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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הוראות כלליות

• מח抃ת הבניהحتיאוריות שבידכם מכילה 57 דפים.
• אamateכליים ותקנים (חיוביים! נא ברע לשיעי lakhai) להתחלה לפטור את המבחנים ממorate שינהープוקודה.
• Startברשותכם 5 שעות להשלמת הבניה.
• יש לכם את התשובה והתאוצה לבחינה, בוכנה ובחרו את התשובה המיטבית لكل בוכנה 찾아זאת. ושובו שכנובש בוכנה.
• קיבלו בד צהוב עם מח歩いて הבניה 3 דפים נוספים. אם אתם羰וקים לزواج זה, השתמשו בד האזרי של מח歩いて הבニア.
• הבニア. זכרו שהשניים דרים מוחים ליר必要があります התשובה לא יקבלו.
• הנבולה המתחוורית וס펙טרום האור והתאוצה אין חלים למחترنت 2, והייחולים לכמ בדפים.
• השתמשו רק בעט ובמחשבון שקיבלתם.
• הגדרת האופטימנט האגנולית של מח歩いて הבניה התאוצה לפסקת התחלימה, וממשיתرك לזרכי הבניה.
• אם מצליחו לשלוח את המח歩いて הבניה (בעזרת שיחותוס ולשון), נتقدم מחונית-המחנה IChO-המחנה. משנית הבניה
• יש Inserts את הכפרים.
• משנית הבניה ידייע מושך ישאר 30 דקות לסיום הבניה.
• תปรับปร לפסיקיה לוחות ולא להשתמש מח نطושו מידי עם השתייפה הפוקודה לא לא ת pwm 30 שניות.
• ת冶金 מרגוע השתייפה הפוקודה, מחנה שולחן יסוי!
• לאחר השתייפה הפוקודה, תניין את מח歩いて הבניה במשתתפת הבניה ושיירה ישים על הכיס.
• משניי הבניה יבוא לאסף את מפעטי הבניה ממכ.
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: \( P = U I \)
where \( U \) is voltage and \( I \) electric current
Enthalpy: \( H = U + pV \)
Gibbs free energy: \( G = H - TS \)
\( \Delta G^0 = -RT \ln K = -zF E_{\text{cell}}^0 \)
\( \Delta G = \Delta G^0 + RT \ln Q \)

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 \( c_m \):
\( \Delta q = n c_m \Delta T \)
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: \[E = E^0 - \frac{RT}{2F} \ln Q\]

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

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

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

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

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

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

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: \[\frac{1}{[A]} = \frac{1}{[A]_0} + kt\]
Theoretical Problem 1

<table>
<thead>
<tr>
<th>Question</th>
<th>1.1</th>
<th>1.2</th>
<th>1.3</th>
<th>1.4</th>
<th>1.5</th>
<th>1.6</th>
<th>Total</th>
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<td>4</td>
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**DNA. **

A double-stranded DNA molecule is defined as DNA that has two strands. One DNA strand is read in the direction 5′-CGCGAATTCGCG-3′, while the other makes the complementary strand 3′-GCGCTTAAGCGC-5′. Examples of such DNA molecules are known as Drew-Dickerson dodecanucleotides.

1. How many double-stranded DNA dodecanucleotides are there?

2. How many double-stranded DNA undecanucleotides are there?
The International Chemistry Olympiad / Slovakia & Czech Republic, 2018

Theoretical Problems

Official English Version

6

\[ T_m, \text{ the melting temperature of dsDNA, is defined as the temperature at which 50}\% \text{ of the original double-stranded DNA is converted into single-stranded DNA. (A-T)} \]

1.3 In double-stranded DNA, \( T_m \) is defined as the temperature at which 50% of the original dsDNA molecule is converted into single-stranded DNA. The DNA strand with G-C bonds has a higher \( T_m \) than the DNA strand with A-T bonds.

(1) Drew-Dickerson dodecanucleotide seems to be a suitable choice for studying the melting temperature of dsDNA.

1.4 The probability that a randomly chosen A-T base pair will be replaced by a G-C base pair is calculated as follows:

\[ \text{Probability} = \frac{\text{number of G-C pairs in the sequence}}{\text{total number of base pairs}} \]

Now we focus on the thermodynamics of creating a double-stranded DNA molecule from single-stranded DNA, and its dependence on the length of the DNA molecule and temperature. There is a different equilibrium constant for the association (binding) of single-stranded DNA molecules to form dsDNA, whether it is palindromic or non-palindromic.

Non-palindromic dsDNA

Calculation:

\[ K = \text{Palindromic dsDNA} \]

Calculation:
The contribution of the entropy of the formation of a double-stranded DNA to the overall entropy of the reaction of association of two individual bases to form dsDNA was examined within a certain range of experimental conditions, and the values 1 - 6.07 kJ mol\(^{-1}\) were obtained for each pair C-G that appears in dsDNA, and 1 - 1.30 kJ mol\(^{-1}\) for each pair T-A that appears in dsDNA.

The contribution of the transition state entropy, that of the transition state of the association of individual bases to form dsDNA, is calculated as follows:

\[
K = \frac{1}{1.00 \times 10^6} \times \frac{1.00 \times 10^5}{K_{A} - 1.30 \times 10^5}
\]

For dsDNA that is not palindromic, the shortest oligonucleotide double-stranded for a given \(T_m\) is:

\[
T_m = \frac{1}{330} K
\]

Is the shortest oligonucleotide double-stranded palindromic or not?

Calculation of the number of base pairs:

The needed length of a non-palindromic dsDNA:
The needed length of a palindromic dsDNA:

The shortest oligonucleotide is

- [ ] palindromic (P)
- [ ] non-palindromic (NP).

The shortest oligonucleotide is palindromic (P).

