

CHE-4 C-0 C-1

CHE-4 C-0 C
Anastasia Sandamirskaya

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>



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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		300	100

Physical Constants and Equations

Constants

Speed of light in vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Planck constant	$h = 6.62607015 \times 10^{-34} \text{ J s}$
Elementary charge	$e = 1.602176634 \times 10^{-19} \text{ C}$
Electron mass	$m_e = 9.10938370 \times 10^{-31} \text{ kg}$
Electric constant (permittivity of vacuum)	$\varepsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$
Avogadro constant	$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$
Faraday constant	$F = N_A \times e = 9.64853321233100184 \times 10^4 \text{ C mol}^{-1}$
Gas constant	$R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 8.2057366081 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$
Unified atomic mass unit	$u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$
Standard pressure	$p = 1 \text{ bar} = 10^5 \text{ Pa}$
Atmospheric pressure	$p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa}$
Zero degree Celsius	$0^\circ \text{C} = 273.15 \text{ K}$
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Part-per-million	$1 \text{ ppm} = 10^{-6}$
Part-per-billion	$1 \text{ ppb} = 10^{-9}$
Part-per-trillion	$1 \text{ ppt} = 10^{-12}$
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	$F = k_e \frac{q_1 q_2}{r^2}$, where F is the electrostatic force, $k_e (\simeq 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2})$ is Coulomb's constant, q_1 and q_2 are the magnitudes of the charges, and r is the distance between the charges.
The first law of thermodynamics	$\Delta U = q + w$, where 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	$S = k_B \ln W$, where W is the number of microstates.
The change of entropy ΔS	$\Delta S = \frac{q_{\text{rev}}}{T}$, where q_{rev} is the heat for the reversible process.
Gibbs free energy G	$G = H - TS$ $\Delta_r G^\circ = -RT \ln K = -zFE^\circ$, where K is the equilibrium constant, z is the number of electrons, E° is the standard electrode potential.
Reaction quotient Q	$\Delta_r G = \Delta_r G^\circ + RT \ln Q$ For a reaction $aA + bB \rightleftharpoons cC + dD$ $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$, where $[A]$ is the concentration of A.

Heat change Δq	$\Delta q = nc_m \Delta T$, where c_m is the temperature-independent molar heat capacity.
Nernst equation for redox reaction	$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration of reduced substance.
Arrhenius equation	$k = A \exp\left(-\frac{E_a}{RT}\right)$, 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	$A = \varepsilon lc$, 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 $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, where equilibrium constant is K_a , $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
Energy of a photon	$E = h\nu = h\frac{c}{\lambda}$, where ν is the frequency, λ is the wavelength of the light.
The sum of a geometric series	When $x \neq 1$, $1 + x + x^2 + \dots + x^n = \sum_{i=0}^n x^i = \frac{1 - x^{n+1}}{1 - x}$
Approximation equation that can be used to solve problems	When $x \ll 1$, $\frac{1}{1 - x} \simeq 1 + x$

Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H Hydrogen 1.008																	2 He Helium 4.003	
3 Li Lithium 6.968	4 Be Beryllium 9.012																9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.306																17 Cl Chlorine 35.452	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798	
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium [99]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.293	
55 Cs Caesium 132.905	56 Ba Barium 137.327	57-71 La-Lu Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.384	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium [210]	85 At Astatine [210]	86 Rn Radon [222]	
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Key:

113 Nh Nihonium [278]	atomic number	Symbol	name	atomic weight [in parenthesis for the radioactive element]
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¹H NMR Chemical Shifts



