IChO
General instructions
Cover sheet

Please return this cover sheet together with all the related question sheets.
International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July - 2nd August, 2021
https://www.icho2021.org

Chemistry! It's Cool!
General Instruction

• You are allowed to use only pen to write the answer.
• Your calculator must be non-programmable.
• This examination has 9 problems.
• You can solve the problems in any order.
• You will have 5 hours to solve all problems.
• You can begin working only after the START command is given.
• All results must be written in the appropriate answer boxes with pen on the answer sheets. Use the back of the question sheets if you need scratch paper. Remember that answers written outside the answer boxes will not be graded.
• Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
• The invigilator will announce a 30-minute warning before the STOP command.
• You must stop working when the STOP command is given. Failure to stop writing will lead to the nullification of your examination.
• The official English version of this examination is available on request only for clarification.
• You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to visit a restroom, etc), raise your hand and wait until an invigilator arrives.

GOOD LUCK!

Problems and Grading Information

<table>
<thead>
<tr>
<th>Title</th>
<th>Total Score</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Hydrogen at a Metal Surface</td>
<td>24</td>
<td>11</td>
</tr>
<tr>
<td>2 Isotope Time Capsule</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>3 Lambert–Beer Law?</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>4 The Redox Chemistry of Zinc</td>
<td>32</td>
<td>11</td>
</tr>
<tr>
<td>5 Mysterious Silicon</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>6 The Solid-State Chemistry of Transition Metals</td>
<td>45</td>
<td>13</td>
</tr>
<tr>
<td>7 Playing with Non-benzenoid Aromaticity</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>8 Dynamic Organic Molecules and Their Chirality</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>9 Likes and Dislikes of Capsules</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
### Physical Constants and Equations

#### Constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed of light in vacuum</td>
<td>$c = 2.99792458 \times 10^8$ m s$^{-1}$</td>
</tr>
<tr>
<td>Planck constant</td>
<td>$h = 6.62607015 \times 10^{-34}$ J s</td>
</tr>
<tr>
<td>Elementary charge</td>
<td>$e = 1.602176634 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Electron mass</td>
<td>$m_e = 9.10938370 \times 10^{-31}$ kg</td>
</tr>
<tr>
<td>Electric constant (permittivity of vacuum)</td>
<td>$\varepsilon_0 = 8.85418781 \times 10^{-12}$ F m$^{-1}$</td>
</tr>
<tr>
<td>Avogadro constant</td>
<td>$N_A = 6.02214076 \times 10^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>$k_B = 1.380649 \times 10^{-23}$ J K$^{-1}$</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>$F = N_A \times e = 9.6485321233100184 \times 10^{4}$ C mol$^{-1}$</td>
</tr>
<tr>
<td>Gas constant</td>
<td>$R = N_A \times k_B = 8.31446261815324$ J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Unified atomic mass unit</td>
<td>$u = 1$ Da $= 1.66053907 \times 10^{-27}$ kg</td>
</tr>
<tr>
<td>Standard pressure</td>
<td>$p = 1$ bar $= 10^5$ Pa</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>$p_{atm} = 1.01325 \times 10^5$ Pa</td>
</tr>
<tr>
<td>Zero degree Celsius</td>
<td>$0$ °C $= 273.15$ K</td>
</tr>
<tr>
<td>Ångstrom</td>
<td>$1$ Å $= 10^{-10}$ m</td>
</tr>
<tr>
<td>Picometer</td>
<td>$1$ pm $= 10^{-12}$ m</td>
</tr>
<tr>
<td>Electronvolt</td>
<td>$1$ eV $= 1.602176634 \times 10^{-19}$ J</td>
</tr>
<tr>
<td>Part-per-million</td>
<td>$1$ ppm $= 10^{-6}$</td>
</tr>
<tr>
<td>Part-per-billion</td>
<td>$1$ ppb $= 10^{-9}$</td>
</tr>
<tr>
<td>Part-per-trillion</td>
<td>$1$ ppt $= 10^{-12}$</td>
</tr>
<tr>
<td>pi</td>
<td>$\pi = 3.141592653589793$</td>
</tr>
<tr>
<td>The base of the natural logarithm (Euler's number)</td>
<td>$e = 2.718281828459045$</td>
</tr>
</tbody>
</table>
Equations

The ideal gas law  
\[ PV = nRT \]
where \( P \) is the pressure, \( V \) is the volume, \( n \) is the amount of substance, \( T \) is the absolute temperature of ideal gas.

Coulomb's law  
\[ F = \frac{k_e q_1 q_2}{r^2} \]
where \( F \) is the electrostatic force, \( k_e \approx 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2} \) is Coulomb's constant, \( q_1 \) and \( q_2 \) are the magnitudes of the charges, and \( r \) is the distance between the charges.

The first law of thermodynamics  
\[ \Delta U = q + w \]
where \( \Delta U \) is the change in the internal energy, \( q \) is the heat supplied, \( w \) is the work done.

Enthalpy \( H \)  
\[ H = U + PV \]

Entropy based on Boltzmann's principle \( S \)  
\[ S = k_B \ln W \]
where \( W \) is the number of microstates.

The change of entropy \( \Delta S \)  
\[ \Delta S = \frac{q_{\text{rev}}}{T} \]
where \( q_{\text{rev}} \) is the heat for the reversible process.

Gibbs free energy \( G \)  
\[ G = H - TS \]
\[ \Delta_r G^\circ = -RT \ln K = -zFE^\circ \]
where \( K \) is the equilibrium constant, \( z \) is the number of electrons, \( E^\circ \) is the standard electrode potential.

Reaction quotient \( Q \)  
For a reaction \( aA + bB \rightleftharpoons cC + dD \)
\[ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
where \([A]\) is the concentration of A.
<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta q = n c_m \Delta T$</td>
<td>Heat change, $c_m$ is the temperature-independent molar heat capacity.</td>
</tr>
<tr>
<td>$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$</td>
<td>Nernst equation for redox reaction, $C_{\text{ox}}$ is the concentration of oxidized substance, $C_{\text{red}}$ is the concentration of reduced substance.</td>
</tr>
<tr>
<td>$k = A \exp \left( - \frac{E_a}{RT} \right)$</td>
<td>Arrhenius equation, $k$ is the rate constant, $A$ is the pre-exponential factor, $E_a$ is the activation energy.</td>
</tr>
<tr>
<td>$A = \varepsilon l c$</td>
<td>Lambert–Beer equation, $A$ is the absorbance, $\varepsilon$ is the molar absorption coefficient, $l$ is the optical path length, $c$ is the concentration of the solution.</td>
</tr>
<tr>
<td>$\text{pH} = p K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$</td>
<td>Henderson–Hasselbalch equation, For an equilibrium $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, where equilibrium constant is $K_a$.</td>
</tr>
<tr>
<td>$E = h \nu = \frac{h \lambda}{\nu}$</td>
<td>Energy of a photon, $\nu$ is the frequency, $\lambda$ is the wavelength of the light.</td>
</tr>
<tr>
<td>$1 + x + x^2 + \cdots + x^n = \frac{1 - x^{n+1}}{1 - x}$</td>
<td>The sum of a geometric series, When $x \neq 1$,</td>
</tr>
<tr>
<td>$1 \approx 1 + x$</td>
<td>Approximation equation that can be used to solve problems, When $x \ll 1$.</td>
</tr>
</tbody>
</table>
§1 H NMR Chemical Shifts

\[ \Delta \delta \text{ for one alkyl group-substitution: } ca. +0.4 \text{ ppm} \]
Međunarodna hemijska olimpijada 2021 Japan
53. IChO 2021 Japan
25. jul – 2. avgust, 2021
https://www.icho2021.org

Chemistry! It's Cool!
Opšta uputstva

- Pišite samo hemijskom olovkom
- Kalkulator mora biti neprogramabilni.
- Ispit se sastoji od 9 zadataka.
- Zadatke ne morate rešavati redom.
- Imate 5 sati na raspolaganju za izradu ispita.
- Sa radom možete početi tek nakon što čujete komandu START.
- Svi rezultati moraju biti upisani hemijskom olovkom u predviđenom prostoru za odgovore (označeni sa A). Koristite poleđinu papira na kojima su pitanja ukoliko vam treba papir za koncept. Zapamтite da odgovori koji su napisani van prostora za odgovore neće biti ocijenjivani.
- Napišite relevantne proračune u odgovarajući prostor. Tačan odgovor će biti ocijenjen samo ukoliko je vaš rad prikazan.
- Supervizor će vas upozoriti 30 minuta ranije na kraj ispita. Kraj ispita će biti proglašen komandom STOP.
- Morate prestatи sa radom čim čujete komandу STOP. Ukoliko odmah ne prestanete sa radom bićete diskvalifikовани.
- Zvanična engleska verzija ovог testа dostupna vam je na zahtjev i služi samo за pojašnjenje.
- Nije vam dozvoljeno da napuštate radni prostor bez dozvole. Ukoliko vam zatreba pomoć (zbog pokvareног kalkulatora, odlaska u toalet...), podignite ruku i sačekajte da dođe supervizor do vas.

SREĆNO!

Zadaci i informacije o ocjenjivanju

<table>
<thead>
<tr>
<th>Naslov</th>
<th>Ukupan broj poena</th>
<th>Procenat</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Vodonik na metalnoj površini</td>
<td>24</td>
<td>11</td>
</tr>
<tr>
<td>2 Izotop - vremenska kapsula</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>3 Lambert–Beer-ov zakon?</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>4 Oksido-redukcija hemija cinka</td>
<td>32</td>
<td>11</td>
</tr>
<tr>
<td>5 Tajanstven silicijum</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>6 Hemija čvrstog stanja prelaznih meta</td>
<td>45</td>
<td>13</td>
</tr>
<tr>
<td>7 Igre s nebenzoidnom aromatičnošću</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>8 Dinamički organski molekuli i njihova hiralnost</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>9 Za i protiv kapsula</td>
<td>23</td>
<td>10</td>
</tr>
</tbody>
</table>

Total: 100
### Fizičke konstante i jednačine

#### Konstante

<table>
<thead>
<tr>
<th>Konstanta</th>
<th>vrijednost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brzina svjetlosti u vakuum</td>
<td>$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Plankova konstanta</td>
<td>$h = 6.62607015 \times 10^{-34} \text{ J s}$</td>
</tr>
<tr>
<td>Elementarno naelektrisanje</td>
<td>$e = 1.602176634 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>Masa elektrona</td>
<td>$m_e = 9.10938370 \times 10^{-31} \text{ kg}$</td>
</tr>
<tr>
<td>Konstanta električne permeabilnosti vakuuma</td>
<td>$\varepsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$</td>
</tr>
<tr>
<td>Avogadrova konstanta</td>
<td>$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Bolcmanova konstanta</td>
<td>$k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$</td>
</tr>
<tr>
<td>Faradejeva konstanta</td>
<td>$F = N_A \times e = 9.6485321233100184 \times 10^4 \text{ C mol}^{-1}$</td>
</tr>
<tr>
<td>Univerzalna gasna konstanta</td>
<td>$R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Unificirana jedinica atomske mase</td>
<td>$u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$</td>
</tr>
<tr>
<td>Standardni pritisak</td>
<td>$p = 1 \text{ bar} = 10^5 \text{ Pa}$</td>
</tr>
<tr>
<td>Atmosferski pritisak</td>
<td>$p_{atm} = 1.01325 \times 10^5 \text{ Pa}$</td>
</tr>
<tr>
<td>Nula stepeni Celzijusa</td>
<td>$0 ^\circ \text{C} = 273.15 \text{ K}$</td>
</tr>
<tr>
<td>Ångstrem</td>
<td>$1 \text{ Å} = 10^{-10} \text{ m}$</td>
</tr>
<tr>
<td>Pikometar</td>
<td>$1 \text{ pm} = 10^{-12} \text{ m}$</td>
</tr>
<tr>
<td>Elektronvolt</td>
<td>$1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}$</td>
</tr>
<tr>
<td>Djelova na milion</td>
<td>$1 \text{ ppm} = 10^{-6}$</td>
</tr>
<tr>
<td>Djelova na bilion</td>
<td>$1 \text{ ppb} = 10^{-9}$</td>
</tr>
<tr>
<td>Djelova na trilion</td>
<td>$1 \text{ ppt} = 10^{-12}$</td>
</tr>
<tr>
<td>Pi</td>
<td>$\pi = 3.141592653589793$</td>
</tr>
<tr>
<td>Osnova prirodnog logaritma (Ojlerov broj)</td>
<td>$e = 2.718281828459045$</td>
</tr>
</tbody>
</table>
Jednačine

<table>
<thead>
<tr>
<th>Jednačina stanja idealnog gasa</th>
<th>$PV = nRT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuleskog zakona</td>
<td>$F = k \frac{q_1 q_2}{r^2}$</td>
</tr>
<tr>
<td>Prvi zakon termodinamike</td>
<td>$\Delta U = q + w$</td>
</tr>
<tr>
<td>Entalpija $H$</td>
<td>$H = U + PV$</td>
</tr>
<tr>
<td>Entropija $S$</td>
<td>$S = k B \ln W$</td>
</tr>
<tr>
<td>Promjena entropije $\Delta S$</td>
<td>$\Delta S = \frac{q_{rev}}{T}$</td>
</tr>
<tr>
<td>Slobodna Gibbsova energija $G$</td>
<td>$G = H - TS$</td>
</tr>
<tr>
<td>Reakcionki koeficijent $Q$</td>
<td>$\Delta G = \Delta G^0 + RT \ln Q$</td>
</tr>
</tbody>
</table>

- $P$ pritisak
- $V$ zapremina
- $n$ količina supstance
- $T$ apsolutna temperatura idealnog gasa.
- $F$ elektrostatična sila
- $k$ Kušlova konstanta
- $q_1$ i $q_2$ količine naelektrisanja
- $r$ rastojanje između naelektrisanja.
- $\Delta U$ promjena unutrašnje energije
- $q$ količina prenesene toplote
- $w$ izvršeni rad.
- $S$ broj mikrostanja
- $\frac{q_{rev}}{T}$ toplota reverzibilnog procesa
- $G^0$ standardna Gibbsova energija
- $K$ konstanta ravnoteže
- $z$ broj elektrona
- $E^0$ standardni elektrodni potencijal
- $A$, $B$ koncentracija A.
Promjena toplote $\Delta q$:

$\Delta q = n c m \Delta T$, gdje je $c_m$ molarni toplotni kapacitet nezavisan od temperature.

