THEORETICAL PROBLEMS

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<td>Name as in passport:</td>
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50th IChO 2018
International Chemistry Olympiad
SLOVAKIA & CZECH REPUBLIC

BACK TO WHERE IT ALL BEGAN
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Instructions

- This theoretical exam booklet contains 59 pages.
- You may begin writing as soon as the Start command is given.
- You have 5 hours to complete the exam.
- All results and answers must be clearly written in pen in their respective designed areas on the exam papers. Answers written outside the answer boxes will not be graded.
- You were provided with 3 sheets of scratch paper. If you need more, use the backside of the exam sheets. Remember that nothing outside the designed areas will be graded.
- The periodic table and visible light spectrum are not part of this booklet; they are provided separately.
- Use only the pen and calculator provided.
- The official English version of the exam booklet is available upon request and serves for clarification only.
- If you need to leave the exam room (to use the toilet or have a snack), wave the blue IChO card. The exam supervisor will come to accompany you.
- The supervisor will announce a 30-minute warning before the Stop command.
- You must stop your work immediately when the Stop command is announced. Failure to stop writing by ½ minute or longer will lead to nullification of your theoretical exam.
- After the Stop command has been given, place your exam booklet back in your exam envelope and wait at your seat. The exam supervisor will come to collect the envelope.
Physical constants and equations

Avogadro’s constant: \( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \)
Universal gas constant: \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
Speed of light: \( c = 2.998 \times 10^8 \text{ m s}^{-1} \)
Planck’s constant: \( h = 6.626 \times 10^{-34} \text{ J s} \)
Faraday constant: \( F = 9.6485 \times 10^4 \text{ C mol}^{-1} \)
Standard pressure: \( p = 1 \text{ bar} = 10^5 \text{ Pa} \)
Normal (atmospheric) pressure: \( p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} \)
Zero of the Celsius scale: \( 273.15 \text{ K} \)
Mass of electron: \( m_e = 9.109 \times 10^{-31} \text{ kg} \)
Unified atomic mass unit: \( u = 1.6605 \times 10^{-27} \text{ kg} \)
Ångström: \( 1 \text{ Å} = 10^{-10} \text{ m} \)
Electronvolt: \( 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \)
Watt: \( 1 \text{ W} = 1 \text{ J s}^{-1} \)

Ideal gas equation: \( pV = nRT \)
The first law of thermodynamics: \( \Delta U = q + W \)
Power input for electrical device: \( P = UI \)
where \( U \) is voltage and \( I \) electric current
Enthalpy: \( H = U + pV \)
Gibbs free energy: \( G = H - TS \)
\( \Delta G^\circ = -RT \ln K = -zF E_{\text{cell}}^\circ \)
\( \Delta G = \Delta G^\circ + RT \ln Q \)

Reaction quotient \( Q \) for a reaction \( a A + b B \rightleftharpoons c C + d D \): \( Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \)

Entropy change: \( \Delta S = \frac{q_{\text{rev}}}{T} \)
where \( q_{\text{rev}} \) is heat for the reversible process
Heat change for temperature-independent \( c_m \): \( \Delta q = nc_m \Delta T \)
where \( c_m \) is molar heat capacity
Van 't Hoff equation: \[ \frac{d \ln K}{dT} = \frac{\Delta H_m}{RT^2} \Rightarrow \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

Henderson–Hasselbalch equation: \[ pH = pK_a + \log \frac{[A^-]}{[HA]} \]

Nernst–Peterson equation: \[ E = E^o - \frac{RT}{2F} \ln Q \]

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

Relation between \(E\) in eV and in J: \[ \frac{E}{\text{eV}} = \frac{E}{J} \frac{eV}{q_e/C} \]

Lambert–Beer law: \[ A = \log \frac{I_0}{I} = \varepsilon l c \]

Wavenumber: \[ \tilde{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

Reduced mass \(\mu\) for a molecule AX: \[ \mu = \frac{m_A m_X}{m_A + m_X} \]

Energy of harmonic oscillator: \[ E_n = h\nu \left( n + \frac{1}{2} \right) \]

Arrhenius equation: \[ k = A e^{-\frac{E_a}{RT}} \]

Rate laws in integrated form:

Zero order: \[ [A] = [A]_0 - kt \]

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

Second order: \[ \frac{1}{[A]} = \frac{1}{[A]_0} + kt \]
Problem 1. DNA

Palindromic sequences are an interesting class of DNA. In a palindromic double-stranded DNA (dsDNA) species, the sequence of one strand read in the 5′→3′ direction matches the sequence read in the 5′→3′ direction of the complementary strand. Hence, a palindromic dsDNA consists of two identical strands that are complementary to each other. An example is the Drew–Dickerson dodecanucleotide (1):

\[
\begin{align*}
5'\text{-CGCGAATTCGCG-3'} \\
| | | | | | | | | | | | \\
3'\text{-GCGCTTAAGCGC-5'}
\end{align*}
\]

(1)

1.1 How many different palindromic double-stranded DNA dodecanucleotides (dsDNA species with twelve base pairs) exist?

1.2 How many different palindromic double-stranded DNA undecanucleotides (dsDNA species with eleven base pairs) exist?
The melting temperature of dsDNA, $T_m$ is defined as the temperature at which 50% of the original number of DNA double strands are dissociated into separate strands.

1.3 Consider the Drew–Dickerson dodecanucleotide (1). Assume that a G–C nucleobase pair contributes to the DNA duplex stability more than an A–T pair does. What is the probability that the Drew-Dickerson dodecanucleotide’s $T_m$ increases when a single randomly selected base pair is replaced by a G–C pair?

Probability
Let us analyze the thermodynamics of formation of double-helical DNA from single strands, and its dependence on the length of the DNA and on the temperature. The equilibrium constant of association of single strands to form dsDNA differs for palindromic and non-palindromic dsDNA. A solution of dsDNA with an initial concentration of $c_{\text{init}} = 1.00 \times 10^{-6} \text{ mol dm}^{-3}$ was heated to $T_m$ and equilibrium was reached.

1.4 Calculate the equilibrium constant of association of single strands at $T_m$ for both non-palindromic and palindromic DNA.

