MNE-4 C-0 C
Ksenija Tadic

IChO
General instructions
Cover sheet

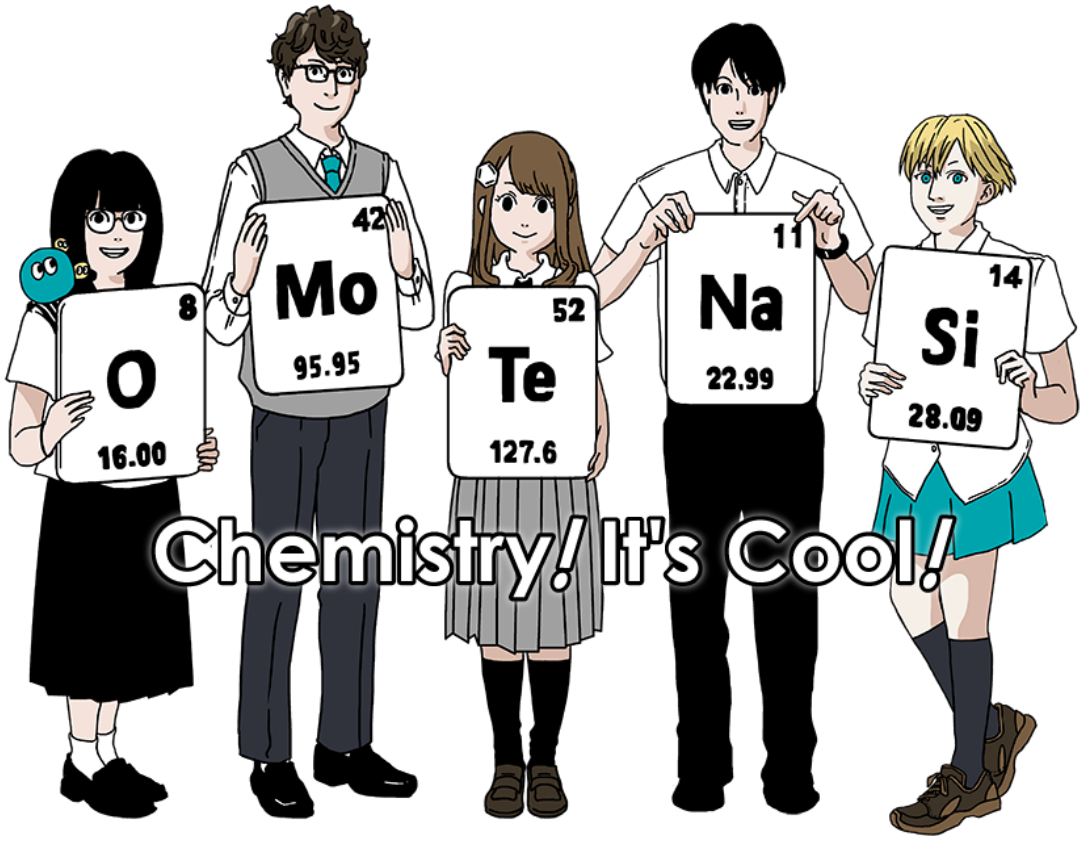
Please return this cover sheet together with all the related question sheets.

International Chemistry Olympiad 2021 Japan

53rd IChO2021 Japan

25th July – 2nd August, 2021

https://www.icho2021.org



G0-2

English (Official)

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

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

Physical Constants and Equations

Constants

Speed of light in vacuum	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Planck constant	$h = 6.62607015 \times 10^{-34}\ \mathrm{J\ s}$
Elementary charge	$e = 1.602176634 \times 10^{-19}\ \mathrm{C}$
Electron mass	$m_{\mathrm{e}} = 9.10938370 \times 10^{-31}\ \mathrm{kg}$
Electric constant (permittivity of vacuum)	$\varepsilon_0 = 8.85418781 \times 10^{-12}\ \mathrm{F\ m^{-1}}$
Avogadro constant	$N_{\mathrm{A}} = 6.02214076 \times 10^{23}\ \mathrm{mol^{-1}}$
Boltzmann constant	$k_{\mathrm{B}} = 1.380649 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
Faraday constant	$F = N_{\mathrm{A}} \times e = 9.64853321233100184 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
Gas constant	$R = N_{\mathrm{A}} \times k_{\mathrm{B}} = 8.31446261815324\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $= 8.2057366081 \times 10^{-2}\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
Unified atomic mass unit	$u = 1\ \mathrm{Da} = 1.66053907 \times 10^{-27}\ \mathrm{kg}$
Standard pressure	$p = 1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$
Atmospheric pressure	$p_{\mathrm{atm}} = 1.01325 \times 10^{5}\ \mathrm{Pa}$
Zero degree Celsius	$0\ ^{\circ}\mathrm{C} = 273.15\ \mathrm{K}$
Ångstrom	$1\ \text{Å} = 10^{-10}\ \mathrm{m}$
Picometer	$1\ \mathrm{pm} = 10^{-12}\ \mathrm{m}$
Electronvolt	$1\ \mathrm{eV} = 1.602176634 \times 10^{-19}\ \mathrm{J}$
Part-per-million	$1\ \mathrm{ppm} = 10^{-6}$
Part-per-billion	$1\ \mathrm{ppb} = 10^{-9}$
Part-per-trillion	$1\ \mathrm{ppt} = 10^{-12}$
pi	$\pi = 3.141592653589793$
The base of the natural logarithm (Euler's number)	$e = 2.718281828459045$

Equations

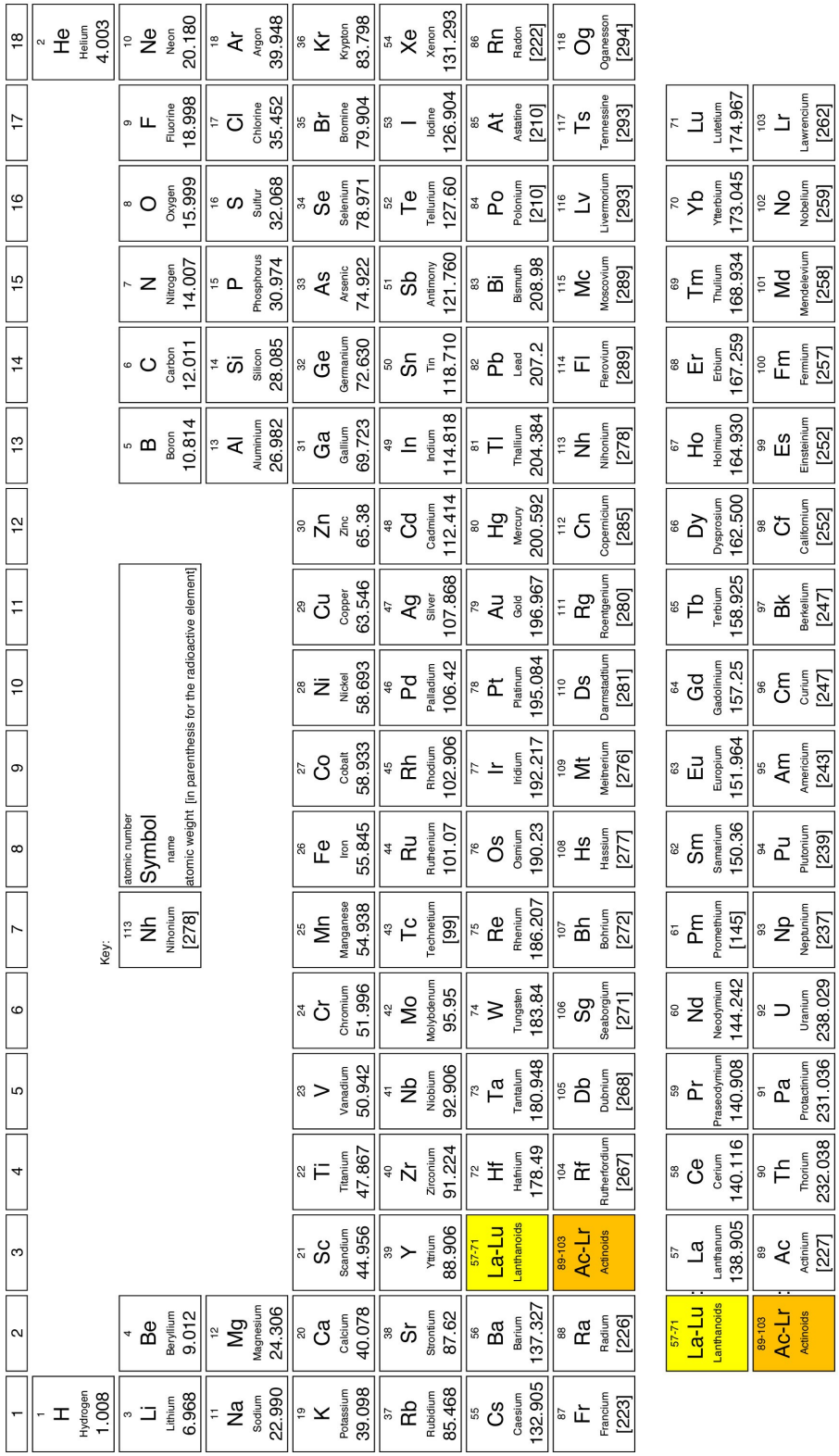
The ideal gas law	$PV = nRT$, where P is the pressure, V is the volume, n is the amount of substance, T is the absolute temperature of ideal gas.
Coulomb's law	$F = k_{\mathrm{e}} \dfrac{q_1 q_2}{r^2}$, where F is the electrostatic force, $k_{\mathrm{e}} (\simeq 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}})$ 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 ΔU 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	$S = k_{\mathrm{B}} \ln W$, where W is the number of microstates.
The change of entropy ΔS	$\Delta S = \dfrac{q_{\mathrm{rev}}}{T}$, where q_{rev} is the heat for the reversible process.
Gibbs free energy G	$G = H - TS$ $\Delta_{\mathrm{r}} G^\circ = -RT \ln K = -zFE^\circ$, where K is the equilibrium constant, z is the number of electrons, E° is the standard electrode potential.
Reaction quotient Q	$\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^\circ + RT \ln Q$ For a reaction $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$ $Q = \dfrac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b}$, where $[\mathrm{A}]$ is the concentration of A.

Heat change Δq	$\Delta q = nc_{\mathrm{m}}\Delta T$, where c_{m} is the temperature-independent molar heat capacity.
Nernst equation for redox reaction	$E = E^{\circ} + \dfrac{RT}{zF} \ln \dfrac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}$, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration of reduced substance.
Arrhenius equation	$k = A \exp\left(-\dfrac{E_a}{RT}\right)$, where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy. $\exp(x) = e^x$
Lambert–Beer equation	$A = \varepsilon l c$, where A is the absorbance, ε is the molar absorption coefficient, l is the optical path length, c is the concentration of the solution.
Henderson–Hasselbalch equation	For an equilibrium $\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$, where equilibrium constant is K_{a}, $\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log\left(\dfrac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
Energy of a photon	$E = h\nu = h\dfrac{c}{\lambda}$, where ν is the frequency, λ is the wavelength of the light.
The sum of a geometric series	When $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \dfrac{1 - x^{n+1}}{1 - x}$
Approximation equation that can be used to solve problems	When $x \ll 1$, $\dfrac{1}{1 - x} \simeq 1 + x$

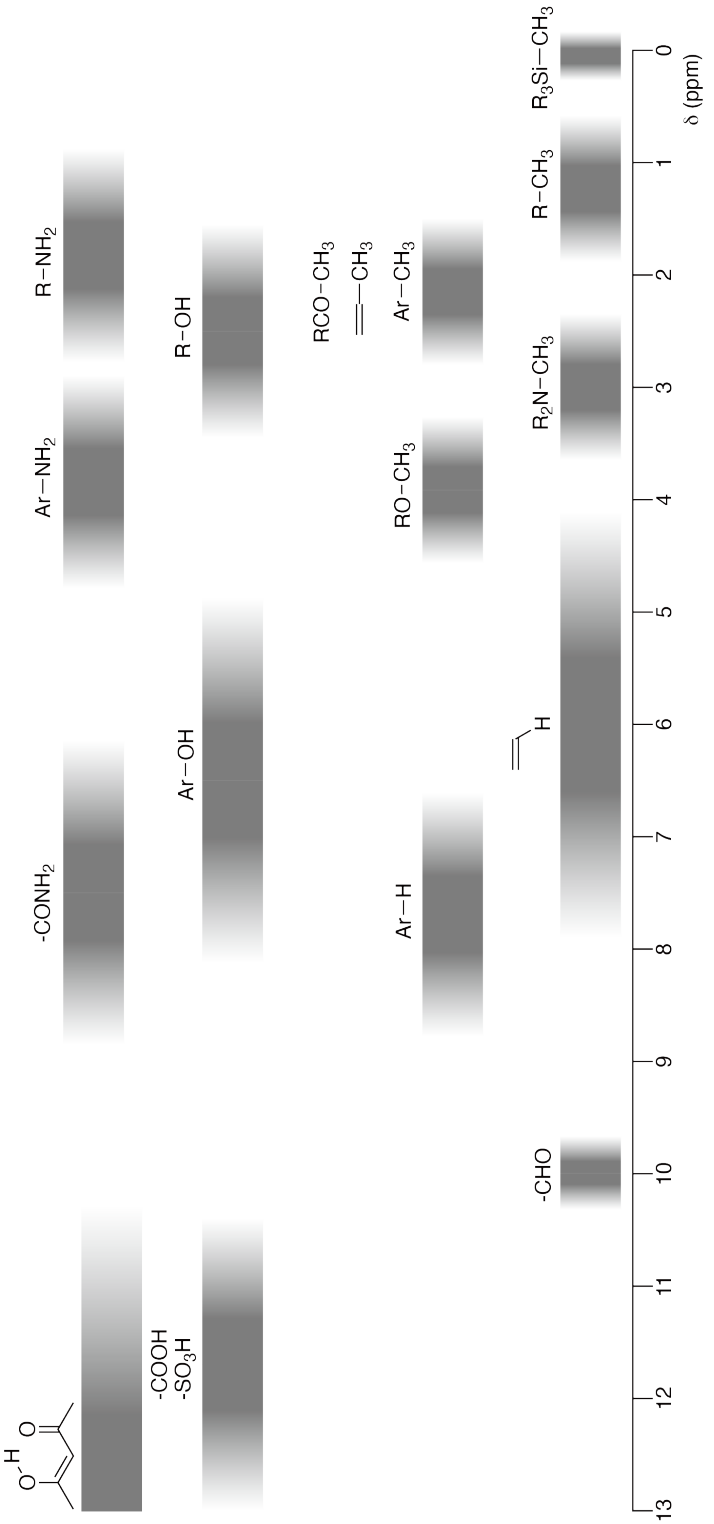
G0-6

English (Official)

Periodic Table



^{1}H NMR Chemical Shifts



$\Delta\delta$ for one alkyl group-substitution: *ca.* +0.4 ppm

G0-1

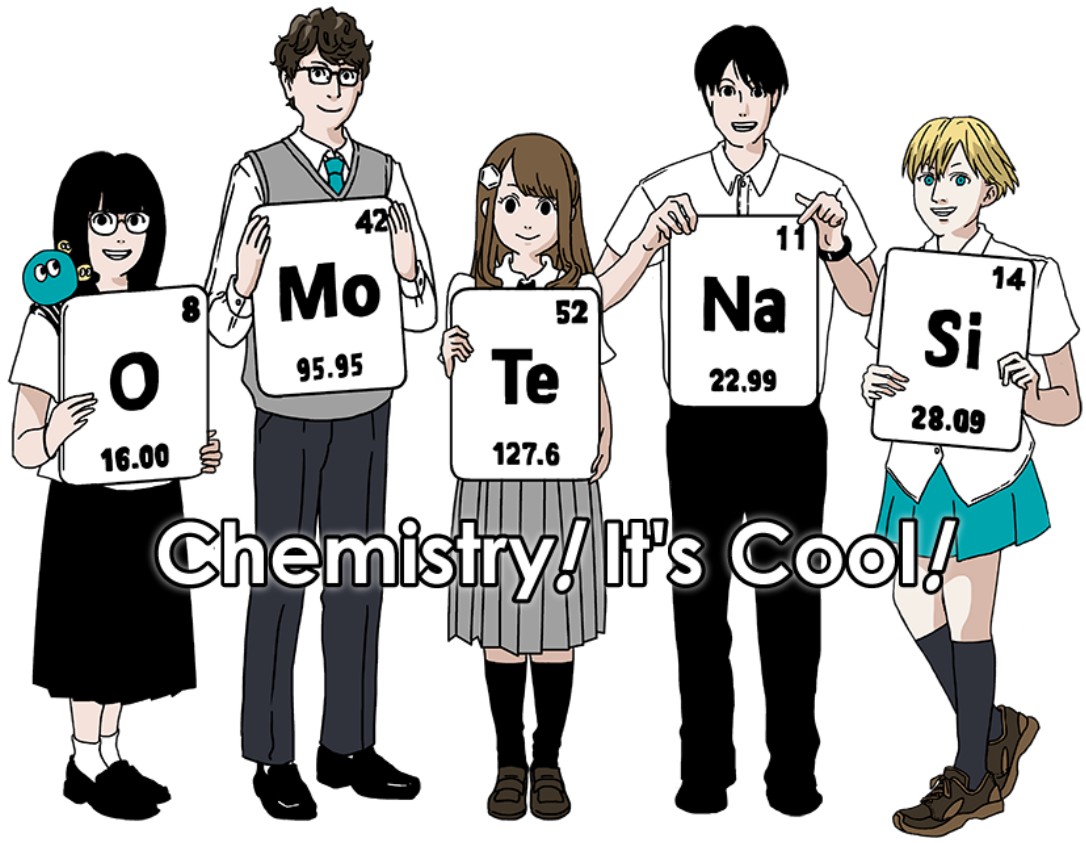
Montenegrin (Montenegro)

Međunarodna hemijska olimpijada 2021 Japan

53. IChO 2021 Japan

25. jul – 2. avgust, 2021

https://www.icho2021.org



G0-2

Montenegrin (Montenegro)

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. Zapamtite 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 prestati sa radom** čim čujete komandu **STOP**. Ukoliko odmah ne prestanete sa radom bićete diskvalifikovani.

• Zvanična engleska verzija ovog testa dostupna vam je na zahtjev i služi samo za pojašnjenje.

• Nije vam dozvoljeno da napuštate radni prostor bez dozvole. Ukoliko vam zatreba pomoć (zbog pokvarenog kalkulatora, odlaska u toalet...), podignite ruku i sačekajte da dođe supervizor do vas.

SREĆNO!

Zadaci i informacije o ocjenjivanju

	Naslov	Ukupan broj poena	Procenat
1	Vodonik na metalnoj površini	**24**	**11**
2	Izotop - vremenska kapsula	**35**	**11**
3	Lambert–Beer-ov zakon?	**22**	**8**
4	Oksido-redukciona hemija cinka	**32**	**11**
5	Tajanstveni silicijum	**60**	**12**
6	Hemija čvrstog stanja prelaznih metala	**45**	**13**
7	Igre s nebenzoidnom aromatičnošću	**36**	**13**
8	Dinamički organski molekuli i njihova hiralnost	**26**	**11**
9	Za i protiv kapsula	**23**	**10**
		Total	**100**

Fizičke konstante i jednačine

Konstante

Brzina svjetlosti u vakumu	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Plankova konstanta	$h = 6.62607015 \times 10^{-34}\ \mathrm{J\ s}$
Elementarno naelektrisanje	$e = 1.602176634 \times 10^{-19}\ \mathrm{C}$
Masa elektrona	$m_\mathrm{e} = 9.10938370 \times 10^{-31}\ \mathrm{kg}$
Konstanta električne permeabilnosti vakuuma	$\varepsilon_0 = 8.85418781 \times 10^{-12}\ \mathrm{F\ m^{-1}}$
Avogadrova konstanta	$N_\mathrm{A} = 6.02214076 \times 10^{23}\ \mathrm{mol^{-1}}$
Bolcmanova konstanta	$k_\mathrm{B} = 1.380649 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
Faradejeva konstanta	$F = N_\mathrm{A} \times e = 9.64853321233100184 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
Univerzalna gasna konstanta	$R = N_\mathrm{A} \times k_\mathrm{B} = 8.31446261815324\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $= 8.2057366081 \times 10^{-2}\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
Unificirana jedinica atomske mase	$u = 1\ \mathrm{Da} = 1.66053907 \times 10^{-27}\ \mathrm{kg}$
Standardni pritisak	$p = 1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$
Atmosferski pritisak	$p_\mathrm{atm} = 1.01325 \times 10^{5}\ \mathrm{Pa}$
Nula stepeni Celzijusa	$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
Ångstrem	$1\ \text{Å} = 10^{-10}\ \mathrm{m}$
Pikometar	$1\ \mathrm{pm} = 10^{-12}\ \mathrm{m}$
Elektronvolt	$1\ \mathrm{eV} = 1.602176634 \times 10^{-19}\ \mathrm{J}$
Djelova na milion	$1\ \mathrm{ppm} = 10^{-6}$
Djelova na bilion	$1\ \mathrm{ppb} = 10^{-9}$
Djelova na trilion	$1\ \mathrm{ppt} = 10^{-12}$
Pi	$\pi = 3.141592653589793$
Osnova prirodnog logaritma (Ojlerov broj)	$e = 2.718281828459045$