Nernstova jednačina za redoks reakciju:

$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{ox}}{C_{red}}$, gdje je $C_{ox}$ koncentracija oksidovane supstance, $C_{red}$ je koncentracija redukovane supstance.

Arenijusova jednačina:

$k = A \exp \left(- \frac{E_a}{RT} \right)$, gdje je $k$ konstanta brzine, $A$ je predeksponencijalni koeficijent, $E_a$ je energija aktivacije.

Exp(x) = $e^x$.

Lambert–Beer-ova jednačina:

$A = \varepsilon l c$, gdje je $A$ apsorbanca, $\varepsilon$ je molarni apsorpcioni koeficijent, $l$ je dužina optičkog puta, $c$ je koncentracija rastvora.

Henderson-Haselbalhova jednačina:

Za ravnotežu HA $\rightleftharpoons$ H$^+$ + A$^-$, gdje je konstanta ravnoteže $K_a$,

$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)$.

Energija fotona:

$E = h \nu = \frac{h c}{\lambda}$, gdje je $\nu$ frekvencija, $\lambda$ je talasna dužina svjetlosti.

Suma geometrijskog niza:

Kada je $x \neq 1$,

$1 + x + x^2 + \ldots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$.

Aproksimaciona jednačina koja se može koristiti za rješavanje zadataka:

Kada je $x \ll 1$,

$\frac{1}{1 - x} \approx 1 + x$.
## Periodni sistem elemenata

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Symbol</th>
<th>Name</th>
<th>Massa u u (apneni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>Hidrogen</td>
<td>1.008</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>Helijum</td>
<td>4.003</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>Lithijum</td>
<td>6.941</td>
</tr>
<tr>
<td>4</td>
<td>Be</td>
<td>Barijum</td>
<td>9.012</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>Bor</td>
<td>10.814</td>
</tr>
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<td>6</td>
<td>C</td>
<td>Karbon</td>
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<td>7</td>
<td>N</td>
<td>Azot</td>
<td>14.007</td>
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<td>Oksijen</td>
<td>15.999</td>
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<td>F</td>
<td>Fosfor</td>
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<td>Klor</td>
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<td>Argon</td>
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<td>Titan</td>
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<td>24</td>
<td>Cr</td>
<td>Krom</td>
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<tr>
<td>25</td>
<td>Mn</td>
<td>Mangan</td>
<td>54.938</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>Fer</td>
<td>55.845</td>
</tr>
<tr>
<td>27</td>
<td>Co</td>
<td>Kobalt</td>
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<td>Ni</td>
<td>Nikel</td>
<td>58.693</td>
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<tr>
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<td>Cu</td>
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Δδ za supstituciju jedne alkil grupe: približno +0,4 ppm
Please return this cover sheet together with all the related question sheets.
Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

**Part A**

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, \( \text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad}) \), where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (\( \text{H}_2 \)) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of \( \text{H}_2 \) is represented by two variables: the interatomic distance, \( d \), and the height relative to the surface metal atom, \( z \). It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the potential energy in units of kJ per mole of \( \text{H}_2 \). The solid line spacing is 20 kJ mol\(^{-1}\), the dashed line spacing is 100 kJ mol\(^{-1}\), and the spacing between solid and dashed lines is 80 kJ mol\(^{-1}\). The zero-point vibration energy is ignored.
Fig. 1 Definition of variables. Drawing is not in scale.

Fig. 2
A.1 For each of the following items (i)–(iii), select the closest value from A–G.

(i) The interatomic distance for a gaseous H\(_2\) molecule
(ii) The interatomic distance between metal atoms (\(d_M\) in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface (\(h_{ad}\) in Fig. 1)

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<th>B. 0.07 nm</th>
<th>C. 0.11 nm</th>
<th>D. 0.15 nm</th>
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A.2 For each of the following items (i)–(ii), select the closest value from A–H.

(i) the energy required for the dissociation of gaseous H\(_2\) to gaseous H
   \([H_2(g) \rightarrow 2H(g)]\)
(ii) the energy released during the adsorption of a gaseous H\(_2\) \([H_2(g) \rightarrow 2H(ad)]\)

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<th>C. 60 kJ mol(^{-1})</th>
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<td>G. 300 kJ mol(^{-1})</td>
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Part B

The adsorbed hydrogen atoms are then either absorbed into the bulk, or recombine and desorb back into the gas phase, as shown in the reactions (1a) and (1b). \( H(ab) \) represents a hydrogen atom absorbed in the bulk.

\[
\begin{align*}
H_2(g) & \xrightleftharpoons[k_2]{k_1} 2H(ad) \quad (1a) \\
H(ad) & \rightarrow H(ab) \quad (1b)
\end{align*}
\]

The reaction rates per surface site for adsorption, desorption, and absorption are \( r_1 \, [s^{-1}] \), \( r_2 \, [s^{-1}] \) and \( r_3 \, [s^{-1}] \), respectively. They are expressed as:

\[
\begin{align*}
r_1 &= k_1 P_{H_2} (1 - \theta)^2 \\
r_2 &= k_2 \theta^3 \\
r_3 &= k_3 \theta
\end{align*}
\]

where \( k_1 \, [s^{-1} \text{Pa}^{-1}] \), \( k_2 \, [s^{-1}] \) and \( k_3 \, [s^{-1}] \) are the reaction rate constants and \( P_{H_2} \) is the pressure of \( H_2 \).

Among the sites available on the surface, \( \theta \) (0 ≤ \( \theta \) ≤ 1) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption (\( r_1, r_2 \gg r_3 \)) and that \( \theta \) remains constant.

\[ r_3 \text{ can be expressed as:} \]

\[
r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{H_2} C}}}
\]

Express \( C \) using \( k_1 \) and \( k_2 \).
A metal sample with a surface area of $S = 1.0 \times 10^{-3} \text{ m}^2$ was placed in a container (1L = $1.0 \times 10^{-3} \text{ m}^3$) with $\text{H}_2$ ($P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18} \text{ m}^{-2}$. The surface temperature was kept at $T = 400 \text{ K}$. As the reaction (1) proceeded, $P_{\text{H}_2}$ decreased at a constant rate of $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$. Assume that $\text{H}_2$ is an ideal gas and that the volume of the metal sample is negligible.

**B.2** Calculate the amount of H atoms in moles absorbed per unit area of the surface per unit time, $A \text{ [mol s}^{-1} \text{ m}^{-2}]$.  

**B.3** At $T = 400 \text{ K}$, $C$ equals $1.0 \times 10^2 \text{ Pa}^{-1}$. **Calculate** the value of $k_3$ at 400 K. If you did not obtain the answer to **B.2**, use $A = 3.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2}$.  

**B.4** At a different $T$, $C = 2.5 \times 10^3 \text{ Pa}^{-1}$ and $k_3 = 4.8 \times 10^{-2} \text{ s}^{-1}$ are given. For $r_3$ as a function of $P_{\text{H}_2}$ at this temperature, select the correct plot from (a)–(h).

![Graphs of $r_3$ vs. $P_{\text{H}_2}$ at different temperatures](image)
Realno se očekuje da će vodonik u budućnosti biti izvor energije koji ne zavisi od fosilnih goriva. Ovdje ćemo razmotriti postupak skladištenja vodonika u metalu, koji je povezan sa tehnologijom transporta i skladištenja vodonika.

**Dio A**

Kako se vodonik apsorbuje u unutrašnjost metala preko površine, prvo razmotrimo proces adsorpcije vodonika na površini metala, \( \text{H}_2(g) \rightarrow 2\text{H(ad)} \), gdje su gasovito i adsorbovano stanje vodonika dati kao (g) i (ad). Molekuli vodonika (H\(_2\)) koji dospiju do metalne površine (M) disosuju na površini i adsorbuju se kao atomi H (Slika 1). Ovdje je potencijalna energija \( \text{H}_2 \) predstavljena sa dvije promjenljive: međuatomskom udaljenošću, \( \mathbf{d} \), i visinom u odnosu na površinu atoma metala, \( \mathbf{h} \). Pretpostavljeno je da je osa duž dva atoma H paralelna sa površinom i da je centar gravitacije uvijek na vertikalnoj isprekidanoj liniji na Slici 1. Na Slici 2 je prikazana kontura potencijalne energije za disocijaciju na površini. Numeričke vrijednosti predstavljaju potencijalnu energiju u jedinicama \( \text{kJ} \) po molu \( \text{H}_2 \). Udaljenost između punih linija je 20 kJ \( \text{mol}^{-1} \), udaljenost između isprekidanih linija je 100 kJ \( \text{mol}^{-1} \) i udaljenost između punih i isprekidanih linija je 80 kJ \( \text{mol}^{-1} \). Energija vibracije nulte tačke se zanemaruje.
Slika 1. Definicija promjenljivih. Crtež nije dat u srazmjeri.

Slika 2
### A.1

Za svaku od sledećih stavki (i)–(iii), izaberite najbližu vrijednost iz A – G.

(i) Međuatomska udaljenost za gasoviti molekul H\(_2\)

(ii) Međuatomska udaljenost između atoma metala (\(d_{M}\) na Slici 1)

(iii) Udaljenost adsorbovanih atoma H od površine (\(h_{ad}\) na Slici 1)

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### A.2

Za svaku od sledećih stavki (i) - (ii), izaberite najbližu vrijednost iz A–H.

(i) Energija potrebna za disocijaciju gasovitog H\(_2\) do gasovitog H.

\[ \text{H}_2(g) \rightarrow 2\text{H}(g) \]

(ii) Energija koja se oslobađa tokom adsorpcije gasovitog H\(_2\) [ \(\text{H}_2(g) \rightarrow 2\text{H}(ad)\) ]

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Dio B

Adsorbovani atomi vodonika se zatim ili apsorbjuju u površinu metala ili se rekombinuju i desorbjuju nazad u gasnu fazu, kao što je prikazano u reakcijama (1a) i (1b). H(ab) predstavlja atom vodonika apsorbovan u površinu metala.

\[
\begin{align*}
    H_2(g) & \xrightarrow{k_1} 2H(ad) \\
    H(ad) & \xrightarrow{k_3} H(ab)
\end{align*}
\]

(1a)  
(1b)

Brzine reakcije po površini za adsorpciju, desorpciju i apsorpciju su \( r_1[s^{-1}] \), \( r_2[s^{-1}] \) i \( r_3[s^{-1}] \). Izražavaju se kao:

\[
    r_1 = k_1P_{H_2}(1-\theta)^2 \\
    r_2 = k_2\theta^2 \\
    r_3 = k_3\theta
\]

gdje su \( k_1[s^{-1}Pa^{-1}] \), \( k_2[s^{-1}] \) i \( k_3[s^{-1}] \) konstante brzine reakcije i \( P_{H_2} \) je pritisak \( H_2 \). Među mjestima koja su dostupna na površini, dio koji je zauzet H atomima označen je kao \( \theta \) (0 ≤ \( \theta \) ≤ 1). Pretpostavlja se da su adsorpcija i desorpcija brže od apsorpcije \( r_1, r_2 \gg r_3 \) i da \( \theta \) ostaje konstantno.

B.1 \( r_3 \) se može izraziti kao:

\[
r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{H_2}C}}}
\]

Izrazite \( C \) koristeći \( k_1 \) i \( k_2 \).
Uzorak metala površine $S = 1.0 \times 10^{-3}$ m$^2$ je smješten u posudu (1L = $1.0 \times 10^{-3}$ m$^3$) sa H$_2$ ($P_{H_2} = 1.0 \times 10^2$ Pa). Gustina adsorpcionih mjesta za vodonik je $N = 1.3 \times 10^{18}$ m$^{-2}$. Temperatura na površini je održavana na $T = 400$ K. Daljim odvijanjem reakcije (1), $P_{H_2}$ se smanjivala konstantnom brzinom od $v = 4.0 \times 10^{-4}$ Pa s$^{-1}$. Pretpostavite da je H$_2$ idealan gas i da se zapremina metala može zanemariti.

**B.2** Izračunajte količinu atoma H u molovima koji su apsorbovani po jedinici površine u jedinici vremena, $A$ [mol s$^{-1}$ m$^{-2}$].

**B.3** Na $T = 400$ K, $C$ je jednako $1.0 \times 10^2$ Pa$^{-1}$. Izračunajte vrijednost $k_3$ na $400$ K. Za dalji rad koristite vrijednost $A = 3.6 \times 10^{-7}$ mol s$^{-1}$ m$^{-2}$.

**B.4** Na drugoj temperaturi $T$, date su $C = 2.5 \times 10^3$ Pa$^{-1}$ i $k_3 = 4.8 \times 10^{-2}$ s$^{-1}$. Za $r_3$ u funkciji od $P_{H_2}$ na ovoj temperaturi, izaberite ispravan grafik od datih (a)–(h).
# Vodonik na metalnoj površini

## Dio A

### A.1 (6 pt)

<table>
<thead>
<tr>
<th>(i)</th>
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<th>(iii)</th>
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### A.2 (4 pt)

<table>
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</tbody>
</table>
Dio B

B.1 (5 pt)

C =

B.2 (3 pt)

A = \text{mol s}^{-1} \text{m}^{-2}
B.3 (3 pt)

\[ k_3 = \quad \text{s}^{-1} \]

B.4 (3 pt)

____________________
IChO
Problem 2
Cover sheet

Please return this cover sheet together with all the related question sheets.
Molecular entities that differ only in isotopic composition, such as CH$_4$ and CH$_3$D, are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

Assume that all of the substances shown in this Question are in a gas phase.

Let us consider the following equilibrium:

$$^{12}\text{C}^{16}\text{O}_2 + ^{12}\text{C}^{18}\text{O}_2 \rightleftharpoons 2^{12}\text{C}^{16}\text{O}^{18}\text{O}$$

$$K = \frac{[^{12}\text{C}^{16}\text{O}^{18}\text{O}]^2}{[^{12}\text{C}^{16}\text{O}_2][^{12}\text{C}^{18}\text{O}_2]}$$

(1)

The entropy, $S$, increases with increasing the number of possible microscopic states of a system, $W$:

$$S = k_B \ln W$$

(2)

$W = 1$ for $^{12}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}_2$. In contrast, $W = 2$ for a $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecules, $W = 2^2 = 4$. 

