38 °C is

P = 0.6011 bar (1')

From the oxygen content of 21% , the partial pressure of oxygen is:

P_{O2} = 0.126 bar

$$\Delta G(-38\,^\circ\mathrm{C}) = \Delta G^\circ(-38\,^\circ\mathrm{C}) - \frac{1}{2}RT\ln P_{O_2}\ (2')$$

$$= -3.24 \times 10^2\ \mathrm{kJ\ mol^{-1}}$$

$$E(-38\,^\circ\mathrm{C}) = -\frac{\Delta G(-38\,^\circ\mathrm{C})}{2F}\ (3')$$

$$= 1.68\,\mathrm{V}$$

4.6 From (10):

$Zn^{2+} + 2e^- \rightarrow Zn$, E° = −0.77 V

$\Delta G^\circ = -2F \times -0.77$ (1')

= 148.59 kJ mol^{-1}

From (8):

$Zn + ½\ O_2 \rightarrow ZnO$, E° = 1.65 V

$\Delta G^\circ = -2F \times 1.65$ (2')

= −318.40 kJ mol^{-1}

From (11):

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, E° = 1.23 V

$\Delta G^\circ = -4F \times 1.23$ (3')

= −474.71 kJ mol^{-1}

From (1):

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2(s)$, K_{sp} = 1.74×10^{-17}

$\Delta G^\circ = -RT\ \ln K_{sp}^{-1}$ (4')

= −95.662 kJ mol^{-1}

From (4):

$H^+ + OH^- \rightarrow H_2O$, K_w = 1 × 10^{-14}

$\Delta G° = -RT \ln K_w^{-1}$ (5')

$= -79.912$ kJ mol^{-1}

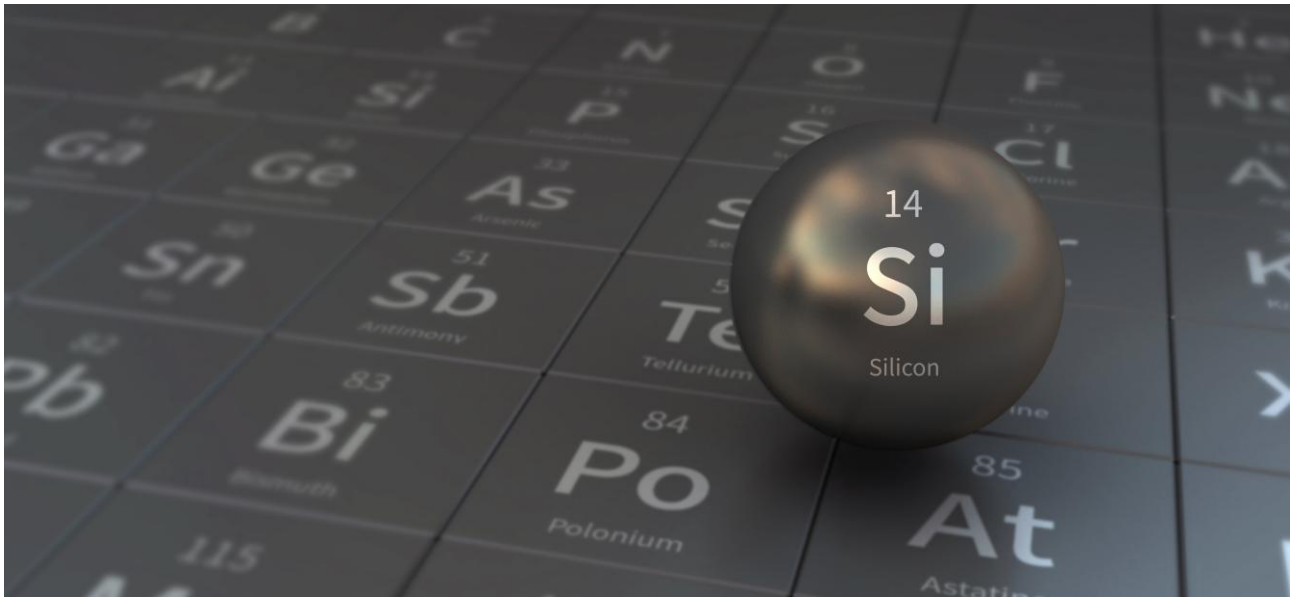
From $\frac{(1')\times 2+(2')\times 2-(3')-(4')\times 2+(5')\times 4}{2}$

$Zn(OH)_2 \rightarrow ZnO + H_2O$, $\Delta G° = 3.0 \sim 3.4 \times 10^3$ J mol^{-1}

(distributed depending on the handling of figures)

THEORETICAL PROBLEM 5

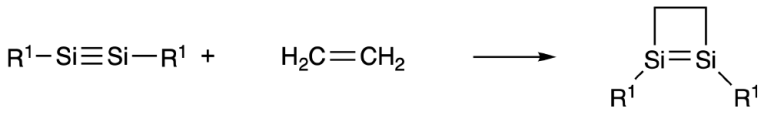
Mysterious Silicon



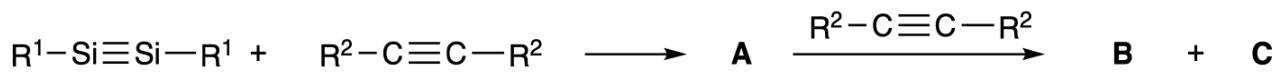
Although silicon is also a group 14 element like carbon, their properties differ significantly.

PART A

Unlike the carbon–carbon triple bond, the silicon–silicon triple bond in a compound formulated as R^1–Si≡Si–R^1 (R: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.



When R^1–Si≡Si–R^1 is treated with an alkyne (R^2–C≡C–R^2), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of R^2–C≡C–R^2 with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called ‘disilabenzenes’ that contain a six-membered ring and can be formulated as $(R^1–Si)_2(R^2–C)_4$.



The ^{13}C NMR analysis of the corresponding six-membered ring skeletons Si_2C_4 shows two signals for **B** and one signal for **C**.

5.1 **Draw** the structural formulae of **A**, **B**, and **C** using R^1, R^2, Si, and C, with one of the possible resonance structures.

5.2 Calculate the aromatic stabilization energy (ASE) for benzene and **C** (in the case of $R^1 = R^2 = H$) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1).

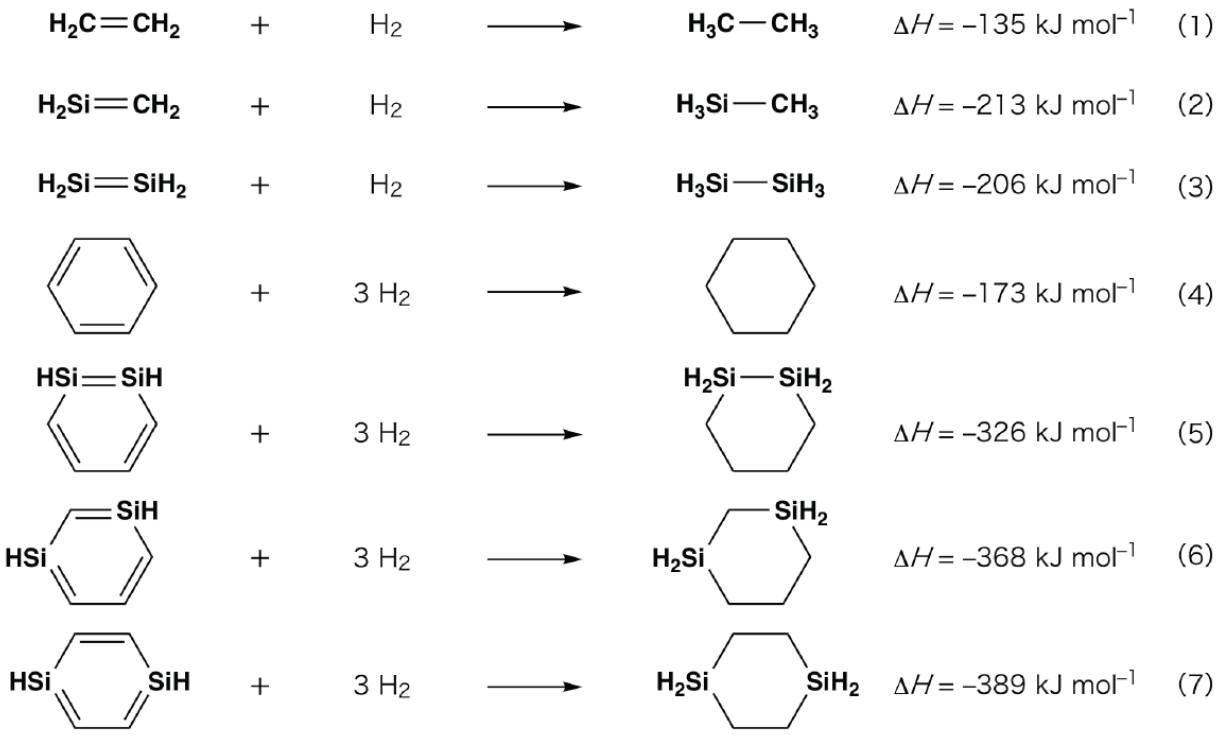


Fig. 1

When a xylene solution of **C** is heated, it undergoes isomerization to give an equilibrium mixture of compounds **D** and **E**. The molar ratio is **D** : **E** = 1 : 40.0 at 50.0 °C and **D** : **E** = 1 : 20.0 at 120.0 °C.

5.3 **Calculate** ΔH for the transformation of **D** to **E**. Assume that ΔH does not depend on temperature.

The isomerization from **C** to **D** and to **E** proceeds via transformations of π-bonds into σ-bonds without breaking any σ-bonds. A ^{13}C NMR analysis revealed one signal for the Si_2C_4 skeleton of **D** and two signals for that of **E**. The skeleton of **D** does not contain any three-membered rings, while **E** has two three membered rings that share an edge.

5.4 **Draw** the structural formulae of **D** and **E** using R^1, R^2, Si, and C

PART B

Silicon is able to form highly coordinated compounds (> four substituents) with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

The fluorination reaction of CCl_4 using Na_2SiF_6 was carried out as follows.

Standardization of Na_2SiF_6 solution:

• Preparation

Aqueous solution **F**: 0.855 g of Na_2SiF_6 (188.053 g mol^{-1}) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ (568.424 g mol^{-1}) dissolved in water (total volume: 200 mL).

• Procedure

Precipitation titration of a solution **F** (50.0 mL) by dropwise adding solution **G** in the presence of xylenol orange, which coordinates to Ce^{3+}, as an indicator. After adding 18.8 mL of solution **G**, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce^{3+}, and the only resulting silicon compound is $Si(OH)_4$.

5.5 Write the balanced equation for the reaction of Na_2SiF_6 with $Ce_2(SO_4)_3$.

• Reaction of CCl_4 with Na_2SiF_6:

(Substance losses by *e.g.* evaporation are negligible during the following operations.)

Na_2SiF_6(x [g]) was added to CCl_4 (500.0 g) and heated to 300˚C in a sealed pressure-resistant reaction vessel. The unreacted Na_2SiF_6 and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with CCl_4 (solution **H**). The ^{29}Si and ^{19}F NMR spectra of solution **H** showed SiF_4 as the only silicon compound. In the ^{19}F NMR spectrum, in addition to SiF_4, signals corresponding to $CFCl_3$, CF_2Cl_2, CF_3Cl, and CF_4 were observed (*cf.* Table 1). The integration ratios in the ^{19}F NMR spectrum are proportional to the number of fluorine nuclei.

Table 1

^{19}F NMR data	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
Integration ratio	45.0	65.0	18.0	2.0

SiF_4 is hydrolyzed to form H_2SiF_6 according to the following eq. 8:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \quad (8)$$

Solution **H** (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF_4. After separation, the H_2SiF_6 generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na_2SiF_6 (aqueous solution **J**).

The precipitate of unreacted Na_2SiF_6 and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution **K**; 10.0 L).

Then, additional precipitation titrations using solution **G** were carried out, and the endpoints of the titrations with **G** were as follows:

· For solution **J** (entire amount): 61.6 mL.

· For 100 mL of solution **K**: 44.4 mL.

It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

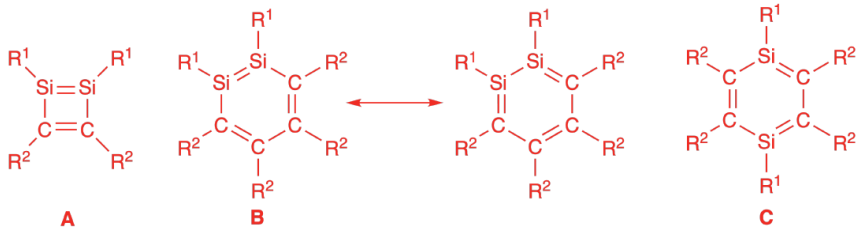
5.6 Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and calculate the mass (x [g]) of the Na_2SiF_6 used as a starting material.

5.7 77.8% of the CCl_4 used as a starting material was unreacted. Calculate the mass of CF_3Cl generated.

———————————

SOLUTION OF THE PROBLEM 5

5.1 Any resonance structure is acceptable.



5.2 The aromatic stabilization energy (ASE) can be calculated as the difference of the sum of the heat of hydrogenation of each double bond and the heat of hydrogenation of the aromatic compound.

ASE for benzene: 135 × 3 − 173 = 232 kJ mol^{-1}

ASE for 1,4-disilabenzene (C=C + 2 Si=C): (135 + 213 × 2) − 389 = 172 kJ mol^{-1}

5.3

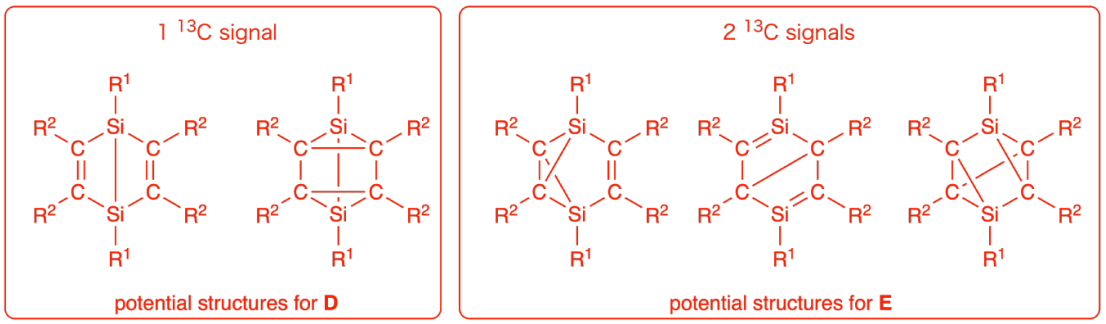
$$\text{T} = 50\ ^\circ\text{C} = 323.15\ \text{K}\ \left(\frac{1}{RT} = 0.3722\right) : K_{\text{DE}} = 40$$

$$\text{T} = 120\ ^\circ\text{C} = 393.15\ \text{K}\ \left(\frac{1}{RT} = 0.3095\right) : K_{\text{DE}} = 20$$

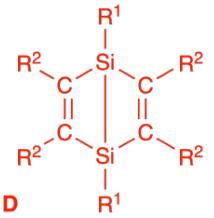
$$\text{According to ln}\ K_{\text{DE}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta H = -\frac{\ln(K_{\text{DE50}}) - \ln(K_{\text{DE120}})}{\frac{1}{RT_{50}} - \frac{1}{RT_{120}}} = -\frac{\ln 40 - \ln 20}{0.3722 - 0.3059} = -10.5\ \text{kJ mol}^{-1}$$

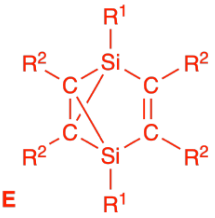
5.4 Based on the signals observed in the ^{13}C NMR spectra, the following structures could be suggested for **D** and **E**:



In addition, considering that **D** has no three-membered ring in its skeleton while **E** has two three membered rings that share an edge, the structures of **D** and **E** can be determined to be those shown below:



D



E

5.5 $M(Na_2SiF_6)$ = 188.053 g mol^{-1}. The concentration of Na_2SiF_6 in solution **F** is

$$\frac{0.855\ \text{g}}{200\ \text{mL}} = \frac{4.548 \times 10^{-3}\ \text{mol}}{0.2\ \text{L}} = 2.274 \times 10^{-2}\ \text{mol L}^{-1}\ (\textbf{F})$$

$M(Ce_2(SO_4)_3)$ = 568.424 g mol^{-1}. The concentration of $Ce_2(SO_4)_3$ in solution **G** is

$$\frac{6.860\ \text{g}}{200\ \text{mL}} = \frac{1.207 \times 10^{-2}\ \text{mol}}{0.2\ \text{L}} = 6.034 \times 10^{-2}\ \text{mol L}^{-1}\ (\textbf{G})$$

The concentration of Ce^{3+} ions in **G** is $6.034\times10^{-2}\times2 = 1.207\times10^{-2}$ mol L^{-1}.

In 50.0 mL of solution **F**: $2.274\times10^{-2}\times50.0 / 1000 = 1.137\times10^{-3}$ mol of Na_2SiF_6 was included.

In 18.8 mL of solution **G**: $6.034\times10^{-2}\times18.8 / 1000 = 1.134\times10^{-3}$ mol of $Ce_2(SO_4)_3$ was included.

Accordingly, Na_2SiF_6 should react with $Ce_2(SO_4)_3$ in a 1:1 ratio.

Ans. $Na_2SiF_6 + Ce_2(SO_4)_3 + 4\ H_2O \longrightarrow 2\ CeF_3 + Si(OH)_4 + Na_2SO_4 + 2\ H_2SO_4$

5.6 $3\ SiF_4 + 2\ H_2O \longrightarrow SiO_2 + 2\ H_2SiF_6$

The ratio of the consumed SiF_4 and the generated H_2SiF_6 should be 3:2.

As Na_2SiF_6 reacts with $Ce_2(SO_4)_3$ in a 1:1 ratio, the amount of SiF_6^{2-} in the aqueous solution **J** is (6.034×10^{-2} mol L^{-1}) × (61.6×10^{-3} L) = 3.717×10^{-3} mol. Considering the equation shown above, 10 mL of the diluted solution **H** contains

3.717×10^{-3} mol ×3/2 = 5.576×10^{-3} mol of SiF_4.

Thus, 1.00 L of diluted solution **H** contains

5.576×10^{-3} mol×1000 / 10 = 5.576×10^{-1} mol of SiF_4.

The amount of fluorine atoms that replace the chlorine atoms of CCl_4 should be twice the amount of SiF_4 formed during the reaction. Thus, 2×0.5576 = 1.115 mol of F– should replace Cl– to result in the formation of NaCl.

1.115 mol × 58.44 g mol^{-1} = 65.17 g of NaCl was formed.

Ans.: 65.2 g (NaCl)

As Na_2SiF_6 reacts with $Ce_2(SO_4)_3$ in a 1:1 ratio, the amount of SiF_6^{2-} in 100 mL of aqueous solution **K** is 44.4×10^{-3} L × (6.034×10^{-2} mol L^{-1}) = 2.679×10^{-3} mol. Accordingly, the residual amount of Na_2SiF_6 in 10.0 L of aqueous solution **K** is

2.679×10^{-3} mol ×10.0 L / 100 mL = 0.2679 mol. In total, the amount of Na_2SiF_6 used as a starting material is (0.2679 mol + 0.5576 mol) × 188.0 g mol^{-1} = 155.2 g

Ans.: 155 g (Na_2SiF_6)

5.7 500.0 g, thus 3.250 mol of CCl_4 was initially used as a starting material. Thus, the amount of the products that contain at least one F atom is 3.250 mol × 0.222 = 0.721 mol.

The ratio of integrals in the ^{19}F NMR spectrum is $CFCl_3$: CF_2Cl_2 : CF_3Cl : CF_4 = 45.0 : 65.0 : 18.0 : 2.0. Thus, the mole ratio of these compounds should be $CFCl_3$: CF_2Cl_2 : CF_3Cl : CF_4 = 45.0 : 32.5 : 6.0 : 0.5 = 90 : 65 : 12 : 1. Accordingly, the amount of CF_3Cl (104.46 g mol^{-1}) is 0.721 mol ×12 / (90 + 65 + 12 + 1) = 0.0515 mol, thus 0.0515 mol × 104.46 g mol^{-1} = 5.38 g

Ans.: 5.38 g

THEORETICAL PROBLEM 6

The Solid-State Chemistry of Transition Metals

Volcano at Sakurajima island

PART A

Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions (M^{n+}) in the magma is incorporated into the silicate minerals. The M^{n+} studied in the problem are coordinated by oxide ions (O^{2-}) and adopt a four-coordinate tetrahedral (T_d) geometry in the magma and six-coordinate octahedral (O_h) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration. The distribution coefficient of M^{n+} between the silicate minerals and magma, D, can be expressed by:

$$D = \frac{[M]_s}{[M]_l}$$

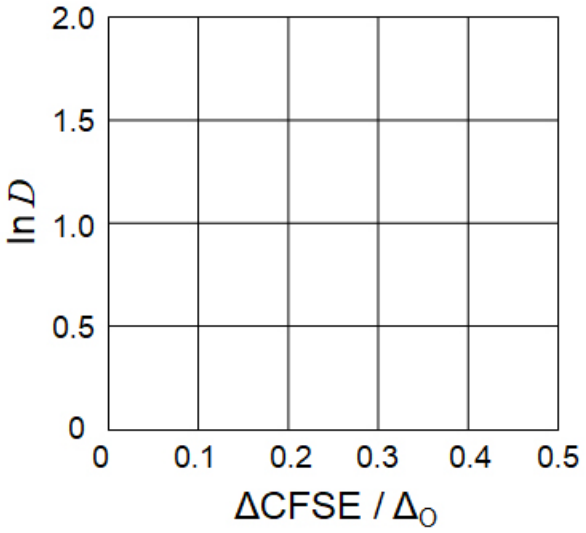
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

	Cr^{2+}	Mn^{2+}
D	7.2	1.1

Let Δ_O and $CFSE^O$ be the energy separation of the d-orbitals of M^{n+} and the crystal-field stabilization energy in a O_h field, respectively. Let Δ_T and $CFSE^T$ be those in a T_d field.

6.1 Calculate $|CFSE^O - CFSE^T| = \Delta CFSE$ in terms of Δ_O for Cr^{2+}, Mn^{2+}, and Co^{2+}; assume $\Delta_T = 4/9\Delta_O$.

6.2 A linear relationship is observed by plotting ln D against ΔCFSE / Δ_O in the Cartesian coordinate system shown below. Estimate D for Co^{2+}.



Metal oxides MO (M: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure wherein the M^{n+} adopts an O_h geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is mainly governed by the Coulomb interactions based on the radius and charge of the ions and some contributions from the CFSE of M^{n+} in the O_h field.

6.3 Choose the appropriate set of lattice enthalpies [kJ mol^{-1}] from one of the options (a) to (f).

	CaO	TiO	VO	MnO	CoO
(a)	3460	3878	3913	3810	3916
(b)	3460	3916	3878	3810	3913
(c)	3460	3913	3916	3810	3878
(d)	3810	3878	3913	3460	3916
(e)	3810	3916	3878	3460	3913
(f)	3810	3913	3916	3460	3878

PART B

A mixed oxide **A**, which contains La^{3+} and Cu^{2+}, crystallizes in a tetragonal unit cell shown in Fig.1. In the [CuO_6] octahedron, the Cu–O length along the *z*-axis (l_z) is longer than that of the *x*-axis (l_x), and [CuO_6] is distorted from the regular O_h geometry. This distortion removes the degeneracy of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}).

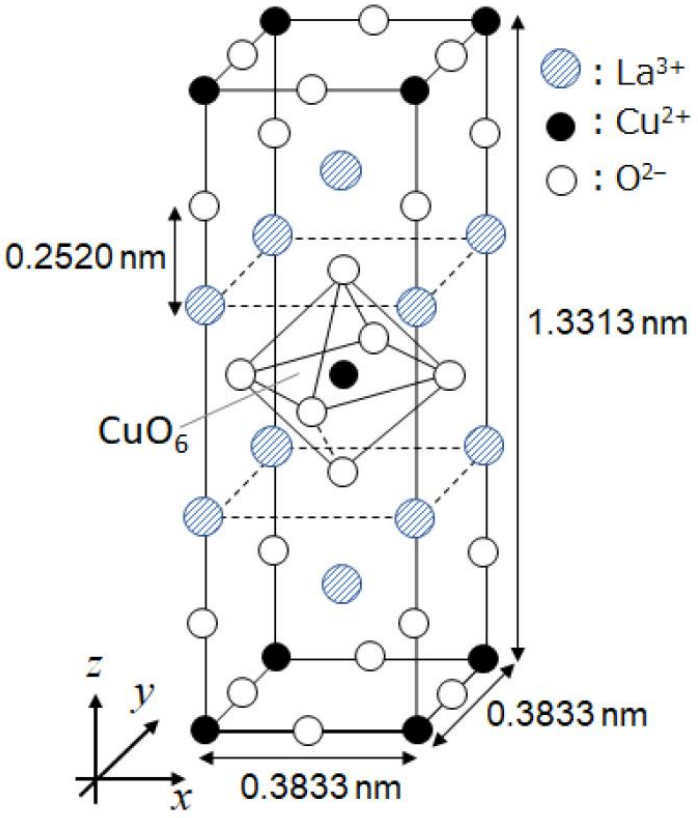


Fig. 1

A can be synthesized by thermal decomposition (pyrolysis) of complex **B**, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid $C_4H_2O_4$, i.e., a diacid. The pyrolysis behavior of **B** in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of CO_2. The total weight loss during the formation of **A** from **B** is 63.6%. It should be noted that only water and CO_2 are released in the pyrolysis reaction.

6.4 Write the chemical formulae for **A** and **B**.

6.5 Calculate l_x and l_z using Fig. 1.

6.6 For Cu^{2+} in the distorted $[CuO_6]$ octahedron in A of Fig. 1, write the names of the split e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet.

A is an insulator. When one La^{3+} is substituted with one Sr^{2+}, one hole is generated in the crystal lattice that can conduct electricity. As a result, the Sr^{2+}-doped **A** shows superconductivity below 38 K. When a substitution reaction took place for **A**, 2.05×10^{27} holes m^{-3} were generated.

6.7 Calculate the percentage of Sr^{2+} substituted for La^{3+} based on the mole ratio in the substitution reaction. Note that the valences of the constituent ions and the crystal structure are not altered by the substitution reaction

PART C

$Cu_2(CH_3CO_2)_4$ is composed of four $CH_3CO_2^-$ coordinated to two Cu^{2+} (Fig. 2A). $Cu_2(CH_3CO_2)_4$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four $CH_3CO_2^-$ and an axis passing through the two Cu^{2+}, all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of $CH_3CO_2^-$, a "cage complex" is formed. The cage complex Cu_4(**L1**)$_4$ is composed of planar dicarboxylate **L1** (Fig. 2B) and Cu^{2+} (Fig. 2C). The angle θ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The θ is 0° for **L1**. Note that hydrogen atoms are not shown in Fig. 2.

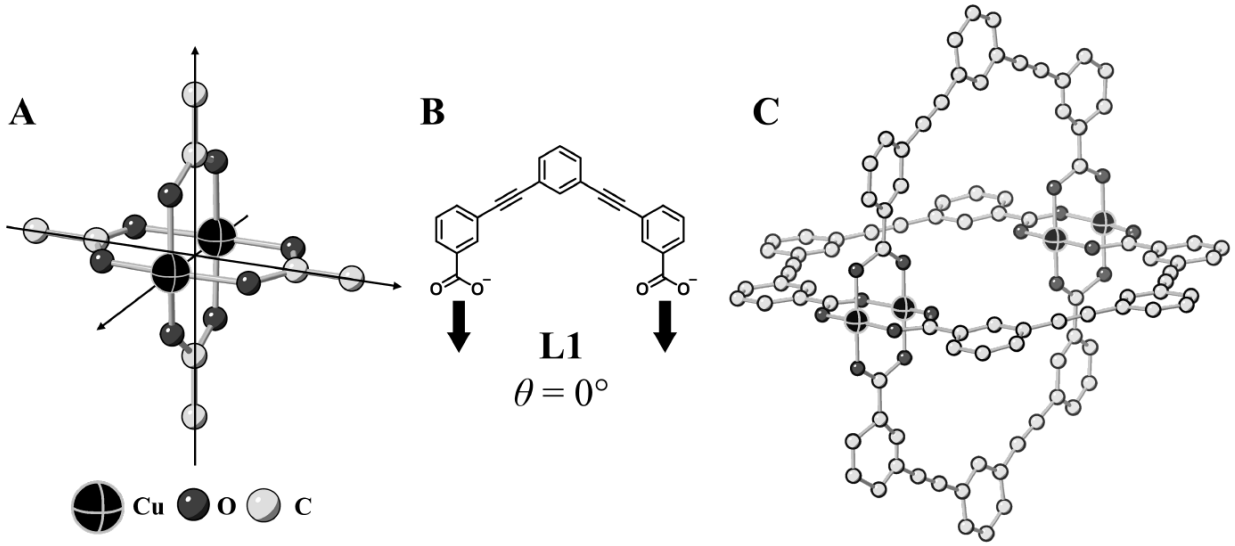
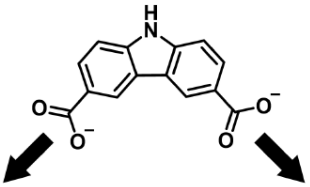


Fig. 2

6.8 The θ of the planar dicarboxylate **L2** below is fixed to 90˚. If the composition of the cage complex formed from **L2** and Cu^{2+} is Cu_n(**L2**)$_m$, give the smallest integer combination of n and m. Assume that only the CO_2− groups of **L2** form a coordination bond to Cu^{2+} ions.



L2

$\theta = 90°$

A zinc complex, $Zn_4O(CH_3CO_2)_6$, contains four tetrahedral Zn^{2+}, six $CH_3CO_2^-$, and one O^{2-} (Fig. 3A). In $Zn_4O(CH_3CO_2)_6$, the O^{2-} is located at the origin, and the three axes passing through the carbon atoms of $CH_3CO_2^-$ are oriented orthogonal relative to each other. When *p*-benzenedicarboxylate (Fig. 3B, **L3**, θ = 180°) is used instead of $CH_3CO_2^-$, the Zn^{2+} clusters are linked to each other to form a crystalline solid (**X**) that is called a "porous coordination polymer" (Fig. 3C). The composition of **X** is $[Zn_4O(\mathbf{L3})_3]_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral Zn^{2+} cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

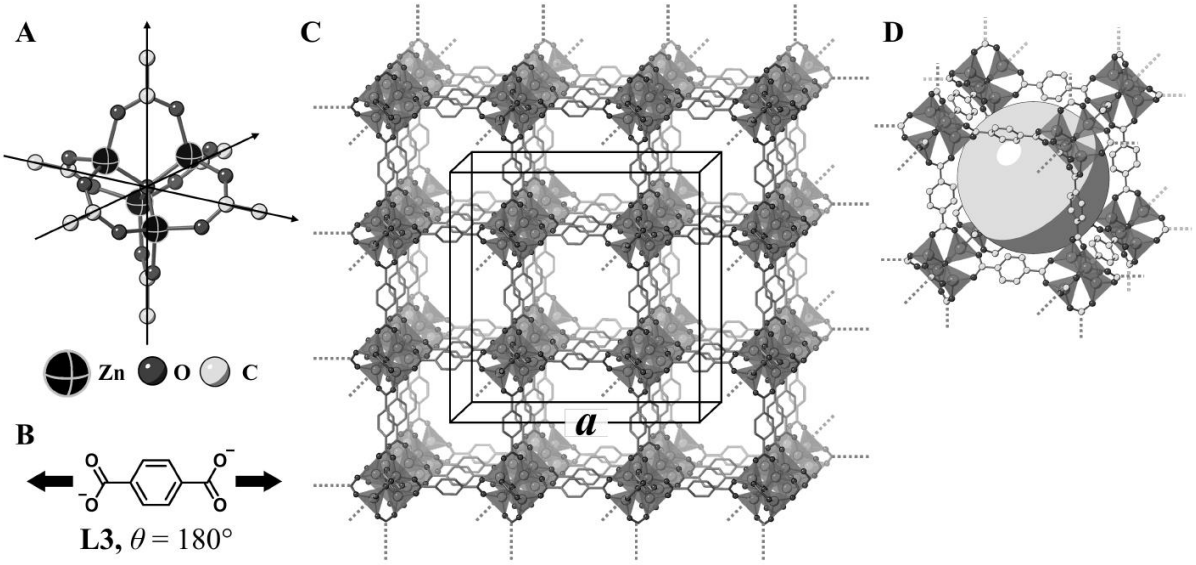


Fig. 3

6.9 **X** has a cubic unit cell with a side length of a (Fig. 3C) and a density of 0.592 g cm^{-3}. **Calculate** a in [cm].

6.10 **X** contains a considerable number of pores, and 1 g of **X** can accommodate 3.0 × 10^2 mL of CO_2 gas in the pores at 1 bar and 25 °C. Calculate the average number of CO_2 molecules per pore.

SOLUTION OF THE PROBLEM 6

6.1 The d-orbitals of a six-coordinate octahedral complex split into two groups e_g ($d_{x^2-y^2}$, d_{z^2}), and t_{2g} (d_{xy}, d_{yz}, d_{zx}) with an energy separation of Δ_O. The energies of the e_g and t_{2g} orbitals relative to the barycenter are $+0.60\Delta_O$ and $-0.40\Delta_O$, respectively. Likewise, the d-orbitals of a four-coordinate tetrahedral complex split into two groups t_2 (d_{xy}, d_{yz}, d_{zx}) and e ($d_{x^2-y^2}$, d_{z^2}) with an energy separation of Δ_T. The energies of the t_2 and e orbitals relative to the barycenter are $+0.40\Delta_T$ and $-0.60\Delta_T$, respectively.

Therefore, in the case of a high-spin electron configuration, $CFSE^O$ and $CFSE^T$ for Cr^{2+} ($3d^4$: $t_{2g}^3\ e_g^1$ or $e^2t_2^2$) are $-0.60\Delta_O$ and $-0.40\Delta_T$ (= $-0.18\Delta_O$), respectively. $CFSE^O$ and $CFSE^T$ for Mn^{2+} ($3d^5$: $t_{2g}^3e_g^2$ or $e^2t_2^3$) are both zero. $CFSE^O$ and $CFSE^T$ for Co^{2+} ($3d^7$: $t_{2g}^4e_g^3$ or $e^4t_2^3$) are $-0.80\Delta_O$ and $-1.2\Delta_T$ (= $-0.53\Delta_O$), respectively. Accordingly, $|CFSE^O - CFSE^T| = \Delta CFSE$ values for each metal ion are,

Cr^{2+}: $|-0.60\Delta_O - (-0.18\Delta_O)| = 0.42\Delta_O$,

Mn^{2+}: 0,

Co^{2+}: $|-0.80\Delta_O - (-0.53\Delta_O)| = 0.27\Delta_O$

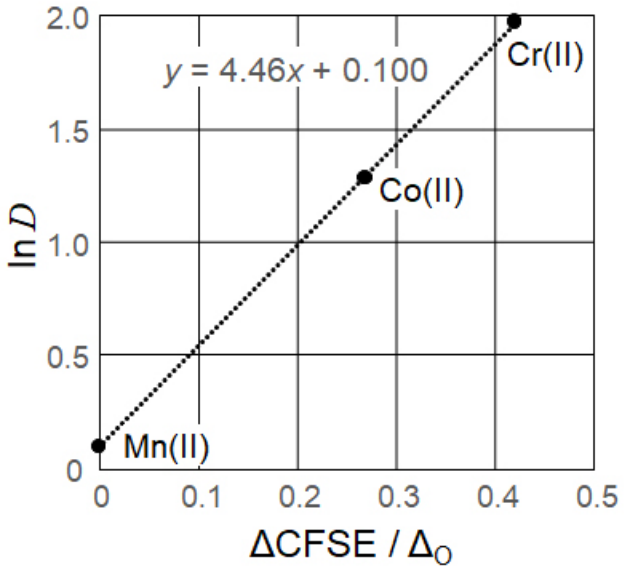
6.2 The coordinates of Mn^{2+} and Cr^{2+} are (0, 0.095) and (0.42, 1.97), respectively. The linear regression line calculated from these coordinates would be $y = 4.46x + 0.100$

$\Delta CFSE$ of Co^{2+} is $0.27\Delta_O$

Therefore, $D = \exp(4.46 \times 0.27 + 0.100) = 3.68$ (= 3.7)

Whether the graph is drawn does not affect grading.

If the coordinates of Mn^{2+} and Cr^{2+} are correctly plotted and the D is estimated with guide of the graph, full mark is given.



6.3 The lattice enthalpy is determined by the Coulomb interactions, which are proportional to the product of the valences of the constituent ions and inversely proportional to the sum of the ionic radii. As the target compounds are oxides of divalent metal ions, we should consider the ionic radii of the metal ions. The radii of divalent metal ions within the same period decrease with increasing atomic number. Let us compare the lattice enthalpies of CaO and MnO with no contribution from the CFSE: The ionic radius of Mn^{2+} is smaller than that of Ca^{2+}, and therefore, the lattice enthalpy is higher for MnO. So, the participants should choose (a), (b), or (c). Then, let us compare the lattice enthalpies of TiO (d^2) and VO (d^3): The ionic radius of V^{2+} is smaller than that of Ti^{2+}, and the CFSE is higher for VO than for TiO. Accordingly, the lattice enthalpy is also higher for VO. Based on these observations, the answer should be (a) or (c). Finally, let us compare the lattice enthalpies of TiO (d^2) and CoO (d^7): The ionic radius of Co^{2+} is smaller than that of Ti^{2+}, while their CFSEs are equal. Thus, the lattice enthalpy is higher for CoO. Thus, the correct answer is (a). Partial credit is given for (b) and (c).

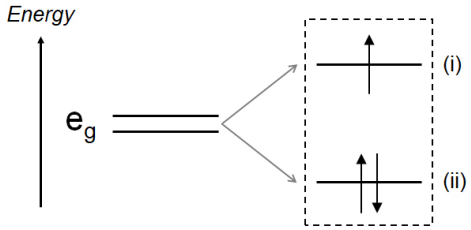
6.4 The unit cell shown in Fig. 1 contains four La^{3+}, two Cu^{2+}, and eight O^{2-} ions. Therefore, **A**: La_2CuO_4. As the formula weight of La_2CuO_4 is 405.3, that of **B** should be 1113.5 considering the following equation: 405.3 ÷ (1 – 0.636). Given that the weight loss due to crystallization water is 29.1%, the number of molecules of crystallization water is 18.00 considering the following equation: (1113.5 × 0.291) ÷ 18 ($18H_2O$; M = 324). Complex **B** is a trinuclear complex that consists of two La^{3+} and one Cu^{2+} ions. Considering that the synthetic solution is basic, the squaric acid

is deprotonated and coordinates to the metal ion as $C_4O_4^{2-}$. The number of squaric acid molecules is 4.00 based on the following equation: (1113.5 – 138.9 × 2 – 63.5 – 324) ÷ 112 ($C_4O_4^{2-}$; M = 112). B: $La_2Cu(C_4O_4)_4(H_2O)_{18}$ ($La_2CuC_{16}O_{34}H_{36}$)

6.5 l_x: 0.3833 ÷ 2 = 0.1917 (= 0.192 nm).

l_z: (1.3313 – 0.2520 × 2) ÷ 4 = 0.2068 (= 0.207 nm)

6.6 (i) $d_{x^2-y^2}$, (ii) d_{z^2}



6.7 The corresponding reaction equation, where the amount of Sr^{2+} is x%, is:

$La_2CuO_4 + (2x/100)Sr^{2+} \rightarrow [La_{2(1-x/100)}Sr_{(2x/100)}CuO_4]^{(2x/100)-} + (2x/100)La^{3+}$

The charge of $[La_{2(1-x/100)}Sr_{(2x/100)}CuO_4]$ is negative, and the amount of doped holes is $(2x/100)h^+$ per mole. The volume of the unit cell is $0.3833^2 \times 1.3313 = 0.1956$ nm^3. The unit cell contains four La^{3+}, two Cu^{2+}, and eight O^{2-} ions, i.e., the unit contains two La_2CuO_4. Accordingly, the number of holes per unit cell is (4x/100).

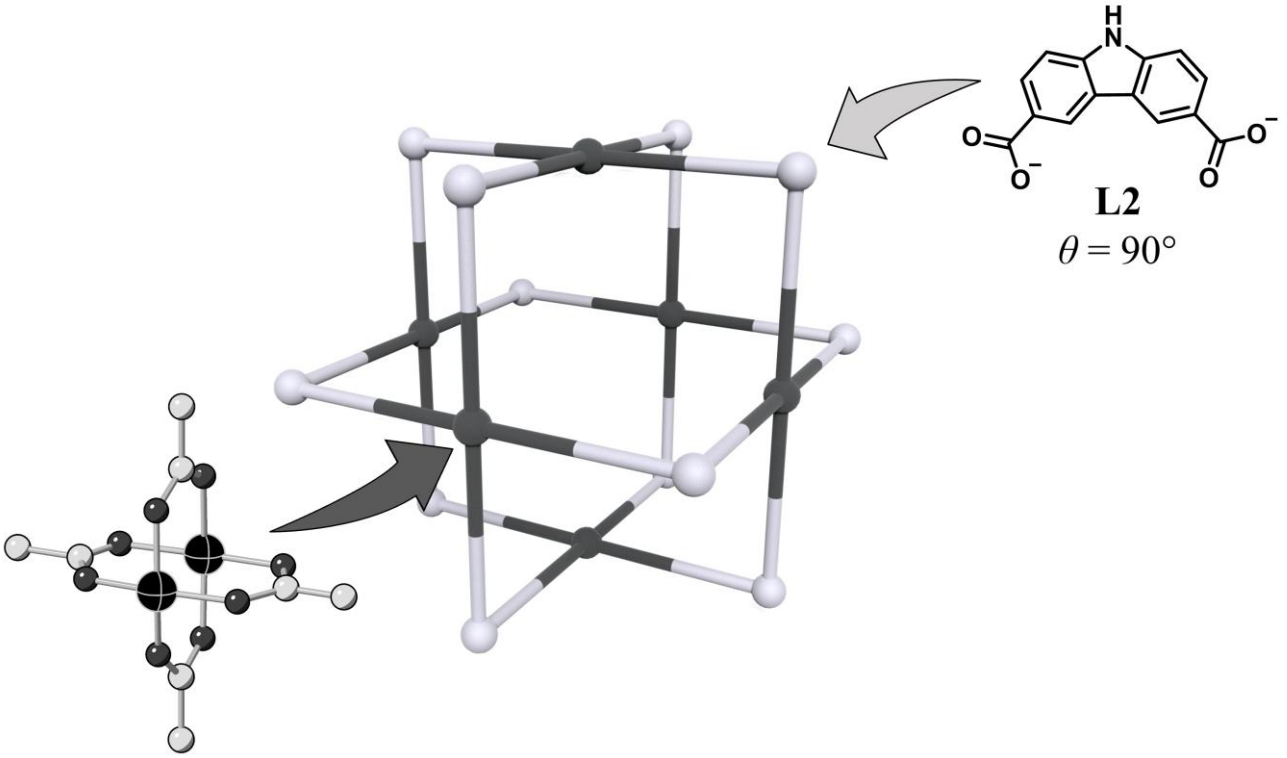
Since the concentration of holes is the number of holes divided by the unit cell volume, the following equation is satisfied: $(4x/100)/(0.1956 \times 10^{-27}) = 2.05 \times 10^{-27}$, x = 10%.

Alternative answer without giving the substitution reaction; density of La^{3+} in the unit cell $4/(0.3833^2 \times 1.3313) = 20.45$ nm^{-3}

Density of holes in the unit cell is 2.05 nm^{-3}

Therefore, the percentage of substitution is 2.05/20.45 × 100 = 10%.

6.8 *n* = *m* = 12



6.9 The molecular weight of Zn_4O(**L3**)$_3$ is 770.

According to Figure 3C, there are eight Zn_4O(**L3**)$_3$ units in the unit cell. Therefore, the molecular weight per unit cell can be calculated as 770 × 8 = 6160.

The weight of the unit cell is 6160 ÷ N_A = 1.02 × 10^{-20} g.

Let the length of the side of the unit cell be a [cm], then, (1.02 × 10^{-20}) g / a^3 [cm^3] = 0.592 g cm^{-3}.

a = 2.6 × 10^{-7} cm

6.10 There is one pore per Zn_4O(**L3**)$_3$ unit.

Number of pores [mol] per 1 [g] of **X**: 1 [g] / 770 = 0.00130.

Based on the ideal gas equation, 3.0 × 10^2 [mL] of adsorbed CO_2 corresponds to: (1×10^5 [Pa] × 3.0×10^{-4} [m^3]) / (8.31×298 [K]) = 0.0121 [mol] of CO_2.

Therefore, 0.0121 ÷ 0.00130 = 9.3 molecules of CO_2 per pore.

THEORETICAL PROBLEM 7

Playing with Non-benzenoid Aromaticity

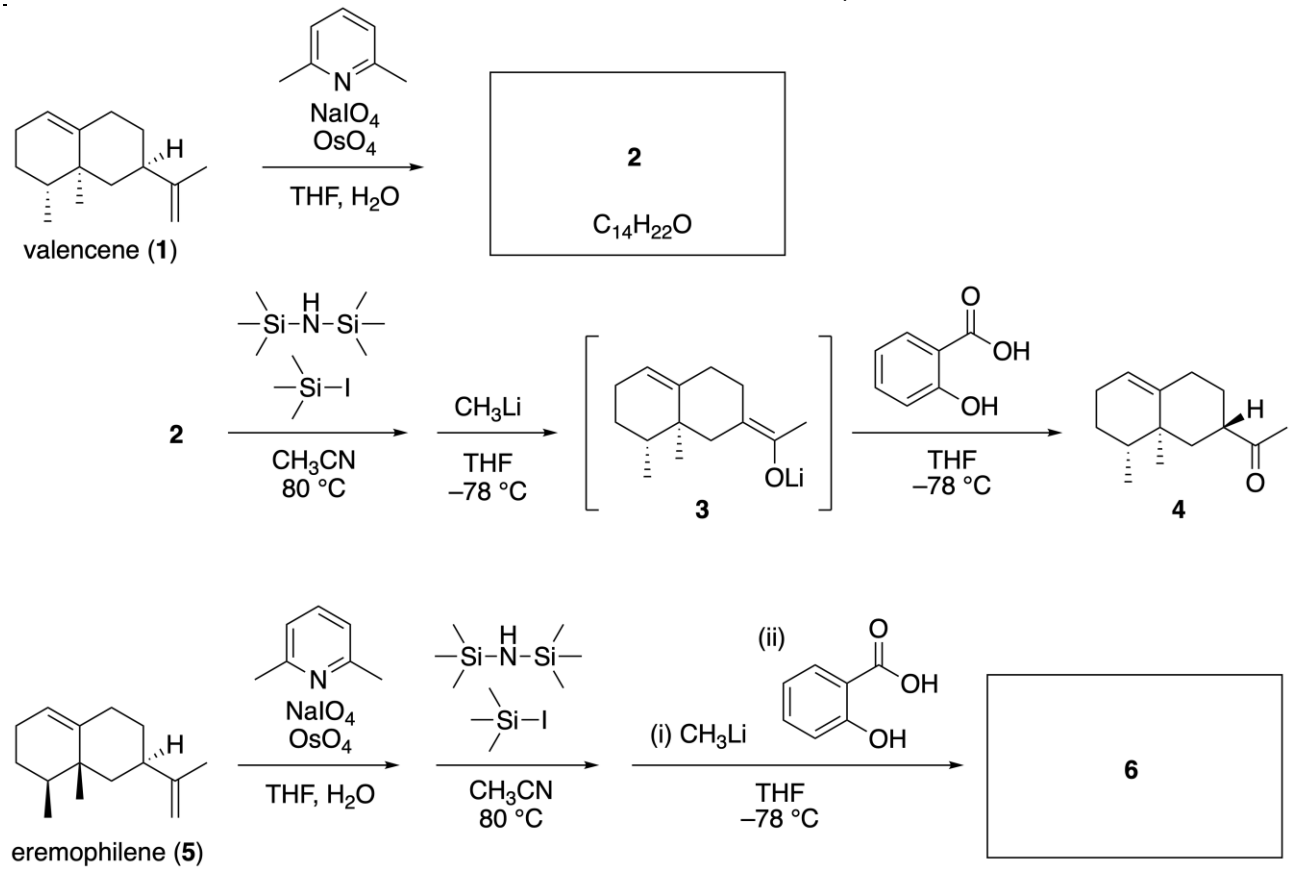
Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

Photo courtesy: Tohoku Univ.

PART A

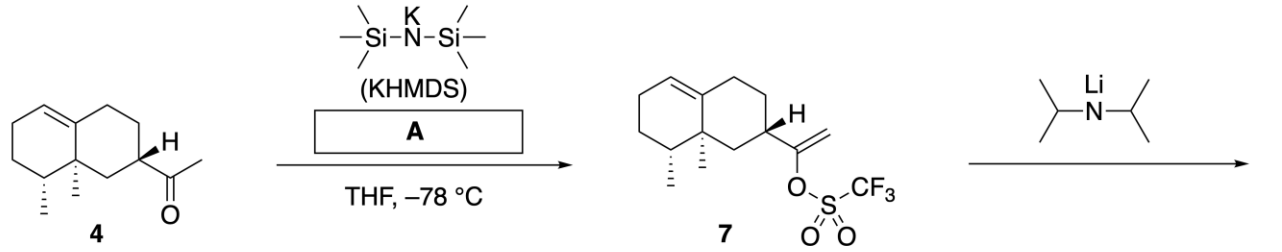
Lineariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (**1**), a one-step conversion yields **2**, before a three-step conversion via **3** yields ketone **4**. Eremophilene (**5**) is converted into **6** by performing the same four-step conversion.

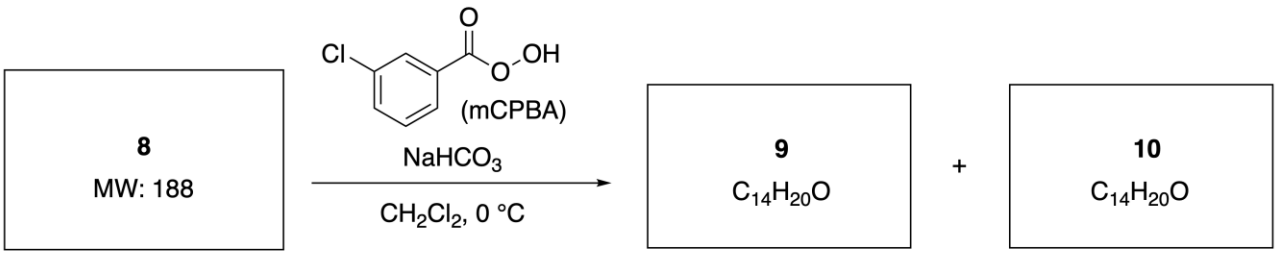
Inula linariifolia

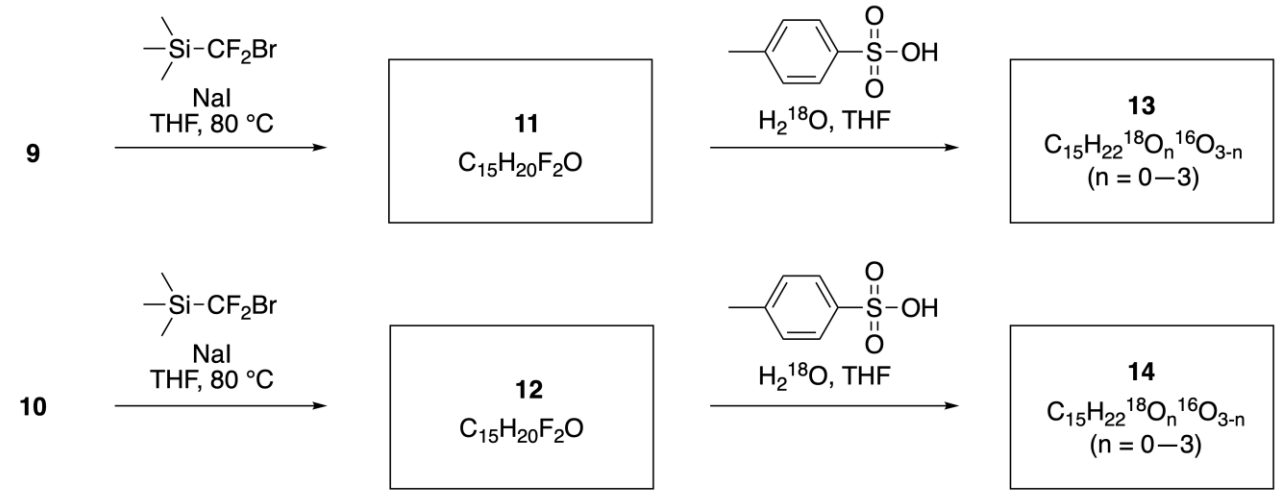


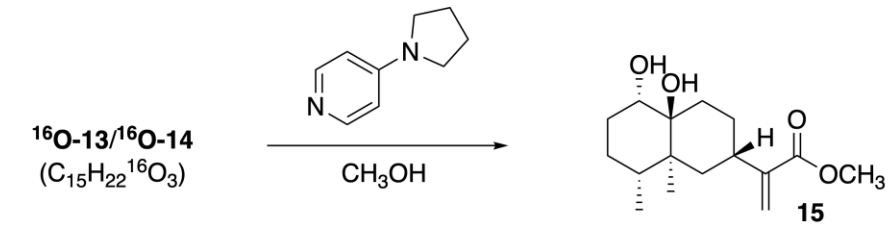
7.1 Draw the structures of **2** and **6** and clearly identify the stereochemistry where necessary.

Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.

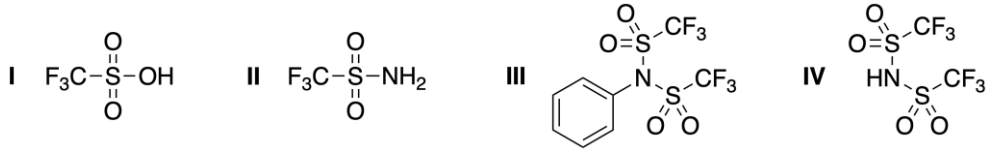




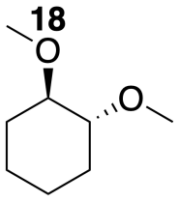




7.2 Choose the appropriate structure for **A**.

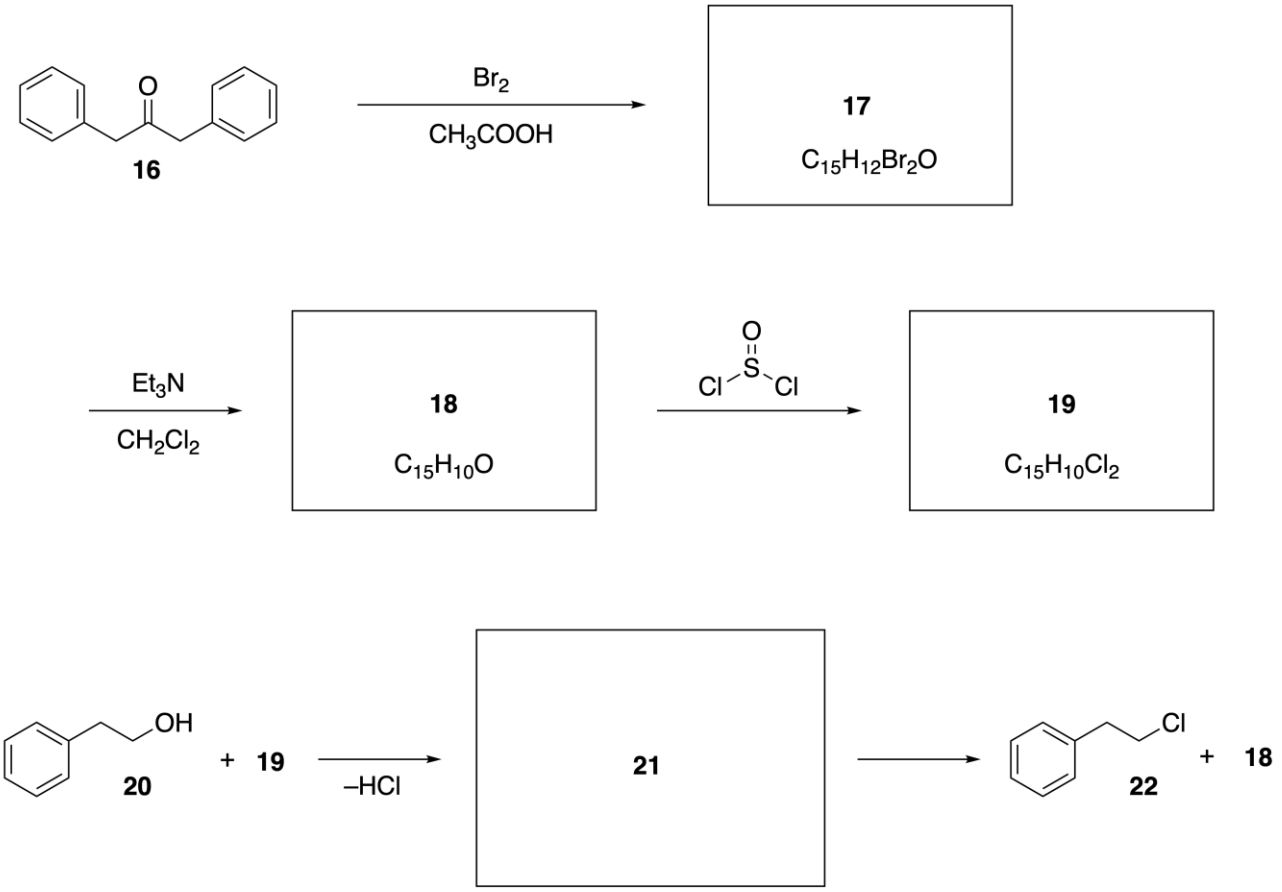


7.3 Draw the structures of **8**–**14** and clearly identify the stereochemistry where necessary. Also, indicate the introduced ^{18}O atoms for **13** and **14** as shown in the example below.