G0-4

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Jednačine

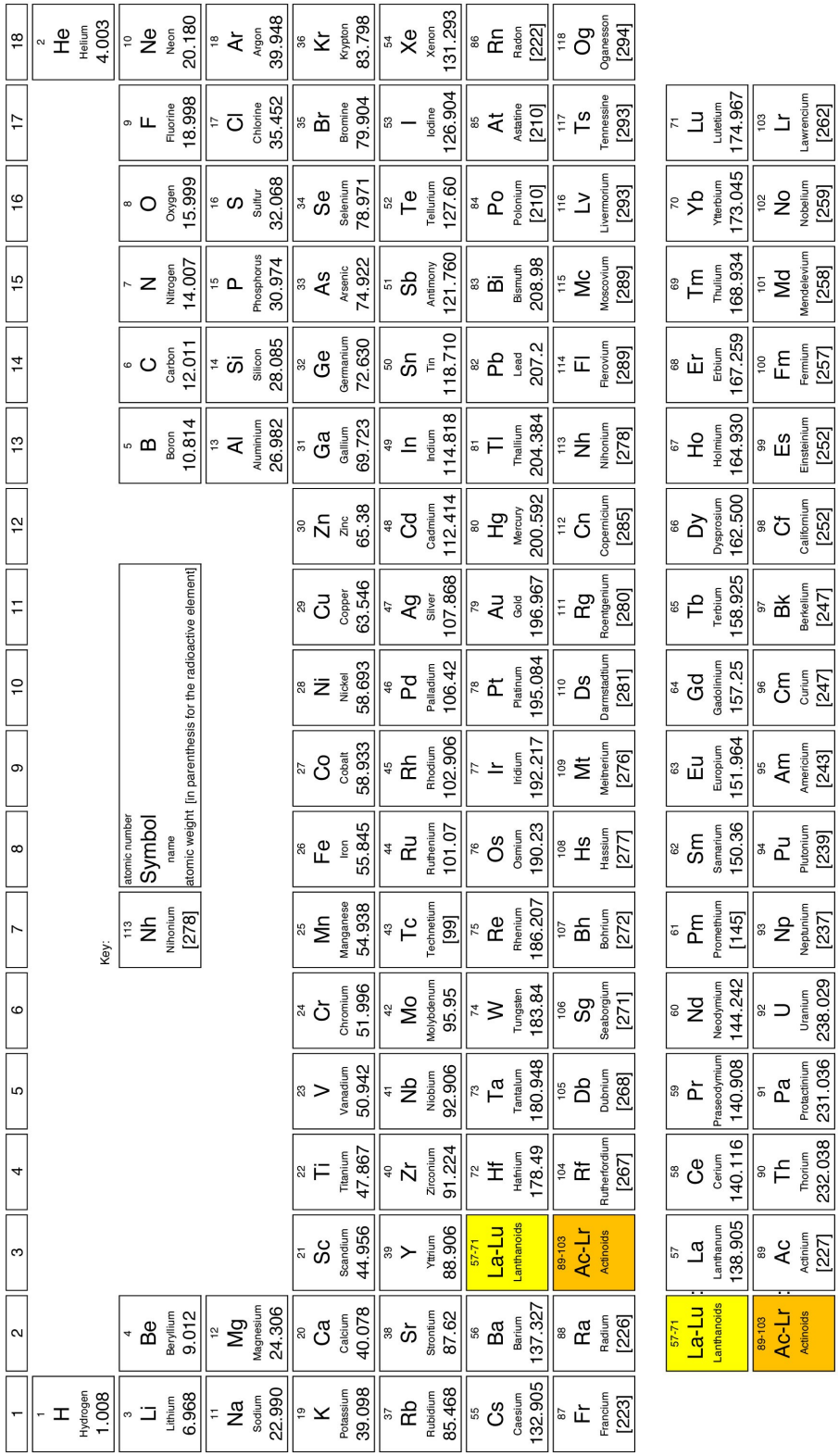
Jednačina stanja idealnog gasa	$PV = nRT$, gdje je P pritisak, V je zapremina, n je količina supstance, T je apsolutna temperatura idealnog gasa.
Kulonov zakon	$F = k_\mathrm{e}\frac{q_1 q_2}{r^2}$, gdje je F elektrostatična sila, $k_\mathrm{e}(\simeq 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}})$ Kulonova konstanta, q_1 i q_2 su količine naelektrisanja i $r$rastojanje između naelektrisanja.
Prvi zakon termodinamike	$\Delta U = q + w$, gdje je ΔU promjena unutrašnje energije, q je količina prenesene toplote, w je izvršeni rad.
Entalpija H	$H = U + PV$
Entropija zasnovana na Bolcmanovom principu S	$S = k_\mathrm{B} \ln W$, gdje je W broj mikrostanja
Promjena entropije ΔS	$\Delta S = \frac{q_\mathrm{rev}}{T}$, gdje je q_rev toplota reverzibilnog procesa
Slobodna Gibsova energija *G*	$G = H - TS$ $\Delta_\mathrm{r} G^\circ = -RT \ln K = -zFE^\circ$, gdje je K konstanta ravnoteže, z je broj elektrona, E° je standardni elektrodni potencijal.
Reakcioni koeficijent Q	$\Delta_\mathrm{r} G = \Delta_\mathrm{r} G^\circ + RT \ln Q$ Za reakciju $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$ $Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$, gdje je $[\mathrm{A}]$ koncentracija A.

Promjena toplote Δq	$\Delta q = nc_{\mathrm{m}}\Delta T$, gdje je c_{m} molarni toplotni kapacitet nezavistan od temperature
Nernstova jednačina za redoks reakciju	$E = E^{\circ} + \frac{RT}{zF}\ln\frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}$, gdje jeC_{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, ε je molarni apsorpcioni koeficijent, l je dužina optičkog puta, c je koncentracija rastvora.
Hendersen-Haselbalhova jednačina	Za ravnotežu $\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$, gdje je konstanta ravnoteže K_{a}, $\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
Energija fotona	$E = h\nu = h\frac{c}{\lambda}$, где је ν frekvencija, λ je talasna dužina svjetlosti.
Suma geometrijskog niza	Kada je $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$
Aproksimaciona jednačina koja se može koristiti za rješavanje zadataka	Kada je $x \ll 1$, $\frac{1}{1-x} \simeq 1 + x$

G0-6

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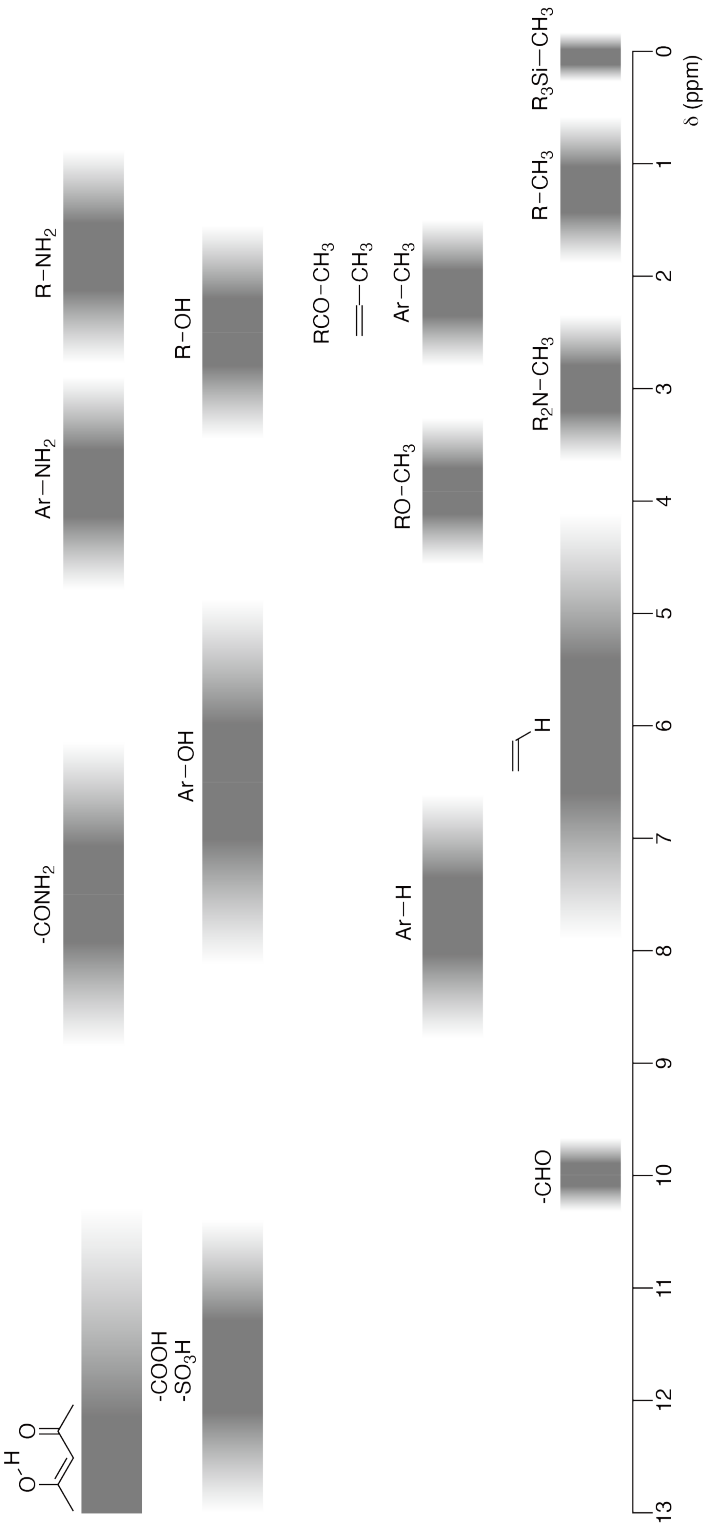
Periodni sistem elemenata



G0-7

Montenegrin (Montenegro)

^{1}H NMR hemijska pomjeranja



G0-8

Montenegrin (Montenegro)

$\Delta\delta$ za supstituciju jedne alkil grupe: približno +0,4 ppm

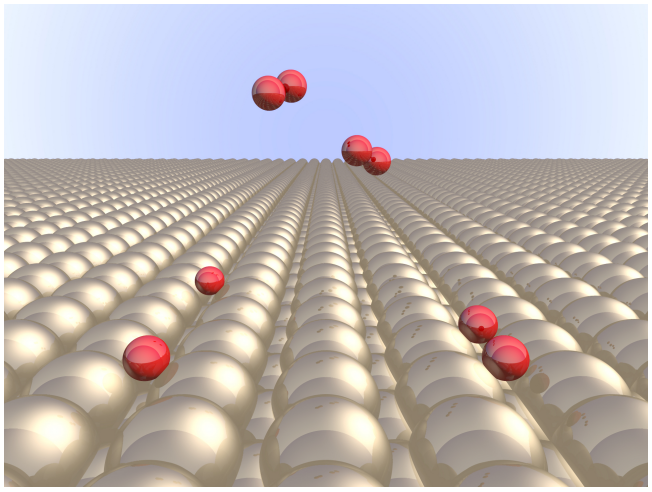
MNE-4 C-1 C
Ksenija Tadic

IChO
Problem 1
Cover sheet

Please return this cover sheet together with all the related question sheets.

Hydrogen at a Metal Surface

11 % of the total							
Question	A.1	A.2	B.1	B.2	B.3	B.4	**Total**
Points	6	4	5	3	3	3	**24**
Score							



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

Part A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $H_2(g) \rightarrow 2H(ad)$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (H_2) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of H_2 is represented by two variables: the interatomic distance, d, and the height relative to the surface metal atom, z. It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the potential energy in units of kJ per mole of H_2. The solid line spacing is 20 kJ mol^{-1}, the dashed line spacing is 100 kJ mol^{-1}, and the spacing between solid and dashed lines is 80 kJ mol^{-1}. The zero-point vibration energy is ignored.

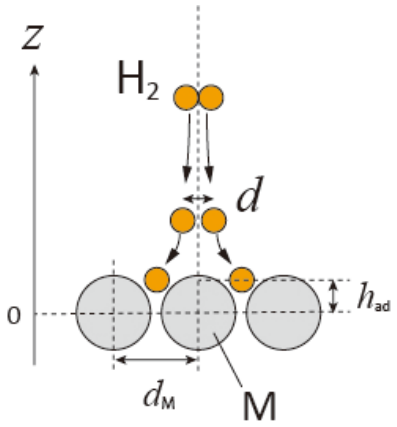


Fig.1 Definition of variables. Drawing is not in scale.

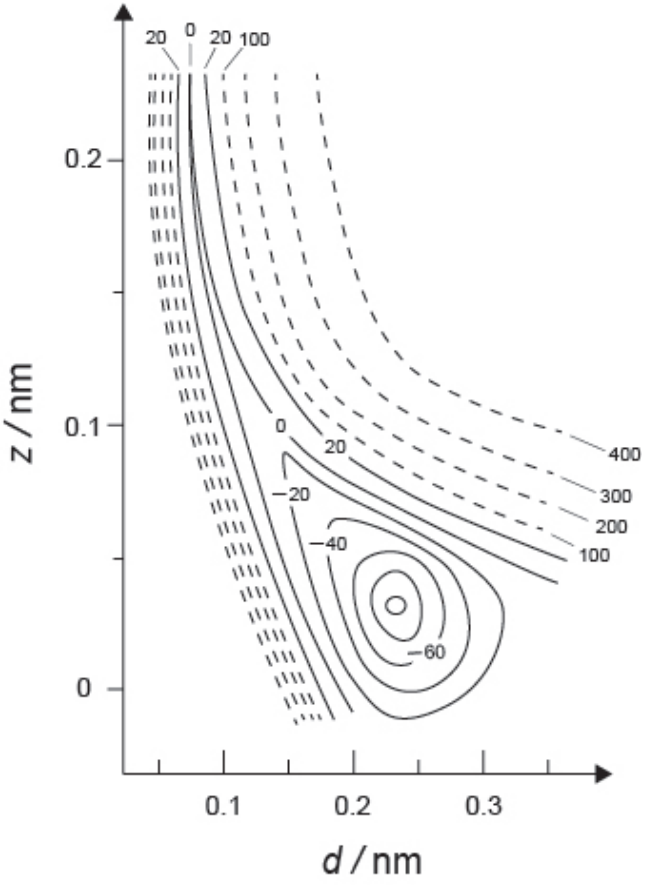


Fig.2

A.1 For each of the following items (i)–(iii), **select** the closest value from A–G. 6pt

(i) The interatomic distance for a gaseous H_2 molecule
(ii) The interatomic distance between metal atoms (d_M in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface (h_{ad} in Fig. 1)

A. 0.03 nm	B. 0.07 nm	C. 0.11 nm	D. 0.15 nm
E. 0.19 nm	F. 0.23 nm	G. 0.27 nm	

A.2 For each of the following items (i)–(ii), **select** the closest value from A–H. 4pt

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

A. 20 kJ mol^{-1}	B. 40 kJ mol^{-1}	C. 60 kJ mol^{-1}	D. 100 kJ mol^{-1}
E. 150 kJ mol^{-1}	F. 200 kJ mol^{-1}	G. 300 kJ mol^{-1}	H. 400 kJ mol^{-1}

Part B

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

$$\mathrm{H_2(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{2H(ad)} \tag{1a}$$

$$\mathrm{H(ad)} \xrightarrow{k_3} \mathrm{H(ab)} \tag{1b}$$

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

$$r_1 = k_1 P_{\mathrm{H_2}} (1-\theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

where $k_1\,[\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}], k_2\,[\mathrm{s}^{-1}]$ and $k_3\,[\mathrm{s}^{-1}]$ are the reaction rate constants and $P_{\mathrm{H_2}}$ is the pressure of $\mathrm{H_2}$. Among the sites available on the surface, θ ($0 \leq \theta \leq 1$) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption ($r_1, r_2 \gg r_3$) and that θ remains constant.

B.1 r_3 can be expressed as: 5pt

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{1}{P_{\mathrm{H_2}} C}}} \tag{5}$$

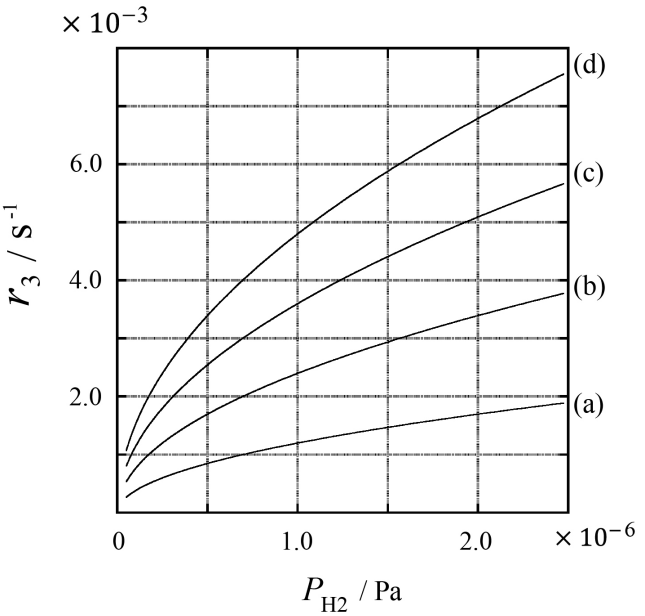
Express C using k_1 and k_2.

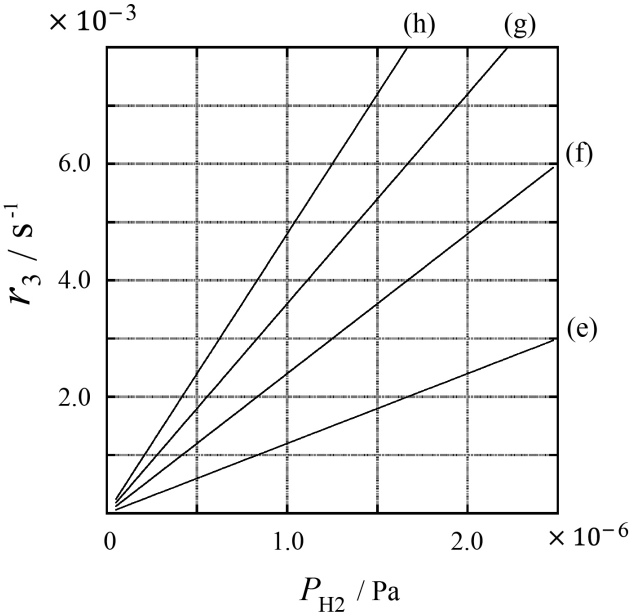
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m^2 was placed in a container (1L = 1.0×10^{-3} m^3) with H_2 ($P_{H_2} = 1.0 \times 10^2$ Pa). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m^{-2}. The surface temperature was kept at $T = 400$ K. As the reaction (1) proceeded, P_{H_2} decreased at a constant rate of $v = 4.0 \times 10^{-4}$ Pa s^{-1}. Assume that 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 [mol s^{-1} m^{-2}]. 3pt

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

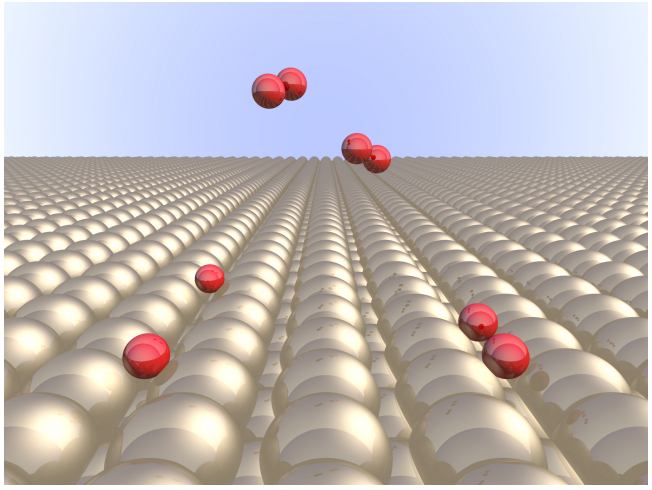
B.4 At a different T, $C = 2.5 \times 10^3$ Pa^{-1} and $k_3 = 4.8 \times 10^{-2}$ s^{-1}are given. For r_3 as a function of P_{H_2}at this temperature, **select** the correct plot from (a)–(h). 3pt





Vodonik na metalnoj površini

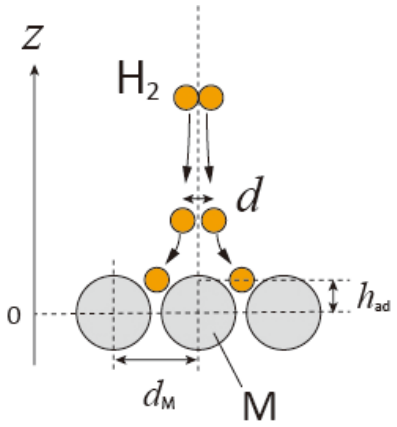
11 % od ukupnog broja poena							
Zadatak	A.1	A.2	B.1	B.2	B.3	B.4	**Ukupno**
Poeni	6	4	5	3	3	3	**24**
Rezultat							



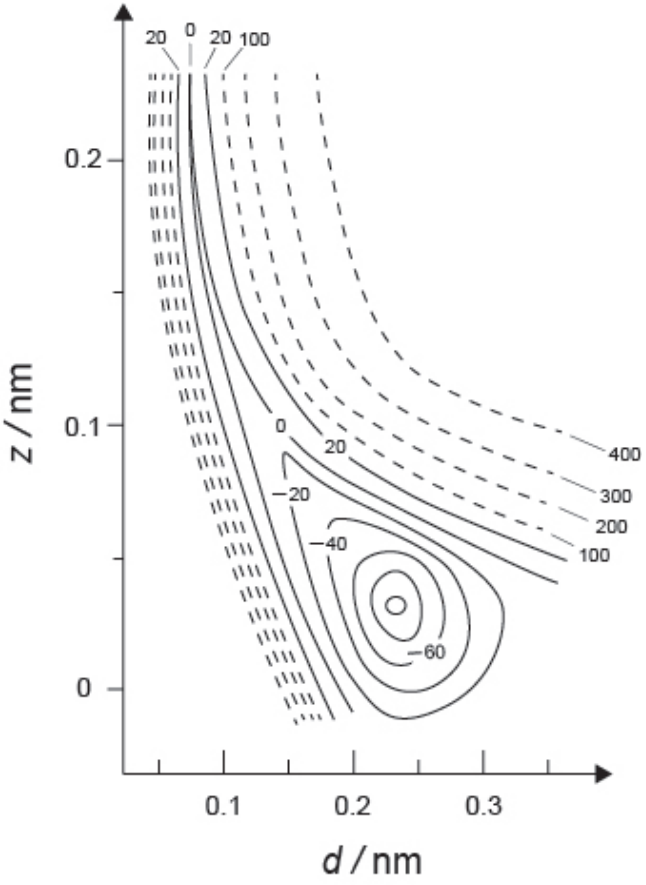
Realno se očekuje da će vodonik u budućnosti biti izvor energije koji ne zavisi od fosilnih goriva. Ovdje ćemo razmotriti postupak skladištenja vodonika u metalu, koji je povezan sa tehnologijom transporta i skladištenja vodonika.

Dio A

Kako se vodonik apsorbuje u unutrašnjost metala preko površine, prvo razmotrimo proces adsorpcije vodonika na površini metala, $H_2(g) \rightarrow 2H(ad)$, 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 H_2 predstavljena sa dvije promjenljive: međuatomskom udaljenošću, $\square$, i visinom u odnosu na površinu atoma metala, $\square$. 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 kJ po molu H_2. Udaljenost između punih linija je 20 kJ mol^{-1}, udaljenost između isprekidanih linija je 100 kJ mol^{-1} i udaljenost između punih i isprekidanih linija je 80 kJ mol^{-1}. Energija vibracije nulte tačke se zanemaruje.



Slika1. Definicija promjenljivih. Crtež nije dat u srazmjeri



Slika 2

Q1-3

Montenegrin (Montenegro)

A.1 Za svaku od sledećih stavki (i)–(iii), **izaberite** najbližu vrijednost iz A – G. 6pt

(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)

A. 0.03 nm	B. 0.07 nm	C. 0.11 nm	D. 0.15 nm
E. 0.19 nm	F. 0.23 nm	G. 0.27 nm	

A.2 Za svaku od sledećih stavki (i) - (ii), **izaberite** najbližu vrijednost iz A–H. 4pt

(i) energija potrebna za disocijaciju gasovitog H_2 do gasovitog **H**.