<table>
<thead>
<tr>
<th>Non-palindromic dsDNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation:</td>
</tr>
</tbody>
</table>

$$K =$$

<table>
<thead>
<tr>
<th>Palindromic dsDNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation:</td>
</tr>
</tbody>
</table>

$$K =$$
The mean contributions to the Gibbs energy of association of two single strands to form dsDNA were estimated over a certain range of experimental conditions, and they amounted to −6.07 kJ mol\(^{-1}\) per G–C pair, and −1.30 kJ mol\(^{-1}\) per A–T pair present in dsDNA.

1.5 How many base pairs are there in the shortest dsDNA oligonucleotide that has \(T_m\) greater than 330 K? At this \(T_m\), consider the following values of the equilibrium constant of association of single strands to form a dsDNA: \(K_{np} = 1.00 \times 10^6\) for non-palindromic dsDNA, \(K_p = 1.00 \times 10^5\) for palindromic dsDNA. Is the shortest oligonucleotide palindromic or non-palindromic?

<table>
<thead>
<tr>
<th>Calculation of the number of base pairs:</th>
</tr>
</thead>
<tbody>
<tr>
<td>The needed length of a non-palindromic dsDNA:</td>
</tr>
<tr>
<td>The needed length of a palindromic dsDNA:</td>
</tr>
<tr>
<td>The shortest oligonucleotide is</td>
</tr>
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</table>
The Gibbs energy of individual base pair contribution to the association of DNA strands is actually temperature dependent. The dependence of the inverse of $T_m$ of the Drew–Dickerson dodecanucleotide (1) on the logarithm of the initial duplex concentration $c_{\text{init}}$ is shown below. (Note: a standard concentration $c_0 = 1 \text{ mol dm}^{-3}$ is introduced.)
1.6 Calculate the standard enthalpy $\Delta H^\circ$ and the standard entropy $\Delta S^\circ$ of the association of DNA single strands to form the palindromic double-stranded Drew–Dickerson dodecanucleotide (1). Assume that $\Delta H^\circ$ and $\Delta S^\circ$ are temperature independent.

Calculation:
Problem 2. Repatriation of remains in the middle ages

At ambient temperatures, racemization is a slow reaction. As such, it can be used for dating biological objects and for studying their thermal history. Let us take L-isoleucine (L-ile) ((2S,3S)-2-amino-3-methylpentanoic acid) as an example. It isomerizes on the α-carbon and forms (2R,3S)-2-amino-3-methylpentanoic acid, also known as D- allo-isoleucine. As the configuration changes on only one of the two stereocentres, this process is called epimerization rather than racemization.

2.1 Choose all true statements.

☐ D- allo-isoleucine and L-isoleucine have the same values of specific optical rotation but they have different melting points.

☐ D- allo-isoleucine has an identical absolute value of specific optical rotation as L-isoleucine but the sign is opposite. The melting point is the same for both isomers.

☐ D- allo-isoleucine and L-isoleucine have different values of specific optical rotation but they have the same melting points.

☐ D- allo-isoleucine and L-isoleucine have different values of specific optical rotation and different melting points.

☐ D- allo-isoleucine is not optically active.

2.2 Assign the absolute configurations for each stereoisomer of isoleucine.

A

2S, 3R (L- allo-isoleucine)

B

2R, 3S (D- allo-isoleucine)

C

2S, 3S (L-isoleucine)

D

2R, 3R (D-isoleucine)
2.3 The equilibrium constant $K_{\text{eq}}$ for L-isoleucine epimerization has the value of 1.38 (at 374 K). If we set molar Gibbs free energy of L-isoleucine to $G_m^\circ = 0 \, \text{kJ mol}^{-1}$, determine the Gibbs free energies for all structures A–D from question 2.2 at 374 K.

<p>| | | | |</p>
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<tbody>
<tr>
<td>A</td>
<td>kJ mol$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>kJ mol$^{-1}$</td>
<td></td>
<td></td>
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<tr>
<td>C</td>
<td>kJ mol$^{-1}$</td>
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</tr>
<tr>
<td>D</td>
<td>kJ mol$^{-1}$</td>
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2.4 If we take into account stereoisomerism at all stereocentres, what is the maximum possible number of the stereoisomers of the isoleucine tripeptide Ile-Ile-Ile?

The number of stereoisomers is
At the start of the epimerization, we can neglect the reverse reaction. The epimerization follows first-order kinetics in the reaction:

\[
\text{L-isoleucine} \xrightarrow{k_1} \text{D-allo-isoleucine}
\]

The value of the rate constant at 374 K is: \( k_1(374 \text{ K}) = 9.02 \times 10^{-5} \text{ h}^{-1} \) and at 421 K, the rate constant is: \( k_1(421 \text{ K}) = 1.18 \times 10^{-2} \text{ h}^{-1} \).

In the following calculation, represent the concentration of L-isoleucine as [L] and of D-allo-isoleucine as [D].

We can define a quantity \( de \) (diastereomeric excess):

\[
de = \frac{[L] - [D]}{[L] + [D]} \times 100(\%).
\]

2.5 Let us boil L-isoleucine for 1,943 hours at 374 K. What is the value of \( de \) (with three significant figures) for L-isoleucine a) before boiling and b) after boiling?

<table>
<thead>
<tr>
<th></th>
<th>Before boiling</th>
<th>After boiling</th>
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<tbody>
<tr>
<td>a) Before boiling</td>
<td>Calculation:</td>
<td>( de = ) %</td>
</tr>
<tr>
<td>b) After boiling</td>
<td>Calculation:</td>
<td>( de = ) %</td>
</tr>
</tbody>
</table>
2.6 How long does it take to convert 10% of L-isoleucine to D-allo-isoleucine at 298 K?

Calculation:

\[ t = \text{years} \]
The correct kinetic scheme for the reverse reaction is:

\[
\text{L-isoleucine} \quad \xrightarrow{k_1} \quad \text{D-allo-isoleucine}
\quad \quad \xlongleftarrow{k_2}
\]

The deviation of concentration from its equilibrium value \([L]_{eq}\) is defined by the equation:

\[x = [L] - [L]_{eq}\]

\(x\) evolves with time according to the following equation:

\[x = x(0) \times e^{-(k_1 + k_2)t},\]

where \(x(0)\) is the deviation from equilibrium at \(t = 0\) h.