PART B

Compound **19** is synthesized as shown below. In relation to non-benzenoid aromaticity, **19** can be used as an activator for alcohols, and **20** was converted to **22** via ion-pair intermediate **21**. Although the formation of **21** was observed by NMR, **21** gradually decomposes to give **18** and **22**.

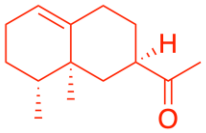
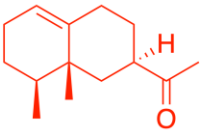


^{1}H NMR (CD_3CN, ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

7.4 **Draw** the structures of **17**–**19** and **21**. Identifying the stereochemistry is not necessary.

SOLUTION OF THE PROBLEM 7

7.1

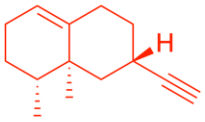
2 (2 pt)	**6** (3 pt)
	

7.2 III

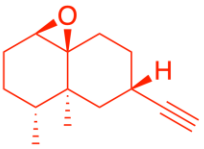
A is reacted with the potassium enolate of **4**, thus **I**, **II**, **IV** are inappropriate because these reagents have acidic protons.

7.3

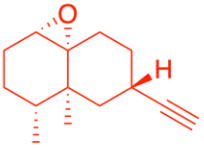
8 (3 pt)



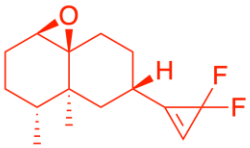
9 (2 pt)



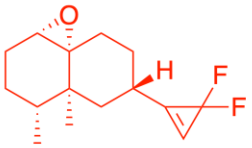
10 (2 pt)



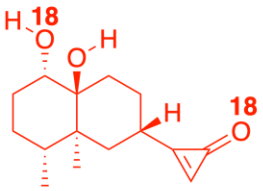
11 (2 pt)



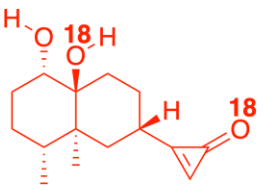
12 (2 pt)



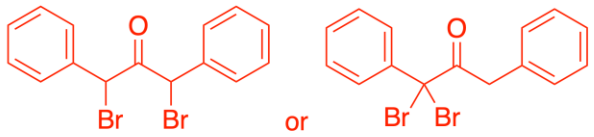
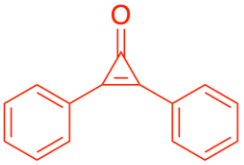
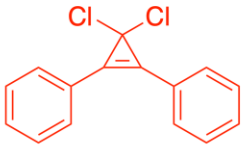
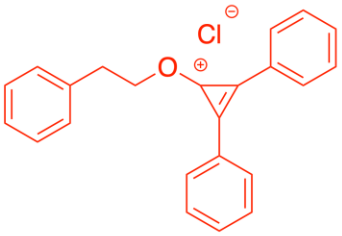
13 (4 pt)



14 (4 pt)



7.4

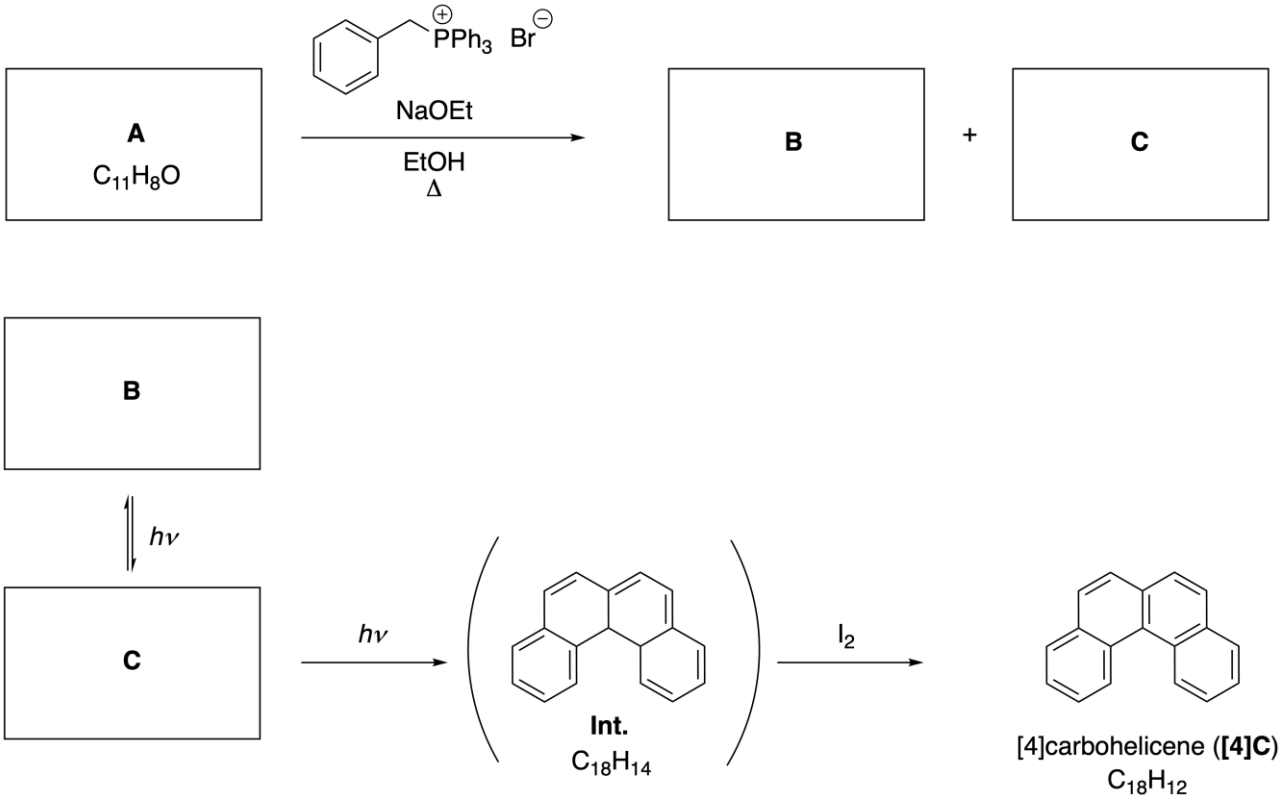
17 (2 pt) 	**18** (2 pt) 
19 (3 pt) 	**21** (3 pt) 

THEORETICAL PROBLEM 8

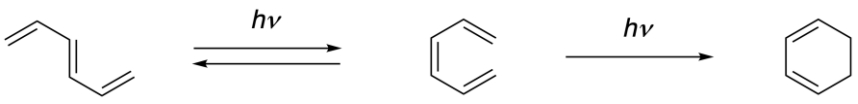
Dynamic Organic Molecules and Their Chirality

PART A

Polycyclic aromatic hydrocarbons with successive ortho-connections are called [n]carbohelicenes (here, n represents the number of six-membered rings) (see below). [4]Carbohelicene (**[4]C**) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (**Int.**) that is readily oxidized by iodine.



The photoreaction proceeds in a manner similar to the following example.

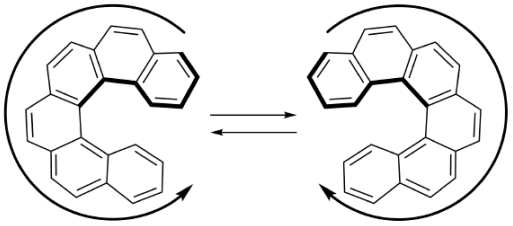


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

8.1 Draw the structures of **A**–**C**. Stereoisomers should be distinguished.

8.2 Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product **D** whose molecular weight was 2 Da lower than that of [5]carbohelicene. The ^{1}H NMR chemical shifts of **D** are listed below. **Draw** the structure of **D**. [**D** (δ, ppm in CS_2, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]

[5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (*M*) or (*P*) as shown below.



[n]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.

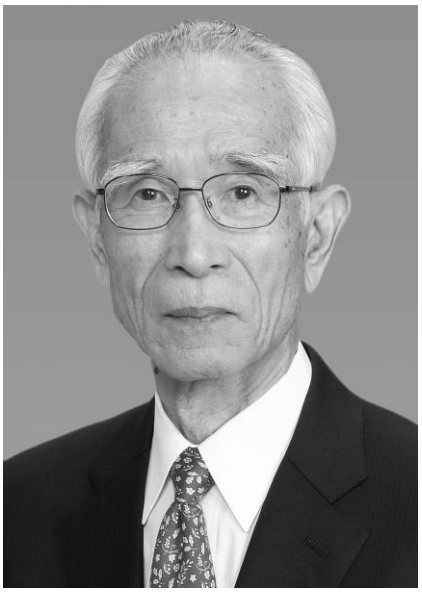
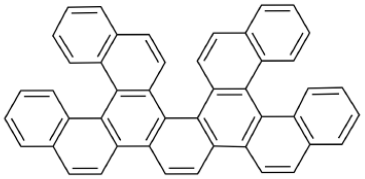
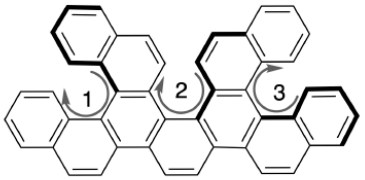


Photo courtesy: The Japan Prize Foundation

Multiple helicenes are molecules that contain two or more helicene-like structures. If its helical chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound **E** contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as (*P*, *P*, *P*) as shown below.

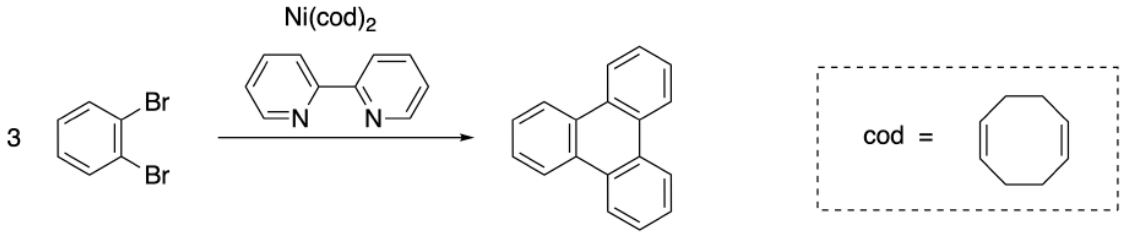


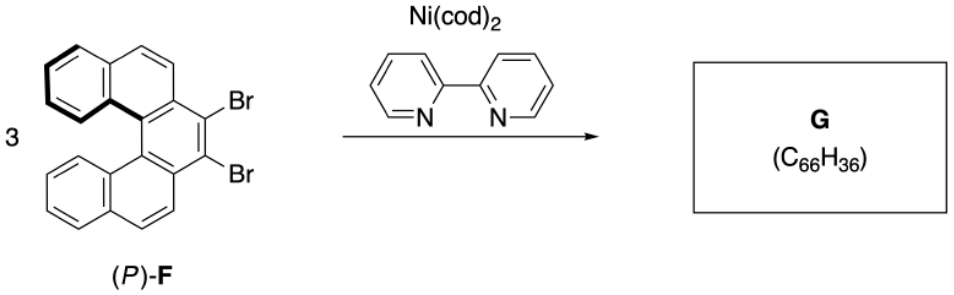
E



(1, 2, 3) = (*P*, *P*, *P*)

8.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, identify all the possible stereoisomers of **G** formed in this process, without duplication. As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and *M* and *P* labels according to the same numbering. For instance, the other stereoisomers of **E** should be listed as (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *M*, *P*), (*M*, *P*, *P*), and (*M*, *P*, *M*).

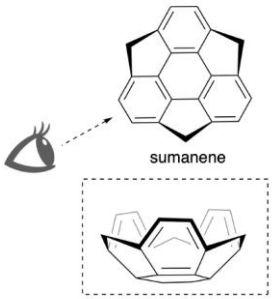




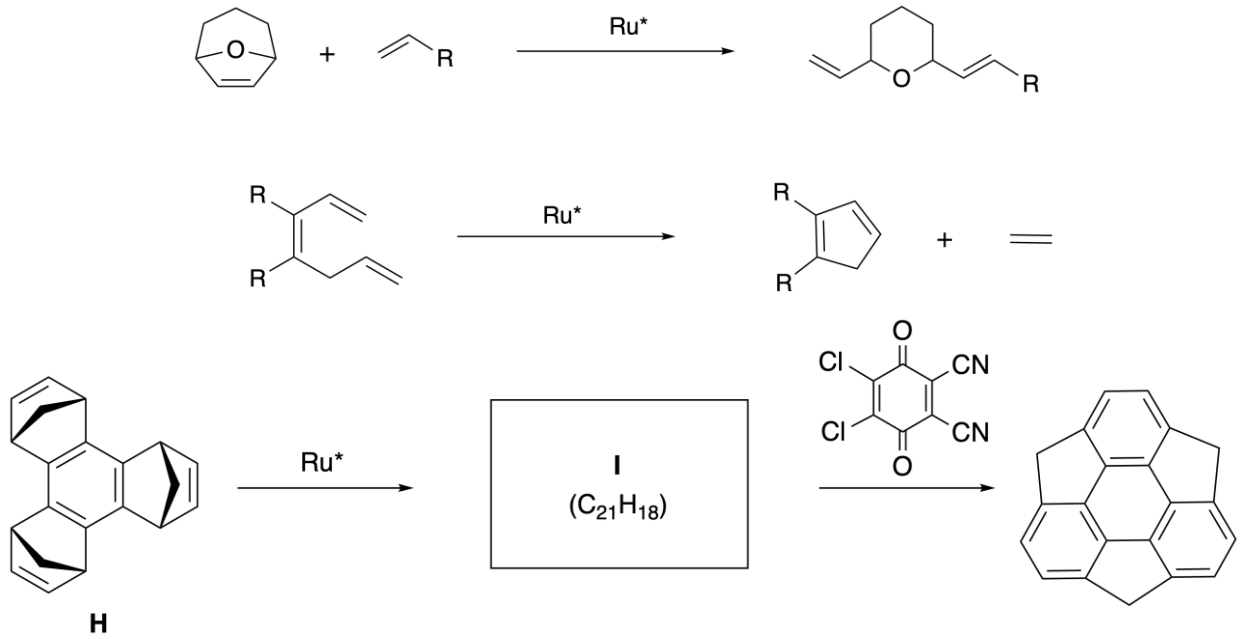
(*P*)-**F**

PART B

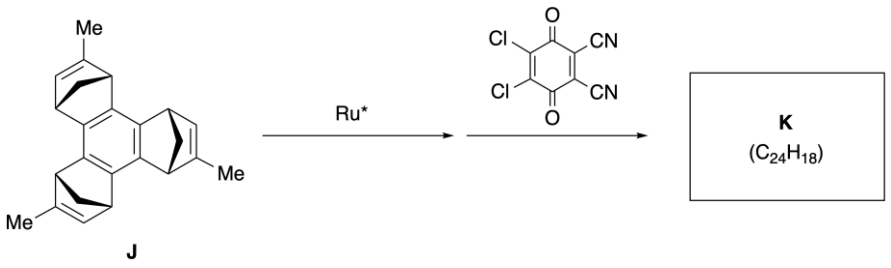
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.



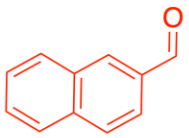
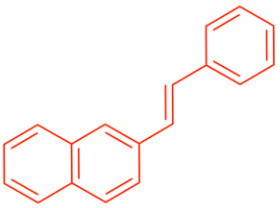
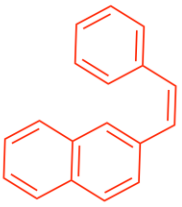
8.4 Draw the structure of intermediate **I** (its stereochemistry is not required).



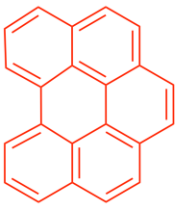
8.5 Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. Draw the structure of **K** with the appropriate stereochemistry.

SOLUTION OF THE PROBLEM 8

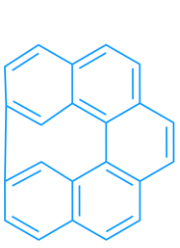
8.1

A (3 pt)	**B** (3 pt)	**C** (3 pt)
		

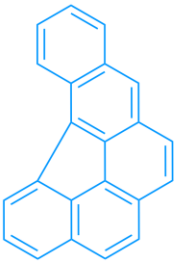
8.2



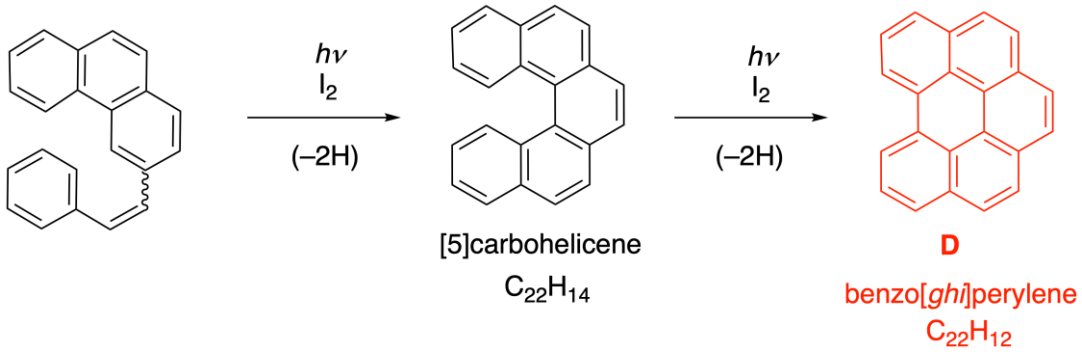
D



D'



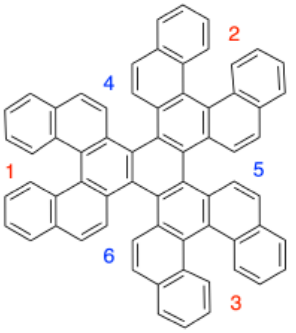
D"



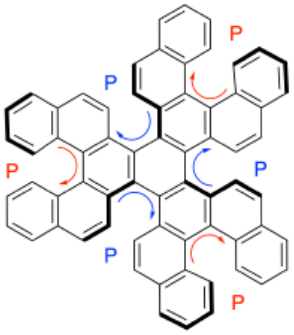
[5]carbohelicene
$C_{22}H_{14}$

D
benzo[*ghi*]perylene
$C_{22}H_{12}$

8.3

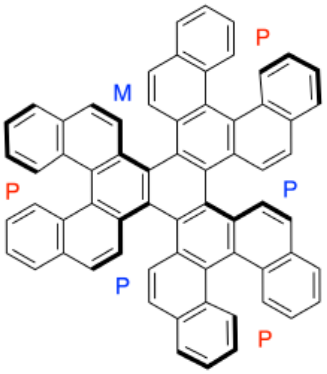


(1, 2, 3, 4, 5, 6)

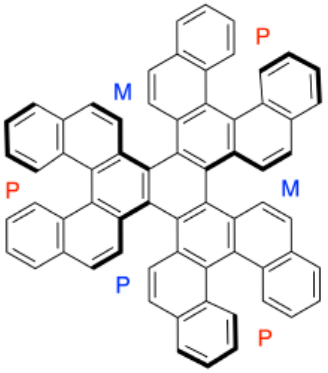


(P, P, P, P, P, P)

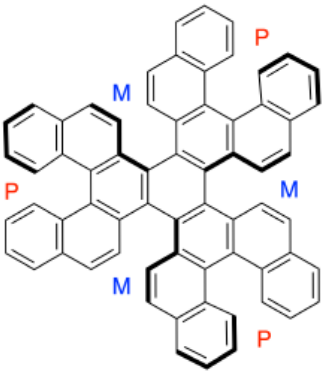
A representative example



(P, P, P, M, P, P)

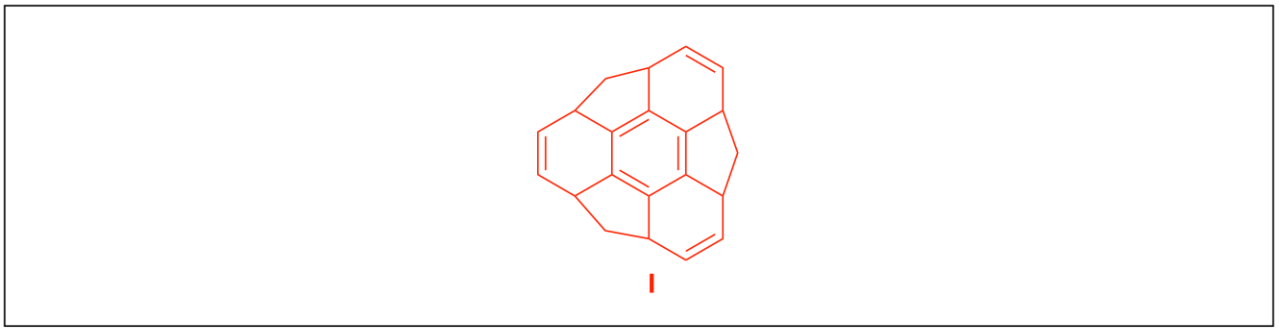


(P, P, P, M, M, P)

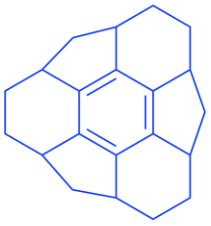


(P, P, P, M, M, M)

8.4

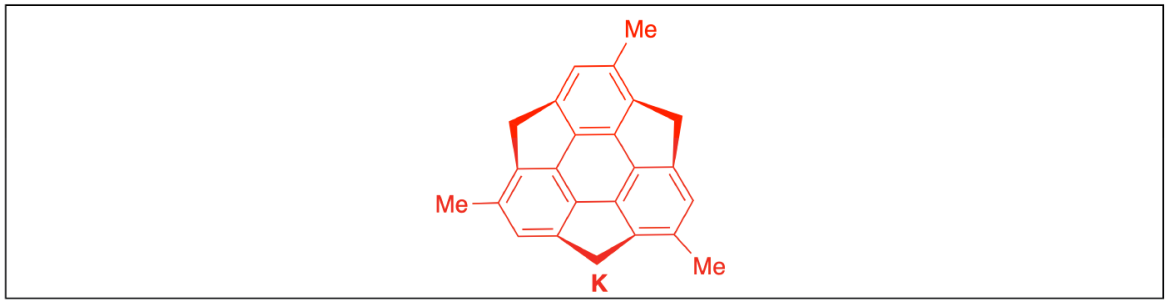


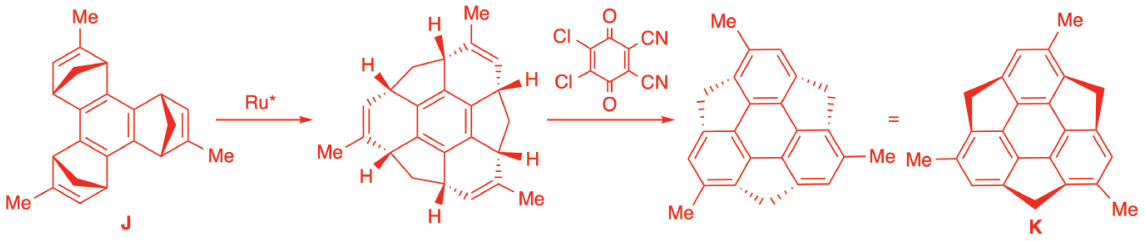
I



I'

8.5


Me
Me
Me
K

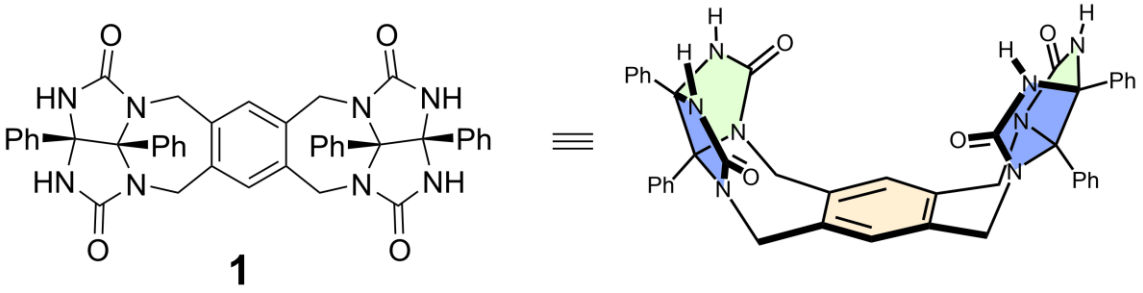

Me
Me
Me
J
Ru*
H
Me
H
H
Me
H
H
Me
O
Cl
CN
Cl
CN
O
Me
Me
Me
=
Me
Me
Me
K

THEORETICAL PROBLEM 9

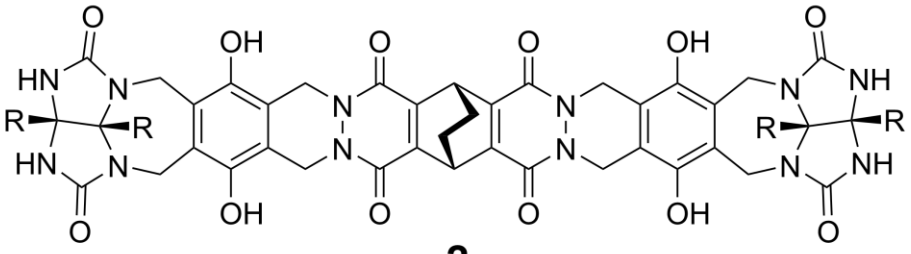
Likes and Dislikes of Capsule

Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.

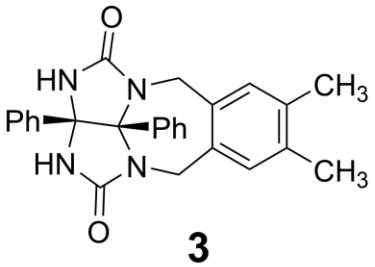
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

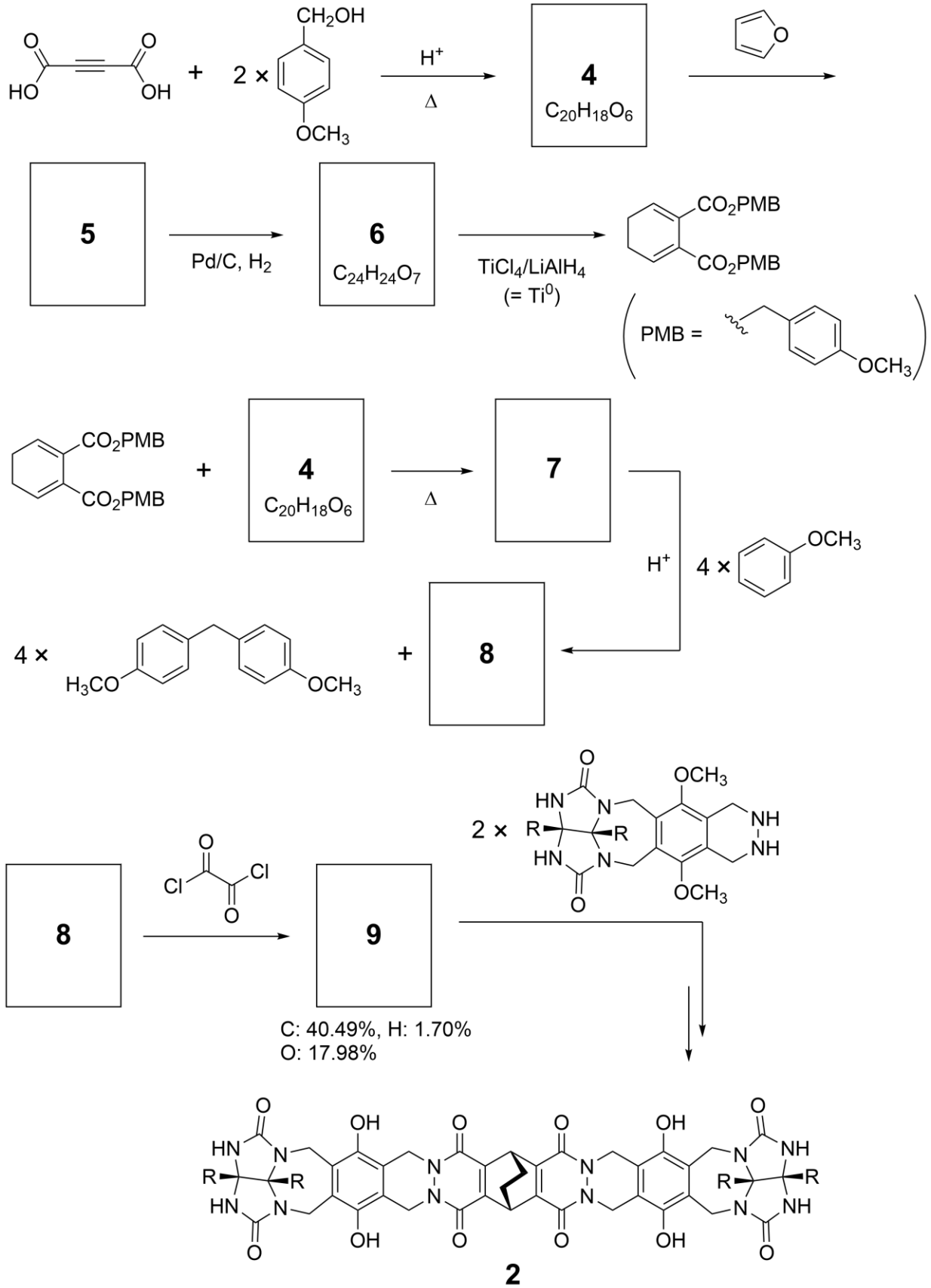


2



3

The synthetic route to **2** is shown below. The elemental composition of compound **9**: C; 40.49%, H; 1.70%, and O; 17.98% by mass.



2

9.1 **Draw** the structures of **4**–**9**; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above.

In the mass spectrum of **1**, the ion peak corresponding to its dimer (**1_2**) was clearly observed, whereas an ion peak for **3_2** was not observed in the spectrum of **3**. In the ^{1}H NMR spectra of a solution of **1_2**, all the NH protons derived from **1** were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of **3**. These data indicate that hydrogen bonds are formed between the NH moieties of **1** and atoms **X** of another molecule of **1** to form the dimeric capsule.

9.2 **Circle** all the appropriate atom(s) **X** in **1**.

9.3 **Give** the number of the hydrogen bonds in the dimeric capsule (**1_2**).

The dimeric capsule of **1** (**1_2**) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

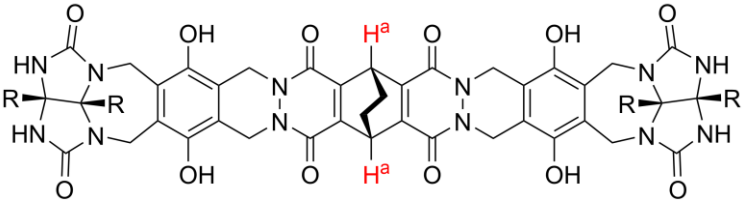
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \quad (1)$$

The equilibrium constant of the encapsulation of Z into **1_2** is given as below:

$$K_\mathrm{a} = \frac{[\mathrm{Z}@\mathbf{1}_2]}{[\mathrm{Z}][\mathbf{1}_2]} \quad (2)$$

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, **1_2** in C_6D_6 gave different signals in the ^{1}H NMR spectra before and after addition of CH_4.

Compound **2** also forms a rigid and larger dimeric capsule (**2_2**). The ^{1}H NMR spectrum of **2_2** was measured in C_6D_6, C_6D_5F, and a C_6D_6/C_6D_5F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H^a proton of **2** in the above solvents are summarized below, and no other signals from the H^a in **2**, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.



2

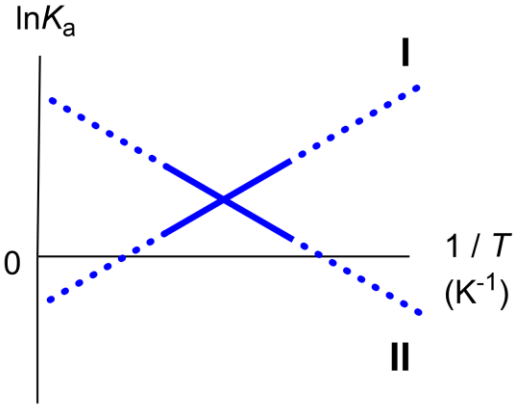
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

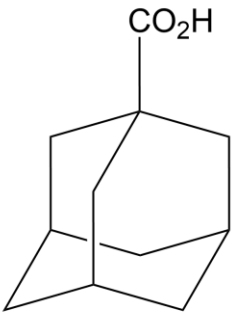
9.4 Determine the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2_2}$ giving each H^a signal.

^{1}H NMR measurements in C_6D_6 revealed that $\mathbf{2_2}$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants (K_a) which are expressed below were determined for various temperatures. [solvent@$\mathbf{2_2}$] denotes a species containing one or more solvent molecules.

$$K_a = \frac{[Z@\mathbf{2}_2]}{[Z][\text{solvent}@\mathbf{2}_2]} \quad (3)$$

Similarly, the K_a values of CH_4 and $\mathbf{1_2}$ given as eq (2) at various temperatures in C_6D_6 were also determined by $_1$H NMR measurements. The plots of the two association constants (as ln K_a vs $1/T$) are shown below.





AdA

No C_6D_6 molecule is encapsulated in **1₂**. In line **II**, the entropy change (ΔS) is (1) and enthalpy change (ΔH) is (2), indicating that the driving force for the encapsulation in line **II** is (3). Therefore, line **I** corresponds to (4), and line **II** corresponds to (5).

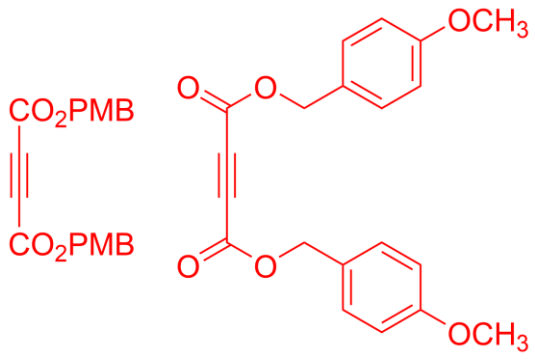
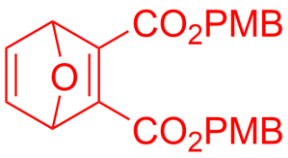
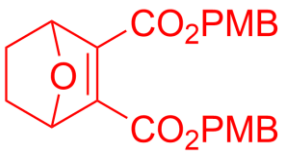
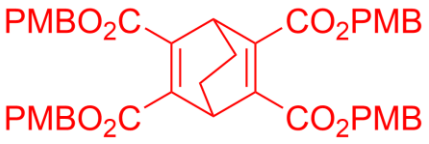
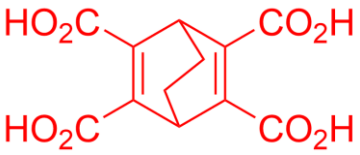
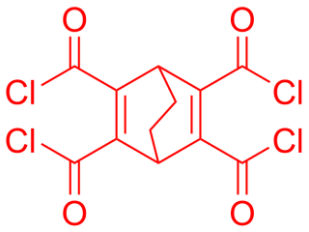
9.5 Choose the correct options in gaps (1)–(5) in the following paragraph from A and B.

	A	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	**1₂** and CH_4	**2₂** and AdA
(5)	**1₂** and CH_4	**2₂** and AdA

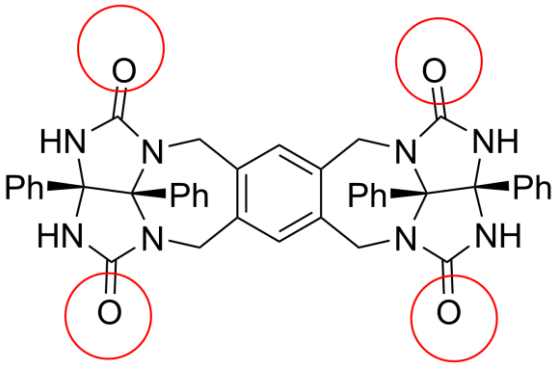
———————

SOLUTION OF THE PROBLEM 9

9.1

4 	**5** 
6 	**7** 
8 	**9** 

9.2



9.3 8 (because 8 NH protons were observed equally in the ^{1}H NMR spectrum of the dimer.)

9.4 The observation of the third signal in the mixed solvent indicates that two solvent molecules are initially encapsulated in the capsule. Thus, the signal at 4.82 ppm is ascribed to a capsule containing one molecule of C_6D_6 and one molecule of C_6D_5F.

δ (ppm) of H[a]	numbers of C_6D_6	numbers of C_6D_5F
4.60 ppm	2	0
4.71 ppm	0	2
4.82 ppm	1	1

9.5 (1): A (2): A (3): A (4): A (5): B

Transforming $\Delta G = -RT \ln K_a = \Delta H - T\Delta S$ gives

$$\ln K_A = -\frac{\Delta \mathrm{H}}{RT} + \frac{\Delta S}{R}$$

(If ΔH is negative, the slope is positive; if the y-intercept is negative, ΔS is negative.)

The relationship between **1₂** and CH_4 is that the entropy change is unfavorable ($\Delta S < 0$) given that the two components become one component. Nevertheless, the encapsulation of CH_4 occurs ($\Delta G < 0$), indicating that the enthalpy change is exothermic and favorable ($\Delta H < 0$). This result indicates a plot with a positive slope and a negative y-intercept for **1₂** and CH_4.

Therefore, the plot with a negative slope ($\Delta H > 0$) and positive y-intercept ($\Delta S > 0$) is **2₂** and AdA. This is due to the release of the two molecules of C_6D_6 that were initially encapsulated and the encapsulation of one molecule of AdA.

54th

9 theoretical problems

The original front page:

THEORETICAL EXAM

54th IChO2022

International Chemistry Olympiad

TIANJIN, CHINA

10th July – 18th July

CHANGE CREATION FUSION

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THE FIFTY-FOURTH

INTERNATIONAL CHEMISTRY OLYMPIAD

10–18 JULY 2022, Tianjin, China

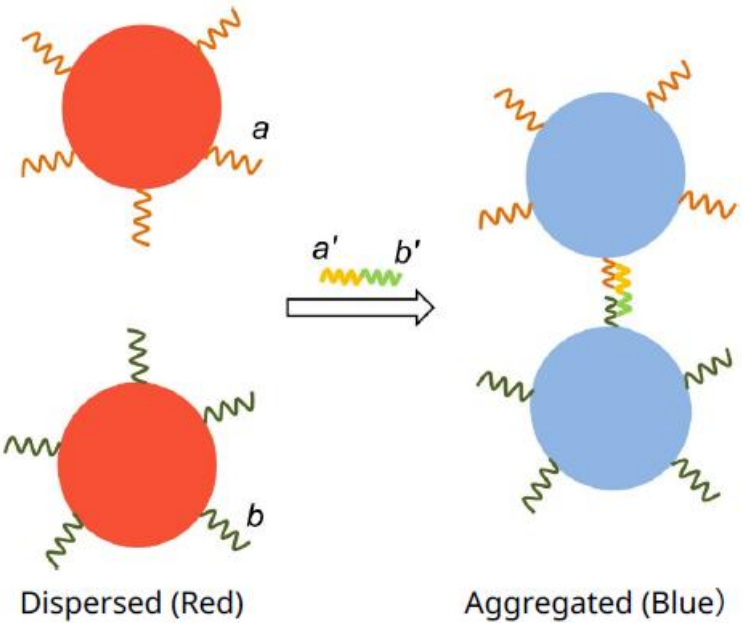
THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

Rapid and Visual Nucleic Acid Testing for COVID-19

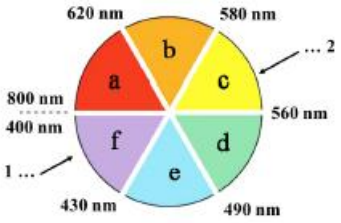
Fast and simple methods for early detection of COVID-19 are urgently needed. Gold nanoparticles-aided detection is one of the promising methods. Gold nanoparticles are widely used as a visible readout for test strips due to their high molar extinction coefficients (molar absorptivity). The color appearance of gold nanoparticles is closely associated with their sizes and dispersity. Generally, the larger the gold nanoparticles, the more reddish the color is. Once the nanoparticles are aggregated, the color shifts from red to blue.

When the surface of gold nanoparticles is modified with two kinds of single-stranded nucleic acid fragments *a* and *b*, the gold nanoparticles would aggregate in the presence of the target nucleic acid (*a*'*b*'), causing the color change of the solution from red to blue in several minutes (as indicated below). Based on this principle, the target nucleic acids collected from the coronavirus in a sample can be detected.



1.1 **Indicate** the absorption band region of the dispersed gold nanoparticles with an appropriate letter (a-f in the color wheel of **Figure 0.1** in **General Instructions**).

The Color Wheel



a: red b: orange c: yellow d: green e: blue f: violet
1: If a substance absorbs here 2: it appears as this color.

Figure 0.1

1.2 Indicate the change in the absorption spectrum of the gold nanoparticles once they are aggregated. Compared to the absorption wavelength of the dispersed gold nanoparticles, the wavelength of the aggregated nanoparticles

(a) becomes longer

(b) becomes shorter

(c) does not change

Gold nanoparticles are composed of gold atoms that are closely packed as solid gold

(density ρ = 19.3 g cm−3).

1.3 Calculate how many gold atoms (N) are there in a spherical gold nanoparticle with a diameter of 30.0 nm.

The synthesis of gold nanoparticles depends on the redox reaction between hydrogen tetrachloroaurate(III) ($HAuCl_4 \cdot 3H_2O$, *M*W = 394) and reducing substances (such as sodium citrate). 5.2 mg of $HAuCl_4 \cdot 3H_2O$ was completely converted into uniform spherical gold nanoparticles with a diameter of 30.0 nm in a 100.0 mL reaction solution. The absorbance of the resulting red solution was 0.800 measured at 530 nm by a UV-Vis spectrometer.

1.4 Calculate the molar extinction coefficient (molar absorptivity) of the resulting gold nanoparticles solution at 530 nm per mol of gold nanoparticles. The optical path of the cuvette used is 1 cm. If you failed to get the number of gold atoms (N) in 1.3 , use $N = 1.00 \times 10^5$.

The standard addition method was used for colorimetric detection of the target nucleic acid. The original throat swab sample was collected and divided equally into two portions. After addition of the probe solutions and water (as indicated below), the absorbance of the two resulting solutions was measured at 600 nm separately.

No.	Volume of throat swab sample (mL)	Volume of solution of gold nanoparticles modified with nucleic acid fragments (mL)	Volume of standard solution containing 2.0 μg mL^{-1} target nucleic acid (mL)	Volume of water (mL)	Absorbance
1	0.10	0.80	0.00	0.10	0.400
2	0.10	0.80	0.10	0.00	0.900

1.5 **Calculate** the concentration of the viral nucleic acids in the original throat swab sample.

_____

Solution of the problem 1

1.1 d)

1.2 a)

1.3

The volume of a gold nanoparticle:

$$V_{NP} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 = \frac{4}{3} \times 3.14 \times \left(\frac{30.0 \times 10^{-7}}{2}\right)^3 = 1.41 \times 10^{-17}\ \text{cm}^3 \text{ or } 1.41 \times 10^{-23}\ \text{m}^3$$

The mass of a gold nanoparticle:

$$m_{NP} = \rho V_{NP} = 19.3 \times 1.41 \times 10^{-17} = 2.72 \times 10^{-16}\ \text{g}$$

The number of gold atoms in each particle:

$$N = \frac{m_{NP}}{AW_{Au}} \cdot N_A = \frac{2.72 \times 10^{-16}}{197.0} \times 6.022 \times 10^{23} = 8.31 \times 10^5$$

OR

$$N = \frac{V_{NP}}{V_{\text{atom}}} = \frac{\pi\rho N_A D^3}{6M} = \frac{3.14 \times 19.3 \times 6.022 \times 10^{23} \times (30.0 \times 10^{-7})^3}{6 \times 197.0} = 8.34 \times 10^5$$

OR

The volume of a gold nanoparticle:

$$V_{NP} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 = \frac{4}{3} \times 3.14 \times \left(\frac{30.0 \times 10^{-7}}{2}\right)^3 = 1.41 \times 10^{-17}\ \text{cm}^3 \text{ or } 1.41 \times 10^{-23}\ \text{m}^3$$

The mass of each gold atom:

$$m = \frac{AW_{Au}}{N_A} = \frac{197.0}{6.022 \times 10^{23}} = 3.271 \times 10^{-22}\ \text{g}$$

The volume of each gold atom:

$$V_{\text{atom}} = \frac{m}{\rho} = \frac{3.271 \times 10^{-22}}{19.3} = 1.69 \times 10^{-23}\ \text{cm}^3$$

The number of gold atoms in each particle:

$$N = \frac{V_{NP}}{V_{\text{atom}}} = \frac{1.41 \times 10^{-17}}{1.69 \times 10^{-23}} = 8.34 \times 10^5$$

1.4

The total number of gold atoms:

$$N_{\text{Total}} = \frac{5.2 \times 10^{-3}}{394} \times 6.022 \times 10^{23} = 7.9 \times 10^{18}$$

The concentration of gold nanoparticles:

$$C = \frac{N_{\text{Total}}}{NVN_A} = \frac{7.9 \times 10^{18}}{8.34 \times 10^5 \times 100 \times 10^{-3} \times 6.022 \times 10^{23}} = 1.6 \times 10^{-10}\ \text{mol L}^{-1}$$

The extinction coefficient:

$$\varepsilon = \frac{A}{lC} = \frac{0.800}{1 \times 1.6 \times 10^{-10}} = 5.0 \times 10^9\ \text{L mol}^{-1}\ \text{cm}^{-1}$$

1.5

$$A_1 = \varepsilon l C_1 = \varepsilon l \frac{0.10 C_x}{1.0} = 0.400$$

$$A_2 = \varepsilon l C_2 = \varepsilon l \frac{0.10 C_x + 2.0 \times 0.10}{1.0} = 0.900$$

OR

$$\frac{0.400}{0.900} = \frac{\frac{0.10 C_x}{1.0}}{\frac{0.10 C_x + 2.0 \times 0.10}{1.0}}$$

$$C_x = 1.6\ \mu\text{g mL}^{-1}$$

THEORETICAL PROBLEM 2

Chromium in Ancient and Modern Times

(The photo is from the website of Palace Museum)

Black glazed porcelain is a special Chinese porcelain and was popular in the Tang and Song dynasties (ca. 1000 years ago). The ceramic ware contained iron oxides as the main color rendering agent, which was mixed with other transition metal oxides to exhibit different color appearance such as auburn, dark brown or black. Currently, the black glazed porcelain is still popular in China.

The typical black glaze is composed of Fe-containing oxides with a spinel structure. Spinel oxides have the general formula AB_2O_4 and the structure consists of a cubic close packing array of O^{2-} ions in which the **A** cations occupy one-eighth of the tetrahedral vacancies and the **B** cations occupy half of the octahedral vacancies, as shown in Figure 2.1(a) for a unit cell.

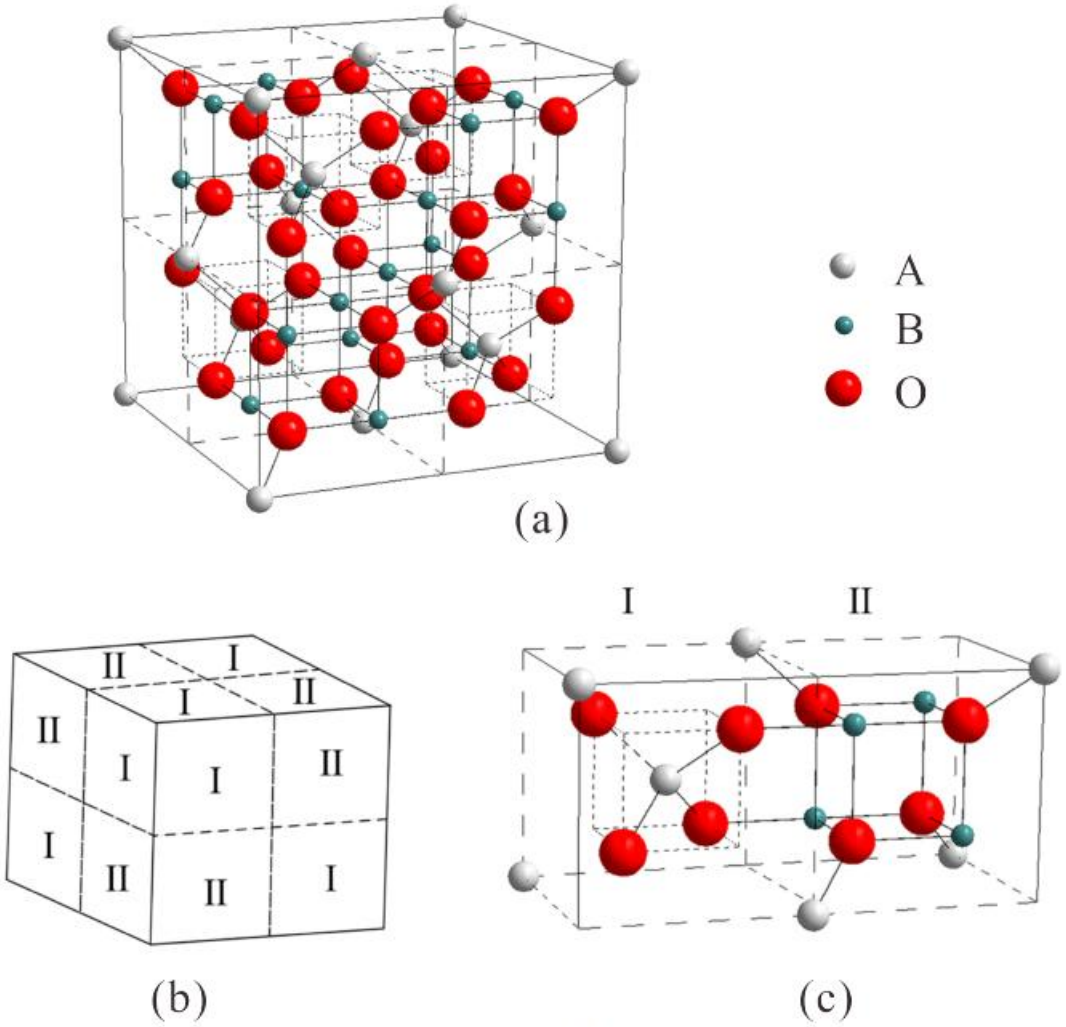


Figure 2.1 Illustration of spinel structure

The cubic unit cell of a spinel structure can be divided into 8 cubic subunits, and the dashed lines represent the internal edges of the subunits. 4 of the subunits belong to type I, and the other 4 subunits are type II (Figure 2.1(b)). The details of adjacent subunits of type I and type II are shown in Figure 2.1(c).

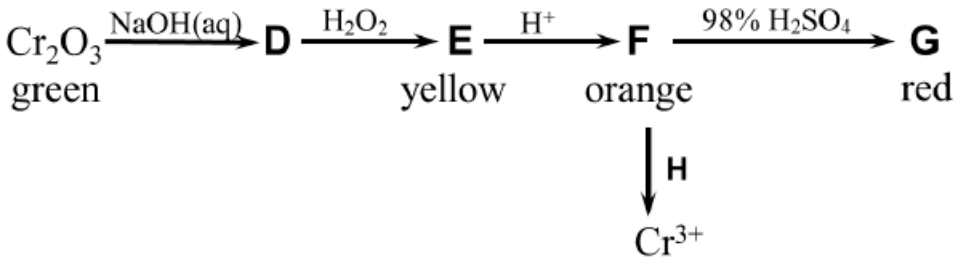
2.1 How many cations of type **A** and **B** are there in a unit cell?

The black ceramic glaze with spinel structure can be produced by roasting Fe_2O_3 and Cr_2O_3 in a certain proportion in a reducing atmosphere (reaction (I)). When Fe_2O_3 and Cr_2O_3 are reacted with the mass ratio of 63.6 : 36.4, they completely transform into a pure stoichiometric compound. The product has a spinel structure, in which the tetrahedral **A** sites are occupied by iron cations only.

2.2 In reaction (I), which element is reduced?

2.3 Calculate the numbers of Fe^{3+} and Cr^{3+} in the **B** sites of one unit cell.

Besides doping in black ceramic glaze, chromium-containing pigments are used in painting and printing due to the abundant color originating from chromium with different oxidation states, such as +2, +3 and +6. The pigment, chrome green (Cr_2O_3) can be converted into a series of other compounds (**D**-**G**) in the following process, where **E**, **F**, **G** are yellow, orange and red respectively.



2.4 Write the chemical formula of **E**.

2.5 Write the reaction equation of **F** ⟶ **G**.

2.6 Choose the agent which could be **H.**

(A) $FeSO_4$

(B) $FeCl_3$

(C) $ZnSO_4$

(D) $CuSO_4$

The variable valence of chromium is not only important for the production of pigments, but also useful for catalysis. For example, a typical Phillips catalyst for the polymerization of ethylene consists of chromium oxide species grafted onto a porous support material such as amorphous silica. The tetracoordinated Cr(VI) specie is the core in the pre-catalyst (**1**), which is proposed to be reduced quickly into a six-coordinated Cr(II) species (**2**) by the ethylene molecules at the beginning. **2** is proposed to further catalyze polymerization of ethylene molecules.

2.7 The reaction of **1** with ethylene can be traced by UV–vis spectra, which show the light absorption of **1** at 21500 cm^{-1} and the light absorption of **2** at 16700 cm^{-1} in the visible region, respectively. Choose the appropriate combination of colors of **1** and **2**.

(A) orange and white, respectively

(B) orange and blue, respectively

(C) blue and orange, respectively

(D) blue and white, respectively

2.8 Assuming that the Cr(II) ion in **2** is located in a regular octahedral crystal field with a splitting energy Δ_o of 16000 cm^{-1}, draw the configurations of d electrons of the Cr(II) ion in **2**, and calculate the crystal field stabilization energy (CFSE) for the Cr(II) ion in **2**. (Note: The pairing energy *P* for Cr(II) in **2** is 23500 cm^{-1})

2.9 Coordination compounds/ions exhibit paramagnetism when containing unpaired electrons, and the corresponding magnetic moment (μ) of transition metal cations is calculated by the function $\mu = \sqrt{n(n+2)}\mu_B$ where n is the number of unpaired electrons. Calculate the magnetic moment in term of μB for the Cr(II) ion in **2**.

Solution of the problem 2

2.1 **A:** 8; **B:** 16

2.2 Fe (or iron)

2.3

Fe^{3+} : 7, Cr^{3+} : 9

Solution 1:

Assume there are x Fe ions (including Fe^{2+} and Fe^{3+}) and y Cr^{3+} ions in a cubic cell, then

$$\frac{x}{y} = \frac{63.6 \times (52.00 \times 2 + 16.00 \times 3)}{36.4 \times (55.85 \times 2 + 16.00 \times 3)}$$

which gives the result: $\frac{x}{y} = 1.66$

Considering that the total amount of the cations in each crystal cell is 24, it can be obtained

$$(1 + 1.66)y = 24$$

which gives the result: $y \approx 9$

Thus, the amount of Fe^{3+} occupying the octahedral vacancies is

$$16 - 9 = 7$$

Solution 2:

Assume there are x Fe ions (including Fe^{2+} and Fe^{3+}) in the final compound, then, the number of Cr^{3+} should be $3-x$ because the summary of A+B should be 3 in AB_2O_4, and the formula of the compound should be $Fe_xCr_{3-x}O_4$, then

$$\frac{x}{3-x} = \frac{63.6 \times (52.00 \times 2 + 16.00 \times 3)}{36.4 \times (55.85 \times 2 + 16.00 \times 3)} = \frac{5}{3}$$

which gives the result: $x = 1.875$

Accordingly, Fe^{2+} in the tetrahedral vacancies is 1, and the number of Fe^{3+} in the octahedral vacancies is

$$x - 1 = 1.875 - 1 = 0.875$$

and the number of Cr^{3+} occupying the octahedral is

$$3 - x = 3 - 1.875 = 1.125$$

In one unit cell, there are 8 Fe^{2+}, thus the numbers of Fe^{3+} and Cr^{3+} are

$$\frac{8}{1} \times 0.875 = 7 \quad \text{and} \quad \frac{8}{1} \times 1.125 = 9$$

respectively.