---

Isotope Time Capsule

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
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</tbody>
</table>
A.1 The enthalpy change, $\Delta H$, of eq. 3 is positive regardless of the temperature. Calculate the equilibrium constants, $K$, for eq. 3 at very low (think of $T \to 0$) and very high (think of $T \to +\infty$) temperatures. Assume that the reaction remains unchanged at these temperatures and that $\Delta H$ converges to a constant value for high temperatures.

The $\Delta H$ of the following process can be explained by molecular vibrations.

$$2\text{HD} \rightleftharpoons \text{H}_2 + \text{D}_2 \quad K = \frac{[\text{H}_2][\text{D}_2]}{[\text{HD}]^2}$$

At $T = 0$ K, the vibrational energy of a diatomic molecule whose vibration frequency is $\nu$ [s$^{-1}$] is expressed as:

$$E = \frac{1}{2} h \nu$$

Wherein $k$ is the force constant and $\mu$ the reduced mass, which is expressed in terms of the mass of the two atoms in the diatomic molecule, $m_1$ and $m_2$, according to:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

A.2 The vibration of $\text{H}_2$ is at 4161.0 cm$^{-1}$ when reported as a wavenumber. Calculate the $\Delta H$ of the following equation at $T = 0$ K in units of J mol$^{-1}$.

$$2\text{HD} \rightarrow \text{H}_2 + \text{D}_2$$

Assume that:
- only the vibrational energy contributes to the $\Delta H$.
- the $k$ values for $\text{H}_2$, HD, and $\text{D}_2$ are identical.
- the mass of H to be 1 Da and the mass of D to be 2 Da.
The molar ratio of H₂, HD, and D₂ depends on the temperature in a system in equilibrium. Here, \( \Delta_{D_2} \) is defined as the change of the molar ratio of D₂.

\[
\Delta_{D_2} = \frac{R_{D_2}}{R_{D_2}^*} - 1
\]  

(9)

Here, \( R_{D_2} \) refers to \( \frac{[D_2]}{[H_2]} \) in the sample and \( R_{D_2}^* \) to \( \frac{[D_2]}{[H_2]} \) at \( T \to +\infty \). It should be noted here that the distribution of isotopes becomes random at \( T \to +\infty \).

A.3 **Calculate** \( \Delta_{D_2} \) with natural D abundance when the isotopic exchange is in equilibrium at the temperature where \( K \) in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are \( 1.5576 \times 10^{-4} \) and \( 1 - 1.5576 \times 10^{-4} \), respectively.
In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO$_2$ molecules with molecular weights of 44 and 47, which are described as CO$_2[44]$ and CO$_2[47]$ below. The quantity $\Delta_{47}$ is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1$$

(10)

$R_{47}$ refers to $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ in the sample and $R_{47}^*$ to $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ at $T \to +\infty$. The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

<table>
<thead>
<tr>
<th></th>
<th>$^{12}\text{C}$</th>
<th>$^{13}\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural abundance</td>
<td>0.988888</td>
<td>0.011112</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$^{16}\text{O}$</th>
<th>$^{17}\text{O}$</th>
<th>$^{18}\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural abundance</td>
<td>0.997621</td>
<td>0.0003790</td>
<td>0.0020000</td>
</tr>
</tbody>
</table>

The temperature dependence of $\Delta_{47}$ is determined as follows, where $T$ is given as the absolute temperature in units of K:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4}$$

(11)

**A.4** The $R_{47}$ of fossil plankton obtained from the Antarctic seabed was $4.50865 \times 10^{-5}$. Estimate the temperature using this $R_{47}$. This temperature is interpreted as the air temperature during the era in which the plankton lived. Consider only the most common isotopologue of CO$_2[47]$ for the calculation.
Izotop - vremenska kapsula

<table>
<thead>
<tr>
<th>Zadatak</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
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</tr>
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<tbody>
<tr>
<td>Poeni</td>
<td>8</td>
<td>8</td>
<td>10</td>
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<td>35</td>
</tr>
</tbody>
</table>

Molekulske vrste koje se razlikuju samo po izotopskom sastavu, kao što su CH₄ i CH₃D, nazivaju se izotopolozi. Smatra se da izotopolozi imaju iste hemijske osobine. U realnosti, međutim, postoje male razlike.

Pretpostavimo da su sve supstance date u ovom zadatku u gasovitoj fazi.

Razmotrimo sledeću ravnotežu:

\[ ^{12}\text{C}^{16}\text{O}_2 + ^{12}\text{C}^{18}\text{O}_2 \rightleftharpoons 2^{12}\text{C}^{16}\text{O}^{18}\text{O} \]

\[ K = \frac{[^{12}\text{C}^{16}\text{O}^{18}\text{O}]^2}{[^{12}\text{C}^{16}\text{O}_2][^{12}\text{C}^{18}\text{O}_2]} \] (1)

Entropija, \( S \), raste sa povećanjem broja mogućih mikroskopskih stanja sistema, \( W \):

\[ S = k_B \ln W \] (2)

\( W = 1 \) za \(^{12}\text{C}^{16}\text{O}_2 i ^{12}\text{C}^{18}\text{O}_2\). Za razliku od prethodnog, \( W = 2 \) za molekul \(^{12}\text{C}^{16}\text{O}^{18}\text{O} \) jer su atomi kiseonika međusobno različiti u ovom molekulu. Kako se na desnoj strani ravnoteže koja je prikazana jednačinom 1 nalaze dva \(^{12}\text{C}^{16}\text{O}^{18}\text{O} \) molekula, slijedi da je \( W = 2^2 = 4 \).
Promjena entalpije, $\Delta H$, za jednačinu 3 je pozitivna bez obzira na tamperaturu. 8pt

$$H_2 + DI \rightleftharpoons HD + HI$$  (3)

Izračunajte konstantu ravnoteže, $K$, za jednačinu 3 na veoma niskim temperaturama (uzeti da je $T \to 0$) i veoma visokim temperaturama (uzeti da je $T \to +\infty$). Uzmite da reakcija ostaje nepromijenjena na ovim temperaturama i da $\Delta H$ konvergira u konstantnu vrijednost na visokim temperaturama.

$\Delta H$ sledećeg procesa može se objasniti molekulskim vibracijama.

$$2HD \rightleftharpoons H_2 + D_2 \quad K = \frac{[H_2][D_2]}{[HD]^2}$$  (4)

Na $T = 0$ K, vibraciona energija dvoatomskog molekula čija je vibraciona frekvencija $\nu$ [s$^{-1}$] izražena je kao:

$$E = \frac{1}{2} \hbar \nu$$  (5)

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$  (6)

gdje je $k$ konstanta sile i $\mu$ je redukovana masa koja je izražena u funkciji masa dva atoma u dvoatomskom molekulu, $m_1$ i $m_2$, prema sledećoj jednačini:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$  (7)

A.2 Vibracija $H_2$ je na 4161.0 cm$^{-1}$ kada se izrazi kao talasni broj. Izračunajte $\Delta H$ 8pt za sledeću jednačinu pri $T = 0$ K u jedinicama J mol$^{-1}$.

$$2HD \to H_2 + D_2$$  (8)

Pretpostavite da:
• samo vibraciona energija doprinosi $\Delta H$.
• su $k$ vrijednosti za $H_2$, HD, i $D_2$ identične.
• je masa H 1 Da i da je masa D 2 Da.
Molarni odnos H₂, HD, i D₂ zavisi od temperature sistema u ravnoteži. Ovdje se Δᵟ definiše kao promjena u molarnom odnosu D₂.

\[ \Delta_{D_2} = \frac{R_{D_2}}{R'_{D_2}} - 1 \]

Ovdje se \( R_{D_2} \) odnosi na \( \left[ \frac{D_2}{H_2} \right] \) u uzorku i \( R'_{D_2} \) na \( \left[ \frac{D_2}{H_2} \right] \) pri \( T \rightarrow +\infty \). Ovdje treba uzeti u obzir da raspodjela izotopa postaje nasumična na \( T \rightarrow +\infty \).

A.3 Izračunajte \( \Delta_{D_2} \) sa prirodnom zastupljenošću D kada je izotopska izmjena u ravnoteži na temperaturi na kojoj \( K \) u jednačini 4 iznosi 0.300. Pretpostavlja se da odnos prirodne zastupljenošti D i H iznosi \( 1.5576 \times 10^{-4} \) i \( 1 - 1.5576 \times 10^{-4} \), redom.
Uopšteno, molarni odnos dvostruko supstituisanog izotopologa, koji sadrži dva teža atoma izotopa u jednom molekulu, raste sa smanjenjem temperature. Razmotrimo molarni odnos molekula CO$_2$ sa relativnim molekulskim masama 44 i 47, koje su dolje date kao CO$_2[44]$ i CO$_2[47]$. $\Delta_{47}$ se definiše kao:

$$\Delta_{47} = \frac{R_{47}}{R_{47}} - 1$$

$R_{47}$ se odnosi na $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ u uzorku i $R_{47}^*$ na $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ pri $T \to +\infty$. Prirodne zastupljenosti atoma ugljenika i kiseonika su prikazane dolje; zanemarite izotope koji ovdje nisu prikazani.

<table>
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<td>0.011112</td>
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<td>0.0020000</td>
</tr>
</tbody>
</table>

Temperaturna zavisnost $\Delta_{47}$ je određena kao što slijedi, gdje je $T$ dato kao apsolutna temperatura izražena u K:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4}$$

$R_{47}$ fosilnog planktona pronađenog na morskom dnu Antarktika iznosi $4.50865 \times 10^{-5}$. **Izračunajte** temperaturu koristeći datu vrijednost $R_{47}$. Ova temperatura je predstavljena kao temperatura vazduha tokom perioda kada je plankton živio. Za ovaj proračun uzmite u obzir samo najrasprostranjeniji izotopolog CO$_2[47]$.  

A.4
**Izotop - vremenska kapsula**

A.1 (8 pt)

\[ T \to 0 : K = \ldots, \quad T \to +\infty : K = \ldots \]
$\Delta H = \underline{\text{J mol}^{-1}}$
Δ_{D_2} =
\[ T = \text{K} \]
IChO
Problem 3
Cover sheet

Please return this cover sheet together with all the related question sheets.
Lambert–Beer Law?

<table>
<thead>
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<th>B.1</th>
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</tr>
</tbody>
</table>

In this problem, ignore the absorption of the cell and the solvent. The temperatures of all solutions and gases are kept constant at 25 °C.

**Part A**

An aqueous solution \( X \) was prepared using HA and NaA. The concentrations \([A^-], [HA], \) and \([H^+]\) in solution \( X \) are \(1.00 \times 10^{-2} \text{ mol L}^{-1}, 1.00 \times 10^{-3} \text{ mol L}^{-1}, \) and \(1.00 \times 10^{-4} \text{ mol L}^{-1}, \) respectively, which are correlated via the following acid-base equilibrium:

\[
HA \rightleftharpoons A^- + H^+ \quad K = \frac{[A^-][H^+]}{[HA]} \tag{1}
\]

The optical path length is \( l \) in Part A. Ignore the density change upon dilution. Assume that no chemical reactions other than eq 1 occur.

**A.1** The absorbance of \( X \) was \( A_1 \) at a wavelength of \( \lambda_1 \). Then, solution \( X \) was diluted to twice its initial volume using hydrochloric acid with \( \text{pH} = 2.500 \). After the dilution, the absorbance was still \( A_1 \) at \( \lambda_1 \). **Determine** the ratio \( \varepsilon_{HA}/\varepsilon_{A^-} \), where \( \varepsilon_{HA} \) and \( \varepsilon_{A^-} \) represent the absorption coefficients of HA and of \( A^- \), respectively, at \( \lambda_1 \).
Part B

Let us consider the following equilibrium in the gas phase.

\[ \text{D} \rightleftharpoons 2\text{M} \quad (2) \]

Pure gas D is filled into a cuboid container that has a transparent movable wall with a cross-section of \( S \) (see the figure below) at a pressure \( P \), and equilibrium is established while the total pressure is kept at \( P \). The absorbance of the gas is \( A = \varepsilon (n/V)l \), where \( \varepsilon \), \( n \), \( V \), and \( l \) are the absorption coefficient, amount of the gas in moles, volume of the gas, and optical path length, respectively. Assume that all components of the gas mixture behave as ideal gases.

Use the following definitions if necessary.

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<thead>
<tr>
<th>Initial state</th>
<th>After equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
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<td>D ( n_0 ) ( V_0 )</td>
</tr>
<tr>
<td>Partial pressure</td>
<td>( P )</td>
</tr>
<tr>
<td>Amount in moles</td>
<td>( n_0 )</td>
</tr>
</tbody>
</table>

B.1 The absorbance of the gas at \( \lambda_{B1} \) measured from direction \( x \) (\( l = l_x \)) was \( A_{B1} \) both at the initial state and after the equilibrium. **Determine** the ratio \( \varepsilon_D/\varepsilon_M \) at \( \lambda_{B1} \), where \( \varepsilon_D \) and \( \varepsilon_M \) represent the absorption coefficients of D and of M, respectively.

B.2 The absorbance of the gas at \( \lambda_{B2} \) measured from direction \( y \) was \( A_{B2} \) both at the initial state (\( l = l_y \)) and after the equilibrium (\( l = l_y \)). **Determine** the ratio \( \varepsilon_D/\varepsilon_M \) at \( \lambda_{B2} \).
**Lambert-Beerov-ov zakon?**

<table>
<thead>
<tr>
<th>Zadatak</th>
<th>A.1</th>
<th>B.1</th>
<th>B.2</th>
<th>Ukupno</th>
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<td>Poeni</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>22</td>
</tr>
</tbody>
</table>

U ovom zadatku možete zanemariti apsorpciju čelije i rastvarača. Temperature svih rastvora i gasova se održavaju konstantnim i iznose 25°C.