2.7 Let us boil 1.00 mol dm\(^{-3}\) L-isoleucine solution for 1,943 hours at 374 K. The rate constant for the forward reaction is \(k_1(374\text{ K}) = 9.02 \times 10^{-5} \text{ h}^{-1}\); \(K_{ep}\) for L-isoleucine epimerization has the value of 1.38 (at 374 K). In the following calculation, represent the concentration of L-isoleucine as \([L]\) and of D-allo-isoleucine as \([D]\). Evaluate to three significant figures:

a) \([L]_{eq}\),

b) diastereomeric excess \((de)\) after boiling.

\[\text{a) Calculation:}\]

\[\text{[L]_{eq} = mol dm}^{-3}\]
b) Calculation:

\[ de = \% \]
Amino acids with a single stereocentre undergo racemization, e.g. L-arginine racemizes as follows:

\[
\text{L-arginine} \xrightarrow{k_1} \text{D-arginine}
\]

The time evolution of concentrations is governed by:

\[
\ln \left( \frac{1 + \frac{[D]}{[L]}}{1 - \frac{[D]}{[L]}} \right) = 2k_1 t + C
\]

Here \([D]\) and \([L]\) are concentrations of D- and L-arginine at time \(t\), \(k_1\) is the rate constant, and the term \(C\) is just a constant set according to the initial concentrations.

Holy Roman Emperor Lothar III passed away during his journey to Sicily in 1137. To facilitate the repatriation of the remains, his body was boiled in water (373 K) immediately after his death. We know that the rate constant \(k_1\) of arginine racemization is \(5.10 \times 10^{-3}\) h\(^{-1}\) at 373 K and pH = 7.

To analyse the isomeric composition of arginine in Lothar’s bones, we need to transfer arginine into solution. Lothar’s bones were hydrolyzed in a highly acidic environment for 4 hours at 383 K. It was determined that the ratio of the optical isomers, \(\frac{[D]}{[L]}\) = 0.090. Lothar’s wife Richenza was not boiled after her death. Her bones were hydrolysed and the ratio was \(\frac{[D]}{[L]}\) = 0.059. (Note that the racemization also takes place during the hydrolysis, with a rate constant \(k_1'\), which is different from \(k_1\)).

2.8 How long was the Holy Roman Emperor Lothar III boiled in water in 1137?

\textit{Note:} The racemization of arginine is an extremely slow process at temperatures typically encountered in graves. As both bodies are only some 880 years old, we can neglect the natural racemization during this time.

\begin{center}
\textbf{Calculation:}
\end{center}
$t_{boiling} = h$
### Problem 3. Emerging electro-mobility

Contemporary means of transportation rely on burning fossil fuels, although the efficiency of real combustion engines is limited and ranges between 20 and 40%.

3.1 Mark the factors that can make the efficiency of a heat engine higher:
- ☐ Increasing the friction in the mechanical parts of the engine
- ☐ Increasing the burning temperature of the fuel in the engine
- ☐ Narrowing the working temperature interval of the engine
- ☐ Increasing the working pressure of the gas

Engine efficiency can be improved by using hydrogen-based fuel cells.

3.2 The standard enthalpy of formation of liquid water is $\Delta_{f}H^\circ(\text{H}_2\text{O},l) = -285.84 \text{ kJ mol}^{-1}$, and the standard combustion enthalpy of isooctane is $\Delta_{c}H^\circ(\text{C}_8\text{H}_{18},l) = -5065.08 \text{ kJ mol}^{-1}$ (both at 323.15 K). Calculate the values of specific (per unit of mass) combustion enthalpy of pure liquid isooctane and pure gaseous hydrogen.

\[
\Delta_{c}H^\circ(\text{C}_8\text{H}_{18}) = \\
\Delta_{c}H^\circ(\text{H}_2) = 
\]
3.3 Calculate the standard electromotive force (EMF) of a fuel cell, which uses gaseous oxygen and hydrogen, both ideal gases at 100 kPa and 323.15 K, to produce liquid water. Use the following entropy data for 323.15 K:

\[ S°(H_2O,l) = 70 \text{ J K}^{-1} \text{ mol}^{-1}, \quad S°(H_2,g) = 131 \text{ J K}^{-1} \text{ mol}^{-1}, \quad S°(O_2,g) = 205 \text{ J K}^{-1} \text{ mol}^{-1}. \]

Calculations:

\[ \text{EMF} = V \]

3.4 Determine the ideal thermodynamic efficiency (\( \eta \)) of a fuel cell producing liquid water at 353.15 K. At this temperature, the enthalpy of formation of water is \( \Delta_f H°(H_2O,l) = -281.64 \text{ kJ mol}^{-1} \) and the corresponding reaction Gibbs energy change is \( \Delta r G° = -225.85 \text{ kJ mol}^{-1} \).

\[ \eta = \% \]
3.5 A polymer membrane electrolyzer facility operates at the voltage of 2.00 V and is powered by a 10.0 MW wind turbine plant which runs at full power from 10 pm to 6 am. The electrolysis yielded 1,090 kg of pure hydrogen. Calculate the electrolysis yield, defined as the mass of produced hydrogen divided by its theoretically produced mass.

Calculations:

\[ \eta_{\text{electrolysis}} = \% \]
3.6 Calculate the mass of hydrogen required to drive between Prague and Bratislava (330 km) at an average speed of 100 km h\(^{-1}\) in a car fitted with a 310 kW electric engine running at a 15\% rate of its maximum power. Assume that the efficiency of the hydrogen cell producing electrical energy is 75\%, the efficiency of the electric engine is 95\%, and the Gibbs energy change for combustion of hydrogen fuel is \(\Delta G = -226 \text{ kJ mol}^{-1}\).

\[
\text{Calculations:}
\]

\[
m = \text{kg}
\]
The low efficiency of hydrogen production and the safety issues connected with hydrogen storage impede the use of hydrogen-based transportation technology. Hydrazine (N₂H₄) fuel cells might be a suitable alternative.