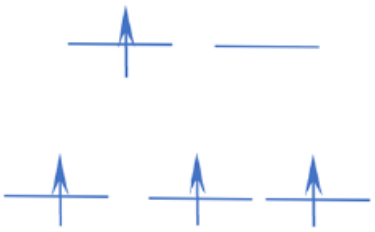
2.4 Na_2CrO_4

2.5 $Na_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + H_2O + 2NaHSO_4$ (ionic form is acceptable)

2.6 (A)

2.7 (B)

2.8



$$\text{CFSE} = 0 - E_{\text{octa}} = 0 - [(-2/5\Delta_o) \times 3 + 3/5\Delta_o] = 3/5\Delta_o = 9600\ \text{cm}^{-1}$$

2.9

$\mu = \sqrt{4(4+2)}\mu_B = 4.9\mu_B$

THEORETICAL PROBLEM 3

Capture and Transformation of Carbon Dioxide

Climate change is one of the most critical global challenges nowadays. The increase of CO_2 concentration in the atmosphere has been recognized as the primary driver of global warming. The study of the capture and transformation of CO_2 has attracted considerable attention.

Direct air capture (DAC) technology which aims to extract CO_2 directly from ambient air is promising. The conventional method of DAC is wet scrubbing with alkaline hydroxide solutions (typically NaOH), where CO_2 in air is absorbed till pH ≈ 10 (step 1). The spent sorbent is regenerated by dosing calcium hydroxide into the system (step 2). The white precipitate **A** received in step 2 decomposes at 700 °C, giving rise to CO_2 and another white compound **B** (step 3). Finally, calcium hydroxide can be generated by the hydration of **B**. This process is highly energy-demanding. (H_2CO_3 : K_{a1} = 4.5×10^{-7}, K_{a2} = 4.7×10^{-11}).

3.1 Write the formulas for **A** and **B** respectively.

3.2 Write the balanced equations of all possible reactions in steps 1-3. NaOH solution is used as sorbent.

Recently, an electrochemical process was developed for regenerating the alkaline solution in the wet scrubbing process for DAC application, and pure CO_2 gas could be recovered that is suitable for storage or utilization. The process is based on a H_2-recycling electrochemical system (HRES), as shown in Figure 3.1.

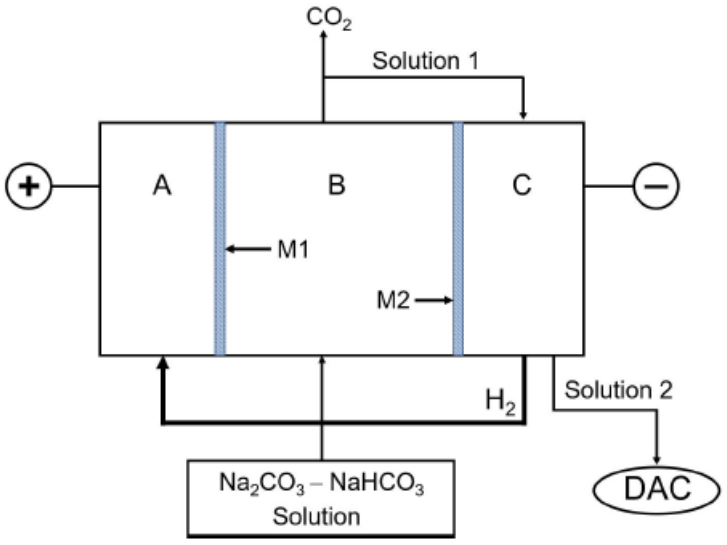


Figure 3.1 Schematic drawing of the experimental setup

The electrochemical cell contains three compartments: an anode region (A), an acidifying region (B), and a cathode region (C). They are separated by ion-selective permeable membranes M1 and M2. During the operation, protons produced from H_2 oxidation at the anode are transported to the acidifying compartment where the spent solution (Na_2CO_3-$NaHCO_3$) coming from the air contactor is fed. The decreasing pH of the solution leads to the conversions of carbonate to hydrocarbonate (reaction 1) and hydrocarbonate to carbonic acid (reaction 2). When the solution is saturated by dissolved CO_2 (solubility: 0.033 mol L^{-1}), a further pH decrease leads to the release of CO_2 gas (reaction 3). H_2 generated in the cathode is introduced to the anode and the solution from the cathode can be reused as a DAC absorbent.

3.3 Write the electrode reactions in the anode (A) and the cathode (C) respectively.

3.4 Write the balanced equations for the reactions **1–3** in the acidifying region (B).

3.5 Check all that correctly describe the movement of cations during the system operation.

(a) H^+ ions permeate through M1 from A to B.

(b) H^+ ions permeate through M2 from B to C.

(c) Na^+ ions permeate through M1 from B to A.

(d) Na^+ ions permeate through M2 from B to C.

(e) Both H^+ and Na^+ ions can permeate through M1and M2.

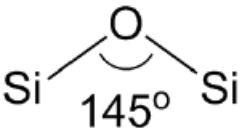
The cell works at a steady state when the current passing through the cell is 2.00 A and the flow rate of the solution (0.050 mol L^{-1} Na_2CO_3 - 0.10 mol L^{-1} NaHCO3) into the region

B is 10.0 mL min^{-1}. The pH in the anode compartment is maintained at 1 in the steady state.

3.6 Calculate the generation rate of CO_2 gas (in mmol min^{-1}).

Zeolitic imidazolate frameworks (ZIFs), a sub-class of metal–organic frameworks (MOFs) are promising materials for the capture and utilization of CO_2. The structures of ZIFs resemble zeolites. They form 3D frameworks with tetrahedrally coordinated metal ions (e.g. Zn^{2+}, Co^{2+}) bridged by imidazolate (Im^-) and its derivatives. As the conjugated base of imidazole (HIm), imidazolate anion binds to metal cations (M) by its two N atoms. The fact that the M-Im-M angle is similar to the Si-O-Si angle (145°) preferred in zeolites (as shown below) has led to the synthesis of a large number of ZIFs with zeolite-type tetrahedral topologies.

M—Im-M



Si—O—Si

ZIF-8 is one of the representative ZIFs, which adopts a sodalite framework (SOD), as shown in Figure 3.2. ZIF-8 was firstly synthesized by Chinese scientists Xiao-Ming Chen et al. (they named it as MAF-4) by the reaction of Zn^{2+} with 2-methylimidazole ($CH_3(C_3N_2H_3)$, HmIm). It crystalizes in the cubic system with the cell parameter a = 1.632 nm for a solvent-free phase with the effective pore diameter (shown by the inside virtual sphere in Figure 3.2d) of 1.16 nm.

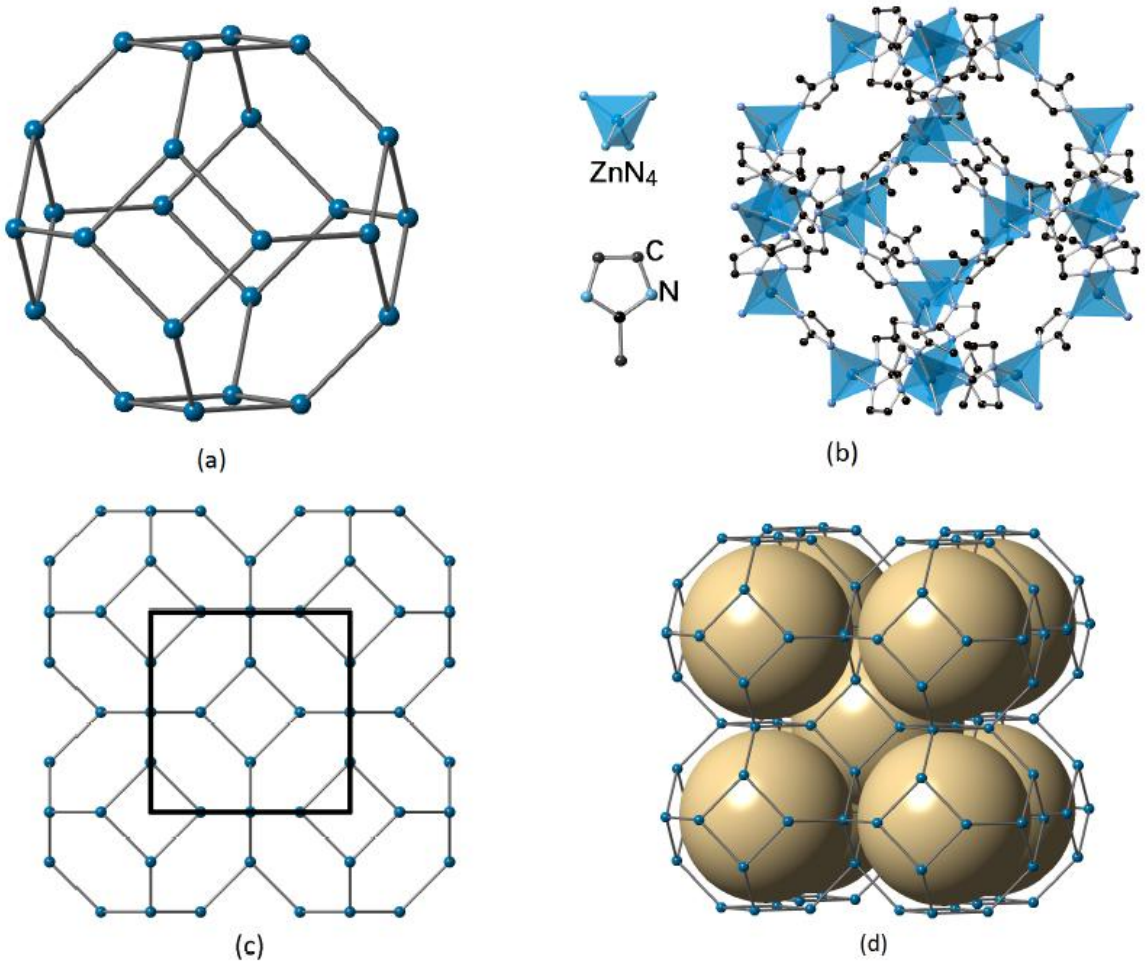


Figure 3.2 Topology of SOD and structure of ZIF-8

(a) Topology of SOD cage;

(b) SOD cage in ZIF-8 formed by Zn^{2+} (at the centers of the tetrahedra) and imidazolate (H atoms are omitted for clarity);

(c) Framework of SOD with the unit cell shown by the square box;

(d) Some of the pores are highlighted by virtual spheres in ZIF-8.

Note: .If you wish, you may use the symbol "HmIm" and "mIm" representing 2-methylimidazole and 2-methylimidazolate respectively in solving the following questions.

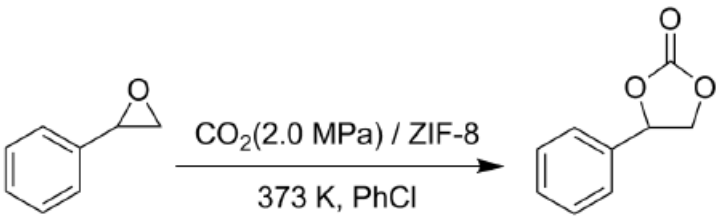
3.7 Write the formula of the single sodalite cage.

3.8 Write the composition of the unit cell of ZIF-8.

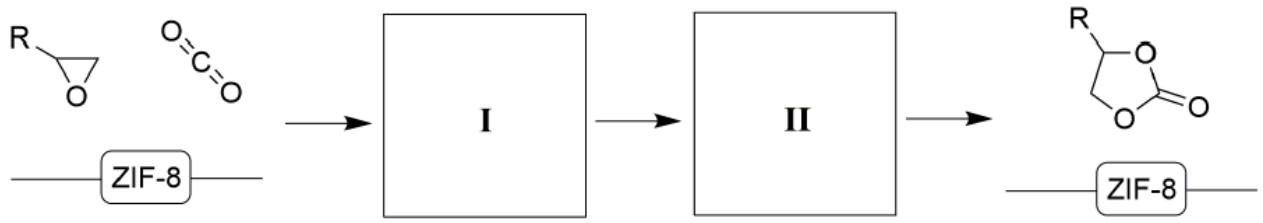
3.9 Calculate the inner surface area (S) of the pores (modeled by the virtual spheres) of 1 g ZIF-8 (in m^2). If you failed to get the composition of the unit cell, use 3500 as the formula weight of the unit cell.

3.10 Calculate the porosity R of ZIF-8 (R is the ratio of pore volume to the actual volume of the material) and the pore volume of 1 g ZIF-8 (V_p, in cm^3).

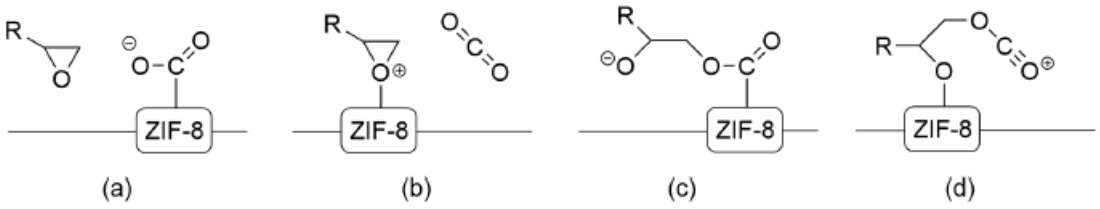
ZIF-8 can also act as a catalyst to promote the conversion of CO_2 to high value-added chemicals. One of the most promising routes for CO_2 fixation is the preparation of cyclic carbonates *via* CO_2 cycloaddition. An example is shown as below:



A mechanism of catalytic conversion of CO_2 to cyclic carbonate over ZIF-8 catalyst is proposed:



3.11 If ZIF-8 provides acid sites in the above catalytic process, complete the mechanism by choosing the reasonable intermediates from the following species:



Choose the intermediates corresponding to I and II respectively.

ZIF-8 shows a relatively high thermal stability. However, a recent study revealed that its structure would be destroyed if applied in a wet acidic environment. The co-existence of CO_2 and H_2O with ZIF-8 resulted in the formation of $ZnCO_3$.

3.12 Write the balanced equation of ZIF-8 with CO_2 and H_2O.

_____

Solution of the problem 3

3.1 **A:** CaCO3 **B:** CaO

3.2

step 1: (2a) $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

or $2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O$

(2b) $NaOH + CO_2 \longrightarrow NaHCO_3$

or $OH^- + CO_2 \longrightarrow HCO_3^-$

or $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

or $CO_3^{2-} + CO_2 + H_2O \longrightarrow 2HCO_3^-$

step 2: (2c) $Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$

(2d) $NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + NaOH + H_2O$

step 3: (2e) $CaCO_3 \longrightarrow CaO + CO_2$

3.3

A: $H_2 \rightarrow 2H^+ + 2e^-$

C: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

3.4

1 $H^+ + CO_3^{2-} \longrightarrow HCO_3^-$

2 $H^+ + HCO_3^- \longrightarrow H_2CO_3$

3 $H_2CO_3 \longrightarrow H_2O + CO_2$

3.5 a), d)

3.6

Rate of H^+ production:

$r(H^+) = 60\ \text{s min}^{-1} \times 2.00\ \text{A}/(96485\ \text{C mol}^{-1})$

$= 1.24 \times 10^{-3}\ \text{mol min}^{-1} = 1.24\ \text{mmol min}^{-1}$

Input rate of HCO_3^- to zone B:

$r(HCO_3^-) = 0.10\ \text{mol L}^{-1} \times 10.0\ \text{mL min}^{-1} = 1.0\ \text{mmol min}^{-1}$

Input rate of CO_3^{2-} to zone B:

$r(CO_3^{2-}) = 0.050\ \text{mol L}^{-1} \times 10.0\ \text{mL min}^{-1} = 0.50\ \text{mmol min}^{-1}$

$H^+ + CO_3^{2-} \longrightarrow HCO_3^-$ $\qquad$ $H^+ + HCO_3^- \longrightarrow CO_2 + H_2O$

The amount of dissolved CO_2 in the flow:

$10.0\ \text{mL min}^{-1} \times 0.033\ \text{mol L}^{-1} = 0.33\ \text{mmol min}^{-1}$

Rate of CO_2 production:

$r(CO_2) = r(H^+) - r(CO_3^{2-}) - 0.33\ \text{mmol min}^{-1}$

$= 1.24\ \text{mmol min}^{-1} - 0.50\ \text{mmol min}^{-1} - 0.33\ \text{mmol min}^{-1} = 0.41\ \text{mmol min}^{-1}$

3.7 $Zn_{24}(C_4H_5N_2)_{36}^{12+}$ or $Zn_{24}(C_4H_5N_2)_{60}^{12-}$

3.8 $Zn_{12}(C_4H_5N_2)_{24}$

3.9

$$M_{Zn(C_4H_5N_2)_2} = [65.38 + (12.01 \times 4 + 1.01 \times 5 + 14.02 \times 2) \times 2]\ \text{g mol}^{-1} = 227.6\ \text{g mol}^{-1}$$

$$S = \frac{2 \times 4\pi r^2 \times N_A \times 1\ \text{g}}{12 \times M_{Zn(C_4H_5N_2)_2}}$$

$$= \frac{2 \times 4 \times 3.14 \times \left(\frac{1.16 \times 10^{-9}\ \text{m}}{2}\right)^2 \times 6.02 \times 10^{23}\ \text{mol}^{-1} \times 1\ \text{g}}{12 \times [65.38 + (12.01 \times 4 + 1.01 \times 5 + 14.01 \times 2) \times 2]\ \text{g mol}^{-1}}$$

$$= \frac{50.8 \times 10^5}{12 \times 227.6}\text{m}^2 = 1.86 \times 10^3\ \text{m}^2$$

3.10

Volume of one spherical cage:

$$V_{\text{Cage}} = (4/3) \times 3.14 \times (1.16\ \text{nm}/2)^3 = 0.817\ \text{nm}^3$$

Volume of the unit cell:

$$V_{\text{cell}} = (1.632\ \text{nm})^3 = 4.347\ \text{nm}^3$$

Porosity:

$$R = 2 \times V_{\text{Cage}}/V_{\text{cell}} = 2 \times 0.817\ \text{nm}^3/4.347\ \text{nm}^3 = 0.376$$

$$V_{\text{p}} = \frac{2 \times V_{\text{cage}} \times N_{\text{A}} \times 1\,\text{g}}{12 \times M_{\text{Zn(C}_4\text{H}_5\text{N}_2)_2}} = \frac{\frac{4}{3}\pi r^3 \times N_{\text{A}} \times 1\,\text{g}}{6 \times M_{\text{Zn(C}_4\text{H}_5\text{N}_2)_2}}$$
$$= \frac{0.817 \times 10^{-21}\ \text{cm}^3 \times 6.02 \times 10^{23}\ \text{mol}^{-1} \times 1\,\text{g}}{6 \times 227.6\ \text{g mol}^{-1}} = 0.360\ \text{cm}^3$$

3.11 **I** (b); **II** (d)

3.12 $Zn(C_4H_5N_2)_2 + CO_2 \rightarrow ZnCO_3 + 2C_4H_6N_2$ or

$Zn(mIm)2 + CO_2 + H_2O \rightarrow ZnCO_3 + 2HmIm$

THEORETICAL PROBLEM 4

A New Journey for Ancient Sulfur

Sulfur has been known and used since the ancient times. Nowadays, sulfur is widely used in chemical production and pharmaceutical industry as an inexpensive chemical raw material.

Pyrite (FeS_2) is commonly used as a raw material in the industrial production of elemental sulfur. By heating pyrite in the presence of limited air supply, the theoretical yield of elemental sulfur is 100% and a black magnetic oxide (Fe_3O_4) is the other product.

4.1 Write the balanced reaction equation that describes the above conversion.

In addition to sulfur, a small amount of SO_2 is generated as a by-product during the actual process. This reaction can be monitored by measuring the amount of SO_2. The following recipe is used for the monitoring:

Raw ore powder is heated in a temperature-controlled tube furnace. The generated SO_2 is absorbed by 2 mol L^{-1} NaOH solution. When the reaction is completed, the solution is transferred to a 500 mL volumetric flask and diluted by distilled water to the mark. 25.00 mL of this diluted solution is then added into an iodine flask containing 50.00 mL 0.05122 mol L^{-1} I_2 standard solution and 5 mL 20% H_2SO_4 solution. After maintaining the iodine flask in dark for 5 min, the solution is titrated with 0.1012 mol L^{-1} $Na_2S_2O_3$ standard solution. When the color of the solution turns light brown, 3 mL 0.5% starch indicator is added. Continue the titration until the blue color disappears.

4.2 Write the balanced reaction equations involving I_2 in the above measurement.

4.3 In such a test experiment starting from pyrite, 17.6 g of elemental sulfur was collected. The analysis of the by-product gases according to the above procedure resulted in the consumption of 18.47 mL of $Na_2S_2O_3$ standard solution. Assuming that no other sulfur containing species were produced, calculate what percentage of the sulfur in pyrite was lost as the by-product?

The lithium-sulfur battery is a compelling energy storage system because its high theoretical energy density exceeds conventional Li-ion batteries. The net reaction of a lithium-sulfur battery can be simplified as: $16\ Li + S_8 \longrightarrow 8\ Li_2S$. Sulfur is the cathode and metallic lithium is the anode active material during discharge.

4.4 Write the balanced equations for reactions that take place at cathode (a) and anode (b) during discharge.

4.5 Calculate the mass ratio of the cathode active material to the anode active material, according to the net battery reaction.

A lithium-ion battery (LIB) that possesses an average operating voltage of 3.8 V and a deliverable capacity of 3110 mAh can provide energy for a mobile phone to play videos continuously for 22 hours upon a full charge.

4.6 If the LIB is replaced by an ideal lithium-sulfur battery pack, which has an average operating voltage of 4.2 V and contains 23 g sulfur as the active electrode material that can react stoichiometrically during discharge, calculate how many hours the new battery pack will provide energy for the phone to play videos continuously after a full charge.

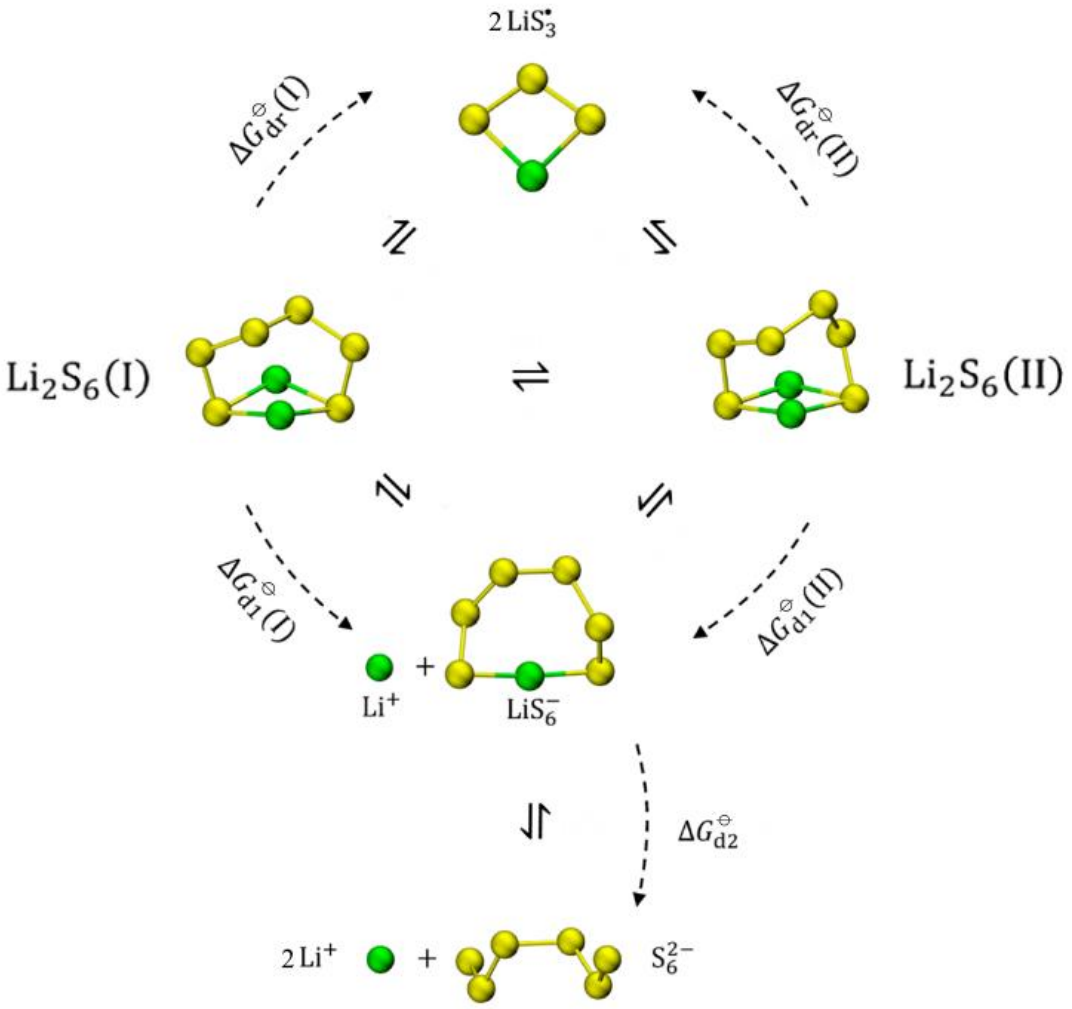
Elemental sulfur generally exists as S_8 molecules. In real lithium-sulfur batteries, S_8 is not directly reduced to Li_2S during discharge, but it undergoes stepwise reactions generating different soluble lithium polysulfides (Li_2S_n, n = 3 − 8). These lithium polysulfides could diffuse to the anode and corrode it, which results in the loss of active electrode materials. This phenomenon is called "shuttle effect".

4.7 Write the balanced reaction equation for the corrosion of anode by soluble lithium polysulfides (Li_2S_n) that produces Li_2S.

In order to suppress the "shuttle effect", the forms of polysulfides in an electrolyte have been extensively studied. Li_2S_6 is one of the most representative intermediate products:

$$2Li^+ + S_8 + 2e^- \longrightarrow Li_2S_6 + 2S$$

A theoretical study shows that two conformers with comparable energies, Li_2S_6(I) and Li_2S_6(II) coexist in 1,2-dimethoxyethane (DME), a common electrolyte solvent in lithium-sulfur batteries. The dissociation of Li_2S_6 in DME is shown below:



Chemical equilibria of Li_2S_6, LiS_6^-, S_6^{2-} and $LiS_3^\bullet$ in DME

Table 4.1 Dissociation Gibbs energies (kJ mol^{-1}) of different reactions in DME (298.15 K, 1 bar)

$\Delta G_{d1}^{\ominus}$(I)	$\Delta G_{d1}^{\ominus}$(II)	$\Delta G_{d2}^{\ominus}$	$\Delta G_{dr}^{\ominus}$(I)	$\Delta G_{dr}^{\ominus}$(II)
20.68	18.92	100.55	45.13	43.37

4.8 Using the data from Table 4.1, calculate the equilibrium concentration ratio of two conformers in DME (298.15 K, 1 bar), $\frac{Li_2S_6(II)}{Li_2S_6(I)}$.

4.9 Using the data from Table 4.1, calculate the apparent dissociation constant of $Li_2S_6 \longrightarrow Li^+ + LiS_6^-$ in DME (298.15 K, 1 bar).

4.10 Sort the following equilibrium concentrations in decreasing order: [Li_2S_6], [LiS_6^-], [S_6^{2-}], [$LiS_3^\bullet$] in DME.

4.11 The standard reduction potential of metallic lithium in water at 298.15 K and 1 bar is:

$$E^{\ominus}\left(\mathrm{Li}^{+}/\mathrm{Li}\right) = -3.040\ \mathrm{V}$$

The standard solvation Gibbs energies of gaseous $Li^+(g)$ to $Li^+(sol)$ in different solvents.

	$Li^+(H_2O)$	$Li^+(DME)$
$\Delta G^{\ominus}$/kJ mol^{-1}	−116.9	−114.6

Calculate the standard reduction potential of metallic lithium electrode in DME.

Studies have shown that electromotive force of a lithium-sulfur battery would be increased by replacing DME with dimethyl sulfoxide (DMSO). Therefore, the forms of polysulfides in DMSO also attract researchers' attention.

In a test, a certain amount of Li_2S and 4.81 mg sulfur powder were added into 10.00 mL DMSO, then heated and stirred until completely dissolved (ignoring the change in volume). Suppose that only the following polysulfides were present in the DMSO: $S_3^{\bullet -}, S_4^{2-}, S_5^{2-}, S_6^{2-}, S_7^{2-}, S_8^{2-}$. The equilibrium concentration ratio of the sulfur containing species was:

$$[S_3^{\bullet -}] : [S_4^{2-}] : [S_5^{2-}] : [S_6^{2-}] : [S_7^{2-}] : [S_8^{2-}] = 17.50 : 1.00 : 4.50 : 55.00 : 5.00 : 0.75$$

4.12 Calculate the original mass m (in mg) of Li_2S added to DMSO.

Solution of the problem 4

4.1

$$3\,FeS_2 + 2\,O_2 \xrightarrow{\Delta} 6\,S + Fe_3O_4 \quad \text{or} \quad 12\,FeS_2 + 8\,O_2 \xrightarrow{\Delta} 3\,S_8 + 4\,Fe_3O_4$$

4.2

(a) $Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$

or

$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2I^-$

(b) $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

or

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

4.3

$$0.05122\,\text{mol}\,L^{-1} \times 50.00\,\text{mL} = 2.561\,\text{mmol}$$

$$\frac{1}{2} \times 0.1012\,\text{mol}\,L^{-1} \times 18.47\,\text{mL} = 0.9346\,\text{mmol}$$

$$(2.561\,\text{mmol} - 0.9346\,\text{mmol}) \times 10^{-3} \times 20 \times 32.06\,\text{g}\,\text{mol}^{-1} = 1.043\,\text{g}$$

$$\frac{1.043\,\text{g}}{(1.043\,\text{g} + 17.6\,\text{g})} \times 100\% = 5.59\%$$

4.4

(a) $S_8 + 16Li^+ + 16e^- \longrightarrow 8Li_2S$

(b) $Li \longrightarrow Li^+ + e^-$ or $16Li \longrightarrow 16Li^+ + 16e^-$

4.5

$$\frac{8 \times 32.06}{16 \times 6.941} = 2.3$$

4.6

The total energy of the LIB is $3.8\,\text{V} \times 3.110\,\text{A h} \times 3600\,\text{s/h} = 4.25 \times 10^4\,\text{J}$

Energy consumed by the mobile phone per hour is $\frac{4.25 \times 10^4\,\text{J}}{22\,\text{h}} = 1.93 \times 10^3\,\text{J h}^{-1}$

The capacity of the ideal lithium-sulfur battery pack is

$$\frac{23\,\text{g} \times 16 \times 96485\,\text{C mol}^{-1}}{8 \times 32.06\,\text{g mol}^{-1}} = \frac{23\,\text{g} \times 2 \times 96485\,\text{C mol}^{-1}}{32.06\,\text{g mol}^{-1}} = 1.4 \times 10^5\,\text{C}$$

The total energy of the ideal lithium-sulfur battery pack is

$4.2\,\text{V} \times 1.4 \times 10^5\,\text{C} = 5.9 \times 10^5\,\text{J}$

After a full charge, the new battery pack can provide energy for the phone to play videos continuously for: $\frac{5.9 \times 10^5\,\text{J}}{1.93 \times 10^3\,\text{J h}^{-1}} = 306\,\text{h}$

4.7

$(2n-2)\,\text{Li} + \text{Li}_2\text{S}_n \longrightarrow n\text{Li}_2\text{S}$

4.8

$\text{Li}_2\text{S}_6(\text{I})(\text{DME}) \longrightarrow \text{Li}_2\text{S}_6(\text{II})(\text{DME})$

$\Delta G^{\ominus}_{\text{I}\longrightarrow\text{II}} = \Delta G^{\ominus}_{\text{d1}}(\text{I}) - \Delta G^{\ominus}_{\text{d1}}(\text{II}) = 20.68\,\text{kJ mol}^{-1} - 18.92\,\text{kJ mol}^{-1} = 1.76\,\text{kJ mol}^{-1}$

or

$\Delta G^{\ominus}_{\text{I}\longrightarrow\text{II}} = \Delta G^{\ominus}_{\text{dr}}(\text{I}) - \Delta G^{\ominus}_{\text{dr}}(\text{II}) = 45.13\,\text{kJ mol}^{-1} - 43.37\,\text{kJ mol}^{-1} = 1.76\,\text{kJ mol}^{-1}$

$\Delta G^{\ominus}_{\text{I}\longrightarrow\text{II}} = -RT \ln K^{\ominus}_{\text{I}\longrightarrow\text{II}}$

$$K^{\ominus}_{\text{I}\longrightarrow\text{II}} = \exp\left(-\frac{1.76\,\text{kJ mol}^{-1} \times 1000}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}}\right) = 0.492$$

$$K^{\ominus}_{\text{I}\longrightarrow\text{II}} = \frac{[\text{Li}_2\text{S}_6(\text{II})]/c^{\ominus}}{[\text{Li}_2\text{S}_6(\text{I})]/c^{\ominus}} = \frac{[\text{Li}_2\text{S}_6(\text{II})]}{[\text{Li}_2\text{S}_6(\text{I})]} = 0.492$$

4.9

$$\frac{[Li_2S_6(II)]}{[Li_2S_6(I)]} = 0.492,\ [Li_2S_6(II)] = 0.492[Li_2S_6(I)]$$

$$Li_2S_6 \longrightarrow Li^+ + LiS_6^-$$

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{[Li_2S_6]} = \frac{[Li^+][LiS_6^-]}{[Li_2S_6(I)] + [Li_2S_6(II)]}$$

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{1.492[Li_2S_6(I)]} = \frac{K_{d1}^{\ominus}(I)}{1.492}$$

or

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{3.03[Li_2S_6(II)]} = \frac{K_{d1}^{\ominus}(II)}{3.03}$$

or

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{[Li_2S_6(I)] + [Li_2S_6(II)]} = \frac{1}{\frac{1}{K_{d1}^{\ominus}(I)} + \frac{1}{K_{d1}^{\ominus}(II)}}$$

$$Li_2S_6(I) \longrightarrow Li^+ + LiS_6^-,\ \Delta G_{d1}^{\ominus}(I) = -RT \ln K_{d1}^{\ominus}(I)$$

$$K_{d1}^{\ominus}(I) = \exp\left(-\frac{20.68\,kJ\,mol^{-1} \times 1000}{8.314\,J\,mol^{-1}\,K^{-1} \times 298.15K}\right) = 2.37 \times 10^{-4}$$

or

$$Li_2S_6(II) \longrightarrow Li^+ + LiS_6^-,\ \Delta G_{d1}^{\ominus}(II) = -RT \ln K_{d1}^{\ominus}(II)$$

$$K_{d1}^{\ominus}(II) = \exp\left(-\frac{18.92\,kJ\,mol^{-1} \times 1000}{8.314\,J\,mol^{-1}\,K^{-1} \times 298.15K}\right) = 4.84 \times 10^{-4}$$

$$K_{d1}^{\ominus} = \frac{2.37 \times 10^{-4}}{1.492} = 1.59 \times 10^{-4}$$

or

$$K_{d1}^{\ominus} = \frac{4.84 \times 10^{-4}}{3.03} = 1.59 \times 10^{-4}$$

or

$$K_{d1}^{\ominus} = \frac{1}{\frac{1}{K_{d1}^{\ominus}(I)} + \frac{1}{K_{d1}^{\ominus}(II)}} = \frac{1}{\frac{1}{2.37 \times 10^{-4}} + \frac{1}{4.84 \times 10^{-4}}} = 1.59 \times 10^{-4}$$

4.10

$$[Li_2S_6] > [LiS_6^-] > [LiS_3^\bullet] > [S_6^{2-}]$$

$LiS_6^-(DME) \longrightarrow Li^+(DME) + S_6^{2-}(DME)$

$$\Delta G_{d2}^\ominus = -RT \ln K_{d2}^\ominus,\ K_{d2}^\ominus = \exp\left(-\frac{100.55\ \text{kJ mol}^{-1} \times 1000}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}}\right) = 2.418 \times 10^{-18}$$

$Li_2S_6 \rightarrow 2LiS_3^\bullet$

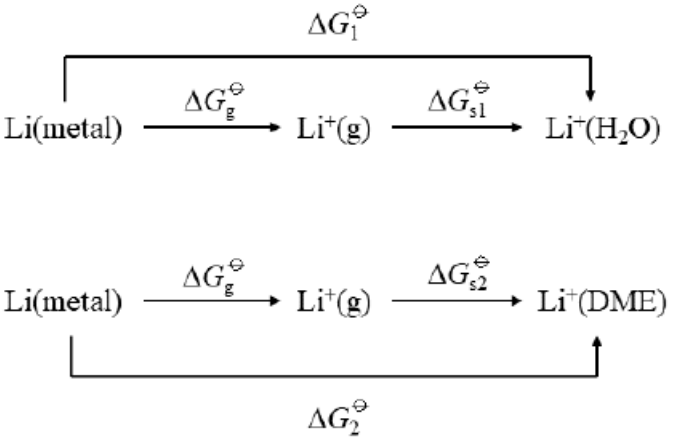
$$K_{dr}^\ominus = \frac{[LiS_3^\bullet]^2}{[Li_2S_6]} = \frac{[LiS_3^\bullet]^2}{[Li_2S_6(I)] + Li_2S_6(II)]} = \frac{[LiS_3^\bullet]^2}{1.492\,[Li_2S_6(I)]} = \frac{K_{dr}^\ominus(I)}{1.492}$$

$Li_2S_6(I) \rightarrow 2LiS_3^\bullet, \Delta G_{dr}^\ominus(I) = -RT \ln K_{dr}^\ominus(I)$

$$K_{dr}^\ominus(I) = \exp\left(-\frac{45.13\ \text{kJ mol}^{-1} \times 1000}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}}\right) = 1.24 \times 10^{-8}$$

$$K_{dr}^\ominus = \frac{1.24 \times 10^{-8}}{1.492} = 8.31 \times 10^{-9}$$

4.11



$$\Delta G_1^\ominus = \Delta G_g^\ominus + \Delta G_{s1}^\ominus \qquad (1)$$

$$\Delta G_2^\ominus = \Delta G_g^\ominus + \Delta G_{s2}^\ominus \qquad (2)$$

$(2) - (1)$: $\Delta G_2^\ominus - \Delta G_1^\ominus = \Delta G_{s2}^\ominus - \Delta G_{s1}^\ominus$

$Li(metal) \longrightarrow Li^+(H_2O) + e^-,\ \Delta G_1^\ominus = nFE^\ominus(Li^+(H_2O)/Li)$

$Li(metal) \longrightarrow Li^+(DME) + e^-,\ \Delta G_2^\ominus = nFE^\ominus(Li^+(DME)/Li)$

$$nFE^\ominus(Li^+(DME)/Li) = nFE^\ominus(Li^+(H_2O)/Li) - \Delta G_{s1}^\ominus + \Delta G_{s2}^\ominus$$

$$E^\ominus(Li^+(DME)/Li) = -3.040 - \frac{[(-116.9\ \text{kJ mol}^{-1}) - (-114.6\ \text{kJ mol}^{-1})] \times 1000}{96485\ \text{C mol}^{-1}} = -3.016\ \text{V}$$

4.12

Assume $[S_4^{2-}] = c_1$, the original concentration of Li_2S is c_0
According to the charge balance:

$$2c_0 = 1 \times [S_3^{\bullet-}] + 2 \times [S_4^{2-}] + 2 \times [S_5^{2-}] + 2 \times [S_6^{2-}] + 2 \times [S_7^{2-}] + 2 \times [S_8^{2-}]$$

$$2c_0 = 17.50c_1 + 1.00 \times 2c_1 + 4.50 \times 2c_1 + 55.00 \times 2c_1 + 5.00 \times 2c_1 + 0.75 \times 2c_1 = 150c_1$$

$$c_0 = 75c_1$$

According to the material balance:

$$c_0 + \frac{4.81\ \text{mg}}{32.07\ \text{g mol}^{-1} \times 10.00\ \text{mL}}$$

$$= 17.50 \times 3c_1 + 1.00 \times 4c_1 + 4.50 \times 5c_1 + 55.00 \times 6c_1 + 5.00 \times 7c_1 + 0.75 \times 8c_1$$

$$75c_1 + 0.0150\ \text{mmol mL}^{-1} = 450c_1$$

$$c_1 = 4.00 \times 10^{-5}\ \text{mmol mL}^{-1}$$

$$m(Li_2S) = 75 \times 4.00 \times 10^{-5}\ \text{mmol mL}^{-1} \times 10.00\ \text{mL} \times 45.96\ \text{g mol}^{-1} = 1.38\ \text{mg}$$

THEORETICAL PROBLEM 5

Interconversion among Nitrogen Oxides

Nitrogen oxides (including N_2O, NO, NO_2, N_2O_4 and etc., usually written as NO_x) are one of the main air pollutants that can cause a series of problems such as ozone depletion, acid rain, photochemical smog, and greenhouse effect. Therefore, the emission and conversion of NO_x must be controlled to improve air quality. Here let us investigate the oxidation of NO to NO_2 *via* the reaction of $2NO + O_2 \longrightarrow 2NO_2$.

Part A

It is generally accepted that this reaction proceeds through the following mechanism in the atmosphere:

$$2\,NO \rightleftharpoons N_2O_2 \qquad (1)$$

$$N_2O_2 + O_2 \longrightarrow 2\,NO_2 \qquad (2)$$

Reaction (1) and (2) and the reverse of reaction (1) are elementary reactions. Reaction (1) is a preequilibrium reaction, and its equilibrium constant in terms of concentrations is denoted as K_{c1}. Reaction (2) is the rate-determining step of the overall reaction, and its rate constant is k_2.

5.1 Deduce the rate expression for the overall reaction of $2NO + O_2 \longrightarrow 2NO_2$ as a function of [NO], [O_2], K_{c1} and k_2.

The temperature dependence of K_{c1} could be approximately described as $\ln K_{c1} = M - (N/T)$ (M and N are constants). The change of k_2 with temperature follows the Arrhenius equation with the preexponential factor of A_2 and apparent activation energy of $E_{a,2}$. Assume that $E_{a,2}$ and A_2 are independent of the temperature.

5.2 Deduce the expressions for the pre-exponential factor (A_+) and apparent activation energy (E_{a+}) of the reaction of $2NO + O_2 \longrightarrow 2NO_2$ as functions of M, N, A_2 and $E_{a,2}$.

The apparent rate constant (k_+) of the overall reaction is 6.63 × 10^5 L^2 mol^{-2} min^{-1} at 600 K, and its apparent activation energy is 1.20 kJ mol^{-1}.

5.3 Calculate the rate constant (in L^2 mol^{-2} min^{-1}) of this reaction at 700 K.

The standard enthalpies of formation ($\Delta_f H_m^{\emptyset}$) and standard entropies ($S_m^{\emptyset}$) at 298.15 K are as follows:

	NO(g)	O_2(g)	NO_2(g)
$\Delta_f H_m^{\ominus}$ (kJ mol^{-1})	91.3		33.1
$S_m^{\ominus}$ (J K^{-1} mol^{-1})	210.8	205.2	240.1

The standard reaction enthalpy and entropy changes of 2NO + O_2 ⟶ 2NO_2 can be regarded as temperature independent. All the gases are taken to be ideal for the following questions.

5.4 Calculate the thermodynamic equilibrium constant ($K_p^{\emptyset}$) of this reaction at 600 K.

5.5 Calculate the standard internal energy change $\Delta_r U_m^{\emptyset}$ (in kJ mol−1) of this reaction at 600 K.

Experimental observation shows that the rate of the reaction of 2NO_2 ⟶ 2NO + O_2 is independent on the concentration of NO and O_2.

5.6 Deduce the expression of the rate for this reaction (the apparent rate constant could be directly used as k_-) and calculate the value of k_- apparent at 600 K. (If you failed to find the $K_p^{\emptyset}$ (600 K) in question 5.4, use $K_p^{\emptyset}$ (600 K) = 350.0).

NO_2 gas is introduced to a container with a fixed volume which is held at 600 K and allowed to reach equilibrium. 20 percent of the reactant is converted to NO and O_2. All the gases are taken to be ideal.

5.7 Calculate the total pressure of this reaction system at equilibrium. (If you failed to find the $K_p^{\emptyset}$ (600 K) in question 5.4, use $K_p^{\emptyset}$ (600 K) = 350.0)

Part B

Industrial exhaust is a main source of NO_x. One of the approaches to reduce the emission of NO_x is through the oxidation of NO to NO_2 and the subsequent absorption of the formed NO_2 by absorbents. However, because of the low concentration of NO in exhaust, its spontaneous oxidation in the atmosphere is too slow to meet the demand of industry.

Generally, solid catalysts are used to accelerate this reaction. The NO oxidation proceeds on the surface of a specific catalyst (CatX) through the following mechanism (adsorption site is denoted as Site):

Assume that the adsorptions of NO, NO_2 and O (from the dissociation of O_2) cannot proceed beyond a monolayer coverage, and these species are adsorbed by the same kind of surface sites. Their fractional coverages (θ, defined as the ratio of the number of adsorption sites occupied to the number of total adsorption sites) are denoted as θ_{NO}, θ_{NO2} and θ_O, respectively. Thus, the fraction of unoccupied adsorption sites (θ_v) is $\theta_v = 1 - \theta_{NO} - \theta_{NO2} - \theta_O$. Assume that all the adsorption and desorption processes are much faster than reaction (S3).

$$O_2(g) + 2\,\text{Site} \underset{k_{S-1}}{\overset{k_{S+1}}{\rightleftharpoons}} 2\,\text{O-Site}$$

$$r_{S+1} = k_{S+1}\,[O_2]\,\theta_v^2 \qquad r_{S-1} = k_{S-1}\theta_O^2$$

$$NO\,(g) + \text{Site} \underset{k_{S-2}}{\overset{k_{S+2}}{\rightleftharpoons}} \text{NO-Site}$$

$$r_{S+2} = k_{S+2}[NO]\theta_v \qquad r_{S-2} = k_{S-2}\theta_{NO}$$

$$NO\,(g) + \text{O-Site} \xrightarrow{k_{S+3}} NO_2\text{-Site}$$

$$r_{S+3} = k_{S+3}[NO]\theta_O$$

$$NO_2\text{-Site} \underset{k_{S-4}}{\overset{k_{S+4}}{\rightleftharpoons}} NO_2(g) + \text{Site}$$

$$r_{S+4} = k_{S+4}\theta_{NO_2} \qquad r_{S-4} = k_{S-4}\,[NO_2]\,\theta_v$$

5.8 Deduce the expression for θ_v as a function of [NO], [O_2], [NO_2] and the rate constants involved in reactions (S1)−(S4).

5.9 Choose the correct expression for the rate of 2 NO(g) + O_2(g) ⟶ 2 NO_2(g) at the beginning of the reaction. Assume that the concentration and adsorption of NO_2 are both negligible.

$$\text{(A) } r_{S+} = \frac{k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[NO][O_2]^{0.5}}{1+(k_{S+1}[O_2]/k_{S-1})^{0.5}+k_{S+2}[NO]/k_{S-2}}$$

$$\text{(B) } r_{S+} = \frac{0.5k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[NO][O_2]^{0.5}}{1+(k_{S+1}[O_2]/k_{S-1})^{0.5}+k_{S+2}[NO]/k_{S-2}}$$

$$\text{(C) } r_{S+} = \frac{k_{S+3}(k_{S+1}/k_{S-1})[NO][O_2]^{0.5}}{1+k_{S+1}[O_2]/k_{S-1}+k_{S+2}[NO]/k_{S-2}}$$

$$\text{(D) } r_{S+} = \frac{k_{S+4}k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[NO][O_2]^{0.5}/k_{S-4}}{1+k_{S+1}([O_2]/k_{S-1})^{0.5}+k_{S+2}[NO]/k_{S-2}}$$

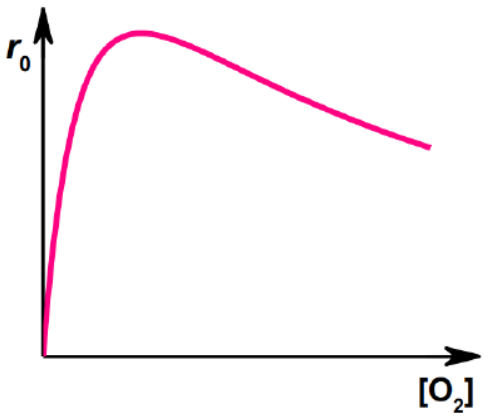
For some catalysts, the surface reaction proceeds via an alternative way instead of reaction (S3):

$$\text{NO-Site} + \text{O-Site} \xrightarrow{k_{S+5}} \text{Site} + \text{NO}_2\text{-Site} \qquad \text{(S5)}$$

$$r_{S+5} = k_{S+5}\theta_{NO}\theta_O$$

This step is also rate-determining for the overall reaction.

A catalyst (CatY) is used to promote the reaction of 2NO + O_2 ⟶ 2NO_2. When the temperature and NO concentration are constant, the initial reaction rate changes with the concentration of O_2 as follows:



5.10 Choose a mechanism that is consistent with this curve.

(A) S3

(B) S5

(C) cannot be determined

Solution of the problem 5

5.1

Using the definition of $K_{c1} = \frac{[N_2O_2]}{[NO]^2}$, $[N_2O_2] = K_{c1}[NO]^2$ is obtained.
Thus, $r_+ = k_2[N_2O_2][O_2] = k_2K_{c1}[NO]^2[O_2]$

5.2

Combining $K_{c1} = \exp(M - N/T)$, $k_2 = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right)$ and $k_+ = k_2K_{c1}$,
$k_+ = k_2K_{c1} = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right) \exp\left(M - \frac{NR}{RT}\right) = A_2 \exp(M) \exp\left(-\frac{E_{a,2} + NR}{RT}\right)$.
Comparing this equation with Arrhenius equation,
$A_+ = A_2 \exp(M)$ and $E_{a+} = E_{a,2} + NR$ are obtained.

5.3

Calculation:
According to Arrhenius equation, $\ln\frac{k_+(T_2)}{k_+(T_1)} = \frac{E_{a+}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ is obtained.
Thus, $k_+(700\ \text{K}) = 6.86 \times 10^5\ \text{L}^2\ \text{mol}^{-2}\ \text{min}^{-1}$

5.4

Calculation:
Because $\Delta_r H_m^\ominus$ and $\Delta_r S_m^\ominus$ do not change with temperature,
$\Delta_r H_m^\ominus(600\text{K})$
$= \Delta_r H_m^\ominus(298\text{K})$
$= 2\Delta_f H_m^\ominus(NO_2, 298\text{K}) - \Delta_f H_m^\ominus(NO, 298\text{K}) - \Delta_r H_m^\ominus(O_2, 298\text{K})$
$= -116.4\ \text{kJ mol}^{-1}$

$\Delta_r S_m^\ominus(600\text{K})$
$= \Delta_r S_m^\ominus(298\text{K})$
$= 2S_m^\ominus(NO_2, 298\text{K}) - 2S_m^\ominus(NO, 298\text{K}) - S_m^\ominus(O_2, 298\text{K})$

$-146.6\ \text{J K}^{-1}\ \text{mol}^{-1}$
For a thermostatic process, $\Delta G = \Delta H - T\Delta S$, thus $\Delta_r G_m^\ominus(600\ \text{K}) = -28.44\ \text{kJ mol}^{-1}$
Using the equation of $K_p^\ominus = \exp(-\Delta_r G_m^\ominus/RT)$, $K_p^\ominus(600\ \text{K}) = 299.2$ is obtained.

5.5

Calculation:
Using the equation of $\Delta_r U_m^\ominus = \Delta_r H_m^\ominus - \sum \nu RT$ and $\sum \nu$ value of -1 ($\nu_{NO_2} - \nu_{NO} - \nu_{O_2} = 2 - 2 - 1 = -1$),
$\Delta_r U_m^\ominus(600\ \text{K}) = -111.4\ \text{kJ mol}^{-1}$ is obtained.

5.6

Calculation:

When chemical equilibrium is reached, $K_c = \dfrac{[\mathrm{NO_2}]_{eq}^2}{[\mathrm{NO}]_{eq}^2 [\mathrm{O_2}]_{eq}}$ and $r_{-eq} = r_{+eq}$.

Thus, $r_{-eq} = r_{+eq} = k_+ [\mathrm{NO}]_{eq}^2 [\mathrm{O_2}]_{eq} = k_+ \dfrac{[\mathrm{NO_2}]_{eq}^2}{K_c} = k_- [\mathrm{NO_2}]_{eq}^2$

Therefore, $r_- = k_- [\mathrm{NO_2}]^2$

Using the equation of $K_c = K_p^{\ominus} \left(\dfrac{RT}{p^{\ominus}}\right)^{-\sum_B \nu_B}$ and $K_p^{\ominus}(600\ \mathrm{K})$ value of 299.2, $K_c = 1.49 \times 10^4\ \mathrm{L\ mol^{-1}}$ is obtained.

According to $k_- = k_+ / K_c$, the value of k_- is calculated to be $44.4\ \mathrm{L\ mol^{-1}\ min^{-1}}$ If the $K_p^{\ominus}(600\ \mathrm{K})$ value is used as 350.0, the result should be 38.0.

5.7

Calculation:

According to the stoichiometry of the reaction and setting $p_{\mathrm{NO_2}} = 0.8p_0, p_{\mathrm{NO}} = 0.2p_0$ and $p_{\mathrm{O_2}} = 0.1p_0$ are obtained.

$$K_p^{\ominus} = \frac{\left(p_{\mathrm{NO_2}}/p^{\ominus}\right)^2}{\left(p_{\mathrm{NO}}/p^{\ominus}\right)^2 \left(p_{\mathrm{O_2}}/p^{\ominus}\right)} = \frac{\left(0.8p_0/p^{\ominus}\right)^2}{\left(0.2p_0/p^{\ominus}\right)^2 \left(0.1p_0/p^{\ominus}\right)} = \frac{160p^{\ominus}}{p_0}$$

Therefore, $p_0 = 53.5$ kPa. $p_{\mathrm{total}} = p_{\mathrm{NO_2}} + p_{\mathrm{NO}} + p_{\mathrm{O_2}} = 1.1p_0 = 58.8$ kPa

If the $K_p^{\ominus}(600\ \mathrm{K})$ value is used as 350.0, the result of 50.3 kPa is obtained.

5.8

The given mechanism involves a pre-equilibrium:

$r_{S+1} = r_{S-1}, k_{S+1} [\mathrm{O_2}] \theta_v^2 = k_{S-1} \theta_O^2, \theta_O / \theta_v = \left(k_{S+1} [\mathrm{O_2}] / k_{S-1}\right)^{0.5}$

$r_{S+2} = r_{S-2}, k_{S+2} [\mathrm{NO}] \theta_v = k_{S-2} \theta_{\mathrm{NO}}, \theta_{\mathrm{NO}} / \theta_v = k_{S+2} [\mathrm{NO}] / k_{S-2}$

$r_{S+4} = r_{S-4}, k_{S+4} \theta_{\mathrm{NO_2}} = k_{S-4} [\mathrm{NO_2}] \theta_v, \theta_{\mathrm{NO_2}} / \theta_v = k_{S-4} [\mathrm{NO_2}] / k_{S+4}$

Because $\theta_v + \theta_{\mathrm{NO}} + \theta_{\mathrm{NO_2}} + \theta_O = 1$, using the ratios among these coverages,

$\theta_v = \dfrac{1}{1 + \left(k_{S+1} [\mathrm{O_2}] / k_{S-1}\right)^{0.5} + k_{S+2} [\mathrm{NO}] / k_{S-2} + k_{S-4} [\mathrm{NO_2}] / k_{S+4}}$ is obtained.

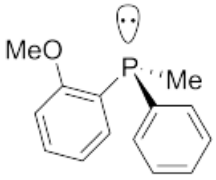
5.9 (B)

5.10 (B)

THEORETICAL PROBLEM 6

Enabling Phosphines

Phosphines are phosphorus analogues of amines. They also carry a lone pair of electrons at the phosphorus atom and thus exhibit Lewis basicity or nucleophilicity. But in contrast with tertiary amines, chiral phosphines like P1 with three different substituents can be isolated as single enantiomers. Chiral phosphines are often used as chiral ligands in transition metal catalysis.



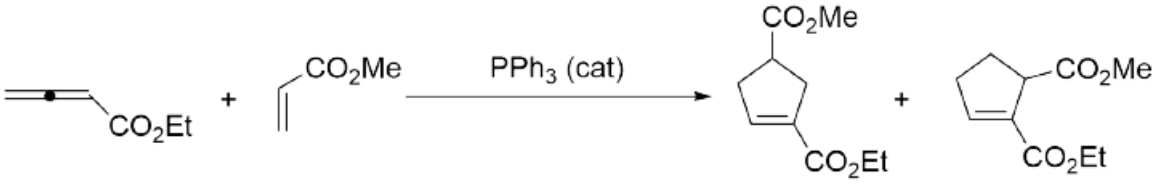
P1

$[\alpha]_D^{20}$ = +46

6.1 Using *R/S* symbol, assign the absolute configuration of P1.

In the past two decades, as organocatalysis grew rapidly, a large number of nucleophilic phosphinecatalyzed synthetic reactions have emerged. Among them, one of the most famous phosphine-catalyzed reactions is the Lu (3+2) cycloaddition reaction, which was first developed by Chinese scientist Xiyan Lu. For instance, under the catalysis of triphenylphosphine, ethyl allenoate **1** and methyl acrylate **2** smoothly produce two cyclopentene derivatives **3** (major) and **4** (minor).

