THEORETICAL PROBLEMS

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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 52 pages.
- You may begin writing as soon as the Start command is announced to indicate the commencement of the exam.
- You have 5 hours to complete the exam.
- All results and answers must be clearly written in pen in their respective designated areas in the answer boxes provided on the exam paper.
- You are provided with 3 sheets of paper for the purpose of rough work. If you need additional space, use the back of the exam paper sheets. Only answers given in the designated areas of the answer boxes provided will be graded. Any answer given outside these areas will not be graded.
- The periodic table and the visible light spectrum are not part of this booklet; these 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 purposes 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 exam supervisor will announce a 30-minute warning before the Stop command is announced, indicating the end of the exam.
- You must stop your work immediately when the Stop command is announced. Failure to stop writing past ½ a minute or longer will lead to nullification of your theoretical exam.
- After the Stop command has been announced, 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 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 \( I \) is 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 \( aA + bB \rightleftharpoons cC + dD \):
\[ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

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: \[ \frac{d \ln K}{d T} = \frac{\Delta H_m}{RT^2} \Rightarrow \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

Henderson-Hasselbalch equation: \[ \text{pH} = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

Nernst-Peterson equation: \[ E = E^0 - \frac{RT}{zF} \ln Q \]

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

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

Beer-Lambert law: \[ A = \log \left( \frac{l_0}{l} \right) = \varepsilon c \]

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

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 of its complementary strand read in the 5′→3′ direction. Hence, a palindromic dsDNA consists of two identical strands that are complementary to each other. An example is the so-called Drew–Dickerson dodecanucleotide (1):

\[
\begin{array}{c}
5' - \text{CGCGAATTCGCG}-3' \\
| | | | | | | | \\
3' - \text{GCGCTTAAGCGC}-5'
\end{array}
\]

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

1.2 How many different palindromic double-stranded DNA undecanucleotides (i.e., 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 amount 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 its $T_m$ increases when a single randomly selected base pair is replaced by a G–C pair?
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 $c_{\text{init}} = 1.00 \times 10^{-6}$ 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 dsDNA.

Non-palindromic dsDNA
Calculation:

$$K = \ldots$$

Palindromic dsDNA
Calculation:
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 to be \(-6.07\, \text{kJ mol}^{-1}\) per one G–C pair and \(-1.30\, \text{kJ mol}^{-1}\) per one A–T pair present in a dsDNA.

1.5 How many base pairs are there in the shortest dsDNA oligonucleotide that has \(T_m\) above 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 a non-palindromic dsDNA, \(K_p = 1.00 \times 10^5\) for a palindromic dsDNA. Is the shortest oligonucleotide palindromic or non-palindromic?

<table>
<thead>
<tr>
<th>Calculation of the number of base pairs:</th>
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<tbody>
<tr>
<td>Length needed for a non-palindromic dsDNA:</td>
</tr>
<tr>
<td>Length needed for a palindromic dsDNA:</td>
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</table>

The shortest oligonucleotide is
- ☐ palindromic (P)
- ☐ non-palindromic (NP)
Finally, let us abandon the simplified idea of base pairs contributing individually to the association of DNA strands. The Gibbs energy of this process may be considered explicitly dependent on temperature. The dependence of the inverse of $T_m$ for 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 to make the logarithm unitless).

\[
\begin{array}{c|cccccc}
\ln(2c_{\text{init}}/c_0) & -15 & -14 & -13 & -12 & -11 \\
\hline
1/T_m (K^{-1}) & 0.00314 & 0.00312 & 0.00310 & 0.00308 & 0.00306 \\
c_{\text{init}} (10^{-6} \text{ mol dm}^{-3}) & 0.25 & 0.50 & 1.00 & 2.0 & 4.0 & 8.0 \\
T_m (K) & 319.0 & 320.4 & 321.8 & 323.3 & 324.7 & 326.2 \\
\end{array}
\]
1.6 Calculate the standard enthalpy change $\Delta H^\circ$ and the standard entropy change $\Delta S^\circ$ of the association of DNA single strands to form the palindromic double-stranded Drew–Dickerson dodecanucleotide (1). Assume that $\Delta H^\circ$ and $\Delta S^\circ$ do not vary with temperature.