The following standard reduction potentials for aqueous hydrazine systems are:

\[
\begin{align*}
N_2(g) + 5 H^+(aq) + 4 e^- &\rightarrow N_2H_5^+(aq) \quad E^0 = -0.23 \text{ V} \\
N_2H_5^+(aq) + 3 H^+(aq) + 2 e^- &\rightarrow 2 NH_4^+(aq) \quad E^0 = +1.28 \text{ V} \\
N_2(g) + 4 H_2O(l) + 4 e^- &\rightarrow N_2H_4(aq) + 4 OH^- (aq) \quad E^0 = -1.16 \text{ V} \\
N_2H_4(aq) + 2 H_2O(l) + 2 e^- &\rightarrow 2 NH_3(aq) + 2 OH^- (aq) \quad E^0 = +0.10 \text{ V} \\
2 H_2O(l) + 2 e^- &\rightarrow H_2(g) + 2 OH^- (aq) \quad E^0 = -0.83 \text{ V}.
\end{align*}
\]

3.7 Fill in the following Latimer diagrams with the forms of hydrazine and ammonia prevailing at the given conditions and write the redox potential value for each arrow representing the electrochemical half-reaction. Record all the necessary calculations.

a) Acidic environment (pH = 0)

\[
\begin{align*}
N_2 &\rightarrow \boxed{\text{N2H5+}} \rightarrow \boxed{\text{NH4}} \\
&\rightarrow \boxed{\text{NH3}} \\
\end{align*}
\]

b) Basic environment (pH = 14)

\[
\begin{align*}
N_2 &\rightarrow \boxed{\text{N2H5+}} \rightarrow \boxed{\text{NH4}} \\
&\rightarrow \boxed{\text{NH3}} \\
\end{align*}
\]

Calculations:
Due to ammonia’s toxicity, odour and environmental impact, it is extremely undesirable to produce ammonia in fuel cells.

3.8 Write down the net reaction for the decomposition of hydrazine under basic conditions to (i) ammonia and nitrogen and (ii) nitrogen and hydrogen, and calculate the corresponding equilibrium constants at $T = 298.15$ K.

### Equations for hydrazine decomposition:

- **Hydrazine decomposition to NH$_3$ and N$_2$ in a basic environment:**
  
  $$K =$$

- **Hydrazine decomposition to H$_2$ and N$_2$ in a basic environment:**
  
  $$K =$$
Rechargeable lithium-based batteries are an alternative to fuel cells. Lithium-ion batteries commonly use graphite for one of the electrodes, in which lithium clusters intercalate in between the graphite sheets. The other electrode is made of lithium cobalt oxide, which can reversibly absorb lithium ions moving from one electrode to the other during the charge and discharge processes. The half-reactions relevant for the system can be formally written as:

\[
\begin{align*}
(C)_n + Li^+ + e^- & \rightarrow Li(C)_n & E^\circ = -3.05 \text{ V}, \\
CoO_2 + Li^+ + e^- & \rightarrow LiCoO_2 & E^\circ = +0.19 \text{ V}.
\end{align*}
\]

3.9 Using the formalism given above, write down the overall chemical reaction occurring in the battery during the discharge process. Give the oxidation states of the cobalt atom.

3.10 Tick the boxes to get the correct statements which are valid for the discharge of the lithium-based battery described in 3.9:

- **Li(C)_n** electrode is
  - cathode
  - anode

- **LiCoO_2** electrode is
  - cathode
  - anode

**because lithium ions are reduced here.**

**because lithium atoms are oxidized here.**

**because cobalt ions are reduced here.**

**because cobalt ions are oxidized here.**
3.11 Assume that a C₆ unit, a CoO₂ unit and Li atom form the active battery mass required to transfer one electron between the electrodes. Using the corresponding standard EMF, calculate the theoretical specific reversible charge capacity (in mAh g⁻¹) and the energy density (in kWh kg⁻¹) of such a model lithium ion battery related to the whole active battery mass.

Calculations:

Charge capacity \( c_{q,s} \) = \text{mAh g}^{-1}

Calculations:

Energy density \( \rho_{el} \) = \text{kWh kg}^{-1}
Theoretical Problem 4

<table>
<thead>
<tr>
<th>Question</th>
<th>4.1</th>
<th>4.2</th>
<th>4.3</th>
<th>4.4</th>
<th>4.5</th>
<th>4.6</th>
<th>4.7</th>
<th>4.8</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
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<td>7</td>
<td>2</td>
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<td>2</td>
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<td>Score</td>
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6% of the total

**Problem 4. Column chromatography of radioactive copper**

$^{64}\text{Cu}$ for positron emission tomography is prepared by the bombardment of a zinc target with deuterium nuclei (further referred to as the activated target).

4.1 Write down the balanced equation for the $^{64}\text{Zn}$ nucleus bombardment with deuterium nuclei, giving $^{64}\text{Cu}$. Specify the corresponding atomic and mass numbers of all species. Disregard the charges.

$$... + ... \rightarrow ... + ...$$

The activated target is dissolved in concentrated hydrochloric acid (HCl (aq)) to give a mixture containing $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ ions and their respective chlorido complexes.

4.2 You will be calculating the mole fraction of negatively charged copper species with respect to the amount of copper prepared by zinc target activation. Assume $[\text{Cl}^-] = 4 \text{ mol dm}^{-3}$. For the overall complexation constants, $\beta$, see Table 1.

Before you start the calculation, write down the charges in the upper right boxes for all of the species:

| Cu | [CuCl] | [CuCl$_2$] | [CuCl$_3$] | [CuCl$_4$] |

Table 1. Overall complexation constants $\beta$ of Cu (charges were omitted in the formulas). $\beta_i = \frac{[\text{CuCl}_i]}{[\text{Cu}][\text{Cl}]^i}$

<table>
<thead>
<tr>
<th>$i$ in [CuCl]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_i$</td>
<td>2.36</td>
<td>1.49</td>
<td>0.690</td>
<td>0.055</td>
</tr>
</tbody>
</table>
Calculation:

Mole fraction =

(answer with 2 digits after decimal point)
The mixture containing Cu$^{2+}$ and Zn$^{2+}$ ions and their respective chlorido complexes was separated with an anion exchange resin. Dry resin in OH$^-$ form was dispersed in water and the suspension was transferred into a column. To occupy all sites with Cl$^-$ ions (i.e. to obtain resin in a Cl$^-$ form), the resin was washed with hydrochloric acid and then with deionized water to remove all the unbound Cl$^-$ ions.