Lu (3+2) cycloaddition:

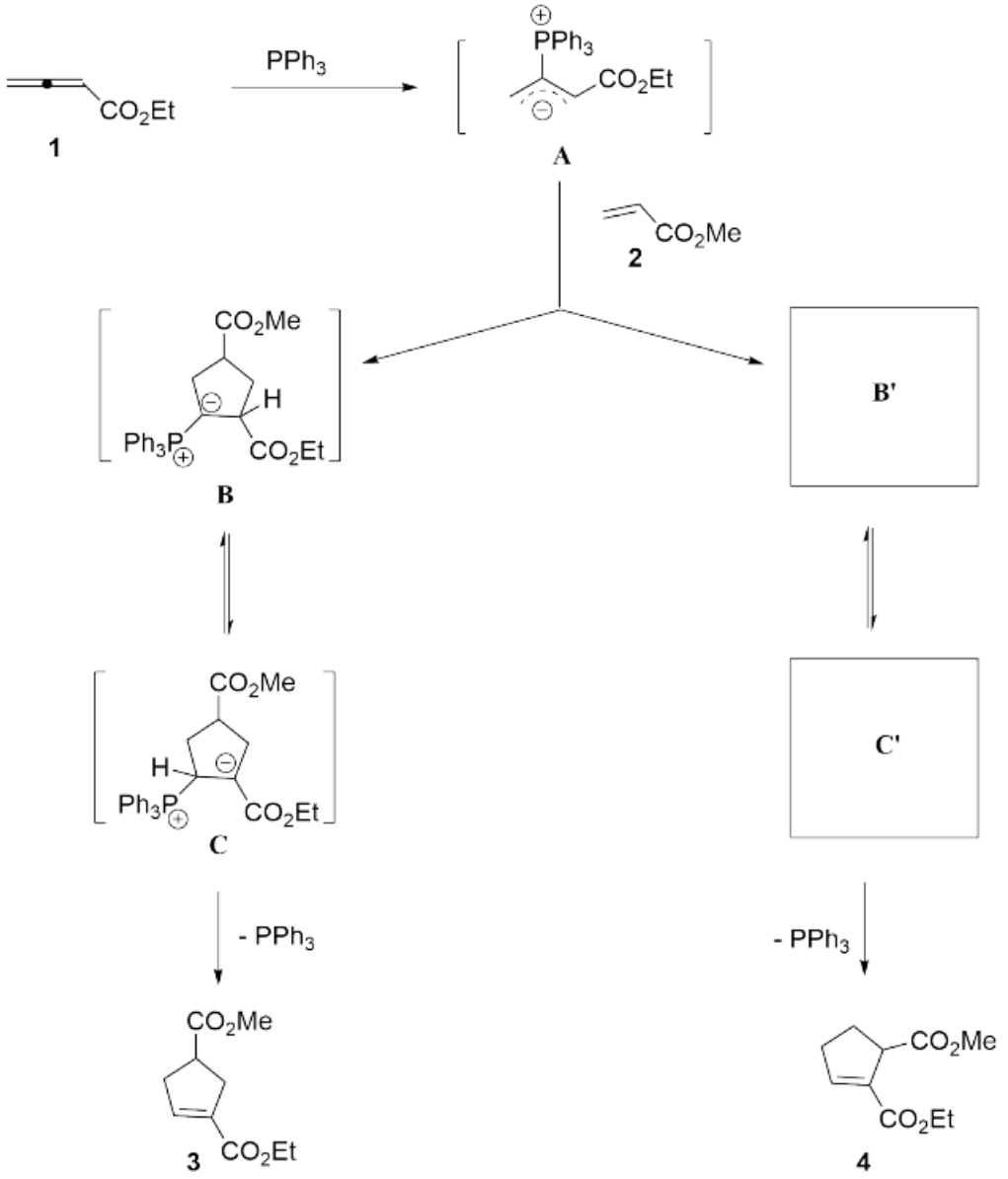


1 **2** **3** **4**

In a generally accepted mechanism, the Lu (3+2) reaction is a *formal* cycloaddition reaction. Initially, the catalyst triphenylphosphine engages in a nucleophilic addition to ethyl allenoate **1** to generate a zwitterionic intermediate **A**, which subsequently cyclizes with methyl acrylate **2** by two paths. In the path leading to compound **3**, an *in situ* generated phosphorus ylide intermediate **B** reversibly converts into intermediate **C** *via* proton transfer; **C** undergoes an elimination to deliver the major product **3** and release the

phosphine catalyst. In the path leading to compound **4**, a phosphorus ylide intermediate **B'** is formed, which also reversibly converts into intermediate **C'** *via* proton transfer; **C'** undergoes an elimination to give the minor product **4** and regenerate the phosphine catalyst.

Mechanism:

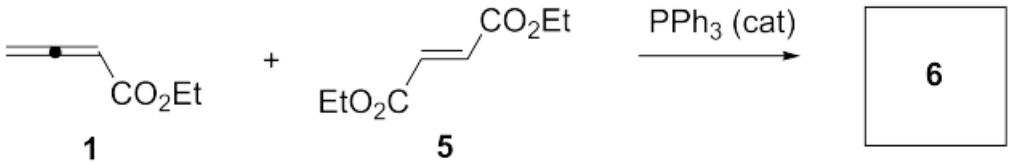


6.2 Draw the two major resonance structures that make up the shown resonance hybrid **A** (the involvement of ester group is not considered, and stereochemistry is not required).

6.3 Draw the structures of intermediates **B'** and **C'** (stereochemistry is not required).

Under similar conditions, ethyl allenoate **1** and diethyl fumarate **5** readily deliver the

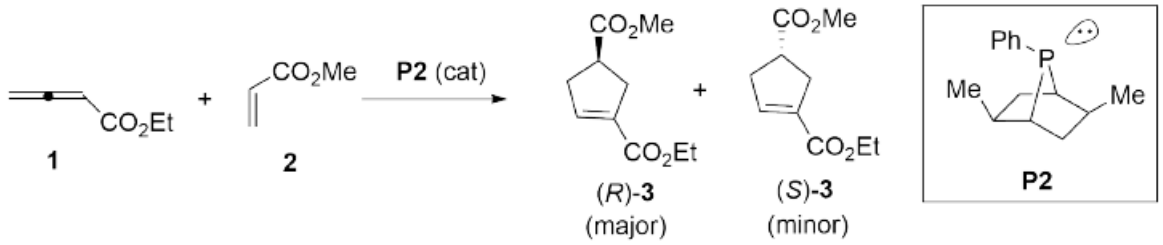
corresponding cycloaddition product **6**.



6.4 Draw the structure of compound **6** (stereochemistry is not required).

Asymmetric Lu (3+2) cycloaddition reaction can be readily realized by utilizing chiral phosphine catalysts. For example, under the catalysis of a chiral bicyclic phosphine **P2**, ethyl allenoate **1** and methyl acrylate **2** smoothly delivered an enantio-enriched cycloaddition product **3** in 80% ee (enantiomeric excess).

Asymmetric Lu (3+2) cycloaddition:



Calculation equation of ee:

$$\mathrm{ee} = \frac{n_{\mathrm{major}} - n_{\mathrm{minor}}}{n_{\mathrm{major}} + n_{\mathrm{minor}}} \times 100\%$$

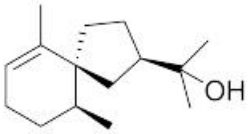
n_{major} = the amount of major enantiomer

n_{minor} = the amount of minor enantiomer

6.5 Mark the chirality centers in the chiral phosphine **P2** by using asterisks. (Note: points will be deducted for every wrong asterisk until 0 points)

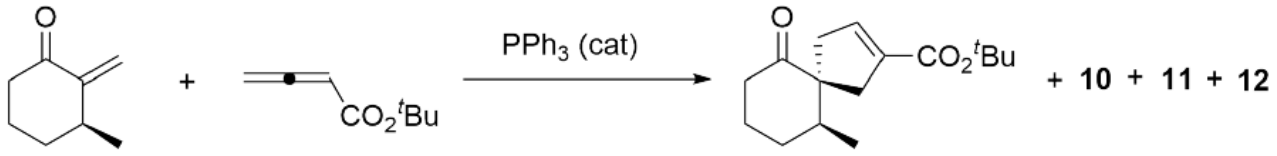
6.6 Give the ratio of n_{major}/n_{minor} of product 3.

Lu (3+2) cycloaddition reaction is a versatile tool in organic synthesis. For example, it was successfully used to synthesize (–)-hinesol, an important component of the Chinese medicinal herb Chang Zhu (*Atractylodes lancea var Chinensis*). Under the catalysis of PPh_3, a chiral cyclohexanone **7** cyclized with *tert*butyl allenoate **8**, affording a major product **9** and three minor products **10**, **11** and **12**. Minor products **10**−**12** are all the isomers of **9**. Compound **9** could be readily transformed into (–)-hinesol by a multistep process.

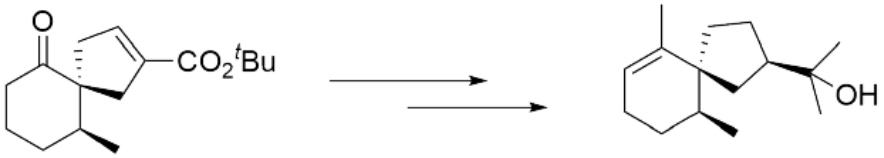


(–)-hinesol

Chang Zhu

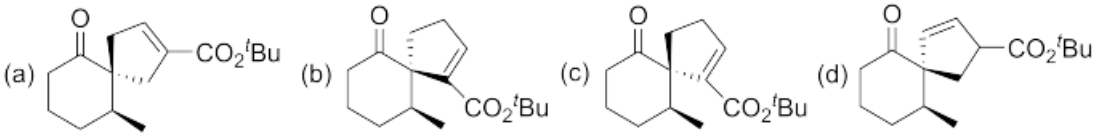


7 **8** **9**



9 (–)-hinesol

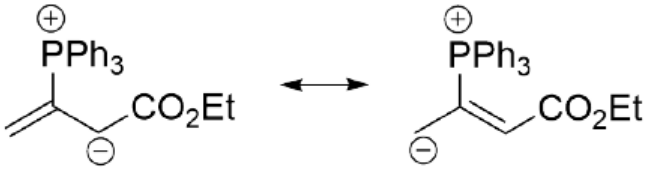
6.7 In the following compounds, choose which one does not belong to the minor products **10**–**12**.



Solution of the problem 6

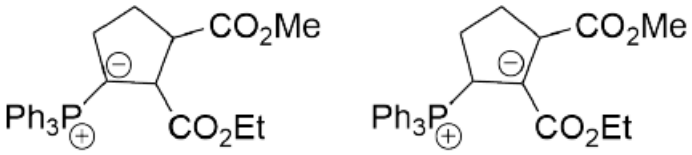
6.1 *R*

6.2



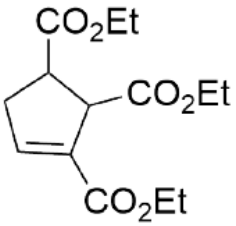
A **A'**

6.3



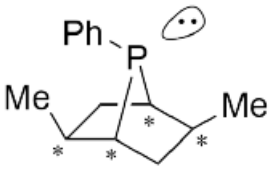
B' **C'**

6.4



6

6.5



P2

6.6 90:10

6.7 d)

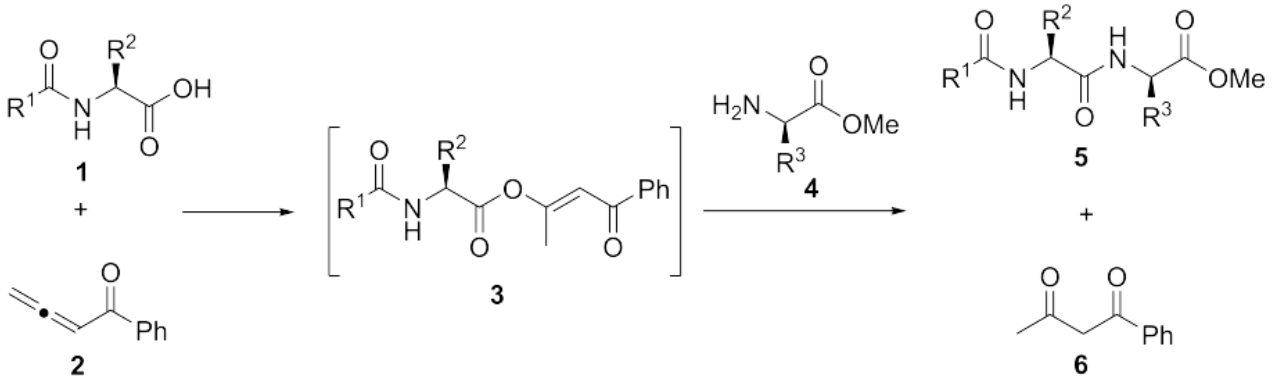
THEORETICAL PROBLEM 7

Organic Molecules in Life

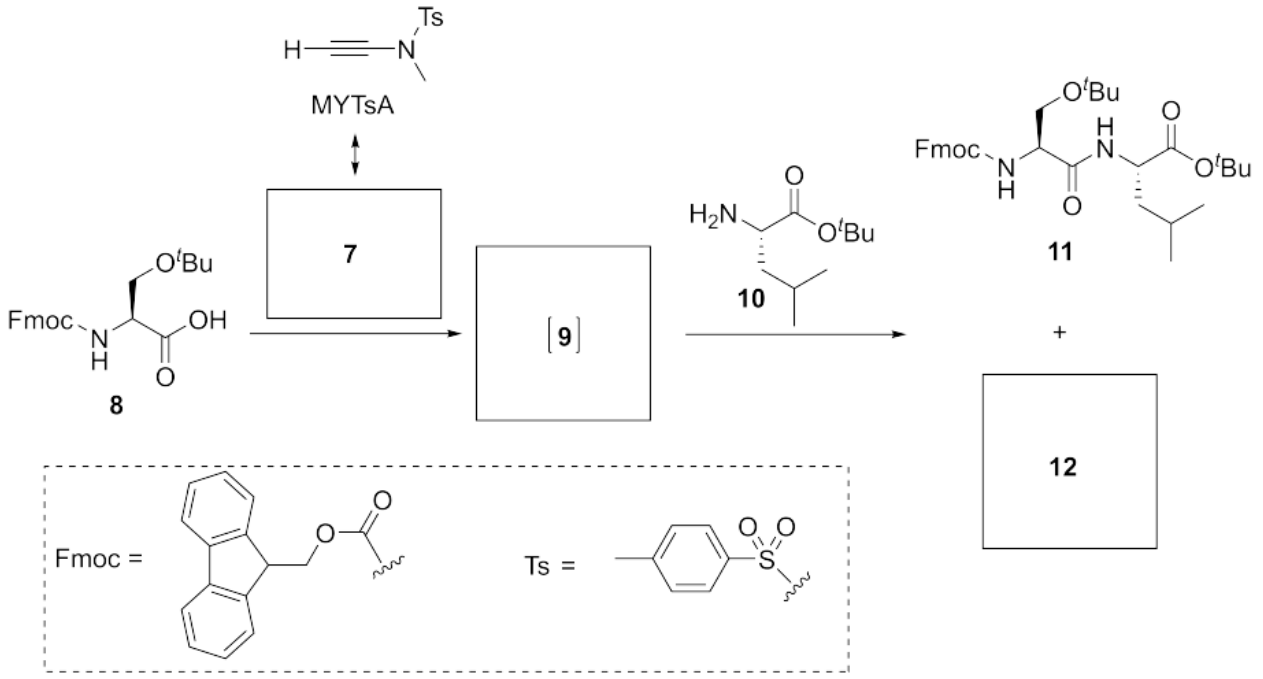
The synthesis of complex peptides and proteins is a challenging task. On September 17, 1965, Chinese scientists synthesized crystalline bovine insulin artificially for the first time, marking a crucial step in the journey of exploring the secret of life and opening the era of protein synthesis.

Stamp issued on the 50th anniversary (2015) of the first synthesis of crystalline bovine insulin.

Coupling of carboxylic acid groups with amine groups to forge an amide bond is the most elementary reaction in the synthesis of peptides and proteins. Allenone **2** was reported to be able to activate the carboxylic acid **1** under mild reaction conditions forming the intermediate **3**. Intermediate **3** then reacts with amine **4** to give amide **5** with high yield, along with the byproduct **6**.

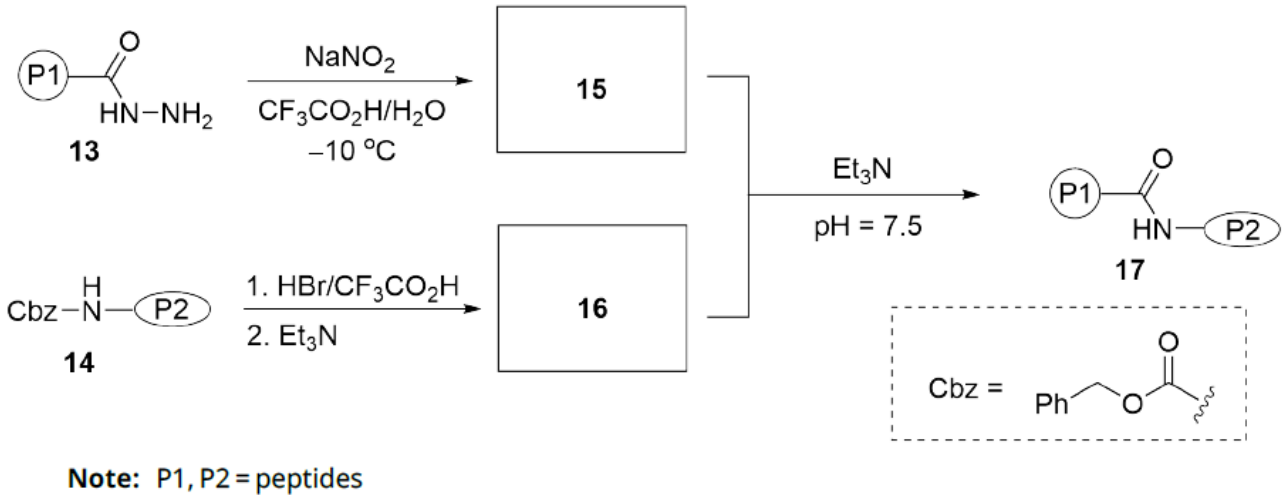


Similarly, *N*-ethynyl-*N*-methyl-*p*-toluenesulfonamide (MYTsA) with its major resonance structure **7** (involvement of Ts group is not considered) can activate carboxylic acid in the same way as allenone **2**.



7.1 Draw the structures of **7**, intermediate **9** and compound **12**. Show the stereochemistry of any stereocenters.

As the length of peptide chain grows, formation of amide bonds becomes more difficult, and conventional condensation methods are not applicable in the synthesis of proteins. In the first synthesis of crystalline bovine insulin, a method based on the chemistry of acylhydrazine **13** was developed to achieve the challenging amide coupling between two peptides. As the following equations, compound **15** reacts with **16** smoothly in the presence of triethylamine.

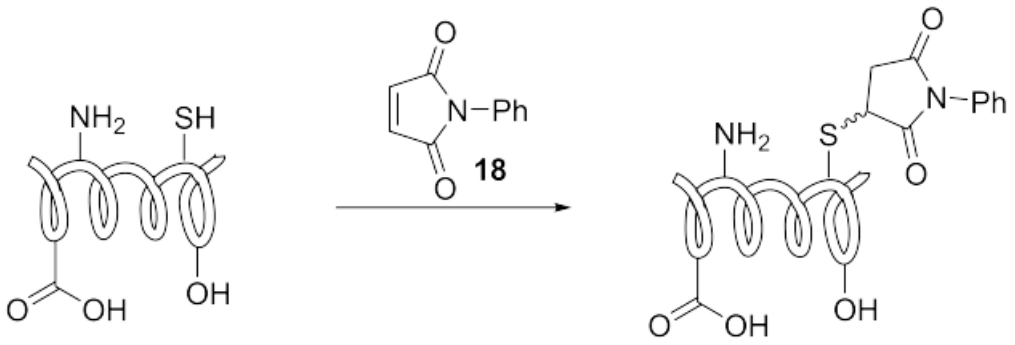


Note: P1, P2 = peptides

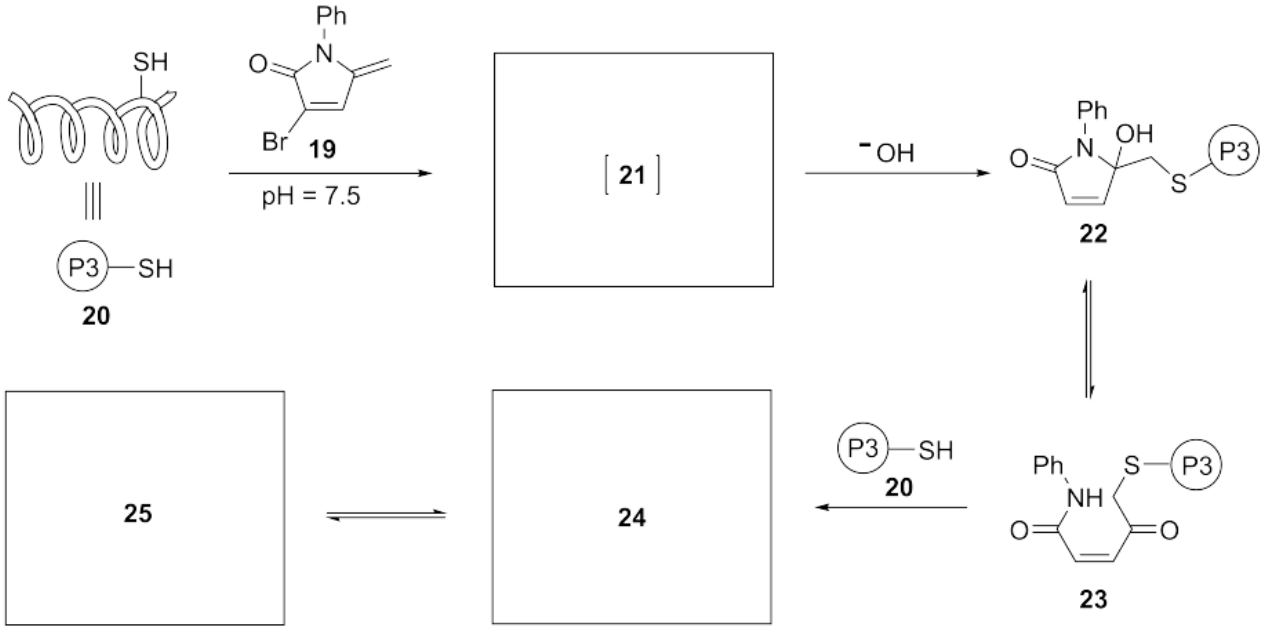
7.2 Draw the structures of compounds **15** and **16**.

In addition to *de novo* synthesis, scientists can modify existing proteins. Although there are multiple reactive sites on the surface of protein, such as amino groups, thiol groups, and

carboxyl groups, the most nucleophilic thiol groups are the preferred site when the protein is treated with electrophilic reagents such as *N*-phenyl maleimide **18** *via* Michael addition.



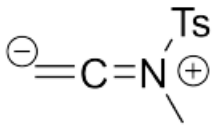
Under mild basic conditions (pH = 7.5), reagent **19** was proposed to react with the thiol group of protein **20** to give a neutral intermediate **21** which is attacked by hydroxide to give compound **22**. Compound **22** can equilibrate with an acyclic form **23**, and subsequently react with another protein **20**. The resulting major product can exist either in the acyclic form **24** or in the cyclic form **25** in a similar way as the equilibration between **22** and **23**.



7.3 Draw the structures of intermediate **21**, compounds **24** and **25**. Stereochemistry is not required**.**

Solution of the problem 7

7.1



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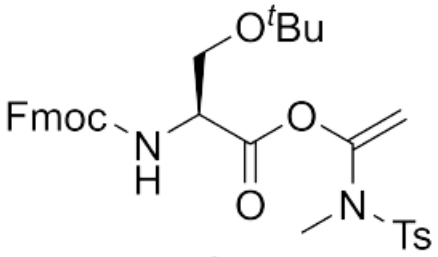

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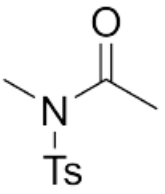

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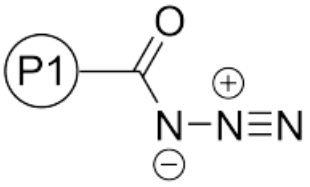
7.2



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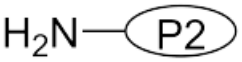

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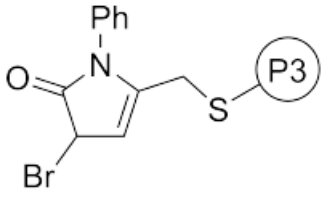
7.3



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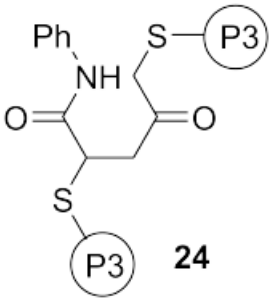
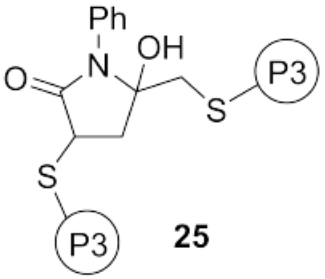


24

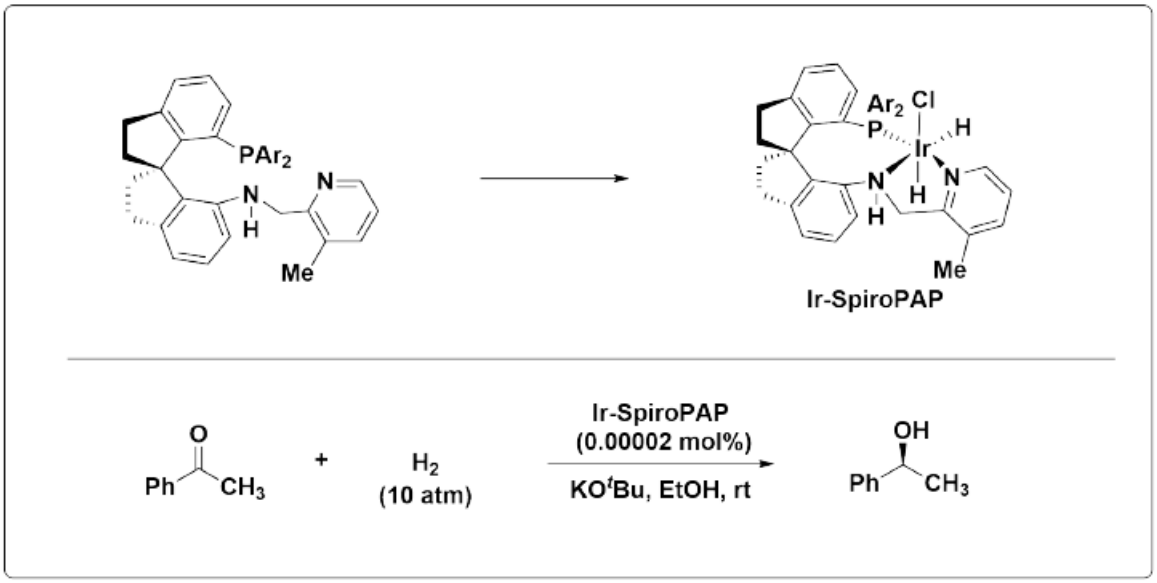


25

THEORETICAL PROBLEM 8

Amazing Chiral Spiro catalyst

Chiral compounds are important for human health, for example, more than 50% of the medicines currently in clinical use are single enantiomers of chiral molecules. However, synthesizing chiral molecules in enantio-enriched form is a great challenge. Professor Qilin Zhou's team in Nankai University in China developed a series of chiral spiro catalysts with high activity, raising the efficiency of asymmetric synthesis to a new height, and being widely used in the pharmaceutical industry. These catalysts can give up to (reach up to) 99.9% ee and can be used down to 0.00002 mol% loading. This research result won the first prize of the 2019 National Natural Science Award of China.

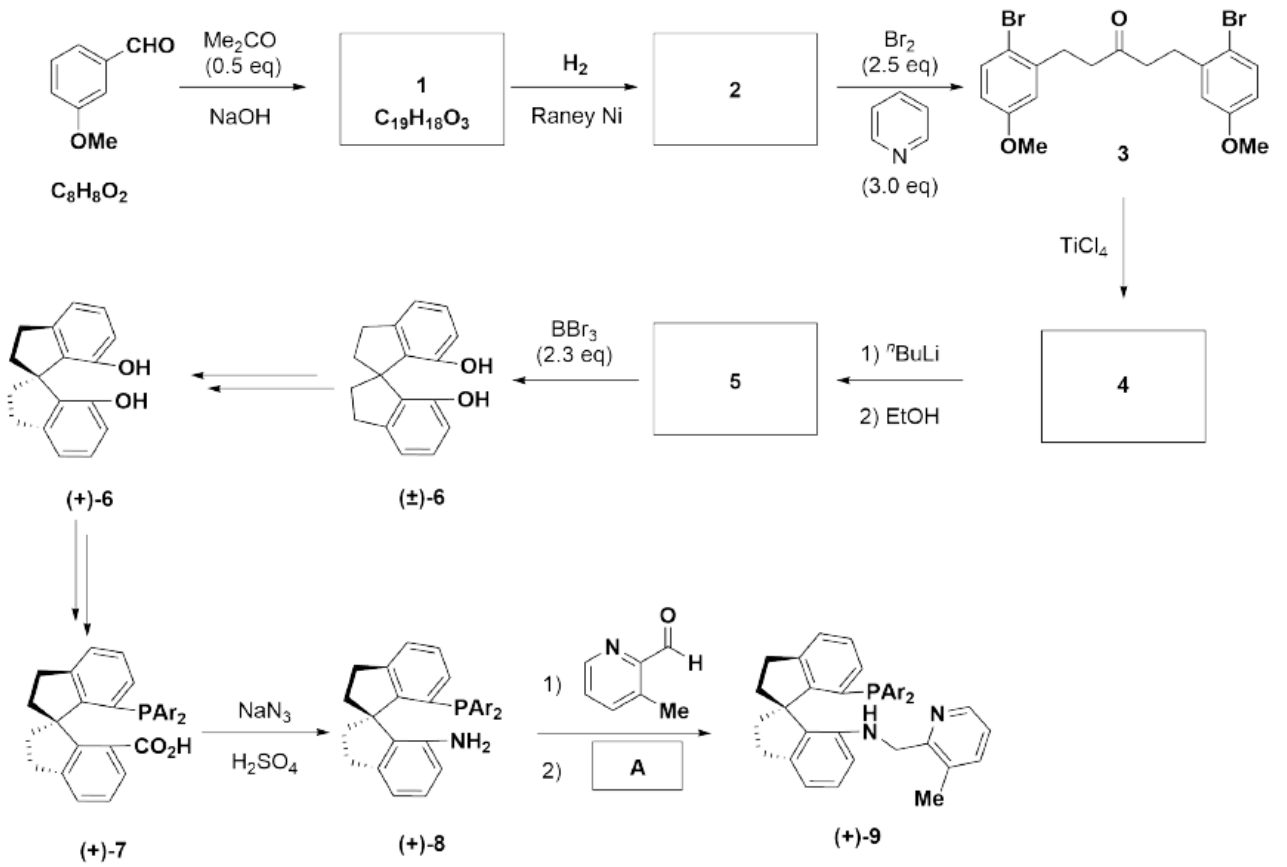


Note:

Ar = 3, 5-(^{t}Bu)$_2$C$_6$H$_3$

Part A

The synthetic route of the chiral ligand SpiroPAP is shown in the following scheme.



Note:

eq = equivalent

Ar = 3, 5-(^{t}Bu)$_2$C$_6$H$_3$

8.1 Draw the structures of **1, 2, 4, 5**. (Stereochemistry is not considered).

8.2 From the following reagents, which reagent **A** can NOT be used for the transformation of **8** to **9**?

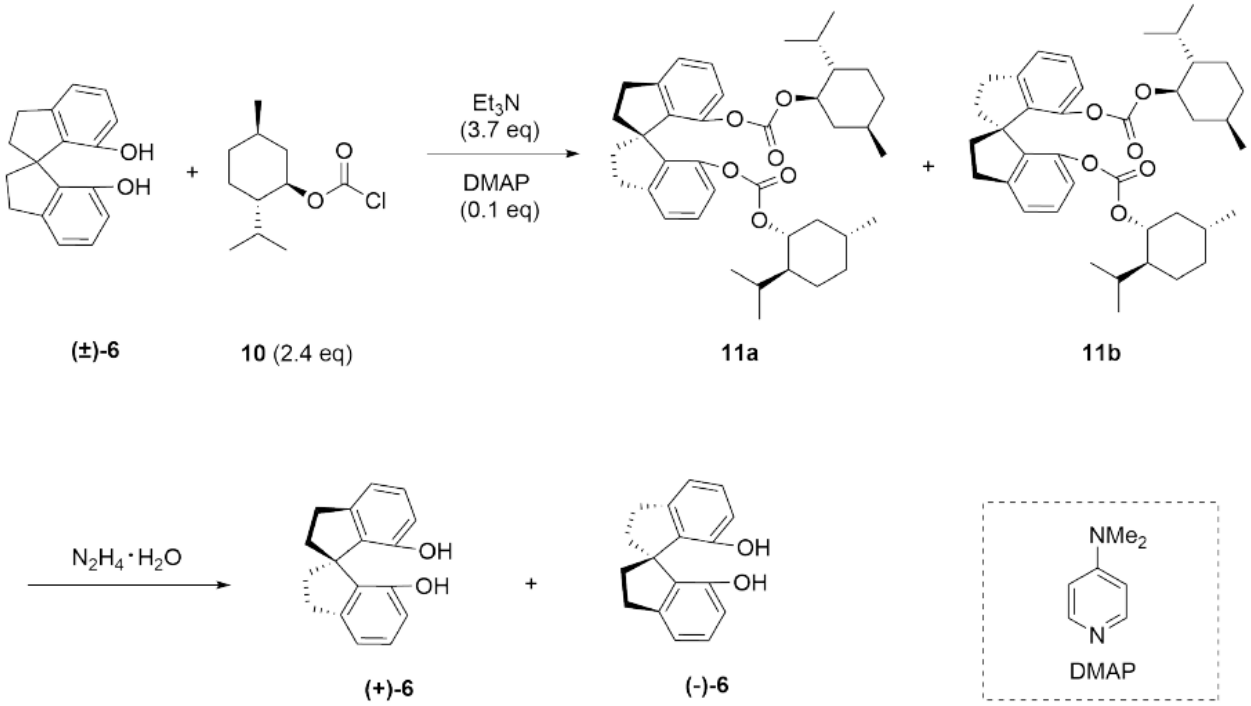
(a) $NaBH(OAc)_3$

(b) $NaBH_3CN$

(c) NH_2NH_2, NaOH

(d) $NaBH_4$

The racemic spiro compound **6** reacts with (–)-menthyl chloroformate (**10**) to generate compounds **11a** and **11b**, which can be separated by column chromatography, followed by hydrazinolysis to obtain optically pure (+)-**6** and (–)-**6**.



Note:

eq = equivalent

8.3 Choose the correct statement below.

(a) Compounds **11a** and **11b** are a pair of enantiomers.

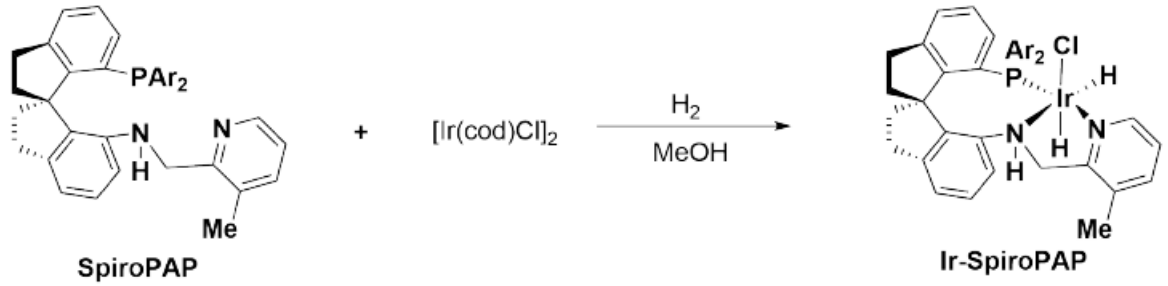
(b) Compounds **11a** and **11b** are a pair of diastereomers.

(c) Compounds **11a** and **11b** are a pair of *cis-trans* isomers.

(d) Compounds **11a** and **11b** are a pair of conformational isomers.

Part B

The Ir-SpiroPAP was prepared by reaction of SpiroPAP with $[Ir(cod)Cl]_2$ (cod is cycloocta-1,5-diene) in MeOH under hydrogen as shown below.



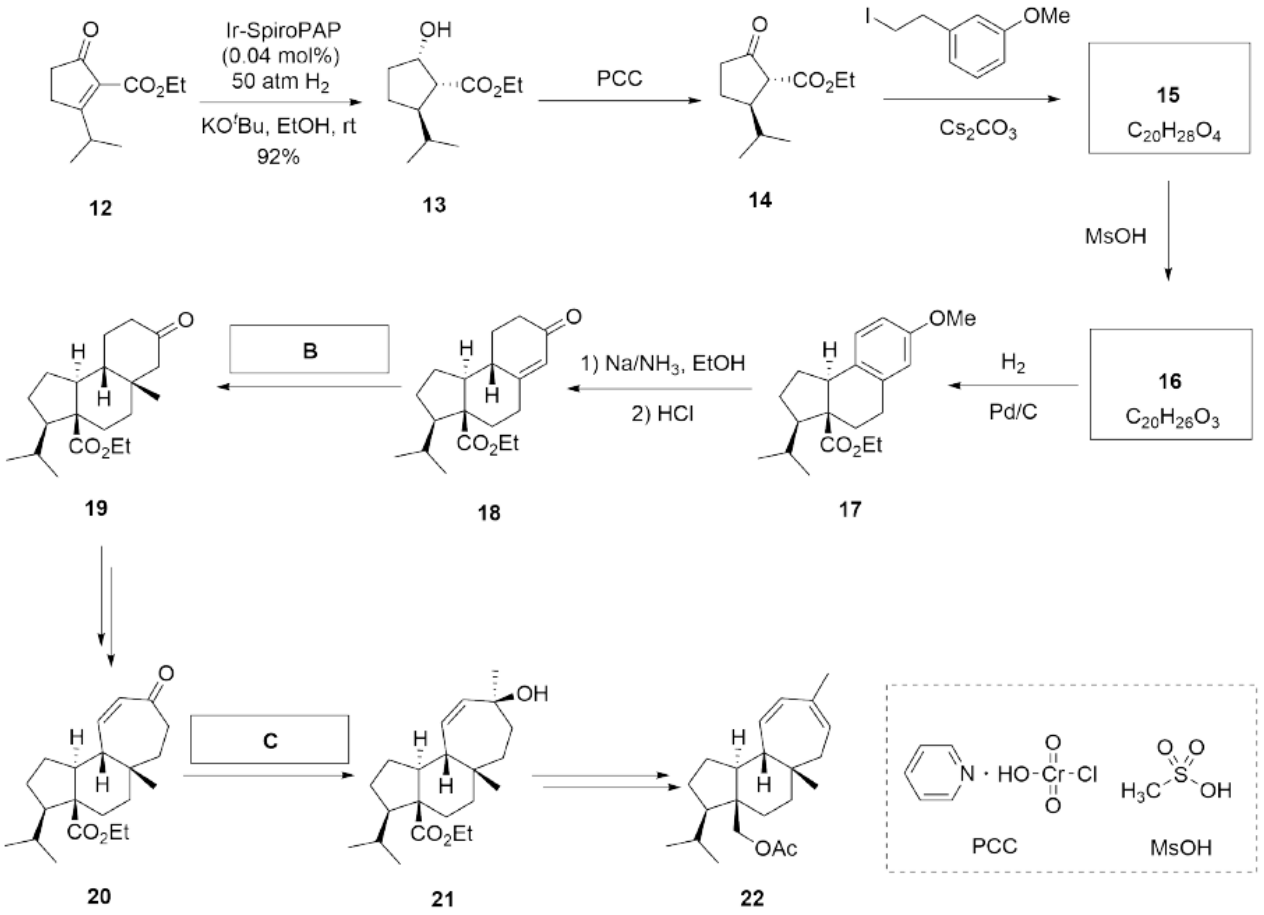
Note:

Ar = 3, 5-(^{t}Bu)$_2$C$_6$H$_3$

8.4 Write the oxidation number of Ir in the catalyst Ir-SpiroPAP.

8.5 Write the number of valence electrons of d orbitals for metal Ir in the catalyst Ir-SpiroPAP.

The chiral spiro catalyst Ir-SpiroPAP was used for the asymmetric total synthesis of Mulinane-type diterpene **22** as shown below.



8.6 Draw the structures of **15** and **16**, including the appropriate stereochemistry.

8.7 From the following reagents, choose the best for **B**.

(a) $MeLi/CeCl_3$

(b) MeLi/CuI

(c) $MePh_3P^+I^-$, ^nBuLi

(d) $Me_3S^+I^-$, NaH

8.8 From the following reagents, choose the best for **C**.

(a) $MeLi/CeCl_3$

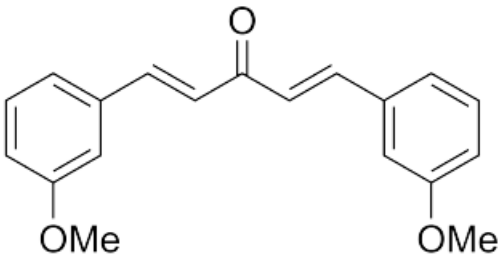
(b) MeLi/CuI

(c) $MePh_3P^+I^-$, ^nBuLi

(d) $Me_3S^+I^-$, NaH

Solution of the problem 8

8.1



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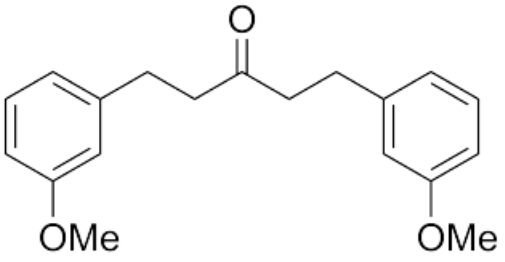

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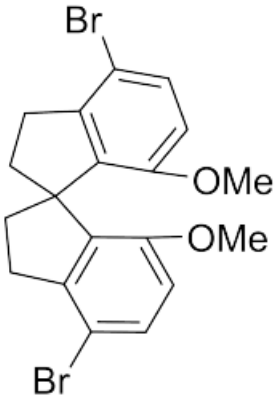

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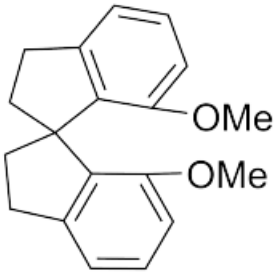


5

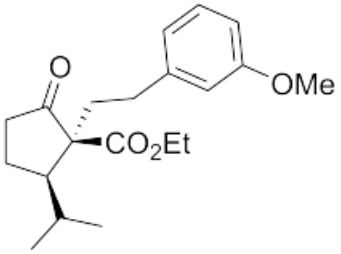
8.2 c)

8.3 b)

8.4 Ir(III) or +3

8.5 6

8.6



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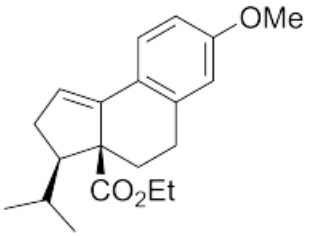

16

8.7 b)

8.8 a)

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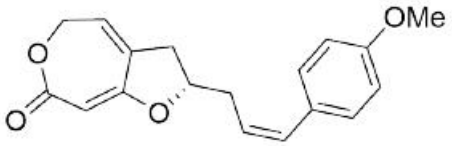
THEORETICAL PROBLEM 9

Total Synthesis of Capitulactone

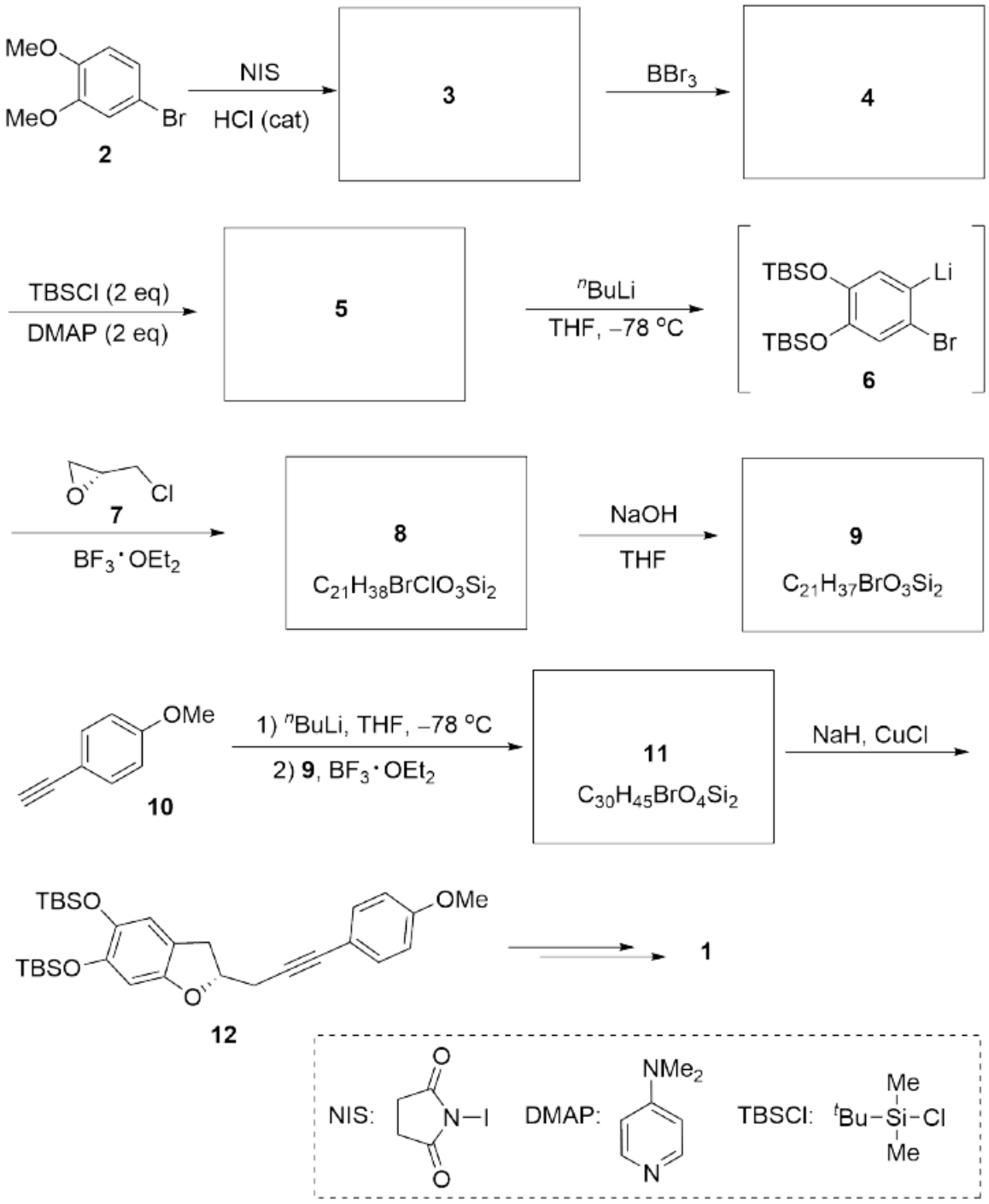
The plant of *Curculigo capitulata* grows in the Southern China and has long been used in traditional Chinese herbal medicine for the treatment of many diseases. Capitulactone (**1**) was isolated from the roots of *Curculigo capitulata*. Its structure with absolute configuration was unambiguously established by a combination of spectroscopic data and total synthesis.

Curculigo capitulata



Capitulactone (**1**)

The total synthesis of **1** began with the iodination of commercially available 4-bromoveratrole **2** through a key intermediate **12** as shown in the following scheme.



Note:

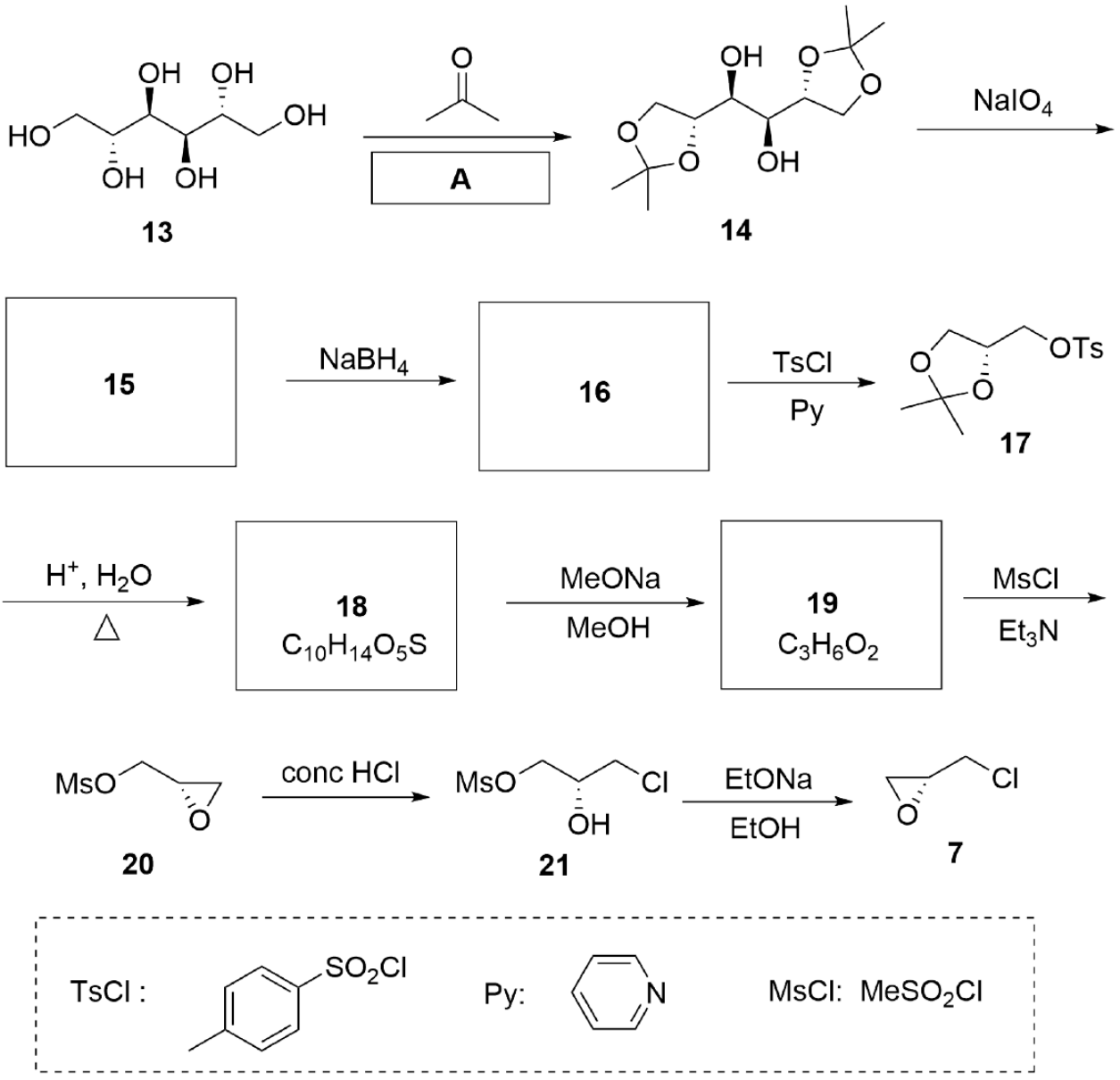
cat = catalyst

eq = equivalent

9.1 Draw the structures of compounds **3-5**, **8**, **9** and **11** and show the stereochemistry of any stereocenters.

(*R*)-Epichlorohydrin (**7**) was prepared from (+)-mannitol (**13**) through a route as shown

below.



Note:

eq = equivalent

conc = concentrated

9.2 From the following conditions, choose the best for **A**.

(a) Pyridine

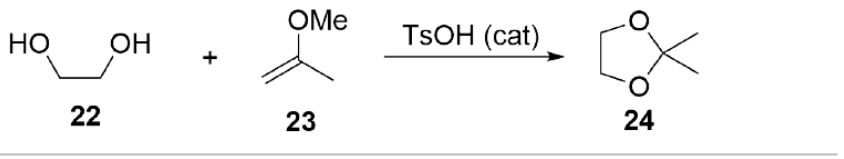
(b) 5% KOH/H_2O

(c) 1% HCl/H_2O

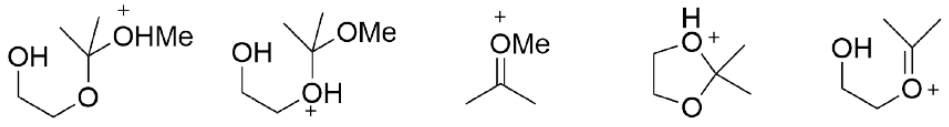
(d) Anhydrous $ZnCl_2$

9.3 Draw the structures of intermediate products **15, 16, 18** and **19** and show the stereochemistry of any stereocenters.

The diketal **14** can also be prepared by treating (+)-mannitol (**13**) with 2-methoxypropene (**23**) in the presence of catalytic amount of tolunesulfonic acid (TsOH) in anhydrous toluene. The model reaction is shown below.



22 **23** **24**



I **II** **III** **IV** **V**

9.4 The proposed mechanism for this reaction involves key intermediates (**I-V**) as shown above, choose the correct order of the formation of the key intermediates during the reaction process.

(a) **I, II, III, IV, V**

(b) **III, II, I, V, IV**

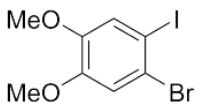
(c) **III, I, II, IV, V**

(d) **III, I, II, V, IV**

_____

Solution of the problem 9

9.1



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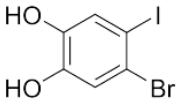

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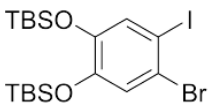

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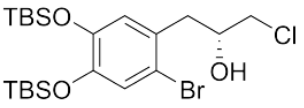

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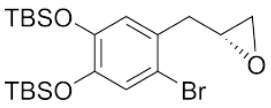

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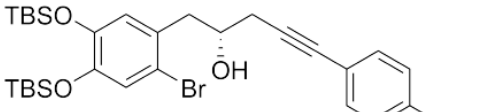
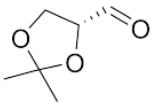


11

9.2 d)

9.3



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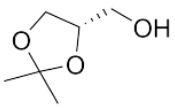

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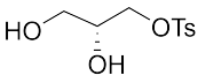

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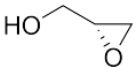

19

9.4 b)

55th

10 theoretical problems

3 practical problems

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55TH INTERNATIONAL CHEMISTRY OLYMPIAD SWITZERLAND 2023

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THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

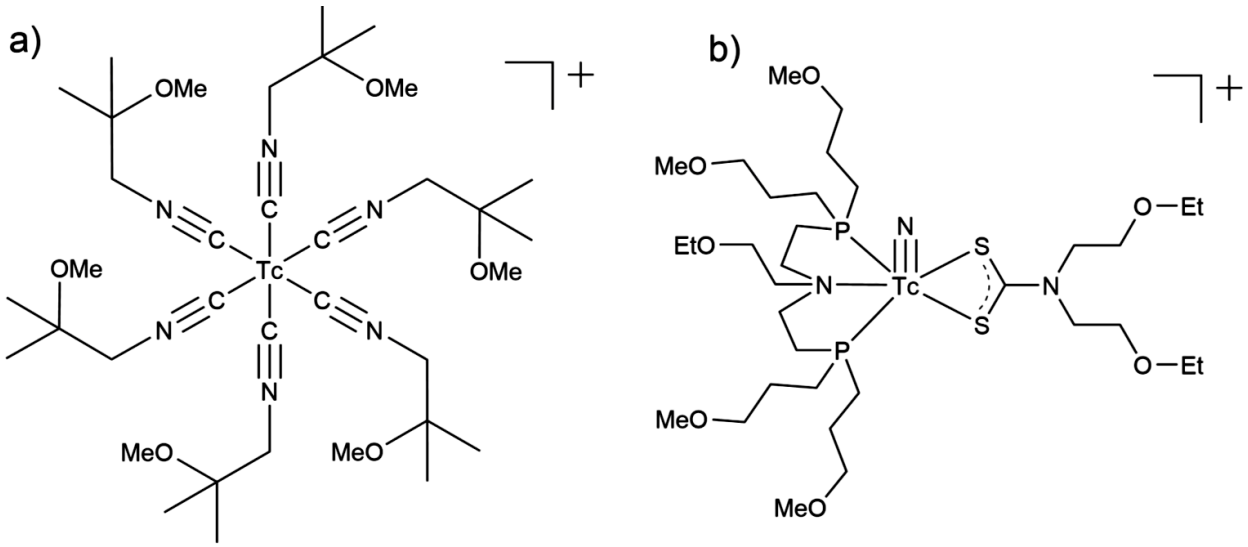
Molecular Imaging

Molecular imaging is a powerful tool in medical diagnostics. The nuclear isomer ^{99m}Tc (m = metastable) of the isotope ^{99g}Tc (g = ground state) has excellent radiation properties (γ-emitter, $t_{1/2}$ = 6.015 h) for radioimaging. ^{99m}Tc is obtained by β^- decay of a mother nuclide in a so-called technetium generator as ^{99m}Tc-pertechnetate $[^{99m}TcO_4]^-$.