$H_2(g) \rightarrow 2H(g)$

(ii) energija koja se oslobađa tokom adsorpcije gasovitog H_2 [$H_2(g) \rightarrow 2H(ad)$]

A. 20 kJ mol^{-1}	B. 40 kJ mol^{-1}	C. 60 kJ mol^{-1}	D. 100 kJ mol^{-1}
E. 150 kJ mol^{-1}	F. 200 kJ mol^{-1}	G. 300 kJ mol^{-1}	H. 400 kJ mol^{-1}

Dio B

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

$$\mathrm{H_2(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{2H(ad)} \tag{1a}$$

$$\mathrm{H(ad)} \xrightarrow{k_3} \mathrm{H(ab)} \tag{1b}$$

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

$$r_1 = k_1 P_{\mathrm{H_2}} (1-\theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

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

B.1 r_3 se može izraziti kao: 5pt

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{1}{P_{\mathrm{H_2}} C}}} \tag{5}$$

Izrazite C koristeći k_1 i k_2.

Q1-5

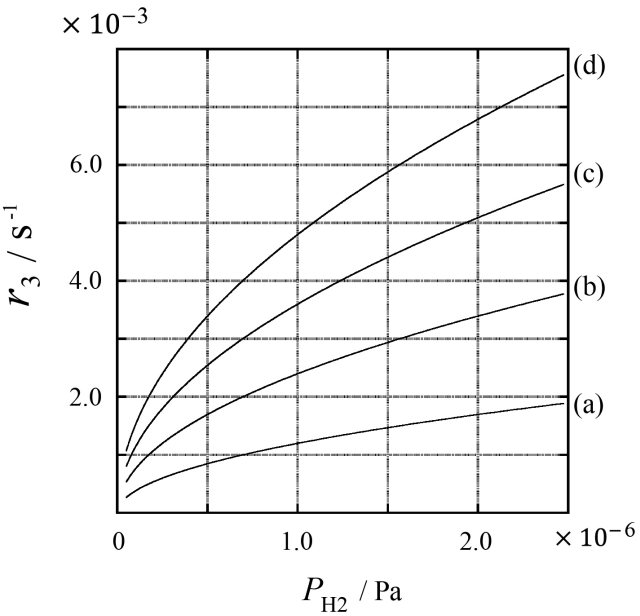
Montenegrin (Montenegro)

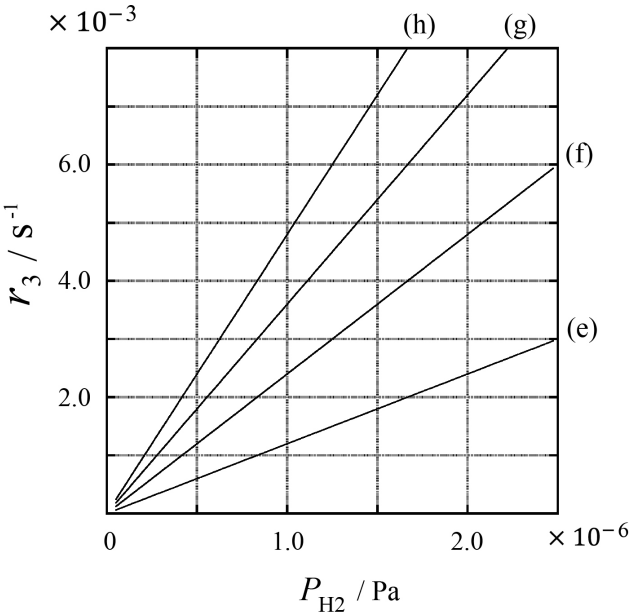
Uzorak metala površine $S = 1.0\times10^{-3}$ m^2 je smješten u posudu (1L = 1.0×10^{-3} m^3) sa H_2 ($P_{H_2} = 1.0\times10^{2}$ Pa). Gustina adsorpcionih mjesta za vodonik je $N = 1.3\times10^{18}$ m^{-2}. Temperatura na površini je održavana na $T = 400$ K. Daljim odvijanjem reakcije (1), P_{H_2} se smanjivala konstantnom brzinom od $v = 4.0\times10^{-4}$ 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}]. 3pt

B.3 Na $T = 400$ K, C je jednako 1.0×10^{2} Pa^{-1}. I**zračunajte** vrijednost k_3 na 400 K. Ukoliko nijeste dobili odgovor za zadatak **B.2**, za dalji rad koristite vrijednost $A = 3.6 \times 10^{-7}$ mol s^{-1} m^{-2}. 3pt

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). 3pt





Vodonik na metalnoj površini

Dio A

A.1 (6 pt)

(i)	(ii)	(iii)

A.2 (4 pt)

(i)	(ii)

Dio B

B.1 (5 pt)

$C =$ _____

B.2 (3 pt)

$A =$ _____ $\mathrm{mol\ s^{-1}\ m^{-2}}$

B.3 (3 pt)

$k_3 =$ _____ s^{-1}

B.4 (3 pt)

_____

MNE-4 C-2 C
Ksenija Tadic

IChO
Problem 2
Cover sheet

Please return this cover sheet together with all the related question sheets.

Isotope Time Capsule

11 % of the total					
Question	A.1	A.2	A.3	A.4	**Total**
Points	8	8	10	9	**35**
Score					



Molecular entities that differ only in isotopic composition, such as CH_4 and CH_3D, are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

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

Let us consider the following equilibrium:

$$^{12}C^{16}O_2 + {}^{12}C^{18}O_2 \rightleftharpoons 2\,{}^{12}C^{16}O^{18}O \qquad K = \frac{[{}^{12}C^{16}O^{18}O]^2}{[{}^{12}C^{16}O_2][{}^{12}C^{18}O_2]} \tag{1}$$

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

$$S = k_B \ln W \tag{2}$$

$W = 1$ for $^{12}C^{16}O_2$ and $^{12}C^{18}O_2$. In contrast, $W = 2$ for a $^{12}C^{16}O^{18}O$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}C^{16}O^{18}O$ molecules, $W = 2^2 = 4$.

A.1 The enthalpy change, ΔH, of eq. 3 is positive regardless of the temperature. 8pt

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

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 ΔH converges to a constant value for high temperatures.

The Δ*H* of the following process can be explained by molecular vibrations.

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

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

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

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

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

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

A.2 The vibration of H_2 is at 4161.0 cm^{-1} when reported as a wavenumber. 8pt
Calculate the ΔH of the following equation at T = 0 K in units of J mol^{-1}.

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

Assume that:
- only the vibrational energy contributes to the ΔH.
- the k values for H_2, HD, and D_2 are identical.
- the mass of H to be 1 Da and the mass of D to be 2 Da.

The molar ratio of H_2, HD, and D_2 depends on the temperature in a system in equilibrium. Here, Δ_{D_2} is defined as the change of the molar ratio of D_2.

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 \tag{9}$$

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

A.3 **Calculate** Δ_{D_2} with natural D abundance when the isotopic exchange is in equilibrium at the temperature where K in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, respectively. 10pt

In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO_2 molecules with molecular weights of 44 and 47, which are described as $CO_2[44]$ and $CO_2[47]$ below. The quantity Δ_{47} is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \tag{10}$$

R_{47} refers to $\frac{[CO_2[47]]}{[CO_2[44]]}$ in the sample and R_{47}^* to $\frac{[CO_2[47]]}{[CO_2[44]]}$ at $T \to +\infty$. The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

	^{12}C	^{13}C
natural abundance	0.988888	0.011112

	^{16}O	^{17}O	^{18}O
natural abundance	0.997621	0.0003790	0.0020000

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

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4} \tag{11}$$

A.4 The R_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-5}. **Estimate** the temperature using this R_{47}. This temperature is interpreted as the air temperature during the era in which the plankton lived. Consider only the most common isotopologue of $CO_2[47]$ for the calculation. 9pt

Q2-1

Montenegrin (Montenegro)

Izotop - vremenska kapsula

11 % od ukupnog broja poena					
Zadatak	A.1	A.2	A.3	A.4	**Ukupno**
Poeni	8	8	10	9	**35**
Rezultat					



Molekulske vrste koje se razlikuju samo po izotopskom sastavu, kao što su CH_4 i CH_3D, 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:

$$^{12}C^{16}O_2 + {}^{12}C^{18}O_2 \rightleftharpoons 2\,{}^{12}C^{16}O^{18}O \qquad K = \frac{[{}^{12}C^{16}O^{18}O]^2}{[{}^{12}C^{16}O_2][{}^{12}C^{18}O_2]} \tag{1}$$

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

$$S = k_B \ln W \tag{2}$$

$W = 1$ za $^{12}C^{16}O_2$ i $^{12}C^{18}O_2$. Za razliku od prethodnog, $W = 2$ za molekul $^{12}C^{16}O^{18}O$ jer su atomi kiseonika međusobno različiti u ovom molekulu. Kako se na desnoj strani ravnoteže koja je prikazana jednačinom 1 nalaze dva $^{12}C^{16}O^{18}O$ molekula, slijedi da je $W = 2^2 = 4$.

A.1 Promjena entalpije, ΔH, za jednačinu 3 je pozitivna bez obzira na tamperaturu. 8pt

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

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 ΔH konvergira u konstantnu vrijednost na visokim temperaturama.

Δ*H* sledećeg procesa može se objasniti molekulskim vibracijama.

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

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

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

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

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

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

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

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

Pretpostavite da:
- samo vibraciona energija doprinosi ΔH.
- 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 H_2, HD, i D_2 zavisi od temperature sistema u ravnoteži. Ovdje se Δ_{D_2} definiše kao promjena u molarnom odnosu D_2.

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 \tag{9}$$

Ovdje se R_{D_2} odnosi na $\frac{[D_2]}{[H_2]}$ u uzorku i $R^*_{D_2}$ na $\frac{[D_2]}{[H_2]}$ pri $T \to +\infty$. Ovdje treba uzeti u obzir da raspodjela izotopa postaje nasumična na $T \to +\infty$.

A.3 **Izračunajte** Δ_{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 zastupljenosti D i H iznosi 1.5576×10^{-4} i $1 - 1.5576 \times 10^{-4}$, redom. 10pt

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 $CO_2[47]$. Δ_{47} se definiše kao:

$$\Delta_{47} = \frac{R_{47}}{R^*_{47}} - 1 \tag{10}$$

R_{47} se odnosi na $\frac{[CO_2[47]]}{[CO_2[44]]}$ u uzorku i R^*_{47}na $\frac{[CO_2[47]]}{[CO_2[44]]}$ pri $T \rightarrow +\infty$. Prirodne zastupljenosti atoma ugljenika i kiseonika su prikazane dolje; zanemarite izotope koji ovdje nisu prikazani.

	^{12}C	^{13}C
Prirodna zastipljenost	0.988888	0.011112

	^{16}O	^{17}O	^{18}O
Prirodna zastupljenost	0.997621	0.0003790	0.0020000

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

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4} \tag{11}$$

A.4 R_{47} fosilnog planktona pronađenog na morskom dnu Antarktika iznosi 4.50865×10^{-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 $CO_2[47]$. 9pt

Izotop - vremenska kapsula

A.1 (8 pt)

$T \to 0 : K =$ _____ , $T \to +\infty : K =$ _____

A2-2

Montenegrin (Montenegro)

A.2 (8 pt)

$\Delta H =$ _____ J mol^{-1}

A.3 (10 pt)

$\Delta_{D_2} =$ _____

A.4 (9 pt)

$T =$ _____ K

MNE-4 C-3 C
Ksenija Tadic

IChO
Problem 3
Cover sheet

Please return this cover sheet together with all the related question sheets.

Lambert–Beer Law?

8 % of the total				
Question	A.1	B.1	B.2	**Total**
Points	10	6	6	**22**
Score				

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

Part A

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

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

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

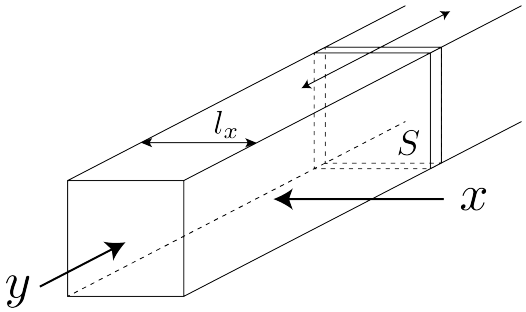
A.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. **Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-} represent the absorption coefficients of HA and of A^-, respectively, at λ_1. 10pt

Part B

Let us consider the following equilibrium in the gas phase.

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \tag{2}$$

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



Use the following definitions if necessary.

	Initial state		After equilibrium	
	D	M	D	M
Partial pressure	P	0	p_{D}	p_{M}
Amount in moles	n_0	0	n_{D}	n_{M}
Volume	V_0		V	

B.1 The absorbance of the gas at λ_{B1} measured from direction x ($l = l_x$) was A_{B1} both at the initial state and after the equilibrium. **Determine** the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at λ_{B1}, where ε_{D} and ε_{M} represent the absorption coefficients of D and of M, respectively. 6pt

B.2 The absorbance of the gas at λ_{B2} measured from direction y was A_{B2} both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). **Determine** the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at λ_{B2}. 6pt

Lambert-Beerov-ov zakon?

8 % od ukupnog broja poena				
Zadatak	A.1	B.1	B.2	**Ukupno**
Poeni	10	6	6	**22**
Rezultat				

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

Dio A

Vodeni rastvor **X** pripremljen je korišćenjem HA i NaA. Koncentracije $[A^-]$, $[HA]$ i $[H^+]$ u rastvoru **X** su 1.00×10^{-2} mol L^{-1}, 1.00×10^{-3} mol L^{-1}, i 1.00×10^{-4} mol L^{-1}, redom, i povezane su sledećom kiselinsko-baznom ravntotežom:

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

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.

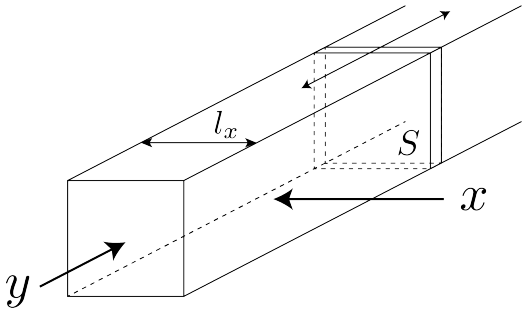
A.1 Apsorbanca rastvora **X** je bila A_1 pri talasnoj dužini λ_1. Dalje, početni rastvor **X** je razblažen do dvostruko veće zapremine hloridnom kiselinom (pH=2,500). Posle razblaženja, apsorbanca je i dalje bila A_1 na talasnoj dužini λ_1. **Izračunajte** odnos $\varepsilon_{HA}/\varepsilon_{A^-}$, gdje su ε_{HA} i ε_{A^-} apsorpcioni koeficijenti za HA i A^-, tim redom, na talasnoj dužini λ_1. 10pt

Dio B

Razmotrimo sledeću ravnotežu u gasnoj fazi.

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \tag{2}$$

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 ε, n,V i l apsorbcioni koeficijent, količina gasa u molovima, zapremina gasa i dužina optičkog puta, redom. Pretpostavite da se sve komponente gasne smješe ponašaju kao idealni gasovi.



Koristite sledeće podatke ukoliko je potrebno

	Početno stanje		Nakon uspostavljanja ravnoteže	
	D	M	D	M
Parcijalni pritisak	P	0	p_{D}	p_{M}
Količina u molovima	n_0	0	n_{D}	n_{M}
Zapremina	V_0		V	

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

B.2	Apsorbanca gasa na λ_{B2} koja je mjerena iz pravca y bila je A_{B2} i na samom početku ($l = l_{y0}$) i nakon uspostavljanja ravnoteže ($l = l_y$). **Odredite** odnos $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ na λ_{B2}.	6pt

Lambert–Beerov zakon?

Dio A

A.1 (10 pt)

(Nastavak je na sledećoj stranici)

A.1 (cont.)

$\varepsilon_{HA}/\varepsilon_{A^-} =$ _____

Dio B

B.1 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

B.2 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

MNE-4 C-4 C
Ksenija Tadic

IChO
Problem 4
Cover sheet

Please return this cover sheet together with all the related question sheets.

The Redox Chemistry of Zinc

11 % of the total							
Question	A.1	A.2	B.1	B.2	B.3	B.4	**Total**
Points	6	5	4	3	5	9	**32**
Score							



Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

Part A

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

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

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

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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14} \tag{4}$$

The solubility, S, of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

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

A.1	When the equilibria in eq. 1–4 are established, **calculate** the pH range in which $[\mathrm{Zn(OH)_2(aq)}]$ is the greatest among $[\mathrm{Zn^{2+}(aq)}]$, $[\mathrm{Zn(OH)_2(aq)}]$ and $[\mathrm{Zn(OH)_4^{2-}(aq)}]$.	6pt

A.2	A saturated aqueous solution of $\mathrm{Zn(OH)_2(s)}$ with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. **Calculate** the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.	5pt

Part B

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

$$\mathrm{Zn(OH)_2(s)} \rightarrow \mathrm{ZnO(s)} + \mathrm{H_2O(l)} \tag{6}$$

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

$$\mathrm{ZnO(s)} + \mathrm{H_2(g)} \rightarrow \mathrm{Zn(s)} + \mathrm{H_2O(g)} \tag{7}$$

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 °C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are $\Delta G_{\mathrm{ZnO}}(300^\circ\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ and $\Delta G_{\mathrm{H_2O}}(300^\circ\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\,mol^{-1}}$, respectively.	4pt

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

$$\mathrm{Zn(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{ZnO(s)} \qquad E^\circ = 1.65\,\mathrm{V} \tag{8}$$

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.	3pt



Mt. Fuji

B.3 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 $-38\,^{\circ}\mathrm{C}$ (February) and 3776 m, respectively. The atmospheric pressure is represented by 5pt

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

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

B.4 **Calculate** the Gibbs energy change for reaction (6) at $25\,^{\circ}\mathrm{C}$. Note that the standard reduction potentials, $E^{\circ}(\mathrm{Zn^{2+}/Zn})$ and $E^{\circ}(\mathrm{O_2/H_2O})$ at $25\,^{\circ}\mathrm{C}$ and 1 bar are given as (10) and (11), respectively. 9pt

$$\mathrm{Zn^{2+} + 2e^- \rightarrow Zn} \qquad E^{\circ}(\mathrm{Zn^{2+}/Zn}) = -0.77\,\mathrm{V} \tag{10}$$

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \qquad E^{\circ}(\mathrm{O_2/H_2O}) = 1.23\,\mathrm{V} \tag{11}$$

Q4-1

Montenegrin (Montenegro)

Oksido-redukciona hemija cinka

11 % od ukupnog broja bodova							
Zadatak	A.1	A.2	B.1	B.2	B.3	B.4	**Ukupno**
Poeni	6	5	4	3	5	9	**32**
Rezultat							



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.**

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

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

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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14} \tag{4}$$

Rastvorljivost cinka **S** (koncentracija cinka u zasićenom vodenom rastvoru) data je jednačinom 5.

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

A.1	Kada su uspostavljene ravnoteže u jednačinama 1–4, **izračunajte** opseg pH-vrijednosti u kojem je $[\mathrm{Zn(OH)_2(aq)}]$ veća u odnosu na svaku od $[\mathrm{Zn^{2+}(aq)}]$ i $[\mathrm{Zn(OH)_4^{2-}(aq)}]$.	6pt

A.2	Pripremljen je zasićeni vodeni rastvor $\mathrm{Zn(OH)_2(s)}$ sa pH=7.00 i profiltriran je. Dobijenom filtratu je dodat NaOH do povećanja pH-vrijednosti na 12.00. **Izračunajte** molarni procenat istaloženog cinka kada pH poraste sa 7.00 do 12.00. Zanemarite promjene temperature i zapremine.	5pt

Dio B

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

$$\mathrm{Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(l)} \tag{6}$$

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

$$\mathrm{ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g)} \tag{7}$$

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 $\Delta G_{\mathrm{ZnO}}(300^{\circ}\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ i $\Delta G_{\mathrm{H_2O}}(300^{\circ}\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\,mol^{-1}}$.	4pt

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° na 25 °C i pritisku od 1 bara.

$$\mathrm{Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)} \qquad E^{\circ} = 1.65\,\mathrm{V} \tag{8}$$

B.2	Baterija cink-vazduh se isprazni pri 20 mA za 24 časa. **Izračunajte** promjenu mase negativne elektrode (anode) baterije.	3pt

Q4-3

Montenegrin (Montenegro)



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 $-38\,^{\circ}$C, a nadmorska visina iznosi 3776 m. Atmosferski pritisak je predstavljen kao: 5pt

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

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

B.4 **Izračunajte** promjenu Gibsove energije za jednačinu (6) na $25\,^{\circ}$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 $25\,^{\circ}$C i 1 bar dati u jednačinama (10) i (11). 9pt

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

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \qquad E^{\circ}(\text{O}_2/\text{H}_2\text{O}) = 1.23\,\text{V} \quad (11)$$

Oksido-redukciona hemija cinka

Dio A

A.1 (6 pt)

_____ < pH < _____

A.2 (5 pt)

_____ %

Dio B

B.1 (4 pt)

$p_{H_2O=}$ _____ bar

B.2 (3 pt)

_____ g

B.3 (5 pt)

V

B.4 (9 pt)

$\Delta G^\circ =$ _____ $\mathrm{J\,mol^{-1}}$

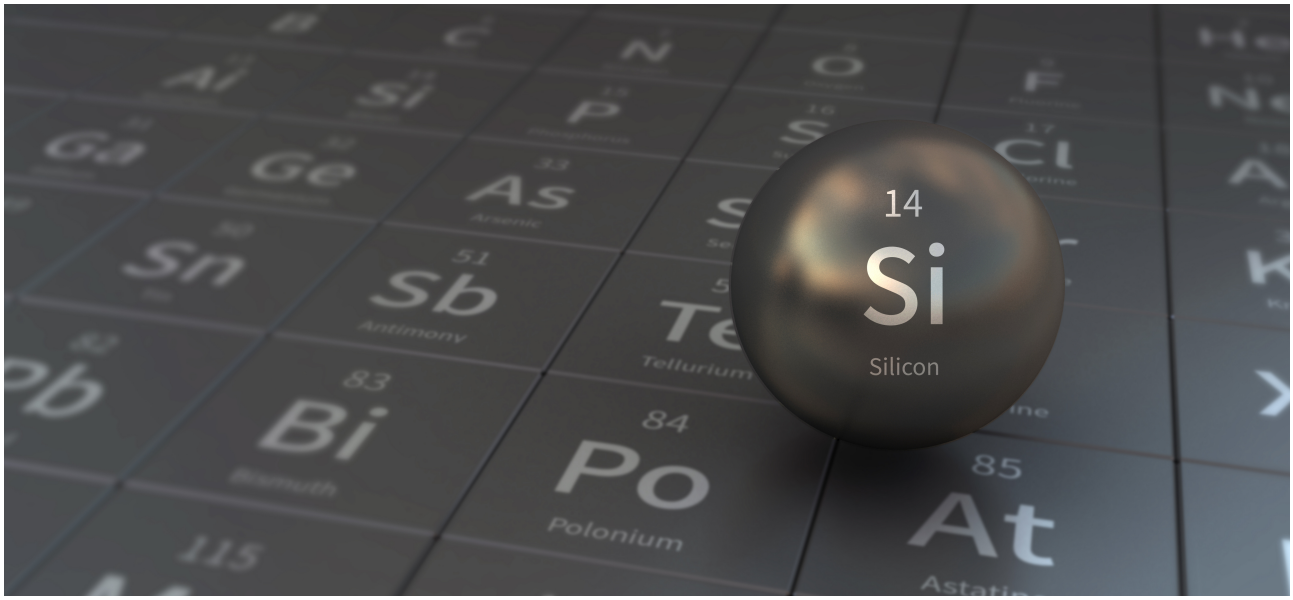
MNE-4 C-5 C
Ksenija Tadic

IChO
Problem 5
Cover sheet

Please return this cover sheet together with all the related question sheets.