4.3 Assuming the resin system was at room temperature before washing with hydrochloric acid, does the column temperature change during the washing with hydrochloric acid?

☐ No.
☐ Yes, the temperature decreases.
☐ Yes, the temperature increases.

The mixture containing Cu$^{2+}$ and Zn$^{2+}$ ions and their respective chlorido complexes was transferred onto the resin-filled column. Hydrochloric acid solution was used as an eluent.

You can calculate quantities that determine average elution properties of both copper species and zinc species on the column using the equation for the retention volume $V_R$

The retention volume $V_R$ (the mobile phase volume at which 50% of the compound has been eluted from the column) can be calculated as follows:

$$V_R = D_g \times m_{\text{resin,dry,OH form}} + V_0$$

4.4 Using average mass distribution coefficients $D_g$ ($D_g$(Cu species) = 17.4 cm$^3$ g$^{-1}$, $D_g$(Zn species) = 78.5 cm$^3$ g$^{-1}$), calculate the retention volumes $V_R$ in cm$^3$ of both copper species and zinc species if the mass of dry resin in OH$^-$ form $m_{\text{resin,dry,OH form}} = 3.72$ g and the void volume of a column $V_0 = 4.93$ cm$^3$.

Calculation:

$$V_R(\text{Cu species}) = \quad \text{cm}^3 \quad \text{(answer with 1 digit after the decimal point)}$$

$$V_R(\text{Zn species}) = \quad \text{cm}^3 \quad \text{ (answer with 0 digit after the decimal point)}$$

If you cannot find the answer, use $V_R$(Cu species) = 49.9 cm$^3$ and $V_R$(Zn species) = 324 cm$^3$ in further calculations.
Separation of two sets of species, A and B, can be considered complete if

\[ V_{0.001}(A) - V_{0.999}(B) > 10V_c \]

where \( V_{0.001} \) is the mobile phase volume at which 0.1% of A has been eluted from the column, and \( V_{0.999} \) is the mobile phase volume at which 99.9% of B has been eluted from the column.

\[
V_{0.001}(A) = V_R(A) \times \left(1 - 6.91 \sqrt{\frac{d_p}{L_c}}\right)
\]

\[
V_{0.001}(B) = V_R(B) \times \left(1 - 6.91 \sqrt{\frac{d_p}{L_c}}\right)
\]

\[
V_{0.999}(B) = 2V_R(B) - V_{0.001}(B)
\]

4.5 Based on a calculation, decide whether copper species were separated completely from zinc species. The volume of the column filled with the swollen resin \( V_c = 10.21 \text{ cm}^3 \), the resin particle diameter \( d_p = 0.125 \text{ mm} \), and the height of the wet resin in a swollen state in the column \( L_c = 13.0 \text{ cm} \).

\[
V_{0.001}(A) = \text{ cm}^3
\]

\[
V_{0.999}(B) = \text{ cm}^3
\]

It is possible to separate copper species from zinc species.

☐ True  ☐ False

4.6 Calculate the theoretical value of the total ion exchange mass capacity of the dry resin used in this problem, \( Q_{m,\text{theor}} \), in mmol g\(^{-1}\). Consider tetraalkylammonium groups were the only ones responsible for ion exchange of the resin. No other nitrogen containing groups were present. The mass fraction of nitrogen in the dry resin was 4.83%.

\[
Q_{m,\text{theor}} = \text{ mmol g}^{-1}\ (\text{answer with 2 digits after decimal point})
\]

If you cannot find the answer, use \( Q_{m,\text{theor}} = 4.83 \text{ mmol g}^{-1}\) for further calculations.
In reality, not all tetraalkylammonium groups are involved in the ion exchange. To determine the total ion exchange volume capacity, $Q_v$, the column filled with 3.72 g dry resin converted to the Cl$^-$ form was washed with the excess of sodium sulfate solution. The eluent was collected in a 500 cm$^3$ volumetric flask, which was then filled with water to the mark. An aliquot of 100 cm$^3$ was potentiometrically titrated with 0.1027 mol dm$^{-3}$ silver nitrate. The silver nitrate solution volume at the equivalence point was 22.20 cm$^3$. The volume of the column filled with the swollen resin, $V_c$, was 10.21 cm$^3$.

4.7 Calculate the $Q_v$ of the swollen resin in mmol of active tetraalkylammonium groups per cm$^3$ of the swollen resin.

$$Q_v = \text{mmol cm}^{-3} \text{ (answer with 2 digits after decimal point)}$$

If you cannot find the answer, use $Q_v = 1.00 \text{ mmol cm}^{-3}$ for further calculations.

4.8 Calculate the mole fraction ($x$) of the tetraalkylammonium groups actively involved in the ion exchange.

$$x = \text{ (answer with 3 digits after decimal point)}$$
Problem 5. Bohemian garnet

Bohemian garnet (pyrope) is a famous Czech blood-red coloured semi-precious stone. The chemical composition of natural garnets is expressed by the general stoichiometric formula of $A_3B_2(SiO_4)_3$, where $A^{II}$ is a divalent cation and $B^{III}$ is a trivalent cation. Garnets have a cubic unit cell that contains 8 formula units. The structure includes 3 types of polyhedra: the $A^{II}$ cation occupies a dodecahedral position (it is surrounded with eight O atoms), the $B^{III}$ cation occupies an octahedral position (it is surrounded with six O atoms) and Si$^{IV}$ is surrounded with four O atoms arranged into a tetrahedron.

The most common garnet mineral is almandine with the formula of $Fe_3Al_2(SiO_4)_3$. Its unit cell parameter is $a = 11.50$ Å.