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, moreover, 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 chiral centres, this process is called epimerization rather than racemization.

### 2.1 Choose all true statements:

- ☐ D-allo-isoleucine and L-isoleucine have the same values for the specific optical rotation but they have different melting points.
- ☐ D-allo-isoleucine and L-isoleucine have identical absolute values for the specific optical rotation but with opposite signs. The melting point is the same for both isomers.
- ☐ D-allo-isoleucine and L-isoleucine have different values for the specific optical rotation but they have the same melting points.
- ☐ D-allo-isoleucine and L-isoleucine have different values for the 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:

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

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

The number of stereoisomers is:

At the start of the epimerization, we can neglect the reverse reaction. The epimerization then follows first-order kinetics:

$$\text{L-isoleucine} \xrightarrow{k_1} \text{D-allo-isoleucine}$$

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 is $k_1(421 \text{ K}) = 1.18 \times 10^{-2} \text{ h}^{-1}$.

In the following calculation, abbreviate the concentration of L-isoleucine as [L] and of D-allo-isoleucine as [D]. We can then define the diastereomeric excess ($de$) as:

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

2.5 Let us boil L-isoleucine for 1943 h at 374 K. What is the value of $de$ (with three significant figures) for L-isoleucine a) before boiling and b) after boiling?

a) Before boiling

Calculation:
de = % (answer with 3 significant figures)

b) After boiling
Calculation:

de = % (answer with 3 significant figures)

2.6 How long does it take to convert 10% of L-isoleucine to D-allo-isoleucine at 298 K?
Calculation:
In fact, the reverse reaction cannot be neglected. The correct kinetic scheme is expressed as:

\[
\text{L-isoleucine} \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad \text{D-allo-isoleucine}
\]

Let us define the deviation of concentration from its equilibrium value \([L]_{\text{eq}}\) as:

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

It is possible to derive the following equation showing that \(x\) evolves with time:

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

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

2.7 Let us boil 1.00 mol dm\(^{-3}\) of L-isoleucine solution for 1943 h at 374 K. The rate constant for the forward reaction is \(k_1(374 \text{ K}) = 9.02 \times 10^{-5} \text{ h}^{-1}\); \(K_{\text{ep}}\) for L-isoleucine epimerization has the value of 1.38 (at 374 K). In the following calculation, abbreviate the concentration of L-isoleucine as [L] and of D-allo-isoleucine as [D]. Determine (with three significant figures):

a) \([L]_{\text{eq}},\) b) diastereomeric excess \((de)\) after boiling.

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

b) Calculation:
Amino acids with a single chiral centre undergo racemization, e.g. L-arginine racemizes:

\[
\text{L-arginine} \quad \xrightleftharpoons[k_1]{k_1} \quad \text{D-arginine}
\]

The time evolution of concentrations is governed by

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

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

The Holy Roman Emperor Lothar III passed away during his journey to Sicily in 1137. To facilitate the repatriation of his remains, immediately after his death his body was boiled in water (373 K) for a certain time. Let us try to estimate the boiling time with the help of chemical kinetics. We know that the rate constant \(k_1\) of arginine racemization within the protein at 373 K and pH = 7 has the value of \(5.10 \times 10^{-3}\) h\(^{-1}\).

In order to analyse the isomeric composition of arginine in Lothar’s bones, we need to start by releasing the arginine into solution via hydrolysis of the bone. Lothar’s bones were hydrolyzed in a highly acidic environment at 383 K for 4 h. The ratio of the optical isomers was \(\frac{[D]}{[L]} = 0.090\). Lothar’s wife Richenza was not boiled after her death, but her bones were hydrolyzed using the same procedure. In this case the ratio was \(\frac{[D]}{[L]} = 0.059\).

(Note that the racemization also takes place during the hydrolysis, with the rate constant \(k_1'\), different from \(k_1\)).
2.8 In 1137, for how long was the Holy Roman Emperor Lothar III boiled in water?

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

Calculation:

\[ t_{\text{boiling}} = h \]
### Problem 3. Emerging electro-mobility

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

3.1 Mark the factors that can increase the efficiency of a heat engine:
- ☐ 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

Fuel cells represent a way of improving the engine efficiency for future vehicles. The engine efficiency can be improved by using hydrogen-based fuel cells.