**Dio A**

Vodeni rastvor X pripremljen je korišćenjem HA i NaA. Koncentracije \([\text{A}^-], [\text{HA}]\) i \([\text{H}^+]\) u rastvoru X su \(1.00 \times 10^{-2} \text{ mol L}^{-1}\), \(1.00 \times 10^{-3} \text{ mol L}^{-1}\), i \(1.00 \times 10^{-4} \text{ mol L}^{-1}\), redom, i povezane su sledećom kiselinsko-baznom ravnotežom:

\[
\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+ \quad K = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \quad (1)
\]

Dužina optičkog puta je \(l\) u Dijelu A ovog zadatka. Zanemarite promjenu gustine nakon razblaživanja. Pretpostavite da se ne odvijaju druge hemijske reakcije sem one koja je prikazana jednačinom 1.

**A.1**

Apsorbanca rastvora X je bila \(A_1\) pri talasnoj dužini \(\lambda_1\). Dalje, početni rastvor X je razblažen do dvostrukoj veće zapremine hloridnom kiselinom (pH=2,500). Posle razblaženja, apsorbanca je i dalje bila \(A_1\) na talasnoj dužini \(\lambda_1\). Izračunajte odnos \(\varepsilon_{\text{HA}}/\varepsilon_{\text{A}^-}\) gdje su \(\varepsilon_{\text{HA}}\) i \(\varepsilon_{\text{A}^-}\) apsorpcioni koeficijenti za HA i A⁻, tim redom, na talasnoj dužini \(\lambda_1\).
**Dio B**

Razmotrimo sledeću ravnotežu u gasnoj fazi.

\[
D \rightleftharpoons 2M \tag{2}
\]

Posuda odlika kvadra je ispunjena čistim gasom D pri pritisku \(P\). Posuda ima providni pokretni zid sa poprečnim presjekom \(S\) (vidjeti sliku ispod) i uspostavljena je ravnoteža, pri čemu je ukupni pritisak održavan konstantnim, \(P\). Apsorbanca gasa je \(A = \varepsilon (n/V)l\), gdje su \(\varepsilon\), \(n\), \(V\) i \(l\) apsorbcijski koeficijent, količina gasa u molovima, zapremina gasa i dužina optičkog puta, redom. Pretpostavite da se sve komponente gasne smiješte ponašaju kao idealni gasovi.

Koristite sledeće podatke ukoliko je potrebno

<table>
<thead>
<tr>
<th>Početno stanje</th>
<th>Nakon uspostavljanja ravnoteže</th>
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</thead>
<tbody>
<tr>
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<td>Parcijalni pritisak</td>
</tr>
<tr>
<td></td>
<td>Količina u molovima</td>
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<tr>
<td></td>
<td>Zapremina</td>
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</tbody>
</table>

**B.1** Apsorbanca gasa na \(\lambda_{B1}\) koja je mjerena iz pravca \(x\) \((l = l_x)\) bila je \(A_{B1}\) i na samom početku i nakon uspostavljanja ravnoteže. **Odredite** odnos \(\varepsilon_D/\varepsilon_M\) na \(\lambda_{B1}\), gdje su \(\varepsilon_D\) i \(\varepsilon_M\) apsorbcijski koeficijenti od D i od M. 6pt

**B.2** Apsorbanca gasa na \(\lambda_{B2}\) koja je mjerena iz pravca \(y\) bila je \(A_{B2}\) i na samom početku \((l = l_y)\) i nakon uspostavljanja ravnoteže \((l = l_y)\). **Odredite** odnos \(\varepsilon_D/\varepsilon_M\) na \(\lambda_{B2}\). 6pt
Lambert–Beerov zakon?

Dio A

A.1 (10 pt)
A.1 (cont.)

\[ \varepsilon_{HA} / \varepsilon_{A^-} = \]
Dio B

B.1 (6 pt)

\[ \frac{\varepsilon_D}{\varepsilon_M} = \]
B.2 (6 pt)

\[ \frac{\varepsilon_D}{\varepsilon_M} = \]
Please return this cover sheet together with all the related question sheets.
Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

**Part A**

The dissolution equilibrium of zinc hydroxide $\text{Zn(OH)}_2(\text{s})$ at 25 °C and the relevant equilibrium constants are given in eq. 1–4.

$$\text{Zn(OH)}_2(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \quad K_{\text{sp}} = 1.74 \times 10^{-17} \quad (1)$$

$$\text{Zn(OH)}_2(\text{s}) \rightleftharpoons \text{Zn(OH)}_2(\text{aq}) \quad K_1 = 2.62 \times 10^{-6} \quad (2)$$

$$\text{Zn(OH)}_2(\text{s}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Zn(OH)}_4^{2-}(\text{aq}) \quad K_2 = 6.47 \times 10^{-2} \quad (3)$$

$$\text{H}_2\text{O(}l\text{)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_w = 1.00 \times 10^{-14} \quad (4)$$
The solubility, \( S \), of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

\[
S = [\text{Zn}^{2+}(\text{aq})] + [\text{Zn(OH)}_2(\text{aq})] + [\text{Zn(OH)}_4^{2-}(\text{aq})]
\]  

**A.1** When the equilibria in eq. 1-4 are established, **calculate** the pH range in which \([\text{Zn(OH)}_2(\text{aq})]\) is the greatest among \([\text{Zn}^{2+}(\text{aq})]\), \([\text{Zn(OH)}_2(\text{aq})]\) and \([\text{Zn(OH)}_4^{2-}(\text{aq})]\).

**A.2** A saturated aqueous solution of \(\text{Zn(OH)}_2(\text{s})\) with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. **Calculate** the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.

**Part B**

Next, the recovered zinc hydroxide is heated to obtain zinc oxide according to the reaction below:

\[
\text{Zn(OH)}_2(\text{s}) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)}
\]  

The zinc oxide is then reduced to metallic zinc by reaction with hydrogen:

\[
\text{ZnO(s)} + \text{H}_2(\text{g}) \rightarrow \text{Zn(s)} + \text{H}_2\text{O(g)}
\]

**B.1** In order for reaction (7) to proceed at a hydrogen pressure kept at 1 bar, it is necessary to reduce the partial pressure of the generated water vapor. **Calculate** the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 \(^\circ\) C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 \(^\circ\) C and 1 bar for all gaseous species are \(\Delta G_{\text{ZnO}}(300\,^\circ\,\text{C}) = -2.90 \times 10^2\,\text{kJ mol}^{-1}\) and \(\Delta G_{\text{H}_2\text{O}}(300\,^\circ\,\text{C}) = -2.20 \times 10^2\,\text{kJ mol}^{-1}\), respectively.

Metallic zinc is used as a negative electrode (anode) material for metal-air batteries. The electrode consists of Zn and ZnO. It uses the following redox reaction to generate electricity with the electromotive force (e.m.f.) at 25 \(^\circ\) C and pressure of 1 bar, \(E^\circ\).

\[
\text{Zn(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{ZnO(s)} \quad E^\circ = 1.65\,\text{V}
\]  

**B.2** A zinc-air battery was discharged at 20 mA for 24 hours. **Calculate** the change in mass of the negative electrode (anode) of the battery.
Consider the change of e.m.f. of a zinc–air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are $−38$ °C (February) and 3776 m, respectively. The atmospheric pressure is represented by

$$P \text{ [bar]} = 1.013 \times \left( 1 - \frac{0.0065h}{T + 0.0065h + 273.15} \right)^{5.257} \tag{9}$$

at altitude $h \text{ [m]}$ and temperature $T \text{ [°C]}$. The molar ratio of oxygen in the atmosphere is $21\%$. The Gibbs energy change of reaction (8) is $\Delta G_{\text{ZnO}}(−38 \text{ °C}) = −3.26 \times 10^2 \text{ kJ mol}^{-1}$ at $−38 \text{ °C}$ and 1 bar.

**Calculate** the Gibbs energy change for reaction (6) at 25 °C. Note that the standard reduction potentials, $E^\circ(\text{Zn}^{2+}/\text{Zn})$ and $E^\circ(\text{O}_2/\text{H}_2\text{O})$ at 25 °C and 1 bar are given as (10) and (11), respectively.

$$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn} \quad E^\circ(\text{Zn}^{2+}/\text{Zn}) = −0.77 \text{ V} \tag{10}$$

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V} \tag{11}$$
Oksido-redukciona hemija cinka

<table>
<thead>
<tr>
<th>Zadatak</th>
<th>A.1</th>
<th>A.2</th>
<th>B.1</th>
<th>B.2</th>
<th>B.3</th>
<th>B.4</th>
<th>Ukupno</th>
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<td>5</td>
<td>4</td>
<td>3</td>
<td>5</td>
<td>9</td>
<td>32</td>
</tr>
</tbody>
</table>

Cink je dugo vremena korišćen kao sastojak legure mesinga i za zaštitu čelika. Cink koji se nalazi u industrijskim otpadnim vodama odvaja se taloženjem u cilju prečišćavanja vode, a dobijeni talog se redukuje i koristi se za ponovno dobijanje metalnog cinka.

Dio A

Ravnotežne reakcije koje se uspostavljaju prilikom rastvaranja cink-hidroksida Zn(OH)$_2$(s) na 25 °C i odgovarajuće konstante tih ravnoteža su date jednačinama od 1 do 4.

\[
\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \quad K_{sp} = 1.74 \times 10^{-17} \quad (1)
\]

\[
\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn(OH)}_2(aq) \quad K_1 = 2.62 \times 10^{-6} \quad (2)
\]

\[
\text{Zn(OH)}_2(s) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn(OH)}_4^{2-}(aq) \quad K_2 = 6.47 \times 10^{-2} \quad (3)
\]

\[
\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad K_w = 1.00 \times 10^{-14} \quad (4)
\]
Rastvorljivost cinka $S$ (koncentracija cinka u zasićenom vodenom rastvoru) data je jednačinom 5.

$$ S = [\text{Zn}^{2+}(aq)] + [\text{Zn(OH)}_2(aq)] + [\text{Zn(OH)}_4^{2-}(aq)] $$ (5)

A.1 Kada su uspostavljene ravnoteže u jednačinama 1–4, izračunajte opseg pH-vrijednosti u kojem je $[\text{Zn(OH)}_2(aq)]$ veća u odnosu u svaku od $[\text{Zn}^{2+}(aq)]$ i $[\text{Zn(OH)}_4^{2-}(aq)]$.

A.2 Pripremljen je zasićeni vodeni rastvor $\text{Zn(OH)}_2(s)$ sa pH=7.00 i profitiran je. Dobijenom filtratu je dodat NaOH do povećanja pH-vrijednosti na 12.00. Izračunajte molarni procenat istalozenog cinka kada pH poraste sa 7.00 do 12.00. Zanemarite promjene temperature i zapremine.

Dio B

Dalje, dobijeni zink-hidroksid se zagrijava da bi se dobio cink-oksid prema sledećoj jednačini:

$$ \text{Zn(OH)}_2(s) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} $$ (6)

Zink-oksid se dalje redukuje do metalnog cinka u reakciji sa vodonikom:

$$ \text{ZnO(s)} + \text{H}_2(g) \rightarrow \text{Zn(s)} + \text{H}_2\text{O(g)} $$ (7)

B.1 Da bi se odvijala reakcija (7) pri konstantnom pritisku vodonika od 1 bar, neophodno je smanjiti parcijalni pritisak dobijene vodene pare. Izračunajte gornju granicu parcijalnog pritiska vodene pare koji omogućava odvijanje reakcije (7) na 300 °C. Ovdje su date Gibsove energije nastajanja cink-oksida i vodene pare na 300 °C i 1 bar za sve gasovite vrste $\Delta G_{\text{ZnO}(300\,^\circ\text{C})} = -2.90 \times 10^2$ kJ mol$^{-1}$ i $\Delta G_{\text{H}_2\text{O}(300\,^\circ\text{C})} = -2.20 \times 10^2$ kJ mol$^{-1}$.

Metalni cink se koristi kao negativna elektroda (anoda) za metal-vazduh baterije. Elektroda se sastoji od Zn i ZnO. Električna struja u bateriji se stvara na osnovu sledeće redoks reakcije sa elektromotornom silom (EMS) $E^\circ$ na 25 °C i pritisku od 1 bara.

$$ \text{Zn(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{ZnO(s)} \quad E^\circ = 1.65$ \text{V} $$(8)

B.2 Baterija cink-vazduh se isprazni pri 20 mA za 24 časa. Izračunajte promjenu mase negativne elektrode (anode) baterije.
Planina Fudži

B.3  Uzmite u obzir promjenu EMS baterije cink-vazduh u zavisnosti od okoline. Izračunajte EMS na vrhu planine Fudži gdje je temperatura u februaru −38°C, a nadmorska visina iznosi 3776 m. Atmosferski pritisak je predstavljen kao:

\[ P [\text{bar}] = 1.013 \times \left( 1 - \frac{0.0065h}{T + 0.0065h + 273.15} \right)^{5.257} \]  (9)

na nadmorskoj visini \( h [\text{m}] \) i temperaturi \( T [\text{°C}] \). Molarni udio kiseonika u atmosferi iznosi 21%. Promjena Gibsove energije za reakciju (8) je \( \Delta G_{\text{ZnO}}(-38°C) = -3.26 \times 10^2 \text{kJ mol}^{-1} \) na −38°C i 1 bar.

B.4  Izračunajte promjenu Gibsove energije za jednačinu (6) na 25°C. Uzmiite u obzir da su standardni redoks potencijali \( E^\circ(\text{Zn}^{2+}/\text{Zn}) \) i \( E^\circ(\text{O}_2/\text{H}_2\text{O}) \) na 25°C i 1 bar dati u jednačinama (10) i (11).

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \]  \( E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.77 \text{V} \)  (10)

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]  \( E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{V} \)  (11)
Dio A

A.1 (6 pt)

< pH <
A.2 (5 pt)
Dio B

B.1 (4 pt)

\[ p_{H_2O} = \text{bar} \]

B.2 (3 pt)

\[ \text{g} \]
B.3 (5 pt)

V
\[ \Delta G^* = J \text{ mol}^{-1} \]
Please return this cover sheet together with all the related question sheets.
Although silicon is also a group 14 element like carbon, their properties differ significantly.