\( T_m = \text{The shortest oligonucleotide is palindromic (P).} \)

\( \frac{1}{T_m} \) vs. \( \ln(2c_{\text{init}}/c_0) \)

<table>
<thead>
<tr>
<th>( c_{\text{init}} \times 10^{-6} \text{ mol dm}^{-3} )</th>
<th>0.25</th>
<th>0.50</th>
<th>1.00</th>
<th>2.0</th>
<th>4.0</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_m / \text{K} )</td>
<td>319.0</td>
<td>320.4</td>
<td>321.8</td>
<td>323.3</td>
<td>324.7</td>
<td>326.2</td>
</tr>
</tbody>
</table>

(בבולון: נעשתה שיטות בריכוז סטנדרטי של \( c_0 = 1 \text{ mol dm}^{-3} \) ד"מ שباشرול הגלרים הוא בטון צהוב.)
Consider the standard enthalpy change at standard conditions, $\Delta H^\circ$, and the standard entropy change, $\Delta S^\circ$, for the association of individual DNA strands to form the Drew-Dickerson dodecanucleotide (1). Assume $\Delta H^\circ$ and $\Delta S^\circ$ are independent of temperature.

**Calculation:**
Theoretical Problem 2

Question

Points

1

2.1

4

2.2

4

2.3

2

2.4

6

2.5

10

2.6

17

2.7

14

2.8

Total

58

% of the total

8%

Repatriation of remains in the middle ages

רטריג' 2

רטריג' 2

The theoretical reaction

רטריג' 2

The theoretical reaction

2.1

Termination of the racemization reaction (racemization) is a slow reaction. Therefore, it can be used for the dating of biological objects, and more specifically, to study their thermal history.

We take as an example the L-isoleucine (L-Ile) L-isoleucine (2S,3S)-2-amino-3-methylpentanoic acid - (L-Ile) L-isoleucine (2S,3S)-2-amino-3-methylpentanoic acid.

D-allo-isoleucine (2R,3S)-2-amino-3-methylpentanoic acid - D-allo-isoleucine (2R,3S)-2-amino-3-methylpentanoic acid.

2.2

Align the absolute configuration of all stereo-isomers of isoleucine.

2.3

The value of the equilibrium constant for the epimerization of isoleucine-L is 1.38 (at 374 K). If we know the activation energy for D-allo-isoleucine lower than for L-isoleucine, L-isoleucine

The enthalpy change for the reaction from A to D at 374 K is 2.2 kJ/mol.
The number of stereoisomers is

 boca selections from two possible states of the tripeptide Ile-Ile-Ile?

The rate constant of the racemization reaction can be neglected in the forward direction. In this case, the kinetic of the racemization reaction occurs as a first-order reaction:

\[
k_1(374 \text{ K}) = 9.02 \times 10^{-5} \text{ h}^{-1}
\]

\[
k_1(421 \text{ K}) = 1.18 \times 10^{-2} \text{ h}^{-1}
\]

We have, therefore, the following expressions for the diastereomeric excess (de):

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

Marinetti's bench length was 1943 cm. At 374 K, the value of de (3 digits) was

\[
L-\text{isoleucine}
\]

For a)

Before boiling

Calculation:
b) After boiling
Calculation:

\[ de = \% \]

\[ de = \% \]

Calculation:
\[ t = \text{years} \]

In the process, it is not possible to ignore the reaction in the second direction. It is possible to describe the actual kinetics according to the following agreement:

\[
\text{L-isoleucine} \xrightleftharpoons[k_2]{k_1} \text{D-allo-isoleucine}
\]

Define the deviation of the concentration \( L \) at a certain time from the equilibrium concentration (denoted \( [L]_{\text{eq}} \)) as:

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

After calculation, you can reach an expression for \( x \) as a function of time for the following equation:

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

When \( x(0) \) is the deviation of the concentration of \( L \)-isoleucine from equilibrium at 0 h.

2.7

Calculate the concentration of \( L \)-isoleucine at 0.14 mol dm\(^{-3}\) for 1943 K.

\[ k_f(374 \text{ K}) = 9.02 \times 10^{-5} \text{ h}^{-1} \]

\[ K_{\text{eq}}(374 \text{ K}) = 1.38 \]

a) Calculation:

\[ \text{deviation at time } t = \text{years} \]
\[ [L]_{eq} = \text{mol dm}^{-3} \]

b) Calculation:
The reaction of L-arginine with a single chiral center also undergoes racemization. For example, the racemization of L-arginine:

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

The reaction is described by the equation:

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

where \( t \) is the time, \([D] \) and \([L] \) are the concentrations of D-arginine and L-arginine at time \( t \), respectively, \( k_1 \) is the rate constant of the reaction, and \( C \) is determined by the initial conditions of the reaction.

The concentration of \( C \) is calculated by the formula:

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

The concentration of L-arginine after racemization is found by the equation:

\[ t = \frac{[L]}{[D]} \]

Furthermore, the concentration of L-arginine in the original body of Luther can be calculated by the equation:

\[ \text{de} = \% \text{ of 3 significant figures} \]

It is known that the rate constant of racemization of arginine within the protein in the body at 373 K and \( pH = 7 \) is equal to \( k = 5.10 \times 10^{-3} \text{ h}^{-1} \).

The concentration of D-arginine in the original body of Luther can be calculated by the equation:

\[ ([D]) = 0.090 \]

In order to achieve the racemization of arginine within the protein, the bones of Luther were subjected to hydrolysis in an extremely acidic environment for 4 hours at 383 K (boiling point). The ratio of the bones after hydrolysis to arginine is determined for each reactant at 383 K.

THEORETICAL PROBLEMS, OFFICIAL ENGLISH VERSION
In the same process as Luther's bones (during our time), in this case the ratio was $[D]/[L] = 0.059$. (Note that deamidation occurs during hydrolysis, with first-order rate constant $k_1$ which is different from the rate constant $k$.)