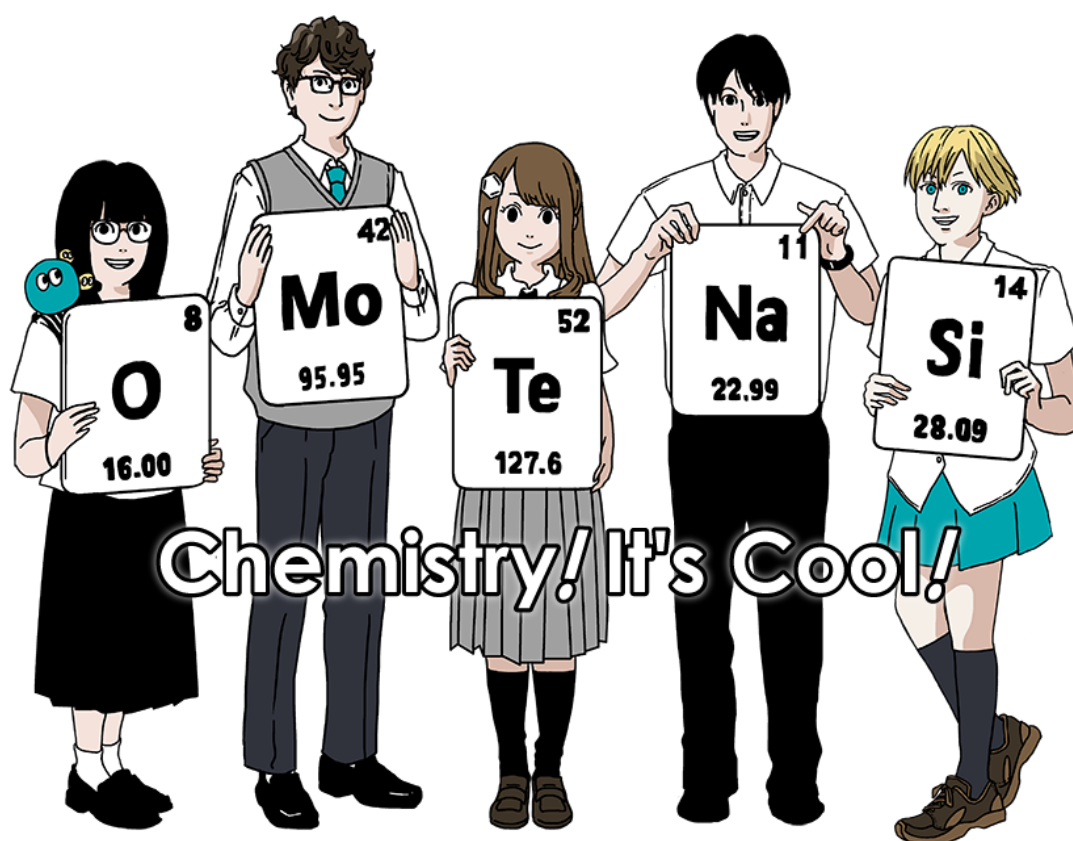
$\Delta\delta$ for one alkyl group-substitution: *ca.* +0.4 ppm

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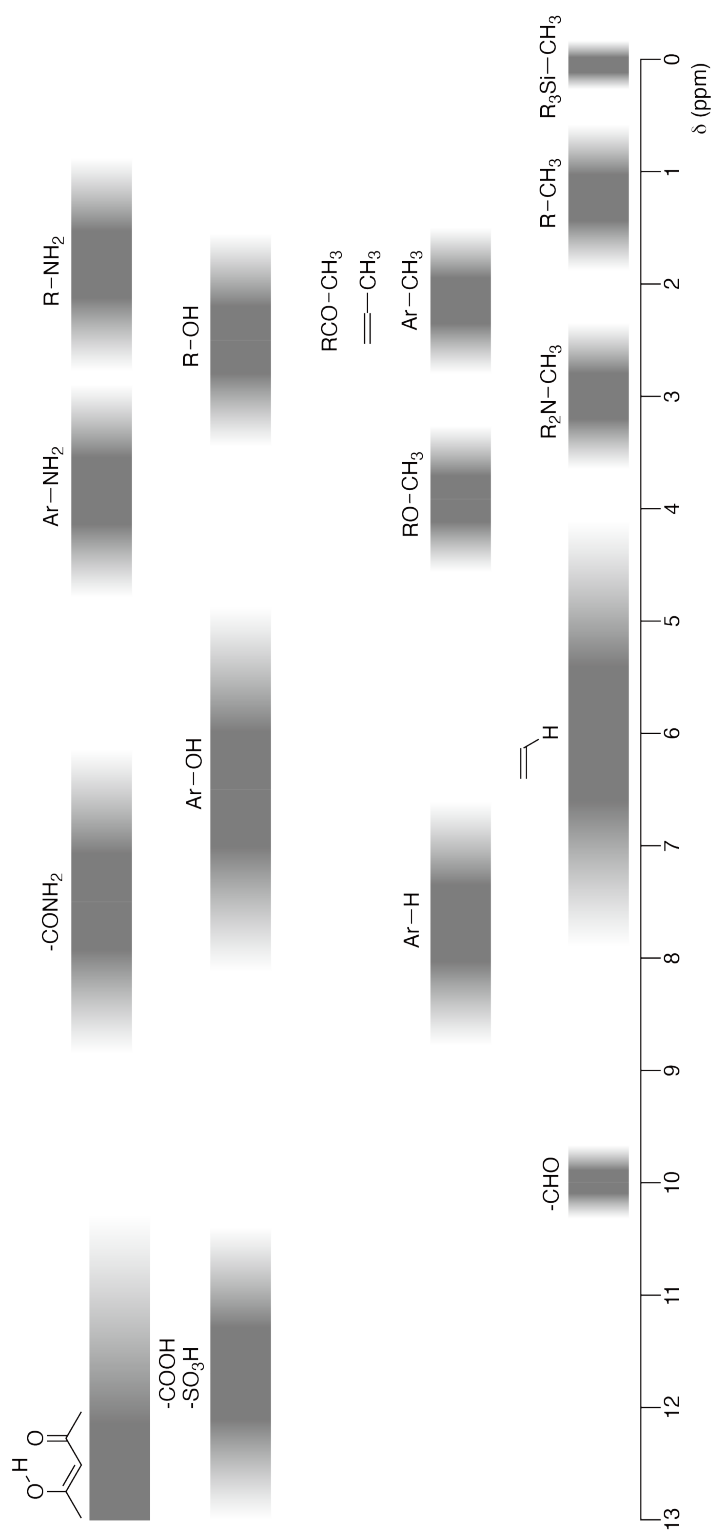
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Key:

113 Nh Nihonium [278]	atomic number	Symbol	atomic weight [in parenthesis for the radioactive element]
		name	

¹H NMR Chemical Shifts



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

CHE-4 C-1 C-1

CHE-4 C-1 C
Anastasia Sandamirskaya

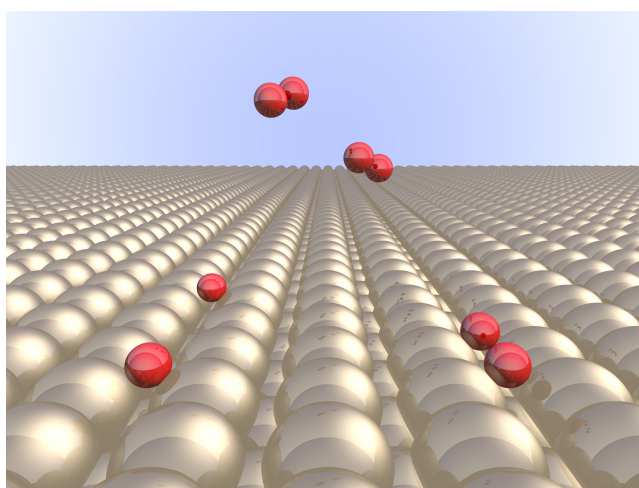
ICHO Problem 1

Cover sheet

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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, $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad})$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (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.

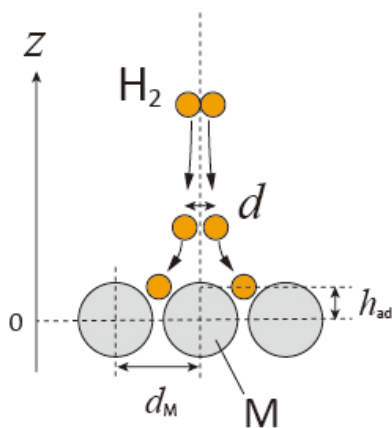


Fig.1 Definition of variables. Drawing is not in scale.