**Part A**

Unlike the carbon–carbon triple bond, the silicon–silicon triple bond in a compound formulated as $R^1$-$Si≡Si-R^1$ ($R$: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.

$$R^1$-$Si≡Si-R^1 + H_2C≡CH_2 \rightarrow \quad \begin{array}{c} \text{Si=} \\ \text{Si} \end{array}$

When $R^1$-$Si≡Si-R^1$ is treated with an alkyne ($R^2\text{-C}≡C\text{-R}^2$), the four-membered-ring compound $A$ is formed as an initial intermediate. Further reaction of another molecule of $R^2\text{-C}≡C\text{-R}^2$ with $A$ affords isomers $B$ and $C$, both of which have benzene-like cyclic conjugated structures, so-called ‘disilabenzenes’ that contain a six-membered ring and can be formulated as $(R^1$-$Si)_2(R^2\text{-C})_4$. 
The $^{13}$C NMR analysis of the corresponding six-membered ring skeletons $\text{Si}_2\text{C}_4$ shows two signals for B and one signal for C.

A.1 Draw the structural formulae of A, B, and C using $R^1$, $R^2$, Si, and C, with one of the possible resonance structures.

A.2 Calculate the aromatic stabilization energy (ASE) for benzene and C (in the case of $R^1 = R^2 = H$) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1).

$$
\begin{align*}
\text{H}_2\text{C} &= \text{CH}_2 + \text{H}_2 & \rightarrow & & \text{H}_3\text{C} &= \text{CH}_3 & \Delta H &= -135 \text{ kJ mol}^{-1} \quad (1) \\
\text{H}_2\text{Si} &= \text{CH}_2 + \text{H}_2 & \rightarrow & & \text{H}_3\text{Si} &= \text{CH}_3 & \Delta H &= -213 \text{ kJ mol}^{-1} \quad (2) \\
\text{H}_2\text{Si} &= \text{SiH}_2 + \text{H}_2 & \rightarrow & & \text{H}_3\text{Si} &= \text{SiH}_3 & \Delta H &= -206 \text{ kJ mol}^{-1} \quad (3) \\
\text{H}_2\text{C} &= \text{H}_2 + 3 \text{H}_2 & \rightarrow & & \text{C}_6\text{H}_6 & & \Delta H &= -173 \text{ kJ mol}^{-1} \quad (4) \\
\text{H}_2\text{Si} &= \text{SiH} + 3 \text{H}_2 & \rightarrow & & \text{H}_2\text{Si} &= \text{SiH}_2 & \Delta H &= -326 \text{ kJ mol}^{-1} \quad (5) \\
\text{H}_2\text{Si} &= \text{SiH} + 3 \text{H}_2 & \rightarrow & & \text{H}_2\text{Si} &= \text{SiH}_2 & \Delta H &= -368 \text{ kJ mol}^{-1} \quad (6) \\
\text{H}_2\text{Si} &= \text{SiH} + 3 \text{H}_2 & \rightarrow & & \text{H}_2\text{Si} &= \text{SiH}_2 & \Delta H &= -389 \text{ kJ mol}^{-1} \quad (7)
\end{align*}
$$

Fig. 1
When a xylene solution of C is heated, it undergoes isomerization to give an equilibrium mixture of compounds D and E. The molar ratio is $D : E = 1 : 40.0$ at 50.0 °C and $D : E = 1 : 20.0$ at 120.0 °C.

**A.3 Calculate $\Delta H$ for the transformation of D to E. Assume that $\Delta H$ does not depend on temperature.**

The isomerization from C to D and to E proceeds via transformations of $\pi$-bonds into $\sigma$-bonds without breaking any $\sigma$-bonds. A $^{13}$C NMR analysis revealed one signal for the Si$_2$C$_4$ skeleton of D and two signals for that of E. The skeleton of D does not contain any three-membered rings, while E has two three-membered rings that share an edge.

**A.4 Draw the structural formulae of D and E using R$^1$, R$^2$, Si, and C.**

**Part B**

Silicon is able to form highly coordinated compounds (> four substituents) with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

The fluorination reaction of CCl$_4$ using Na$_2$SiF$_6$ was carried out as follows.

- **Standardization of Na$_2$SiF$_6$ solution**
  - Preparation
    Aqueous solution F: 0.855 g of Na$_2$SiF$_6$ (188.053 g mol$^{-1}$) dissolved in water (total volume: 200 mL).
    Aqueous solution G: 6.86 g of Ce$_2$(SO$_4$)$_3$ (568.424 g mol$^{-1}$) dissolved in water (total volume: 200 mL).
  - Procedure
    Precipitation titration of a solution F (50.0 mL) by dropwise adding solution G in the presence of xylene orange, which coordinates to Ce$^{3+}$, as an indicator. After adding 18.8 mL of solution G, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce$^{3+}$, and the only resulting silicon compound is Si(OH)$_4$.

**B.1 Write the balanced equation for the reaction of Na$_2$SiF$_6$ with Ce$_2$(SO$_4$)$_3$.**

**Reaction of CCl$_4$ with Na$_2$SiF$_6$:**

( Substance losses by e.g. evaporation are negligible during the following operations.)

Na$_2$SiF$_6$(x [g]) was added to CCl$_4$ (500.0 g) and heated to 300 °C in a sealed pressure-resistant reaction vessel. The unreacted Na$_2$SiF$_6$ and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with CCl$_4$ (solution H). The $^{29}$Si and $^{19}$F NMR spectra of solution H showed SiF$_4$ as the only silicon compound. In the $^{19}$F NMR spectrum, in addition to SiF$_4$, signals corresponding to CFCl$_3$, CF$_2$Cl$_2$, CF$_3$Cl, and CF$_4$ were observed (cf. Table 1). The integration ratios in the $^{19}$F NMR spectrum are proportional to the number of fluorine nuclei.

<table>
<thead>
<tr>
<th>$^{19}$F NMR data</th>
<th>CFCl$_3$</th>
<th>CF$_2$Cl$_2$</th>
<th>CF$_3$Cl</th>
<th>CF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integration ratio</td>
<td>45.0</td>
<td>65.0</td>
<td>18.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
SiF₄ is hydrolyzed to form H₂SiF₆ according to the following eq. 8:

\[
3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6
\] (8)

Solution H (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF₄. After separation, the H₂SiF₆ generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na₂SiF₆ (aqueous solution J).

The precipitate of unreacted Na₂SiF₆ and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution K; 10.0 L).

Then, additional precipitation titrations using solution G were carried out, and the endpoints of the titrations with G were as follows:
- For solution J (entire amount): 61.6 mL.
- For 100 mL of solution K: 44.4 mL.

It should be noted here that the coexistence of NaCl or SiO₂ has no effect on the precipitation titration.

| B.2 Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and calculate the mass (x [g]) of the Na₂SiF₆ used as a starting material. |
| B.3 77.8% of the CCl₄ used as a starting material was unreacted. Calculate the mass of CF₃Cl generated. |
Tajanstveni silicijum

<table>
<thead>
<tr>
<th>Zadatak</th>
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<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
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<th>B.3</th>
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<td>8</td>
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</table>

Iako silicijum pripada 14. grupi elemenata kao i ugljenik, njegove osobine se bitno razlikuju.

 Dio A

Za razliku ugljenik-ugljen trstrukih veza, trostruka veza silicijum-silicijum u jedinjenjima opšte formule $R^1\cdot Si \equiv Si \cdot R^1$ (R: organski supstituent) je veoma reaktivna. Na primjer, ova jedinjenja reaguju sa etenom i grade ciklične proizvode koji sadrže četvoročlane prstenove.

Kada se $R^1\cdot Si \equiv Si \cdot R^1$ tretira alkinom ($R^2\cdot C \equiv C \cdot R^2$), nastaje jedinjenje A koje se formira kao inicijalni intermedijer. Daljom reakcijom jedinjenja $R^2\cdot C \equiv C \cdot R^2$ sa A dobijaju se izomeri B i C, koji oba imaju ciklične konjugovane strukture nalik strukturni benzena, takozvani „disilabenzeni“ koji sadrže šestočlani prsten i mogu se predstaviti na sledeći način: $(R^1\cdot Si)_2(R^2\cdot C)_4$. 

\[
\begin{align*}
R^1\text{Si} \equiv \text{Si} \equiv R^1 + & \quad H_2C \equiv CH_2 \quad \rightarrow \quad \text{Si} \equiv \text{Si} \\
R^1 & \quad R^1
\end{align*}
\]
Analizom $^{13}$C NMR spektara odgovarajućeg šestočlanog prstena Si$_2$C$_4$ pokazuje postojanje dva signala kod izomera B i jedan signal za izomer C.

A.1 **Nacrtajte** strukturne formule jedinjenja A, B i C koristeći oznake R$^1$, R$^2$, Si i C. 9pt

Nije potrebno crtati više rezonancijskih struktura.

A.2 **Izračunajte** energiju stabilizacije aromatičnog sistema (ASE) za benzen i jedinjenje C (u slučaju: R$^1$ = R$^2$ = H), izražene kao pozitivne vrijednosti, uzimajući u obzir da su promjene entalpija reakcije hidrogenizacije nekoliko nezasićenih sistema date ispod (Slika 1).

\[
\begin{align*}
\text{H}_2\text{C} = \text{CH}_2 & \quad + \quad \text{H}_2 & \quad \rightarrow & \quad \text{H}_3\text{C} \quad \text{CH}_3 & \quad \Delta H = -135 \text{ kJ mol}^{-1} \quad (1) \\
\text{H}_2\text{Si} = \text{SiH}_2 & \quad + \quad \text{H}_2 & \quad \rightarrow & \quad \text{H}_3\text{Si} \quad \text{SiH}_3 & \quad \Delta H = -213 \text{ kJ mol}^{-1} \quad (2) \\
\text{H}_2\text{Si} = \text{SiH}_2 & \quad + \quad 3 \text{ H}_2 & \quad \rightarrow & \quad \text{H}_2\text{Si} \quad \text{SiH}_2 & \quad \Delta H = -173 \text{ kJ mol}^{-1} \quad (4) \\
\text{H}_2\text{Si} = \text{SiH}_2 & \quad + \quad 3 \text{ H}_2 & \quad \rightarrow & \quad \text{H}_2\text{Si} \quad \text{SiH}_2 & \quad \Delta H = -326 \text{ kJ mol}^{-1} \quad (5) \\
\text{H}_2\text{Si} = \text{SiH}_2 & \quad + \quad 3 \text{ H}_2 & \quad \rightarrow & \quad \text{H}_2\text{Si} \quad \text{SiH}_2 & \quad \Delta H = -368 \text{ kJ mol}^{-1} \quad (6) \\
\text{H}_2\text{Si} = \text{SiH}_2 & \quad + \quad 3 \text{ H}_2 & \quad \rightarrow & \quad \text{H}_2\text{Si} \quad \text{SiH}_2 & \quad \Delta H = -389 \text{ kJ mol}^{-1} \quad (7)
\end{align*}
\]

\[\text{Slika 1}\]
Zagrijavanjem rastvora jedinjenja C u ksilenu, ono podliježe izomerizaciji pri čemu nastaje ravnotežna smješa jedinjenja D i E. Molarni odnos D : E = 1 : 40,0 na 50.0 °C, a D : E = 1 : 20,0 na 120.0 °C.

A.3 Izračunajte $\Delta H$ za transformaciju D u E. Pretpostavite da veličina $\Delta H$ ne zavisi od temperature.

Izomerizacija C u D i u E odvija se na račun transformacije $\pi$-veza u $\sigma$-veze bez raskidanja $\sigma$-veza. Analiza $^{13}$C NMR-spektra otkriva jedan signal koji odgovara skeletu Si$_2$C$_4$ u spektru jedinjenja D i dva signala za isti fragment koji se uočavaju u spektru jedinjenja E. Skelet jedinjenja D ne sadrži tročlani prsten, dok jedinjenje E sadrži dva tročlana prstena kojima je zajednička jedna stranica.

A.4 Nacrtajte strukturne formule jedinjenja D i E koristeći oznake R$^1$, R$^2$, Si i C.

Dio B
Silicijum ima mogućnost da gradi jedinjenja sa visokim koordinacionim brojem (više od 4 supstituenta) sa elektronegativnim elementima kao što je fluor. Pošto se metalni fluoridi često koriste kao reagensi za fluorovanje, tako i jedinjenja silicijuma i fluora sa visokim koordinacionim brojevima mogu imati osobine takvih reagenasa.

Reakcija fluorovanja CCl$_4$ pomoću Na$_2$SiF$_6$ odvija se na sledeći način.

- Standardizacija rastvora Na$_2$SiF$_6$:
  - Priprema
    Voden rastvor F: 0,855 g Na$_2$SiF$_6$ (188,053 g mol$^{-1}$) rastvoreno je u vodi (ukupna zapremina rastvora: 200 mL).
    Voden rastvor G: 6,86 g Ce$_2$(SO$_4$)$_3$ (568,424 g mol$^{-1}$) rastvoreno je u vodi (ukupna zapremina rastvora: 200 mL).
  - Postupak
    Taložna titracija rastvora F (50,0 mL) izvodi se ukapavanjem rastvora G u prisustvu ksileno-oranža koji koordinuje Ce$^{3+}$-jone, kao indikatora. Nakon dodatka 18.8 mL rastvora G, boja rastvora se mijenja iz žute u svijetloljubičastu (magenta boja). Nastali talog je binarno jedinjenje koje sadrži Ce$^{3+}$, a jedino dobijeno silicijumovo jedinjenje je Si(OH)$_4$.