5.1 Calculate the theoretical density of almandine.

$$\rho = \text{g cm}^{-3}$$
The Bohemian garnet has the composition of Mg$_3$Al$_2$(SiO$_4$)$_3$. The pure compound is colourless and the colour of natural garnets comes from chromophores – transition metal cations that substitute the host material cations. The red colour of the Bohemian garnet comes from trace amounts of Cr$^{III}$ ions in the octahedral sites and Fe$^{II}$ ions in the dodecahedral sites.

5.2 Draw the splitting diagram for the [Cr$^{III}$O$_6$]$^{2-}$ d-orbitals and fill it with electrons.

5.3 Identify the 1$^{st}$ transition row element(s) whose trivalent cation(s) M$^{III}$ placed in an octahedral position is/are diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

5.4 The figure below shows d-orbitals splitting in the dodecahedral crystal field. Fill in the electrons for the [Fe$^{II}$O$_8$]$^{3-}$ chromophore for both existing arrangements.

5.5 Derive the inequalities (e.g. $P < E_1 + E_2 + E_3$) for the pairing energy ($P$) magnitude in relation to energies $E_1$, $E_2$ and $E_3$ for both arrangements.

<table>
<thead>
<tr>
<th>a) high-spin arrangement</th>
<th>b) low-spin arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>$E_2$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>$E_3$</td>
</tr>
</tbody>
</table>

| a) high-spin arrangement: | $P$ |
| b) low-spin arrangement:  | $P$ |
5.6 Assuming that \( P > E_3 \), identify the 1st transition row element(s) whose divalent cation \( M^{II} \) placed in dodecahedral position is diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

The figures below show simplified absorption spectra of four coloured minerals – blood-coloured Bohemian garnet, green uvarovite, blue sapphire and yellow-orange citrine.

5.7 Match the spectra with the minerals.

<table>
<thead>
<tr>
<th>Bohemian garnet:</th>
<th>Sapphire:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uvarovite:</td>
<td>Citrine:</td>
</tr>
</tbody>
</table>

5.8 If illuminated with monochromatic blue-green light, how will the Bohemian garnet look?

- Red
- Yellow
- Blue
- Blue-green
- Yellow-orange
- Violet
- Black
- White
Andradite is another garnet mineral; its chemical composition is $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$. A double cation substitution – Ti$^{IV}$ for Fe$^{III}$ in the octahedral position and Fe$^{III}$ for Si$^{IV}$ in the tetrahedral position – gives rise to black schorlomite. Its chemical composition can be expressed as $\text{Ca}_3[\text{Fe,Ti}^{IV}]_{\text{oct}}([\text{Si,Fe}^{III}]_{\text{tet}}\text{O}_4)_3$.

5.9 Calculate the percentage of Si$^{IV}$ ions in a sample of schorlomite that must be substituted with Fe$^{III}$, if we know that 5% of Fe$^{III}$ ions in octahedral position are substituted with Ti$^{IV}$.

$$p = \%$$

The colour of the mineral is caused by two chromophores: $[\text{Fe}^{III}\text{O}_6]_{\text{oct}}$ and $[\text{Fe}^{III}\text{O}_4]_{\text{tet}}$. The central ions of both chromophores have an equal number of unpaired electrons.

5.10 Draw the $d$-orbitals splitting diagrams for both chromophores and fill in the electrons.

$[\text{Fe}^{III}\text{O}_6]_{\text{oct}}$:  

$[\text{Fe}^{III}\text{O}_4]_{\text{tet}}$:  

Tetrahedral field causes a smaller splitting than the octahedral field ($\Delta_{\text{tet}} = \frac{4}{9} \Delta_{\text{oct}}$). Surprisingly for the Fe$^{\text{III}}$ ion, the energy of the first d–d transition (although very weak) for the octahedral chromophore is smaller (11 000 cm$^{-1}$) than for the tetrahedral one (22 000 cm$^{-1}$).

5.11 Calculate the size of pairing energy ($P$) and the sizes of $\Delta_{\text{oct}}$ and $\Delta_{\text{tet}}$ splitting. Assume that the pairing energy is equal in both chromophores.

\[
P = \text{ cm}^{-1} \\
\Delta_{\text{oct}} = \text{ cm}^{-1} \\
\Delta_{\text{tet}} = \text{ cm}^{-1}
\]

Synthetic garnet YAG (YttriumAluminiumGarnet), used in optoelectronics, has the composition of $\text{Y}_3\text{Al}_5\text{O}_{12}$. Its structure is derived from the general garnet structure $\text{A}_3\text{B}_2(\text{SiO}_4)_3$ by placing the ions $\text{Y}^{\text{III}}$ and $\text{Al}^{\text{III}}$ to the A, B and Si positions.

5.12 Based on your knowledge of the relative ion radii, determine which cation in the synthetic garnet occupy positions A, B and Si.

A:  
B:  
Si:

5.13 For the use in LED technology, YAG is doped with Ce$^{\text{III}}$. Determine the values of $x$ and $y$ in the formula of YAG in which 5% of yttrium atoms are substituted with cerium.

\[
\text{Y}_x\text{Ce}_y\text{Al}_5\text{O}_{12}
\]

$x = \quad y =

If you don’t get result, use $x = 2.25$ and $y = 0.75.$
5.14 The Ce$^{III}$-doped YAG is prepared by annealing the mixture of $\text{Y}_2\text{O}_3$, $\text{Al}_2\text{O}_3$ and $\text{CeO}_2$ in $\text{H}_2$ atmosphere. Use the formula you determined in 5.13 and write down a balanced equation for this reaction with the smallest whole-number stoichiometric coefficients.
Doping the YAG structure with rare-earth ions enables the production of lasers with emission wavelengths ranging from the UV to the mid-IR region. In the scheme below, simplified $f-f$ energy transitions of selected rare-earths ions are shown.