Mysterious Silicon

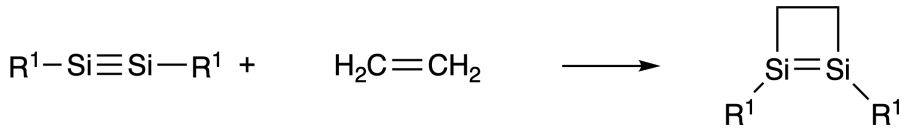
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



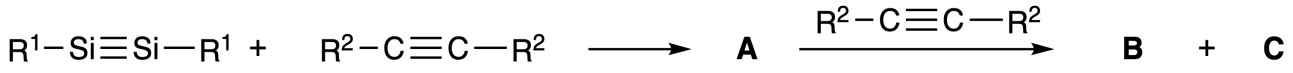
Although silicon is also a group 14 element like carbon, their properties differ significantly.

Part A

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



When R^1–Si ≡ Si–R^1 is treated with an alkyne (R^2–C ≡ C–R^2), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of R^2–C ≡ C–R^2 with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called 'disilabenzenes' that contain a six-membered ring and can be formulated as $(R^1\text{–Si})_2(R^2\text{–C})_4$.



The ^{13}C NMR analysis of the corresponding six-membered ring skeletons Si_2C_4 shows two signals for **B** and one signal for **C**.

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. 9pt

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). 7pt

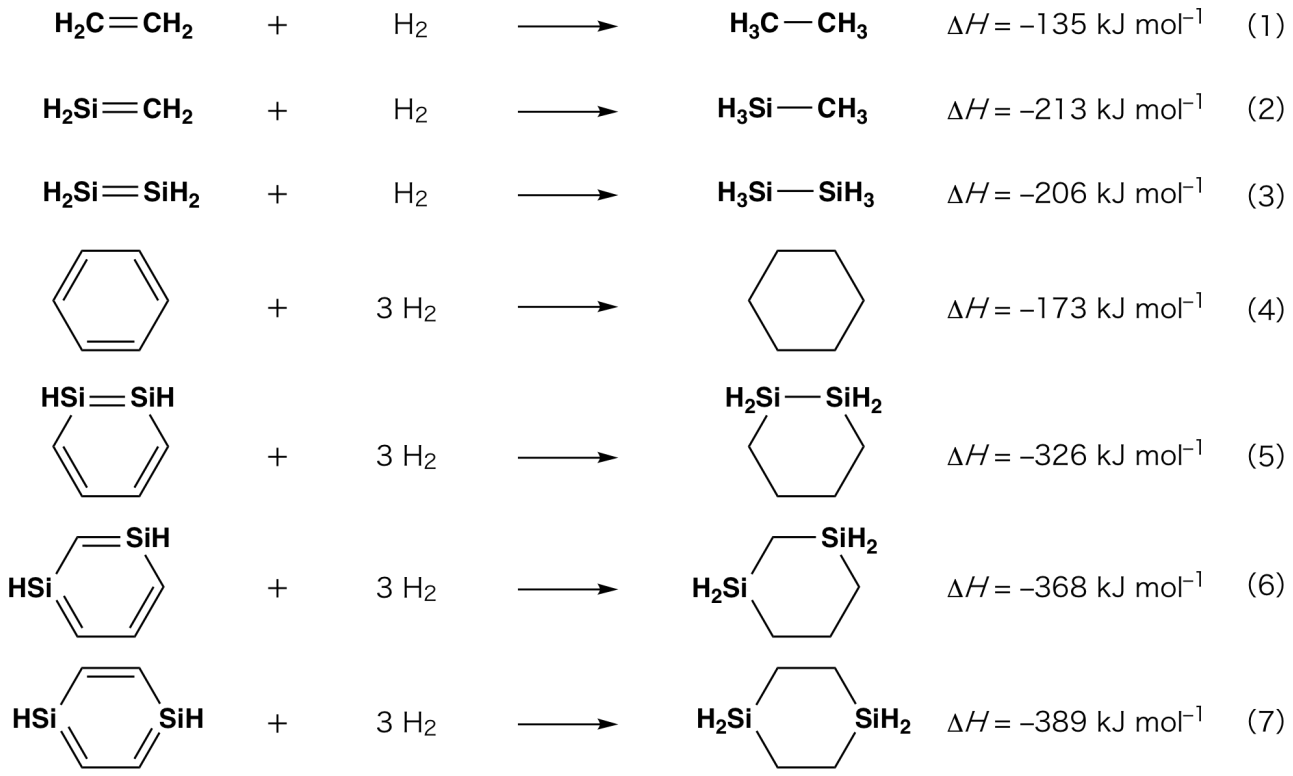


Fig. 1

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** ΔH for the transformation of **D** to **E**. Assume that ΔH does not depend on temperature. 6pt

The isomerization from **C** to **D** and to **E** proceeds via transformations of π-bonds into σ-bonds without breaking any σ-bonds. A ^{13}C NMR analysis revealed one signal for the Si_2C_4 skeleton of **D** and two signals for that of **E**. The skeleton of **D** does not contain any three-membered rings, while **E** has two three-membered rings that share an edge.

A.4 **Draw** the structural formulae of **D** and **E** using R^1, R^2, Si, and C. 10pt

Part B

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

The fluorination reaction of CCl_4 using Na_2SiF_6 was carried out as follows.

- **Standardization of Na_2SiF_6 solution** :

· Preparation

Aqueous solution **F**: 0.855 g of Na_2SiF_6 (188.053 g mol^{-1}) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ (568.424 g mol^{-1}) dissolved in water (total volume: 200 mL).

· Procedure

Precipitation titration of a solution **F** (50.0 mL) by dropwise adding solution **G** in the presence of xylenol orange, which coordinates to Ce^{3+}, as an indicator. After adding 18.8 mL of solution **G**, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce^{3+}, and the only resulting silicon compound is $Si(OH)_4$.

B.1 **Write** the balanced equation for the reaction of Na_2SiF_6 with $Ce_2(SO_4)_3$. 5pt

- **Reaction of CCl_4 with Na_2SiF_6:**

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

Na_2SiF_6(x [g]) was added to CCl_4 (500.0 g) and heated to 300˚C in a sealed pressure-resistant reaction vessel. The unreacted Na_2SiF_6 and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with CCl_4 (solution **H**). The ^{29}Si and ^{19}F NMR spectra of solution **H** showed SiF_4 as the only silicon compound. In the ^{19}F NMR spectrum, in addition to SiF_4, signals corresponding to $CFCl_3$, CF_2Cl_2, CF_3Cl, and CF_4 were observed (*cf.* Table 1). The integration ratios in the ^{19}F NMR spectrum are proportional to the number of fluorine nuclei.

Table 1

^{19}F NMR data	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
Integration ratio	45.0	65.0	18.0	2.0

SiF_4 is hydrolyzed to form H_2SiF_6 according to the following eq. 8:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \quad (8)$$

Solution **H** (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF_4. After separation, the H_2SiF_6 generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na_2SiF_6 (aqueous solution **J**).

The precipitate of unreacted Na_2SiF_6 and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution **K**; 10.0 L).

Then, additional precipitation titrations using solution **G** were carried out, and the endpoints of the titrations with **G** were as follows:

·For solution **J** (entire amount): 61.6 mL.

·For 100 mL of solution **K**: 44.4 mL.

It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

B.2	**Calculate** the mass of the NaCl produced in the reaction vessel (information underlined), and **calculate** the mass (x [g]) of the Na_2SiF_6 used as a starting material.	15pt

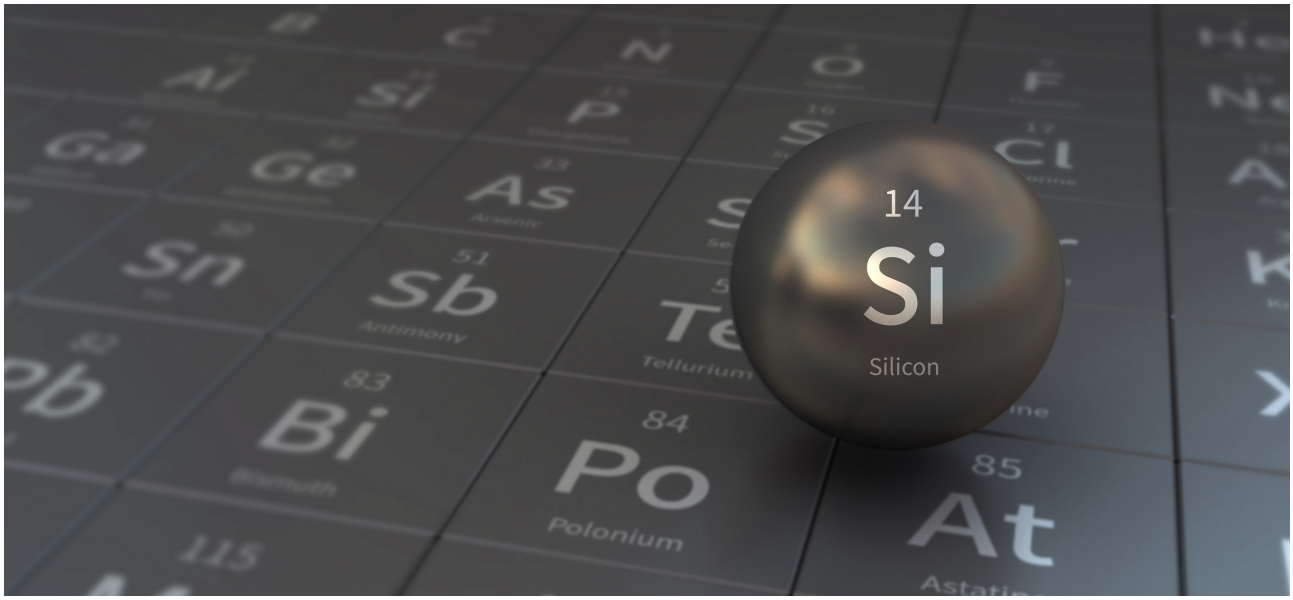
B.3	77.8% of the CCl_4 used as a starting material was unreacted. **Calculate** the mass of CF_3Cl generated.	8pt

Q5-1

Montenegrin (Montenegro)

Tajanstveni silicijum

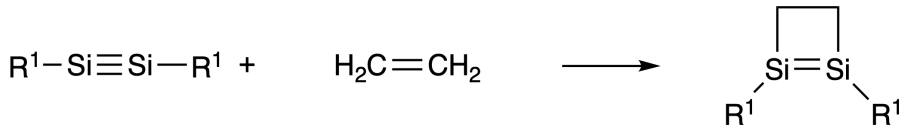
12 % od ukupnog broja poena								
Zadatak	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Ukupno**
Poeni	9	7	6	10	5	15	8	**60**
Rezultat								



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

Dio A

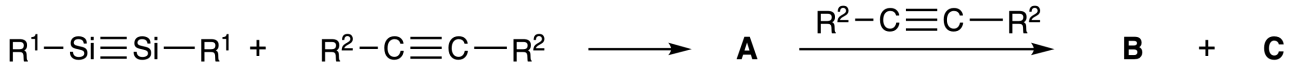
Za razliku ugljenik-ugljenik trstrukih veza, trostruka veza silicijum-silicijum u jedinjenjima opšte formule $R^1–Si \equiv Si–R^1$ (R: organski supstituent) je veoma reaktivna. Na primjer, ova jedinjenja reaguju sa etenom i grade ciklične proizvode koji sadrže četvoročlane prstenove.



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

Q5-2

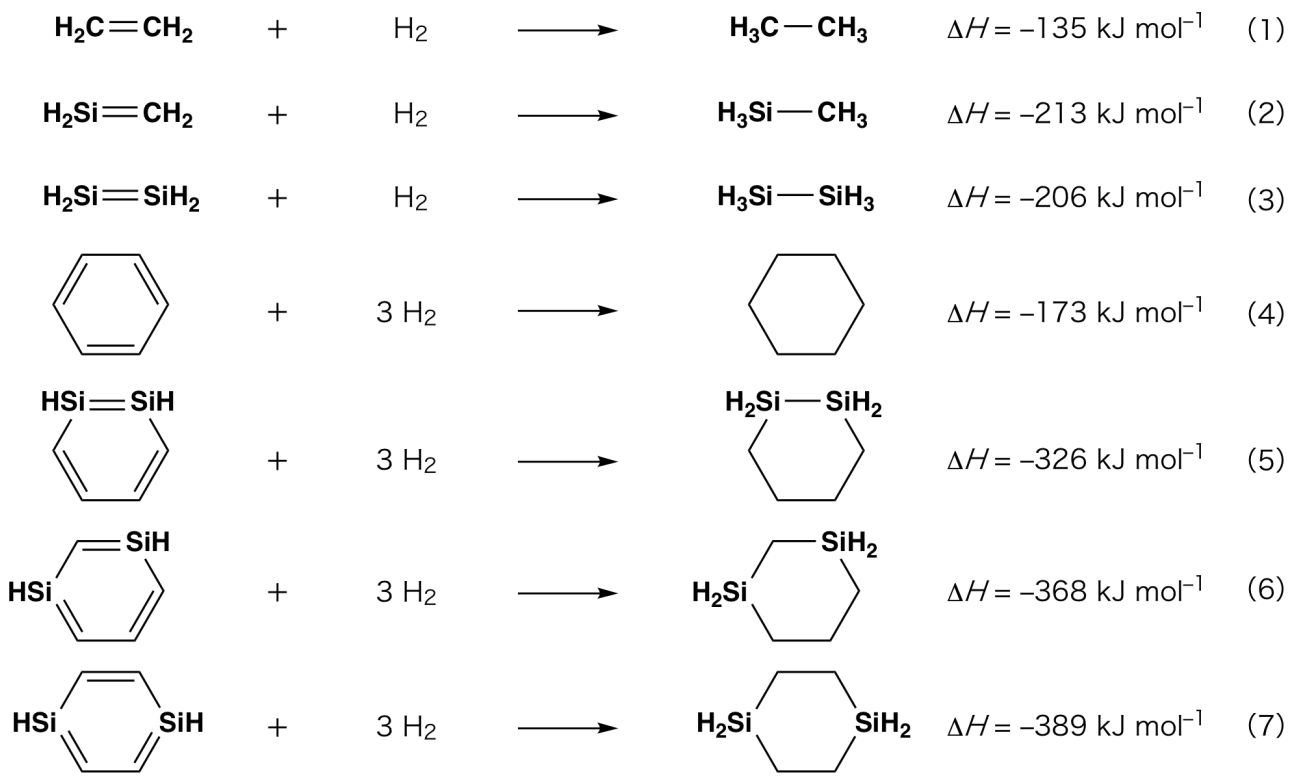
Montenegrin (Montenegro)



Analizom ^{13}C NMR spektara odgovarajućeg šestočlanog prstenaSi_2C_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. Nije potrebno crtati više rezonancionih struktura. 9pt

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). 7pt



Slika 1

Q5-3

Montenegrin (Montenegro)

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** ΔH za transformaciju **D** u **E**. Pretpostavite da veličina ΔH ne zavisi od temperature. 6pt

Izomerizacija **C** u **D** i u **E** odvija se na račun transformacije π-veza u σ-veze bez raskidanja σ-veza. Analiza ^{13}C NMR-spektra otkriva jedan signal koji odgovara skeletu Si_2C_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. 10pt

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_2SiF_6 odvija se na sledeći način.

- **Standardizacija rastvora Na_2SiF_6** :

· Priprema

Vodeni rastvor **F**: 0,855 g Na_2SiF_6 (188,053 $g\,mol^{-1}$) rastvoreno je u vodi (ukupna zapremina rastvora: 200 mL).

Vodeni 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 ksilenol-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_2SiF_6 i $Ce_2(SO_4)_3$. 5pt

- **Reakcija CCl_4i Na_2SiF_6:**

(Gubici supstance prilikom isparavanja tokom rada su zanemarljive za dalji postupak)

Na_2SiF_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_2SiF_6 i nastali NaCl su odvojeni filtracijom. Filtrat se razblaži sa CCl_4 do ukupne zapremine od 1.00 L (rastvor **H**). ^{29}Si i ^{19}F NMR spektri 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 $CFCl_3$, CF_2Cl_2, CF_3Cl i CF_4 (Tabela 1). Odnos integrala signala u ^{19}F NMR spektru je proporcionalan broju jezgara fluora.

Tabela 1

^{19}F NMR podaci	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
Odnos integrala	45.0	65.0	18.0	2.0

SiF_4 se hidrolizuje do H_2SiF_6 prema sledećoj jednačini reklacije (8):

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \quad (8)$$

Rastvor **H** (10 mL) je dodat u veću količinu vode, što rezultuje potpunom hidrolizom SiF_4. Nakon odvajanja, H_2SiF_6 , nastao u reakciji hidrolize, neutralisan je i potpuno preveden u Na_2SiF_6 (vodeni rastvor **J**).

Talog neizreagovalog Na_2SiF_6 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** (cjelokupna količina): 61.6mL.
- Za 100 ml rastvora **K:** 44.4 ml.

Ovdje je važno napomenuti da istovremeno prisustvo NaCl i SiO_2 ne utiče na taložnu titraciju.

B.2	**Izračunajte** masu NaCl koja je nastala u reakcionom sudu (podvučeni dio teksta) i **izračunajte** masu (x [g]) Na_2SiF_6 koji je korišćen kao polazna supstanca.	15pt

B.3	77,8% CCl_4 koji je korišćen kao polazna supstanca ostalo je neizreagovano. **Izračunajte** masu dobijenog CF_3Cl.	8pt

Tajanstveni silicijum

Dio A

A.1 (9 pt)

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

A.2 (7 pt)

C_6H_6 : kJ mol^{-1}, **C** : kJ mol^{-1}

A.3 (6 pt)

ΔH = _____ 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, Na_2SiF_6 : g

B.3 (8 pt)

CF_3Cl : _____ g

MNE-4 C-6 C
Ksenija Tadic

IChO
Problem 6
Cover sheet

Please return this cover sheet together with all the related question sheets.

Q6-1

English (Official)

The Solid-State Chemistry of Transition Metals

13 % of the total											
Question	A.1	A.2	A.3	B.1	B.2	B.3	B.4	C.1	C.2	C.3	**Total**
Points	6	3	3	6	4	4	4	5	5	5	**45**
Score											



Volcano at Sakurajima island

Part A

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

$$D = \frac{[\mathrm{M}]_\mathrm{s}}{[\mathrm{M}]_\mathrm{l}}$$

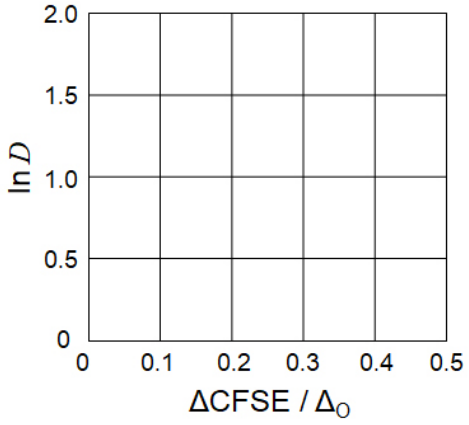
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

	Cr^{2+}	Mn^{2+}
D	7.2	1.1

Let Δ_O and $CFSE^O$ be the energy separation of the d-orbitals of M^{n+} and the crystal-field stabilization energy in a O_h field, respectively. Let Δ_T and $CFSE^T$ be those in a T_d field.

A.1 **Calculate** $|CFSE^O - CFSE^T| = \Delta CFSE$ in terms of Δ_O for Cr^{2+}, Mn^{2+}, and Co^{2+}; assume $\Delta_T = 4/9\Delta_O$. 6pt

A.2 A linear relationship is observed by plotting $\ln D$ against $\Delta CFSE / \Delta_O$ in the Cartesian coordinate system shown below. 3pt
Estimate D for Co^{2+}.



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

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

	CaO	TiO	VO	MnO	CoO
(a)	3460	3878	3913	3810	3916
(b)	3460	3916	3878	3810	3913
(c)	3460	3913	3916	3810	3878
(d)	3810	3878	3913	3460	3916
(e)	3810	3916	3878	3460	3913
(f)	3810	3913	3916	3460	3878

Part B

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

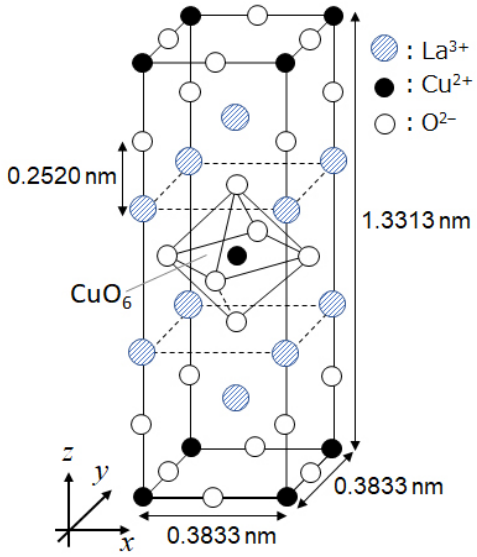


Fig. 1

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

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**, 2.05×10^{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.	4pt

Part C

$Cu_2(CH_3CO_2)_4$ is composed of four $CH_3CO_2^-$ coordinated to two Cu^{2+} (Fig. 2A). $Cu_2(CH_3CO_2)_4$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four $CH_3CO_2^-$ and an axis passing through the two Cu^{2+}, all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of $CH_3CO_2^-$, a "cage complex" is formed. The cage complex $Cu_4(\mathbf{L1})_4$ is composed of planar dicarboxylate **L1** (Fig. 2B) and Cu^{2+} (Fig. 2C). The angle θ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The θ is 0° for **L1**. Note that hydrogen atoms are not shown in Fig. 2.