3.2 The standard enthalpy change of formation of liquid water is $\Delta_f H^\circ(H_2O,l) = -285.84 \text{ kJ mol}^{-1}$, and the standard combustion enthalpy change of isooctane is $\Delta_c H^\circ(C_8H_{18},l) = -5065.08 \text{ kJ mol}^{-1}$, both at 323.15 K. Calculate the values of specific (per unit of mass) combustion enthalpy at 323.15 K of pure liquid isooctane and pure gaseous hydrogen.

\[
\Delta_c H_s^\circ(C_8H_{18}) = \]

\[
\Delta_c H_s^\circ(H_2) = \]

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<tr>
<th>Theoretical Problem 3</th>
<th>Question</th>
<th>3.1</th>
<th>3.2</th>
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**THEORETICAL PROBLEMS, OFFICIAL ENGLISH VERSION**

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3.3 Calculate the standard electromotive force (EMF) of a fuel cell using gaseous oxygen and hydrogen, both ideal gases at 100 kPa and 323.15 K, to produce liquid water. Use the following entropy data at 323.15 K: 
\[ S^\circ(H_2O,l) = 70 \text{ J K}^{-1} \text{ mol}^{-1}, \quad S^\circ(H_2,g) = 131 \text{ J K}^{-1} \text{ mol}^{-1}, \quad S^\circ(O_2,g) = 205 \text{ J K}^{-1} \text{ mol}^{-1}. \]

**Calculations:**

\[ \text{EMF} = \text{V} \]

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

\[ \eta = \% \]

3.5 A polymer membrane electrolyzer facility operated at a voltage of 2.00 V and powered by a 10.0 MW wind turbine plant was running at full power from 10 pm to 6 am. The electrolysis yielded 1090 kg of pure hydrogen. Calculate the electrolysis yield, defined as the mass of hydrogen produced divided by its theoretical produced mass.

**Calculations:**
3.6 Calculate the mass of hydrogen required to drive the distance 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 on average 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 $\Delta G = -226$ kJ mol$^{-1}$.

Calculations:

\[
\eta_{\text{electrolysis}} = \%
\]

\[
m = \text{kg}
\]

The low efficiency of hydrogen production and the safety issues connected with its storage impede the spread of the hydrogen-based transportation technology. Hydrazine ($N_2H_4$) fuel cells might be a suitable alternative.
The following standard reduction potentials for aqueous hydrazine systems are available:

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

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. Show all the necessary calculations.

a) Acidic environment (pH = 0)

\[
\begin{array}{c}
N_2 \\
\downarrow \\
\downarrow \\
N_2H_5^+ \\
\downarrow \\
\downarrow \\
NH_4^+ \\
\downarrow \\
\downarrow \\
H^+ \\
\downarrow \\
\downarrow \\
H_2O \\
\end{array}
\]

b) Basic environment (pH = 14)

\[
\begin{array}{c}
N_2 \\
\downarrow \\
\downarrow \\
N_2H_4 \\
\downarrow \\
\downarrow \\
NH_3 \\
\downarrow \\
\downarrow \\
OH^- \\
\downarrow \\
\downarrow \\
OH^- \\
\downarrow \\
\downarrow \\
H_2O \\
\end{array}
\]

Calculations:

Due to its toxicity, odour and environmental impact, it is extremely undesirable to produce ammonia in fuel cells.
3.8 Write 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:

Calculations:
Hydrazine decomposition to \( \text{NH}_3 \) and \( \text{N}_2 \) in a basic environment:

\[ K = \]

Hydrazine decomposition to \( \text{H}_2 \) and \( \text{N}_2 \) in a basic environment:

\[ K = \]

Rechargeable lithium-based batteries are an alternative to fuel cells. Lithium-ion batteries commonly use graphite as 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 to this system can be formally written as:

\[
\begin{align*}
(C)_n + \text{Li}^+ + e^- &\rightarrow \text{Li(C)}_n & E^\circ = -3.05 \, \text{V}, \\
\text{CoO}_2 + \text{Li}^+ + e^- &\rightarrow \text{LiCoO}_2 & E^\circ = +0.19 \, \text{V}.
\end{align*}
\]