2.8. Boil the bones of the king and the bones of Emperor Luther III in water for how long after death in 1137?

Note: Deamidation of arginine is a very slow process at body temperatures usually found in cemeteries. Since the two bodies were buried about 880 years ago, we can neglect the naturally occurring deamidation that occurred.

Calculation:

\[ t_{\text{boiling}} = h \]
Emerging electro-mobility

3.1: Mark the factors which can increase the efficiency of a hot engine:
☐ Increased mechanical friction of the engine
☐ Increased combustion temperature of the fuel
☐ Decreased working temperature range of the engine
☐ Increased gas pressure during work

In the future, tank fuels can be used to improve engine efficiency. This can be done by using tank fuels based on

3.2: The standard enthalpy of formation of water vapor is $\Delta H_f^\circ (H_2O, l) = 285.84 \text{ kJ mol}^{-1}$ and the standard enthalpy of isooctane $\Delta H_f^\circ (C_8H_{18}, l) = -5065.08 \text{ kJ mol}^{-1}$.

Calculate the specific enthalpy of combustion (per mass) of pure water vapor $\Delta cH_s^\circ$ (H_2O) and pure isooctane $\Delta cH_s^\circ$ (C_8H_{18}).
3.3 Think about the standard electromotive force (EMF) of the fuel cell using oxygen and water vapor, both at 100 kPa and 323.15 K (ideal gases under these conditions). Calculate the water vapor and the entropy values at 323.15 K:

- $S^\circ_{\text{(H}_2\text{O, l)}} = 70 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S^\circ_{\text{(H}_2, \text{ g)}} = 131 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S^\circ_{\text{(O}_2, \text{ g)}} = 205 \text{ J K}^{-1} \text{ mol}^{-1}$

Calculations:

$$\text{EMF} = V$$

3.4 Electrons transfer to the oxygen, forming water. The standard free energy change is $\Delta G^\circ = -225.85 \text{ kJ mol}^{-1}$ and the enthalpy change is $\Delta H^\circ = -281.64 \text{ kJ mol}^{-1}$. Calculate the efficiency ($\eta$) of the fuel cell at 353.15 K (323.15 K to 353.15 K).

$$\eta = \%$$
3.5 The rate constant for the reaction of aqueous chlorine with solid silver is 2.00 V.

3.6 Shown as the diagram is the silver chloride produced, the concentration of silver chloride is 1.00 M. The volume is 0.50 L. Calculate the concentration of silver ions in the solution.
The low efficiency of hydrogen production and the safety issues arising from its storage are hindering the expansion of hydrogen-based transportation technologies. Hydrogen fuel cells (\(\text{N}_2\text{H}_4\)) could perhaps serve as a suitable and potential substitute for the standard combustion processes in water solutions for materials containing hydrogen.

Complete the following electron transfer reactions for the materials containing hydrogen using the Latimer scale and write the values of the standard cell potential for each half-cell reaction. Show all calculations.

(a) In acidic solution (\(\text{pH} = 0\))

\[
\begin{align*}
\text{N}_2(g) + 5 \text{H}^+(aq) + 4 \text{e}^- & \rightarrow \text{N}_2\text{H}_5^+(aq) & E^\circ &= -0.23 \text{ V} \\
\text{N}_2\text{H}_5^+(aq) + 3 \text{H}^+(aq) + 2 \text{e}^- & \rightarrow 2 \text{NH}_4^+(aq) & E^\circ &= +1.28 \text{ V} \\
\text{N}_2(g) + 4 \text{H}_2\text{O}(l) + 4 \text{e}^- & \rightarrow \text{N}_2\text{H}_4(aq) + 4 \text{OH}^- (aq) & E^\circ &= -1.16 \text{ V} \\
\text{N}_2\text{H}_4(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{e}^- & \rightarrow 2 \text{NH}_3(aq) + 2 \text{OH}^- (aq) & E^\circ &= +0.10 \text{ V} \\
2 \text{H}_2\text{O}(l) + 2 \text{e}^- & \rightarrow \text{H}_2(g) + 2 \text{OH}^- (aq) & E^\circ &= -0.83 \text{ V}.
\end{align*}
\]

(b) In basic solution (\(\text{pH} = 14\))

3.7 Draw and label the electron transfer reactions for the materials containing hydrogen using the Latimer scale and write the values of the standard cell potential for each half-cell reaction. Show all calculations.

\[
\begin{align*}
\text{N}_2(g) + 5 \text{H}^+(aq) + 4 \text{e}^- & \rightarrow \text{N}_2\text{H}_5^+(aq) & E^\circ &= -0.23 \text{ V} \\
\text{N}_2\text{H}_5^+(aq) + 3 \text{H}^+(aq) + 2 \text{e}^- & \rightarrow 2 \text{NH}_4^+(aq) & E^\circ &= +1.28 \text{ V} \\
\text{N}_2(g) + 4 \text{H}_2\text{O}(l) + 4 \text{e}^- & \rightarrow \text{N}_2\text{H}_4(aq) + 4 \text{OH}^- (aq) & E^\circ &= -1.16 \text{ V} \\
\text{N}_2\text{H}_4(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{e}^- & \rightarrow 2 \text{NH}_3(aq) + 2 \text{OH}^- (aq) & E^\circ &= +0.10 \text{ V} \\
2 \text{H}_2\text{O}(l) + 2 \text{e}^- & \rightarrow \text{H}_2(g) + 2 \text{OH}^- (aq) & E^\circ &= -0.83 \text{ V}.
\end{align*}
\]

Calculations:
Due to the reactivity, the explosion, and environmental impact, it is very undesirable to produce ammonia in the fuel cells. Therefore, we wrote the equations for the decomposition of hydrazine in a basic environment:

3.8

We used the following reactions to decompose hydrazine in a basic environment:

(i) Ammonia and nitrogen gas

(ii) Nitrogen gas and nitrogen gas

Moreover, we considered the equilibrium constants for the reactions you wrote in different temperatures.