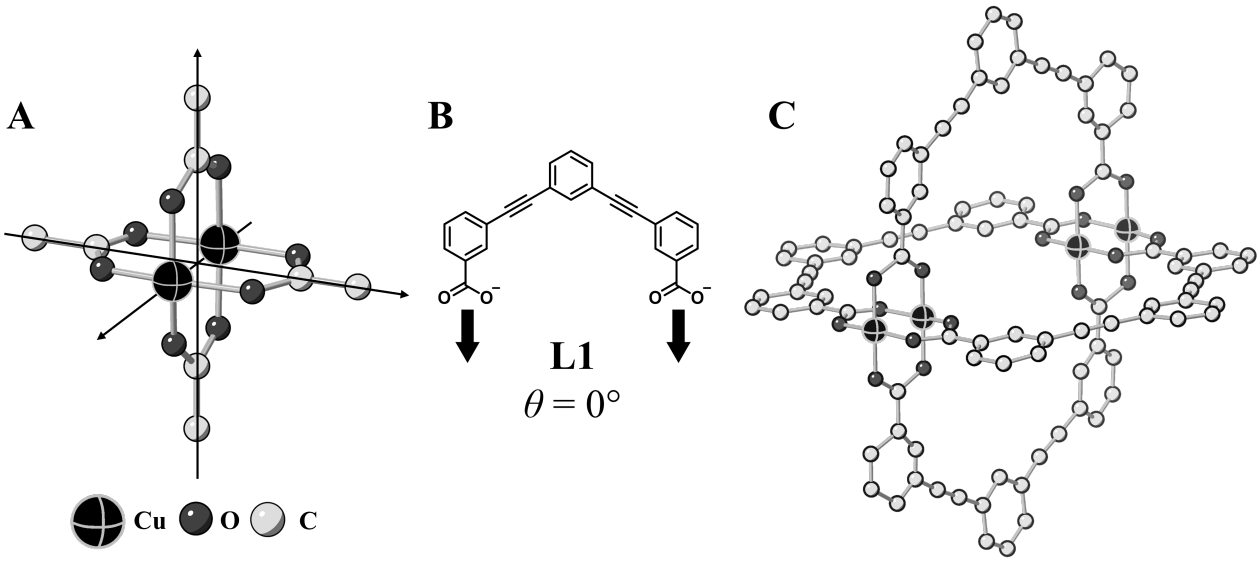
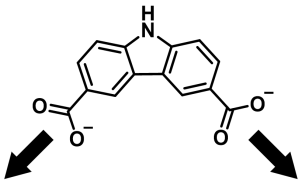


Fig. 2

C.1 The θ of the planar dicarboxylate **L2** below is fixed to 90˚. If the composition of the cage complex formed from **L2** and Cu^{2+} is $Cu_n(\mathbf{L2})_m$, **give** the smallest integer combination of *n* and *m*. Assume that only the CO_2^- groups of **L2** form a coordination bond to Cu^{2+} ions. 5pt



L2

$\theta = 90°$

A zinc complex, $Zn_4O(CH_3CO_2)_6$, contains four tetrahedral Zn^{2+}, six $CH_3CO_2^-$, and one O^{2-} (Fig. 3A). In $Zn_4O(CH_3CO_2)_6$, the O^{2-} is located at the origin, and the three axes passing through the carbon atoms of $CH_3CO_2^-$ are oriented orthogonal relative to each other. When *p*-benzenedicarboxylate (Fig. 3B, **L3**, θ = 180°) is used instead of $CH_3CO_2^-$, the Zn^{2+} clusters are linked to each other to form a crystalline solid (**X**) that is called a "porous coordination polymer" (Fig. 3C). The composition of **X** is $[Zn_4O(\mathbf{L3})_3]_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral Zn^{2+} cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

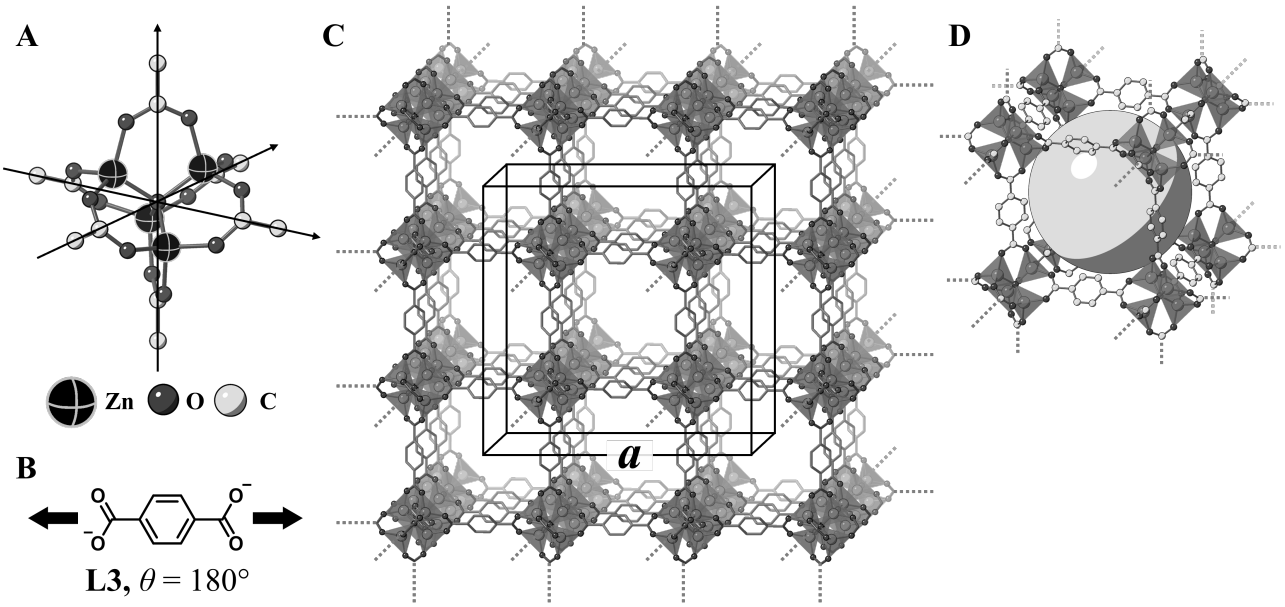


Fig. 3

C.2	**X** has a cubic unit cell with a side length of a (Fig. 3C) and a density of 0.592 g cm^{-3}. **Calculate** a in [cm].	5pt

C.3	**X** contains a considerable number of pores, and 1 g of **X** can accommodate 3.0×10^2 mL of CO_2 gas in the pores at 1 bar and 25 °C. **Calculate** the average number of CO_2 molecules per pore.	5pt

Q6-1

Montenegrin (Montenegro)

Hemija čvrstog stanja prelaznih metala

13 % od ukupnog broja poena											
Zadatak	A.1	A.2	A.3	B.1	B.2	B.3	B.4	C.1	C.2	C.3	**Ukupno**
Poeni	6	3	3	6	4	4	4	5	5	5	**45**
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 minerale. M^{n+} joni koji se razmatraju u ovom zadatku su koordinovani kiseoničnim jonima (O^{2-}) i zadobijaju četvorokoordinovanu 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:

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

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+} :

	Cr^{2+}	Mn^{2+}
D	7.2	1.1

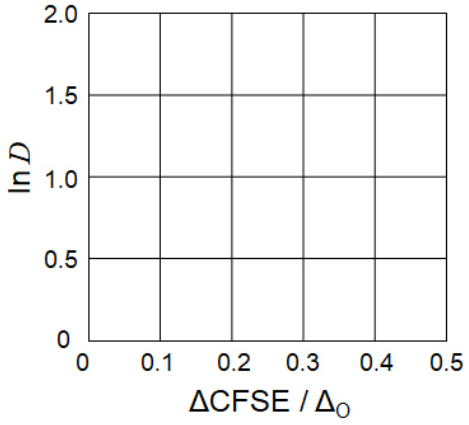
Q6-2

Montenegrin (Montenegro)

Neka Δ_O i $CFSE^O$ predstavljaju energiju razdvajanja *d*-orbitala jona M^{n+} i energiju stabilizacije kristalnog polja u O_h polju, respektivno. Neka Δ_T i $CFSE^T$ budu takođe i u T_d polju.

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

A.2 Posmatran je linearni odnos između $\ln D$ i ΔCFSE / Δ_O u Cartesian-ovom koordinatnom sistemu koji je prikazan ispod. 3pt
Odredite D za 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 stabilizacione 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}]. 3pt

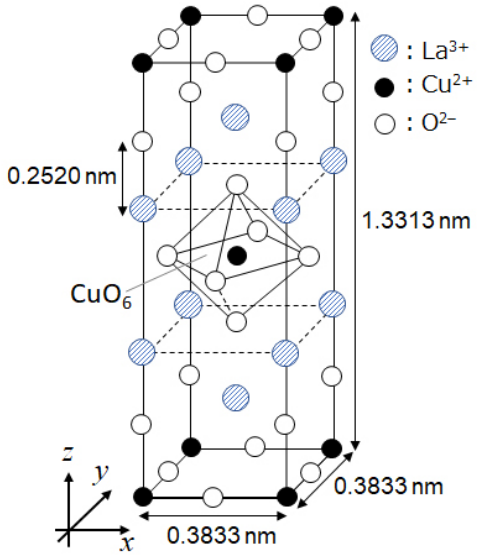
	CaO	**TiO**	**VO**	**MnO**	**CoO**
(a)	3460	3878	3913	3810	3916
(b)	3460	3916	3878	3810	3913
(c)	3460	3913	3916	3810	3878
(d)	3810	3878	3913	3460	3916
(e)	3810	3916	3878	3460	3913
(f)	3810	3913	3916	3460	3878

Q6-3

Montenegrin (Montenegro)

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 $C_4H_2O_4$, (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 .

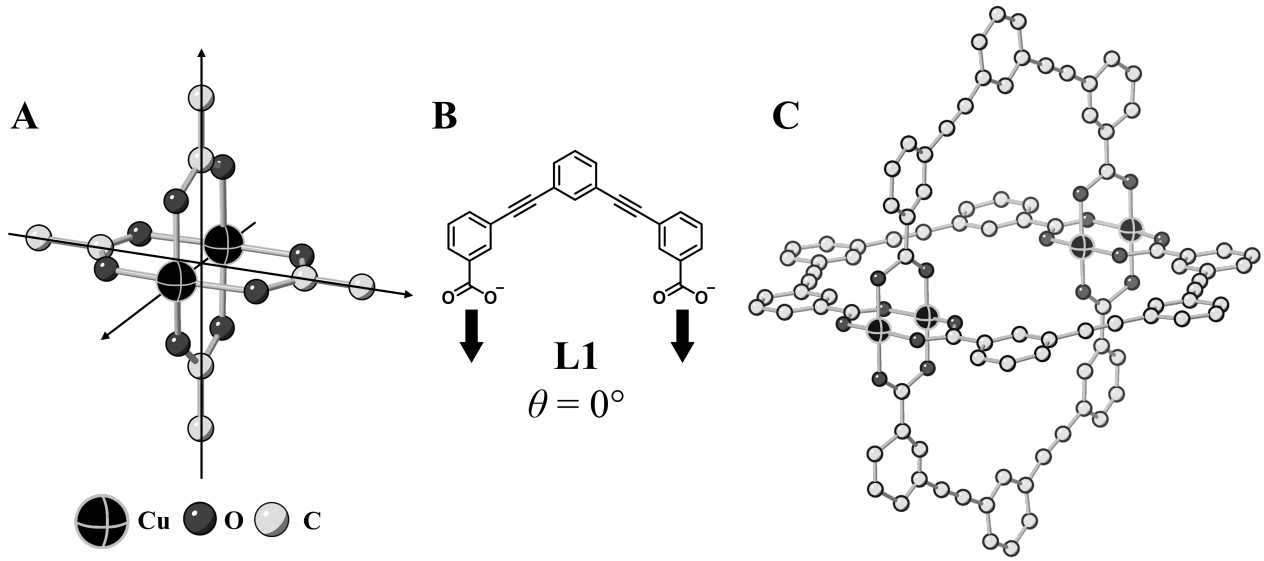
B.1	**Napišite** hemijske formule jedinjenja **A** i **B**.	6pt
B.2	**Izračunajte** l_x i l_z uz pomoć Slike 1.	4pt
B.3	Za Cu^{2+} u nepravilnom $[CuO_6]$ oktaedru u **A** sa Slike 1, **napišite** nazive podijeljenih e_g orbitala ($d_{x^2-y^2}$ i d_{z^2}) u (i) i (ii), i **nacrtajte** elektronsku konfiguraciju u istačkanom pravougaoniku u listu za odgovore.	4pt

A je izolator. Kada se jedan La^{3+} zamijeni 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 je 2.05×10^{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.	4pt

Dio C

$Cu_2(CH_3CO_2)_4$ se sastoji iz četiri $CH_3CO_2^-$ -jona koja su koordinovana sa dva jona Cu^{2+} (Slika 2A). $Cu_2(CH_3CO_2)_4$ posjeduje visok nivo strukturne simetrije, sa dvije ose koje prolaze kroz atome ugljenika od četiri $CH_3CO_2^-$ jona i osom koja prolazi kroz dva Cu^{2+} i sve su ortogonalno orijentisane jedna u odnosu na drugu. Kada se umjesto $CH_3CO_2^-$, koristi dikarboksilatni ligand, formira se „kavez-kompleks“ („cage complex”). Kavez-kompleks $Cu_4(\mathbf{L1})_4$ je sastavljen od planarnog dikarboksilata **L1** (Slika 2B) i Cu^{2+} (Slika 2C). Ugao θ između koordinativnih pravaca od dva karboksilata, označenih strelicama na Slici 3B, određuju strukturu kavez-kompleksa. θ ima vrijednost 0° za **L1**. Atomi vodonika nijesu prikazani na Slici 2.

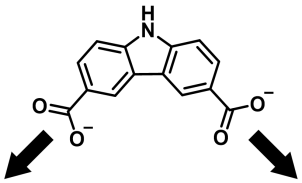


Slika 2

Q6-5

Montenegrin (Montenegro)

C.1 Ugao θ planarnog dikarboksilata **L2** , koji je prikazan ispod, iznosi 90˚. Ako sastav kavez-kompleksa, dobijenog od **L2** i Cu^{2+} može da se prikaže formulom $Cu_n(\mathbf{L2})_m$, **dajte** najmanju cjelobrojnu kombinaciju *n* i *m*. Pretpostavite da samo CO_2^- grupe iz **L2** grade koordinativnu vezu sa Cu^{2+} - jonima. 5pt



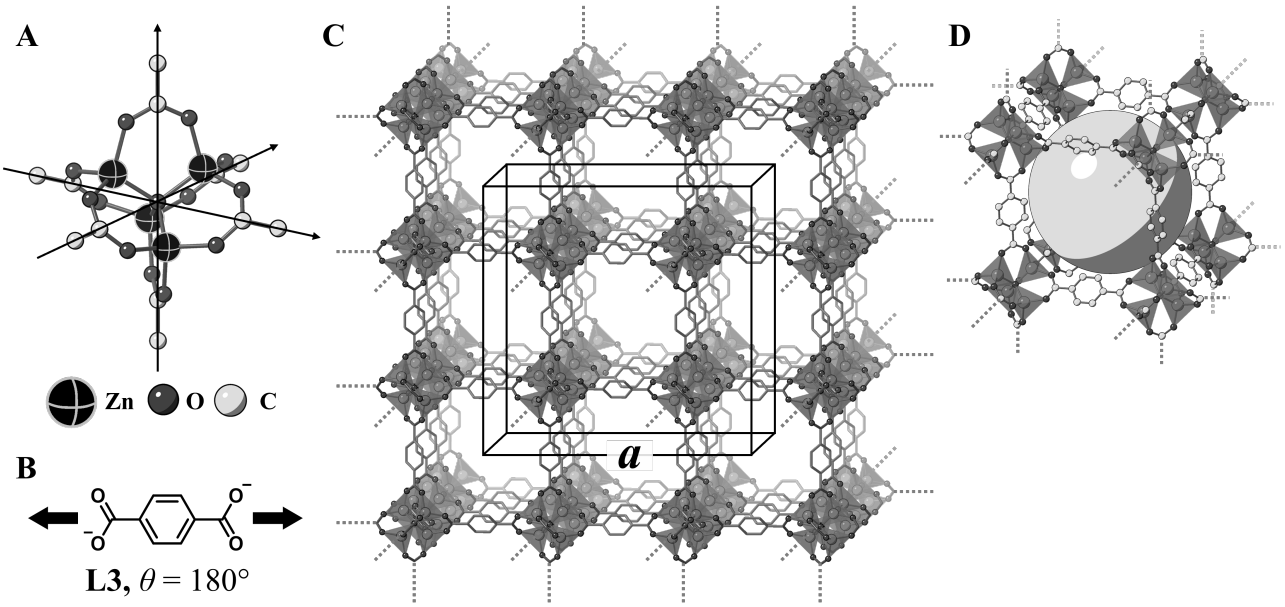
L2

$\theta = 90°$

Q6-6

Montenegrin (Montenegro)

Kompleks cinka, $Zn_4O(CH_3CO_2)_6$, sadrži četiri tetraedarska Zn^{2+}, šest $CH_3CO_2^-$, i jedan O^{2-} (Slika 3A). U kompleksu $Zn_4O(CH_3CO_2)_6$, O^{2-} se nalazi na početku, a tri ose koje prolaze kroz atome ugljenika $CH_3CO_2^-$ su orijentisane ortogonalno (pod uglovima od 90°) jedna u odnosu na drugu. Kada se *p*-benzendikarboksilat (Slika 3B, **L3**, θ = 180°) koristi umjesto $CH_3CO_2^-$, klasteri Zn^{2+} se međusobno povezuju i stvaraju kristalnu čvrstu supstancu (**X**) koja se naziva „porozni koordinacioni polimer" (Slika 3C). Sastav polimera **X** je $[Zn_4O(\mathbf{L3})_3]_n$, i on ima kubnu kristalnu strukturu sa porama nano veličine. Jedna pora je predstavljena kao sfera na Slici 3D, a svaki tetraedarski klaster Zn^{2+} predstavljen je kao tamno-sivi poliedar na slikama 3C i 3D. Atomi vodonika nijesu prikazani na Slici 3.



Slika 3

C.2	**X** posjeduje kubnu jediničnu ćeliju sa dužinom ivice a (Slika 3C) čija je gustina 0.592 g cm^{-3}. **Izračunajte** a u [cm].	5pt

C.3	**X** sadrži priličan broj pora i 1 g polimera **X** može da primi 3.0×10^2 mL gasovitog CO_2 unutar svojih pora na pritisku od 1 bar i na temperaturi od 25 °C. **Izračunajte** prosječan broj molekula of CO_2 po jednoj pori.	5pt

Hemija čvrstog stanja prelaznih metala

Dio A

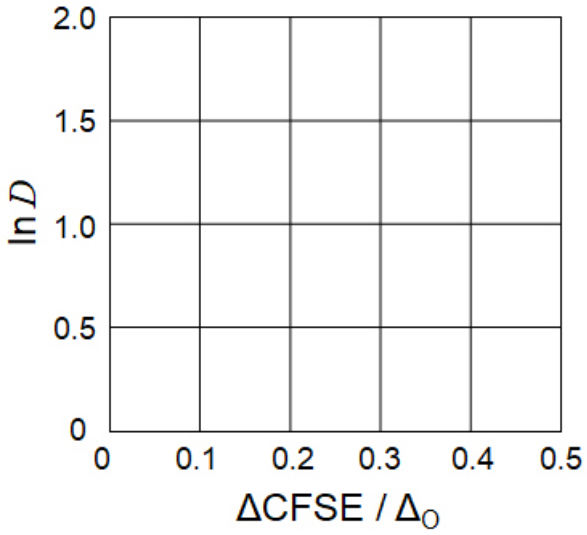
A.1 (6 pt)

Cr^{2+} : _____ Δ_O, Mn^{2+} : _____ Δ_O , Co^{2+} : _____ Δ_O

A6-2

Montenegrin (Montenegro)

A.2 (3 pt)



D : _____

A.3 (3 pt)

_____

Dio B

B.1 (6 pt)

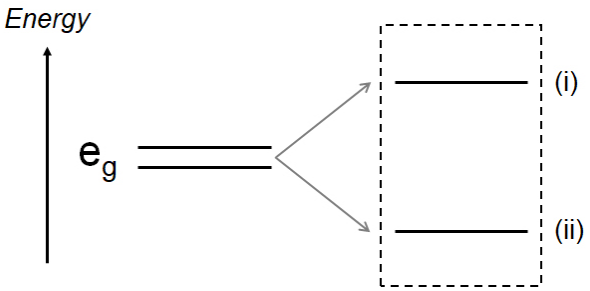
A : _____, B : _____

B.2 (4 pt)

$l_x =$ _____ nm, $l_z =$ _____ nm

B.3 (4 pt)

(i) : _____ , (ii) : _____



B.4 (4 pt)

_____ %

Dio C

C.1 (5 pt)

$n =$ _____, $m =$ _____

C.2 (5 pt)

$a =$ _____ cm

C.3 (5 pt)

MNE-4 C-7 C
Ksenija Tadic

IChO
Problem 7
Cover sheet

Please return this cover sheet together with all the related question sheets.

Playing with Non-benzenoid Aromaticity

13 % of the total					
Question	A.1	A.2	A.3	B.1	**Total**
Points	5	2	19	10	**36**
Score					

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



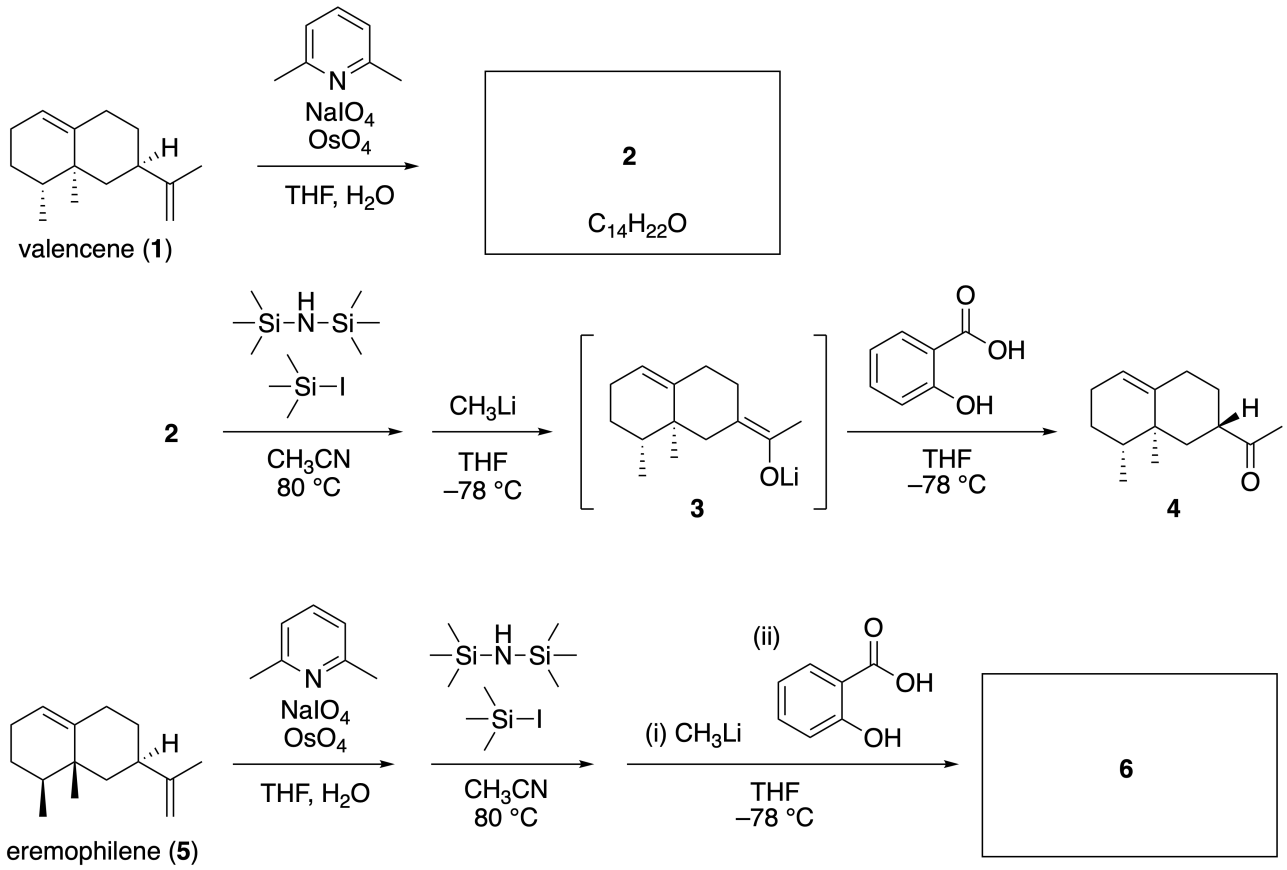
Photo courtesy: Tohoku Univ.