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 with the correct statements valid for the discharge of the lithium-based battery described in 3.9:

Li(C)_n electrode is □ cathode □ anode because lithium ions are reduced here because lithium atoms are oxidized here

LiCoO_2 electrode is □ cathode □ anode because cobalt ions are reduced here because cobalt ions are oxidized here

3.11 Assume that a C_6 unit, a CoO_2 unit and a 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 \((c_{q,s}) = \quad \text{mAh g}^{-1}\)

Calculations:

Energy density \((\rho_{el}) = \quad \text{kWh kg}^{-1}\)
Problem 4. Column chromatography of radioactive copper

$^{64}$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 $^{64}$Zn nucleus bombardment with deuterium nuclei, giving $^{64}$Cu. Specify the corresponding atomic and mass numbers of all species.

\[ ... + ... \overset{\text{...}}{\longrightarrow} ... + ... \]

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

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

Before you start the calculation, add the charges in the upper right boxes:

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

\[
\begin{array}{cccc}
  i & 1 & 2 & 3 & 4 \\
\beta_i & 2.36 & 1.49 & 0.690 & 0.055 \\
\end{array}
\]

Calculation:
Mole fraction =

(4.3) Does the column temperature change during the washing with hydrochloric acid? (Note: All components were initially at room temperature).

☐ 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.

Using a simple experimental formula, you can calculate the retention volume $V_R$ (i.e. the mobile phase volume at which 50% of the compound has been eluted from the column) that characterises the average elution properties of copper and zinc species on the column:

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

4.4 Using the average mass distribution coefficients $D_g$ ($D_g(\text{Cu species}) = 17.4 \text{ cm}^3 \text{ g}^{-1}$, $D_g(\text{Zn species}) = 78.5 \text{ cm}^3 \text{ g}^{-1}$), 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 is $m_{\text{resin,dry,OH form}} = 3.72$ g and the void volume of the column is $V_0 = 4.93 \text{ cm}^3$. 
Calculation:

\[ V_{R(Cu \text{ species})} = \text{cm}^3 \]  
(answer with 1 digit after the decimal point)

\[ V_{R(Zn \text{ species})} = \text{cm}^3 \]  
(answer with 0 digit after the decimal point)

If you cannot find the answer, use \( V_{R(Cu \text{ species})} = 49.9 \text{ cm}^3 \) and \( V_{R(Zn \text{ species})} = 324 \text{ cm}^3 \) for further calculations.

Using a simple experimental formula, 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, and can be obtained as follows:

\[ V_{0.001}(A) = V_R(A) \times \left(1 - 6.91\sqrt{\frac{d_p}{L_c}}\right) \]
\[ V_{0.001}(B) = V_R(B) \times \left(1 - 6.91\sqrt{\frac{d_p}{L_c}}\right) \]
\[ V_{0.999}(B) = 2V_R(B) - V_{0.001}(B) \]

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

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

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

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%.

\[
Q_{m,\text{theor}} = \text{mmol g}^{-1}
\]

(answer with 2 digits after decimal point)

If you cannot find the answer, use $Q_{m,\text{theor}} = 4.83$ 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 excess of a sodium sulfate solution. The effluent 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.

\[
Q_v = \text{mmol cm}^{-3}
\]

(answer with 2 digits after decimal point)

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

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

\[
x =
\]

(answer with 3 digits after decimal point)
**Problem 5. Bohemian garnet**

Bohemian garnet (pyrope) is a famous Czech blood coloured semi-precious stone. The chemical composition of natural garnets is expressed by the general stoichiometric formula $A_{3}B_{2}(SiO_{4})_{3}$, where $A^{II}$ is a divalent cation and $B^{III}$ is a trivalent cation. Garnets have a cubic unit cell which contains 8 formula units. The structure comprises 3 types of polyhedra: the $A^{II}$ cation occupies a dodecahedral position (it is surrounded by eight O atoms), the $B^{III}$ cation occupies an octahedral position (it is surrounded by six O atoms) and $Si^{IV}$ occupies a tetrahedral position (it is surrounded by four O atoms).