B.1 Napisati izjednačenu jendačinu reakcije između Na$_2$SiF$_6$ i Ce$_2$(SO$_4$)$_3$. 5pt

- Reakcija CCl$_4$ i Na$_2$SiF$_6$:
  (Gubici supstance prilikom isparavanja tokom rada su zanemarljive za dalji postupak)
  Na$_2$SiF$_6$($x$ [g]) je dodat u CCl$_4$ (500,0 g) i dobijena smješa je zagrijavana na 300°C u zatvorenom sudu, otpornom na promjene pritiska. Neizreagovali Na$_2$SiF$_6$ i nastali NaCl su odvojeni filtracijom. Filtrat se razbljaži sa CCl$_4$ do ukupne zapremine od 1.00 L (rastvor H). $^{29}$Si i $^{19}$F NMR spekttri rastvora H pokazuju da je jedino silicijumovo jedinjenje koje nastaje SiF$_4$. $^{19}$F NMR spektar, osim signala koji potiču od SiF$_4$, sadrži i signale koji odgovaraju CFC$_3$, CF$_2$Cl$_2$, CF$_3$Cl i CF$_4$ (Tabela 1). Odnos integrala signala u $^{19}$F NMR spektru je proporcionalan broju jezgara fluora.
SiF₄ se hidrolizuje do H₂SiF₆ prema sledećoj jednačini reklacije (8):

\[ 3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6 \]  

Rastvor H (10 mL) je dodat u veću količinu vode, što rezultuje potpunom hidrolizom SiF₄. Nakon odvajanja, H₂SiF₆, nastao u reakciji hidrolize, neutralisan je i potpuno preveden u Na₂SiF₆ (vodeni rastvor J).

Talog neizreagovalog Na₂SiF₆ i NaCl, koji je odvojen filtracijom u početnom koraku (podvučena rečenica), je u potpunosti rastvoren u vodi, pri čemu se dobija vodeni rastvor K (10,0 L).

Nakon toga, dodatne taložne titracije su izvedene upotrebom rastvora G, pri čemu su završne tačke titracija sa G bile:

- Za rastvor J (cijelokupna količina): 61.6 mL.
- Za 100 ml rastvora K: 44.4 mL.

Ovdje je važno napomenuti da istovremeno prisustvo NaCl i SiO₂ ne utiče na taložnu titraciju.

| B.2 Izračunajte masu NaCl koja je nastala u reakcionom sudu (podvučeni dio teksta) i Izračunajte masu (x [g]) Na₂SiF₆ koji je korišćen kao polazna supstanca. 15pt |
|---|---|

| B.3 77,8% CCl₄ koji je korišćen kao polazna supstanca ostalo je neizreagovano. 8pt Izračunajte masu dobijenog CF₂Cl. |
Tajanstveni silicijum

Dio A

A.1 (9 pt)

A (3 pt)  B (3 pt)  C (3 pt)

A.2 (7 pt)

C₆H₆ :  kj mol⁻¹, C :  kj mol⁻¹
A.3 (6 pt)

\[ \Delta H = \text{kj mol}^{-1} \]

A.4 (10 pt)

| D (5 pt) | E (5 pt) |
Dio B

B.1 (5 pt)

B.2 (15 pt)

(Nastavlja se na sledećoj stranici)
B.2 (cont.)

NaCl :  g, Na₂SiF₆ :  g
B.3 (8 pt)

CF₂Cl: _________ g
IChO
Problem 6
Cover sheet

Please return this cover sheet together with all the related question sheets.
The Solid-State Chemistry of Transition Metals

Part A

Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions (\(M^{n+}\)) in the magma is incorporated into the silicate minerals. The \(M^{n+}\) studied in the problem are coordinated by oxide ions (\(O^{2-}\)) and adopt a four-coordinate tetrahedral (\(T_d\)) geometry in the magma and six-coordinate octahedral (\(O_h\)) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration. The distribution coefficient of \(M^{n+}\) between the silicate minerals and magma, \(D\), can be expressed by:

\[
D = \frac{[M]_s}{[M]_l}
\]

where \([M]_s\) and \([M]_l\) are the concentrations of \(M^{n+}\) in the silicate minerals and the magma, respectively. The table below shows the \(D\) values of \(Cr^{2+}\) and \(Mn^{2+}\) as examples.

<table>
<thead>
<tr>
<th></th>
<th>(Cr^{2+})</th>
<th>(Mn^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)</td>
<td>7.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Let $\Delta_O$ and $\text{CFSE}^O$ be the energy separation of the d-orbitals of $M^{n+}$ and the crystal-field stabilization energy in a $O_h$ field, respectively. Let $\Delta_T$ and $\text{CFSE}^T$ be those in a $T_d$ field.

A.1 Calculate $|\text{CFSE}^O - \text{CFSE}^T| = \Delta\text{CFSE}$ in terms of $\Delta_O$ for $\text{Cr}^{2+}$, $\text{Mn}^{2+}$, and $\text{Co}^{2+}$; assume $\Delta_T = 4/9 \Delta_O$.

A.2 A linear relationship is observed by plotting $\ln D$ against $\Delta\text{CFSE} / \Delta_O$ in the Cartesian coordinate system shown below. Estimate $D$ for $\text{Co}^{2+}$.

Metal oxides $MO$ ($M$: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure wherein the $M^{n+}$ adopts an $O_h$ geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is mainly governed by the Coulomb interactions based on the radius and charge of the ions and some contributions from the CFSE of $M^{n+}$ in the $O_h$ field.

A.3 Choose the appropriate set of lattice enthalpies [kJ mol$^{-1}$] from one of the options (a) to (f).

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>TiO</th>
<th>VO</th>
<th>MnO</th>
<th>CoO</th>
</tr>
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<tr>
<td>(a)</td>
<td>3460</td>
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<tr>
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<td>(d)</td>
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<tr>
<td>(f)</td>
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<td>3913</td>
<td>3916</td>
<td>3460</td>
<td>3878</td>
</tr>
</tbody>
</table>
Part B

A mixed oxide $A$, which contains $La^{3+}$ and $Cu^{2+}$, crystallizes in a tetragonal unit cell shown in Fig. 1. In the $[CuO_6]$ octahedron, the Cu–O length along the $z$-axis ($l_z$) is longer than that of the $x$-axis ($l_x$), and $[CuO_6]$ is distorted from the regular $O_h$ geometry. This distortion removes the degeneracy of the $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$).

Fig. 1

$A$ can be synthesized by thermal decomposition (pyrolysis) of complex $B$, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid $C_4H_2O_4$, i.e., a diacid. The pyrolysis behavior of $B$ in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of $CO_2$. The total weight loss during the formation of $A$ from $B$ is 63.6%. It should be noted that only water and $CO_2$ are released in the pyrolysis reaction.

| B.1 | Write the chemical formulae for $A$ and $B$. | 6pt |
| B.2 | Calculate $l_x$ and $l_z$ using Fig. 1. | 4pt |
| B.3 | For $Cu^{2+}$ in the distorted $[CuO_6]$ octahedron in $A$ of Fig. 1, write the names of the split $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet. | 4pt |
A is an insulator. When one La$^{3+}$ is substituted with one Sr$^{2+}$, one hole is generated in the crystal lattice that can conduct electricity. As a result, the Sr$^{2+}$-doped A shows superconductivity below 38 K. When a substitution reaction took place for A, $2.05 \times 10^{27}$ holes m$^{-3}$ were generated.

B.4 **Calculate** the percentage of Sr$^{2+}$ substituted for La$^{3+}$ based on the mole ratio in the substitution reaction. Note that the valences of the constituent ions and the crystal structure are not altered by the substitution reaction.

**Part C**

Cu$_2$(CH$_3$CO$_2$)$_4$ is composed of four CH$_3$CO$_2^-$ coordinated to two Cu$^{2+}$ (Fig. 2A). Cu$_2$(CH$_3$CO$_2$)$_4$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four CH$_3$CO$_2^-$ and an axis passing through the two Cu$^{2+}$, all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of CH$_3$CO$_2^-$, a “cage complex” is formed. The cage complex Cu$_4$(L$_1$L$_1$L$_1$)$_4$ is composed of planar dicarboxylate L$_1$ (Fig. 2B) and Cu$^{2+}$ (Fig. 2C). The angle $\theta$ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The $\theta$ is 0° for L$_1$. Note that hydrogen atoms are not shown in Fig. 2.
C.1 The $\theta$ of the planar dicarboxylate $L_2$ below is fixed to 90°. If the composition of the cage complex formed from $L_2$ and $Cu^{2+}$ is $Cu_n(L_2)_m$, give the smallest integer combination of $n$ and $m$. Assume that only the $CO_2^-$ groups of $L_2$ form a coordination bond to $Cu^{2+}$ ions.

![Diagram of L2 molecule with $\theta = 90^\circ$]
A zinc complex, $\text{Zn}_4\text{O} (\text{CH}_3\text{CO}_2)^6$, contains four tetrahedral $\text{Zn}^{2+}$, six $\text{CH}_3\text{CO}_2^-$, and one $\text{O}^{2-}$ (Fig. 3A). In $\text{Zn}_4\text{O} (\text{CH}_3\text{CO}_2)^6$, the $\text{O}^{2-}$ is located at the origin, and the three axes passing through the carbon atoms of $\text{CH}_3\text{CO}_2^-$ are oriented orthogonal relative to each other. When $p$-benzenedicarboxylate (Fig. 3B, $\text{L}_3$, $\theta = 180^\circ$) is used instead of $\text{CH}_3\text{CO}_2^-$, the $\text{Zn}^{2+}$ clusters are linked to each other to form a crystalline solid ($\text{X}$) that is called a “porous coordination polymer” (Fig. 3C). The composition of $\text{X}$ is $[\text{Zn}_4\text{O} (\text{L}_3)_3]^n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral $\text{Zn}^{2+}$ cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

**Fig. 3**

<table>
<thead>
<tr>
<th><strong>C.2</strong></th>
<th>$\text{X}$ has a cubic unit cell with a side length of $a$ (Fig. 3C) and a density of 0.592 g cm$^{-3}$. <strong>Calculate</strong> $a$ in [cm].</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th><strong>C.3</strong></th>
<th>$\text{X}$ contains a considerable number of pores, and 1 g of $\text{X}$ can accommodate $3.0 \times 10^2$ mL of $\text{CO}_2$ gas in the pores at 1 bar and 25 $^\circ\text{C}$. <strong>Calculate</strong> the average number of $\text{CO}_2$ molecules per pore.</th>
</tr>
</thead>
</table>


Hemija čvrstog stanja prelaznih metala

<table>
<thead>
<tr>
<th>Zadatak</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>B.1</th>
<th>B.2</th>
<th>B.3</th>
<th>B.4</th>
<th>C.1</th>
<th>C.2</th>
<th>C.3</th>
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<tr>
<td>Poeni</td>
<td>6</td>
<td>3</td>
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<td>6</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
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<td><strong>45</strong></td>
</tr>
</tbody>
</table>

Rezultat

Vulkan na ostrvu Sakurajima

Dio A

Japan je jedna od zemalja sa najvećim brojem vulkana na svijetu. Kada silikatni materijali kristališu iz magme, dio jona prelaznih metala (M$^{n+}$) iz magme se ugradi u te silikatne mineralne. M$^{n+}$ joni koji se razmatraju u ovom zadatku su koordinovani kiseoničnim jonima (O$^{2-}$) i zadobijaju četverokoordinovanu tetraedarsku geometriju ($T_d$) u magmi i heksakoordinovanu oktaedarsku geometriju ($O_h$) u silikatnim mineralima, pri čemu obje postoje u visoko-spinskim elektronskim konfiguracijama. Koeficijent raspodjele (D) M$^{n+}$ jona između silikatnih minerala i magme ima sledeći oblik:

\[ D = \frac{[M]^s}{[M]^l} \]

gdje su $[M]^s$ i $[M]^l$ koncentracije M$^{n+}$ -jona u silikatnim mineralima i u magmi, respektivno. U tablici su kao primjeri navedene $D$ vrijednosti za Cr$^{2+}$ i Mn$^{2+}$:

<table>
<thead>
<tr>
<th></th>
<th>Cr$^{2+}$</th>
<th>Mn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>7.2</td>
<td>1.1</td>
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</table>
Neka $\Delta O$ i CFSE$^O$ predstavljaju energiju razdvajanja $d$-orbitala jona $M^{n+}$ i energiju stabilizacije kristalnog polja u $O_h$ polju, respektivno. Neka $\Delta T$ i CFSE$^T$ budu takođe i u $T_d$ polju.

A.1 **Izračunajte** $|\text{CFSE}^O - \text{CFSE}^T| = \Delta \text{CFSE}$ u uslovima $\Delta O$ za $\text{Cr}^{2+}$, $\text{Mn}^{2+}$ i $\text{Co}^{2+}$; 6pt pretpostaviti da je $\Delta T = 4/9 \Delta O$.

A.2 Posmatran je linearni odnos između $\ln D$ i $\Delta \text{CFSE} / \Delta O$ u Cartesian-ovom koordinatnom sistemu koji je prikazan ispod. **Odredite** $D$ za $\text{Co}^{2+}$.

Metalni oksidi MO (M: Ca, Ti, V, Mn ili Co) kristališu u obliku struktura kamene soli gdje joni $M^{n+}$ posjeduju $O_h$ geometriju sa visoko-spinskom elektronskom konfiguracijom. Entalpija kristalne rešetke ovih oksida je uglavnom određena Coulomb-ovim interakcijama zasnovanim na prečniku i naelektrisanju jona, kao i uticajima od strane stabilizacije energije kristalnog polja CFSE jona $M^{n+}$ u $O_h$ polju.

A.3 **Izaberite** opciju među datim (a) - (f) koja predstavlja odgovarajuće entalpije kristalne rešetke [kJ mol$^{-1}$].

<table>
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<td>3460</td>
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</tbody>
</table>
Dio B

Mješoviti oksid A, koji sadrži jone La$^{3+}$ i Cu$^{2+}$, kristališe u obliku tetragonalne jedinične ćelije prikazane na Slici 1. U [CuO$_6$] oktaedaru, udaljenost između Cu – O na z-osi ($l_z$) je veća nego na x-osi ($l_x$), i [CuO$_6$] ima nepravilnu $O_h$ geometriju. Ova nepravilnost uklanja degeneraciju e$_g$ orbitala ($d_{x^2-y^2}$ i $d_{z^2}$).

Slika 1

A se može sintetisati termičkim razlaganjem kompleksa B, koji nastaje miješanjem metalnih hlorida u razblaženom vodenom rastvoru amonijaka koji sadrži skvarinsku kiselinu C$_4$H$_2$O$_4$, (Squaric acid), koja je zapravo dikiselina. Pirolizom jedinjenja B na suvom vazduhu dolazi do gubitka mase od 29,1% na 200 °C usled gubitka kristalne vode, što je praćeno daljim gubitkom mase na 700 °C usled oslobađanja CO$_2$. Ukupan gubitak mase tokom formiranja A iz B je 63.6%. Važno je naglasiti da se u reakciji pirolize oslobađaju samo molekuli vode i CO$_2$.