Equations for hydrazine decomposition:

Calculations:
Hydrazine decomposition to NH₃ and N₂ in a basic environment:

\[ K = \]
In the second paragraph, the lithium ion is used as a replacement for lead batteries. Lithium-ion batteries are usually made of graphite with lithium atoms trapped between graphite layers as one electrode. The other electrode is made of lithium cobalt oxide (Lithium cobalt oxide), which can release lithium ions during the charge-discharge process of the battery. They can be written formally as follows:

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

In the first sentence, use the common symbols and write the chemical reaction that occurs in the battery during the discharge process. Mark the oxidation state of the cobalt atom wherever it appears.

3.9

Complete the following for the discharge process of the lithium-ion battery described in paragraph 3.9:

- \(\text{Li(C)}_n\) electrode is cathode because lithium ions are reduced here.
- \(\text{Li(C)}_n\) electrode is anode because lithium atoms are oxidized here.
- \(\text{LiCoO}_2\) electrode is cathode because cobalt ions are reduced here.
- \(\text{LiCoO}_2\) electrode is anode because cobalt ions are oxidized here.
3.11 Let us consider a lithium battery LiFePO₄, C₆ and CoO₂ units and one Li atom which are the active mass of the battery and should be enough to transfer one electron between the electrodes.

Using the standard EMF (voltage) equation, calculate the specific charge capacity (in units of mAh g⁻¹) and energy density (in units of kWh kg⁻¹) for such a cell.

### Calculations:

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

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

Theoretical Problem 4

<table>
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<th>Question</th>
<th>4.1</th>
<th>4.2</th>
<th>4.3</th>
<th>4.4</th>
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</tbody>
</table>

Column chromatography of radioactive copper. 4

Theoretical Problems, Official English Version

4.1

\[ \text{... } + \text{... } \rightarrow \text{... } + \text{... } \]

\[ \text{Cu}^{64} + \text{Zn}^{64} \rightarrow \text{Cu}^{64} + \text{Cl}^{-} \]

4.2

Calculate the molar ratio of negatively charged copper ions to the total copper content obtained from the fission process.

\[ \beta_i = \frac{[\text{CuCl}_i]}{[\text{Cu}] \cdot [\text{Cl}]^i} \]

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

Mole fraction = "וענה תשובה בעלת דיוק של 2 ספרות אחרי הנקודה העשרונית" (עומת השעון בעלה דים של 2 ספרות אחרי הנקודה העשרונית)

4.3 לrpm השטיפה עם $\text{HCl}$, כל הכלים והחומרים היו בטמפרטורת החדר. האמ תספרוור העמודה שטוחה במקלוי.

ושתיות עם $\text{HCl}$ לא ☐

 recreation תרד ☐

$\text{Cl^-}$ תספרוורית עדלה ☐

המערכת מכילה את יונים $\text{Zn}^{2+}$, $\text{Cu}^{2+}$, יונים $\text{Zn}^{2+}$ והקומפלקסים הכılmışיים שלם הפורדה במ TNT והופרדה בצורת $\text{OH}^{-}$. שרף יבש (dry resin), exchange resin ושלי עבב הפך, הועברה והובירה את כל האתימורים של $\text{Cl}^{-}$ (וכלຮנה עד הש랙 בзван) ושלי, הש랙 נשטף עם $\text{HCl}$ וلاحقה מנשמח עם מים. המוקימי כי, לשון מועמדה אט כי, השרא שיאים קשים לשאר.

בפני השטיפה עם $\text{HCl}$, כל הכלים והחומרים היו בטמפרטורת החדר. האמ תספרוור העמודה שטוחה במקלוי.
Retention volume, $V_R$, of a specific substance on the column describes the volume of the mobile phase (eluent) that must be transferred in the column from the beginning of the separation until 50% of the substance leaves the column. We denote it as follows:

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

We have to calculate the retentions for copper and zinc species, respectively.

For copper species:

- Density of copper species is $D_g(Cu) = 17.4 \text{ cm}^3 \text{ g}^{-1}$
- Mass of dry, OH form resin is $m_{\text{resin,dry,OH form}} = 3.72 \text{ g}$
- Volume of the column is $V_0 = 4.93 \text{ cm}^3$

**Calculation:**

$$V_{R(Cu \text{ species})} = V_R(Cu) = D_g \times (1 - 6.91 \sqrt{d_p/L_c})$$

For zinc species:

- Density of zinc species is $D_g(Zn) = 78.5 \text{ cm}^3 \text{ g}^{-1}$

**Calculation:**

$$V_{R(Zn \text{ species})} = V_R(Zn) = D_g \times (1 - 6.91 \sqrt{d_p/L_c})$$

In order to achieve a complete separation of two sets of columns, A and B, the following condition must be met:

$$V_{0.001}(A) - V_{0.999}(B) > 10 V_c$$

where $V_{0.001}(A)$ and $V_{0.999}(B)$ are the volumes of the mobile phase that must be transferred such that 0.001% and 99.9% of the substance from set A and B, respectively, should leave the column. The condition above is satisfied if the difference between the two volumes is greater than 10 times the volume of the column.
After calculating, it was decided that after passing through the column, it is possible to separate copper species from zinc species. 

\[
V_{0.001} = \text{cm}^3 \\
V_{0.999} = \text{cm}^3
\]

It is possible to separate copper species from zinc species.

\[
\begin{array}{ccc}
\hline
\text{Option} & \text{Value} \\
\hline
\text{A} & \text{cm}^3 \\
\text{B} & \text{cm}^3 \\
\end{array}
\]

4.6. To find the theoretical exchange total ion capacity mass of the resin that we have referred to in this question, denoted as \( Q_{m,\text{theor}} \), in mmol g\(^{-1}\).

We assume that the tetraalkylammonium groups are the only groups that are responsible for the ions exchange properties of the resin. There are no other groups containing nitrogen that contribute to the exchange.