1.1 Identify the mother nuclide (**A**) of 99mTc and the emitted particle (**B**).

A → ^{99m}Tc + **B**

1.2 Provide the oxidation states of the radiometal in the following ^{99m}Tc-probes.



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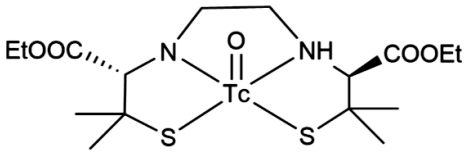

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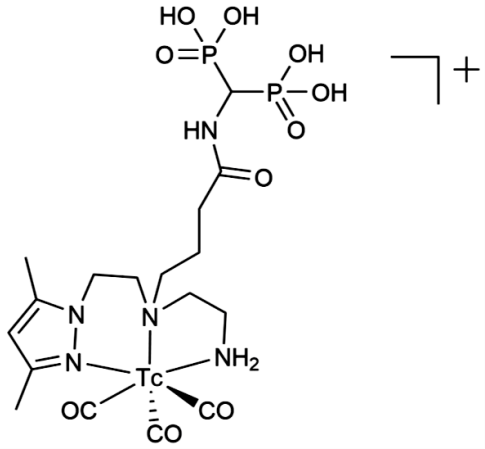


The redox potentials of the group seven elements manganese (**Mn**), technetium (**Tc**) and rhenium (**Re**) follow the general trend in the periodic tables (see **Figure 2** below).

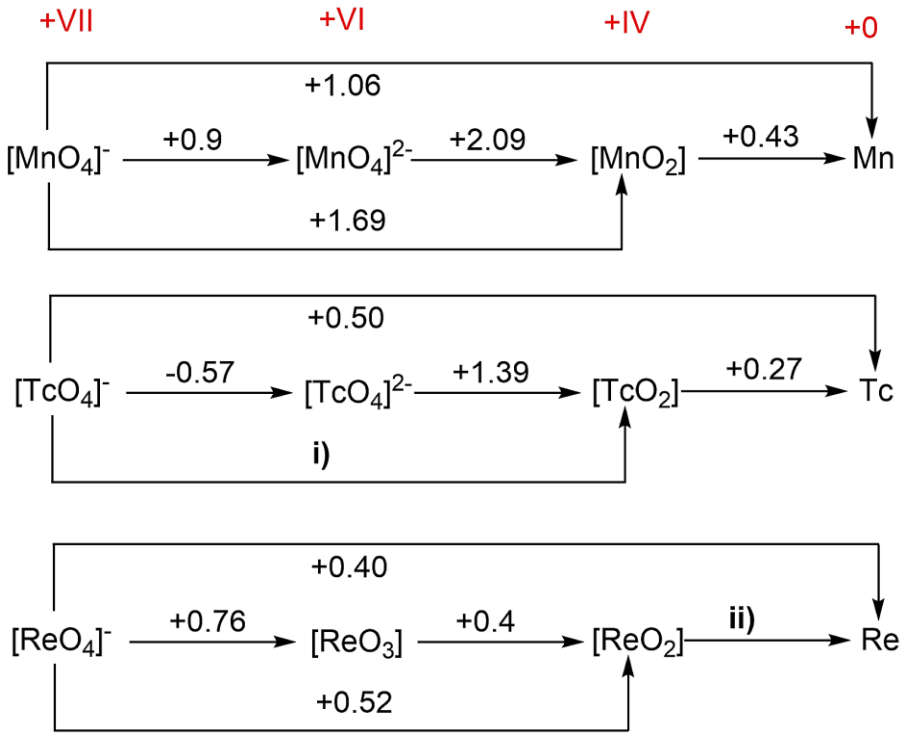


Figure 2

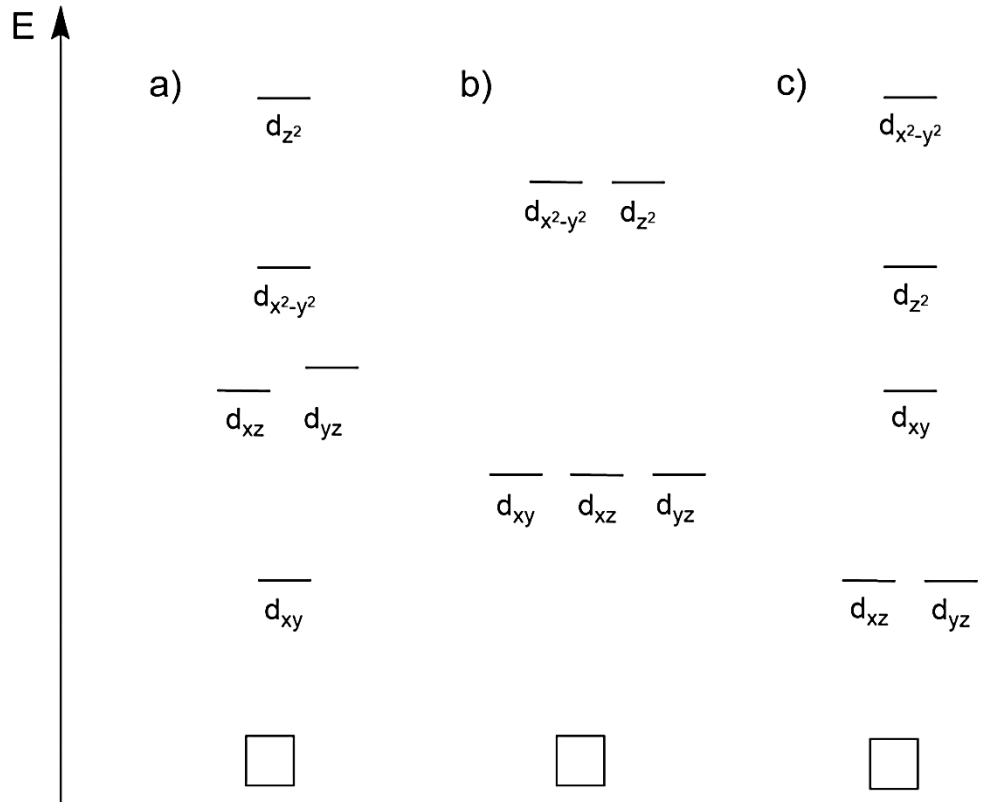
1.3 Calculate the two missing redox potentials **i** and **ii**.

1.4 Compare $[MnO_4]^-$, $[TcO_4]^-$ and $[ReO_4]^-$. Choose the strongest oxidizing agent.

1.5 Based on the values indicated by Figure 2 in the question sheet, select if TcO_2 would disproportionate to Tc and TcO_4^{2-} under acidic conditions.

Tc and Re complexes at the oxidation state +V (d^2 systems) which contain a terminal oxo- (O=) or nitrido ligand (N≡) are diamagnetic. The scheme below shows three possible molecular orbital energy diagrams.

1.6 Choose which orbital energy diagram explains the observed diamagnetism. Draw the corresponding electron configuration in the correct diagram.



$((C_4H_9)_4N)[^{99g}TcO_4]$ is a colorless powder. By the addition of conc. HCl this common starting compound for ^{99g}Tc chemistry is converted into the green complex $((C_4H_9)_4N)[^{99g}TcOCl_4]$.

1.7 Write down both oxidation and reduction half-reactions using the formulas of ions or neutral molecules, and the complete redox reaction.

All ^{99m}Tc radiotracers in clinics are prepared in “one pot” reactions, applying commercialized kits. Typically (^{99m}Tc $t_{1/2}$ = 6.015 h), an eluate of a ^{99m}Tc generator has an activity of 12.5 GBq (GBq = gigabecquerel = 10^9 decays per second).

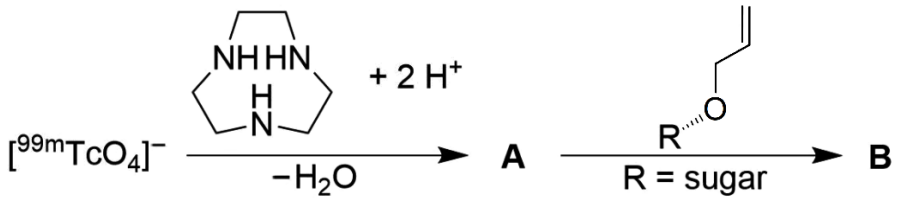
1.8 Calculate how many moles of ^{99m}Tc are present in such samples.

For standard imaging, around 200 MBq ^{99m}Tc are administered to the patient.

1.9 Assume that no activity is lost through excretion. Calculate how many hours the patient has to wait until the injected activity decreases to under 1 % of the starting activity.

Bioconjugation of radiometals is a chemical challenge. A recent example is the (3 + 2)

cycloaddition of $[^{99m}TcO_3(tacn)]^+$ (**A**) (tacn = 1,4,7-triazacyclononane) with alkenes. In this context (3 + 2) refers to the number of atoms involved and not to the numbers of electrons. The following scheme shows an example of this reaction by labeling a protected carbohydrate.



1.10 Draw the structures of compound **A** and **B**. Further, state the oxidation state of the technetium in these compounds.

SOLUTION OF THE PROBLEM 1

1.1 β^- decay: $[^{99}MoO_4]^{2-} \rightarrow [^{99m}TcO_4]^- + e^- + \nu$. *(antineutrino ν is not required)*

Hence: **A** = ^{99}Mo and **B** = e^-.

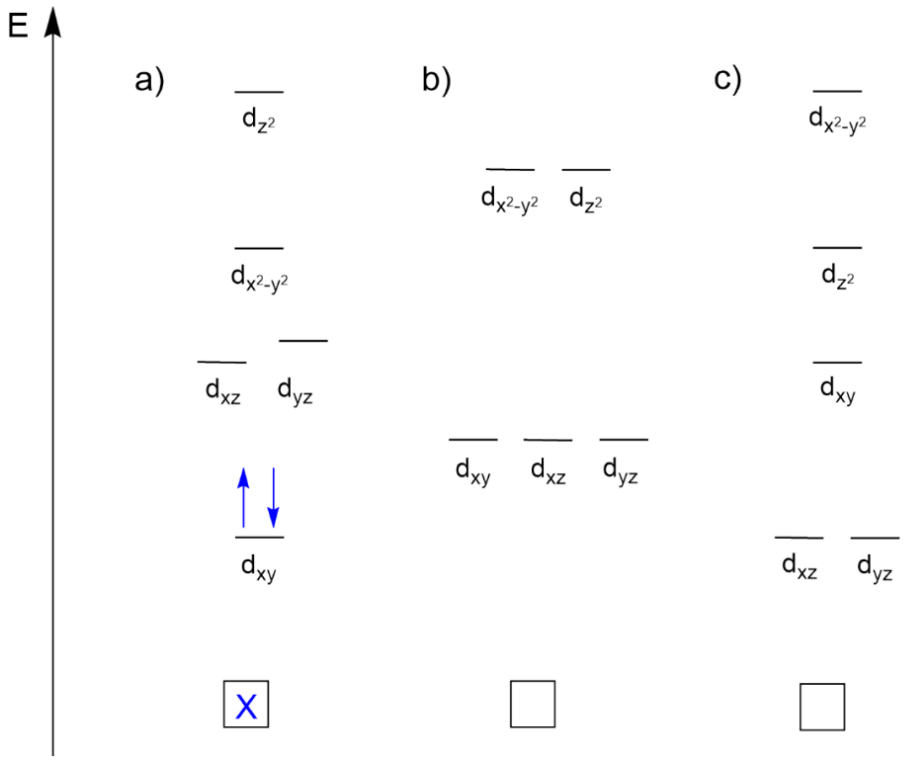
1.2 a) +I b) +V c) +V d) +I

1.3 i) +0.74 V ii) +0.31 V

1.4 $[MnO_4]^-$

1.5 No.

1.6



1.7 Reduction:

$((C_4H_9)_4N)[^{99g}TcO_4] + 2e^- + 6H^+ + 4Cl^- \rightarrow ((C_4H_9)_4N)[^{99g}TcOCl_4] + 3H_2O$

Oxidation:

$2Cl^- \rightarrow Cl_2 + 2e^-$

Overall reaction:

$((C_4H_9)_4N)[^{99g}TcO_4] + 6H^+ + 6Cl^- \rightarrow ((C_4H_9)_4N)[^{99g}TcOCl_4] + Cl_2 + 3H_2O$

or $((C_4H_9)_4N)[^{99g}TcO_4] + 6HCl \rightarrow ((C_4H_9)_4N)[^{99g}TcOCl_4] + Cl_2 + 3H_2O$

1.8 $A = \lambda N$

$\lambda = (\ln 2)/t_{1/2}$

$t_{1/2}$ = 6 h = 21600 s

$\lambda = (\ln 2)/21600\ s = 3.209 \times 10^{-5}\ s^{-1}$

$N = A/\lambda$

$N = (12.5 \times 10^9\ \text{decays}\ s^{-1})/3.209 \times 10^{-5}\ s^{-1}$

$N = 3.895 \times 10^{14}$ (atoms)

$n(^{99m}Tc) = 3.895 \times 10^{14}/6.022 \times 10^{23}\ mol^{-1}$

$n(^{99m}Tc) = 0.647 \times 10^{-9}$ mol

1.9 1% of 200 MBq = 2 MBq

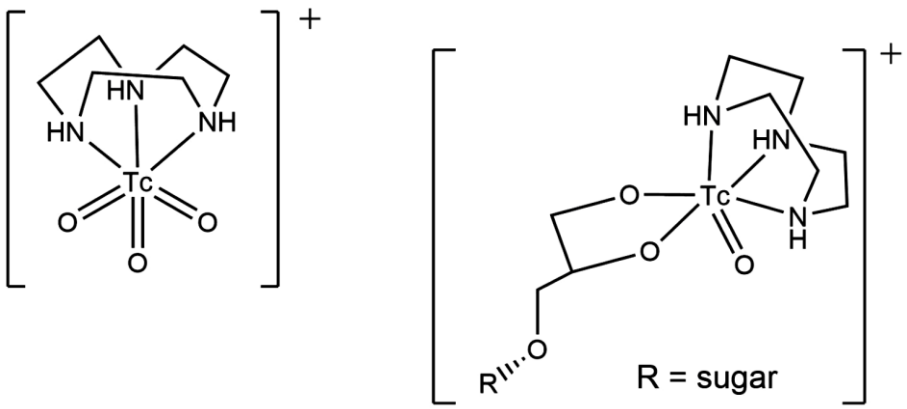
$t = -\ln(A/A_0)/\lambda$

$t = -\ln(2\ MBq/200\ MBq)/3.209 \times 10^{-5}\ s^{-1}$

t = 143508 s = 39.86 h

1.10 **A** oxidation state: +VII

B oxidation state: +V



A) B)

THEORETICAL PROBLEM 2

Electrochemical CO_2 reduction

In recent years, the electrochemical conversion of CO_2 into higher value products has been considered a promising and technologically feasible approach to mitigate the negative climatic effects caused by its increasing levels in the atmosphere. Several technologies have been developed to achieve this goal. Among these, CO_2 reduction through electrochemical means (CO_2RR) warrants particular attention due to its ability to be powered by renewable energy to transform environmentally harmful CO_2 into platform chemicals. Electrocatalysts are essential not only to accelerate the intrinsically slow CO_2RR but also to direct the electrolysis reaction towards the desired reaction products. In this context, it is not only the chemical nature of the catalyst itself which governs the resulting CO_2RR product distribution but also its morphological characteristics on various length scales. A new concept of CO_2RR catalyst design relies on the electrodeposition of foam-type materials, which offer a large surface area that is accessible to reactants (e.g. H_2O, H_2, and CO_2). Copper-based materials are the only known metallic CO_2RR catalysts that can produce hydrocarbons and alcohols in significant amounts by CO_2 electrolysis. Given below are thermodynamic data of selected substances:

	$\Delta_f H^\ominus$ (kJ mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})
H_2O(l)	−285.83	69.95
O_2(g)	0	205.15
H_2(g)	0	130.68
CO_2(g)	−393.52	213.79
ethanol(l)	−276.00	159.86
***n*-propanol(l)**	−302.54	192.80

Table 1. Standard formation enthalpy $\Delta_f H^\ominus$ and standard entropy $S^\ominus$ for some substances under standard conditions (T = 298.15 K, $p^\ominus$ = 1 bar)

Cell reaction	$E^\ominus$ vs. SHE (V)
$Cu^{2+} + 2e^- = Cu$	+0.34
$2H^+ + 2e^- = H_2$	0.00

Table 2. Selected half-cell reactions and standard potentials under standard conditions

2.1 Write and balance the chemical equation of the half-cell reactions for the following electrochemical reduction processes in acidic environment: (i) CO_2 to ethanol; (ii) CO_2 to *n*-propanol.

2.2 Combine the half-cell of the reduction process with an $H_2/2H^+$ half-cell where the latter acts as anode. Calculate the value of the standard cell potential of the CO_2 to **ethanol** reduction.

2.3 Write all the reduction and oxidation half-cell reactions taking place at the cathode and the anode, respectively.

Figure 1 shows the principle of dynamic hydrogen bubble-templated metal deposition.

Figure 2 displays top-down scanning electron microscopy images of five different Cu foams obtained upon interruption of the metal deposition at different times: 5 s, 20 s, 80 s.

Cu foam electrodeposition processes (see **Figure 1**) were carried out in an aqueous 1.5 M sulfuric acid solution containing 0.2 M copper sulfate ($CuSO_4 \cdot 5H_2O$) as the copper source. A Cu disk (1 cm^2) and a Pt foil served as the cathode and the anode, respectively.

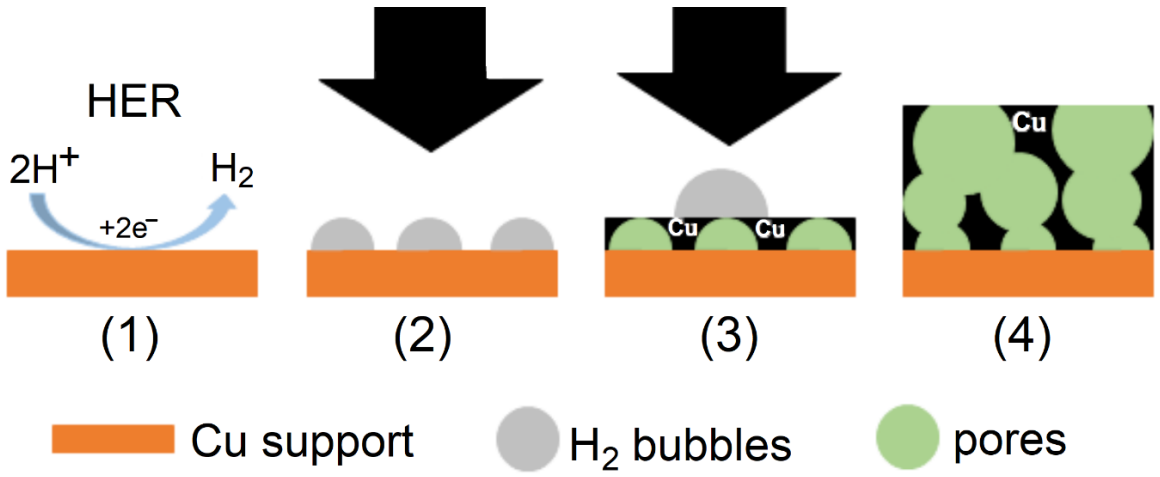


Figure 1. Depiction of the electrodeposition of foam-type materials. In the course of electrochemical metal deposition (black arrows) at high current densities in aqueous media, the Hydrogen Evolution Reaction (HER) takes place on the metallic (Cu) support (1). The surface becomes thus partially covered by H_2 bubbles (2). The H_2 bubbles act as a template for metal deposition (3). As a result a highly porous metal foam emerges (4)

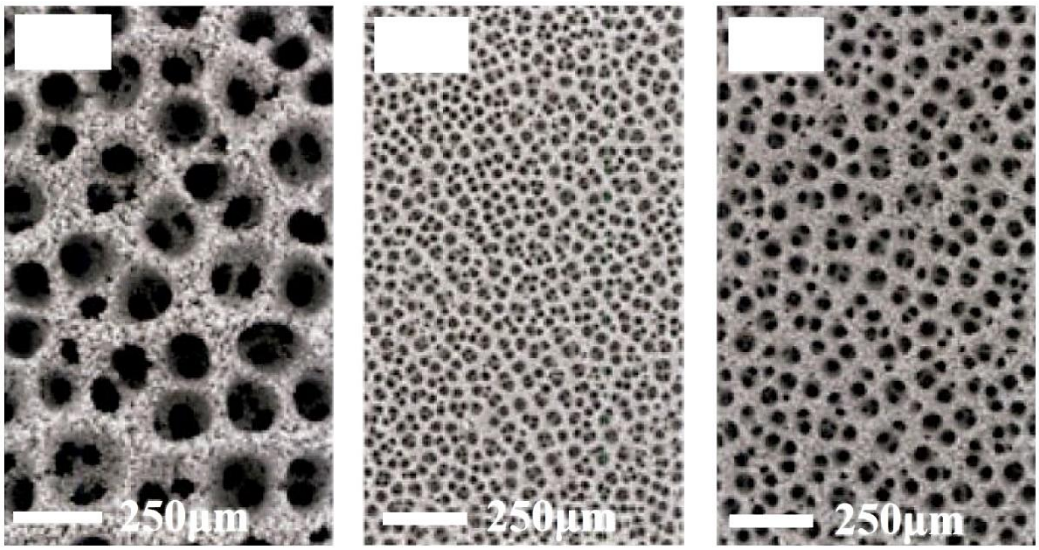


Figure 2. Cu foams obtained by galvanostatic Cu electrodeposition at a current density of $j = -3\ \mathrm{A\,cm^{-2}}$. The deposition was, in each case, interrupted at distinct elapsed duration: 5 s, 20 s and 80 s. The scale bar is the same in all panels

2.4 Considering this mechanism, assign the correct deposition time to the Cu foams shown in **Figure 2** on the answer sheet (white boxes upper left corner).

Bimetallic CuAg systems are excellent catalysts for the electrosynthesis of alcohols from CO_2. 5.4 mg of a bimetallic Cu-Ag foam catalyst (90 wt. % Cu, $M_{Cu} = 63.546\ \mathrm{g\,mol^{-1}}$; 10 wt. % Ag, $M_{Ag} = 107.868\ \mathrm{g\,mol^{-1}}$) was galvanostatically deposited onto a Cu foil (1 $\mathrm{cm^2}$) at a current density of $j = -3\ \mathrm{A\,cm^{-2}}$ applied for 20 s (the minus sign accounts for a reductive/cathodic process).

2.5 Calculate the Faradaic efficiency (FE in %) of this metal deposition process. FE is defined as $(Q_{product}/Q_{total}) \times 100$ %, where Q denotes the charge.

We consider a CO_2 electrolysis experiment carried out in 35 mL CO_2-saturated 0.5 M $KHCO_3$ electrolyte solution over the bimetallic Cu-Ag foam catalyst (90 wt. % Cu; 10 wt. % Ag). The CO_2 electrolysis was carried out at a constant (total) current density of $j(\mathrm{tot}) = -30\ \mathrm{mA\,cm^{-2}}$ for 3600 s (note the current density is normalized to the geometric surface area of 1 $\mathrm{cm^2}$; the minus sign accounts for a reductive/cathodic process). A product analysis, carried out after the electrolysis, revealed mass concentrations of 41.3 $\mathrm{mg\,L^{-1}}$ and 7.4 $\mathrm{mg\,L^{-1}}$ for ethanol and *n*-propanol, respectively. Both alcohols are liquid reaction products and accumulate in the electrolyte in the course of the electrolysis reaction. We assume that gaseous hydrogen (H_2) is formed as the only by-product of the process.

2.6 Calculate the current densities required for the formation of (a) ethanol (M_{EtOH} = 46.08 g mol^{-1}) and (b) *n*-propanol (M_{PrOH} = 60.10 g mol^{-1}) assuming that the current densities do not change with electrolysis time.

2.7 Calculate the volume of the formed hydrogen on the 1 cm^2 catalyst area at 298.15 K and 1 bar, assuming ideal behavior of the formed hydrogen, and its complete release into the gas phase. *If you did not get a result in Task 2.6, continue with FE(EtOH) = 45,1 % and FE(PrOH) = 4.8 %.*

SOLUTION OF THE PROBLEM 2

2.1 (i) Ethanol: $2CO_2 + 12H^+ + 12e^- = C_2H_5OH + 3H_2O$

(ii) Propanol: $3CO_2 + 18H^+ + 18e^- = C_3H_7OH + 5H_2O$

2.2 $2CO_2 + 12H^+ + 12e^- = C_2H_5OH + 3H_2O$ (**R1**) cathode

$H_2 = 2H^+ + 2e^- \times(-6)$

$6H_2 = 12H^+ + 12e^-$ (**R2**) anode

Combining the two half cells we get:

$2CO_2 + 6H_2 = C_2H_5OH + 3H_2O$ (**R3**)

$\Delta_rH_{R3} = -276 + (-3 \times 285.83) - 2 \times (-393.52) = -346.45$ kJ mol^{-1}

$\Delta_rS_{R3} = 3S(H_2O) + S(C_2H_5OH) - 2S(CO_2) - 6S(H_2) = -842$ J K^{-1} mol^{-1}

$\Delta_rG_{R3} = \Delta_rH_{R3} - T\Delta_rS_{R3} = -346.45 \times 10^3$ J mol^{-1} $- 298.15$ K $\times (-842$ J K^{-1} mol$^{-1})$

$\Delta_rG_{R3} = -95.53$ kJ mol^{-1}

$\Delta E_{R3} = -\Delta_rG_{R3}/n_{R3}F = 95\,530$ J mol^{-1}/$(12 \times 96485$ C mol$^{-1})$ $= 0.0825$ V

$\Delta E_{R3} = E_{cathode} - E_{anode}$

$E_{cathode} = \Delta E_{R3} + E_{anode} = 0.0825$ V $+ 0.00$ V $=$ **0.0825 V**

2.3 <u>Anode reaction</u>

Oxidative oxygen evolution reaction (OER): $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

<u>Cathode reactions</u>

Reductive hydrogen evolution reaction (HER): $2H^+ + 2e^- \rightarrow H_2$ (proton reduction)

Metal deposition / reduction of cupric ions: $Cu^{2+} + 2e^- \rightarrow Cu$

2.4 From left to right: 80 s, 5 s, 20 s.

2.5 $m_{Cu\text{-}Ag} = 0.0054$ g $\rightarrow$ $m_{Cu} = 0.00486$ g; $m(Ag) = 0.00054$ g

$n = m/M$ $\rightarrow$ $n_{Cu} = 7.65 \times 10^{-5}$ mol; $n_{Ag} = 5.004 \times 10^{-6}$ mol

$Q_{Cu} = 2 \times 96485$ C mol$^{-1} \times 7.65 \times 10^{-5}$ mol $= 14.7$ C

$Q_{Ag} = 96485$ C mol$^{-1} \times 5.004 \times 10^{-6}$ mol $= 0.48$ C

$Q_{Cu\text{-}Ag} = 14.7$ C $+ 0.48$ C $= 15.18$ C

$Q_{tot} = 20$ s $\times 3$ A $= 60$ C

$FE_{Cu\text{-}Ag} = (Q_{Cu\text{-}Ag}/Q_{tot}) \times 100\ \% = (15.18/60) \times 100\ \% =$ **25.3 %**

2.6 $Q_{area} = 0.03$ A cm$^{-2} \times 3600$ s $= 108$ C cm^{-2}

assuming a geometric surface area of 1 cm^2 $\rightarrow$ $Q_{tot} = 108$ C

c(EtOH) $= 41.3$ mg L$^{-1} = 0.0413$ mg mL^{-1}

m(EtOH) $= 0.0413$ mg mL$^{-1} \times 35$ mL $= 1.446$ mg

n(EtOH) = (1.446 × 10^{-3} g)/(46.08 g mol^{-1}) = 3.14 × 10^{-5} mol

Q(EtOH) = 3.14 × 10^{-5} mol × 12 × 96485 C mol^{-1} = 36.355 C

FE(EtOH) = (36.355/108) × 100 % = 33.6 %

j(EtOH) = 0.336 × (−30 mA cm^{-2}) = **−10.09 mA cm^{-2}**

c(PrOH) = 7.4 mg L^{-1} = 0.0074 mg mL^{-1}

m(PrOH) = 0.0074 mg mL^{-1} × 35 mL = 2.59 × 10^{-4} g

n(PrOH) = (2.59 × 10^{-4} g)/(60.10 g mol^{-1}) = 4.3 × 10^{-6} mol

Q(PrOH) = 4.3 × 10^{-6} mol × 18 × 96485 C mol^{-1}= 7.468 C,

FE(PrOH) = (7.468/108) × 100 % = 6.9 %

j(PrOH) = 0.069 × (−30 mA cm^{-2}) = **−2.07 mA cm^{-2}**

(note the current densities are normalized to geometric surface area of 1 cm^2)

2.7 FE(H_2) = 100 % − (33.6 % + 6.9 %) = 59.5 %

n(H_2) = Q(H_2)/(zF) = FE(H_2)Q_{tot}/(zF) = FE(H_2)jAt/(zF)

n(H_2) = (0.595 × 0.03 A cm^{-2} × 1 cm^2 × 3600 s)/(2 × 96485 C mol^{-1}) = 3.33 × 10^{-4} mol

Ideal behavior of the hydrogen gas: $pV = nRT \rightarrow V = nRT/p$

V(H_2) = (3.33 × 10^{-4} mol × 8.3145 J K^{-1} mol^{-1} × 298.15 K)/(10^5 Pa) = **8.25 mL**

If you used FE(H_2) = 50.1%: n(H_2) = 2.80 × 10^{-4} mol, V(H_2) = **7.00 mL**

THEORETICAL PROBLEM 3

Artificial Photosynthesis

The field of artificial photosynthesis research aims at storing solar energy in chemical bonds. Photons are absorbed by exciting sensitizers, thereby producing a charge-separated state. The excited electron is transferred to a catalyst (hydrogen evolving catalyst, HEC), which is reduced twice and then produces H_2. The photosensitizer or light absorber is often $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), and the HECs are often cobalt complexes.

Energetics of Water Splitting

3.1 Calculate the enthalpy of the reaction $H_2 \rightarrow 2H^+(aq) + 2e^-$.
Solvation enthalpy of proton: $\Delta_{aq}H(H^+) = -1190$ kJ mol^{-1}
Ionization energy of hydrogen: $IE_1 = 13.6$ eV
Dissociation enthalpy of H_2: $\Delta_{diss}H(H_2) = 432$ kJ mol^{-1}

Ideally, electrochemical water splitting into O_2 and H_2 runs at 1.23 V. Since $T\Delta S$ for this process is positive, heat from the environment is needed. If additional voltage produces the heat required to compensate the decrease in temperature the process is called **thermoneutral**. The enthalpy of H_2O formation, $\Delta_f H^\ominus(H_2O)$, is −285 kJ mol^{-1}.

3.2 Calculate (a) the water splitting reaction entropy $\Delta_r S^\ominus$ at 25 °C of 1 mol of H_2O and (b) the voltage at which water splitting is thermoneutral.

Catalysts

Cobalt–salen (salcomin) type complexes are potential catalysts for H_2 formation from protons and electrons. The structure of salcomin is given below:

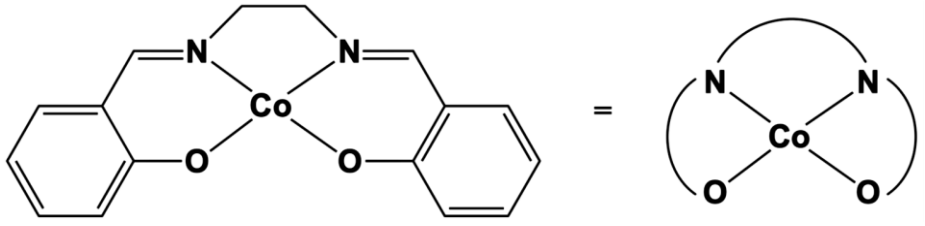


Figure 1. The structure of salcomin

3.3 Determine the oxidation state of the cobalt atom in salcomin. Determine the geometric structure around the cobalt center of salcomin, choosing from these three possibilities: tetrahedral, square planar or octahedral.

In solution, salcomin can bind O_2; that links two salcomin moieties by coordinating to the two Co centers. The oxidation state of both Co centers is then +III.

3.4 Draw the resulting structure.

The H_2 formation takes place exclusively at the cobalt center. The reaction is described by a 4-step catalytic cycle starting with Co^{2+} using 2 H^+ and 2 electrons. During one step a hydride is formed by an intramolecular electron transfer.

3.5 Write down two possible variations of the catalytic cycle with charges of the complex and oxidations states of the Co center. The oxidation state on the Co center should not be larger than +III. Mark the hydride formation step with an asterisk and label H^+ uptake with **C** (chemical reaction), and electron uptake with **E** (electrochemical reaction), see example cycle in **Figure 2** below. [Co^{II}] stands for the Cobalt–salen complex.

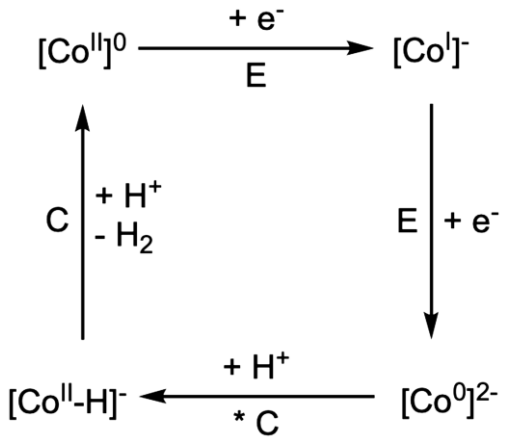


Figure 2. An example cycle for task 3.5

3.6 Using the redox potential values of different cobalt complexes given in Table 1, write down which complex is suitable for a) water oxidation at neutral pH b) water reduction at neutral pH. Write down the corresponding overall reaction for both processes (only for the complexes, capable of performing it) and calculate the cell potentials at neutral pH. The half-cell potential for the proton reduction at pH = 7, T = 298 K is −0.41 V.

Co(III/II) redox couple	$E^{\ominus}$ vs. normal hydrogen electrode
$[Co(H_2O)_6]^{3+/2+}$	+1.92 V
$[Co(C_2O_4)_3]^{3-/4-}$	+0.55 V
$[Co(EDTA)]^{1-/2-}$	+0.38 V
$[Co(NH_3)_6]^{3+/2+}$	+0.06 V
$[Co(en)_3]^{3+/2+}$	−0.18 V
$[Co(CN)_5]^{2-/3-}$	−0.60 V

Table 1. Possible redox couples for task 3.6; $[C_2O_4]^{2-}$ = oxalate, en = 1,2-ethylendiamine.

A Glimpse at the Natural Process

The natural storage of biological H_2 equivalents is NADPH, which is produced from $NADP^+$ through the addition of a hydride ion. The structure of NADPH is shown in **Figure 3**.

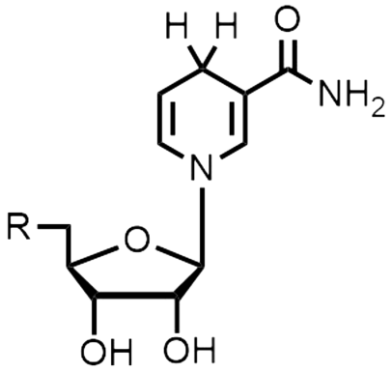


Figure 3. The structure of NADPH

3.7 Draw the structure of $NADP^+$.

Chlorophyll has an extinction coefficient of about $\varepsilon = 8 \times 10^4\ M^{-1}\ cm^{-1}$ at 680 nm.

3.8 Assuming an efficiency (photon to hydrogen atom) of ϕ = 20 % at a 680 nm photon flux of 100 nE s^{-1} cm^{-2} (1 E = 1 mol of photons), calculate a) the number of photons per second and b) the concentration of chlorophyll in a 1×1×1 cm^3 cell needed to get a turnover frequency of 1 nmol (H_2) s^{-1}.

———————————

SOLUTION OF THE PROBLEM 3

3.1 $\Delta_r H^\ominus = \Delta_{diss}H(H_2) + 2IE_1 + 2\Delta_{aq}H(H^+) = 432 + 2625 - 2380 = 677\ kJ\ mol^{-1}$

3.2 $E^\ominus = -1.23\ V \rightarrow \Delta_r G^\ominus = +237\ kJ\ mol^{-1}$ [$= -\Delta_f G^\ominus(H_2O)$]

$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

$-T\Delta_r S^\ominus$ equals the lost heat that must be compensated

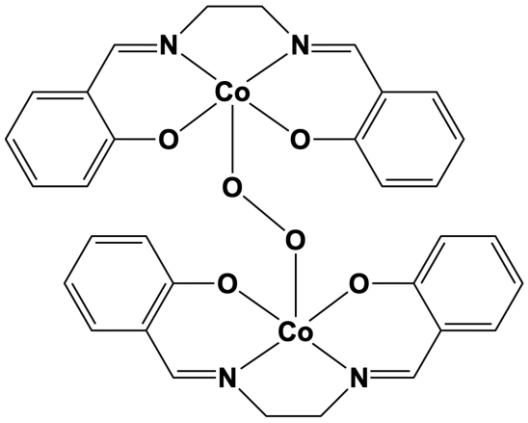
$-T\Delta_r S^\ominus = (237 - 285)\ kJ\ mol^{-1} = -48\ kJ\ mol^{-1}$ and $\Delta_r S^\ominus =$ **161 J mol^{-1} K^{-1}**

$$\frac{48000\ J\ mol^{-1}}{2 \times 96485\ C\ mol^{-1}} = 0.25\ V$$

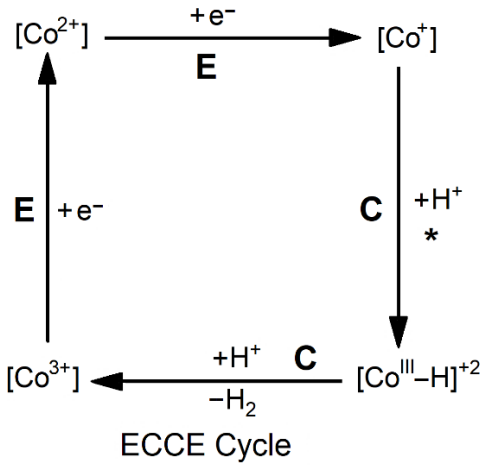
To be thermoneutral, the cell voltage needs to be 1.23 V + 0.25 V = **1.48 V** which corresponds to $\Delta_r H^\ominus$.

3.3 Oxidation number: +II. Geometry: square planar (the ligand is a conjugated system)

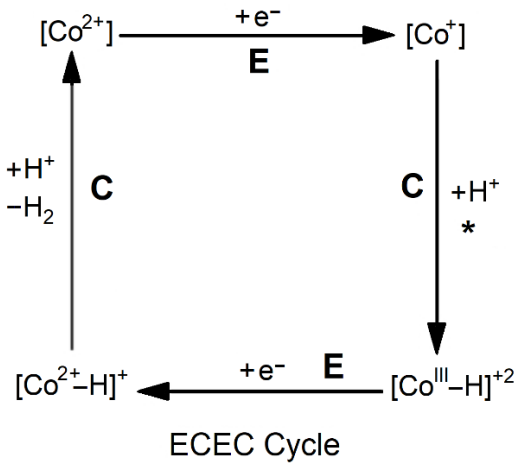
3.4



3.5



ECCE Cycle



ECEC Cycle

3.6 $H_2O \rightarrow ½\ O_2 + 2H^+ + 2e^-$ $E^\ominus(ox) = 1.23$ V (standard conditions)

This potential is pH dependent. According to Nernst, the reduction potential E(ox) at pH = 7 is thus 1.23 V − 0.41 V = +0.817 V.

(a) To be able to oxidize water, the reduction potential must be larger than +0.817 V at pH = 7, which means that only **$[Co(H_2O)_6]^{3+/2+}$** couple is able to do this reaction.

Redox couple for water oxidation:

$[Co(H_2O)_6]^{3+} + e^- \rightarrow [Co(H_2O)_6]^{2+}$ $\quad E^\ominus(red) = +1.92$ V

$H_2O \rightarrow ½\ O_2 + 2H^+ + 2e^-$ $\quad E(ox) = +0.817$ V (pH = 7)

Overall reaction:

$2[Co(H_2O)_6]^{3+} + H_2O \rightarrow 2[Co(H_2O)_6]^{2+} + ½\ O_2 + 2H^+$, E = +1.1 V

(b) The reduction potential for the reduction of water at pH = 7 is −0.41 V. The $E^\ominus$(red) of the redox couple must be smaller than −0.41 V. Only the **$[Co(CN)_5]^{2-/3-}$** couple is able to do this reaction.

Redox couple for water reduction:

$[Co(CN)_5]^{3-} \rightarrow [Co(CN)_5]^{2-} + e^-$ $\quad E^\ominus(ox) = -0.60$ V

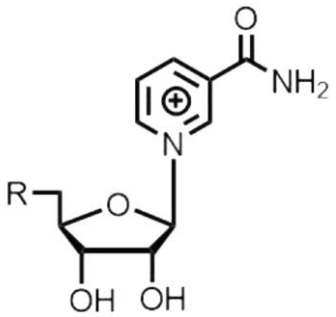
$H_2O + 2e^- \rightarrow H_2 + \text{“}O^{2-}\text{”}$ $\quad E^\ominus(red) = -0.41$ V

(or $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$)

Overall reaction:

$2[Co(CN)_5]^{3-} + H_2O \rightarrow 2[Co(CN)_5]^{2-} + H_2 + \text{“}O^{2-}\text{”}$, E = +0.19 V (pH = 7)

3.7



3.8 1 nmol H_2 per second corresponds to 2 nmol H per second. This corresponds to 1.2×10^{15} H atoms per second. Taking the efficiency into account, this would require 6×10^{15} H photons per second. The Lambert–Beer law states $A = \log(I_0/I) = \varepsilon\, c\, d$. With $I_0 = 6 \times 10^{16}$ photons s^{-1} and $I = (6 \times 10^{16} - 6 \times 10^{15})$ photons s^{-1}:

$A = \log(6 \times 10^{16}/(6 \times 10^{16} - 6 \times 10^{15})) = 0.046$. Hence:

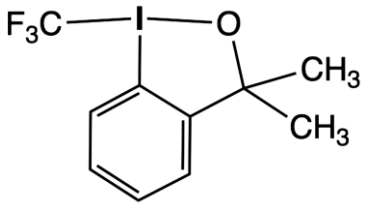
$\varepsilon\, c\, d = 0.046 \rightarrow c = 0.046/(8 \times 10^4\ M^{-1}\, cm^{-1} \times 1\ cm) =$ **5.7×10^{-7} M**

THEORETICAL PROBLEM 4

Fluorinated and Hypervalent Compounds

Fluorine forms stable and isolable compounds with essentially all elements, including the noble gases Kr and Xe. Fluorine-containing molecules often feature uncommon structures. Thus, fluorine is frequently involved in the formation of compounds with elements of groups 14–18, which are defined as hypervalent. The synthesis of fluorinated organic compounds is nowadays heavily based on the availability of specifically designed reagents, compound **4** below being an example.

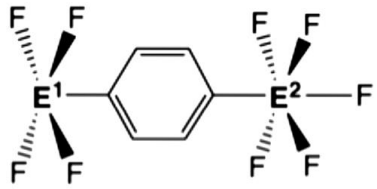
Hint: Any element E in the series ***E*^{1}–*E*^{8}** *may be represented more than once.*



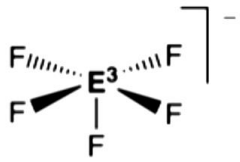
4

Part I. Molecular geometry

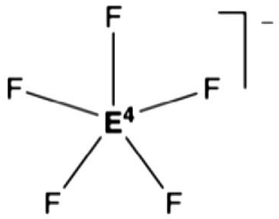
4.1 Identify elements **E^{1}**, **E^{2}**, **E^{3}**, and **E^{4}** in the three species **1**, **[2]$^{-}$**, and **[3]$^{-}$**.



1



[2]$^{-}$



[3]$^{-}$

1: neutral, non-zwitterionic molecule, **E^{1}** square pyramidal, **E^{2}** octahedral, average *d*(E^{1}–F) = 1.91 Å; average *d*(E^{2}–F) = 1.58 Å

[2]$^{-}$: anion, square pyramidal, average *d*(E^{3}–F) = 1.96 Å

[3]$^{-}$: anion, pentagonal planar, *d*(E^{4}–F) = 1.98 Å

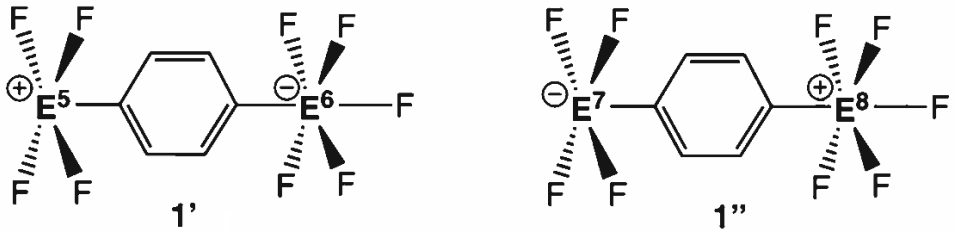
Hints:

1. *The molecular geometries refer to the arrangement of atoms bonding to E^{1}–E^{4}*
2. *The elemental analysis of **1** gives a carbon content of 17.75 % wt.*

Group 15	Group 16	Group 17	Group 18
d(P–F) = 1.50–1.68 Å	*d*(S–F) = 1.52–1.60 Å	*d*(Cl–F) = 1.63–1.85 Å	
d(As–F) = 1.68–1.72 Å	*d*(Se–F) = 1.75–1.80 Å	*d*(Br–F) = 1.77–1.97 Å	*d*(Kr–F) = 1.77–1.89 Å
d(Sb–F) = 1.85–2.05 Å	*d*(Te–F) = 1.80–2.00 Å	*d*(I–F) = 1.90–2.00 Å	*d*(Xe–F) = 1.77–2.00 Å

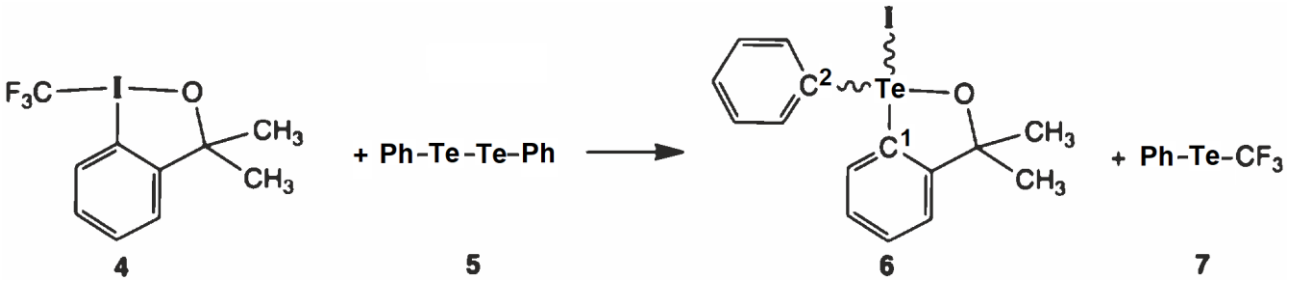
Table 1. Typical E–F bond distance ranges for a selection of elements in groups 15–18

4.2 Choose which elements $\mathbf{E^5/E^6}$ and $\mathbf{E^7/E^8}$, respectively, would display the given geometry, including E–F bond distances close to those in **1** (see Table 1).



Part II. Reactivity and structure

Consider the reaction shown below:



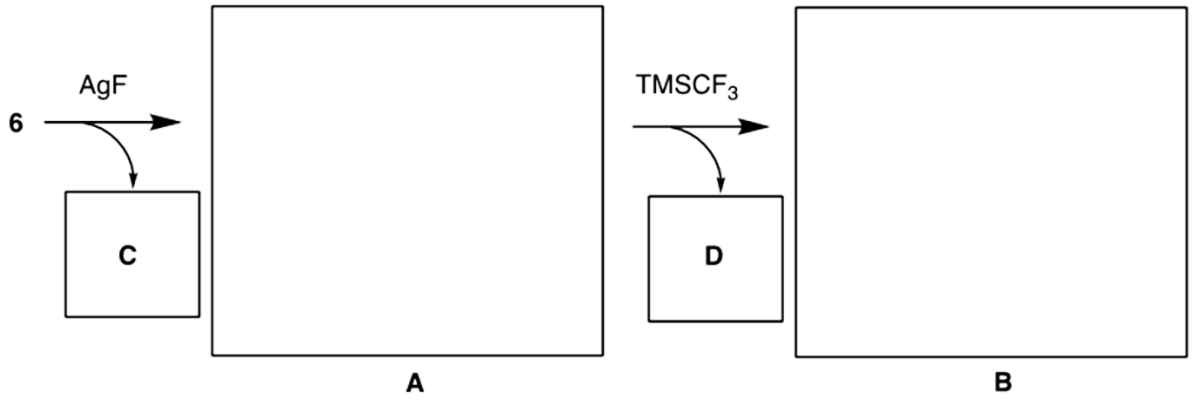
4.3 Choose the ideal geometry of compound 6 in terms of the arrangement of the valence-shell electron-pair domains around the Te atom:

- square planar
- square pyramidal
- trigonal bipyramidal
- tetrahedral
- octahedral

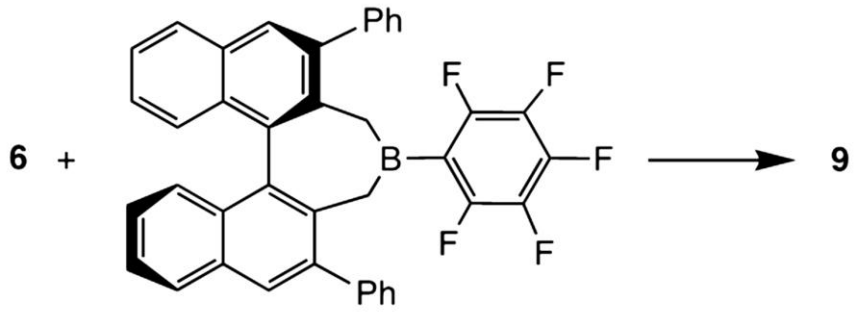
Provide the expected ideal bond angles C^1−Te−I, C^2−Te−I, I−Te−O, and C^1−Te−C^2.

4.4 Write the number ^{1}H-NMR signals you expect for the two methyl groups in compounds **4** and **6**, respectively.

4.5 Compound **6** reacts consecutively with AgF and $(H_3C)_3SiCF_3$ ($TMSCF_3$). Formulate the Te-containing intermediate **A** and final product **B**, including their correct geometry, as well as the byproducts **C** and **D**. Draw **A** and **B** and write the by-products **C** and **D**. *Hint: molecular weight of **D** is 92.08 g mol^{-1}.*



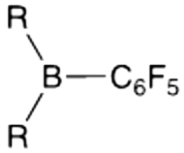
Assume that compound **6** reacts with a sterically bulky, chiral, enantiomerically pure Lewis acid, such as the known boron derivative **8**, as shown below. This reaction should lead to the formation of a new product **9**, the composition of which corresponds to the sum of **6** and **8**. Further assume that **9** is a salt, in which the cation derives from **6** and the anion from **8**.



8

4.6 Draw the structure of both the Te-containing cation and the boron-containing anion and choose the ideal geometry of the cation in terms of the arrangement of the valence-shell electron-pair domains around the Te atom.

*Hint: For **8** (chiral, enantiomerically pure) use the following schematic representation:*



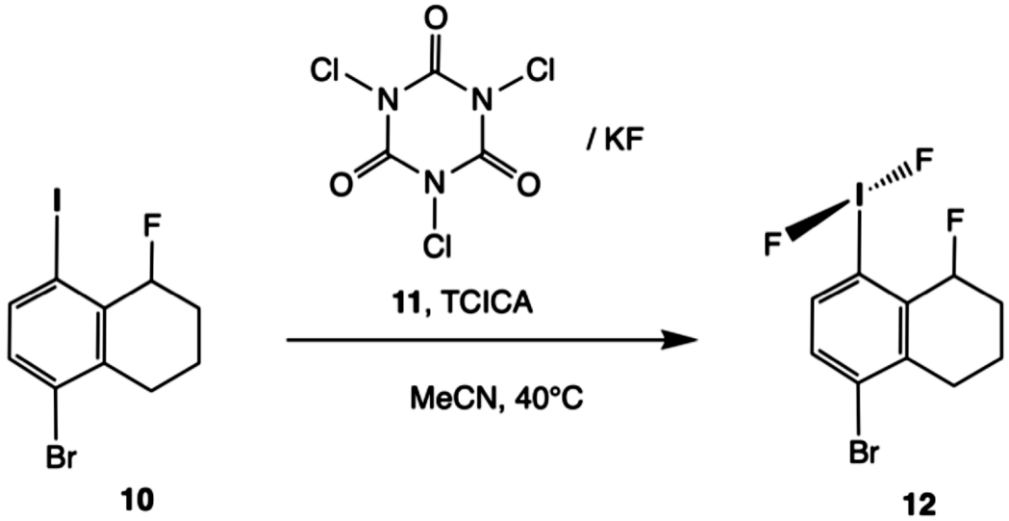
Choose the ideal molecular geometry of the cation:

- square-planar
- trigonal-planar
- trigonal-pyramidal
- trigonal-bipyramidal
- tetrahedral

4.7 State the number of possible stereochemically different salts **9**.

Part III. Synthesis of a λ³-difluoroiodane and rotation around a single bond

Compound **10** is prepared from starting material 8 by oxidation with trichloroisocyanuric acid (TCICA, **9**) in the presence of excess KF in dry acetonitrile as shown below.

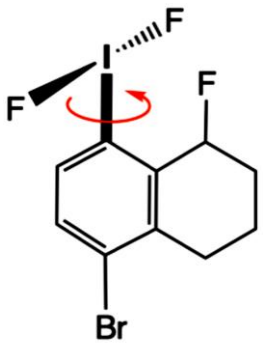


10 **12**

4.8 Write balanced half-cell reactions and a balanced overall reaction for this process.

*Hint: Abbreviate **10** as R–I, **11** as R–IF₂, and TCICA as $C_3Cl_3N_3O_3$. The six-membered ring of TCICA stays intact upon reduction.*

The IF_2 group in **12** can rotate around the I−C bond (imagine a molecular propeller). The corresponding rotation barrier has been measured experimentally, E_a = 30 kJ mol^{-1}. Furthermore, the rate constant for the rotation is k = 2500 s^{-1} at 228 K.



12

4.9 Determine how fast the IF_2 group can in principle rotate at room temperature (298 K). Consider this process as if it were a chemical reaction for which you are determining the rate constant. Write your answer on the answer sheet. The unit of the constant should be given in s^{-1}.

SOLUTION OF THE PROBLEM 4

4.1 E^1 = I, E^2 = S, E^3 = Te, E^4 = Xe.

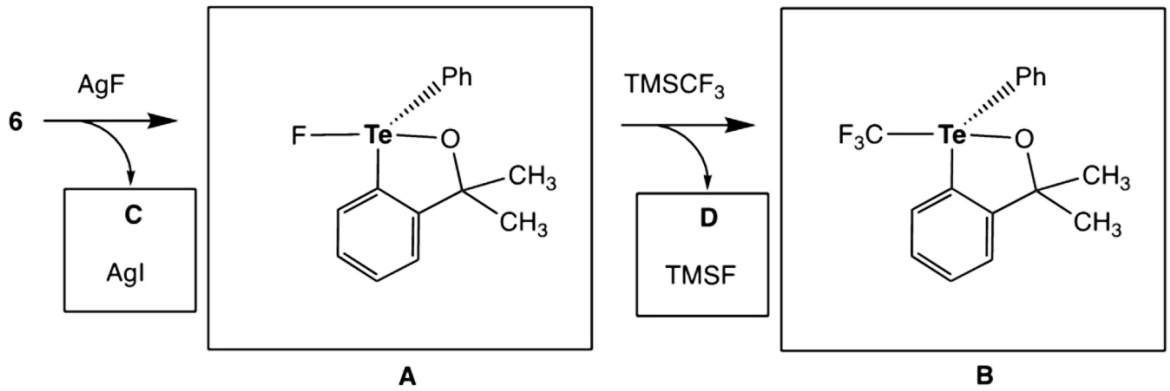
4.2 E^5 = Xe, E^6 = P, E^7 = Te, E^8 = Cl.

4.3 Trigonal bipyramidal.

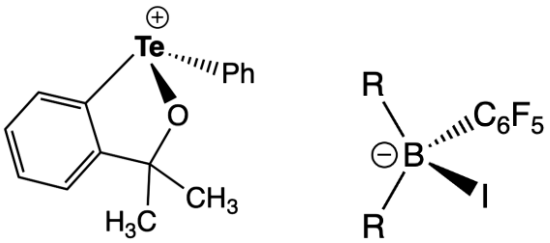
Angles: C^1−Te−I = 90°, C^2−Te−I= 90°, I−Te−O = 180°, C^1−Te−C^2 = 120°.