5.15 Which cation has a transition which corresponds to blue light emission?

- Er$^{3+}$
- Sm$^{3+}$
- Tm$^{3+}$
- Pr$^{3+}$
- Yb$^{3+}$
- Nd$^{3+}$
- Tb$^{3+}$

5.16 Calculate the emission wavelength of this light.

$$\lambda = \text{nm}$$

5.17 According to a legend, Noah used a stick with a garnet stone for illumination during his voyage. Assuming only the photoluminescence effect, determine the colour of the laser light emitted from his stick if the stone were the blood-coloured Bohemian garnet.

- Red
- Blue
- Yellow-orange
- Black
- Yellow
- Blue-green
- Violet
- White
Problem 6. Let’s go mushrooming

Mushrooming is a Czech and Slovak traditional pastime. While some of our mushroom species are edible, some are inedible or even poisonous.

Inky cap (*Coprinopsis atramentaria*) is considered edible and delicious. It contains a natural compound called coprine (E), which can be synthesized from ethyl 3-chloropropanoate (1).

\[
\begin{align*}
\text{Cl} & \\
\text{OEt} & \\
1. \text{Na, Et}_2\text{O, reflux} & \rightarrow \text{C}_{8}\text{H}_{18}\text{O}_2\text{Si} \\
2. (\text{CH}_3)_3\text{SiCl} & \\
\text{A} & \\
\text{B}_4\text{N}^+ & \\
\text{F}^- & \\
\text{MeOH} & \\
\text{B} & \\
\text{NaNH}_2 & \\
\text{NH}_3 (l) & \\
\text{C}_{3}\text{H}_7\text{NO} & \\
\text{C} & \\
\text{HO} & \\
\text{COO}^+ & \\
2. \text{C, THF} & \\
\text{D} & \\
5\% \text{aq. HCl} & \\
40 \degree \text{C} & \\
\text{Coprine (E)} & \\
\text{C}_{8}\text{H}_{14}\text{N}_2\text{O}_4 & \\
\text{E} &
\end{align*}
\]

6.1 Draw the structures of compounds **A**–**E** including stereochemistry when necessary. *Hint: The first reaction affording compound **A** proceeds via an organometallic compound which then cyclizes.*

A

B

C

D

E
In the human body, coprine undergoes hydrolysis to L-glutamic acid (3) and compounds C and 4, which are responsible for the coprine adverse side-effects. They inhibit the enzyme acetaldehyde dehydrogenase, which is involved in the metabolism of alcohol. When the enzyme is inhibited, acetaldehyde formed by alcohol dehydrogenase accumulates in the body, causing strong symptoms of a hangover (also called the antabuse effect). The active site of the enzyme contains a cysteine -SH group, which is blocked either by compound C or 4.

Enzyme = acetaldehyde dehydrogenase

6.2 Using the “Enzyme” pictogram for acetaldehyde dehydrogenase above, draw the structure F of the enzyme inhibited by compound 4.
The antabuse effect got its name after antabuse (5), the most popular drug used for treatment of alcohol-addiction. This drug can be synthesized according to the following scheme:

6.3 Draw the structures of compounds G and H. *Hint: Compound H contains five carbon atoms.*

6.4 Mark all possible reagents which could be used for reagent I from the following list.

- ☐ *m*-chloroperbenzoic acid (*m*CPBA)
- ☐ Zn/CH₃COOH
- ☐ I₂
- ☐ K₂CO₃, H₂O
- ☐ diluted H₂O₂
- ☐ NaBH₄
- ☐ hot concentrated H₂SO₄
- ☐ AlCl₃
The way antabuse inhibits acetaldehyde dehydrogenase is similar to the effect of compounds C and 4.

![Enzyme reaction diagram]

Enzyme = acetaldehyde dehydrogenase

6.5 Using the “Enzyme” pictogram above for acetaldehyde dehydrogenase, draw the structure J of the enzyme inhibited by antabuse (5). *Hint: Three sulfur atoms should be shown in the structure.*

![Structure J]

False morel (*Gyromitra esculenta*) is another interesting mushroom. Although it was considered edible in the past (*esculentus* means edible in Latin), there is clear evidence that this mushroom is poisonous due to the content of gyromitrin (M). Gyromitrin can be prepared from *N*-methylhydrazine (6) as follows:

![Gyromitrin synthesis]

6.6 Draw the structures of compounds K–M.

![Structures K, L, M]
In the human body, gyromitrin (M) hydrolyzes and provides N-methylhydrazine (6), which is strongly hepatotoxic. Gyromitrin (M) hydrolysis occurs as soon as it enters the acidic environment in human stomach where both its amide and imine groups are hydrolyzed.

Let us focus on the hydrolysis of the amide moiety within the gyromitrin molecule. The vibrational wavenumber of the stretching mode of the relevant C−N bond amounts to 1,293.0 cm$^{-1}$ and the potential energy surface does not significantly alter its shape with the isotope substitution effect.

6.7 Calculate the highest possible hypothetical kinetic isotope effect at the temperature of human body, 37 °C, for the given hydrolysis reaction assuming that both relevant nitrogen and carbon atoms were simultaneously substituted, $^{14}$N with the $^{15}$N isotope and $^{12}$C with the $^{13}$C isotope. Consider that only the zero point vibrational energy affects the rate constants. Assume that the molar masses of all isotopes are integers. In all further steps, consider five significant digits.

6.8 After making these isotopic changes, the rates of hydrolysis are not significantly different. Which of the following is most likely to be the rate determining step?

☐ Nucleophilic attack of water on a protonated amidic moiety
☐ C−N bond cleavage
☐ Protonation of the gyromitrin molecule
Problem 7. Cidofovir

Cidofovir (1), originally designed and prepared by the group of Professor Holy in former Czechoslovakia, is a nucleotide analogue with antiviral activity. It is used to treat viral infections, mostly in patients with AIDS.

![Cidofovir (1)](image)

The key intermediate in the synthesis of cidofovir is optically pure diol 2, which can be prepared from L-mannitol (3).
7.1 Draw the structures of compounds A–D, including stereochemistry. One molecule of A produces two molecules of B.
7.2 Draw the structural formulae of all alternative stereoisomers of compound 3 which could be used in the same reaction sequence to afford only the same product 2.

Diol 2 is further modified to provide compound I. The synthesis of phosphonate 4 used to convert compound F to G will be discussed later.
7.3 Draw the structures of compounds E–I, including stereochemistry. Use the abbreviation MMT for the (4-methoxyphenyl)diphenylmethyl group.