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

We need to calculate the exchange capacity of the resin using the following equation:

\[Q_{m,\text{theor}} = 4.83 \text{ mmol g}^{-1}\]

Note: The exchange capacity is calculated per unit mass of the resin.
In this experiment, tetraalkylammonium total ion exchange volume capacity, $Q_v$, of hydrated resin was determined. 3.72 g of hydrated resin was treated with silver nitrate solution, and the volume of the reaction solution was measured. The solution was then filtered, and the filtrate was added to a volume of 3500 cm$^3$ of sodium sulfate solution. The solution was then diluted with water to a specific volume.

After the solution was mixed, a 3100 cm$^3$ sample was taken from the vessel, and its concentration of tetraalkylammonium ions was determined by titration with silver nitrate solution, $0.1027$ mol dm$^{-3}$. The volume of silver nitrate solution required to reach equivalence was 22.20 cm$^3$.

The volume of hydrated resin, $V_c = 10.21$ cm$^3$, was subtracted from the volume of the reaction solution.

The concentration of tetraalkylammonium ions in the solution was calculated as:

$$Q_v = \frac{\text{mmol}}{\text{cm}^3}$$

By solving the above equation for $Q_v$:

$$x = \frac{\text{mmol}}{3 \text{ cm}^3}$$

If you don't reach the solution, substitute the value of 1.00 mmol for $Q_v$.
Bohemian garnet .5

The mineral "Bohemian garnet", also known as almandine, is a well-known gem stone in purple color. Its chemical composition is expressed by the formula:

\[ A_2^{II}A_3^{III}B_2(SiO_4)_3 \]

where \( A_2^{II} \) is a divalent cation, and \( A_3^{III}B_2 \) is a trivalent cation.

Garnets are crystals with a cubic structure containing 8 molecules of the formula unit. The structure consists of 3 types of polyhedra:

1. The first type, where the cation \( A_2^{II} \) takes a dodecahedral position, surrounded by 8 oxygen atoms (O).
2. The second type, where the cation \( A_3^{III}B_2 \) takes an octahedral position, surrounded by 6 oxygen atoms.
3. The third type, where \( IV \) Si is surrounded by 4 oxygen atoms in a tetrahedral arrangement.

The most common garnet is "almandine" (almandine), with the molecular formula:

\[ A_2^{II}B_3^{II}Al_3^{III}Fe_2^{III}(SiO_4)_3 \]

Its edge cell length is: \( a = 11.50 \text{ Å} \).

Calculate the theoretical density of almandine.

\[ \rho = \text{g cm}^{-3} \]
The Bohemian granite is a mineral with the formula Mg₄Al₂(SiO₄)₃. The granite contains tetrahedra of magnesium and silicon tetrahedra, which are key in the formation of the granite.

The granite is a natural colorless mineral, and its coloring is due to the chromophores — these are cations of other transition metals that replace the original cations in the structure.

The red color of the Bohemian granite is due to a small amount of Cr³⁺ in octahedral sites and Fe²⁺ in dodecahedral sites.

5.2 Draw the electronic configuration for the Bohemian granite in the octahedral [Cr³⁺O₆] oct and dodecahedral [Fe²⁺O₈] dod sites.

5.3 Each of the two configurations shows a transition metal from the first transition series (one or more). The octahedral position is diamagnetic in the low-spin state and paramagnetic in the high-spin state.

5.4 The diagram below shows the high-spin and low-spin arrangements. Complete the energy levels for these arrangements.
5.5 Write an expression for the spin state (for example: \( P < E_1 + E_2 + E_3 \)) for the high-spin arrangement \((P)\) in terms of the given energies.

a) high-spin arrangement: \( P \)

b) low-spin arrangement: \( P \)

5.6 Assume \( P > E_3 \) for both high and low spin arrangements (the same as in the previous case). Show that the exchange is a transition of the form dodecahedral position \( M^{II} \) to high spin-

5.7 Pair the absorption spectrum with the given gemstone.

Bohemian Garnet:

Uvarovite:

Sapphire:

Citrine:
If you are exposed to a green-white light and a chromatic blue, how would a granite bohemian mineral look to our eyes?

- Red
- Blue
- Yellow-orange
- Black
- Yellow
- Blue-green
- Violet
- White

Andradite (a mineral of the olivine group) is a colorless mineral that, when exposed to light, changes the color of the mineral. The chemical composition of the mineral is:

\[ \text{Cas}_3\text{Fe}_2(\text{SiO}_4)_3 \]

When a replacement reaction occurs, a black mineral is formed. The chemical changes are:

- \( \text{IV} \text{Ti} \) replaces \( \text{III} \text{Fe} \) in an octahedral position,
- \( \text{III} \text{Fe} \) replaces \( \text{IV} \text{Si} \) in a tetrahedral position.

The chemical composition of the resulting mineral can be expressed as:

\[ \text{C}_{\text{as}}\text{[Fe, Ti]}^\text{oct}_2 \left([\text{Si, Fe}^\text{tet} \text{O}_4]_3\right) \]

Calculate the percentage of the mineral in the octahedral position.

\[ p = \% \]

The green color of the mineral can result from two chromophores:

- \([\text{Fe}^{\text{III}} \text{O}_6]^{\text{oct}}\) - carbonyl group
- \([\text{Fe}^{\text{III}} \text{O}_4]^{\text{tet}}\) - trans-

The central cations of both chromophores have the same number of unpaired electrons.