Part A

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



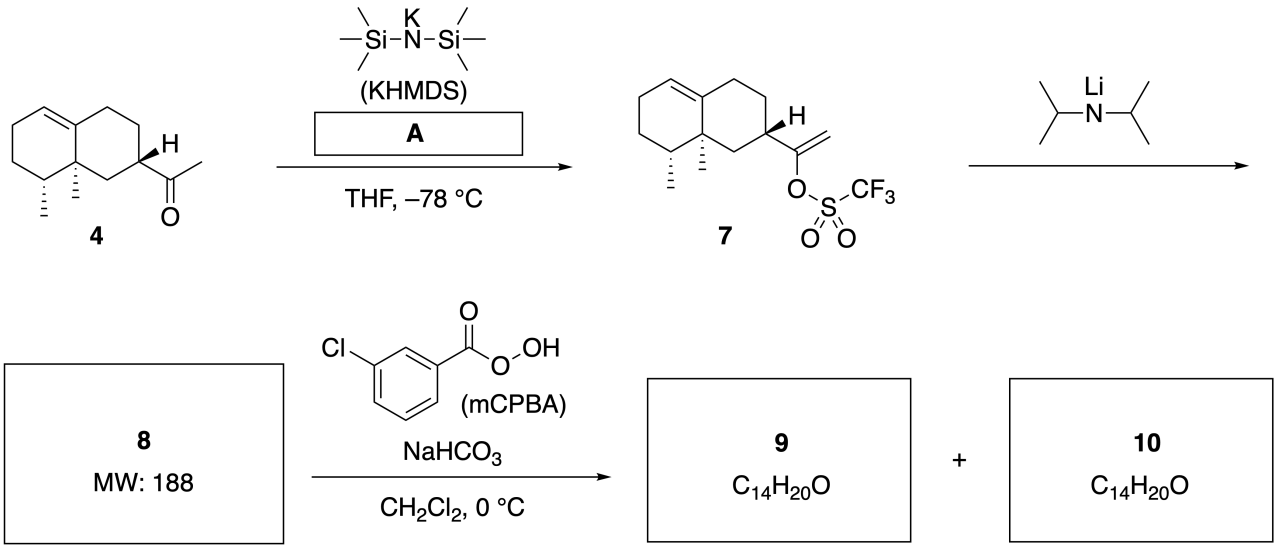
Inula linariifolia

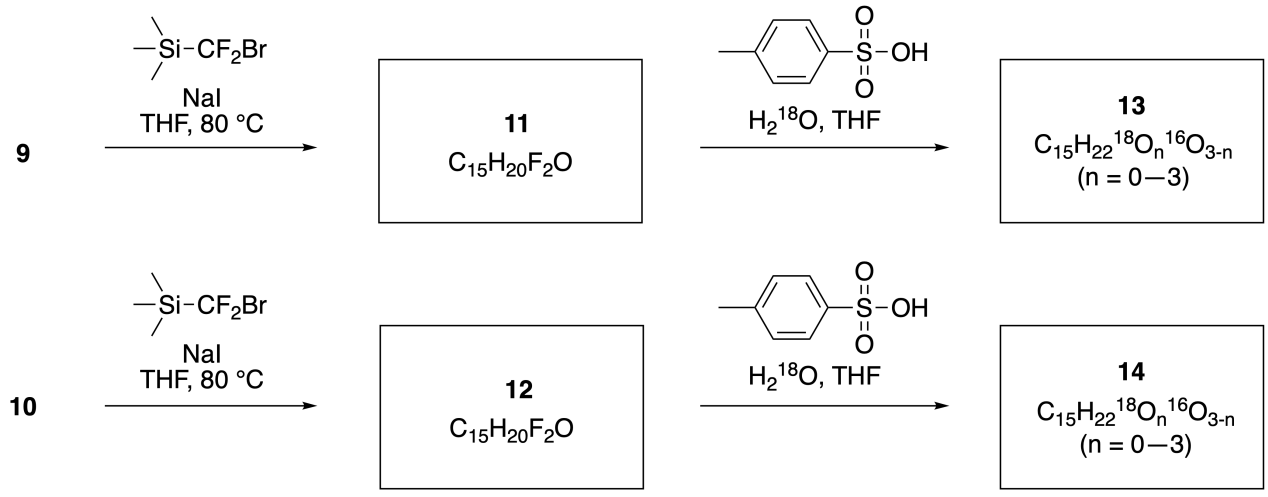


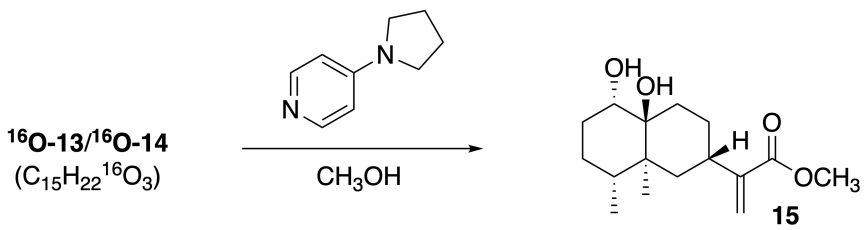
A.1 **Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary. 5pt

Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume

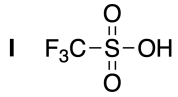
that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.

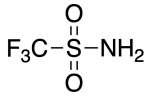


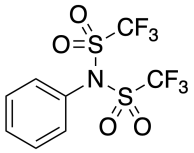


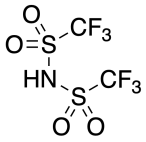


A.2 **Choose** the appropriate structure for **A**. 2pt

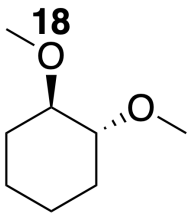
I 

II 

III 

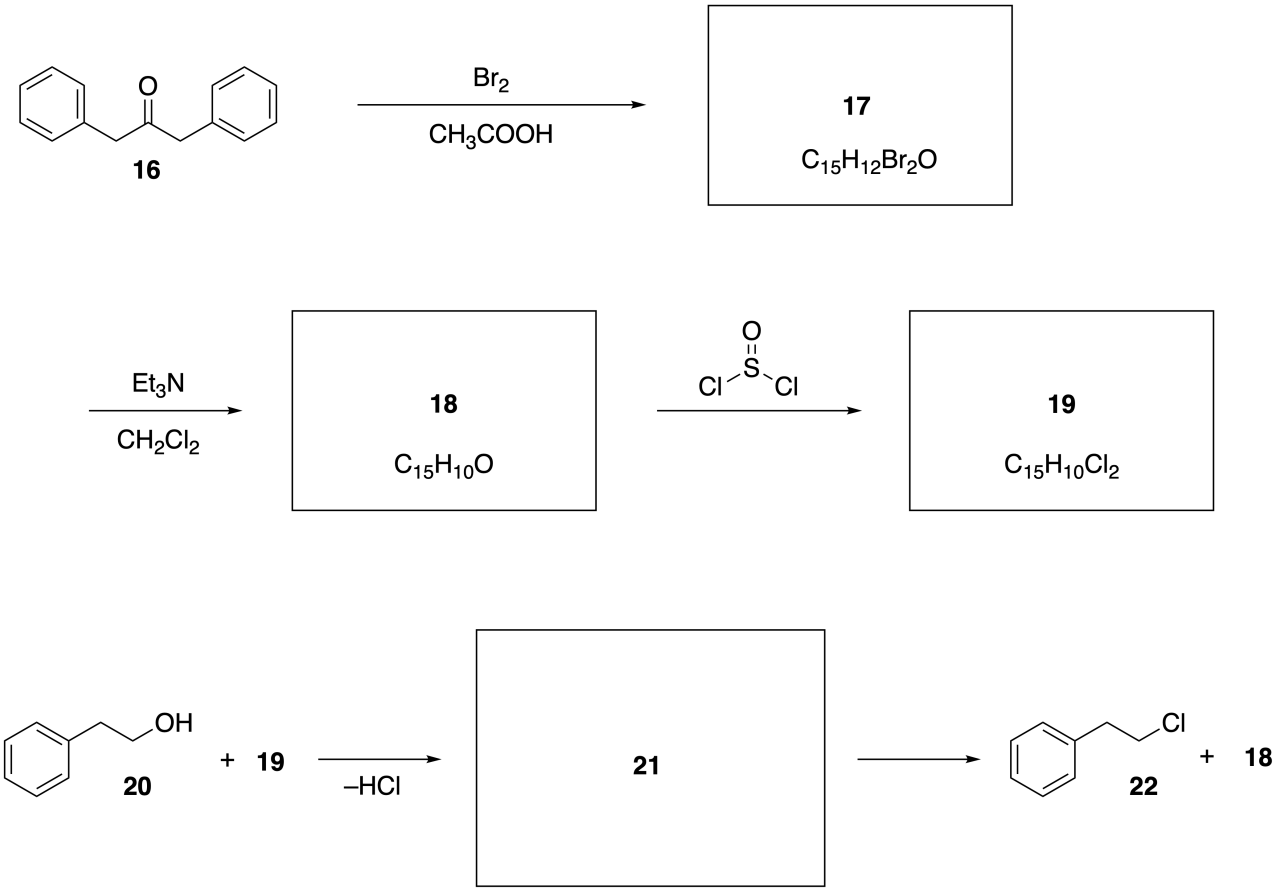
IV 

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**.



^{1}H NMR (CD_3CN, ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

B.1 **Draw** the structures of **17**–**19** and **21**. Identifying the stereochemistry is not necessary. 10pt

Igre s nebenzoidnom aromatičnošću

13 % od ukupnog broja poena					
Zadatak	A.1	A.2	A.3	B.1	**Ukupno**
Poena	5	2	19	10	**36**
Rezultat					

Profesor Nozoe (1902–1996) otvorio je polje istraživanja nebenzenoidnih aromatičnih jedinjenja, koji su danas veoma prisutni u organskoj hemiji.



Fotografija dobijena ljubaznošću Univerziteta Tohoku

Dio A

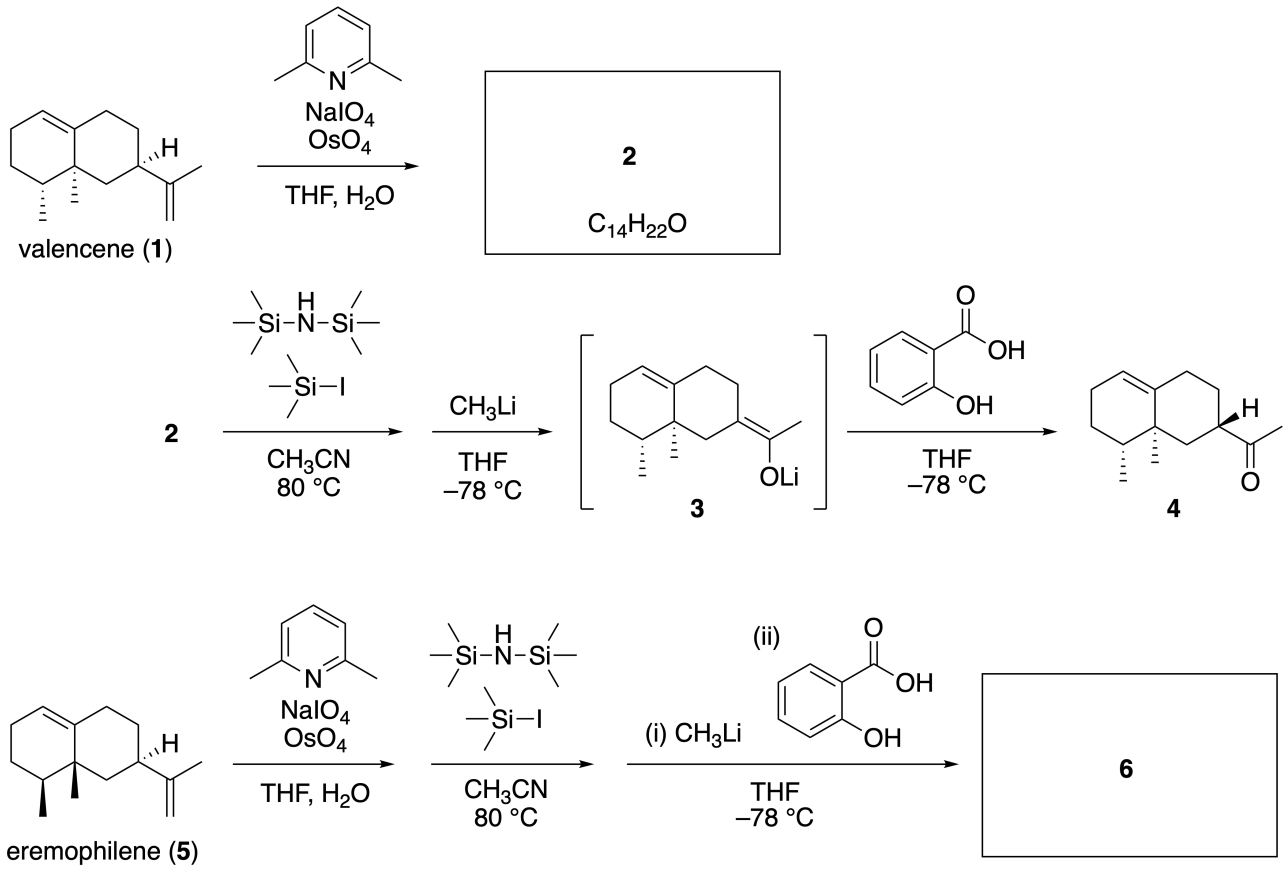
Lineariifolianon je prirodni proizvod sa jedinstvenom strukturom koji je izolovan iz biljke *Inula linariifolia*. Iz valencena (**1**) se u jednom koraku dobija jedinjenje **2**, iz koga se u tri koraka, preko jedinjenja **3**, dobija keton **4**. Na sličan način, iz eremofilena (**5**) se u četiri koraka sinteze dobija jedinjenje **6**.

Q7-2

Montenegrin (Montenegro)



Inula linariifolia



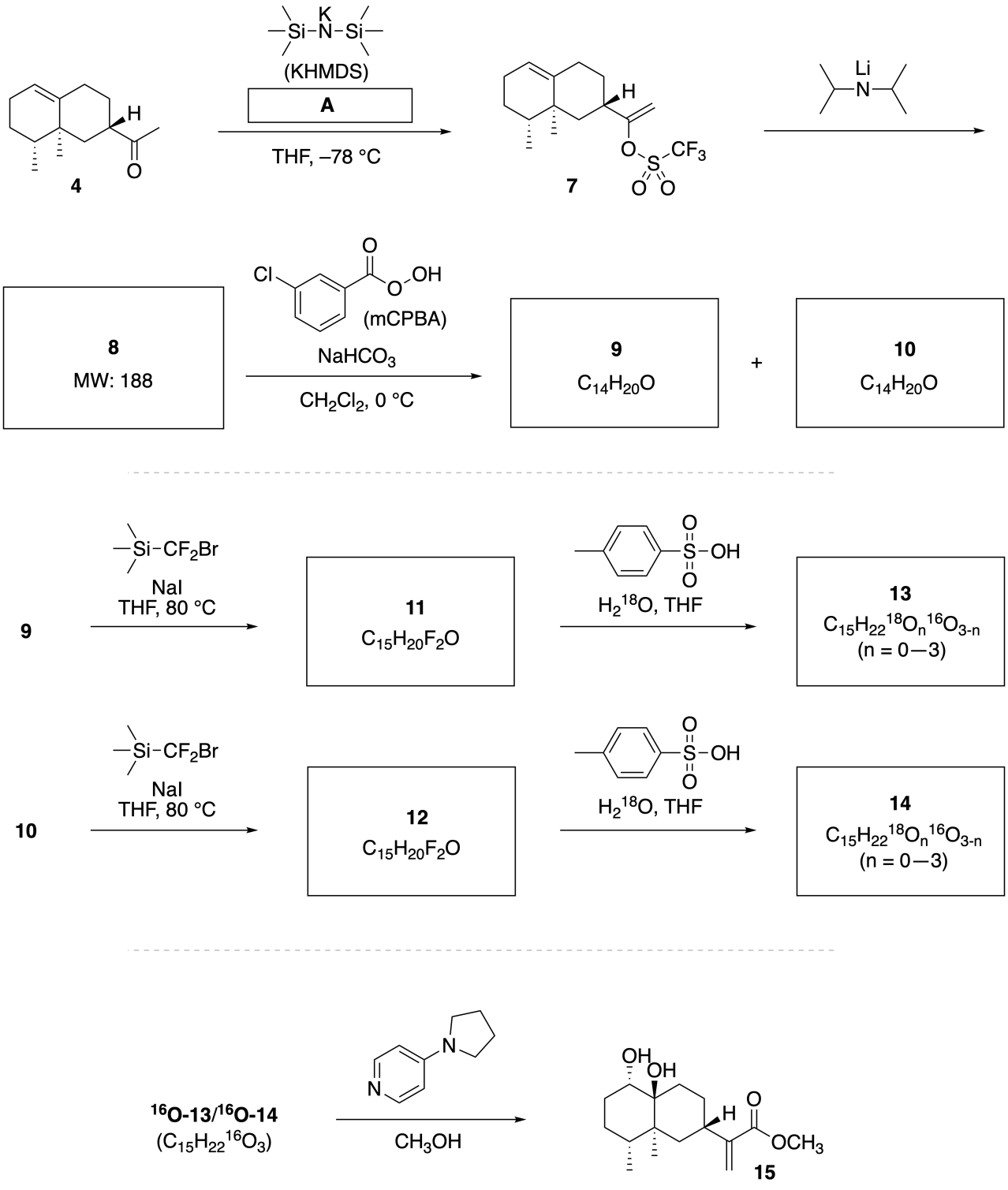
A.1 **Nacrtajte** strukturne formule jedinjenja **2** i **6** uz jasno naznačavanje stereohemijskih centara. 5pt

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-

Q7-3

Montenegrin (Montenegro)

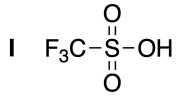
ugljenik dvostruku vezu. Pretpostavite da je $H_2{}^{18}O$ upotrebljena umjesto $H_2{}^{16}O$ u sintezi ^{18}O-obilježenih linearifolianona **13** i **14** iz jedinjenja **11**, odnosno **12**. Jedinjenja **13** i **14** su ^{18}O-obilježeni izotopomeri. Ako zanemarimo izotopsko obilježavanje, oba jedinjenja **13** i **14** vode do istog proizvoda **15** sa identičnom stereohemijom.

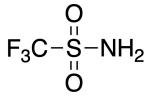


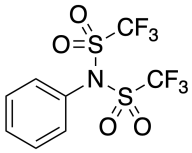
Q7-4

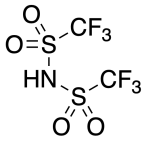
Montenegrin (Montenegro)

A.2 **Izaberite** odgovarajuću strukturu jedinjenja **A**. 2pt

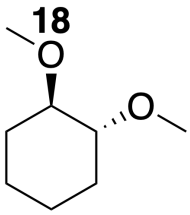
I 

II 

III 

IV 

A.3 **Nacrtajte** strukture jedinjenja **8**–**14** i jasno naznačite streohemijske centre gdje je to potrebno. **Označite** izotope ^{18}O u jedinjenjima **13** i **14** kao što je prikazano u donjem primjeru. 19pt

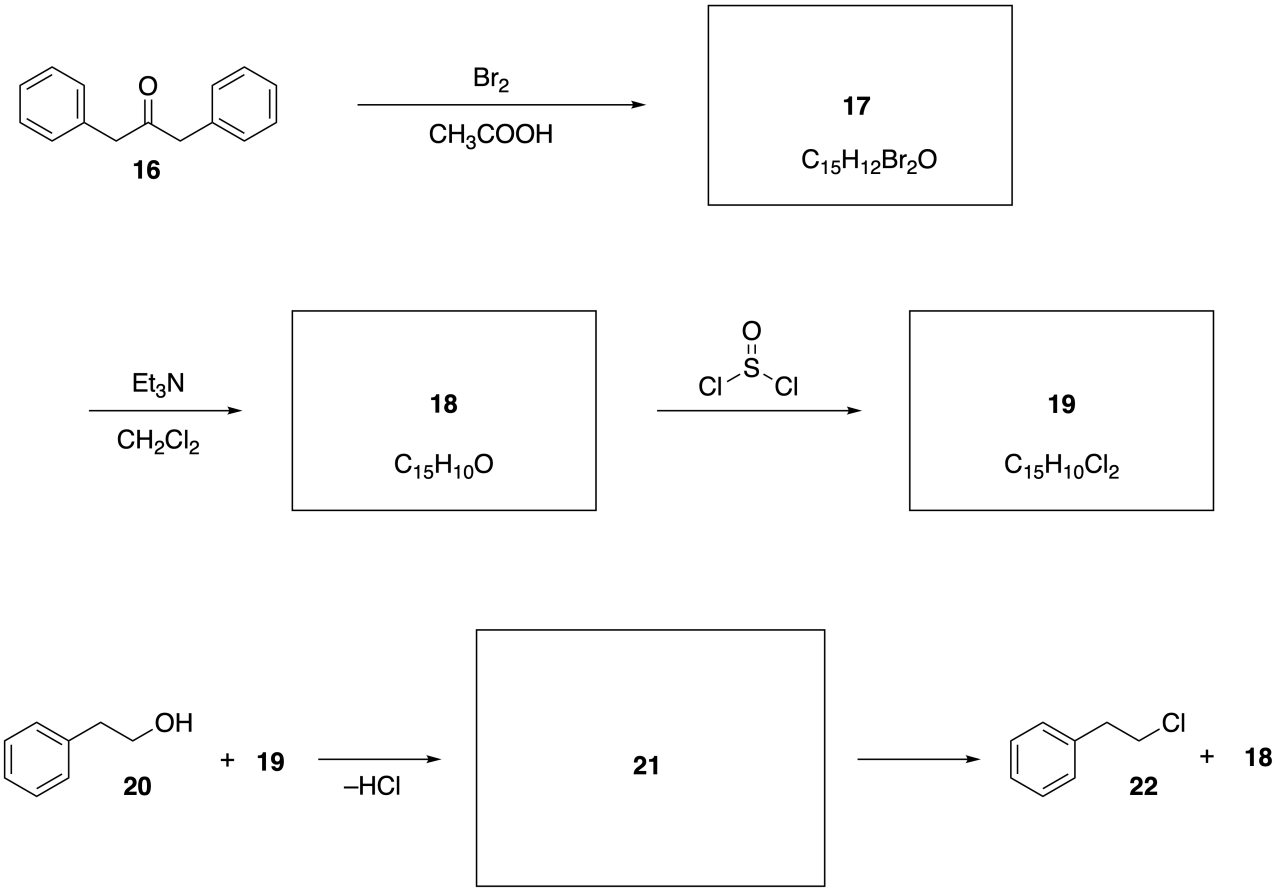


Q7-5

Montenegrin (Montenegro)

Dio B

Jedinjenje **19** se može koristiti kao aktivator alkoholne grupe. Njegova sinteza prikazana je na donjoj slici. Jedinjenje **20** se prevodi u jedinjenje **22**, preko jonskog međuproizvoda **21**. Iako je nastajanje intermedijera **21** dokazano NMR-om, on se postupno raspada, dajući proizvode **18** i **22**.