4.4 **4**: 1 signal; **6**: 2 signals

4.5



4.6 Cation: Anion:



Geometry: tetrahedral.

4.7 Two.

4.8 Oxidation: $R{-}I + 2\ F^- \rightarrow R{-}IF_2 + 2\ e^-$ (×3)

Reduction: $C_3Cl_3N_3O_3 + 6\ e^- = [C_3N_3O_3]^{3-} + 3\ Cl^-$

Overall reaction: $3\ R{-}I + 6\ F^- + C_3Cl_3N_3O_3 \rightarrow 3\ R{-}IF_2 + [C_3N_3O_3]^{3-} + 3\ Cl^-$

or $3\ R{-}I + 6\ KF + C_3Cl_3N_3O_3 \rightarrow 3\ R{-}IF_2 + [C_3N_3O_3]^{3-} + 3\ KCl$

Redox reactions involving one or two Cl per TCICA instead of three can also be considered correct.

For the reduction reaction, two consecutive two-electron reductions of TCICA (leading to the same product $K_3C_3N_3O_3$) are also considered correct.

4.9 Using the Arrheius equation:

$\ln k_1 = -E_a/RT_1 + \ln A$ and $\ln k_2 = -E_a/RT_2$

$\ln k_1 - \ln k_2 = (E_a/R)(1/T_2 - 1/T_1)$

$\ln k_2 = \ln k_1 - (E_a/R)(1/T_2 - 1/T_1)$

Here, $k_1 = 2500\ s^{-1}$, $T_1 = 228\ K$, $T_2 = 298\ K$, and $E_a = 30\ kJ\ mol^{-1}$. Thus:

$\ln k_2 = \ln 2500 - (30000/8.314)(1/298 - 1/228) = 11.542$

$k_2 = \mathbf{1.03 \times 10^5\ s^{-1}}$

THEORETICAL PROBLEM 5

Hydrodesulfurization

The production of sulfur-free fuels is the general trend towards lowering the emission of sulfur-containing compounds that are toxic to the environment. To remove sulfur, the hydrogen-assisted hydrodesulfurization process is used at the refineries.

5.1 Draw the structure of products **A** to **E** of thiophene hydrodesulfurization, knowing that **A** and **B** are cyclic regioisomers and **C** is cyclic.

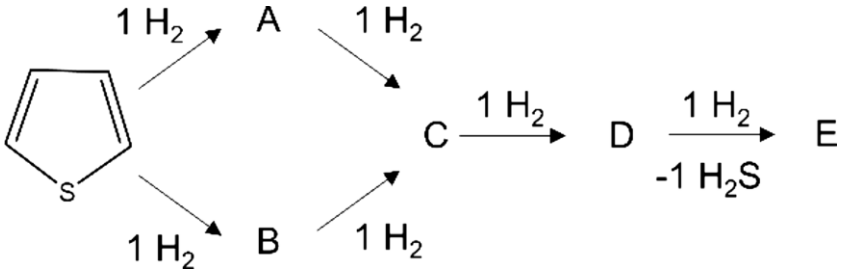


Figure 1. Thiophene hydrodesulfurization process

Sulfur has two most common natural stable isotopes, ^{32}S and ^{34}S, with a relative molar abundance of $x(^{32}S) = 94.8\,\%$ and $x(^{34}S) = 4.37\,\%$, respectively. For hydrogen, the stable natural isotopes are ^{1}H and ^{2}H (D), with a relative molar abundance of $x(^{1}H) = 99.986\,\%$ and $x(^{2}H) = 0.014\,\%$, respectively.

5.2 Considering only the isotopes listed above, list all isotopologues of H_2S.

5.3 Considering only the isotopes listed above, list all isotopologues of H_2S containing simultaneously D and ^{34}S nuclei and for each calculate the respective relative molar abundance in %.

The desulfurization is a catalytic process typically carried out over MoS_2 supported on SiO_2 (MoS_2/SiO_2) catalyst. To study the surface of the catalyst, isotope exchange methods can be employed. The isotope exchange reaction takes place at the gas-solid interface, resulting in the exchange of the surface atoms exclusively. In the first approximation, the bulk atoms do not participate in the exchange (**Figure 2**).

In the experiment, the isotope exchange between the MoS_2/SiO_2 catalyst (Mo mass fraction $w_{Mo} = 4.280\,\%$, initially containing only ^{32}S) and gaseous isotopically-labeled $H_2{}^{34}S$

was studied in a flow reactor (**Figure 2**). The MoS_2/SiO_2 catalyst (m_{cat} = 1.2350 g) was kept in a flow (p = 1.00 bar, v = 20.0 mL min^{-1}, T = 23.0 °C) of gas mixture containing $H_2{}^{34}S$ balanced with Ar (volume fraction $\varphi(H_2{}^{34}S)$ = 1.00 %, ^{34}S isotopic purity α = 99.95 mol. %). The experiment duration was t = 10.0 min and gas from the outlet was collected during the entire experiment. The measured fraction of ^{34}S isotope among the sulfur atoms (γ) in the collected gas phase was γ = 87.3 mol. %. Assume ideal gas behavior, and that the elemental (not isotopic!) composition of MoS_2 on the surface and in the bulk are identical, and by the end of the experiment all sulfur atoms from the surface are exchanged with the gas phase.

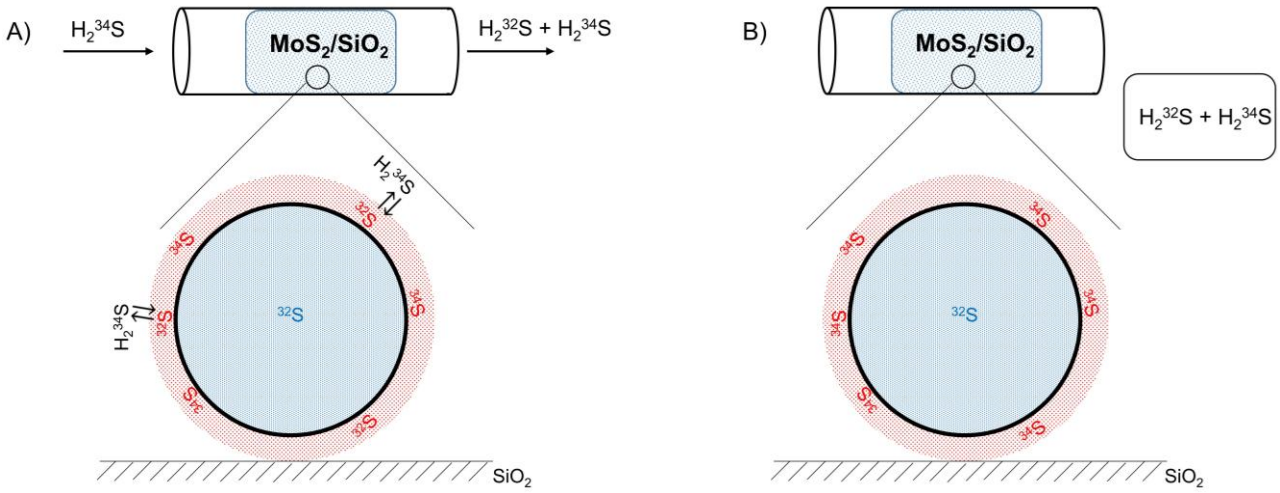


Figure 2. Schematic representation of the experiment in the course (A) and at the final stage (B). Sulfur atoms on the surface are shown in red, sulfur atoms in the bulk are shown in blue. Molybdenum atoms are not shown.

5.4 Calculate the amount of exchanged sulfur atoms $n(S)_{surface}$ in mol.

If you have been unable to calculate the amount of exchanged sulfur atoms, use the value 1.53 × 10^{-5} mol in all the following calculations.

Assume that the MoS_2 phase consists of uniform spherical particles, and at the end of the experiment all sulfur atoms located on the surface are exchanged, while the bulk atoms did not participate in the exchange reaction. The density of MoS_2 is ρ = 5.06 g cm^{-3}, the average area occupied by S and Mo atoms on the surface is equal to A_S = 3.00 × 10^{-19} m^2 and A_{Mo} = 5.00 × 10^{-19} m^2, respectively. The area of a sphere with radius R can be calculated as $S = 4\pi R^2$, and its volume as $V = (4/3)\pi R^3$. Assume that isotopic composition does not affect the density of MoS_2.

5.5 Calculate the particle radius R of the MoS_2 particles. Give your answer in nm.

In reality, the isotopically-labeled atoms from the surface diffuse into the bulk and the non-labeled atoms from the bulk travel to the surface, undergoing a gradual exchange (**Figure 3A**). Therefore, for a given moment, the fraction of the labeled atoms inside the particle decreases from the surface of the particle to its center. Simultaneously, with an increase in time of exchange, the involvement of bulk atoms to the exchange reaction increases, as sketched in **Figure 3B**.

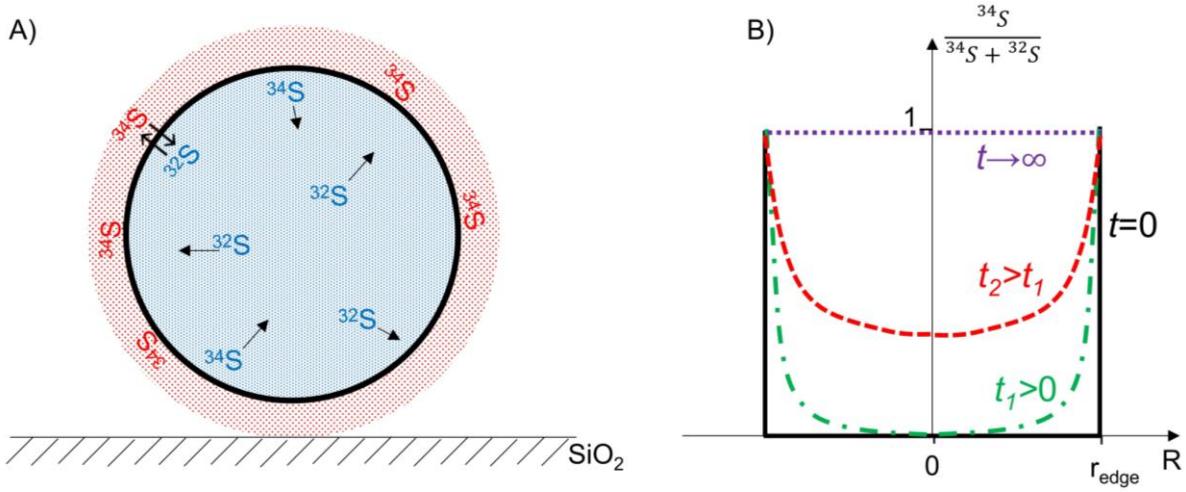


Figure 3. A) Schematic representation of the diffusion of sulfur isotopes from the surface to the bulk in a MoS_2 particle. Sulfur atoms on the surface are shown in red, sulfur atoms in the bulk are shown in blue. Molybdenum atoms are not shown. **B**) The fraction of ^{34}S atoms in the bulk as function of time and distance from center of the particle; r_{edge} corresponds to the radius of MoS_2 particle.

At the end of the experiment, the surface atoms are completely exchanged, and additionally a fraction of the bulk is exchanged via diffusion. The fraction of the exchanged bulk atoms, $n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{bulk}}$, of the total bulk atoms of sulfur, $n(\mathrm{S})^{\mathrm{total}}_{\mathrm{bulk}}$, can be calculated as:

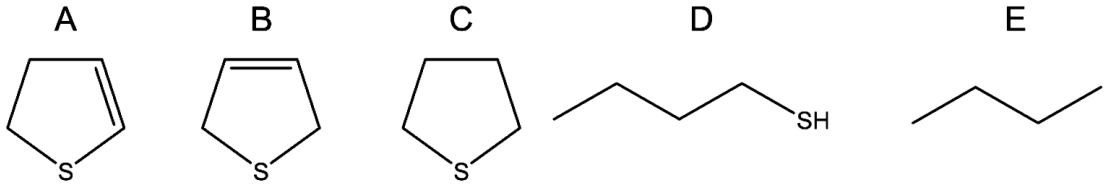
$$F = n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{bulk}} / n(\mathrm{S})^{\mathrm{total}}_{\mathrm{bulk}} = 1 - \exp(-Dt/R^2)$$

Where t is the time of exchange experiment (described above), R is the particle radius, and D is the diffusion coefficient. The catalyst described above was independently studied by means of electron microscopy, which showed that the MoS_2 particles are uniformly distributed spheres with a radius of 35.0 nm.

5.6 Using $R = 35.0$ nm and the data of the exchange experiment described above, calculate the diffusion coefficient D (in $m^2\,s^{-1}$) for the diffusion of sulfur atoms in MoS_2. In your calculations, use the approximation $e^x \approx 1 + x$ for $x \ll 1$.

SOLUTION OF THE PROBLEM 5

5.1



5.2 $^{1}H_2{}^{32}S$, $^{1}H_2{}^{34}S$, $^{1}H^{2}H^{32}S$, $^{1}H^{2}H^{34}S$, $^{2}H_2{}^{32}S$, $^{2}H_2{}^{34}S$.

5.3 $x(D_2{}^{34}S) = (0.00014)^2 \times 0.0437 = 8.57 \times 10^{-10} = 8.57 \times 10^{-8}$ %

$x(^{1}HD^{34}S) = 2 \times 0.00014 \times 0.99986 \times 0.0437 = 1.22 \times 10^{-5} = 1.22 \times 10^{-3}$ %

5.4 All exchanged sulfur atoms are ^{32}S atoms which were initially on the catalyst surface and at the end of experiment appeared in the gas phase. The volume of $H_2{}^{32}S$ can be calculated as difference between volume of $H_2{}^{34}S$ supplied and collected. The volume of supplied $H_2{}^{34}S$ can be calculated as:

$$V(H_2{}^{34}S)_{\text{supplied}} = v\,t\,\varphi(H_2{}^{34}S)\,\alpha = 20\text{ mL min}^{-1} \times 10\text{ min} \times 0.01 \times 0.9995 = 2.00\text{ mL}$$

Applying the same formula, the volume of collected $H_2{}^{34}S$ can be calculated as:

$$V(H_2{}^{34}S)_{\text{collected}} = v\,t\,\varphi(H_2{}^{34}S)\,\gamma = 20\text{ mL min}^{-1} \times 10\text{ min} \times 0.01 \times 0.873 = 1.75\text{ mL}$$

The volume of $H_2{}^{32}S$ with ^{32}S atoms from the catalyst is the difference between the volume of supplied and collected H_2:

$$V(H_2{}^{32}S) = V(H_2{}^{34}S)_{\text{supplied}} - V(H_2{}^{34}S)_{\text{collected}} = 0.25\text{ mL}$$

The number of exchanged sulfur atoms can be calculated from the ideal gas law:

$$n(S)_{\text{surface}} = n(H_2{}^{32}S) = \frac{pV}{RT} = \frac{10^5\text{ Pa} \times 0.25 \times 10^{-6}\text{m}^3}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 296.15\text{ K}} = \mathbf{1.02 \times 10^{-5}\text{ mol}}$$

5.5 Let N be the total number of MoS_2 spherical particles and R be the radius of each sphere. The total volume of all spheres is equal to the total volume of the MoS_2:

$$V_{MoS_2} = \frac{4}{3}\pi R^3 N = \frac{m_{MoS_2}}{\rho_{MoS_2}} = \frac{\frac{m_{cat} w_{Mo}}{M_{Mo}} M_{MoS_2}}{\rho_{MoS_2}} = \frac{\frac{1.235\text{ g} \times 0.0428}{95.95\text{ g mol}^{-1}} \times 160.07\text{g mol}^{-1}}{5.06 \times 10^6\text{ g m}^{-3}}$$

$$= 1.74 \times 10^{-8}\text{ m}^3$$

The total number of sulfur atoms on the surface of all spheres is equal to the total number of exchanged sulfur atoms. Considering only ½ of each MoS_2 unit is exposed on the surface, the total area of all MoS_2 spheres can be calculated as:

$$A_{MoS_2} = 4\pi R^2 N = n(S)_{surface} N_A \frac{2A_S + A_{Mo}}{2}$$

$$= 1.02\times10^{-5}\,\text{mol} \times 6.022\times10^{23}\,\text{mol}^{-1} \times \frac{(2\times3.00 + 5.00)\times10^{-19}\ \text{m}^2}{2}$$

$$= 3.38\ \text{m}^2$$

Radius can be calculated from the ratio of the total volume to the total surface area:

$$\frac{V_{MoS_2}}{A_{MoS_2}} = \frac{R}{3} = \frac{1.74\times10^{-8}\ \text{m}^3}{3.38\,\text{m}^2} = 5.5\times10^{-9}\ \text{m}$$

$$R = 3\times5.5\times10^{-9}\ \text{m} = \mathbf{15.5\ nm}$$

5.6 The number of spherical particles N with R = 35 nm can be calculated from the total volume of the MoS_2 phase divided by the volume of one sphere:

$$N = \frac{V_{MoS_2}}{\frac{4}{3}\pi R^3} = \frac{1.74\times10^{-8}\ \text{m}^3}{\frac{4}{3}\pi\times(3.50\times10^{-8}\ \text{m})^3} = 9.69\times10^{13}$$

The total surface area A_{MoS_2} of all spheres with a radius R = 35.0 nm:

$$A_{MoS_2} = 4\pi R^2 N = 4\pi\times(35\times10^{-9}\text{m})^2\times9.69\times10^{13} = 1.49\,\text{m}^2$$

The amount of sulfur on the surface, $n(S)_{surface(35nm)}$ of spheres can be calculated as:

$$n(S)_{surface(35nm)} = \frac{A_{MoS_2}}{\frac{2A_S + A_{Mo}}{2}} \frac{1}{N_A} = \frac{1.49\,\text{m}^2}{\frac{(2\times3.00 + 5.00)\times10^{-19}\ \text{m}^2}{2}} \frac{1}{6.022\times10^{23}\,\text{mol}^{-1}}$$

$$= 4.50\times10^{-6}\ \text{mol}$$

The total sulfur amount $n(S)_{total}$ can be calculated as:

$$n(S)_{total} = 2n_{Mo} = 2\frac{m_{cat}w_{Mo}}{M_{Mo}} = \frac{1.235\,\text{g}\times0.0428}{95.95\,\text{g mol}^{-1}} = 1.1\times10^{-3}\ \text{mol}$$

The amount of sulfur in the bulk can be calculated as the difference between the total amount of sulfur and the amount of sulfur on the surface:

$$n(S)^{total}_{bulk} = n(S)_{total} - n(S)_{surface(35nm)}$$

The amount of sulfur from the bulk that participated in the exchanged $n(S)^{ex}_{bulk}$ can be calculated as the difference between the total exchanged amount $n(S)^{ex}_{total}$ and the amount of sulfur on the surface $n(S)_{surface(35nm)}$ (all surface atoms were exchanged):

$$n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{bulk}} = n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{total}} - n(\mathrm{S})_{\mathrm{surface(35nm)}}$$

The fraction F of the exchanged bulk atoms from the total bulk atoms of sulfur can be calculated as:

$$F = \frac{n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{bulk}}}{n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{total}}} = \frac{n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{total}} - n(\mathrm{S})_{\mathrm{surface(35nm)}}}{n(\mathrm{S})_{\mathrm{total}} - n(\mathrm{S})_{\mathrm{surface(35nm)}}} = \frac{1.02\times10^{-5} - 4.5\times10^{-6}}{1.1\times10^{-3} - 4.5\times10^{-6}} = 5.2\times10^{-3}$$

$F \ll 1$ indicates that the given approximation is valid:

$$F = 1 - e^{-Dt/R^2} = 1 - (1 - Dt/R^2) = Dt/R^2$$

$$D = \frac{FR^2}{t} = \frac{5.2\times10^{-3}\times(35\times10^{-9}\mathrm{m})^2}{600\ \mathrm{s}} = \mathbf{1.1\times10^{-20}\ m^2 s^{-1}}$$

Calculations using 1.53×10^{-5} mol for $n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{total}}$:

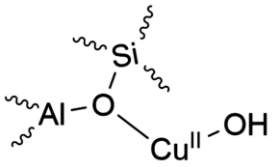
$$F = \frac{n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{bulk}}}{n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{total}}} = \frac{n(\mathrm{S})^{\mathrm{ex}}_{\mathrm{total}} - n(\mathrm{S})_{\mathrm{surface(35nm)}}}{n(\mathrm{S})_{\mathrm{total}} - n(\mathrm{S})_{\mathrm{surface(35nm)}}} = \frac{1.53\times10^{-5} - 4.5\times10^{-6}}{1.1\times10^{-3} - 4.5\times10^{-6}} = 9.86\times10^{-3}$$

$$D = \frac{FR^2}{t} = \frac{9.86\times10^{-3}\times(35\times10^{-9}\mathrm{m})^2}{600\ \mathrm{s}} = 2.0\times10^{-20}\ \mathrm{m^2 s^{-1}}$$

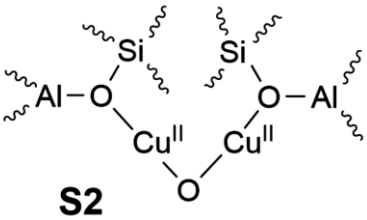
THEORETICAL PROBLEM 6

Direct conversion of methane to methanol

Methane is widely available as natural gas making it an attractive feedstock for the chemical industry, such as for the production of methanol. However, control of this process is challenging as methanol is more easily oxidized than methane. Overoxidation is avoided in a chemical looping process, where active sites of copper-exchanged zeolite catalysts provide only the single oxygen atom required for oxidation to methanol and are consumed. In a second step, the catalyst is regenerated with oxygen in the absence of methane. The scheme below shows two potential catalytic copper sites. During the reaction, Cu(II) is reduced to Cu(I).



S1



S2

6.1 Give the number of **S1** sites and the number of **S2** sites required to oxidize one methane molecule to methanol.

In the absence of oxygen, the methanol formed does not desorb from zeolite. If the reaction is performed in a container with constant volume and temperature (an autoclave), a pressure-drop results only from the consumption of methane, which can be considered as an ideal gas. In a 1 L autoclave containing 200 mg of zeolite loaded with 4.3 % wt. copper, the initial methane pressure p_0 = 933 Pa dropped to p_∞ = 925 Pa after completion of the reaction at 528 K.

6.2 Calculate the percentage of copper that reacted.

6.3 Experimental data are plotted in **Figure 1**. Based on this, decide on the (pseudo) order of the oxidation of CH_4.

(a) The reaction is of (pseudo) zeroth order.

(b) The reaction is of (pseudo) first order.

(c) The reaction is of (pseudo) second order.

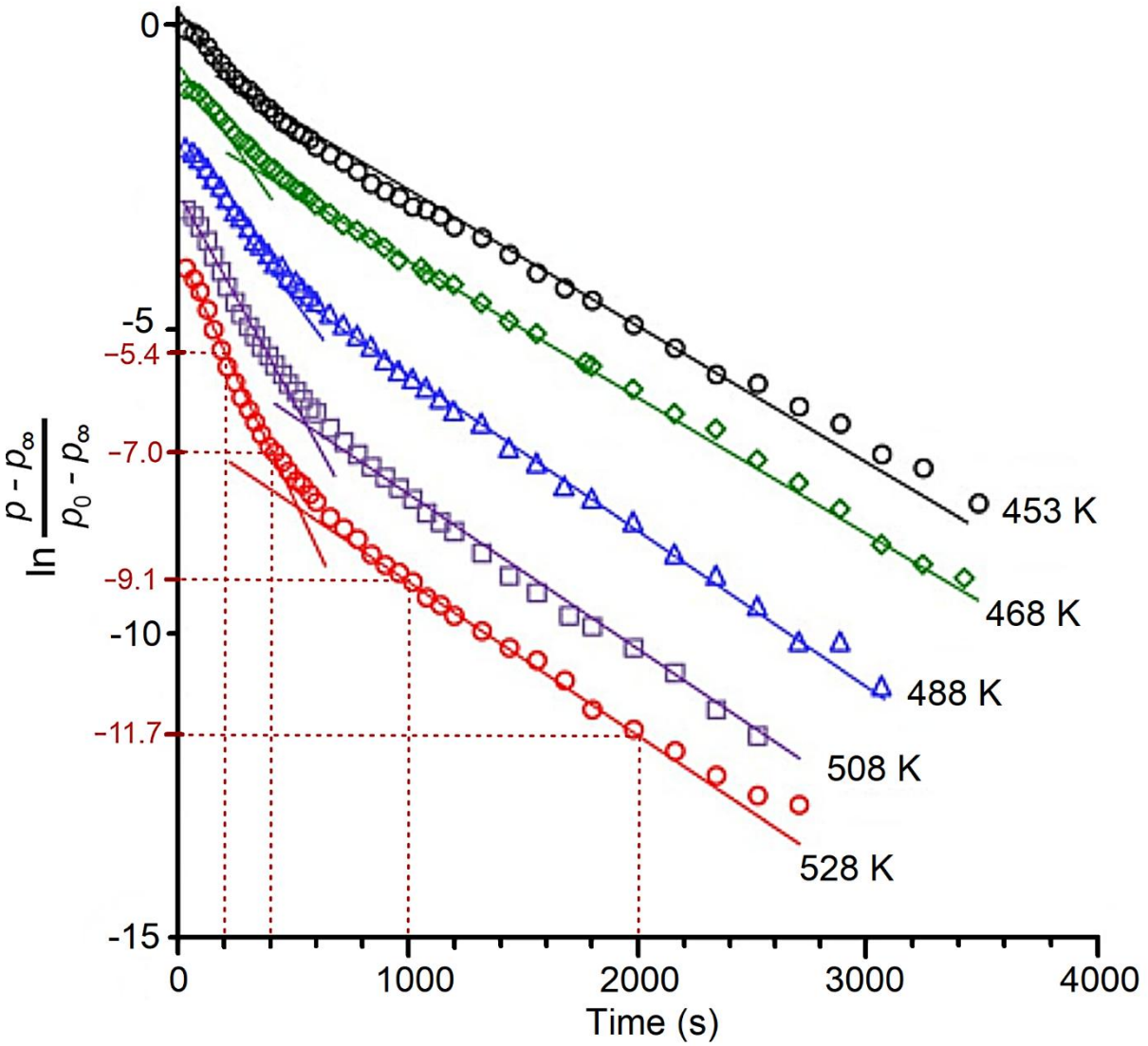


Figure 1. Semi-logarithmic graph of normalized methane pressure versus time for the reaction with copper-loaded zeolite containing sites **S1** and **S2** in an autoclave at various temperatures. The symbols denote experimental data points. The solid lines are linear fits to appropriate time ranges. The dotted lines are guides for the eyes

6.4 Write down the (pseudo) rate law for the oxidation of CH_4 that is consistent with the experimental data under the given conditions. Note that it may depend on the concentrations of CH_4 as well as of sites **S1** and **S2** and on the rate constants.

6.5 Choose the correct statement(s).

(a) At least two types of copper sites react, each with a different rate constant.

(b) The overall methane oxidation by zeolite is faster at higher temperature.

(c) At higher temperature, a larger fraction of the copper sites will have reacted with methane after completion of the reaction.

(d) One of the reactions becomes slower at higher temperature.

Paramagnetic sites **S1** can be observed by electron paramagnetic resonance (EPR) spectroscopy, whereas diamagnetic sites **S2** do not give an EPR signal. EPR spectroscopy measures the number of electron spins. Thus, the number of **S1** sites is proportional to the double integral I_2 of the EPR spectrum, i.e. [**S1**] $\propto I_2$. Spectra were measured at different temperatures T and at each temperature at different times, t, after initiating the reaction.

6.6 Derive the equation, which is linear in time, that relates $I_2(t)$ to the rate constant for the loss of **S1** sites.

6.7 Tick the boxes on the answer sheet for each measurement that needs to be calibrated with a known Cu(II) standard.

(a) Total number of paramagnetic Cu(II) sites in the sample.

(b) Concentration of paramagnetic Cu(II) sites in the sample.

(c) Rate constant.

(d) Types of different paramagnetic Cu(II) species in the sample.

From EPR measurements, it is known that the rate constant for the reaction with **S1** sites at 528 K is $2.604 \times 10^{-3}\ s^{-1}$.

6.8 Considering **Figure 1** and based on a calculation, decide if methane reacts faster or slower with **S2** sites than with **S1** sites.

(a) Methane reacts faster with **S1**.

(b) Both reaction rates are the same.

(c) Methane reacts faster with **S2**.

Methanol can be further converted into valuable olefins with different zeolite catalysts. In this process, one observes an intermediate product with molar mass $86.09\ g\ mol^{-1}$, elemental analysis (55.8 % wt. C, 7.0 % wt. H) and an ^1H NMR spectrum consisting of signals at four different chemical shifts:

a: 12.2 ppm (1H, s), broad, disappears when D_2O is added

b: 6.3 ppm (1H, d)

c: 5.7 ppm (1H, d)

d: 2.0 ppm (3H, s)

6.9 Draw the structure of the intermediate product and assign protons **a** and **d**.

The United States Department of Energy assigned twelve chemical compounds only containing C, H and O as *platform chemicals*. These are the most promising candidates, easy to prepare from renewable resources and with multiple target derivatives to be prepared from them. One of them is compound **A**, that can either be further derivatized or used for example in medicinal applications or in detergents.

- ^{1}H NMR in DMSO: 7.81 ppm (**a**, s), 13.0 ppm (**b**, s, broad, disappears when D_2O is added), both signals have the same integral.
- ^{13}C NMR: 165.1 ppm (**1**), 150.6 ppm (**2**) and 120.6 ppm (**3**).
- M = 156.03 g mol^{-1}. Elemental analysis: 46.15 % wt. C, 2.56 % wt. H.

6.10 Give a possible structure of **A** and assign all protons and carbon **1**.

SOLUTION OF THE PROBLEM 6

6.1 Two **S1** sites or one **S2** site are needed, since oxidation state changes by two units.

6.2 Consumed methane and initial amount of copper atoms:

$$\Delta n(\mathrm{CH_4}) = \frac{\Delta pV}{RT} = \frac{8\ \mathrm{Pa} \times 10^{-3}\ \mathrm{m^3}}{8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 528\ \mathrm{K}} = 1.822 \times 10^{-6}\ \mathrm{mol}$$

$$n_0(\mathrm{Cu}) = \frac{m_{\mathrm{cat}} w(\mathrm{Cu})}{M(\mathrm{Cu})} = \frac{0.200\ \mathrm{g} \times 0.043}{63.55\ \mathrm{g\ mol^{-1}}} = 1.353 \times 10^{-4}\ \mathrm{mol}$$

Two copper atoms are required per methane molecule:

$$\Delta n(\mathrm{Cu}) = 2\Delta n(\mathrm{CH_4}) = 3.644 \times 10^{-6}\ \mathrm{mol}$$

Fraction of Cu reacted:

$$\frac{\Delta n(\mathrm{Cu})}{n_0(\mathrm{Cu})} = \frac{3.644 \times 10^{-6}}{1.353 \times 10^{-4}} = 0.0269 = \mathbf{2.69\ \%}$$

6.3 (b) The reaction is of (pseudo) first order.

*The semi-logarithmic plot is linear, which applies only to first-order reactions. Because the contributing elementary reactions are bimolecular (CH_4 and site **S1** as well as CH_4 and site **S2**), the reactions are (pseudo) first order.*

6.4 $v = -\mathrm{d}[\mathrm{CH_4}]/\mathrm{d}t = k_{\mathrm{S1}}[\mathbf{S1}] + k_{\mathrm{S2}}[\mathbf{S2}]$

Due to the practically constant concentration of methane (small relative pressure drop), the concentration $[\mathrm{CH_4}]$ *does not appear in the rate law. It is not obvious from the plot, but the rate must of course depend on the concentration of the catalytic sites as they are consumed. As **S1** is visited sequentially, the **S1** rate should be proportional to [**S1**] and not [**S1**]^2.*

6.5 (a) and (b) are correct.

*Two processes with different rates are observed. At least for the faster process (**S2** sites), it is seen in Figure 1 that the slope increases with increasing temperature. What fraction of the copper sites reacts, cannot be determined from these plots.*

6.6 Since $I_2(t)$ is proportional to [**S1**](t), we can use the rate law $-\mathrm{d}[\mathbf{S1}]/\mathrm{d}t = k_{\mathrm{S1}}[\mathbf{S1}]$ and the time dependence of [**S1**] that follows from the rate law $[\mathbf{S1}](t) = [\mathbf{S1}]_0 \exp(-k_{\mathrm{S1}}t)$. Hence, $I_2(\mathrm{t}) = I_2(0)\exp(-k_{\mathrm{S1}}t)$. By taking the logarithm, we linearize this equation in time to obtain the desired form: $\mathbf{\ln} I_2(\mathbf{t}) = \mathbf{\ln} I_2(\mathbf{0}) - k_{\mathbf{S1}}\mathbf{t}$.

6.7 (a) and (b) are correct.

For determining absolute number and concentration, we need to calibrate signal

amplitude with respect to number of spins. The rate constant can be derived from relative amplitudes in spectra obtained at different times, which does not require calibration. The types of Cu(II) species can be inferred from the number of spectral components, and this also does not require calibration.

6.8 Option (c) is correct. From Figure 1 we can compute the two rate constants at 528 K. For each process, we have $p(CH_4) = p_0(CH_4)\exp(-k_i t)$. It follows that

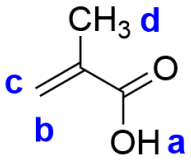
$$\ln p(CH_4, t_2) - \ln p(CH_4, t_1) = -k_i(t_2 - t_1),$$

That is, the rate constants are the negative slopes in Figure 1. At short times, the fast process dominates, but at long times, only the slow process contributes (fast reacting sites are depleted first). For the fast and slow process, we can calculate:

$$k_{fast} = \frac{-5.4-(-7)}{400\ s - 200\ s} = 0.008\ s^{-1} \qquad k_{slow} = \frac{-9.1-(-11.7)}{2000\ s - 1000\ s} = 0.0026\ s^{-1}$$

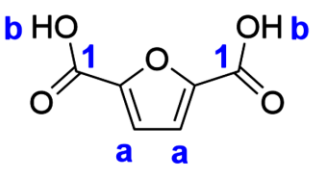
The k_{slow} value is close to the value given for **S1**, meaning that **S2** sites react faster.

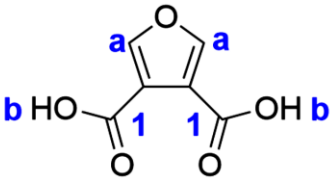
6.9 Correct structure:



The compound has 4 carbon atoms and 6 protons. This leaves 32.02 g mol^{-1} for other elements. From the chemical context, we can expect that this corresponds to two oxygen atoms. Each of the signals **a**, **b**, *and* **c** *corresponds to a single proton, signal* **d** *corresponds to three protons. Together with the chemical shift, we can safely assign signal* **d** *to a methyl group. The very large chemical shift of proton* **a** *suggests an acidic proton. From the number of protons we can infer a carbon–carbon double bond or a cyclic structure. A cyclic structure cannot be constructed with the groups that we have already assigned. The relatively large chemical shift of the methyl protons suggests that the methyl group is next to the carboxylic acid group. The multiplet information safely excludes a structure with the methyl group on the other side of the C=C bond.*

6.10 Two possible structures and assignments:





From the EA: (100 − 46.15 − 2.56) % = 51.29 % remain for O.

Element	M_{rel}	*w (%)*	w/M_{rel}
C	*12.0*	*46.15*	*3.85*
H	*1.0*	*2.56*	*2.56*
O	*16.0*	*51.29*	*3.21*

$C_xH_yO_z \rightarrow x : y : z = 3.85 : 2.56 : 3.21 = 1.5 : 1 : 1.25 \rightarrow (C_{1.5}H_1O_{1.25})_n$

$n = 156.03/(1.5\times12 + 1\times1 + 1.25\times16) = 4 \rightarrow (C_{1.5}H_1O_{1.25})_4$

Thus, the empirical formula is $C_6H_4O_5$. From the NMR data one can conclude that **A** *is a symmetrical molecule with one proton attached to an aromatic ring and one acidic proton in each moiety. There are two possible products in line with this data: 2,5-furandicarboxylic acid (actual data and designated platform chemical) and 3,4-furandicarboxylic acid.*

THEORETICAL PROBLEM 7

Enzyme Kinetics

The Michaelis–Menten (MM) mechanism, introduced in 1913, describes the kinetics of enzyme catalysis. In this mechanism, enzyme **E** catalyzes the conversion of substrate **S** to the product **P**:

$$\mathbf{E} + \mathbf{S} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{ES} \xrightarrow{k_3} \mathbf{E} + \mathbf{P}$$

The initial rate for an enzymatic reaction following the MM mechanism is given as

$$v_0 = v_{\max} \frac{[\mathbf{S}]_0}{K_M + [\mathbf{S}]_0} \tag{1}$$

when the initial concentration of **E** is much lower than the initial concentration of **S**, $[\mathbf{E}]_0 \ll [\mathbf{S}]_0$. The Michaelis constant is defined as $K_M = (k_2 + k_3)/k_1$. The initial rate can also be expressed as the product of the relative flow j and $[\mathbf{E}]_0$:

$$v_0 = j\,[\mathbf{E}]_0 \tag{2}$$

*Note: Questions **7.1** and **7.2** can have one, multiple, or no correct answer(s).*

7.1 Choose the correct alternative form(s) of the initial rate (v_0) expressions (1) and (2). $[\mathbf{ES}]_{max}$ is the maximum concentration of the **ES** complex.

(a) $v_0 = \dfrac{k_3[\mathbf{E}]_0[\mathbf{S}]_0}{K_M + [\mathbf{S}]_0}$ (b) $v_0 = \dfrac{k_3[\mathbf{E}]}{K_M/[\mathbf{S}]_0 + 1}$ (c) $v_0 = j\,[\mathbf{ES}]_{\max}$

(d) $v_0 = \dfrac{k_3[\mathbf{E}]_0[\mathbf{ES}]_{\max}}{K_M + [\mathbf{S}]_0}$ (e) $v_0 = \dfrac{k_3[\mathbf{E}]_0}{K_M/[\mathbf{S}]_0 + 1}$ (f) $v_0 = \dfrac{j[\mathbf{E}]_0}{K_M + [\mathbf{S}]_0}$

7.2 Choose the pair(s) of axes (y vs. x) that are expected to give a *linear plot*.

(a) v_0 vs. $1/[\mathbf{S}]_0$ (b) v_0 vs. v_0/K_M (c) v_0 vs. K_M/v_0

(d) $1/v_0$ vs. $v_0/[\mathbf{S}]_0$ (e) $1/v_0$ vs. v_0/K_M (f) $[\mathbf{S}]_0/v_0$ vs. $[\mathbf{S}]_0$

Many enzymes catalyze multi- rather than single-substrate transformations. However, if the concentration of one of the substrates is much higher than that of the other substrate or it is kept constant, the MM kinetics is also valid. Here we will look at two independent enzymatic systems that follow the MM kinetics.

Enzymatic System I

Enzyme **E** converts substrates **A** and **B** to products $\mathbf{P_A}$ and $\mathbf{P_B}$. At rapid pre-equilibrium between the free enzyme and all enzyme–substrate complexes, the following equation applies:

$$v_0 = \frac{k[\mathbf{E}]_0[\mathbf{A}]_0[\mathbf{B}]_0}{(K+[\mathbf{A}]_0)(K+[\mathbf{B}]_0)} \qquad (3)$$

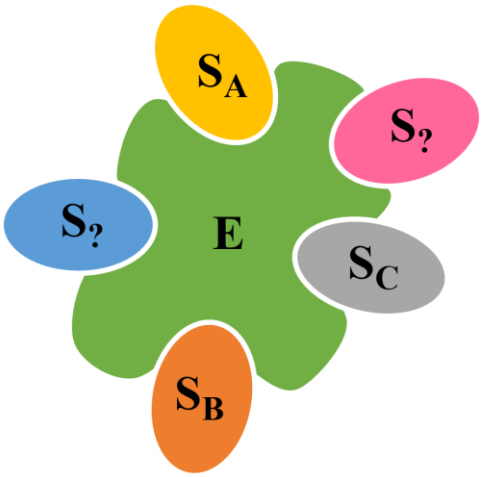
where k is the rate constant of one of the reactions. The same equilibrium constant K characterizes the dissociation of either substrate from the corresponding active site of **E**.

7.3 Show that equation (3) takes the MM form (1) if the concentration of substrate **B** is maintained at a constant value c_0. Give the expression for v_{max} in this case.

7.4 Propose a kinetic scheme for the *Enzymatic System I* consistent with eq. (3), showing all the intermediates and products. Indicate the reaction with a rate constant k.

Enzymatic System II

Enzyme **E** has five active sites, each of which is specific to one of the substrates $\mathbf{S_A}$, $\mathbf{S_B}$, or $\mathbf{S_C}$ that are selectively transformed to products $\mathbf{P_A}$, $\mathbf{P_B}$, or $\mathbf{P_C}$, respectively. There is at least one active site for each substrate. Each active site is independent of the others.



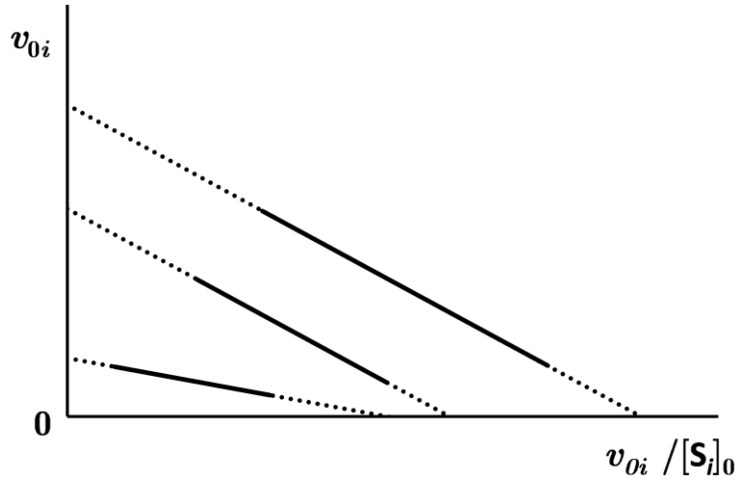
$$\mathbf{E} + \mathbf{S_A} \underset{k_{a2}}{\overset{k_{a1}}{\rightleftharpoons}} \mathbf{ES_A} \xrightarrow{k_{a3}} \mathbf{E} + \mathbf{P_A}$$

$$\mathbf{E} + \mathbf{S_B} \underset{k_{b2}}{\overset{k_{b1}}{\rightleftharpoons}} \mathbf{ES_B} \xrightarrow{k_{b3}} \mathbf{E} + \mathbf{P_B}$$

$$\mathbf{E} + \mathbf{S_C} \underset{k_{c2}}{\overset{k_{c1}}{\rightleftharpoons}} \mathbf{ES_C} \xrightarrow{k_{c3}} \mathbf{E} + \mathbf{P_C}$$

For **E**, it is known that:

1. The affinity for $\mathbf{S_C}$ is higher than for $\mathbf{S_B}$.
2. The plot of v_{0i} vs. $v_{0i}/[\mathbf{S}_i]_0$, known as Eadie–Hofstee plot, for $\mathbf{S_A}$, $\mathbf{S_B}$, $\mathbf{S_C}$, with rate given *per active site* (v_{0i}), is shown below, but the scale and the legend are omitted.



3. When **E** is saturated with $\mathbf{S_A}$, $\mathbf{S_B}$, $\mathbf{S_C}$, the catalytic turnover number (TON) for $\mathbf{S_C}$ per site is 10200 min^{-1}, and 2023 product $\mathbf{P_A}$, $\mathbf{P_B}$, $\mathbf{P_C}$ molecules in total are synthesized per second. At the same time, no more than 5.94×10^6 molecules of $\mathbf{P_A}$ and $\mathbf{P_B}$ are detected to form per hour.
4. At equimolar concentrations of $\mathbf{S_A}$, $\mathbf{S_B}$, $\mathbf{S_C}$, which are at least 1000-times lower than corresponding $K_{M,i}$ values, the $\mathbf{P_A}$, $\mathbf{P_B}$, $\mathbf{P_C}$ concentrations become proportional to the catalytic efficiency ($\varepsilon_i = k_{i3}/K_{M,i}$), and their ratio is 3 : 2 : 5, respectively.
5. Two $\mathbf{ES_i}$ complexes have equal rate constants for dissociation to **E** and $\mathbf{S_i}$. The activation barrier for the reaction of $\mathbf{ES_C}$ into the initial compounds is 1266 J mol^{-1} higher than for the reaction into the final products. Assume that the pre-exponential factors are equal for both reactions and T = 25 °C.
6. For **E** + $\mathbf{S_i}$ reaction: $k_{c1} = 1.57 \times 10^7$ M^{-1} s^{-1} and $k_{a1} = k_{b1}$.

7.5 Fill in the table below and provide your calculations. *Hints:*

- Use information from points 1 and 2 to find the relation (<, >, =) between constants $K_{M,A}$, $K_{M,B}$ and $K_{M,C}$.
- Information from points 3 and 5 allows you to complete the first column (number of active sites for each substrate) and the last row (all the constants for substrate $\mathbf{S_C}$) of the table. Check that the sum of active sites is equal to 5.

	# of active sites	k_1	k_2	k_3	K_M
$\mathbf{S_A}$					
$\mathbf{S_B}$					
$\mathbf{S_C}$		1.57×10^7 M^{-1} s^{-1}			

SOLUTION OF THE PROBLEM 7

7.1 (a), (c), (e). The answers represent the same kinetic equation

$$v_0 = v_{\max}\frac{[\mathbf{S}]_0}{K_\mathrm{M}+[\mathbf{S}]_0} = \frac{k_3[\mathbf{E}]_0[\mathbf{S}]_0}{K_\mathrm{M}+[\mathbf{S}]_0} = j[\mathbf{E}]_0$$

expressed in different ways.

7.2 (b), (f). When the MM equation is inversed, the following is obtained:

$$\frac{1}{v_0} = \frac{1}{v_{\max}}\frac{K_\mathrm{M}+[\mathbf{S}]_0}{[\mathbf{S}]_0} = \frac{1}{v_{\max}} + \frac{K_\mathrm{M}}{v_{\max}}\frac{1}{[\mathbf{S}]_0}$$

The equation matches the linear form $y = ax + b$ with coordinates $y = 1/v_0$ and $x = 1/[\mathbf{S}]_0$. Thus, options v_0 vs. $1/[\mathbf{S}]_0$ and $1/v_0$ vs. $v_0/[\mathbf{S}]_0$ are incorrect. The option $[\mathbf{S}]_0/v_0$ vs. $[\mathbf{S}]_0$ can be checked if the reversed equation is multiplied by $[\mathbf{S}]_0$:

$$\frac{[\mathbf{S}]_0}{v_0} = \frac{[\mathbf{S}]_0}{v_{\max}}\frac{K_\mathrm{M}+[\mathbf{S}]_0}{[\mathbf{S}]_0} = \frac{1}{v_{\max}}(K_\mathrm{M}+[\mathbf{S}]_0) = \frac{K_\mathrm{M}}{v_{\max}} + \frac{[\mathbf{S}]_0}{v_{\max}}$$

making it the correct answer. The other three options don't contain $[\mathbf{S}]_0$ as a variable; thus, the MM equation is not even needed to check them. Only option v_0 vs. v_0/K_M reflects the linear dependence (a straight line with zero intercept).

7.3 If the concentration of substrate **B** is maintained constant at c_0

$$v_0 = \frac{k[\mathbf{E}]_0[\mathbf{A}]_0 c_0}{(K+[\mathbf{A}]_0)(K+c_0)} = \frac{\frac{k[\mathbf{E}]_0 c_0}{(K+c_0)}[\mathbf{A}]_0}{K+[\mathbf{A}]_0} = \frac{v_{\max}[\mathbf{A}]_0}{K+[\mathbf{A}]_0}$$

Thus, the maximum rate $v_{\max}$ corresponds to the expression:

$$v_{\max} = \frac{k[\mathbf{E}]_0 c_0}{(K+c_0)}$$

7.4 One-substrate enzymatic reaction

$$\mathbf{E} + \mathbf{S} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathbf{ES} \xrightarrow{k_3} \mathbf{E} + \mathbf{P}$$

In the case of pre-equilibrium ($k_3 \ll k_2$), the equilibrium constant for the dissociation of a substrate from a catalyst active site is

$$K = \frac{k_2}{k_1} = \frac{[\mathbf{E}][\mathbf{S}]}{[\mathbf{ES}]}$$

The initial rate for this enzymatic reaction is $v_0 = k_3[\mathbf{ES}] = k_3\alpha_{\mathrm{ES}}[\mathbf{E}]_0$ where

$$\alpha_{\mathrm{ES}} = \frac{[\mathbf{ES}]}{[\mathbf{E}]_0} = \frac{[\mathbf{ES}]}{K[\mathbf{ES}]/[\mathbf{S}]+[\mathbf{ES}]} = \frac{[\mathbf{S}]}{K+[\mathbf{S}]}$$

is a fraction of catalyst in the form of enzyme–substrate complex **ES**. As the substrate concentration at the beginning of a reaction is much higher than the enzyme concentration, it can be considered equal to the initial concentration, thus

$$\alpha_{ES} = \frac{[\mathbf{S}]_0}{K + [\mathbf{S}]_0}$$

This is how the initial rate equation takes the Michaelis–Menten form:

$$v_0 = k_3 \alpha_{ES} [\mathbf{E}]_0 = \frac{k_3 [\mathbf{E}]_0 [\mathbf{S}]_0}{K + [\mathbf{S}]_0} = \frac{v_{max} [\mathbf{S}]_0}{K_M + [\mathbf{S}]_0}$$

with $v_{max} = k_3 [\mathbf{E}]_0$ and $K_M = K$, which can be expected from the original expression $K_M = (k_2 + k_3)/k_1$ with the pre-equilibrium condition $k_3 \ll k_2$. Based on this analogy, the expression (3) from the question

$$v_0 = \frac{k [\mathbf{E}]_0 [\mathbf{A}]_0 [\mathbf{B}]_0}{(K + [\mathbf{A}]_0)(K + [\mathbf{B}]_0)}$$

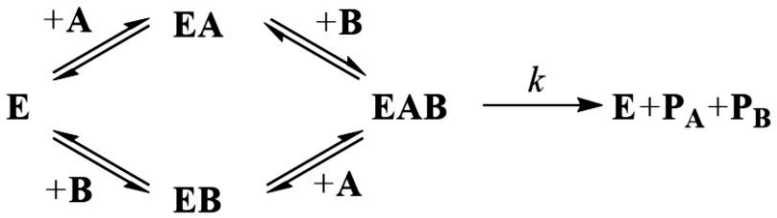
allows us to assume that k corresponds to the rate constant for the step of formation of the products from that form of the enzyme, with a fraction

$$\alpha = \frac{[\mathbf{A}]_0 [\mathbf{B}]_0}{(K + [\mathbf{A}]_0)(K + [\mathbf{B}]_0)} = \frac{[\mathbf{A}]_0 [\mathbf{B}]_0}{K^2 + K[\mathbf{A}]_0 + K[\mathbf{B}]_0 + [\mathbf{A}]_0 [\mathbf{B}]_0}$$

This expression corresponds to the case when four enzyme forms are present: free enzyme **E** and enzyme bound to one or two substrates **EA**, **EB**, and **EAB**. This mole fraction corresponds to **EAB**, meaning that the products are formed from this form,

$$\alpha = \frac{[\mathbf{EAB}]}{[\mathbf{E}]_0}$$

The mechanism is a random sequential reaction:



7.5 From the information given in **1** we know that $K_{M,C} < K_{M,B}$, because the lower the constant is, the higher affinity is observed.

From **2**, the slope of the Eadie–Hofstee plot is $-K_M$ as the corresponding linear form of the MM equation is

$v_0 = v_{max} - K_M(v_0/[\mathbf{S}]_0)$.

We see two parallel lines on the plot; thus, two $K_{M,i}$ values are equal. The absolute value of the third slope is smaller; therefore, it corresponds to $K_{M,C}$, and we know that

$K_{M,A} = K_{M,B}$

From the information given in point **3** we can obtain directly that $k_{c3} = 10200\ \text{min}^{-1} = 170\ \text{s}^{-1}$. The meaning of this constant is turnover number TON — rate when **E** is saturated by **S**; that is, the formation of a given number of product molecules by one site per unit time. Also, we can write the relation:

$$k_{a3}a + k_{b3}b + k_{c3}c = 2023 \ \rightarrow \ k_{a3}a + k_{b3}b + 170c = 2023 \qquad (1^*)$$

where a, b and c are the numbers of $\mathbf{S_A}$, $\mathbf{S_B}$, and $\mathbf{S_C}$ active sites, respectively, with the sum $a + b + c = 5$. The other information tells us that

$$ak_{a3} + bk_{b3} \le 5.94 \times 10^6\ \text{h}^{-1} = 1650\ \text{s}^{-1} \qquad (2^*)$$

From these two expressions, we obtain $170c \ge 2023 - 1650$. Hence, $c \ge 2.19$. The only possible solution is $c = 3$ and $a = b = 1$ (i.e., both unassigned sites are for $\mathbf{S_C}$).

Analysis of the information given in **4** gives the following. For low concentrations of $\mathbf{S_i}$ ($\mathbf{S_A}$, $\mathbf{S_B}$, and $\mathbf{S_C}$), that is when $[\mathbf{S_i}]_0 \ll K_{M,i}$ the rate equation (per active site) can be written as

$$v_{0i} = \frac{k_{i3}[\mathbf{E}]_0[\mathbf{S_i}]_0}{K_{M,i} + [\mathbf{S_I}]_0} = \frac{k_{i3}}{K_{M,i}}[\mathbf{E}]_0[\mathbf{S_i}]_0 \qquad (3^*)$$

As $[\mathbf{S_i}]_0$ are all equal here, and **E** is the same enzyme, we obtain that the concentration of a product $\mathbf{P_i}$ is directly proportional to the ratio $\varepsilon_i = k_{i3}/K_{M,I}$ (catalytic efficiency). Considering the number of sites, we get the following:

$$\frac{k_{a3}}{K_{M,A}} : \frac{k_{b3}}{K_{M,B}} : 3\frac{k_{c3}}{K_{M,C}} = 3:2:5 \qquad (4^*)$$

As $K_{M,A} = K_{M,B}$, the following ratio of constants can be derived: $k_{a3}/k_{b3} = 3/2 = 1.5$. In combination with the equation (1*) with $a = b = 1$ and $c = 3$, we obtain:

$k_{a3} + k_{b3} + 170 \times 3 = 2023$

$1.5k_{b3} + k_{b3} = 1513 \ \rightarrow \ k_{b3} = 605\ \text{s}^{-1}$

and $k_{a3} = 1.5k_{b3} = 1.5 \times 605\ \text{s}^{-1} = 908\ \text{s}^{-1}$. Now we can also find the ratio between $K_{M,A} = K_{M,B}$ and $K_{M,C}$, which will be needed later:

$$\frac{k_{b3}}{K_{M,B}} : 3\frac{k_{c3}}{K_{M,C}} = 2:5 \ \rightarrow \ \frac{K_{M,B}}{K_{M,C}} = \frac{5k_{b3}}{2 \times 3k_{c3}} = \frac{5 \times 605}{2 \times 3 \times 170} = 2.97 \qquad (5^*)$$

From the information given in **5**, using the Arrhenius equation, the ratio between k_{c3} and k_{c2} can be found:

$$\frac{k_{c3}}{k_{c2}} = \frac{A_{c3}\exp(-E_{c3}/RT)}{A_{c2}\exp(-E_{c2}/RT)} = e^{\frac{E_{c2}-E_{c3}}{RT}} = e^{\frac{1266}{8.314\times298}} = 1.667$$

Since $k_{c3} = 170\ s^{-1}$, we get $k_{c2} = (170/1.667)\ s^{-1} = 102\ s^{-1}$.

Since it is stated that two enzyme–substrate complexes dissociate back with the same rate constant, two k_{i2} are equal: $k_{a2} = k_{b2}$ or $k_{a2} = k_{c2}$ or $k_{b2} = k_{c2}$. As $K_{M,A} = K_{M,B}$ and $k_{a1} = k_{b1}$ (information given in **6**), using the definition of Michaelis constant

$$K_{M,i} = (k_{i2} + k_{i3})/k_{i1} \rightarrow k_{a2} + k_{a3} = k_{b2} + k_{b3} \rightarrow k_{a2} + 908\ s^{-1} = k_{b2} + 605\ s^{-1}$$

or $k_{a2} = k_{b2} - 303\ s^{-1}$. This means that $k_{a2} \neq k_{b2}$. Moreover, k_{b2} can't be equal to $k_{c2} = 102\ s^{-1}$, as in that case k_{a2} would be negative. Therefore, the only option is $k_{a2} = k_{c2} = 102\ s^{-1}$. Thus, $k_{b2} = k_{a2} + 303\ s^{-1} = (102 + 303)\ s^{-1} = 405\ s^{-1}$.