The most common garnet mineral is almandine which has the formula $Fe_{3}Al_{2}(SiO_{4})_{3}$. Its unit cell parameter is $a = 11.50 \text{ Å}$.

5.1 Calculate the theoretical density of almandine $\rho$ in g cm$^{-3}$.

$$\rho = \text{ g cm}^{-3}$$

Bohemian garnet has the composition $Mg_{3}Al_{2}(SiO_{4})_{3}$. The pure compound is colourless. 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 $[Cr^{III}O_{6}]^{oct}$ d-orbitals and fill it with electrons.
5.3 Identify the 1st row transition element(s) whose trivalent cation(s) M\textsuperscript{III} placed in an octahedral crystal field is/are diamagnetic in its low-spin configuration and paramagnetic in its corresponding high-spin configuration.

5.4 The figure below shows the splitting of the d-orbitals in the dodecahedral crystal field. Fill in the electrons for the [Fe\textsuperscript{II}O\textsubscript{8}]\textsuperscript{dod} chromophore for both high-spin and low-spin configurations.

\begin{itemize}
  \item [a)] high-spin configuration
  \begin{itemize}
    \item \[E_1 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 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\frac{\text{P}}{\text{E}_2}
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 (A, B, C or D) to 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? Mark an (x) in the correct box.

- [ ] Red  [ ] Blue  [ ] Yellow-orange  [ ] Black
- [ ] Yellow  [ ] Blue-green  [ ] Violet  [ ] 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 $\text{Ca}_3[\text{Fe,Ti}_{\text{oct}}^\text{III}][\text{Si,Fe}_{\text{tet}}^\text{IV}O_4]_3$.

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

\[
p = \ \%\]

The colour of the mineral is due to two chromophores: $[\text{Fe}^{III}O_6]^{\text{oct}}$ and $[\text{Fe}^{III}O_4]^{\text{tet}}$ respectively. The central Fe$^{III}$ ions for both chromophores contain an equal number of unpaired electrons.

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

\[
[\text{Fe}^{III}O_6]^{\text{oct}}: \hspace{2cm} [\text{Fe}^{III}O_4]^{\text{tet}}:
\]

A tetrahedral crystal field causes a smaller splitting than the corresponding octahedral crystal field ($\Delta_{\text{tet}} = \frac{4}{9} \Delta_{\text{oct}}$). Surprisingly for the Fe$^{III}$ ion, the energy of the first d–d electronic 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 value of the pairing energy $P$ in cm$^{-1}$ and the values of both crystal field splitting energies $\Delta_{\text{oct}}$ and $\Delta_{\text{tet}}$ in cm$^{-1}$. Assume that the pairing energy $P$ is equal in both chromophores.

\[
P = \ \text{cm}^{-1}
\]
\[
\Delta_{\text{oct}} = \ \text{cm}^{-1}
\]
\[
\Delta_{\text{tet}} = \ \text{cm}^{-1}
\]
Synthetic garnet YAG (Yttrium Aluminium Garnet), used in optoelectronics, has the composition $Y_3Al_5O_{12}$. Its structure is derived from the general garnet structure $A_3B_2(SiO_4)_3$ by placing the ions $Y^{III}$ and $Al^{III}$ in the A, B and Si positions.

5.12 Based on your knowledge of the relative ionic radii, determine which cation ($Y^{III}$ or $Al^{III}$) occupies each position A, B and Si.

<table>
<thead>
<tr>
<th>A:</th>
<th>B:</th>
<th>Si:</th>
</tr>
</thead>
</table>

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

$Y_xCe_yAl_5O_{12}$

$x = y =$

If you do not get a result, use $x = 2.25$ and $y = 0.75$.

5.14 The Ce$^{III}$-doped YAG is prepared by annealing the mixture of $Y_2O_3$, $Al_2O_3$ and $CeO_2$ in an atmosphere of $H_2$. Using the formula for $Y_xCe_yAl_5O_{12}$ worked out in 5.13, write a balanced equation for this reaction using the smallest whole-number ratio of stoichiometric coefficients.

Equation:
Doping the YAG structure with rare-earth ions enables lasers to be produced with emission wavelengths ranging from the UV to the mid-IR region. In the scheme below, simplified f–f energy transitions of selected rare-earth ions are shown.