^{1}H NMR (CD_3CN, ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

B.1 **Nacrtajte** strukturne formule jedinjenja **17**–**19** i **21**. Naznačite streohemijske centre gdje je to potrebno. 10pt

Igre s nebenzoidnom aromatičnošću

Dio A

A.1 (5 pt)

2 (2 pt)	**6** (3 pt)

A.2 (2 pt)

A7-2

Montenegrin (Montenegro)

A.3 (19 pt)

8 (3 pt)

9 (2 pt)

10 (2 pt)

11 (2 pt)

12 (2 pt)

13 (4 pt)

14 (4 pt)

A7-3

Montenegrin (Montenegro)

Dio B

B.1 (10 pt)

17 (2 pt)	**18** (2 pt)
19 (3 pt)	**21** (3 pt)

MNE-4 C-8 C
Ksenija Tadic

IChO
Problem 8
Cover sheet

Please return this cover sheet together with all the related question sheets.

Q8-1

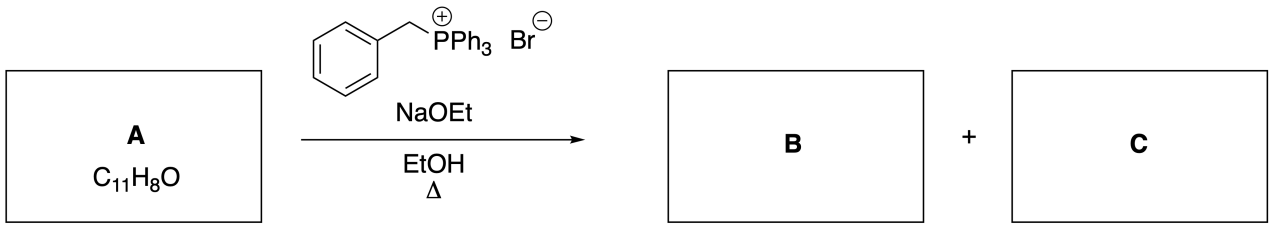
English (Official)

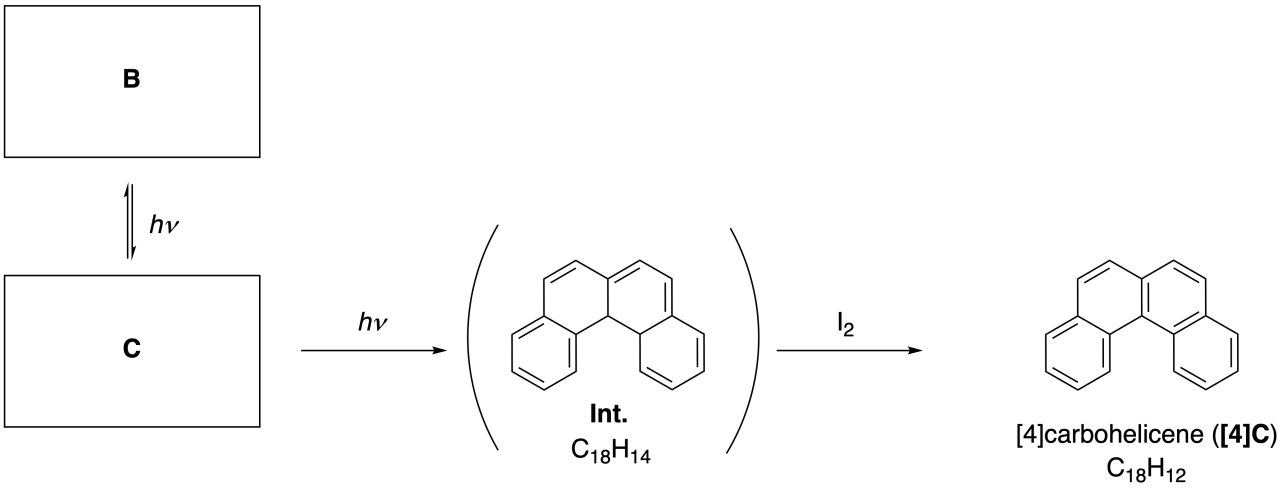
Dynamic Organic Molecules and Their Chirality

11 % of the total						
Question	A.1	A.2	A.3	B.1	B.2	**Total**
Points	9	3	7	3	4	**26**
Score						

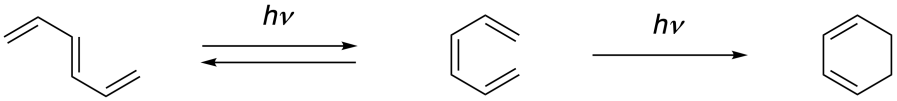
Part A

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





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

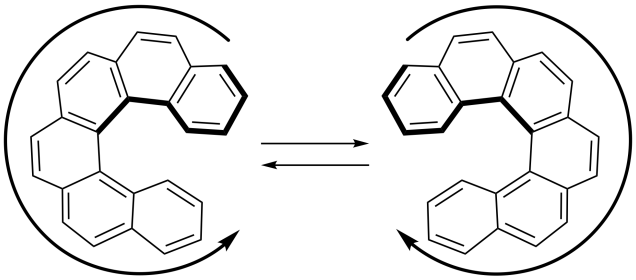


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

A.1	**Draw** the structures of **A**–**C**. Stereoisomers should be distinguished.	9pt

A.2	Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product **D** whose molecular weight was 2 Da lower than that of [5]carbohelicene. The ^{1}H NMR chemical shifts of **D** are listed below. **Draw** the structure of **D**. **[D** (δ, ppm in CS_2, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)**]**	3pt

[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.



(*M*) (*P*)

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

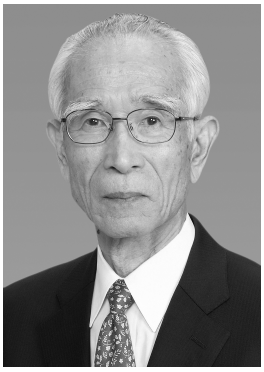
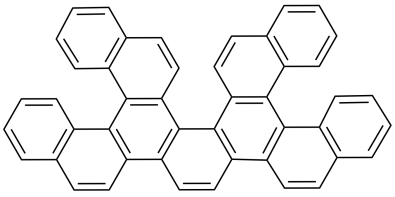


Photo courtesy: The Japan Prize Foundation

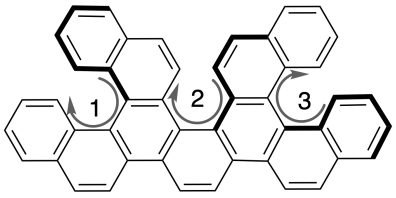
Q8-3

English (Official)

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

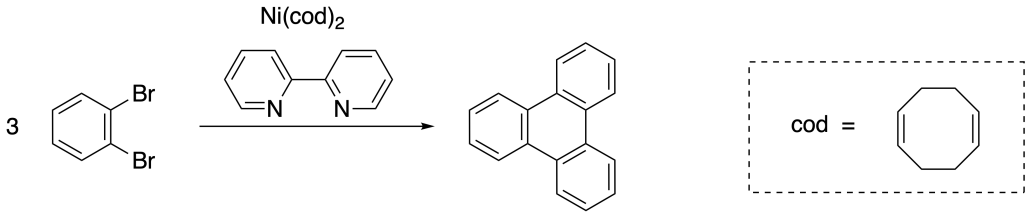


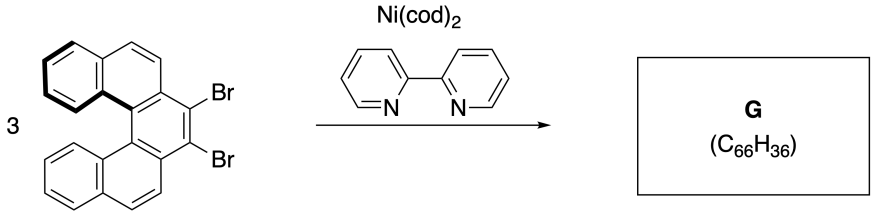
E



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

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*, *P*), (*M*, *P*, *P*), and (*M*, *P*, *M*). 7pt

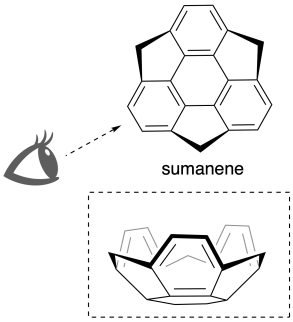




(*P*)-**F**

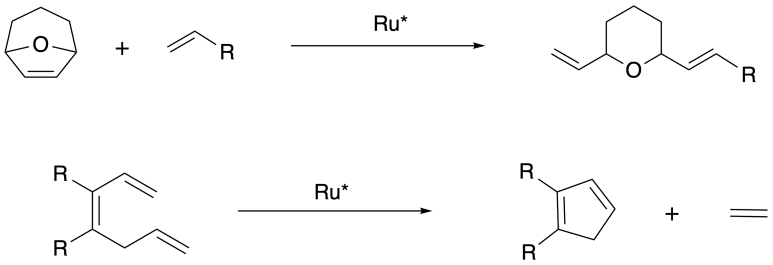
Part B

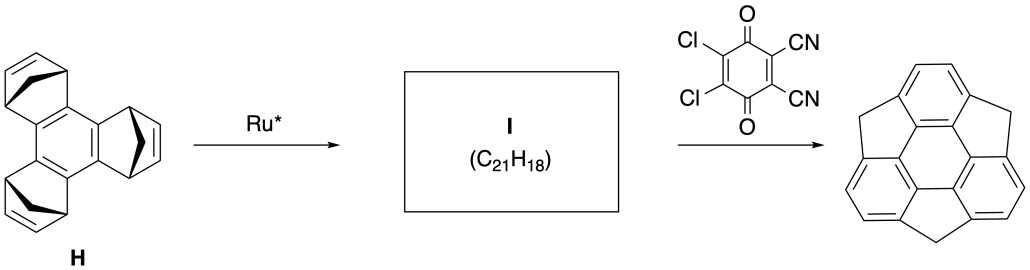
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



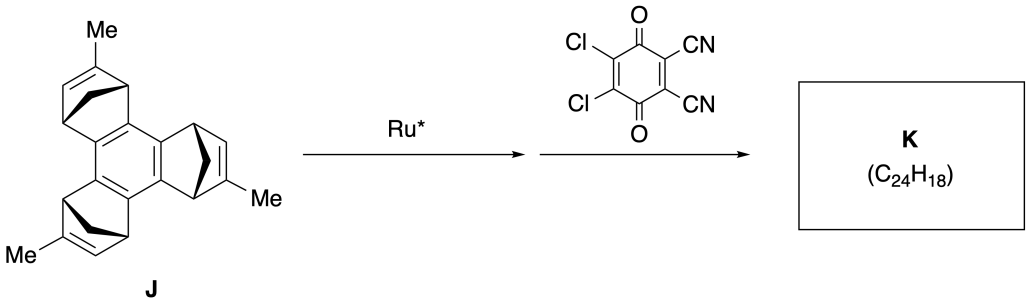


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.





B.1	**Draw** the structure of intermediate **I** (its stereochemistry is not required).	3pt



J

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.	4pt

Q8-1

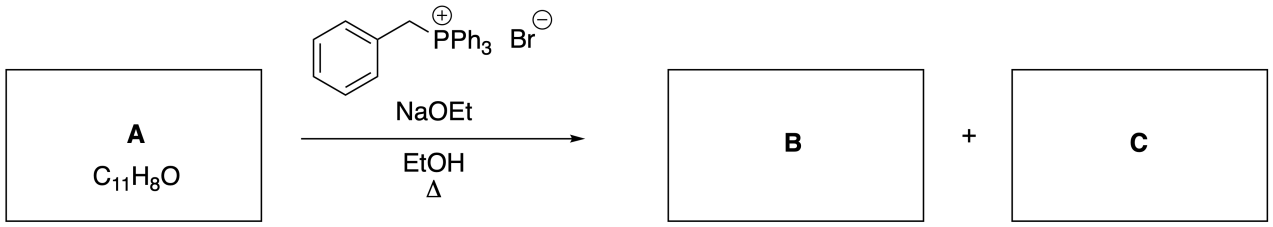
Montenegrin (Montenegro)

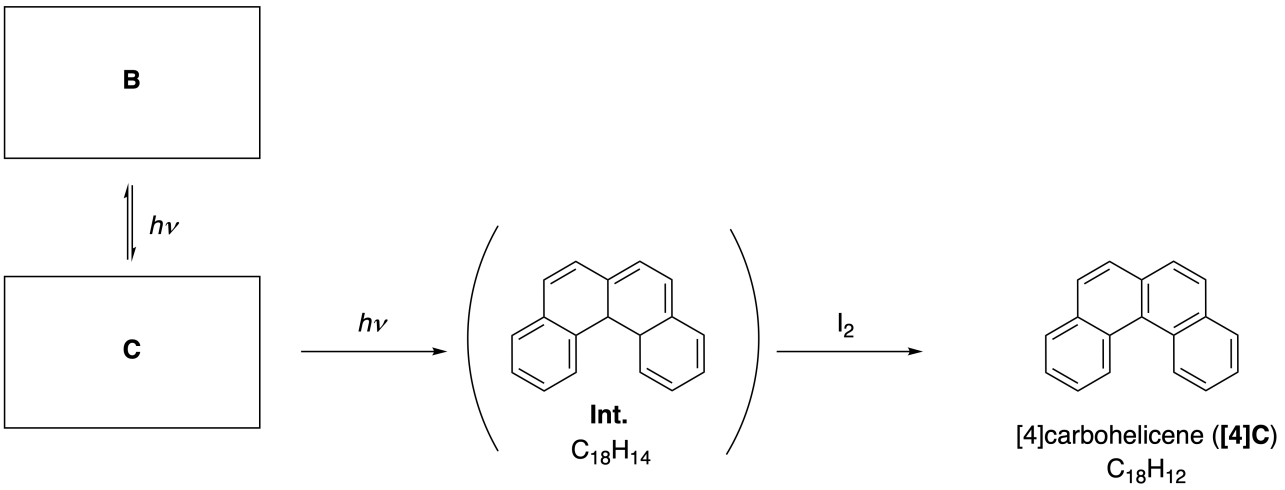
Dinamički organski molekuli i njihova hiralnost

11 % od ukupnog broja poena						
Zadatak	A.1	A.2	A.3	B.1	B.2	**Ukupno**
Poeni	9	3	7	3	4	**26**
Rezultat						

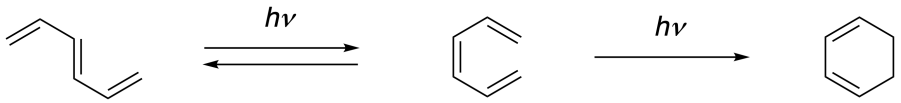
Dio A

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.



Q8-2

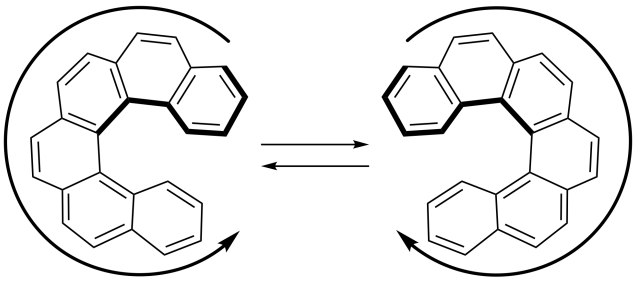
Montenegrin (Montenegro)

Napomena: U cijelom Zadatku 8, za konjugovani π sistem ne koristite kružiće nego naizmjenične dvostruke i jednostruke veze.

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

A.2	Pokušaji sinteze [5]karbohelicena iz iste fosfonijum-soli i odgovarajućeg polaznog jedinjenja kao rezultat su dali to da je [5]karbohelicen nastao u tragovima. Umjesto njega, dobijen je proizvod **D** čija je molekulska masa bila 2 Da (daltona) niža od mase [5]karbohelicena. ^{1}H NMR spektar jedinjenja **D**: **[D** (δ, ppm in CS_2, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)**]** **Nacrtajte** strukturnu formulu jedinjena **D**.	3pt

[5] - i veći [n]karboheliceni pokazuju helikalnu hiralnost. Međusobna konverzija između enantiomera helicena je spora na sobnoj temperaturi. Hiralnost [n]karbohelicena označava se sa (*M*) ili (*P*) kao što je prikazano dolje.



(*M*) (*P*)

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

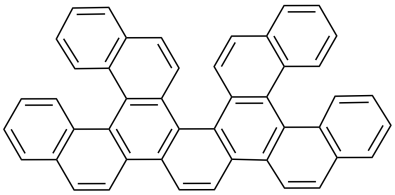


Fotografija dobijena ljubaznošću *The Japan Prize Foundation*

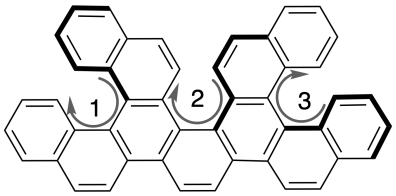
Q8-3

Montenegrin (Montenegro)

Višestruki heliceni su molekuli koji sadrže dva ili više strukturnih motiva helicenskog tipa. Ukoliko se posmatra helikalna hiralnost, postoji nekoliko stereoizomera u višestrukom helicenu. Na primjer, jedinjenje **E** sadrži tri [5]karbohelicenska motiva u molekulu. Jedan od stereoizomera je opisan kao (*P*, *P*, *P*) i prikazan je ispod.

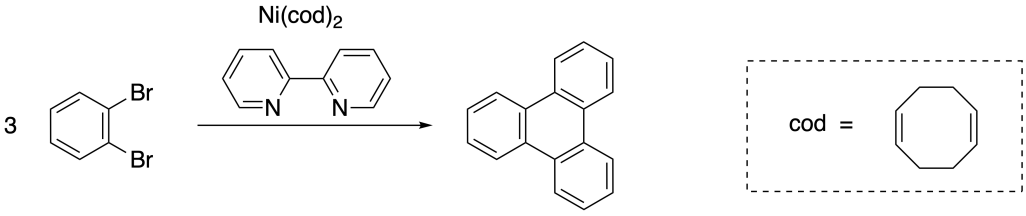


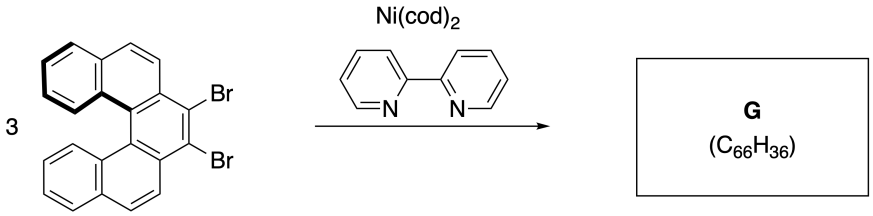
E



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

A.3 Trimerizacija 1,2-dibromobenzena u prisutnosti nikla daje trifenilen. Istom rekacijom 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 streoizomere 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*, *P*) i (*M*, *P*, *M*). 7pt





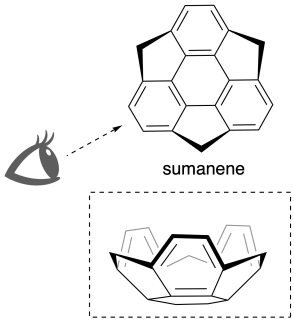
(*P*)-**F**

Q8-4

Montenegrin (Montenegro)

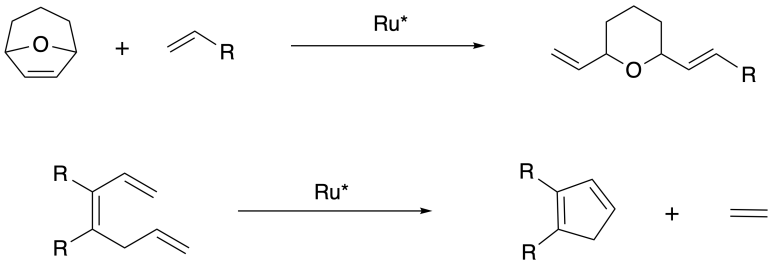
Dio B

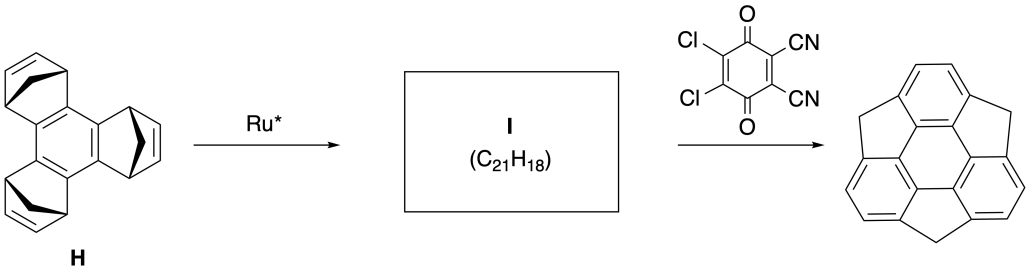
Sumanen je ugljovodonik, koji posmatran sa strane ima oblik činije. Prvi put je sintetisan 2003. godine u Japanu. Naziv sumanen dolazi od riječi ”suman” koja u Sanskrit-Hindu jeziku označava suncokret. Sinteza sumanena vrši se nizom reakcija koje uključuju otvaranje i zatvaranje prstenova.