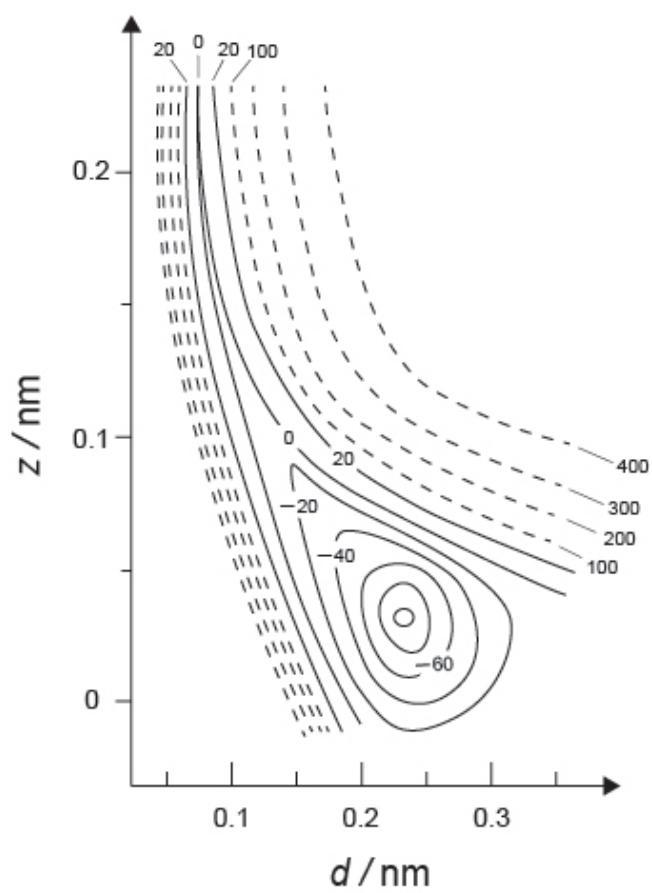


Fig.2

- 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
[$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$]
 - (ii) the energy released during the adsorption of a gaseous H_2 [$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad})$]

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.



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

$$r_1 = k_1 P_{\text{H}_2} (1 - \theta)^2 \quad (2)$$

$$r_2 = k_2 \theta^2 \quad (3)$$

$$r_3 = k_3 \theta \quad (4)$$

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

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\text{H}_2} C}}} \quad (5)$$

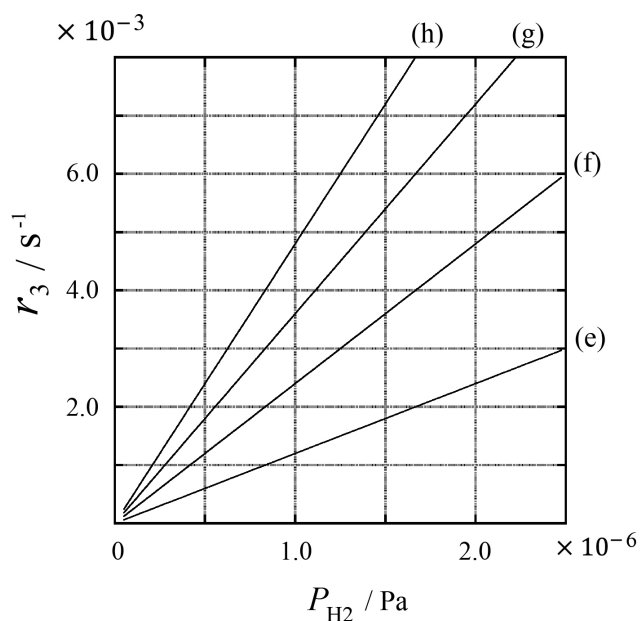
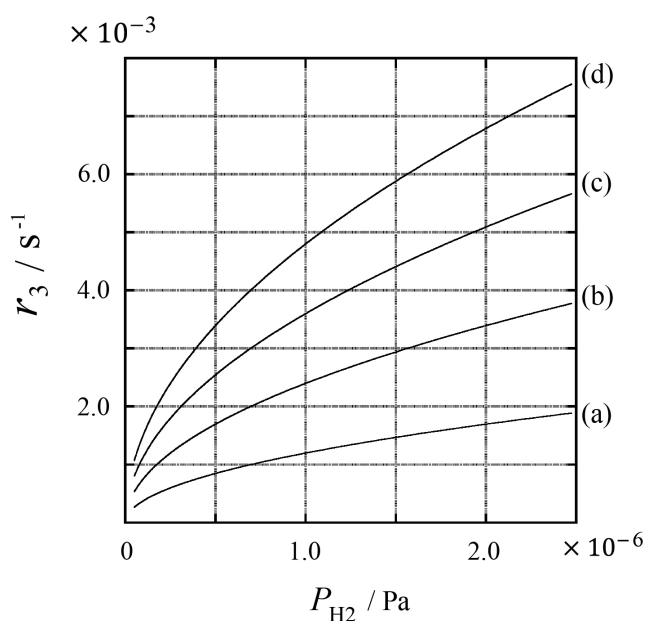
Express C using k_1 and k_2 .