B.1 Napišite hemijske formule jedinjenja A i B. 6pt

B.2 Izračunajte $l_x$ i $l_z$ uz pomoć Slike 1. 4pt

B.3 Za Cu$^{2+}$ u nepravilnom [CuO$_6$] oktaedru u A sa Slike 1, napišite nazive 4pt podijeljenih e$_g$ orbitala ($d_{x^2-y^2}$ i $d_{z^2}$) u (i) i (ii), i nacrtajte elektronsku konfiguraciju u istačkanom pravougaoniku u listu za odgovore.
A je izolator. Kada se jedan La$^{3+}$ zamjeni sa jednim Sr$^{2+}$, u kristalnoj rešetki se stvara jedna rupa koja može provoditi elektricitet. Kao rezultat toga, Sr$^{2+}$-dopingovani izolator A sada pokazuje superprovodljivost ispod 38 K. Kada dođe do reakcije zamjene unutar izolatora A, nastaje $2.05 \times 10^{27}$ rupa po $m^{-3}$.

**B.4 Izračunajte** procenat Sr$^{2+}$ koji su supstituisali (zamijenili) La$^{3+}$ na osnovu molskog odnosa u reakciji zamjene. Smatrajte da se valence jona u izolatoru i kristalna struktura ne mijenjaju tokom reakcije supstitucije.

**Dio C**

$	ext{Cu}_2(\text{CH}_3\text{CO}_2)_4$ se sastoji iz četiri $\text{CH}_3\text{CO}_2^-$ -jona koji su koordinovana sa dva jona Cu$^{2+}$ (Slika 2A). $	ext{Cu}_2(\text{CH}_3\text{CO}_2)_4$ posjeduje visok nivo strukturne simetrije, sa dvije ose koje prolaze kroz atome ugljenika od četiri $\text{CH}_3\text{CO}_2^-$ jona i osom koja prolazi kroz dva Cu$^{2+}$ i sve su ortogonalno orijentisane jedna u odnosu na drugu. Kada se umjesto $\text{CH}_3\text{CO}_2^-$ koristi dikarboksilatni ligand, formira se „kavez-kompleks“ („cage complex“). Kavez-kompleks $	ext{Cu}_4(L_1)_4$ je sastavljen od planarnog dikarboksilata $L_1$ (Slika 2B) i Cu$^{2+}$ (Slika 2C). Ugao $\theta$ između koordinativnih pravaca od dva karboksilata, označenih strelicama na Slici 3B, određuju strukturu kavez-kompleksa. $\theta$ ima vrijednost 0° za $L_1$. Atomi vodonika nijesu prikazani na Slici 2.
C.1 Ugao $\theta$ planarnog dikarboksilata $\text{L}_2$, koji je prikazan ispod, iznosi 90˚. Ako sastav kavez-kompleksa, dobijenog od $\text{L}_2$ i $\text{Cu}^{2+}$ može da se prikaže formulom $\text{Cu}_n(\text{L}_2)_m$, dajte najmanju cijelobrojnu kombinaciju $n$ i $m$. Pretpostavite da samo $\text{CO}_2^-$ grupe iz $\text{L}_2$ grade koordinativnu vezu sa $\text{Cu}^{2+}$ - jonima.
Kompleks cinka, Zn₄O(CH₃CO₂)₄, sadrži četiri tetraedarska Zn²⁺, šest CH₃CO₂⁻, i jedan O²⁻ (Slika 3A). U komplexu Zn₄O(CH₃CO₂)₄, O²⁻ se nalazi na početku, a tri ose koje prolaze kroz atome ugljenika CH₃CO₂⁻ su orijentisane ortogonalno (pod uglom od 90°) jedna u odnosu na drugu. Kada se p-benzendikarboksilat (Slika 3B, L₃, θ = 180°) koristi umjesto CH₃CO₂⁻, klasteri Zn²⁺ se međusobno povezuju i stvaraju kristalnu čvrstu supstancu (X) koja se naziva „porozni koordinacioni polimer“ (Slika 3C). Sastav polimera X je [Zn₄O(L₃)₃]ⁿ⁻, i on ima kubnu kristalnu strukturu sa porama nano veličine. Jedna pora je predstavljena kao sfera na Slici 3D, a svaki tetraedarski klaster Zn²⁺ predstavljen je kao tamno-sivi poliedar na slikama 3C i 3D. Atomi vodonika nijesu prikazani na Slici 3.

Slika 3

<table>
<thead>
<tr>
<th>C.2</th>
<th>X posjeduje kubnu jediničnu čeliju sa dužinom ivice a (Slika 3C) čija je gustina 0.592 g cm⁻³. <strong>Izračunajte</strong> a u [cm].</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.3</td>
<td>X sadrži priličan broj pora i 1 g polimera X može da primi 3.0 × 10² mL gasovitog CO₂ unutar svojih pora na pritisku od 1 bar i na temperaturi od 25 °C. <strong>Izračunajte</strong> prosječan broj molekula of CO₂ po jednoj pori.</td>
</tr>
</tbody>
</table>
Hemija čvrstog stanja prelaznih metala

Dio A

A.1 (6 pt)

\[ \text{Cr}^{2+} : \Delta_0, \text{Mn}^{2+} : \Delta_0, \text{Co}^{2+} : \Delta_0 \]
A.2 (3 pt)

\[ \ln D \]

\[ \Delta \text{CFSE} / \Delta_0 \]

\[ D : \] ______________

A.3 (3 pt)

_______
### Dio B

**B.1 (6 pt)**

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

**B.2 (4 pt)**

\[ l_x = \text{nm}, l_z = \text{nm} \]
B.3 (4 pt)
(i) : ........................................, (ii) :

\[
\begin{align*}
\text{Energy} & \\
\text{e}_g & \quad \text{branch} \quad \text{branch} \\
\text{branch} & \quad \text{branch}
\end{align*}
\]

B.4 (4 pt)
Dio C

C.1 (5 pt)

\[ n = \_\_\_, \quad m = \_\_\_ \]

C.2 (5 pt)

\[ a = \_\_\_ \text{ cm} \]
C.3 (5 pt)
Please return this cover sheet together with all the related question sheets.
Playing with Non-benzenoid Aromaticity

Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

Part A

Lineariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (1), a one-step conversion yields 2, before a three-step conversion via 3 yields ketone 4. Eremophilene (5) is converted into 6 by performing the same four-step conversion.
A.1 **Draw** the structures of 2 and 6 and clearly identify the stereochemistry where necessary.

Then, ketone 4 is converted into ester 15. Compound 8 (molecular weight: 188) retains all the stereocenters in 7. Compounds 9 and 10 have five stereocenters and no carbon-carbon double bonds. Assume
that $\text{H}_2^{18}\text{O}$ is used instead of $\text{H}_2^{16}\text{O}$ for the synthesis of $^{18}\text{O}$-labelled-lineariifolianones 13 and 14 from 11 and 12, respectively. Compounds 13 and 14 are $^{18}\text{O}$-labelled isotopomers. Ignoring isotopic labelling, both 13 and 14 provide the same product 15 with identical stereochemistry.
A.2 Choose the appropriate structure for A. 2pt

I $\overset{\text{O}}{\text{F}}_3\text{C-S-}\overset{\text{O}}{\text{OH}}$ II $\overset{\text{O}}{\text{F}}_3\text{C-S-}\overset{\text{O}}{\text{NH}_2}$ III $\overset{\text{O}}{\text{S}}\text{CF}_3$ IV $\overset{\text{O}}{\text{S}}\text{CF}_3$

A.3 Draw the structures of 8-14 and clearly identify the stereochemistry where necessary. Also, indicate the introduced $^{18}$O atoms for 13 and 14 as shown in the example below. 19pt
Part B

Compound 19 is synthesized as shown below. In relation to non-benzenoid aromaticity, 19 can be used as an activator for alcohols, and 20 was converted to 22 via ion-pair intermediate 21. Although the formation of 21 was observed by NMR, 21 gradually decomposes to give 18 and 22.

\[
\begin{align*}
\text{16} & \quad \text{Br}_2 \quad \text{CH}_3\text{COOH} \\
\text{17} & \quad \text{C}_{15}\text{H}_{12}\text{Br}_2\text{O} \\
\text{18} & \quad \text{C}_{15}\text{H}_{10}\text{O} \\
\text{19} & \quad \text{C}_{15}\text{H}_{10}\text{Cl}_2 \\
\end{align*}
\]

\[\text{20} + 19 \rightarrow \text{21} \rightarrow \text{22} + 18\]

\[^1\text{H NMR (CD}_3\text{CN, ppm)} \]

\[\text{20}: \delta \text{ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)}\]

\[\text{21}: \delta \text{ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)}\]

**B.1** **Draw** the structures of 17–19 and 21. Identifying the stereochemistry is not necessary.
Игра с неbenzoidном ароматићношћу

<table>
<thead>
<tr>
<th>Задатак</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>B.1</th>
<th>Укупно</th>
</tr>
</thead>
<tbody>
<tr>
<td>Пoена</td>
<td>5</td>
<td>2</td>
<td>19</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>Резултат</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Проfесор Nozoe (1902–1996) отворио je поље истраживања неbenzenoidних ароматичних jedinjenja, koji су данас veoma prisutni u organskoj hemiji.

Фотографија добијена лjубазношћу Univerziteta Tohoku

Дio A

Lineariifolianon je priродни proizvod sa jedinstvenom strukturom koji je izolovan iz biljke Inula linariifolia. Iz valencena (1) se у једном koraku добија jedinjenje 2, iz koga se у tri koraka, preko jedinjenja 3, добија keton 4. Na sličan način, из eremofilena (5) se у четiri koraka синтезе добија jedinjenje 6.
Nakon toga, keton 4 je preveden u estar 15. Jedinjenje 8 (relativna molekulska masa: 188) zadržava sve stereocentre od jedinjenja 7. Jedinjenja 9 i 10 imaju 5 stereocentara i ne posjeduju ugljenik-
ugljenik dvostruku vezu. Pretpostavite da je H\textsubscript{2}\textsuperscript{18}O upotrebljena umjesto H\textsubscript{2}\textsuperscript{16}O u sintezi \textsuperscript{18}O-obilježenih lineariifolianona 13 i 14 iz jedinjenja 11, odnosno 12. Jedinjenja 13 i 14 su \textsuperscript{18}O-obilježeni izotopomeri. Ako zanemarimo izotopsko obilježavanje, oba jedinjenja 13 i 14 vode do istog proizvoda 15 sa identičnom stereohemijom.
A.2 Izaberite odgovarajuću strukturu jedinjenja A.

I $\text{F}_3\text{C}-\text{SOH}$  
II $\text{F}_3\text{C}-\text{SONH}_2$  
III $\text{O=S-CF}_3$  
IV $\text{O=S-CF}_3$

A.3 Nacrtajte strukture jedinjenja 8–14 i jasno naznačite stereochemijske centre gdje je to potrebno. Označite izotope $^{18}\text{O}$ u jedinjenjima 13 i 14 kao što je prikazano u donjem primjeru.
Dio B


$$\text{16} \quad \text{Br}_2 \quad \text{CH}_3\text{COOH} \quad \rightarrow \quad \text{17} \quad \text{C}_{15}\text{H}_{12}\text{Br}_2\text{O}$$

$$\text{18} \quad \text{O} \quad \text{Cl}_2\text{Cl} \quad \rightarrow \quad \text{19} \quad \text{C}_{15}\text{H}_{10}\text{Cl}_2$$

$$\text{19} \quad \rightarrow \quad \text{20} \quad \text{21}$$

$$\text{21} \quad \rightarrow \quad \text{22} \quad \text{18}$$

$^{1}$H NMR (CD$_3$CN, ppm) 20: $\delta$ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
21: $\delta$ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

Igre s nebenzoidnom aromatičnošću

Dio A

A.1 (5 pt)

2 (2 pt) 6 (3 pt)

A.2 (2 pt)
## Dio B

**B.1 (10 pt)**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>17</strong> (2 pt)</td>
<td><strong>18</strong> (2 pt)</td>
</tr>
<tr>
<td><strong>19</strong> (3 pt)</td>
<td><strong>21</strong> (3 pt)</td>
</tr>
</tbody>
</table>
IChO
Problem 8
Cover sheet

Please return this cover sheet together with all the related question sheets.
## Dynamic Organic Molecules and Their Chirality

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>B.1</th>
<th>B.2</th>
<th>Total</th>
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</thead>
<tbody>
<tr>
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<td>7</td>
<td>3</td>
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<td>Score</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Part A

Polycyclic aromatic hydrocarbons with successive ortho-connections are called \([n]\)carbohelicenes (here, \(n\) represents the number of six-membered rings) (see below). \([4]\)Carbohelicene \((\text{[4]}C)\) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (\(\text{Int.}\)) that is readily oxidized by iodine.

![Reaction Scheme]

The photoreaction proceeds in a manner similar to the following example.

![Example Reaction]

Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

<table>
<thead>
<tr>
<th>A.1</th>
<th>Draw the structures of A–C. Stereoisomers should be distinguished.</th>
<th>9pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.2</td>
<td>Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product D whose molecular weight was 2 Da lower than that of [5]carbohelicene. The $^1$H NMR chemical shifts of D are listed below. Draw the structure of D.</td>
<td>3pt</td>
</tr>
<tr>
<td>D $\delta$, ppm in CS$_2$, r.t., 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (M) or (P) as shown below.

[5]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.

Photo courtesy: The Japan Prize Foundation
Multiple helicenes are molecules that contain two or more helicene-like structures. If its helical chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound E contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as \((P, P, P)\) as shown below.

![Diagram of compound E and (1, 2, 3) = (P, P, P)]

A.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of F, \((P)-F\), multiple helicene G \((C_{66}H_{36})\) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, identify all the possible stereoisomers of G formed in this process, without duplication. As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and \(M\) and \(P\) labels according to the same numbering. For instance, the other stereoisomers of E should be listed as \((1, 2, 3) = (P, M, P), (P, M, M), (P, P, M), (M, M, M), (M, M, M), (M, M, P), (M, P, P),\) and \((M, P, M)\).
Part B

Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.

Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.

B.1 Draw the structure of intermediate I (its stereochemistry is not required). 3pt
B.2 Starting from the optically active precursor \( J \), the same reaction sequence gives the optically active sumanene derivative \( K \). The stereocenters in \( J \) suffer no inversion during the metathesis reaction. **Draw** the structure of \( K \) with the appropriate stereochemistry.
Dinamički organski molekuli i njihova hiralnost

<table>
<thead>
<tr>
<th>Zadatak</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>B.1</th>
<th>B.2</th>
<th>Ukupno</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poeni</td>
<td>9</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>26</td>
</tr>
</tbody>
</table>

Rezultat

Dio A

Policiklični aromatični ugljovodonici sa naizmjeničnim orto-vezama nazivaju se \([n]\)karboheliceni (ovdje \(n\) predstavlja broj šestočlanih prstenova) (vidi dolje). \([4]\)Karbohelicen (\([4]\)C) se na efikasan način dobija fotohemijskom reakcijom koja je prikazana dolje, preko intermedijera (Int.) koji se lako oksiduje pomoću joda.

Fotoreakcija se odvija na sličan način kao u donjem primjeru.
Napomena: U cijelom Zadatku 8, za konjugovani \( \pi \) sistem ne koristite kružiće nego naizmjenične dvostruke i jednostruke veze.

A.1 **Nacrtajte** strukturne formule jedinjenja A–C. Stereoizomere crtajte odvojeno. 9pt


\[ D (\delta, \text{ppm in CS}_2, \text{r.t.}) \]: 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)

**Nacrtajte** strukturnu formulu jedinjena \( D \).


Enantiomeri [n]karbohelicena u kojima je \( n \) veći od 4 mogu se razdvojiti na hiralnim hromatografskim kolonama koje je razvio profesor Yoshio Okamoto.

Fotografija dobijena ljubaznošću *The Japan Prize Foundation*

![Višestruki helicen E](image)

(1, 2, 3) = \((P, P, P)\)

### A.3

Trimerizacija 1,2-dibromobenzena u prisutnosti nikla daje trifenilen. Istočnom reakcijom iz enantiomera F, \((P)\)-F, nastaje višestruki helicen G \((C_{66}H_{36})\). Ako se pretpostavi da tokom reakcije ne dolazi do interkonverzije stereoizomera, odredite sve moguće stereoizomere jedinjenja G. Jedan izomer nacrtajte i označite brojevima i slovima kao u gornjem primjeru. Ostale stereoizomere samo označite brojevima i slovima; Npr., ostali stereoizomeri jedinjenja E su: \((1, 2, 3) = (P, M, P), (P, M, M), (P, P, M), (M, M, M), (M, M, P), (M, P, M)\) i \((M, P, M)\).
**Dio B**


Reprezentativna reakcija koja se odvija uz rutenijum kao katalizator (Ru*) prikazana je ispod.

**B.1 Nacrta** strukturnu formulu intermedijera I (nije potrebno označavati njegovu střeohemiju).
Dinamički organski molekuli i njihova hiralnost

Dio A

A.1 (9 pt)

A (3 pt)  B (3 pt)  C (3 pt)

A.2 (3 pt)
A.3 (7 pt)
Dio B

B.1 (3 pt)

B.2 (4 pt)
Please return this cover sheet together with all the related question sheets.
Likes and Dislikes of Capsule

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
<th>A.5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
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<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>23</td>
</tr>
</tbody>
</table>

Score

Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.

Based on this idea, compounds 1 and 2 were synthesized as U-shaped molecules with different sizes. Compound 3 was prepared as a comparison of 1 and the encapsulation behavior of these compounds was investigated.
The synthetic route to 2 is shown below. The elemental composition of compound 9: C; 40.49%, H; 1.70%, and O; 17.98% by mass.
A.1 **Draw** the structures of 4-9; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of \( p \)-methoxybenzyl group shown in the scheme above.

In the mass spectrum of 1, the ion peak corresponding to its dimer (1₂) was clearly observed, whereas an ion peak for 3₂ was not observed in the spectrum of 3. In the \( ^1 \)H NMR spectra of a solution of 1₂, all the NH protons derived from 1 were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of 3. These data indicate that hydrogen bonds are formed between the NH moieties of 1 and atoms X of another molecule of 1 to form the dimeric capsule.

A.2 **Circle** all the appropriate atom(s) X in 1.

A.3 **Give** the number of the hydrogen bonds in the dimeric capsule (1₂).
The dimeric capsule of 1 (\(1_2\)) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

\[ Z + 1_2 \rightarrow Z@1_2 \]  

(1)

The equilibrium constant of the encapsulation of Z into \(1_2\) is given as below:

\[ K_a = \frac{[Z@1_2]}{[Z][1_2]} \]  

(2)

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, \(1_2\) in \(C_6D_6\) gave different signals in the \(^1H\) NMR spectra before and after addition of CH\(_4\).

Compound 2 also forms a rigid and larger dimeric capsule (\(2_2\)). The \(^1H\) NMR spectrum of \(2_2\) was measured in \(C_6D_6\), \(C_6D_5F\), and a \(C_6D_6/C_6D_5F\) solvent mixture, with all other conditions being kept constant. The chemical shifts for the H\(^a\) proton of 2 in the above solvents are summarized below, and no other signals from the H\(^a\) in 2, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.

<table>
<thead>
<tr>
<th>solvent</th>
<th>(\delta) (ppm) of H(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_6D_6)</td>
<td>4.60</td>
</tr>
<tr>
<td>(C_6D_5F)</td>
<td>4.71</td>
</tr>
<tr>
<td>(C_6D_6/\ C_6D_5F)</td>
<td>4.60, 4.71, 4.82</td>
</tr>
</tbody>
</table>

A.4 Determine the number of \(C_6D_6\) and \(C_6D_5F\) molecules encapsulated in \(2_2\) giving each H\(^a\) signal.
$^1$H NMR measurements in C$_6$D$_6$ revealed that 2, can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants ($K_a$) which are expressed below were determined for various temperatures. [solvent@2$_2$] denotes a species containing one or more solvent molecules.

$$K_a = \frac{[Z@2_2]}{[Z][\text{solvent@2}_2]}$$

(3)

Similarly, the $K_a$ values of CH$_4$ and 1$_2$ given as eq (2) at various temperatures in C$_6$D$_6$ were also determined by $^1$H NMR measurements. The plots of the two association constants (as ln $K_a$ vs 1/T) are shown below.

No C$_6$D$_6$ molecule is encapsulated in 1$_2$. In line II, the entropy change ($\Delta S$) is (1) and enthalpy change ($\Delta H$) is (2), indicating that the driving force for the encapsulation in line II is (3). Therefore, line I corresponds to (4), and line II corresponds to (5).

**A.5 Choose** the correct options in gaps (1)–(5) in the following paragraph from A and B.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>positive</td>
<td>negative</td>
</tr>
<tr>
<td>(2)</td>
<td>positive</td>
<td>negative</td>
</tr>
<tr>
<td>(3)</td>
<td>$\Delta S$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td>(4)</td>
<td>1$_2$ and CH$_4$</td>
<td>2$_2$ and AdA</td>
</tr>
<tr>
<td>(5)</td>
<td>1$_2$ and CH$_4$</td>
<td>2$_2$ and AdA</td>
</tr>
</tbody>
</table>
Za i protiv kapsula

<table>
<thead>
<tr>
<th>Zadatak</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
<th>A.5</th>
<th>Ukupno</th>
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<tbody>
<tr>
<td>Poeni</td>
<td>13</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>23</td>
</tr>
</tbody>
</table>

Dobra djeca to ne rade, ali ako rasiječete tenisku lopticu, možete je rastaviti na dva dijela u obliku slova U.

Na osnovu ove ideje sintetisana su jedinjenja 1 i 2, kao molekuli u obliku slova U različitih veličina. Jedinjenje 3 je slično jedinjenju 1. Istraživana su njihova svojstva enkapsuliranja.
Sintetička sekvence dobijanja jedinjenja 2 je prikazana spod. Elementarnom analizom jedinjenja 9 dobijeni su sledeći podaci: C; 40,49 %, H; 1,70 % i O; 17,98 % (maseni udjeli).
A.1 Nacrtajte strukurne formule jedinjenja 4-9; stereohemiju možete zanemariti. Koristite "PMB" kao oznaku za supstituent umjesto da crtećete cijelu strukturu p-metoksibenzi-grupe koja je prikazana u gornjoj šemi.

U masnom spektru jedinjenja 1, jonski pik (signal) koji odgovara njegovom dimeru (1₂), dok signal za 3₂ nije primijećen u spektru jedinjenja 3. U ¹H NMR spektru rastvora jedinjenja 1₂, svi NH protoni su hemijski ekvivalenti i njihova hemijska pomjeranja značajno se razlikuju od NH protona u jedinjenju 3. Ovi podaci ukazuju na to da se vodonične veze formiraju između ostataka NH kod jedinjenja 1 i atoma X drugog molekula jedinjenja 1 kako bi se formirala dimerna kapsula.

A.2 Zaokružite sve atome X u jedinjenju 1.

A.3 Koliki je ukupan broj vodoničnih veza u dimernoj kapsuli (1₂)?
Dimerna kapsula od jedinjenja \( 1 (1_2) \) ima unutrašnji prostor u koji se može smjestiti (inkapsulirati) odgovarajući mali molekul \( Z \). Ovaj fenomen se izražava sledećom jednačinom:

\[
Z + 1_2 \rightarrow Z@1_2
\]  \( (1) \)

Konstanta ravnoteže inkapsulacije \( 1_2 \) je data ispod:

\[
K_a = \frac{[Z@1_2]}{[Z][1_2]}
\]  \( (2) \)

Inkapsulacija molekula unutar kapsule može se pratiti NMR spektroskopijom. Na primjer, \( 1_2 \) u \( C_6D_6 \) daje različite signale u \( ^1H \) NMR spektru prije i nakon dodatka \( CH_4 \).

Jedinjenje \( 2 \) takođe gradi rigidnu i veću dimernu kapsulu (\( 2_2 \)). Snimljen je \( ^1H \) NMR spektar od \( 2_2 \) u: \( C_6D_6 it C_6D_5F \, i \, smješi C_6D_6/C_6D_5F \) pri čemu se svi ostali uslovi održavaju konstantnim. Hemijska pomjeranja protona \( H^a \) jedinjenja \( 2 \) u gore navedenim rastvaračima su prikazana ispod, i drugi signali od \( H^a \) iz molekula \( 2 \), osim navedenih, nijesu detektovani. Pretpostavimo da je unutrašnjost kapsule uvijek ispunjena najvećim mogućim brojem molekula rastvarača i da svaki signal odgovara jednoj vrsti.

![Diagram](image)

<table>
<thead>
<tr>
<th>rastvarač</th>
<th>( \delta ) (ppm) od ( H^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6D_6 )</td>
<td>4.60</td>
</tr>
<tr>
<td>( C_6D_5F )</td>
<td>4.71</td>
</tr>
<tr>
<td>( C_6D_6 / C_6D_5F )</td>
<td>4.60, 4.71, 4.82</td>
</tr>
</tbody>
</table>

**A.4** Koliki je broj molekula \( C_6D_6 \) i \( C_6D_5F \) koji su inkapsulirani u \( 2_2 \) za sve date \( H^a \) 3pt signale.
1H NMR mjerenja u C₆D₆ pokazala su da 2 može da ugradi jedan molekul 1-adamantankarboksilne kiseline (AdA) i konstante asocijacije (Kₐ) koje su izražene ispod su određene na različitim temperaturama. [solvent@2₂] označava vrstu koja sadrži jedan ili više molekula rastvarača.

\[ K_a = \frac{[Z@2₂]}{[Z][solvent@2₂]} \]  

(3)

Slično tome, vrijednosti Kₐ za CH₄ i molekul 1₂ date jednačinom (2) na različitim temperaturama u C₆D₆ takođe su određene ¹H NMR mjerenjima. Prikazani su grafici te dvije konstante (ka ln Kₐ vs 1/T).

Molekuli C₆D₆ nijesu inkapsulirani u 1₁. U liniji II, promjena entropije (ΔS) je (1) a promjena entalpije (ΔH) je (2), što ukazuje da je pokretačka sila za inkapsulaciju u liniji III (3). Stoga, linija I odgovara (4), a linija II odgovara (5).

A.5 Izaberite odgovarajuću kombinaciju za (1)-(5) koja je ponuđena među 3pt odgovorima A i B.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pozitivna</td>
<td>negativna</td>
</tr>
<tr>
<td>2</td>
<td>pozitivna</td>
<td>negativna</td>
</tr>
<tr>
<td>3</td>
<td>ΔS</td>
<td>ΔH</td>
</tr>
<tr>
<td>4</td>
<td>1₂ i CH₄</td>
<td>2₂ i AdA</td>
</tr>
<tr>
<td>5</td>
<td>1₁ i CH₄</td>
<td>2₁ i AdA</td>
</tr>
</tbody>
</table>
**Za i protiv kapsula**

<table>
<thead>
<tr>
<th>A.1 (13 pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 (2 pt)</td>
</tr>
<tr>
<td>6 (2 pt)</td>
</tr>
<tr>
<td>8 (2 pt)</td>
</tr>
</tbody>
</table>
A.2 (2 pt)

\[
\begin{array}{c}
\text{HN} \\
\text{O} \\
\text{HN} \\
\text{O} \\
\text{HN} \\
\text{O} \\
\text{HN} \\
\text{O} \\
\end{array}
\]

\[
\text{Ph} \quad \text{Ph} \\
\text{Ph} \quad \text{Ph} \\
\]

A.3 (2 pt)

A.4 (3 pt)

<table>
<thead>
<tr>
<th>( \delta ) (ppm) od H(^a)</th>
<th>broj C(_6)D(_6)</th>
<th>broj C(_6)D(_5)F</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.60 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.71 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.82 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A.5 (3 pt)

(1) : 

(2) : 

(3) : 

(4) : 

(5) :