Draw the orbital splitting diagrams for the two chromophores and fill in the electron configurations:

- \([\text{Fe}^{\text{III}} \text{O}_6]^{\text{oct}}\)
- \([\text{Fe}^{\text{III}} \text{O}_4]^{\text{tet}}\)
\[ \Delta_{\text{tet}} = \frac{4}{9} \Delta_{\text{oct}} \]

It is known that the tetrahedral field is smaller than the octahedral field \((\Delta_{\text{tet}} < \Delta_{\text{oct}})\). Interestingly, for the Fe\(^{III}\) ion, the energy change upon the first d-d transition (although it is very weak) is smaller in the octahedral chromophore compared to the tetrahedral one \((\Delta_{\text{oct}} - \Delta_{\text{tet}} < 1000 \text{ cm}^{-1})\) and for the tetrahedral chromophore, it is smaller again \((\Delta_{\text{tet}} - \Delta_{\text{oct}} < 5110 \text{ cm}^{-1})\). The energy gap between the tetrahedral and octahedral forms is calculated using the following equation:

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

Consider the YAG \((\text{Yttrium-Aluminium-Garnet})\) garnet synthetic crystal. The chromophore \(\text{Y}_{3}\text{Si}_{5}O_{12}\) is used in optoelectronics. The crystal structure of YAG is based on the general formula \(\text{AB}_2(\text{SiO}_4)_3\), where \(\text{A}^{III}\) and \(\text{B}^{III}\) ions are in different sites. To determine which ion is in site A and which in site B, use the following information:

- The radius ratio of \(\text{A}^{III}\) to \(\text{B}^{III}\) is 0.72
- The bond length of \(\text{Si}^{IV}\) is 1.17 Å

Determine the positions of \(\text{A}\) and \(\text{B}\) in the garnet structure.
5.13 By using technology with LED, the mineral YAG (Chlorido-III cerium) is doped with Yttrium (5% of the cerium). Determine the values of $x$ and $y$ in the formula of YAG that contains 5% of yttrium. Use the data $x = 2.25$ and $y = 0.75$.

\[Y_xCe_yAl_5O_{12}\]

\[x = \quad y =\]

5.14 YAG containing Yttrium can be prepared by heating a mixture of $3O_2$, $Al_2O_3$, $Y_2O_3$, and $2CeO_2$ under a flux of $2H_2$. Use the equation you found in section 5.13 to write a balanced equation for the reaction that takes place, with stoichiometric coefficients.
5.15 Which cation among the following, matches with the transitions in the chart?

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

5.16 Calculate the wavelength of the emitted light.

\[ \lambda = \text{nm} \]

5.17 Behrman's legend, which we mention in passing, has chosen a bright phosphor that is often called a "merry phosphorus". As you can see, this is the same word in Hebrew of the word for "phosphorescence".

- Red
- Blue
- Yellow-orange
- Black
- Yellow
- Blue-green
- Violet
- White
**Let’s go mushrooming** 6.0

Kotik fruity sir is a mushroom name. This kind of mushroom is edible, but some are poisonous, and others are not.

Latin name of this mushroom (Coprinopsis atramentaria) Ink cap (pun) is well-known in the Czech and Slovakian literature. It is considered edible and extremely tasty. It contains a natural compound called **coprine** (E), which can be easily synthesized from the compound (1), ethyl 3-chloropropanoate (E),

Theoretical Problem 6

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<th>Question</th>
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### 6.1

Draw the structures **A** - **E**. In your answer, write the stereochemistry if necessary.

**Ripple:**

In the first reaction, **A** passes through an intermediate organometallic compound (organo-metallic compound), which undergoes cyclization.

A B C

**Boc** = , **DCC** = , **HOBt** = , **Bu** =

- **A** is the starting material for the compound.
- **B** is the product of the compound.
- **C** is the reactant in the reaction.
**THEORETICAL PROBLEMS, OFFICIAL ENGLISH VERSION**

**INTERNATIONAL CHEMISTRY OLYMPIAD / SLOVAKIA & CZECH REPUBLIC, 2018**

**THEORETICAL PROBLEMS**

**4.-** Coprine, an alkaloid isolated from certain species of Amanita muscaria, undergoes hydrolysis to L-glutamic acid (3) and an intermediate molecule coprine. This intermediate molecule reacts with l-glutamic acid to form two new compounds (C and 4).

The compounds C and 4 are responsible for the toxic effects of coprine, as they inhibit the enzyme acetaldehyde dehydrogenase, which is responsible for alcohol metabolism in the body. As a result, acetaldehyde (a toxic metabolite of alcohol) accumulates in the body and causes a strong symptom of nausea (commonly referred to as "the antabuse effect").

The active site of the enzyme contains a group of cysteine SH, which is blocked by one of the compounds C or 4.

**Diagram:**

![Diagram showing the reaction between coprine (E) and hydrolysis to form L-glutamic acid (3) and an intermediate molecule coprine. The intermediate molecule reacts with L-glutamic acid to form two new compounds (C and 4). The enzyme acetaldehyde dehydrogenase is shown as a circle with a SH group.](image)

**Enzyme = acetaldehyde dehydrogenase**

The reaction between coprine and L-glutamic acid is shown in the figure. The compound 4 is shown to inhibit the enzyme acetaldehyde dehydrogenase. The figure also shows the formation of two new compounds C and 4.

Thus, the reaction between coprine and L-glutamic acid leads to the formation of two new compounds C and 4, which inhibit the enzyme acetaldehyde dehydrogenase. This results in the accumulation of acetaldehyde in the body and the onset of nausea.
The effect of antabuse is obtained from the drug named Antabuse. It is the most famous treatment for alcoholics. It is synthesized according to the following scheme:

\[ \text{NH}_2 + G \xrightarrow{\text{NaOH}} H \text{ reagent I} \]

The structure of \( H \) is given. Complete the structure of \( H \) according to the following scheme for \( G \). Complete the table 6.3.