A metal sample with a surface area of $S = 1.0 \times 10^{-3} \text{ m}^2$ was placed in a container ($1\text{L} = 1.0 \times 10^{-3} \text{ m}^3$) with H_2 ($P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18} \text{ m}^{-2}$. The surface temperature was kept at $T = 400 \text{ K}$. As the reaction (1) proceeded, P_{H_2} decreased at a constant rate of $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$. 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 [$\text{mol s}^{-1} \text{ m}^{-2}$]. 3pt

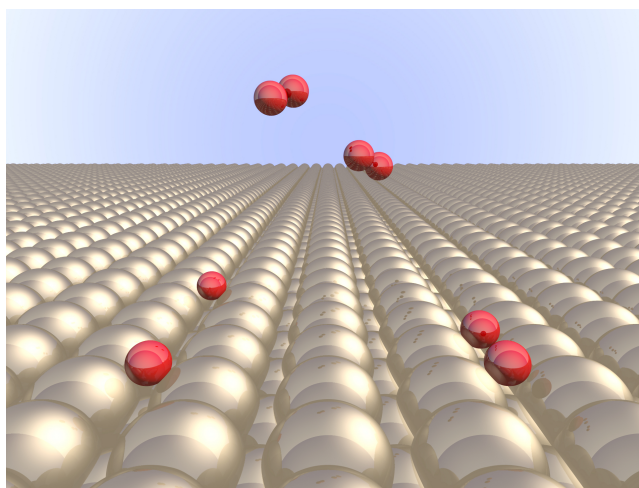
B.3 At $T = 400 \text{ K}$, C equals $1.0 \times 10^2 \text{ Pa}^{-1}$. Calculate the value of k_3 at 400 K . If you did not obtain the answer to **B.2**, use $A = 3.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2}$. 3pt

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



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 anticipated 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 transportation and storage technology.

Part A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad})$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively.

Hydrogen molecules (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 centre 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 mol^{-1} . 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.

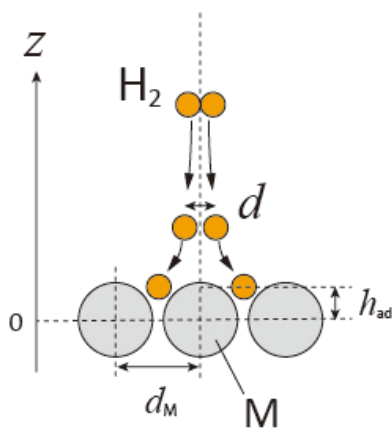


Fig.1 Definition of variables. Drawing is not to scale.

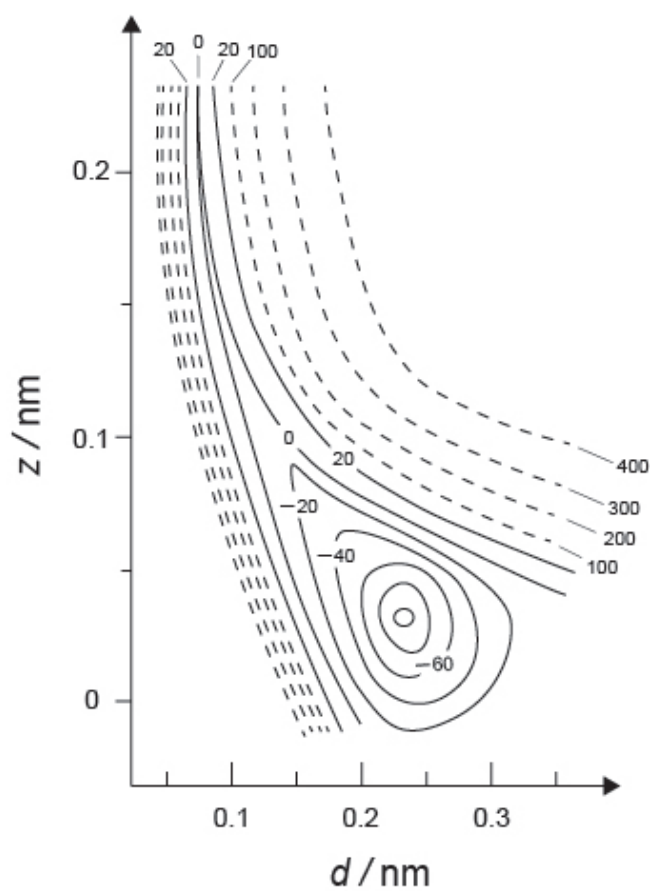


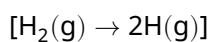
Fig.2

- 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)

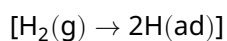
A. 0.03 nm	B. 0.07 nm	C. 0.11 nm	D. 0.15 nm
E. 0.19 nm	F. 0.23 nm	G. 0.27 nm	

- 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



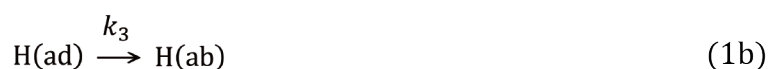
- (ii) the energy released during the adsorption of gaseous H_2



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.