All the rate constants for **Sc** are now known and $K_{M,i}$ can be calculated:

$$K_{M,C} = \frac{k_{c2} + k_{c3}}{k_{c1}} = \frac{(102+170)\ s^{-1}}{1.57\times10^{7}\ M^{-1}\ s^{-1}} = 1.73\times10^{-5}\ M$$

The ratio between $K_{M,A} = K_{M,B}$ and $K_{M,C}$ was determined in (4*). Therefore:

$$K_{M,A} = K_{M,B} = 2.97K_{M,C} = 2.97\times1.73\times10^{-5}\ M = 5.14\times10^{-5}\ M$$

The only remaining constants are $k_{a1} = k_{b1}$. From $K_{M,B}$ we have:

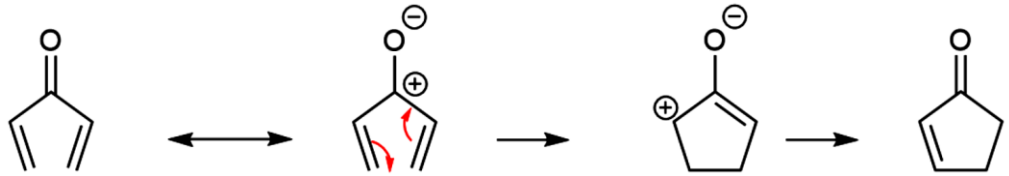
$$k_{b1} = \frac{k_{b2} + k_{b3}}{K_{M,B}} = \frac{(405+605)\ s^{-1}}{5.14\times10^{-5}\ M} = 1.96\times10^{7}\ M^{-1}\ s^{-1}$$

	# of active sites	k_1	k_2	k_3	K_M
SA	1	$1.96 \times 10^7\ M^{-1}\ s^{-1}$	$102\ s^{-1}$	$908\ s^{-1}$	5.14×10^{-5} M
SB	1		$405\ s^{-1}$	$605\ s^{-1}$	5.14×10^{-5} M
SC	3	$1.57 \times 10^7\ M^{-1}\ s^{-1}$	$102\ s^{-1}$	$170\ s^{-1}$	1.73×10^{-5} M

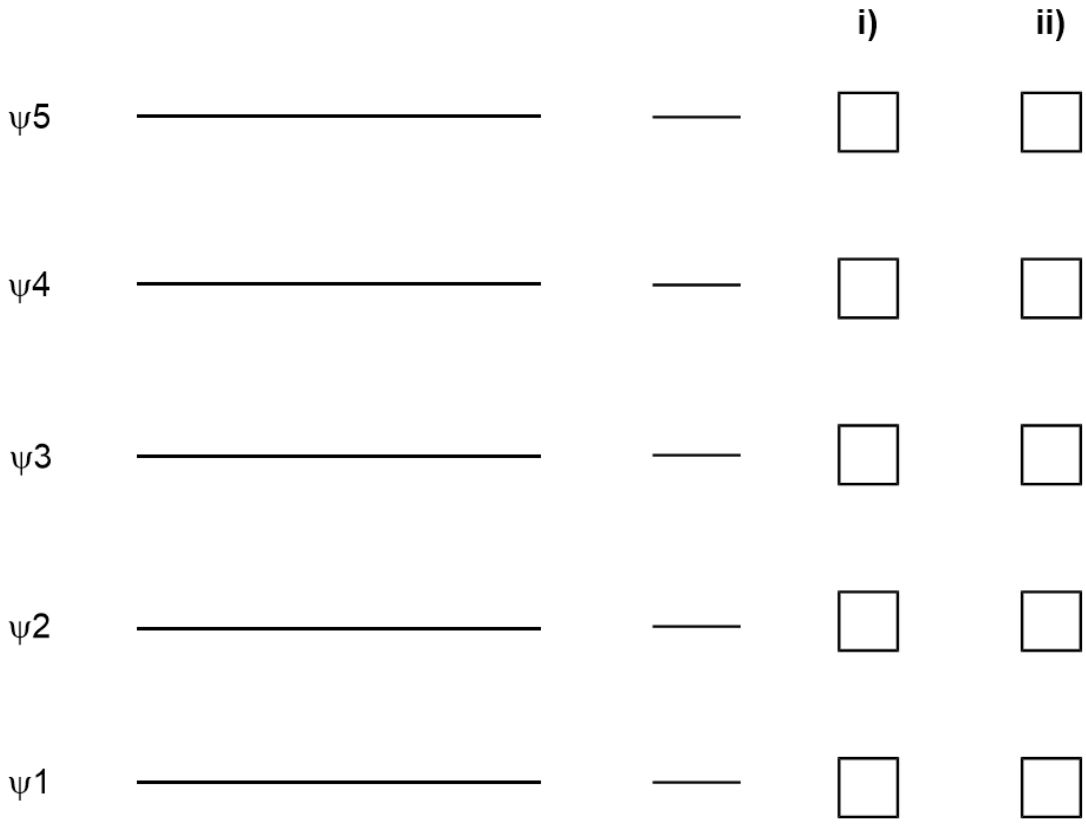
THEORETICAL PROBLEM 8

Nazarov Reaction

The Nazarov reaction is a frequently used reaction of divinyl ketones to give cyclopentenones. It proceeds either photochemically or via acid catalysis and is an electrocyclization, followed by a proton transfer.



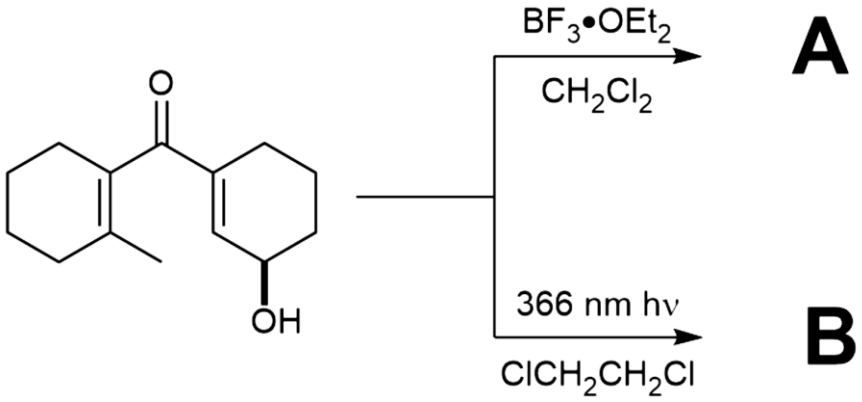
8.1 Draw the π molecular orbitals to describe the Nazarov reaction. Fill in the electrons into the respective energy levels. Mark with an **x** the (i) HOMO (highest occupied molecular orbital) and (ii) LUMO (lowest unoccupied molecular orbital). For this exercise, you can consider the divinyl ketone as a pentadienyl cation with five p-orbitals.



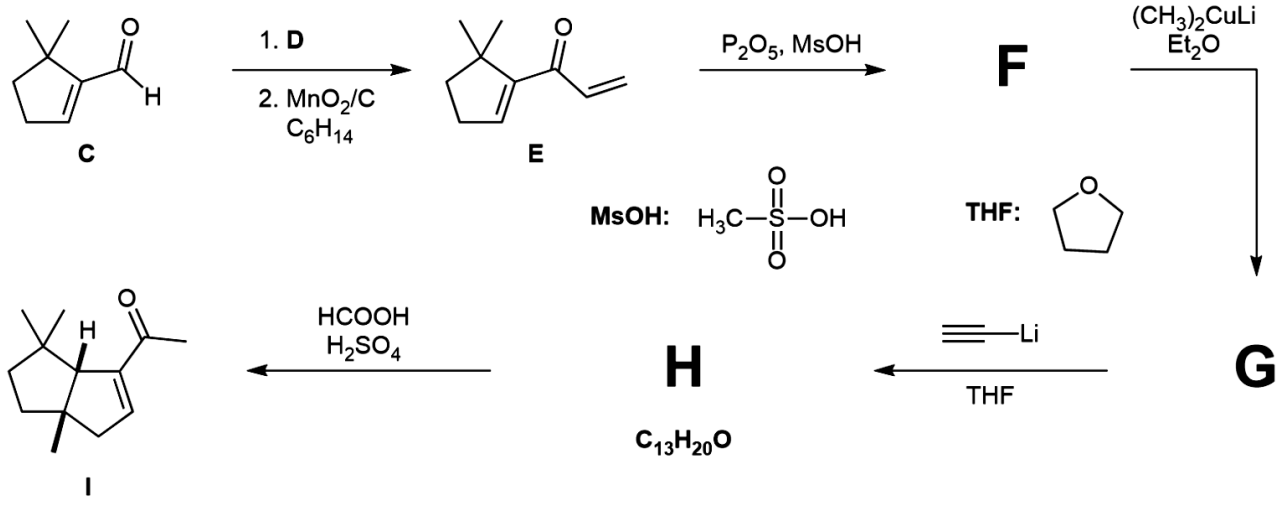
8.2 From the π molecular orbitals you derived in Task **8.1**, predict under which conditions the Nazarov reaction of the divinyl ketone will proceed in a disrotatory or conrotatory fashion. In the table mark with an **x** the conditions under which the reaction is allowed.

	Disrotatory	Conrotatory
Thermal		
Photochemical		

8.3 The Nazarov reaction was used as key reaction in a synthesis of Farnesin. For both conditions below, draw one possible structure for each of **A** and **B**, including stereochemistry. Note that the products of both reactions show ^{1}H NMR a signal at 6.70–6.73 ppm.



The synthesis of Capnellene commences with unsaturated aldehyde **C** shown below. Treatment with **D**, followed by reaction with MnO_2 supported on carbon gave divinyl ketone **E** shown below. Exposure to a mixture of P_2O_5 and MsOH yielded **F**, which was elaborated via a sequence of reactions to the unsaturated ketone **I**.



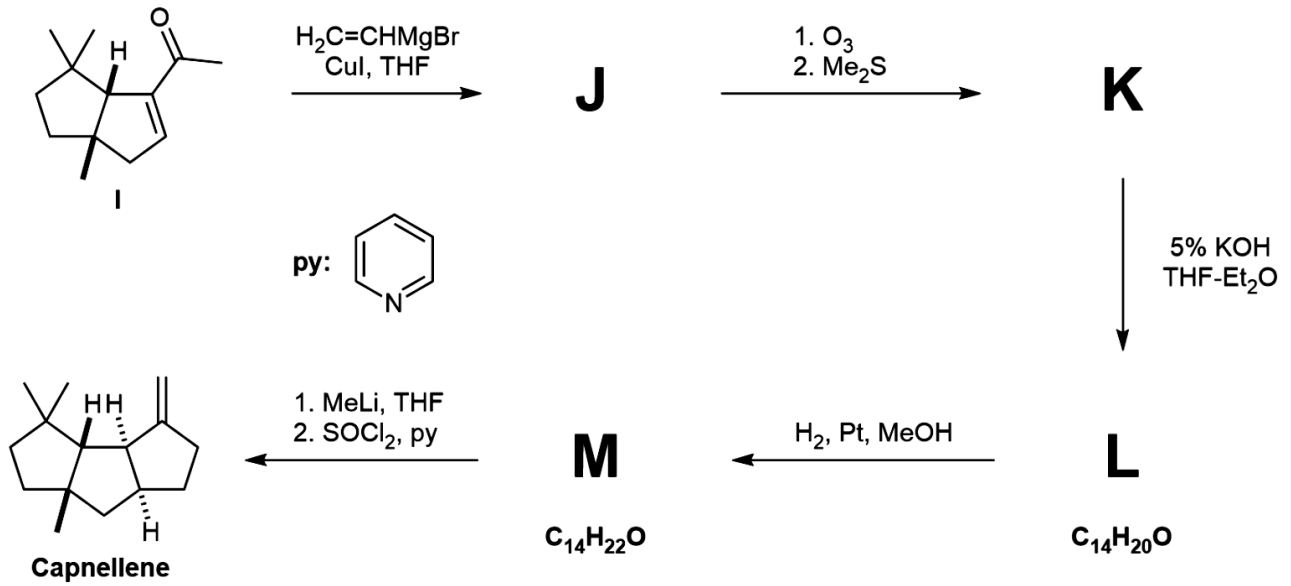
8.4 Choose the reagent(s) from the list that would be suitable as **D**.

(a) H_2C=CHMgBr (c) H_2C=CHBr, $Pd(PPh_3)_4$

(b) 1. $NaBH_4$ 2. H_2C=CHLi (d) H_2C=CHMgBr, CuI

8.5 Give the structures of intermediates **F**, **G**, and **H**, including their stereochemistry.

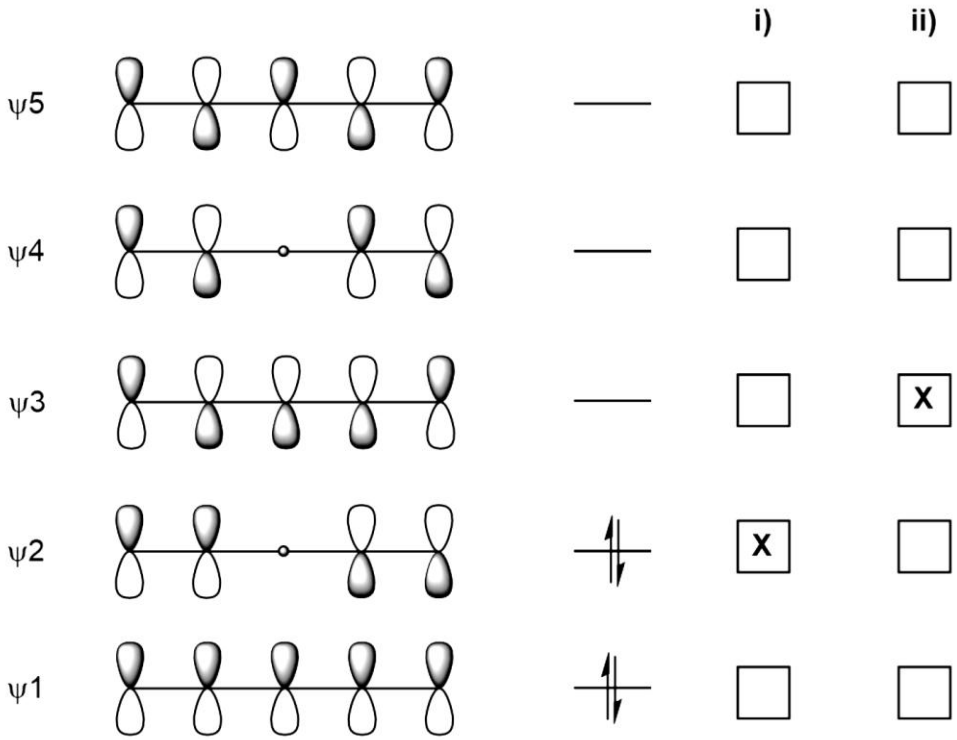
Enone **I** was then subjected to H_2C=CHMgBr and CuI in THF to give intermediate **J**, followed by ozonolysis to yield intermediate **K**, which shows a signal at 9.61 ppm in the ^1H NMR. Treatment with 5-% KOH in a mixture of THF and ether yielded intermediate **L**. Hydrogenation with a Pt catalyst and under an atmosphere of H_2 yielded **M**, which finally gave rise to Capnellene.



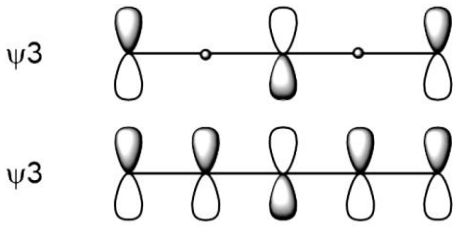
8.6 Give the structures **J**, **K**, **L**, and **M**, including their stereochemistry.

SOLUTION OF THE PROBLEM 8

8.1



For ψ3, the following is also accepted as correct.

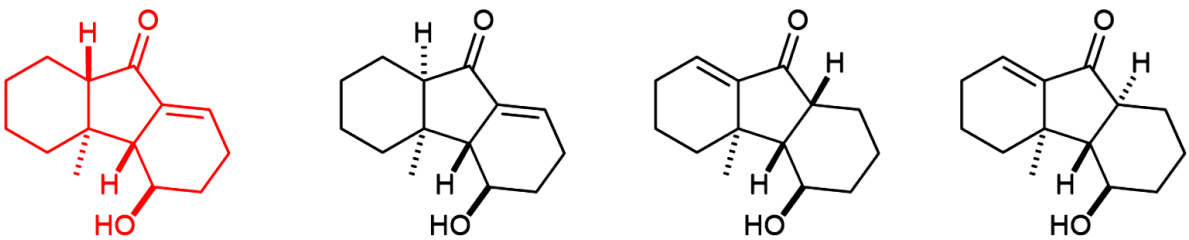


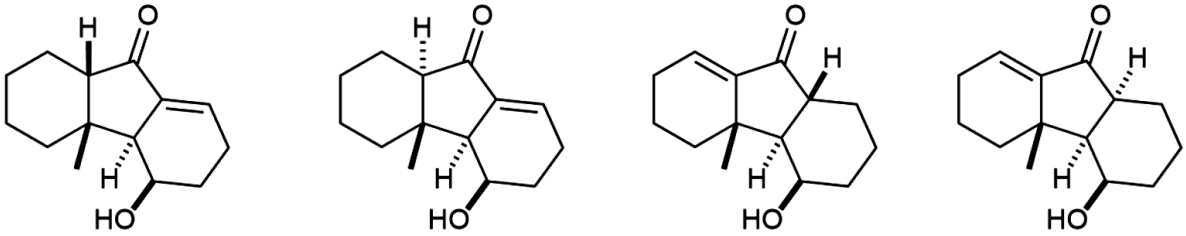
8.2

	Disrotatory	Conrotatory
Thermal		**x**
Photochemical	**x**	

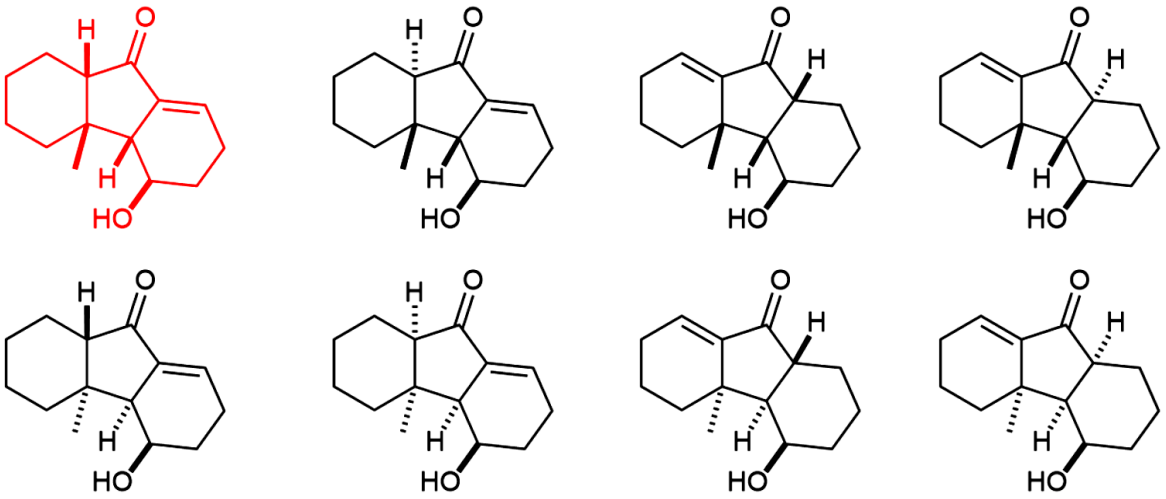
8.3 The red isomer is actually formed. However, all 8 possible combinations of olefin isomer, α-H and torque selectivity in the electrocyclization will be graded as correct.

A:



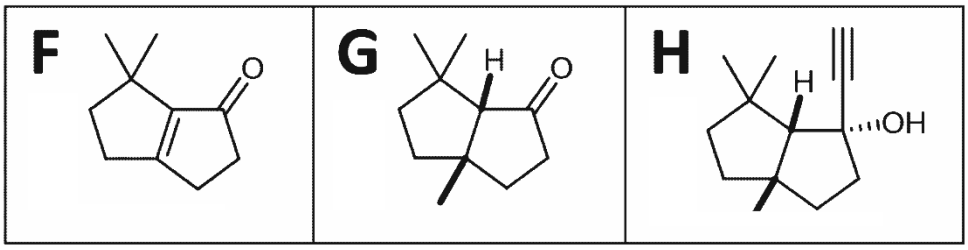


B:

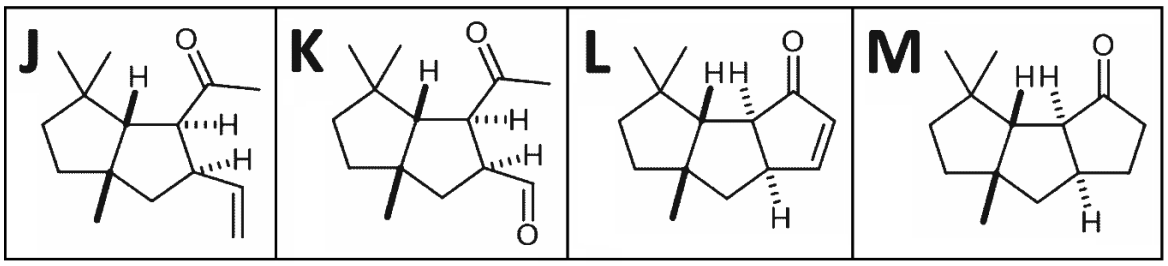


8.4 (a)

8.5



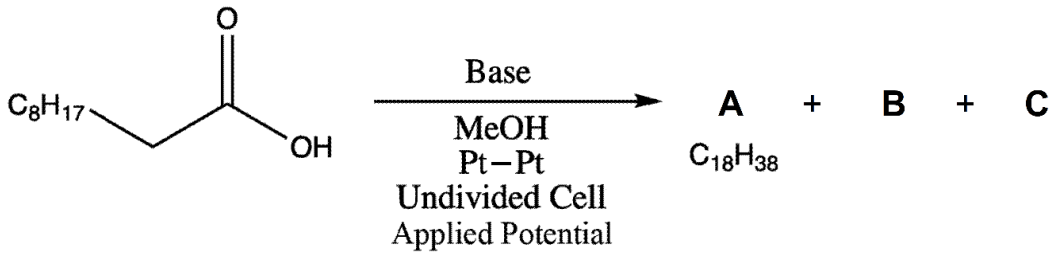
8.6 The stereochemistry of α-hydrogen of **J** and **K** can be considered correct if the epimer is drawn (epimerization under the condensation conditions is conceivable)



THEORETICAL PROBLEM 9

Electrolysis in Organic Synthesis

The Kolbe electrolysis describes the decarboxylative dimerization of two carboxylic acids and only proceeds if the acid is deprotonated. The unbalanced equation is shown here.

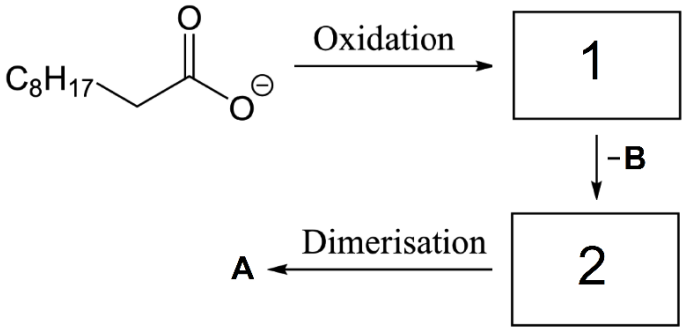


Two gases (**B** and **C**) are produced during the reaction. **B** reacts with $Ca(OH)_2$, while **C** is highly flammable.

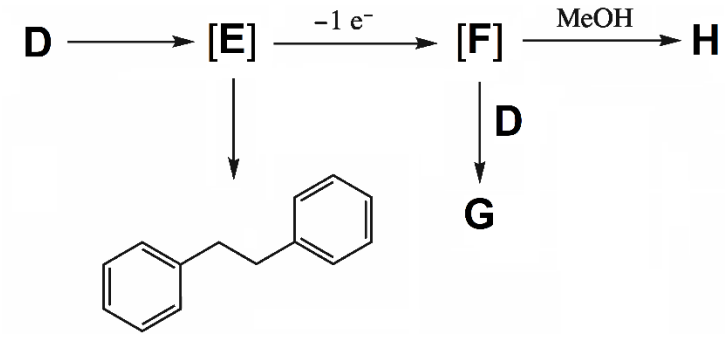
9.1 Provide the structural formulae of **A**, **B**, and **C**.

9.2 The synthesis is formally a redox reaction, where the carboxylate is oxidized and the solvent is reduced. Formulate the oxidative and reductive half reactions and the overall redox reaction.

9.3 Provide the intermediates **1** and **2** in the mechanism for the oxidative decarboxylation and formation of the product.

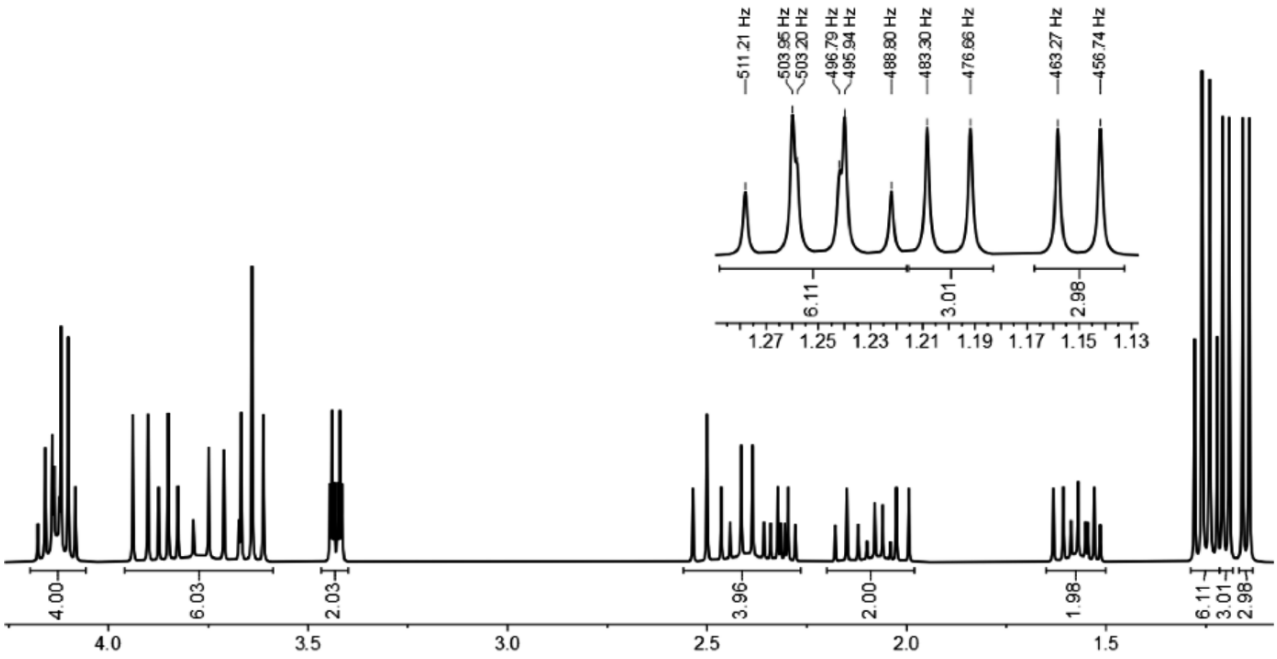


The Kolbe electrolysis is usually only efficient for long-chained saturated carboxylic acids and not for certain carboxylic acids, such as **D**. Here, the overoxidation of the radical intermediate **E** to a positively charged species **F** is facilitated. Intermediate **F** can react with nucleophiles to form different side products, for example it reacts with **D** to form an ester **G**, and with MeOH to form **H**.



9.4 Provide the structures of **D**–**H**.

The electrolysis of carboxylic acid I in the presence of an excess of co-acid **J** yields two main products (by ^{1}H NMR analysis) that are inseparable by silica gel chromatography. Their spectroscopic data are almost identical. In the ^{1}H NMR, the two species are only distinguishable by two signals with small differences in chemical shifts.



The ^{1}H NMR spectrum looks as follows (1:1 mixture of products **K** and **L**):

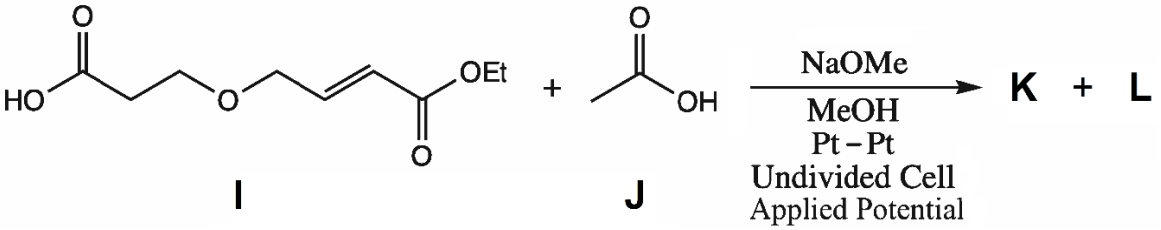
4.18–4.08 (m, 4 H), 3.95–3.60 (m, 6 H), 3.43 (dt, 2 H, *J* = 7.8, 2.2 Hz), 2.55–2.25 (m, 4 H), 2.20–1.95 (m, 2 H), 1.65–1.50 (m, 2 H)

Specific signals for **K**:

1.26 (t, 3 H, *J* = 7.2 Hz), 1.20 (d, 3 H, *J* = 6.6 Hz)

Specific signals for **L**:

1.24 (t, 3 H, *J* = 7.2 Hz), 1.15 (d, 3 H, *J* = 6.6 Hz)

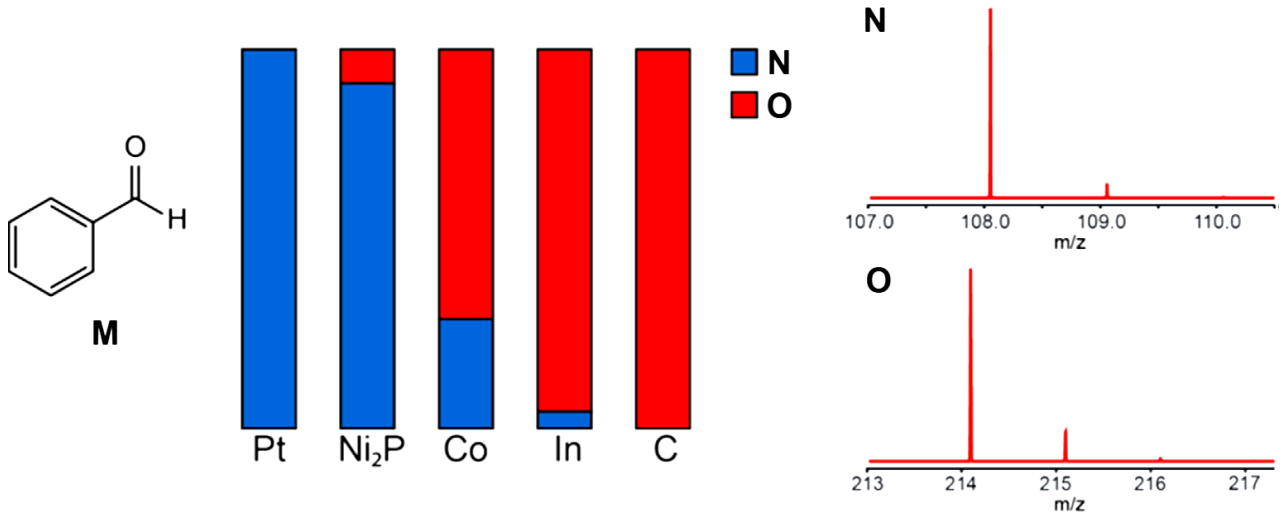


9.5 Provide the structures for products **K** and **L**. Indicate how the products are related.

(a) Epimers (b) Enantiomers

(c) Diastereomers (d) Constitutional Isomers

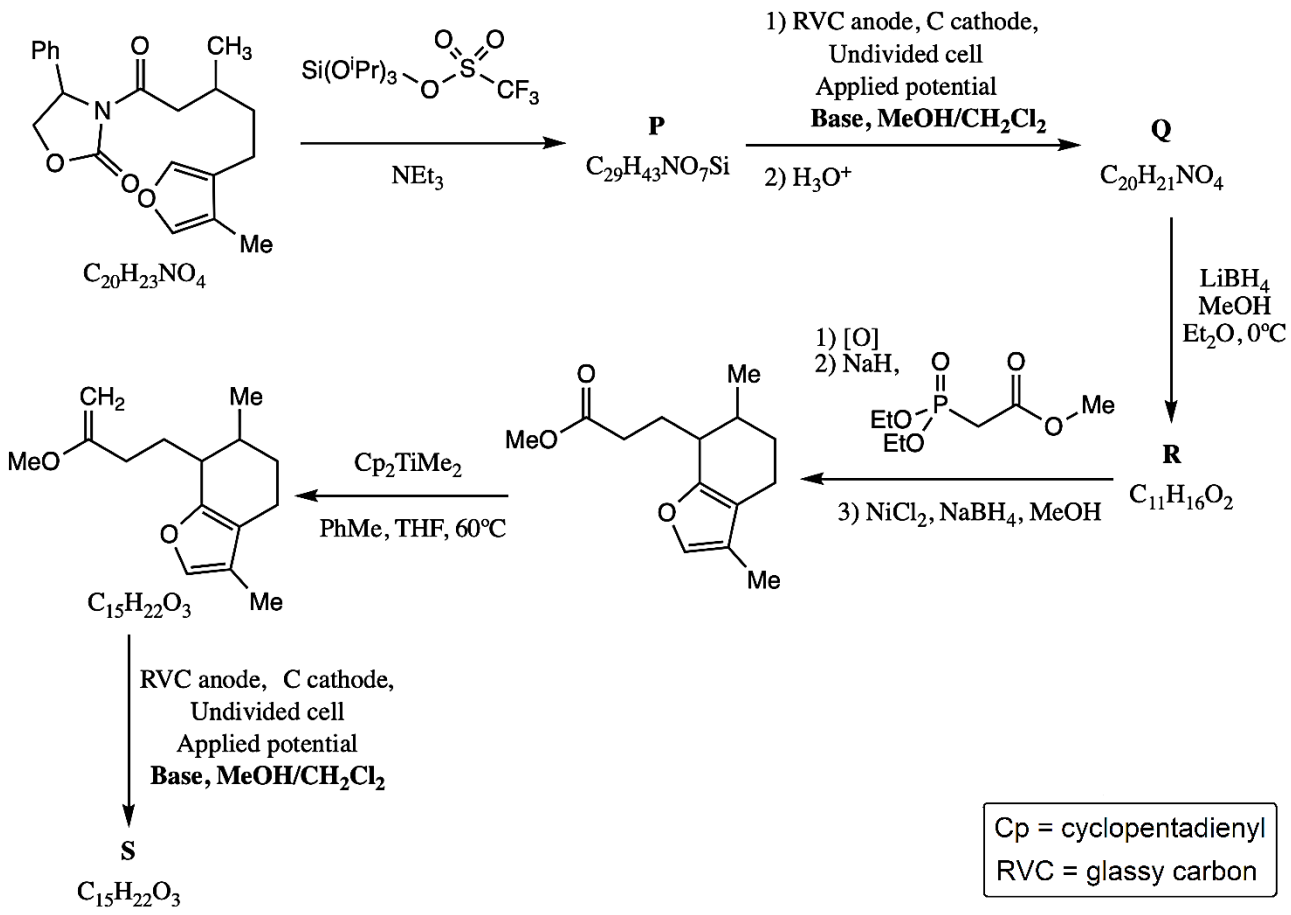
The choice of the electrode material can influence the selectivity of an organic electrosynthetic reaction. The reductive electrolysis of benzaldehyde (**M**) (16 mM in 1 M aqueous KOH, Pt anode, −1.3 V vs. Ag/AgCl) yields different products depending on the cathode material used. Strong binding to the surface favors intermolecular reactions. The figure below shows the product distribution for different cathode materials and the mass spectra of the products.



9.6 Provide the structure of **N** and **O**.

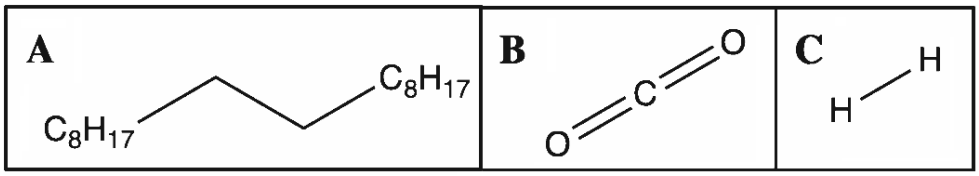
Alkenes, such as enol ethers, can be oxidatively coupled. This typically involves the anodic oxidation of the alkene fragment to yield a radical cation which can be intercepted by a nucleophile.

9.7 Provide the structural formulae of **P**, **Q**, **R**, and **S** in the scheme below. Indicating stereochemistry is not required. *Hint:* **S** is a tricyclic product.


Ph
O
CH3
N
O
O
O
Me
C20H23NO4
Si(OiPr)3
O
S
O
CF3
NEt3
P
C29H43NO7Si
1) RVC anode, C cathode,
Undivided cell
Applied potential
Base, MeOH/CH2Cl2
2) H3O+
Q
C20H21NO4
LiBH4
MeOH
Et2O, 0°C
R
C11H16O2
1) [O]
2) NaH,
EtO
EtO
P
O
O
Me
3) NiCl2, NaBH4, MeOH
MeO
O
Me
Me
Cp2TiMe2
PhMe, THF, 60°C
CH2
MeO
O
Me
C15H22O3
RVC anode, C cathode,
Undivided cell
Applied potential
Base, MeOH/CH2Cl2
S
C15H22O3
Cp = cyclopentadienyl
RVC = glassy carbon

SOLUTION OF THE PROBLEM 9

9.1

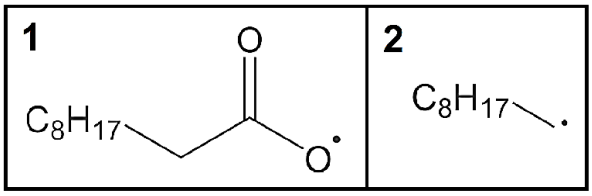


9.2 Reductive half reaction: $2\,MeOH + 2\,e^- \rightarrow 2\,MeO^- + H_2$

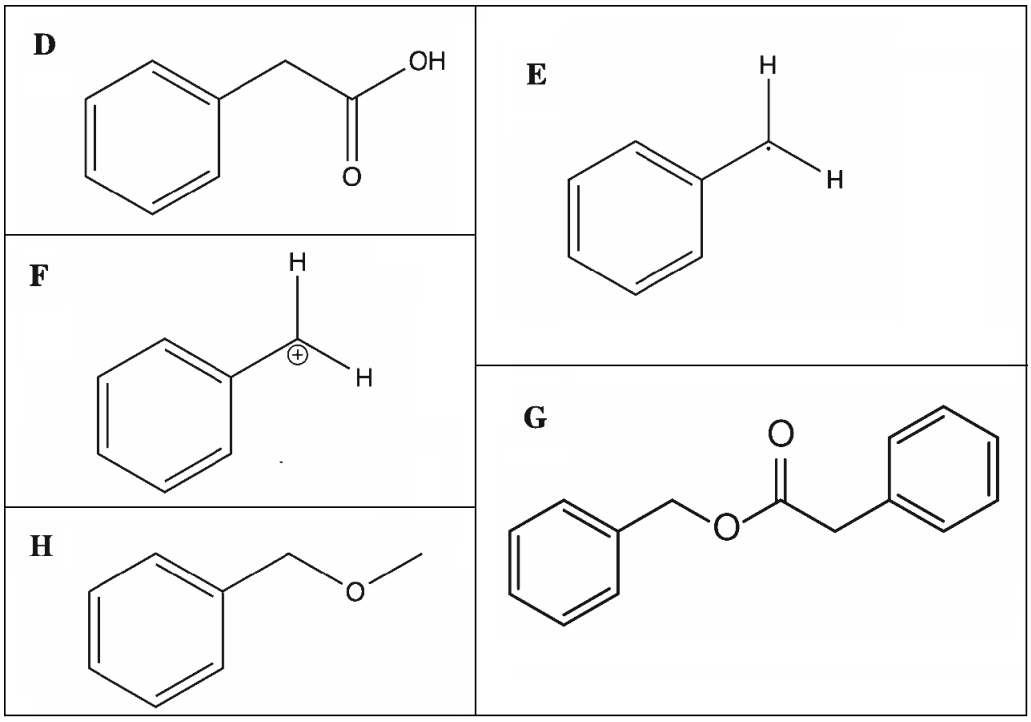
Oxidative half reaction: $2\,R{-}COO^- \rightarrow R{-}R + 2\,CO_2 + 2\,e^-$

Overall reaction: $2\,R{-}COO^- + 2\,MeOH \rightarrow R{-}R + 2\,CO_2 + 2\,MeO^- + H_2$

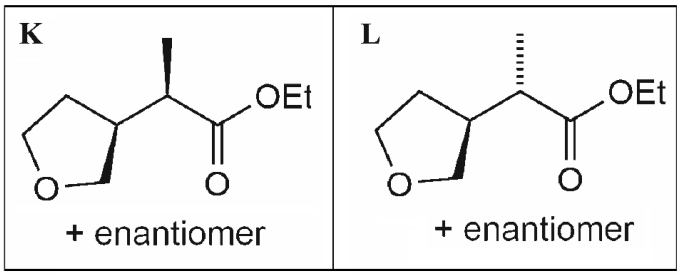
9.3



9.4

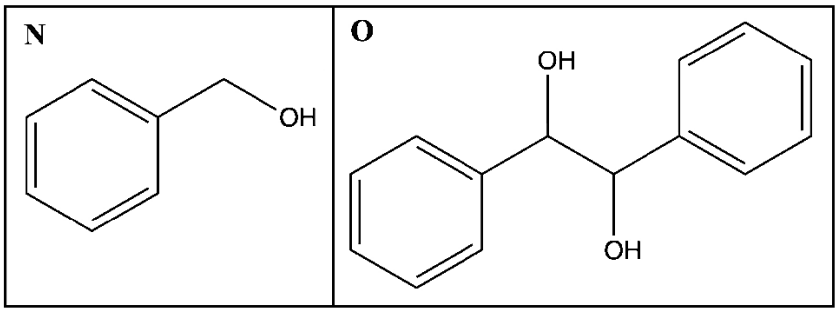


9.5 (a), (c).

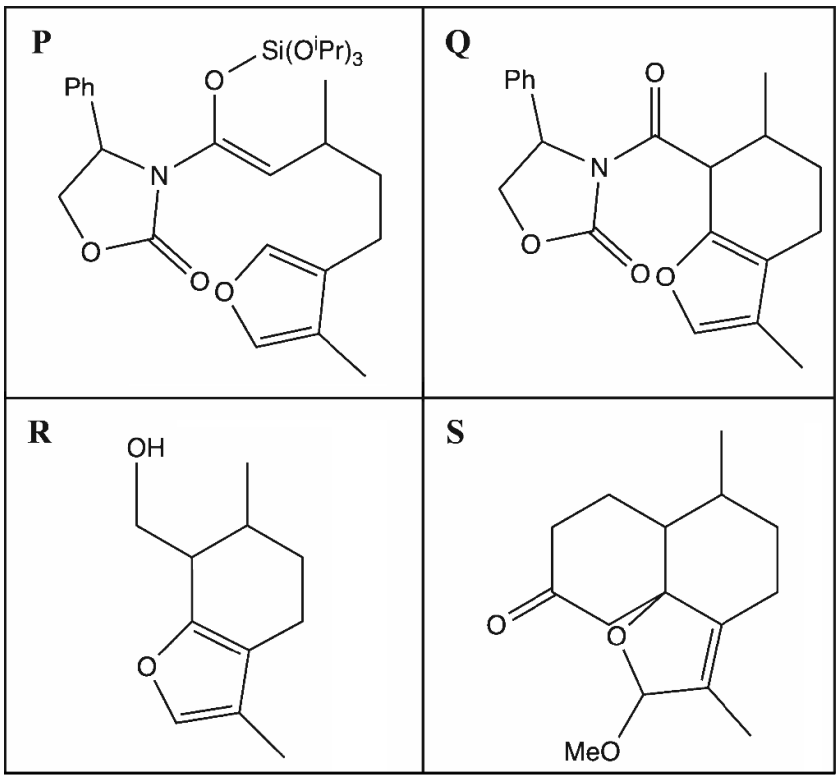


Specification "+ enantiomer" is not necessary.

9.6



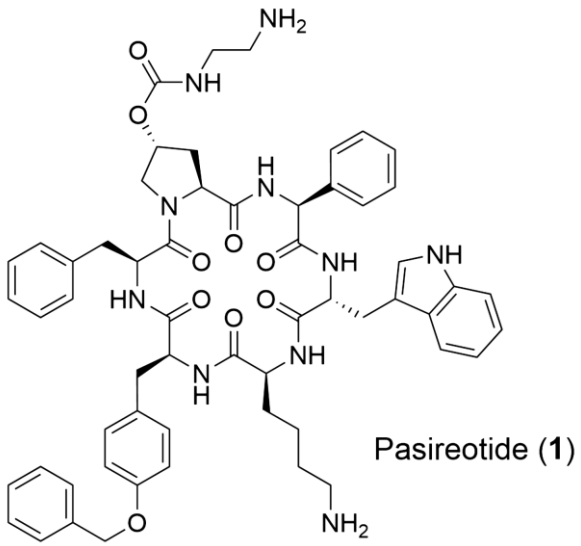
9.7



THEORETICAL PROBLEM 10

Switzerland — The Country of Pharmaceuticals

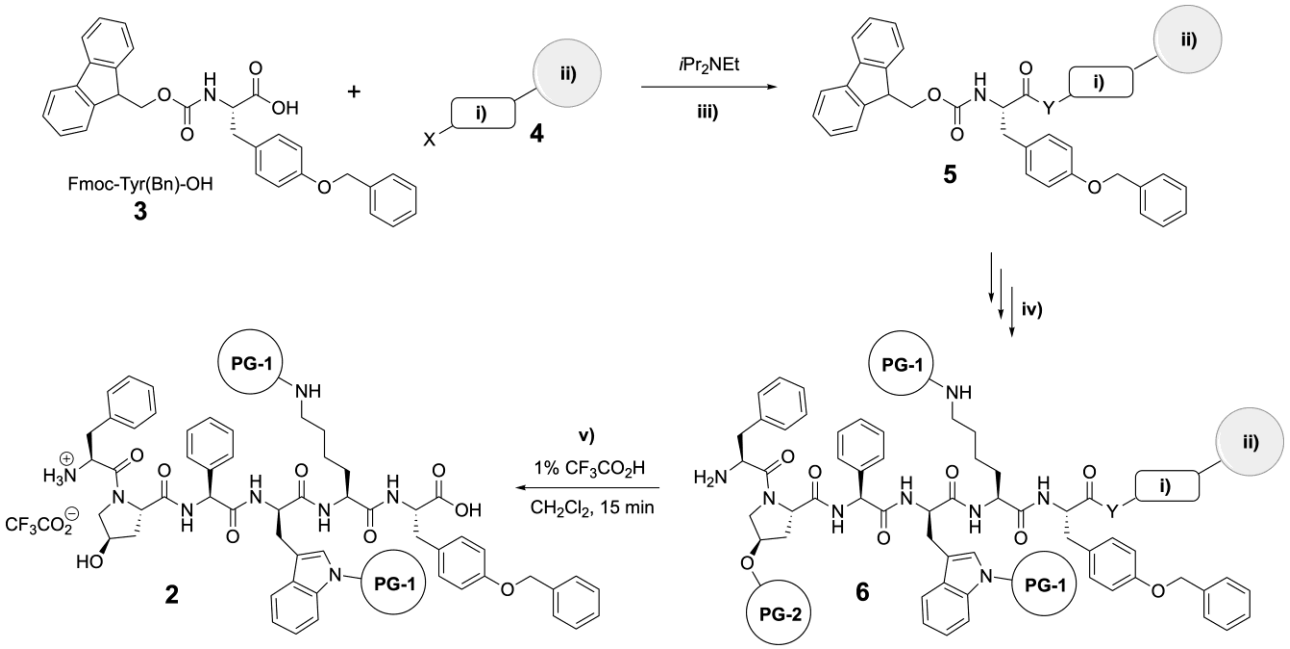
Pasireotide (**1**) is a peptide-based drug developed by the Swiss pharmaceutical company Novartis to treat the Cushing's disease.



Pasireotide (**1**)

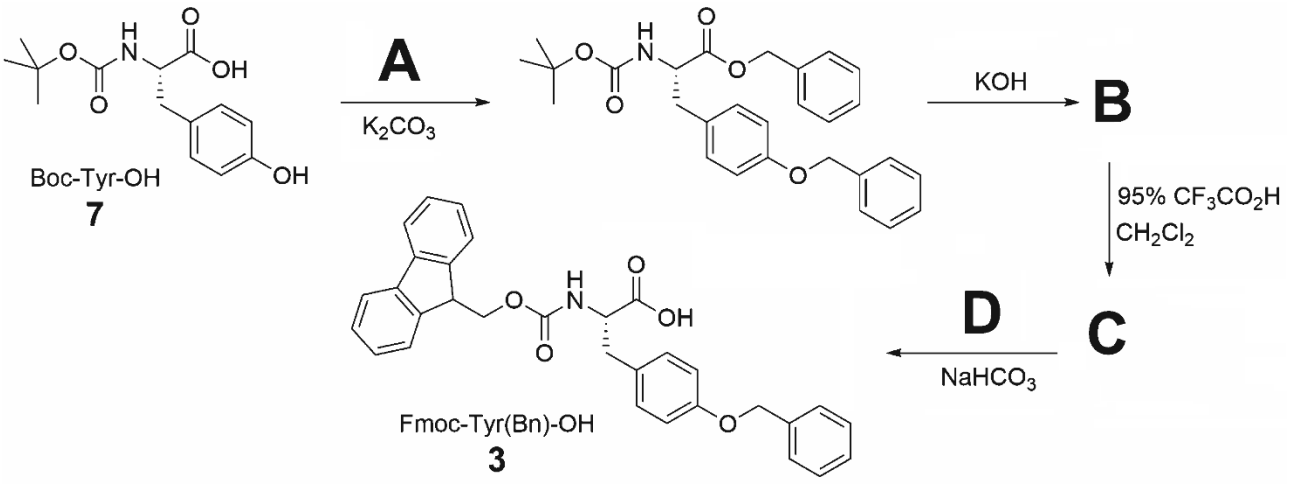
10.1 Determine the number of stereogenic centers (*n*) in Pasireotide (**1**). Calculate the total number of all possible stereoisomers (*t*).

Pasireotide (**1**) is a cyclic peptide. An advanced intermediate in its synthesis (linear peptide **2**) can be prepared by solid-phase peptide synthesis (SPPS) using the Fmoc/tBu strategy as shown in **Scheme 1**.



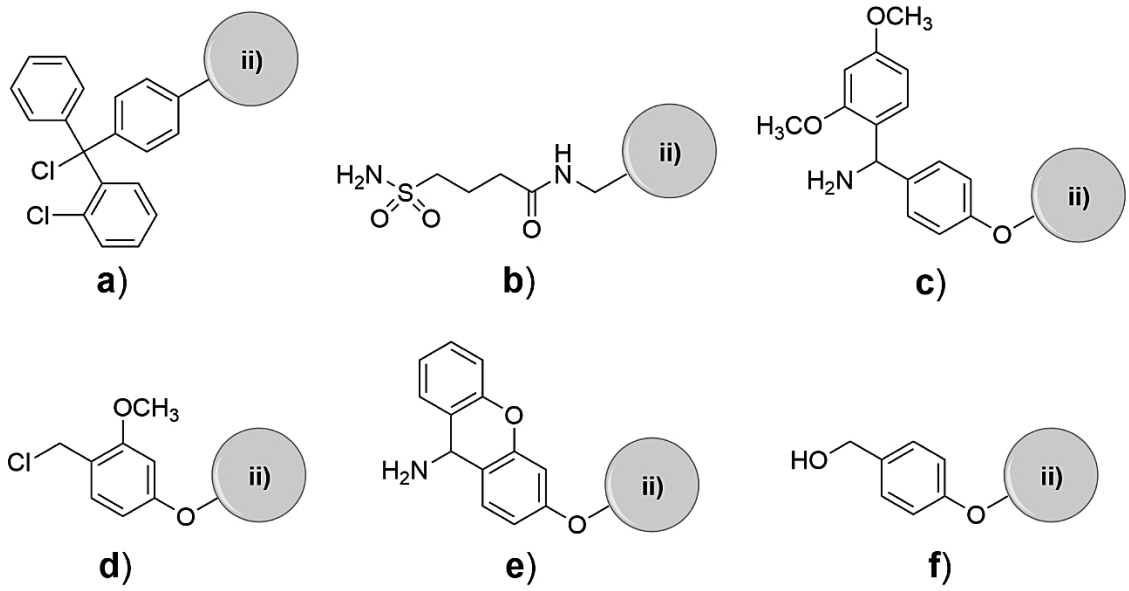
Scheme 1. SPPS of peptide **2**. i) Linker; ii) Resin; iii) Resin loading; iv) SPPS: repetition of 1. Fmoc deprotection 2. amino acid coupling + final Fmoc deprotection; v) Peptide cleavage from resin and deprotection of PG-2.

The synthesis starts with the preparation of Fmoc-Tyr(Bn)-OH (**3**) from Boc-Tyr-OH (**7**).



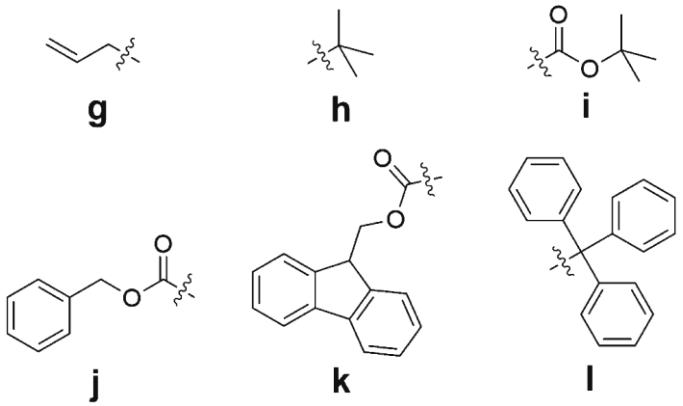
10.2 Draw reagents **A** and **D** and intermediates **B** and **C** in the synthesis of Fmoc-Tyr(Bn)-OH (3) as shown above.

The SPPS of intermediate **2** begins with attaching the Fmoc-Tyr(Bn)-OH (**3**) to a suitable resin-bound linker.



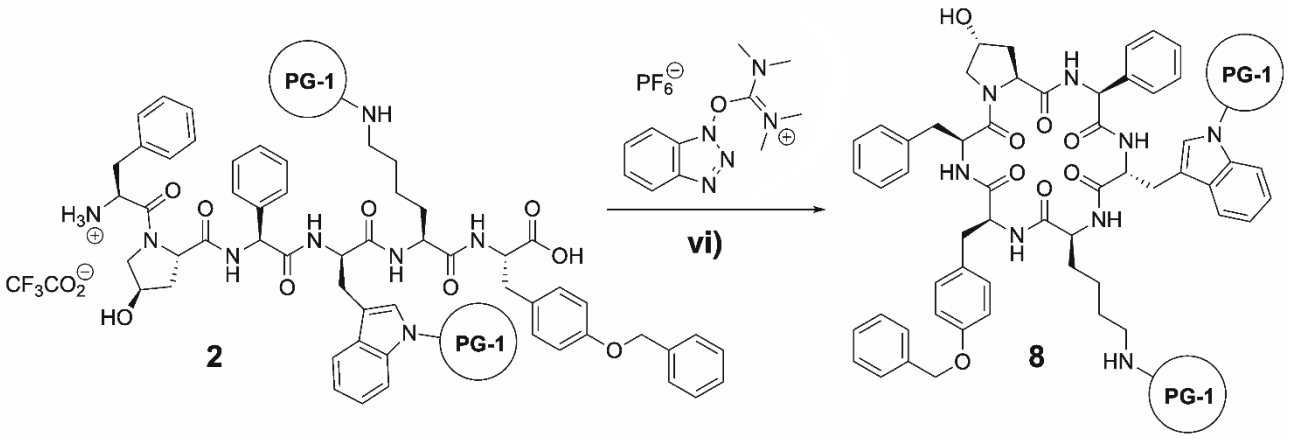
Scheme 2. ii) Resin; a) 2-Chlorotrityl-chloride linker; b) Safety-catch linker; c) Rink amide linker; d) SASRIN-chloride linker; e) Sieber amide linker; f) Wang linker

10.3 Choose the linker(s) **4** from **Scheme 2** that are appropriate for SPPS of peptide **2** according to **Scheme 1**.



10.4 From **g**–**l** choose the most suitable side-chain protecting groups **PG-1** and **PG-2** for SPPS of **2** according to **Scheme 1** that can be orthogonally cleaved in the presence of all other functional groups present in Pasireotide. Only one answer is correct for each of the protecting groups.