5.15 Identify which cation has a transition which corresponds to blue light emission. Mark an (x) in the correct box.

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

5.16 Calculate the emission wavelength of this light $\lambda$ in nm.

$\lambda =$ 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 was the blood-coloured Bohemian garnet. Mark an (x) in the correct box.

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

Going foraging for mushrooms is a traditional Czech and Slovak pastime. While many 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 easily synthesized from ethyl 3-chloropropanoate (1).

6.1 Draw the formulae of compounds A–E including stereochemistry when necessary.

*Hint: The first reaction to form compound A proceeds via an organometallic compound which subsequently cyclizes.*

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>E</td>
<td></td>
</tr>
</tbody>
</table>
In the human body, coprine undergoes hydrolysis to L-glutamic acid (3) and compounds C and 4, which are responsible for the adverse side-effects of coprine. They inhibit the enzyme acetaldehyde dehydrogenase, which is involved in the metabolism of alcohol. When this enzyme is inhibited, acetaldehyde formed by alcohol dehydrogenase accumulates in the body, causing the strong symptoms of a hangover (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 pictogram for acetaldehyde dehydrogenase above, draw the structure F of the enzyme inhibited by compound 4.

The antabuse effect was named after antabuse (5), the most commonly used drug in alcohol-addiction treatment. This drug can be synthesized according to the following scheme:
6.3 Draw the formulae of compounds G and H.

*Hint: Compound H contains five carbon atoms.*

![Formulae of G and H](image)

6.4 Mark with an (x) all possible reagents which could be used as I from the following list:

- [ ] m-chloroperbenzoic acid (mCPBA)
- [ ] dilute H₂O₂
- [ ] Zn/CH₃COOH
- [ ] NaBH₄
- [ ] I₂
- [ ] hot concentrated H₂SO₄
- [ ] K₂CO₃, H₂O
- [ ] AlCl₃

The way antabuse inhibits acetaldehyde dehydrogenase is similar to the effect of compounds C and 4.

![Structure of Enzyme and 5](image)

Enzyme = acetaldehyde dehydrogenase

6.5 Using the pictogram for acetaldehyde dehydrogenase above, draw the structure J of the enzyme inhibited by antabuse (5).

*Hint: Three sulfur atoms should be in the structure.*

![Structure of J](image)
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 since it contains gyromitrin (M). This natural compound can be prepared from *N*\)-methylhydrazine (6):

```
\[
\begin{align*}
\text{HO}_2 & + \text{OCl} \\
\text{NH}_2 & \xrightarrow{\text{(1 equiv.)} \ \text{Et}_3\text{N}} \text{L} \\
\text{K} & \quad \text{M}
\end{align*}
\]
```

6.6 Draw the formulae of compounds K–M.

In the human body, gyromitrin (M) hydrolyzes and can form *N*\)-methylhydrazine (6), which is strongly hepatotoxic. Gyromitrin (M) hydrolysis occurs as soon as it enters the acidic environment of the 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 wavenumber of the stretching mode of vibration of the relevant C–N bond occurs at 1293.0 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 the human body, 37 °C, for the given hydrolysis reaction, assuming both relevant nitrogen and carbon atoms were simultaneously substituted i.e. \(^{14}\text{N}\) with the \(^{15}\text{N}\) isotope and \(^{12}\text{C}\) with the \(^{13}\text{C}\) 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 figures.**
6.8 After making these isotopic changes, the rates of hydrolysis are not significantly different. Which of the following is most likely the rate-determining step? Mark an (x) in the correct box.

☐ 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.

<table>
<thead>
<tr>
<th>A</th>
<th>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.2 Draw the structural formulae of all alternative stereoisomers of compound 3 which could be used in the same reaction sequence to only form the same product 2.