<p>| | |</p>
<table>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>G</td>
<td>H</td>
</tr>
</tbody>
</table>

6.4. Complete the following table, select all reagents that can be used to synthesize Crayons:

- m-chloroperbenzoic acid (mCPBA)
- Zn(CH₃COOH)
- I₂
- K₂CO₃, H₂O
- dilute \( \text{H}_2\text{O}_2 \)
- NaBH₄
- hot concentrated \( \text{H}_2\text{SO}_4 \)
- AlCl₃
The enzyme acetaldehyde dehydrogenase, denoted as antabus, catalyzes the conversion of acetaldehyde to acetic acid.

The enzyme reaction is illustrated as follows:

\[
\text{Enzyme} + \text{acetaldehyde dehydrogenase} \rightarrow \text{J}
\]

**Enzyme = acetaldehyde dehydrogenase**

6.5. Enzymes of the acetaldehyde dehydrogenase family are highly similar to each other. In this context, the reaction catalyzed by the enzyme is the conversion of acetaldehyde to acetic acid.

The reaction takes place in the presence of a cofactor, cofactor 5, which is analogous to antabus. The reaction mechanism involves the formation of a thiolate anion, which then reacts with the substrate.

**Enzyme reaction mechanism**

**False morel** (Gyromitra esculenta) is another mushroom of interest. Unlike in the past, it has been shown to be poisonous due to the presence of the compound gyromitrin (M). Gyromitrin is a natural poison that can be converted into the toxic compounds under acidic conditions. The conversion is catalyzed by the enzyme gyromitrin dehydrogenase, which results in the formation of N-methylhydrizine (6). The same mechanism applies to the conversion of other similar compounds.

**False morel reaction mechanism**

\[
\text{Gyromitrin (M)} \rightarrow \text{N-methylhydrizine (6)}
\]
6.6  ציירו את הנוסחה של החומרים \( K \cdot M \).

<table>
<thead>
<tr>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
</table>

בואו נתרכז בהידרוליזה של הקבוצה האמידיית \( \text{amide moiety} \) (אורטוניטירל) \( \text{gyromitrin} \), ומאמזון \( \text{gyromitrin} \) \( \text{amide moiety} \) במולקה \( L \). מספר הגל עבור ויברציות המתיחה \( \text{amide moiety} \) הרלוונטי הוא \( 1293.0 \, \text{cm}^{-1} \). המשמעותית כאן היא מאפקט התわかって האיזוטופי \( \text{(isotope substitution effect)} \).

6.7 חשב את האפקט האיזוטופי הקнятие החידושי \( \text{(isotope substitution effect)} \) \( \text{gyromitrin} \), הנבנה ביבחר האמפירי \( \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{O} \), להבה \( \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{O} \). המסה המולרית \( \text{gyromitrin} \) \( \text{(isotope substitution effect)} \) \( \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{O} \). התחשב בועברה \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \), ב.width=123 padr=25%حادם \( 37^\circ \text{C} \). נ consect \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \). \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \). \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \).

לאחר \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \) \( \text{amide moiety} \) \( \text{gyromitrin} \).
לאחר השינויים האיזוטופיים, קצב התגובה עבר ההידרוליזה לא השתנה משמעותית.

בחרו ממהבאים הבאים שעליו שיוחיש שלב קובע המהירות מתוך האפשרויות הבאות:

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

The question: 7.1 Cidofovir (nucleotide) is an analog of a nucleotide that has antiviral activity. It is used to treat viral infections, especially in patients with AIDS.

The intermediate important in the synthesis of cidofovir is the diol optically pure (2). Cidofovir can be synthesized from L-mannitol (3) by following the reactions:

1. L-Mannitol (3) → acetone → A
2. A → NaIO₄ → B
3. B → NaBH₄ → C
5. D → aqueous HCl → 2

For questions 7.1, 7.2, 7.3, 7.4, 7.5, and 7.6, please refer to the table below:

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<th>Theoretical Problem 7</th>
<th>Question</th>
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</table>
A. $\text{C}_{12}\text{H}_{22}\text{O}_6$

B. 

C. 

D. 
7.2 ציירו את המבנה של כל הסטרואיזומרים (stereoisomers) של חומר (3) שניטק ליחוש משבחם.

בותונבות אלולן בדיקן את אחת התוצרות (2).

את Diol (2) מהם שניהל הלאה, ליירט החומר 1.

במחלקה התגובה יש לטמך את החומר (4) phosphonate כדי להפוך את התרכובת G⁻ פ' F, כדי להפור את התרכובת C₃₀H₃₅O₄. (עיין שדהו שמשך).

במקביל התגובה יש לטמך את התוצר C₆H₁₇ΟCl.)
7.3: Draw the structures of the molecules E, I, and highlight the stereochemistry. Use MMT (4-methoxyphenyl)diphenylmethyl.

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

\[ \text{Reactions:} \]

\[ \text{MMT-Cl} \xrightarrow{\text{NEt}_3} \text{E} \xrightarrow{\text{NaH}} \text{C}_{30}\text{H}_{30}\text{O}_4 \]

\[ \text{TsO} \xrightarrow{\text{H}^+} \text{(TsOH)H} \]

\[ \text{CH}_2\text{C(OH)} \xrightarrow{\text{H}_2\text{O}} \text{H} \]

\[ \text{Cl}_{3}\text{SO}_2\text{Cl} \xrightarrow{\text{NEt}_3} \text{I} \]

\[ \text{F} \]

\[ \text{G} \]

\[ \text{H} \]

\[ \text{I} \]

\[ \text{C}_{18}\text{H}_{27}\text{O}_8\text{PS} \]
The problem involves the synthesis of phosphonate according to the following reaction scheme:

\[
\begin{align*}
\text{O} & \quad \text{Br} + J \quad \rightarrow \quad K \\
1. \text{EtONa} & \quad 2. \text{H}^+ \quad \rightarrow \quad L \\
\text{TsCl} \quad \text{NEI}_3 \quad \rightarrow \quad \text{TsO} \quad \text{P(OEi)}_2
\end{align*}
\]

Please draw the structures of the compounds J, K, and L as indicated in the scheme.
The reaction of $I$ (from question 7.3) with $5 \text{ cytosine}$ gives a mixture of isomers $M$ and $N$ in a ratio of 3:1. $P$, the aromatic tautomer of cytosine-$5 \text{ (5 cytosine-aryl tautomer)}$, is also formed.