Next, linear peptide **2** undergoes an intramolecular coupling reaction to form cyclic peptide **8** according to the following scheme:



Scheme 3. vi) Base

10.5 Choose the correct statement(s) about the cyclization of peptide **2** to **8**.

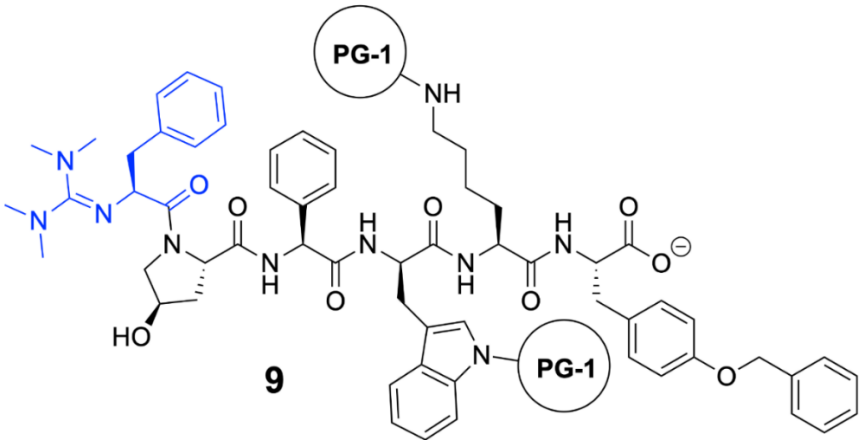
(a) A possible side-product of the reaction is tetramethylguanidylation of the *N*-terminal phenylalanine residue resulting in compound **9** shown below.

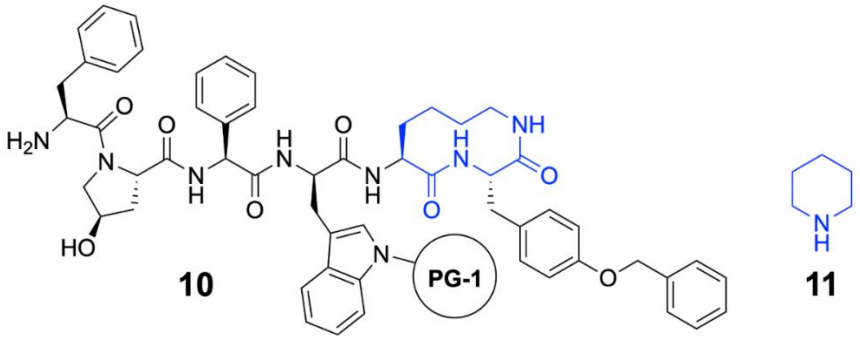
(b) A possible side-product of the reaction is the cleavage of protecting group **PG-1** and cyclization via the amino group of the lysine residue to give compound **10** shown below.

(c) The reaction must be carried out at a high peptide concentration to achieve a sufficient reaction rate.

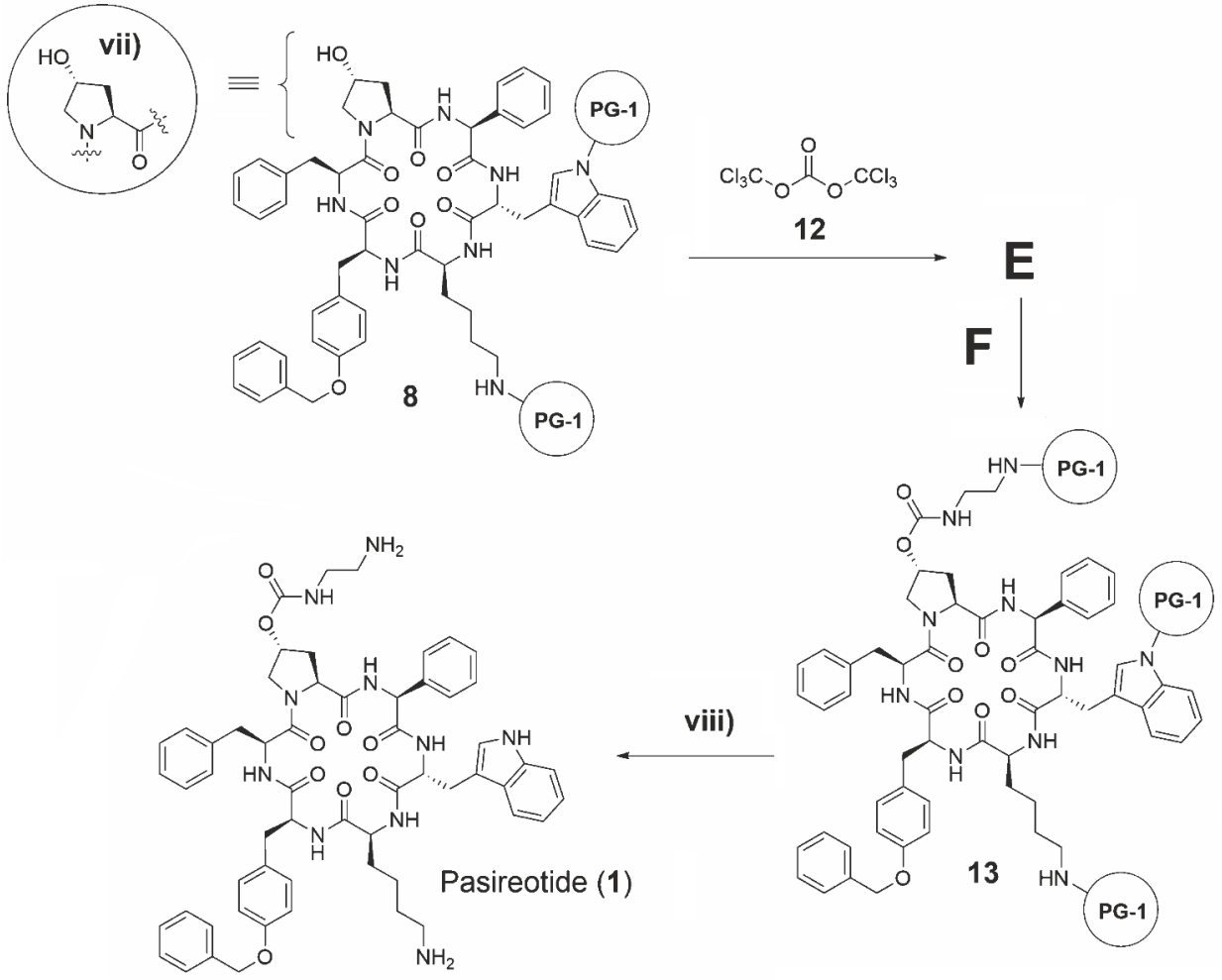
(d) The reaction must be carried out at a low peptide concentration to prevent polycondensation.

(e) Piperidine (**11**) below is a suitable base for the reaction.





The last steps of the synthesis involve functionalization of the OH-group of the 4-hydroxyproline residue in **8**, followed by cleavage of all PGs to give Pasireotide (**1**).



Scheme 4. vii) can be used as simplification of **8**; viii) Cleavage of protecting groups

10.6 Draw the structures of intermediate **E** (including stereochemistry) and reagent **F**. Abbreviate intermediate **8** as (**vii**) and the protecting group as **PG-1** in structures **E** and **F** as depicted in **Scheme 5**.

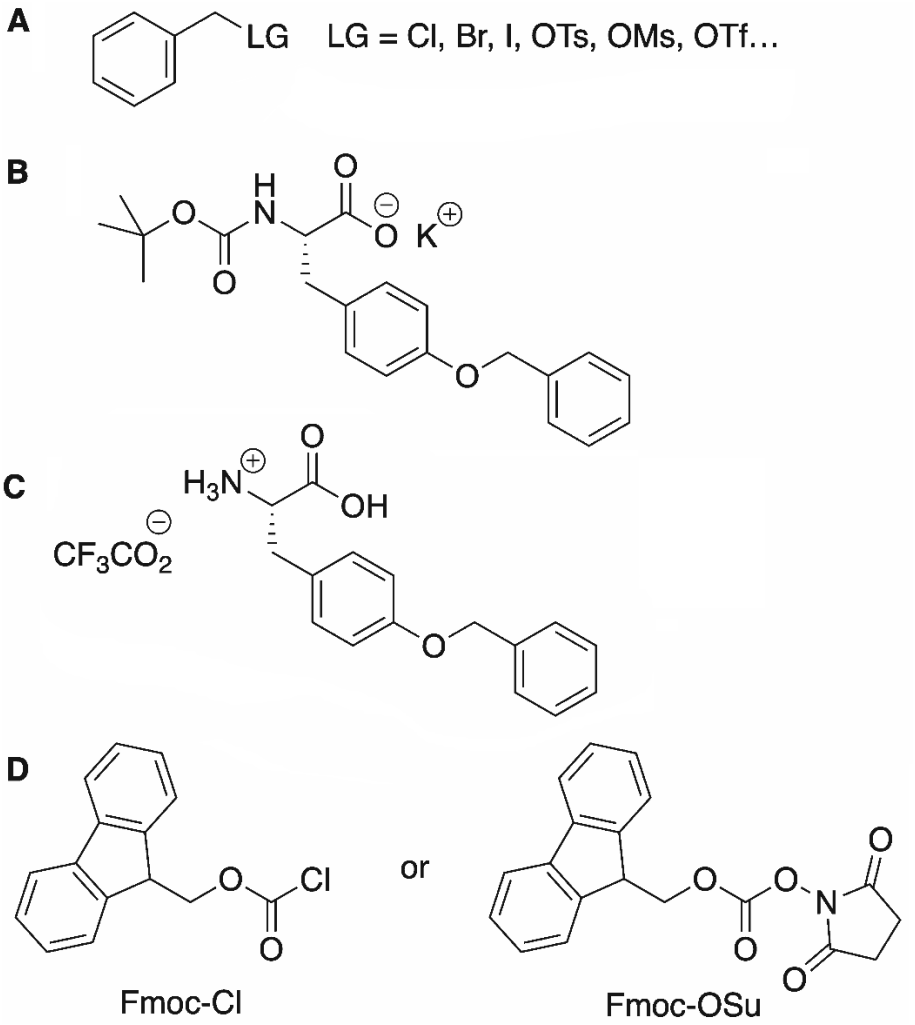
10.7 Determine the lowest possible molar equivalents of compound **12** that are necessary to enable full conversion of **8** to **13**.

SOLUTION OF THE PROBLEM 10

10.1 Number of stereogenic centers: $n = 7$.

In total $t = 2^n = 2^7 = 128$ stereoisomers.

10.2



10.3 (a), (d).

10.4 PG-1: (i); PG-2: (l).

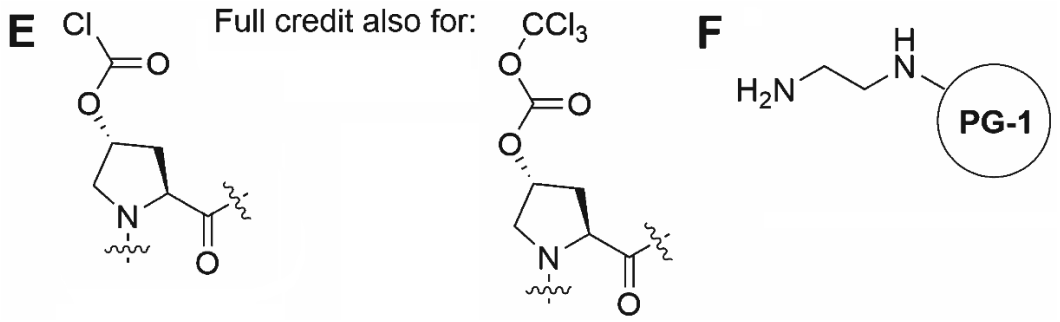
Reasoning for PG-1: (g) and (h) lead to 2° amines in the peptide — not compatible with Fmoc and the coupling conditions; (i) is stable in 1% TFA in CH_2Cl_2 and the correct answer; deprotection conditions of (j) are not orthogonal with Tyr(Bn) which is in the structure of peptide 1; (k) not stable to SPPS deprotection conditions; (l) is not stable in 1% TFA in CH_2Cl_2.

Reasoning for PG-2: Only (l) is cleavable in 1% TFA in CH_2Cl_2 and therefore the only correct answer.

10.5 (a), (d).

Reasoning for incorrect options. (b): PG-1 is stable under cyclization conditions and does not fall off. (c): At high concentrations, intermolecular reactions (undesired polycondensation) are favored over intramolecular reactions (desired cyclization). (e): Piperidine is a nucleophilic base and would compete with the N-terminal amino group for amidation of the C-terminus.

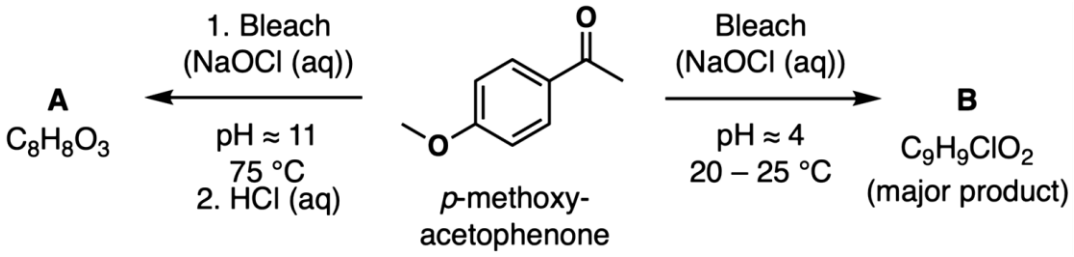
10.6



10.7 1/3 (0.33) equivalents.

PRACTICAL PROBLEM 1

Bleach, a Chameleonic Reagent



Chemicals

- CH_3COOH, 4 mL
- Eluent (C_6H_{14}/EtOAc, 80:20, *v*/*v*), 15 mL
- HCl, 2 M in H_2O, 25 mL
- *p*-Methoxyacetophenone, 2 × 500 mg
- $NaHSO_3$ (ca. 40% in H_2O), 8 mL
- NaOCl (ca. 14% in H_2O),
  - 7.5 mL for preparation of product A,
  - 4.0 mL for preparation of product B
- Na_2SO_4, ca. 5 g
- $C_6H_5CH_3$, 40 mL
- Distilled water
- NaOH (1 M in H_2O), 6.7 mL
- $(CH_3)_2CO$

Personal equipment

- Laboratory stand, 1
- Clamp with clamp holder, 4
- Magnetic stirrer with hotplate, 1
- Magnetic stir bar (rod-shaped, 2.5 cm), 2
- Magnetic stir bar (olive-shaped, 2 cm long, 1 cm thick), 1
- Water bath: crystallization dish (filled 1/3 with water, equipped with magnetic stir bar), 1
- Thermometer (0−100 °C), 1

– Round-bottom flask (50 mL), 2
– Vigreux column, 1
– Hose adapter, bent, connected to gas bubbler, 1
– Gas bubbler with hose, charged with trap solution (EtOH/aq. 1 M NaOH, 10:90, *v*/*v*), 1
– Graduated cylinder (10 mL), 1
– Graduated cylinder (50 mL), 1
– Erlenmeyer flask (50 mL), 1
– Suction flask (500 mL) with rubber protection sleeve and rubber gasket, connected to vacuum trap, 1
– Vacuum trap, connected to vacuum module, 1
– Glass filter crucible (8 mL), 1
– Separatory funnel (50 mL) with plastic stopper, 1
– Glass funnel, 1
– TLC elution chamber with lid, 1
– TLC plate, in the ziplock bag labeled “TLC + [student code]”, 3

Preparation of Product A

1. Turn on the magnetic stirrer hotplate and set the control knob between 100 °C and 150 °C in order to reach the desired water bath temperature of 70–80 °C. While stirring, control the temperature of the water bath with a thermometer clamped to the stand.

2. While the water bath is heating up, take a small sample (small spatula tip) of *p*-methoxyacetophenone from the vial labeled “**SM-A**”, transfer it to the vial labeled “**TLC-SM**” and set it aside for TLC analysis (to be carried out later).

3. To a 50 mL round-bottom flask, add a stir bar (olive-shaped), *p*-methoxyacetophenone (500 mg, entire content of the vial labeled “**SM-A**”, a weighing paper may be used for the transfer), NaOH(aq) (6.7 mL, entire content of the vial labeled “**NaOH(aq**)”), and bleach (7.5 mL, entire content of the vial labeled “**Bleach-A**”).

4. Clamp the flask to the stand and lower it into the water bath by adjusting the position of the clamp. Make sure the reaction mixture is stirring rapidly (ca. 750 rpm).

5. Attach a Vigreux column to the flask (**Figure 1**). To the top of the Vigreux column, attach the bent hose adapter which is connected via tubing to a gas bubbler (filled with a trap solution of NaOH in EtOH/H_2O). Secure the joint with a clip.

6. Let the reaction run at 70–80 °C for 60 minutes.

7. Turn off the heating, raise the flask above the water bath by adjusting the position of the clamps. Raise the technical assistance card for the removal of the water bath by an assistant. Allow the mixture to cool down while stirring and proceeding with the next steps.

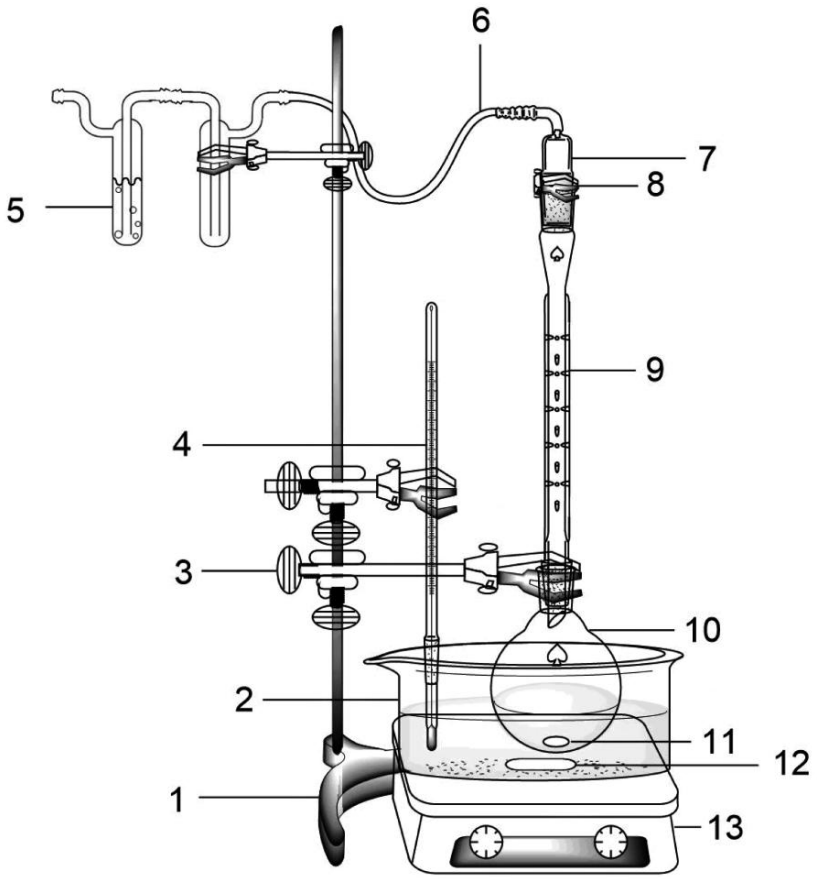


Figure 1. 1 = laboratory stand, 2 = water bath, 3 = clamp holder with clamp, 4 = thermometer, 5 = gas bubbler, 6 = tubing, 7 = hose adapter with inner ground glass joint, 8 = joint clip, 9 = Vigreux column, 10 = round-bottom flask, 11 and 12 = magnetic stir bar, 13 = magnetic stirrer with hotplate

8. Disconnect the gas bubbler from the Vigreux column by removing the bent hose adapter. Remove the Vigreux column (will be reused in the preparation of product **B**).

9. Ask a lab assistant for crushed ice and cool the reaction flask in an ice-water bath while stirring (ca. 5 minutes).

10. With the flask still in the ice-water bath, slowly add NaHSO3 solution (aq, 40 %) (ca. 5 mL from the vial "**$NaHSO_3$(aq)**"; 1 mL corresponds to ½ Pasteur pipette, see **Figure 2**) with a Pasteur pipette. Keep stirring. A white precipitate (product **A**) will form.

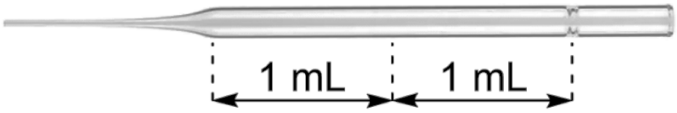


Figure 2. Pasteur pipette with approximate volume indications

11. Adjust the pH to 1–2 by adding 2 M HCl(aq) (ca. 6–8 mL, from the screw cap glass bottle labeled "**2M HCl(aq)**") with a Pasteur pipette. Check the pH of the solution, using pH indicator strips (for reference color pattern see **Figure 3**). To do so, withdraw a small aliquot of the reaction mixture with a fresh Pasteur pipette and drip a drop onto a pH indicator strip, do not dip the strips into the reaction mixture. Continue adding HCl until pH ≈ 1–2, then stop.

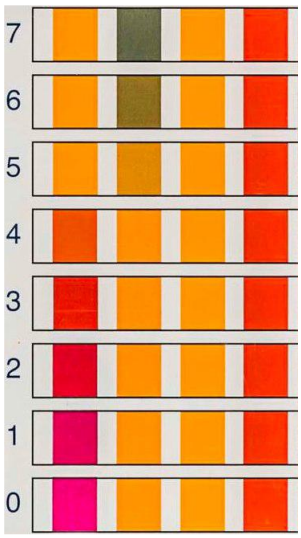


Figure 3. Color scale for pH determination by visual comparison with the reaction zones on the indicator strips. All four reaction zones on the pH paper strip have to match the color scale at the given pH. The pH values are the numbers indicated on the left. You may ask your lab assistant to see the commercial product with the color scale printed on it.

12. Ask a lab assistant for a magnetic stir bar remover, turn off the stirrer and remove the stir bar from the flask. Clean the stir bar by rinsing it first with water (→ "**Waste (aq)**"), then with acetone (→ "**Waste (org)**") and dry it with a paper towel. It will be reused later.
13. Set up a vacuum filtration apparatus: Clamp the suction flask to the laboratory stand and make sure the conical rubber gasket is sitting on the rubber protection sleeve (**Figure 4**).
14. Place the glass filter crucible onto the conical rubber gasket. Make sure it fits tightly.

15. Apply vacuum and pour the suspension of the solid to be filtered into the glass filter crucible. Depending on the amount of liquid, this needs to be done portion-wise.

16. Wash the solid thoroughly with water (2 × 10 mL; a measuring cylinder may be used).

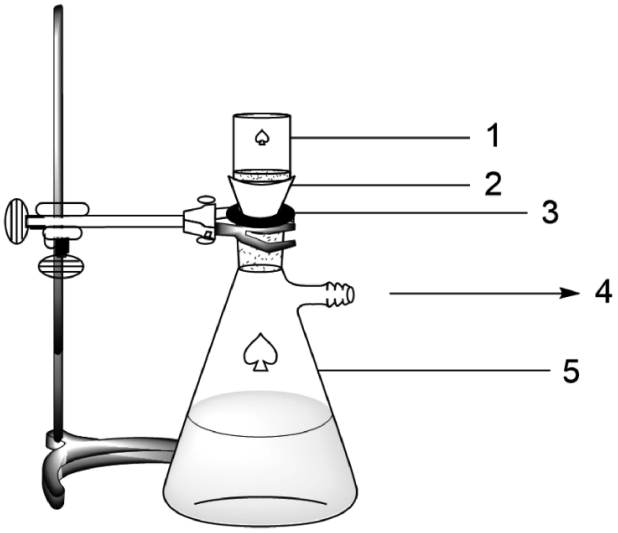


Figure 4. 1 = Glass filter crucible, 2 = conical rubber gasket, 3 = rubber protection sleeve, 4 = towards vacuum, 5 = suction flask

17. Let air suck through the precipitate to remove most of the water (no more than 10 minutes), then turn off the vacuum and disconnect the vacuum source.

18. Set aside a small sample (1 small spatula tip) of product A in the glass vial labeled "TLC-A" for thin layer chromatography (TLC) analysis (to be carried out later).

19. Transfer the product from the glass filter crucible to the vial labeled "**Product A + [student code]**" with a spatula.

20. Cap the vial labeled "**Product A + [student code]**". At the end of the exam, it will be picked up by your lab assistant.

21. Dispose of the filtrate (suction flask) in the "**Waste (aq)**" bottle.

Preparation of product B

1. Take a fresh 50 mL round-bottom flask, add a magnetic stir bar (olive-shaped) and clamp the flask to the stand.

2. Add *p*-methoxyacetophenone (500 mg, entire content of the vial "**SM-B**", a weighing paper may be used for the transfer) and glacial acetic acid (4 mL, entire content of the vial "**AcOH**") to the flask.

3. While stirring, add bleach (4.0 mL, entire content of the vial "**Bleach-B**") dropwise over

a period of 1–2 minutes, using a Pasteur pipette.

4. Attach a Vigreux column to the flask.
5. Rapidly stir the reaction (750 rpm) at room temperature for 45 minutes.
6. Remove the Vigreux column and dropwise add aqueous sodium bisulfite solution (40 %) (ca. 3 mL, remaining content of the vial "**$NaHSO_3$(aq)**") to the mixture over a period of 1 minute, using a Pasteur pipette. The mixture warms up during the addition.
7. Ask a lab assistant for a magnetic stir bar remover, turn off the stirrer and remove the stir bar from the flask.
8. Clamp a 50 mL separatory funnel to the stand. Add 10 mL of water (a measuring cylinder may be used).
9. Pour the reaction mixture from the round-bottom flask via a glass funnel into the separatory funnel.
10. Add toluene (ca. 10 mL, from the screw cap bottle "**Toluene**"; a measuring cylinder may be used), then remove the funnel.
11. Seal the separatory funnel with a stopper and shake it vigorously for a while. Make sure to interrupt shaking and to vent the funnel from time to time, with its spout pointing away from yourself and others.
12. Stop shaking, vent the funnel one more time, then clamp it to the stand. Remove the stopper and let the layers separate.
13. Drain the lower (aqueous) layer into the used reaction flask (round-bottom flask). Pour the top (organic) layer containing product B into a 50 mL Erlenmeyer flask.
14. Extract the aqueous phase two more times with toluene by repeating steps 9 to 13 twice. Collect the organic extracts in the same Erlenmeyer flask.
15. Rinse the glass funnel with acetone (→ "**Waste (org)**") and let it dry.
16. Add sodium sulfate (entire content of the vial "**Na_2SO_4**") to the Erlenmeyer flask with the combined organic extracts. Add a stir bar (rod-shaped) and stir the suspension for 3 minutes on the magnetic stirrer, then turn off the stirrer.
17. Let the glass funnel sit on a clamp have its spout protrude into the volumetric flask labeled "**Product B**". Place a filter paper into the glass funnel and wet it with a small amount of toluene using a Pasteur pipette.

18. Filter the contents of the Erlenmeyer flask into the volumetric flask "**Product B**" (the solution does not reach the mark). Rinse the Erlenmeyer flask with toluene (ca. 5 mL), using the same Pasteur pipette, and pour the solvent into the filter.
19. With a Pasteur pipette, transfer 4 drops of "**Product B**" solution into the vial "**TLC-B**".
20. Stopper the volumetric flask. At the end of the exam, it will be picked up by lab assistant. Dispose of the aqueous phase collected in the reaction flask (→ "**Waste (aq)**").

Thin Layer Chromatography (TLC) Analysis

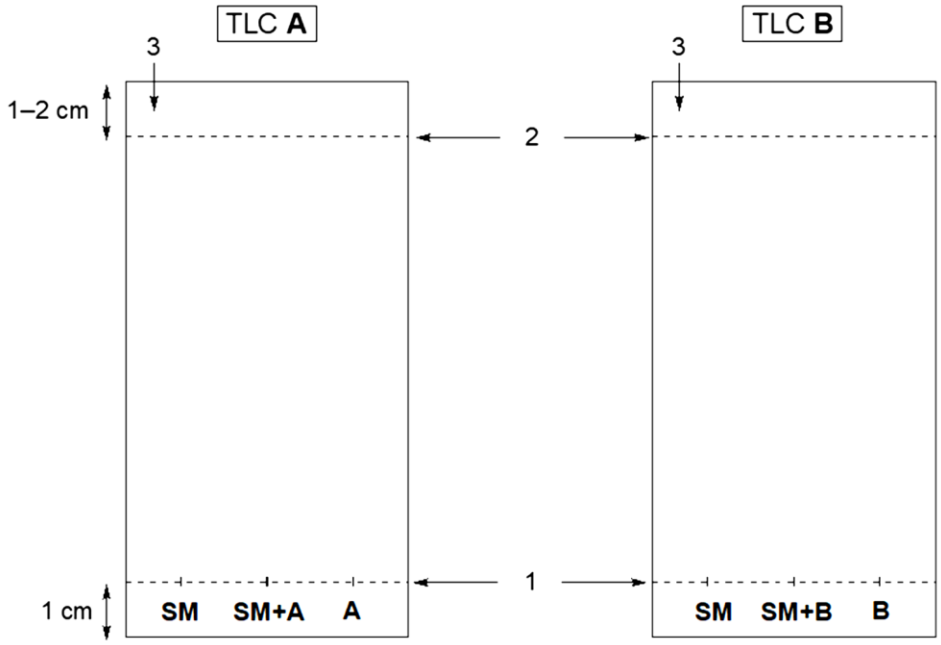


Figure 5. SM = starting material = *p*-methoxyacetophenone, **A** = product A, **SM+A** = co-spot of starting material and product A, **B** = product B, **SM+B** = co-spot of starting material and product B, 1 = starting line, 2 = front line, 3 = position to write down your student code.

1. Prepare the elution chamber: Load it to a level of ca. 0.5 cm with the eluent (mixture hexane/EtOAc in a 80:20 ratio, screw cap bottle "**Eluent**") and cover it with the lid. If necessary, you can get extra eluent from your lab assistant without penalty.
2. Prepare your samples: Using a Pasteur pipette, add ca. 0.5 mL of eluent to each of the vials "**TLCSM**", "**TLC-A**", and "**TLC-B**" to dissolve/dilute the respective samples. Cap the vial "**TLC-A**" and shake it (ca. 0.5 minute) for faster dissolution.
3. Prepare a TLC plate (stationary phase: SiO_2 on aluminum) for the analysis of product A (**Figure 5**, left): With pencil and ruler, draw the starting line ca. 1 cm above the bottom of the plate and mark the positions to spot 3 samples. Label them "**SM**" =

starting material = *p*-methoxyacetophenone, "**A**" = product A, and "**SM+A**" = mixture (co-spot) of SM and product A. On the top left of the plate, write down your Student Code.

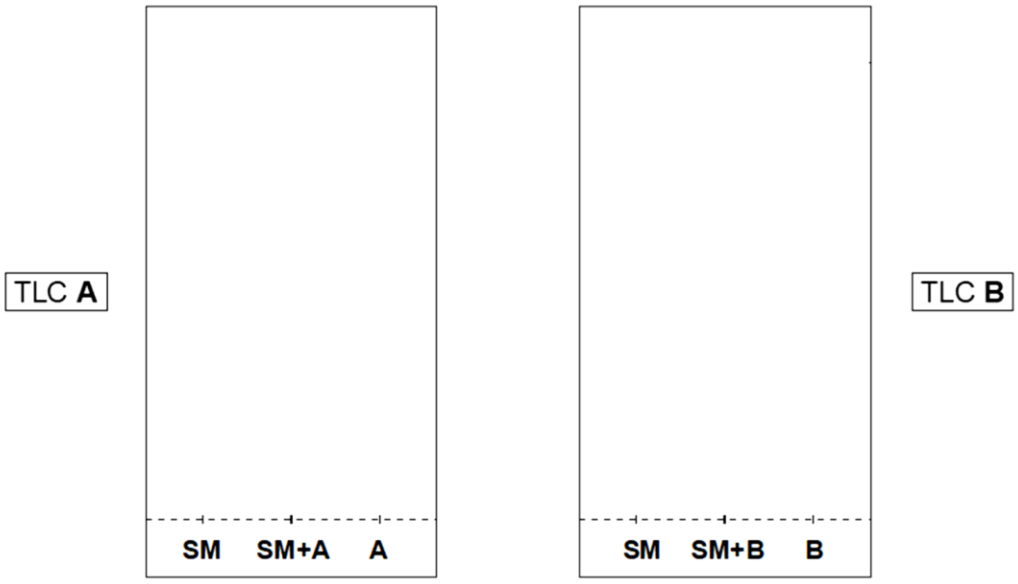
4. Similarly prepare another TLC plate for the analysis of product B (**Figure 5**, right).

5. Using capillary spotters, spot the two TLC plates on the starting line according to the labeling just done (**Figure 5**). Use a different capillary for each sample. Wait until the solvents have evaporated and the spots are dry.

6. Develop the TLC plates (either simultaneously or one after the other): Using tweezers, insert the TLC plate(s) into the elution chamber and cover it with the lid. Let the eluent reach a level of 1–2 cm below the top of each plate. Remove the lid and, using tweezers, remove the plate(s) from the chamber. Mark the eluent front gently with a pencil and let the plate(s) air-dry.

7. Visualize the dry TLC plates under the UV lamp kept on a common bench. With a pencil, gently circle all visible spots.

8. Complete the templates on the answer sheet by sketching in the spots observed under the UV light. Use these sketches to answer the TLC-related questions.



9. Carefully place your dry TLC plates into the zip lock bag with your student code. Avoid the plates scratching each other.

10. Have the following items ready to be picked up by your lab assistant:
    - The glass vial and the volumetric flask with your products. They are labeled with your student code and the designation of the respective product ("**Product A**" and

"**Product B**").

- A zipped bag labeled with your student code and containing the two TLC plates (TLC analysis of products A and B).

Note added post festum:

The elaboration of the present exam question was inspired by the following publication: C. E. Ballard, *J. Chem. Educ.* **2010**, *87*, 190. The yields of products A and B were determined by 1H-NMR spectroscopy and gas chromatography (GC), respectively, using internal standards.

Questions

1.1 Answer questions a–d based on the above sketch of your TLC plates (stationary phase: SiO_2 on aluminum; eluent: hexane/EtOAc 80:20).

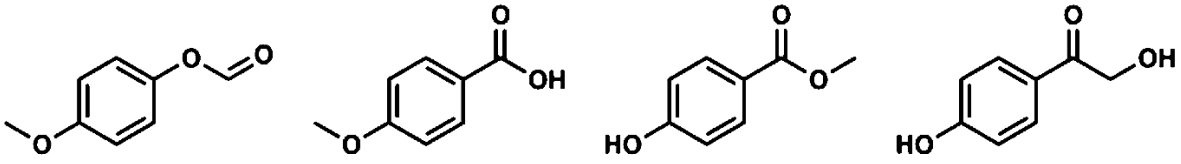
(a) Which of the two products is more polar, **A** or **B**?

(b) Which of the following two compounds is more polar, product **A** or the starting material (**SM**)?

(c) Does your product **A** contain some remaining starting material?

(d) Does your product **B** contain some remaining starting material?

1.2 Identify the structure of product **A** (empirical formula $C_8H_8O_3$).



☐ 1 ☐ 2 ☐ 3 ☐ 4

1.3 As apparent from the empirical formula of product **A** ($C_8H_8O_3$), a C_1 fragment is cleaved off the starting molecule ($C_9H_{10}O_2$) in the course of the formation of **A**. After the reaction, the C_1 fragment ends up containing chlorine. Identify its structure.

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
1	2	3	4

1.4 The formation of product **A** is a redox reaction.

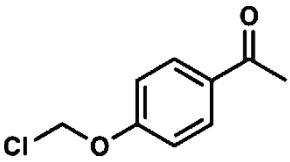
(a) In this reaction, which element is affected by an increase in oxidation number?

C	H_2	O	Cl
1	2	3	4

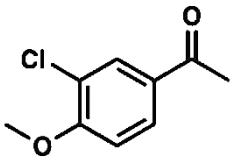
(b) In this reaction, which element is affected by a decrease in oxidation number?

C	H_2	O	Cl
1	2	3	4

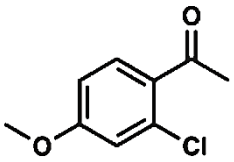
1.5 Identify the structure of product **B** (empirical formula $C_9H_9ClO_2$).



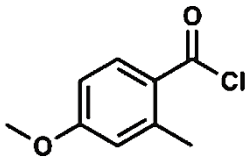
☐ 1



☐ 2



☐ 3



☐ 4

1.6 At some point in the synthesis of product **B**, $NaHSO_3$ (aq) is added to the reaction mixture. While serving its purpose, hydrogensulfite HSO_3^- undergoes a chemical reaction. What is the resulting sulfur-containing species? Choose the correct answer. Note that this question is not aimed at the protonation state of the resulting S-containing species (acid-base equilibria are ignored here).

HS^-	S_8	$HS_2O_3^-$	HSO_4^-
1	2	3	4

SOLUTION OF THE PROBLEM 1

1.1 (a) and (b): product **A** is more polar.

(c) and (d): answer depends on TLC sketch.

1.2 2 (*p*-methoxybenzoic acid)

1.3 3 (chloroform)

1.4 a: 1 (carbon); b: 4 (chlorine)

1.5 2 (1-(3-Chloro-4-methoxyphenyl)ethan-1-one)

1.6 4 (hydrogensulfate)

Practical problem 2

Titration Tango

Introduction

Iron was historically mined and processed in 19 Swiss cantons, meeting local and regional demand. Evidence of this activity remains, particularly in the Swiss Jura. To produce iron and steel efficiently, knowledge of the composition of the iron ore is essential. A versatile method to analyze any metal in solution is the complexometric titration, pioneered by Prof. Gerold Schwarzenbach at ETH in the 1940s. You are provided with a sample containing only hydrates of $FeCl_3$ and $CaCl_2$, dissolved in aqueous HCl. This simulates an iron ore sample, which has been digested with hydrochloric acid. Your task is to determine the iron concentration and the overall composition of the sample by complexometric titrations.
Any aqueous waste of this task should be collected in the beaker labelled "**Waste P2**".

Chemicals

- $CaCl_2 \cdot 2H_2O$(s)
- Distilled water
- EDTA standard solution (10.0 mM), 500 mL
- 0.1 M HCl (10 mL)
- Sample (mixture), dissolved in HCl, pH = 1
- Eriochrome® Black T (solid mixture, 1 % wt. in NaCl), 1 g
- Variamine Blue (solid mixture, 1 % wt. in NaCl), 1 g
- Schwarzenbach buffer (pH = 10, $c_{HB+} + c_B$ = 8.8 M), 10 mL
- Ethanol, 200 mL

Personal equipment

- 20 mL vial, 6
- Volumetric flask (100 mL), 1
- Volumetric flask (250 mL), 1
- Small funnel, fitting the burette, 1
- Spatula, 1
- Erlenmeyer flask (300 mL), 3

– Volumetric pipette (5.0 mL), 1
– Pipette bulb, 1
– Graduated cylinder (50 mL), 1
– Glass Pasteur pipette, 4
– Burette (50 mL), 1
– Laboratory stand with burette holder, 1
– PE bottle (500 mL), labeled “EDTA”, 1
– Bottle (250 mL), labeled “EtOH”), 1
– Beaker (50 mL), 1
– Volumetric pipette (20.0 mL), 1
– Beaker (1000 mL), labeled “Waste (P2)”, 1

Procedure

Part I. Dilution of Unknown Iron Ore Sample

1. You are given a sample of ca. 1200 mg of simulated iron ore. The exact mass is written on the label of your vial. Report it in your Answer Sheet. The sample has already been dissolved in aqueous HCl of pH 1.
2. Prepare 100 mL of sample solution in the 100 mL volumetric flask using the whole content from the vial labelled "Sample + [student code]" and distilled water. You may use a funnel. This solution is called **A**. This solution will be used in Part II and IV.

Part II. Direct Titration of Iron Ore Solution

3. Fill the burette with 10.0 mM EDTA solution, labelled as "**EDTA**". You may use a funnel and a beaker.
4. In a 300 mL Erlenmeyer flask:
   • Add 5.00 mL of solution **A** using a volumetric pipette;
   • Add 10 drops of 0.1 M hydrochloric acid using a glass Pasteur pipette;
   • Fill up to the 100 mL mark of your Erlenmeyer flask with distilled water;
   • Add a small amount of Variamine Blue using a spatula.
5. Titrate the content of the Erlenmeyer flask until the solution becomes yellow. Record the titration volume V_1.
6. Discard the titrated content of the Erlenmeyer flask in the beaker labelled “**Waste P2**”.
7. Repeat the procedure (steps 3–6) as needed.

8. Report your final result in the last row of the table.

Analysis #	V_1**/mL**
1	
2	
…	
Reported value V_1**/mL**	

Part III. Titer preparation

9. You are given a sample of ca. 550 mg of pure calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$). The exact mass is written on the label of your vial. Report it in the table in your Answer Sheet.

10. Prepare 250 mL of calcium chloride solution in the 250 mL volumetric flask using the whole sample of solid $CaCl_2 \cdot 2H_2O$ (M = 147.0 g mol^{-1}) and distilled water. You may need a funnel to transfer the solid. This solution is called **B**. It will be used in part IV.

***m*(CaCl₂ · 2H₂O)/mg (Report the value on the label)**	

Part IV. Indirect Titration of Iron Ore Solution

11. Empty the burette. Rinse the burette well with distilled water and then with solution **B**. You may use a beaker. Discard the rinse solutions in the beaker labelled "**Waste P2**".

12. Fill the burette with solution **B**. You may use a funnel and a beaker.

13. In a 300 mL Erlenmeyer flask, add:
    - 5.00 mL of solution **A** using a volumetric pipette;
    - 40.0 mL of 10.0 mM EDTA solution, labelled as "**EDTA**", using a volumetric pipette;
    - 10 drops of buffer solution using a glass Pasteur pipette (be careful when opening the buffer solution, as there can be evolution of ammonia);
    - 25 mL of distilled water using a graduated cylinder;
    - 30 mL of ethanol using a graduated cylinder.

    Your sample may be turbid.

14. To the 300 mL Erlenmeyer flask, add a small amount of Eriochrome® Black T, from the vial labelled with "**Erio T**". Your sample should now be intense blue-green. Perform the titration immediately after the addition of the indicator.

    Note: After addition of the indicator, the color will change to red after several minutes, regardless of the progress of the titration. At that point, the titration endpoint is no

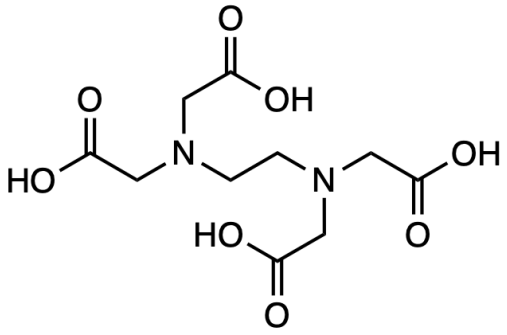
longer detectable.

15. Titrate the content of the Erlenmeyer flask until the solution turns grey. Record the titration volume V_2. Your expected volume is below 15 mL.
16. Discard the titrated content of the Erlenmeyer flask in the beaker labelled "**Waste P2**".
17. Repeat the procedure (steps 12–16) as needed.
18. Report your final result in the last row of the table.

Analysis #	**V_2/mL**
1	
2	
…	
Reported value V_2/mL	

Questions

2.1 Provide the chemical formula of the resulting EDTA complex formed in the direct titration up to the equivalence point. The structure of EDTA is given below. In your chemical formula, abbreviate EDTA as "**H_4Y**", its conjugate bases as "**H_3Y^-**", "**H_2Y^{2-}**" etc. *Hint: Under these conditions, one of the metal ions in solution preferentially forms an EDTA complex.*



Structure of EDTA (equivalent to **H_4Y**)

2.2 Calculate the mass percentage of iron(III) chloride (without water of crystallization), in % wt., of the provided sample. The molar mass of $FeCl_3$ is 162.2 g mol^{-1}.

2.3 Calculate the mass percentage of calcium chloride (without water of crystallization), in % wt., of the provided sample. The molar mass of $CaCl_2$ is 111.0 g mol^{-1}.

2.4 Calculate the mass percentage of water of crystallization, % wt., of the provided sample.

2.5 Why is it necessary to keep the sample solution **A** at pH < 2?

(a) To chemically stabilize Ca^{2+} in solution.

(b) To chemically stabilize Fe^{3+} in solution.

(c) To reduce Ca^{2+} in solution.

(d) To reduce Fe^{3+} in solution.

2.6 The solution you were given simulates the digestion of iron ore with concentrated HCl. Which of the following mixtures could be analyzed by the same procedure?

(a) Hematite (Fe_2O_3) + Limestone ($CaCO_3$).

(b) Magnetite (Fe_3O_4) + Chalcopyrite ($CuFeS_2$).

(c) Ilmenite ($FeTiO_3$) + Goethite ($FeO(OH)$).

(d) Siderite ($FeCO_3$) + Dolomite ($CaMg(CO_3)_2$).

2.7 Why does the sample for the indirect titration show a color change from blue to red regardless of the progress of the titration?

(a) Reduction of Fe^{3+} EDTA complex by ethanol.

(b) Hydrolysis of Eriochrome® Black T under basic conditions.

(c) Irreversible ligand exchange of Fe^{3+} EDTA complex by Eriochrome® Black T.

(d) Eriochrome® Black T adsorption onto precipitated $CaCO_3$.

SOLUTION OF THE PROBLEM 2

2.1 Complex formula: $[FeY]^-$

2.2

$$c_{\text{sample}}(Fe^{3+}) = \frac{V_1}{V_{\text{sample,aliquot}}(Fe^{3+})} c(\text{EDTA})$$

$$n_{\text{sample}}(Fe^{3+}) = c_{\text{sample}}(Fe^{3+}) V_{\text{sample}}(Fe^{3+})$$

$$m_{\text{sample}}(FeCl_3) = n_{\text{sample}}(Fe^{3+}) M(FeCl_3)$$

$$w(FeCl_3) = \frac{m_{\text{sample}}(FeCl_3)}{m_{\text{sample}}} \cdot 100\ \%$$

2.3

$$c_{\text{sample}}(Ca^{2+}) = \frac{[c(\text{EDTA}) V_{\text{ex}}(\text{EDTA}) - c_{\text{sample}}(Fe^{3+}) V_{\text{sample,aliquot}} - c_{\text{std}}(Ca^{2+}) V_2]}{V_{\text{sample,aliquot}}}$$

$$n_{\text{sample}}(Ca^{2+}) = c_{\text{sample}}(Ca^{2+}) V_{\text{sample}}(Ca^{2+})$$

$$m_{\text{sample}}(CaCl_2) = n_{\text{sample}}(Ca^{2+}) M(CaCl_2)$$

$$w(CaCl_2) = \frac{m_{\text{sample}}(CaCl_2)}{m_{\text{sample}}} \cdot 100\ \%$$

2.4 $w(H_2O) = 100\% - w(CaCl_2) - w(FeCl_3)$

2.5 (b). *Reasoning: $[Fe(H_2O)_6]^{3+}$ is a weak acid which give off a proton yielding $[Fe(H_2O)_5(OH)]^{2+}$ which is unstable and results in the precipitation of FeOOH.*

2.6 (a). *Reasoning: Both magnetite and siderite contain Iron(II), which first needs to be fully oxidized to iron(III) to be able to quantify it with the given method. Using indirect titration to determine the amount of bivalent cations, any bivalent cations, which form stronger EDTA complexes than Ca^{2+} can be determined. This is the case for Cu^{2+}, TiO^{2+} and Zn^{2+} but not for Mg^{2+}. The titanium content will not dissolve. Thus, the correct choice is hematite + limestone.*

2.7 (c). *Reasoning:* Reduction of Fe^{3+} EDTA complex by ethanol can be excluded since ethanol is not easily oxidized. Hydrolysis of the indicator under basic conditions can be excluded from the observations in the standardization procedure. Indicator adsorption onto precipitated $CaCO_3$ can be excluded since the samples are free of CO_2 and the absorption from air is slow. This leaves only one option. In fact, the indicator builds a strong enough complex with Fe^{3+} to complete with EDTA. The addition of an organic solvent kinetically inhibits this competition.

PRACTICAL PROBLEM 3

Beauty in simplicity

Introduction

You are provided with 6 solutions **S1**–**S6** of unknown composition. Your task is to identify all cations and anions dissolved in these solutions.

Chemicals

– Solutions **S1**–**S6** (liquid)

Personal equipment

– Bottle (100 mL), labeled "**Waste (P3)**", 1
– Sample vials (20 mL), labeled "**S1–S6** + **[student code]**", 6
– Test tubes, 18
– Glass Pasteur pipettes, 10
– Test tube rack, 1

Hints:

- There are 7 cations and 7 anions which have been dissolved in aqueous solutions S1–S6 from the list:
  – Cations: Ag^+, Ba^{2+}, Ca^{2+}, Fe^{3+}, K^+, Mn^{2+}, Na^+;
  – Anions: CH_3COO^-, Cl^-, I^-, NO_3^-, PO_4^{3-}, S^{2-}, SO_4^{2-}.
- 2 or 3 ions in total were introduced into each solution.
- Each of the ions was introduced only into one solution.
- Na^+ and K^+ are present together in the same solution.
- In some cases, it might take up to 15 minutes before a visible change occurs; fill in the table in Question 3.1 with your final observations.
- Some solutions can get colored or attain some precipitate due to oxidation under air.

Questions

3.1 Perform the cross-reactions between solutions **S1**–**S6**. Fill in the first table of your answer sheet with your observations using these symbols:

- "↓" for precipitation,
- "↑" for gas evolution,
- "S" for colour change of the solution,
- "–" if there are no visible observations.

Report on the colors of the precipitates using the following letters:

- "W" for white/colorless,
- "B" for black,
- "C" for colored.

3.2 Based on your observations and the hints, identify the ions in **S1**–**S6**.

3.3 In the third table of your answer sheet, write the ionic equations of the performed reactions that explain your observations. Use "↓" for precipitates and "↑" for gases.

SOLUTION OF THE PROBLEM 3

3.1 Observations:

Solutions	**S2**	**S3**	**S4**	**S5**	**S6**
S1	C↓ yellowish	C↓ or W↓ pale yellow	W↓ white	C↓ or W↓ beige	W↓ white
S2	×	W↓ white	B↓ black	B↓ metallic, black	C↓ pale yellow
S3	×	×	C↓ or B↓ dark brown, black	S red-brown	S brown
S4	×	×	×	C↓ or W↓ beige	W↓ white
S5	×	×	×	×	W↓ white

3.2 The following ions usually are colored in aqueous solutions: Fe^{3+} (yellow/orange), Mn^{2+} (pinkish in concentrated solutions). Solution **S3** has intense yellow-orange color, while solutions **S4** and **S6** can be also slightly yellow; thus, one of them contains Fe^{3+}. (The coloring of the other two solutions might come from the oxidation of the corresponding iodide and sulfide anions.) The only possible anions for the solution with Fe^{3+} are Cl^-, NO_3^-, SO_4^{2-}, while PO_4^{3-}, and S^{2-} anions give insoluble products with Fe^{3+}, I^- gets oxidized to I_2 and CH_3COO^- forms a distinctly red complex. Only solution **S3** forms dark brown precipitate with **S4**, intense red-brown solution with **S5** and brown solution with **S6**. These observations are consistent with the presence of Fe^{3+} in **S3** and S^{2-} in **S4**. Solutions **S5** and **S6**, therefore, should contain CH_3COO^- and I^-. **S4** containing S^{2-} can form another black precipitate only with Ag^+ in **S2**.

Solutions	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Cations		Ag^+	Fe^{3+}			
Anions				S^{2-}	CH_3COO^- or I^-	CH_3COO^- or I^-

Next, one can use reaction with Ag^+ in order to identify I^-. Upon mixing **S2** containing Ag^+ and **S5**, a metallic precipitate, possibly Ag, is formed, while the only possible reducing agent amongst remaining ions is Mn^{2+}. Plus, the number of beige precipitates observed upon mixing **S5** with the other solutions suggests that Mn^{2+} is

there. The formation of pale-yellow precipitate from **S2** and **S6** and the absence of similarly textured and colored precipitate in the **S2** + **S5** mixture mean that **S6** contains I^- (this also explains the yellow color of S6: oxidation of I^- by air) and **S5** contains CH_3COO^-.

Solutions	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Cations		Ag^+	Fe^{3+}		Mn^{2+}	
Anions				S^{2-}	CH_3COO^-	I^-

Ag^+ can also form precipitates with Cl^- (white), SO_4^{2-}, (white) and PO_4^{3-} (yellow). Indeed, solution **S2** forms yellow precipitate with **S1**, white with **S3**, and yellowish with **S6**. Therefore, **S1** contains PO_4^{3-}. The only cations that do not form precipitates in mixture with PO_4^{3-} are Na^+ and K^+.

Solutions	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Cations	Na^+, K^+.	Ag^+	Fe^{3+}		Mn^{2+}	
Anions	PO_4^{3-}			S^{2-}	CH_3COO^-	I^-

We are left with two cations, Ca^{2+} and Ba^{2+}, that should be contained in solutions **S4** and **S6**. Indeed, both solutions form white precipitates with PO_4^{3-} (**S1**). CaS hydrolyzes stronger than BaS due to a lower solubility of $Ca(OH)_2$. Therefore, most probably Ba^{2+} is contained together with S^{2-} in **S4** and Ca^{2+} is together with I^- in S6. This can be further confirmed by mixing S4 and **S6** leading to a slow formation of white precipitate $Ca(OH)_2$.

Solutions	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Cations	Na^+, K^+.	Ag^+	Fe^{3+}	Ba^{2+}	Mn^{2+}	Ca^{2+}
Anions	PO_4^{3-}			S^{2-}	CH_3COO^-	I^-

Mixing of **S2** (Ag^+) and **S3** leads to the formation of white precipitate at the bottom of the tube. The only possible anions amongst the remaining ones that form precipitate with Ag^+ are Cl^- and SO_4^{2-}. Thus, **S3** contains Cl^-, SO_4^{2-}, or a mixture of both of them. Instead, **S2** should contain NO_3^-. Presence of Cl^- and SO_4^{2-} in **S3** cannot be tested directly due to the formation of other colored products upon mixing

of **S3** with other solutions. Yet, mixing solution **S5** with solution **S6** containing Ca^{2+} leads to a slow formation of colorless precipitate which cannot be explained by the already identified ions. The only option for this precipitate is $CaSO_4$, therefore SO_4^{2-} is contained in **S5**. This experiment also serves as additional proof of absence of Ba^{2+} in **S6**, otherwise a quick formation of highly insoluble white $BaSO_4$ is expected. The remaining anion Cl^- then should be in **S3**. The final table:

Solutions	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Cations	Na^+, K^+.	Ag^+	Fe^{3+}	Ba^{2+}	Mn^{2+}	Ca^{2+}
Anions	PO_4^{3-}	NO_3^-	Cl^-	S^{2-}	CH_3COO^- SO_4^{2-}	I^-

3.3

Solutions	**S2**	**S3**	**S4**	**S5**	**S6**
S1	$Ag_3PO_4\downarrow$	$FePO_4\downarrow$	$Ba_3(PO_4)_2\downarrow$	$Mn_3(PO_4)_2\downarrow$	$Ca_3(PO_4)_2\downarrow$
S2	×	$AgCl\downarrow$	$Ag_2S\downarrow$	$Ag\downarrow$ + $MnO_2\downarrow$	$AgI\downarrow$
S3	×	×	$Fe(OH)_3\downarrow$ or $FeS\downarrow$ + $S\downarrow$	$Fe_3O(AcO)_6$	I_3^- or I_2
S4	×	×	×	$BaSO_4\downarrow$ + $MnS\downarrow$	$Ca(OH)_2\downarrow$
S5	×	×	×	×	$CaSO_4\downarrow$

Combination	Ionic Reaction Equation(s)
S1 + S2	$3Ag^+ + PO_4^{3-} = Ag_3PO_4\downarrow$
S1 + S3	$Fe^{3+} + PO_4^{3-} = FePO_4\downarrow$
S1 + S4	$3Ba^{2+} + 2PO_4^{3-} = Ba_3(PO_4)_2\downarrow$
S1 + S5	$3Mn^{2+} + 2PO_4^{3-} = Mn_3(PO_4)_2\downarrow$
S1 + S6	$3Ca^{2+} + 2PO_4^{3-} = Ca_3(PO_4)_2\downarrow$

S2 + S3	$Ag^+ + Cl^- = AgCl\downarrow$
S2 + S4	$2Ag^+ + S^{2-} = Ag_2S\downarrow$
S2 + S5	$Mn^{2+} + 2Ag^+ + 2H_2O = MnO_2\downarrow + 2Ag\downarrow + 4H^+$
S2 + S6	$Ag^+ + I^- = AgI\downarrow$
S3 + S4	$2Fe^{3+} + 3S^{2-} = 2FeS\downarrow + S\downarrow$ or $2Fe^{3+} + 3S^{2-} + 6H_2O = 2Fe(OH)_3\downarrow + 3H_2S\uparrow$
S3 + S5	$3Fe^{3+} + 6AcO^- + H_2O = [Fe_3O(AcO)_6]^- + 2H^+$
S3 + S6	$2Fe^{3+} + 3I^- = 2Fe^{2+} + I_3^-$ or $2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2\downarrow$
S4 + S5	$Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$ $Mn^{2+} + S^{2-} = MnS\downarrow$
S4 + S6	$Ca^{2+} + S^{2-} + 2H_2O = Ca(OH)_2\downarrow + H_2S\uparrow$
S5 + S6	$Ca^{2+} + SO_4^{2-} = CaSO_4\downarrow$