Diol 2 is further modified to give compound I. The synthesis of the 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 following is the same scheme as given on the previous page, for ease of orientation:
The phosphonate 4 can be prepared according to the following scheme:

\[
\text{O} - \text{Br} + \text{J} \xrightarrow{\text{K}} \text{L} \xrightarrow{\text{TsCl, NEt}} \text{4}
\]

1. EtONa
2. H^+

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 results in the formation of compound O. The phosphonic ester moiety in compound O reacts with bromotrimethylsilane to form cidofovir (1).
7.5 Draw the structures of the two isomers $M$, $N$, and of compound $O$, including stereochemistry, and the structure of the aromatic tautomer $P$ of cytosine (5). The transformation of $M$ to $O$ involves the removal of a protecting group.
7.6 Draw the structures of the two, simple organic side-products \( Q \) and \( R \) formed during the conversion of \( M \) to \( O \).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>from cyclohexadiene</td>
</tr>
<tr>
<td>R</td>
<td>from the protecting group</td>
</tr>
</tbody>
</table>
Problem 8. Caryophyllene

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

The synthesis of β-caryophyllene commences from a single enantiomer of dienone A. The reaction of A with silyl ketene acetal 1 followed by immediate reduction and aqueous work-up results in the formation of ketone 2. This intermediate then undergoes reaction with tosyl chloride to form B. Basic cyclization of this compound results in C. Finally, the reaction of C with ylide D produces β-caryophyllene.
8.1 Draw the structures of compounds A–D, including the appropriate stereochemistry. 
*Hint: In the transformation A → 2, the silyl ketene acetal acts as a nucleophile.*

A

\[ \text{C}_{10}\text{H}_{14}\text{O} \]

B

\[ \text{Ts} \]

\[ \text{H}_3\text{C} \]

\[ \overset{\text{O}}{\text{O}} \]

\[ \overset{\text{O}}{\text{O}} \]

\[ \overset{\text{Ph}}{\text{Ph}} \]

\[ \overset{\text{P} \cdot \text{CH}_3}{\text{Br}} \]

\[ n\text{-BuLi} \]

\[ \text{DIBAL-H} \]

\[ \text{TsCl} \]

\[ \text{pyridine} \]

\[ t\text{-BuOK} \]

\[ \beta\text{-Caryophyllene (3)} \]

C

D
One of the double bonds in 2 as well as in 3 has a 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:

8.2 Draw the structure of reagent E and intermediates F and G, including the appropriate stereochemistry. For F and G, mark the box with an (x) indicating the resultant stereochemical outcome.

<table>
<thead>
<tr>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>achiral</td>
<td>achiral</td>
</tr>
<tr>
<td>single enantiomer</td>
<td>single enantiomer</td>
</tr>
<tr>
<td>racemic mixture</td>
<td>racemic mixture</td>
</tr>
<tr>
<td>mixture of diastereoisomers</td>
<td>mixture of diastereoisomers</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>achiral</td>
</tr>
<tr>
<td>single enantiomer</td>
</tr>
<tr>
<td>racemic mixture</td>
</tr>
<tr>
<td>mixture of diastereoisomers</td>
</tr>
</tbody>
</table>
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 the appropriate 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 \( \beta \)-caryophyllene (3).

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

\[5 \rightarrow \text{Ka + Kb}\]

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 investigations, structure determinations, and mass or NMR spectroscopy studies.

Consider the synthesis of a selection of labelled analogues of \( \beta \)-caryophyllene:
8.6 Draw the structures of compounds L and M, including the appropriate stereochemistry.

\[
\begin{array}{c|c|c}
L & M & C_{14}H_{20}D_{2}O \\
\end{array}
\]

\[\beta\text{-Caryophyllene (3)}\] undergoes acid-catalyzed cyclization, which results in a complex mixture of products. Among them, the pair of diastereomers Na + Nb and the pair of diastereomers 7a + 7b are the most abundant. The reaction starts with protonation of the more reactive internal double bond forming cation O. This cyclizes without the cleavage of a carbon-carbon single bond to yield the diastereomeric tricyclic cations Pa and Pb, which undergo hydration to give the target alcohols Na and Nb. Alternatively, the cations Pa and Pb can rearrange with the cleavage of a carbon-carbon single bond to form cations Qa and Qb, which deprotonate to form compounds 7a and 7b.

8.7 Draw the structures of the three intermediates O, Pa, Qa, including the appropriate stereochemistry, leading to the diastereomer 7a.
8.8 Draw the structures of diastereomers $\text{Na} + \text{Nb}$.