The same scheme as on the previous page, for easier orientation

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{OCH}_2\text{Ph} & \quad \text{2} \\
\end{align*}
\]

\[
\begin{align*}
\text{MMT-Cl} & \quad \text{NET}_3 \\
\text{C}_30\text{H}_30\text{O}_4 & \quad \text{E} \\
\text{NaH} & \quad \text{C}_2\text{H}_5\text{CO}_2\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
\text{TsO} & \quad \text{O} \quad \text{DEt}_2 \\
\text{H}_2\text{O} & \quad \text{CH}_3\text{COOH} \\
\text{H}_2\text{O} & \quad \text{CH}_3\text{SOCl} \\
\text{NET}_3 & \quad \text{C}_4\text{H}_6\text{O}_2\text{PS} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{I} \\
\text{C}_{16}\text{H}_{27}\text{O}_2\text{PS} & \quad \text{C}_30\text{H}_{30}\text{O}_4
\end{align*}
\]
Phosphonate 4 can be prepared according to the following scheme:

\[
\begin{array}{c}
\text{O} & \text{Br} \\
\text{O}
\end{array} + J \rightarrow K \\
K \xrightarrow{1. \text{EtONa} \ 2. \text{H}^+} L \\
L \xrightarrow{\text{TsCl} \ \text{NEt}_3} TsO\text{P(OEt)}_2
\]

7.4 Draw the structures of compounds J–L.

The reaction of I (from question 7.3) with cytosine (5) leads to a 3:1 mixture of isomeric compounds M and N. The formation of these two products may be understood by realizing that cytosine (5) can also exist as an aromatic tautomer P. The reaction of M with cyclohexa-1,4-diene and palladium hydroxide on carbon leads to compound O. The phosphonic ester moiety in compound O reacts with bromotrimethylsilane to provide cidofovir (1).
7.5 Draw the structures of the two isomers M, N, of compound O, including stereochemistry, and the structure of the aromatic tautomer P of cytosine (5). The transformation of M to O is the removal of a protecting group.

<table>
<thead>
<tr>
<th>M (75%)</th>
<th>N (25%)</th>
</tr>
</thead>
</table>

![Diagram](image-url)
7.6 Draw the structures of the two simple organic side products \( Q \) and \( R \) formed during the conversion of \( M \) to \( O \).

\( Q \) from cyclohexadiene

\( R \) from the protecting group
Problem 8. Caryophyllene

β-Caryophyllene (3) is a naturally occurring sesquiterpene present in clove trees and in some traditional Czech and Slovak plants, such as the hop plant or the small-leaved linden.

The synthesis of β-caryophyllene starts from a single enantiomer of dienone A. The reaction of A with silyl ketene acetal 1 followed by immediate reduction and aqueous work-up affords ketone 2. This intermediate then undergoes reaction with tosyl chloride, providing B. Basic cyclization of this compound affords C. Finally, the reaction of C with ylide D provides β-caryophyllene.

\[
\begin{align*}
\text{β-Caryophyllene (3)}
\end{align*}
\]
8.1 Draw the structures of compounds A–D, including the appropriate stereochemistry. *Hint: In transformation A → 2, the silyl ketene acetal acts as a nucleophile.*
One of the double bonds in 2 as well as in 3 has trans configuration and the scaffold is stable enough due to the large ring size. trans-Cyclooctene (4) is the smallest ring that can accommodate a trans double bond. It can be prepared according to the following scheme:

![Chemical reaction scheme]

8.2 Draw the structures of reagent E and intermediates F and G, including stereochemistry. Additionally, for F and G, tick the box indicating the stereochemical outcome.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>F</td>
</tr>
<tr>
<td></td>
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</tr>
</tbody>
</table>

- E: single enantiomer
- F: achiral
- G: racemic mixture
- mixture of diastereoisomers
8.3 Draw the structure of the enantiomer of cycloalkene 4.

The two double bonds in β-caryophyllene display different reactivity: the double bond in the ring (endocyclic) is more reactive than the other one (exocyclic) due to the ring strain.

8.4 Draw the structures of compounds Ha + Hb, I and Ja + Jb, including stereochemistry. Hint: Ha + Hb and Ja + Jb are pairs of diastereomers.
<table>
<thead>
<tr>
<th>Ha + Hb</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
</tr>
<tr>
<td>Ja + Jb</td>
</tr>
</tbody>
</table>
Interestingly, the reactivity of the double bonds is reversed when isocaryophyllene (5) is used instead of β-caryophyllene (3).

\[
\begin{align*}
&\text{1. BH}_3\text{THF (1/3 equiv.)} \\
&\text{2. H}_2\text{O}_2, \text{NaOH} \\
&\text{Ka + Kb}
\end{align*}
\]

8.5 Draw the structures of compounds Ka and Kb. Hint: Ka + Kb are a pair of diastereomers.

Isotope-labelled compounds are invaluable tools for reaction mechanism investigation, structure determination, and mass or NMR spectroscopy studies. Let us have a look at the synthesis of some labelled analogues of β-caryophyllene.
8.6 Draw the structures of compounds L and M including the appropriate stereochemistry

β-Caryophyllene (3) undergoes acid-catalyzed cyclization and the components of the mixture of products which are most abundant include, the pair of diastereomers Na + Nb and the pair of diastereomers 7a + 7b. The reaction starts with protonation of the more reactive internal double bond in 3, producing cation O. This cyclizes without the cleavage of a carbon-carbon single bond to yield diastereomeric tricyclic cations Pa and Pb, which undergo hydration to give the target alcohols Na and Nb. Alternatively, the cations Pa and Pb rearrange with the cleavage of a carbon-carbon single bond to cations Qa and Qb, which deprotonate to give compounds 7a and 7b.
8.7 Including the appropriate stereochemistry, draw the structures of the three intermediates O, Pa, Qa leading to the diastereomer 7a.

O

Pa

Qa

8.8 Draw the structures of diastereomers Na + Nb.

Na + Nb

C_{15}H_{26}O