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

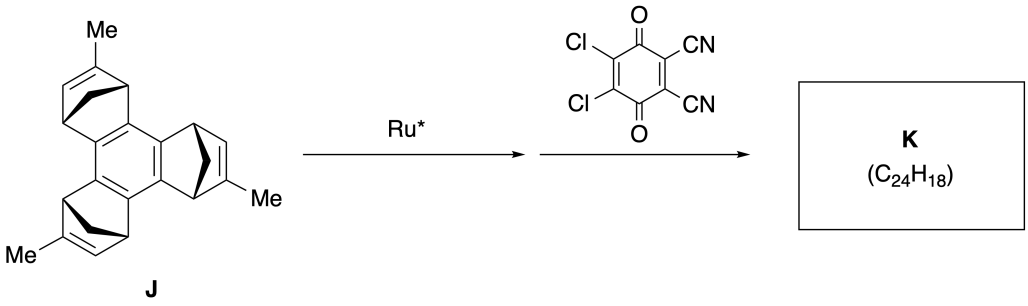




B.1	**Nacrtajte** strukturnu formulu intermedijera **I** (nije potrebno označavati njegovu streohemiju).	3pt

Q8-5

Montenegrin (Montenegro)



J

B.2	Polazeći iz optički aktivnog prekursora **J**, istom sekvencom reakcija dobija se jedinjenje **K** koje je optički aktivni derivat sumanena. Tokom reakcije ne dolazi do inverzije konfiguracije u stereocentrima. **Nacrtajte** strukturnu formulu jedinjenja **K** sa odgovarajućim streohemijskim oznakama.	4pt

A8-1

Montenegrin (Montenegro)

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)

MNE-4 C-9 C
Ksenija Tadic

IChO
Problem 9
Cover sheet

Please return this cover sheet together with all the related question sheets.

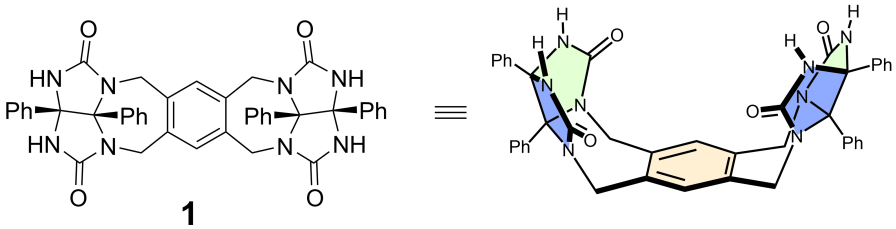
Likes and Dislikes of Capsule

10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	**Total**
Points	13	2	2	3	3	**23**
Score						

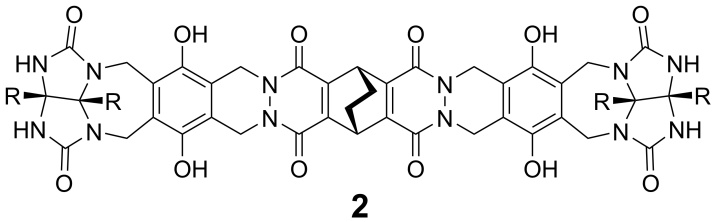
Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



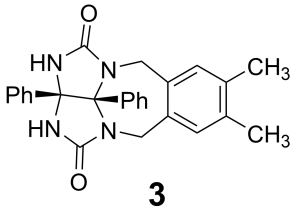
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

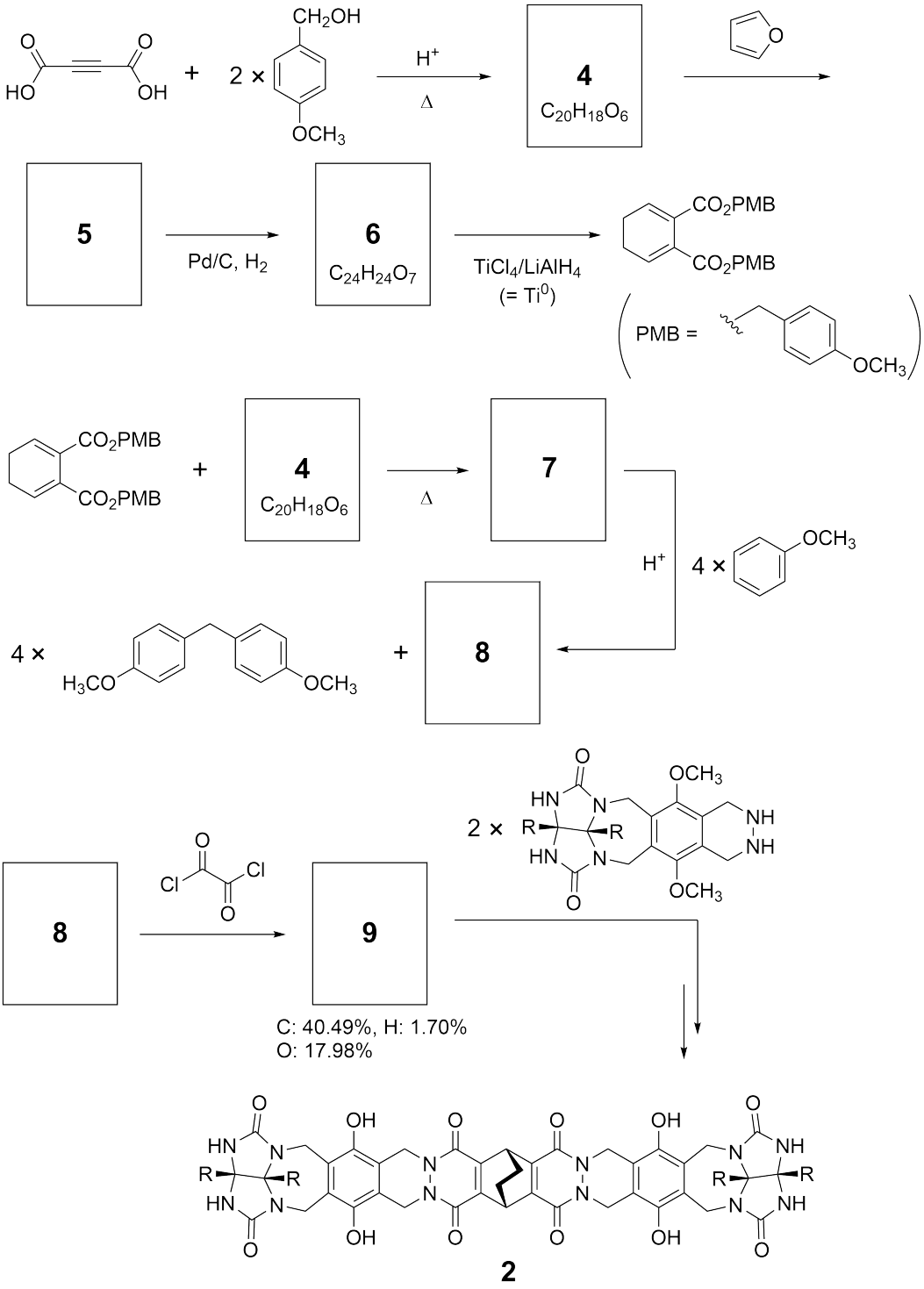


2



3

The synthetic route to **2** is shown below. The elemental composition of compound **9**: C; 40.49%, H; 1.70%, and O; 17.98% by mass.



2

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.	13pt

In the mass spectrum of **1**, the ion peak corresponding to its dimer ($\mathbf{1}_2$) was clearly observed, whereas an ion peak for $\mathbf{3}_2$ was not observed in the spectrum of **3**. In the ^{1}H NMR spectra of a solution of $\mathbf{1}_2$, all the NH protons derived from **1** were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of **3**. These data indicate that hydrogen bonds are formed between the NH moieties of **1** and atoms **X** of another molecule of **1** to form the dimeric capsule.

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

A.3	**Give** the number of the hydrogen bonds in the dimeric capsule ($\mathbf{1}_2$).	2pt

The dimeric capsule of **1** ($\mathbf{1}_2$) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

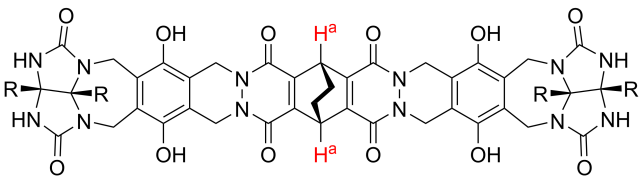
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

The equilibrium constant of the encapsulation of Z into $\mathbf{1}_2$ is given as below:

$$K_\mathrm{a} = \frac{[\mathrm{Z}@\mathbf{1}_2]}{[\mathrm{Z}][\mathbf{1}_2]} \tag{2}$$

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, $\mathbf{1}_2$ in C_6D_6 gave different signals in the ^{1}H NMR spectra before and after addition of CH_4.

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



2

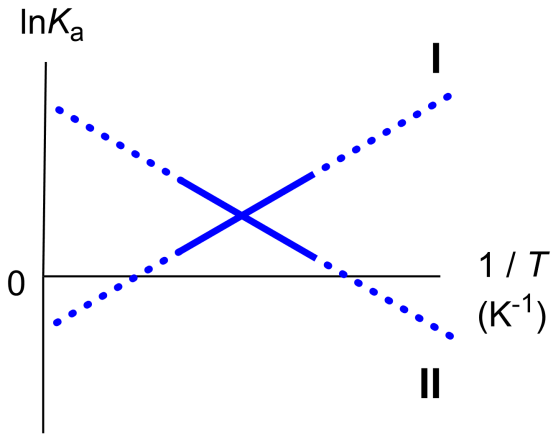
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

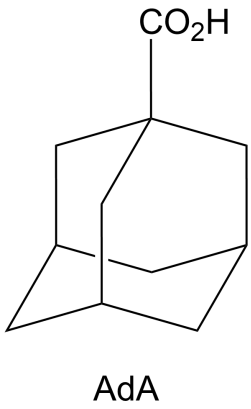
A.4 **<u>Determine</u>** the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2}_2$ giving each H^a signal. 3pt

^{1}H NMR measurements in C_6D_6 revealed that $\mathbf{2}_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants (K_a) which are expressed below were determined for various temperatures. [solvent@$\mathbf{2}_2$] denotes a species containing one or more solvent molecules.

$$K_a = \frac{[Z@\mathbf{2}_2]}{[Z][\text{solvent}@\mathbf{2}_2]} \tag{3}$$

Similarly, the K_a values of CH_4 and $\mathbf{1}_2$ given as eq (2) at various temperatures in C_6D_6 were also determined by ^{1}H NMR measurements. The plots of the two association constants (as ln K_a vs 1/T) are shown below.





No C_6D_6 molecule is encapsulated in $\mathbf{1}_2$. In line **II**, the entropy change (ΔS) is (1) and enthalpy change (ΔH) is (2), indicating that the driving force for the encapsulation in line **II** is (3). Therefore, line **I** corresponds to (4), and line **II** corresponds to (5).

A.5 **Choose** the correct options in gaps (1)–(5) in the following paragraph from A and B. 3pt

	A	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and AdA
(5)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and AdA

Q9-1

Montenegrin (Montenegro)

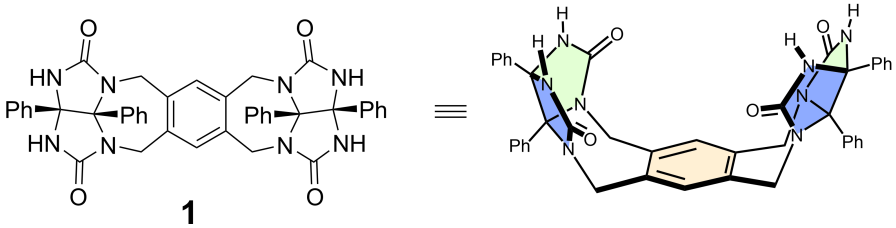
Za i protiv kapsula

10 % od ukupnog broja poena						
Zadatak	A.1	A.2	A.3	A.4	A.5	**Ukupno**
Poeni	13	2	2	3	3	**23**
Rezultat						

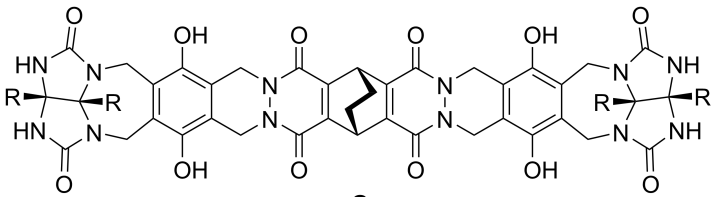
Dobra djeca to ne rade, ali ako rasiječete tenisku lopticu, možete je rastaviti na dva dijela u obliku slova U.



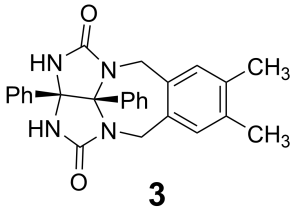
Na osnovu ove ideje sintetisana su jedinjenja **1** i **2** , kao molekuli u obliku slova U različitih veličina. Jedinjenje **3** je slično jedinjenju **1**. Istraživana su njihova svojstva enkapsuliranja.



1



2

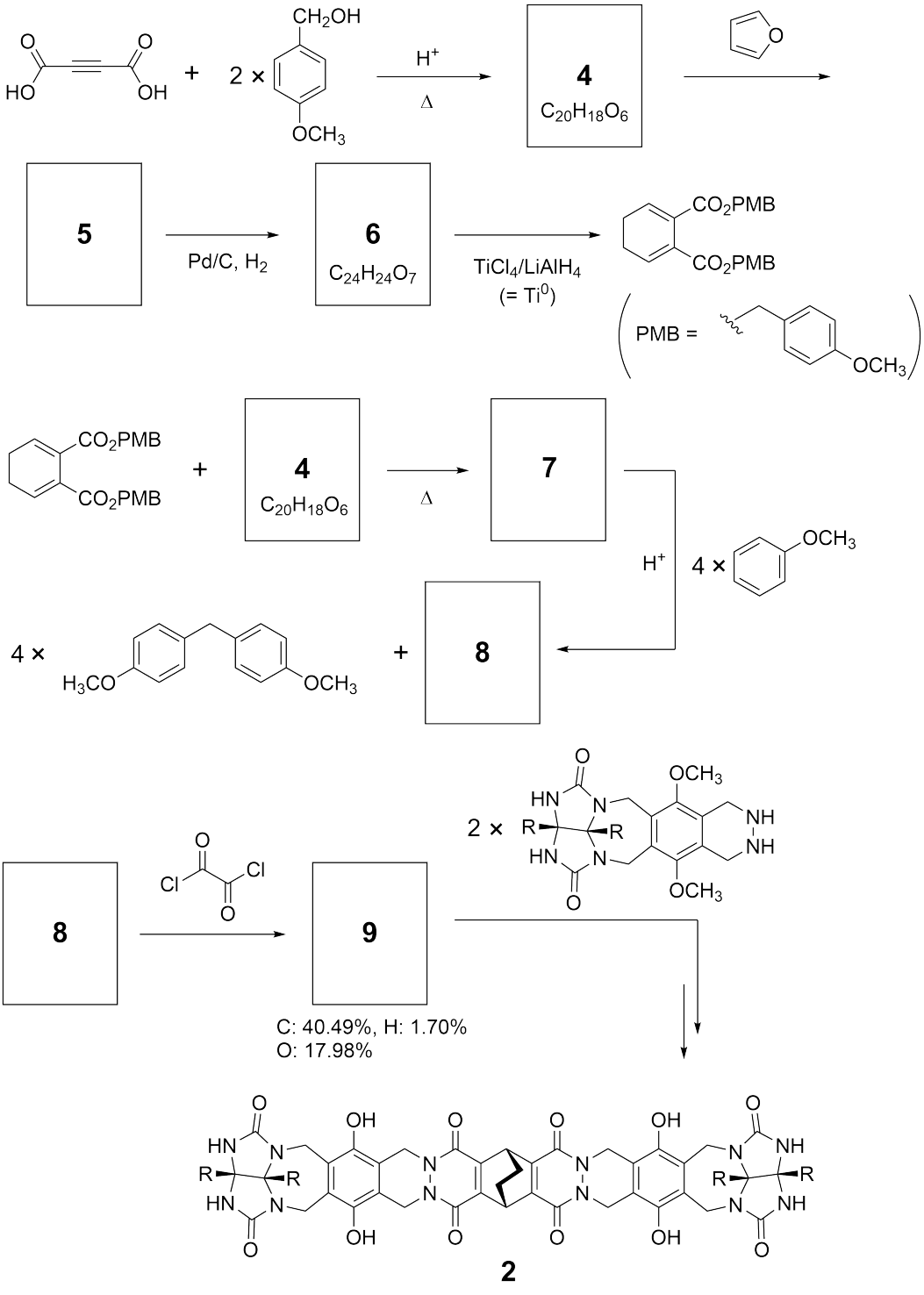


3

Q9-2

Montenegrin (Montenegro)

Sintetička sekvenca 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).



Q9-3

Montenegrin (Montenegro)

A.1	**Nacrtajte** strukturne formule jedinjenja **4**–**9**; stereohemiju možete zanemariti. Koristite "PMB" kao oznaku za supstituent umjesto da crtate cijelu strukturu *p*-metoksibenzil-grupe koja je prikazana u gornjoj šemi.	13pt

U masenom spektru jedinjenja **1**, jonski pik (signal) koji odgovara njegovom dimeru ($\mathbf{1}_2$), dok signal za $\mathbf{3}_2$nije primijećen u spektru jedinjenja **3**. U ^{1}H NMR spektru rastvora jedinjenja $\mathbf{1}_2$, 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**.	2pt

A.3	**Koliki je** ukupan broj vodoničnih veza u dimernoj kapsuli ($\mathbf{1}_2$)?	2pt

Q9-4

Montenegrin (Montenegro)

Dimerna kapsula od jedinjenja **1** ($\mathbf{1}_2$) ima unutrašnji prostor u koji se može smjestiti (inkapsulirati) odgovarajući mali molekul Z. Ovaj fenomen se izražava sledećom jednačinom:

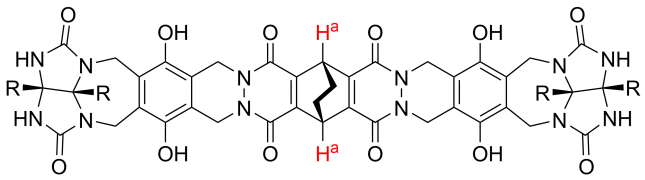
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

Konstanta ravnoteže inkapsulacije $\mathbf{1}_2$ je data ispod:

$$K_\mathrm{a} = \frac{[\mathrm{Z}@\mathbf{1}_2]}{[\mathrm{Z}][\mathbf{1}_2]} \tag{2}$$

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

Jedinjenje **2** takođe gradi rigidnu i veću dimernu kapsulu ($\mathbf{2}_2$). Snimljen je ^{1}H NMR spektar od $\mathbf{2}_2$ u: C_6D_6, 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.



2

rastvarač	δ (ppm) od H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

A.4 Koliki je broj molekula C_6D_6 i C_6D_5F koji su inkapsulirani u $\mathbf{2}_2$ za sve date H^a signale. 3pt

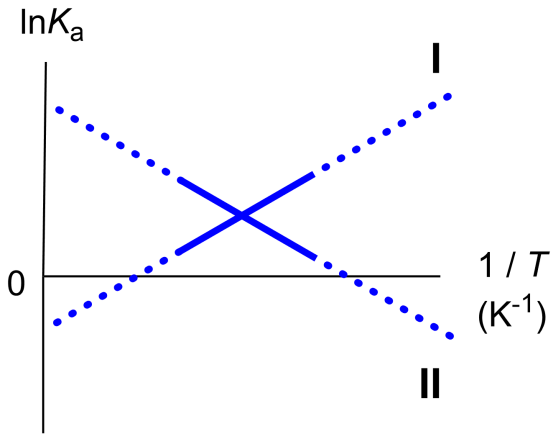
Q9-5

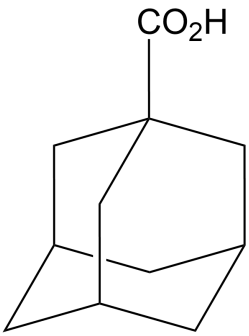
Montenegrin (Montenegro)

^{1}H NMR mjerenja u C_6D_6 pokazala su da $\mathbf{2}_2$ može da ugradi jedan molekul 1-adamantankarboksilne kiseline (AdA) i konstante asocijacije (K_a) koje su izražene ispod su određene na različitim temperaturama. [solvent@$\mathbf{2}_2$] označava vrstu koja sadrži jedan ili više molekula rastvarača.

$$K_a = \frac{[Z@\mathbf{2}_2]}{[Z][solvent@\mathbf{2}_2]} \quad (3)$$

Slično tome, vrijednosti K_a za CH_4 i molekul $\mathbf{1}_2$ date jednačinom (2) na različitim temperaturama u C_6D_6 takođe su određene ^{1}H NMR mjerenjima. Prikazani su grafici te dvije konstante (kao ln K_a vs 1/T).





AdA

Molekuli C_6D_6 nijesu inkapsulirani u $\mathbf{1}_2$. U liniji **II**, promjena entropije (ΔS) je (1) a promjena entalpije (ΔH) je (2), što ukazuje da je pokretačka sila za inkapsulaciju u liniji **II** (3). Stoga, linija **I** odgovara (4), a linija **II** odgovara (5).

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

	A	B
(1)	pozitivna	negativna
(2)	pozitivna	negativna
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ i CH_4	$\mathbf{2}_2$ i AdA
(5)	$\mathbf{1}_2$ i CH_4	$\mathbf{2}_2$ i AdA

A9-1

Montenegrin (Montenegro)

Za i protiv kapsula

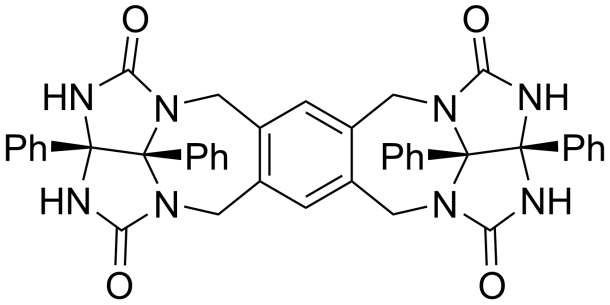
A.1 (13 pt)

4 (2 pt)	**5** (3 pt)
6 (2 pt)	**7** (2 pt)
8 (2 pt)	**9** (2 pt)

A9-2

Montenegrin (Montenegro)

A.2 (2 pt)



A.3 (2 pt)

A.4 (3 pt)

δ (ppm) od H^a	broj C_6D_6	broj C_6D_5F
4.60 ppm		
4.71 ppm		
4.82 ppm		

A.5 (3 pt)

(1) : _____ (2) : _____ (3) : _____

(4) : _____ (5) : _____