The reaction of $M$ with cyclohexa-1,4-diene in the presence of palladium hydroxide on charcoal yields $O$.

A phosphonic ester group reacts with bromotrimethylsilane to form cidofovir. Write the structures of isomers $M$, $N$ and product $O$, and write the structure of the aromatic tautomer $P$ of cytosine-$5 \text{.}$

$O$ is formed by removing a protective group from $M$. $M$ (75%) and $N$ (25%).

## Table

<table>
<thead>
<tr>
<th>Product</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>75%</td>
</tr>
<tr>
<td>$N$</td>
<td>25%</td>
</tr>
</tbody>
</table>
7.6 The structure of the two organic products Q and R formed during the reaction where M is converted 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>
Caryophyllene.

Theoretical Problem 8

<table>
<thead>
<tr>
<th>Question</th>
<th>8.1</th>
<th>8.2</th>
<th>8.3</th>
<th>8.4</th>
<th>8.5</th>
<th>8.6</th>
<th>8.7</th>
<th>8.8</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>14</td>
<td>14</td>
<td>2</td>
<td>16</td>
<td>6</td>
<td>8</td>
<td>9</td>
<td>6</td>
<td>75</td>
</tr>
</tbody>
</table>

Score

9% of the total

A dienone (3) \(\beta\)-Caryophyllene is the major enantiomer yields the ketone

The reaction of \(A\) with silyl ketene acetal (1), and the subsequent work-up with water, followed by \(\text{HCl}\), forms the ketone 2

The ketone forms a yellow solid with tosyl chloride \(B\). The ketone continues to react with \(\text{D}\) to give the product \(\beta\)-caryophyllene.

The final step

\[\text{C_{10}H_{14}O} \xrightarrow{\text{Ph}_{3}C\text{ClO}_{4} \text{(cat.)}} \xrightarrow{i-Bu_{2}AlH \text{(DIBAL-H)}} \xrightarrow{\text{TsCl, pyridine}} \xrightarrow{t-BuOK} \xrightarrow{n-BuLi} \beta\text{-Caryophyllene (3)}\]
8.1 הציירו את המבנים של התרכובות \( A - D \), וציון סטרוקומניות מתאימה.

רמז: במעבר מחומר המוצר \( A \) לחומר הביניים \( 2 \), קבוצת \( \text{silyl ketene acetal} \) מתפקדת כנוקלאופיל.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{10}\text{H}</em>{14}\text{O} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.2 ציירו את המבנה של הריאגנט E והחוברים F,G-1. חכו בתשובותיכם את הסטראוכימיה המתאימה. עبور תומרים 8.2-1 ח专区 F,G, שמום במקום המהווה בפתורון מתי המשבצות המהויות שייכות לא התורן הסטראוכימיה שמצרר.

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

(4) cycloalkane

8.4 

Ja + Jb

Ha + Hb

Ja + Jb

Ha + Hb
Ja + Jb
באופן מעניין, הראקטיביות של הקשרים הכפולים של הקורלט ו-\( \beta \)-כריופיללינן \( \text{isocaryophyllene} \) \( \text{5} \) הופכת כאשר משתמשים בתגובה בראגנט \( \text{isocaryophyllene} \) \( \text{5} \)替换为\( \beta \)-כריופיללינן \( \text{3} \)rather than \( \beta \)-כריופיללינן \( \text{3} \)במקום \( \beta \)-כריופיללינן \( \text{3} \).

8.5 ציירו את המבנים עבור התרכובות \( \text{Ka} \) ו-\( \text{Kb} \).

ה应注意 \( \text{Kb} \)-\( \text{Ka} \) זו זוג דיאסטראומרים.

רמז: \( \text{Ka} + \text{Kb} \) הם זוג דיאסטראומרים.

הרכבויות המסומנות בעוד איזוטופים אצל \( \text{Ka} \) ושני מתודות שחזור בחקירות \( \text{MS} \) ו-\( \text{NMR} \).

בואו נבחן את הסינתזה עבור תרכובות \( \beta \)-כריופיללינן \( \text{3} \) מסמנים של \( \beta \)-כריופיללינן \( \text{3} \)换来 \( \beta \)-כריופיללינן \( \text{3} \).

MS

NMR

בהוא נבנה \( \beta \)-כריופיללינן \( \text{3} \)逵 \( \beta \)-כריופיללינן \( \text{3} \)逵 \( \beta \)-כריופיללינן \( \text{3} \).
The reaction begins with protodeauration of the inner double bond that is more reactive of the two, to form the cation O.

The cationic system undergoes cyclization without breaking a carbon-carbon single bond, to form two diastereomeric tricyclic cations Pa and Pb, which undergo hydration to form products containing an alcohol group Na and Nb.

Alternatively, the cations Pa and Pb undergo reorganization as a result of breaking a carbon-carbon single bond to form the cations Qa and Qb, which undergo protodesaturation to form products 7a and 7b.

In other words, the products of the reaction contain a hydroxyl group Na and Nb.

The reaction proceeds through the formation of two diastereomeric tricyclic cations Pa and Pb, which undergo hydration to form products containing an alcohol group Na and Nb.

Alternatively, the cations Pa and Pb undergo reorganization as a result of breaking a carbon-carbon single bond to form the cations Qa and Qb, which undergo protodesaturation to form products 7a and 7b.

In other words, the products of the reaction contain a hydroxyl group Na and Nb.
8.7 Draw the structures of the intermediate vinyls O, Pa, Qa (write their stereochemistry) involved in the diastereomer 7a.

8.8 Draw the structures of the diastereomers Na + Nb.