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

$$r_1 = k_1 P_{\text{H}_2} (1 - \theta)^2 \quad (2)$$

$$r_2 = k_2 \theta^2 \quad (3)$$

$$r_3 = k_3 \theta \quad (4)$$

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

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\text{H}_2} C}}} \quad (5)$$

Express C using k_1 and k_2 .

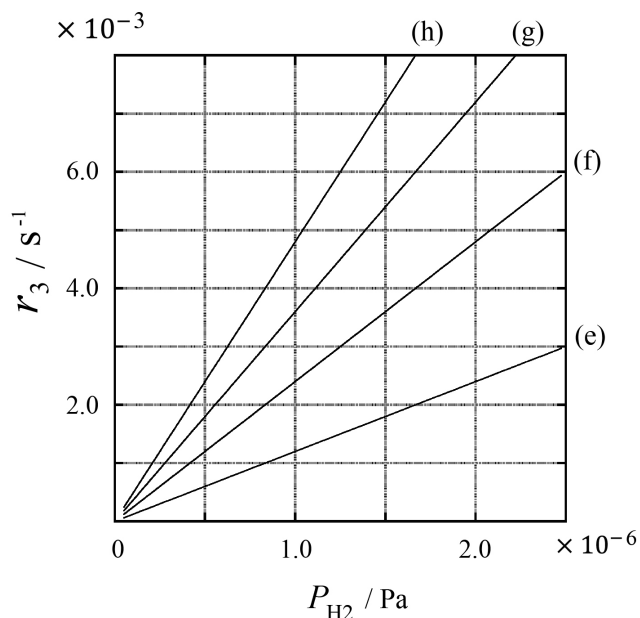
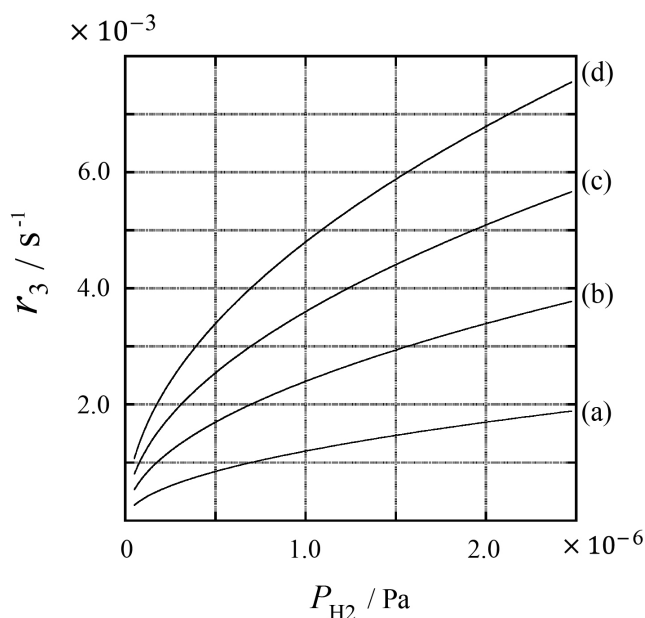
A metal sample with a surface area of $S = 1.0 \times 10^{-3} \text{ m}^2$ was placed in a 1L container ($1\text{L} = 1.0 \times 10^{-3} \text{ m}^3$) with H_2 at pressure $P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$. The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18} \text{ m}^{-2}$. The surface temperature was kept at $T = 400 \text{ K}$.

As the reaction (1) proceeded, P_{H_2} decreased at a constant rate of $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$. Assume that H_2 is an ideal gas and that the volume of the metal sample is negligible.

B.2 Calculate in moles the amount of H atoms absorbed per unit area of the surface per unit time, A [$\text{mol s}^{-1} \text{ m}^{-2}$]. 3pt

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

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



Hydrogen at a Metal Surface

Part A

A.1 (6 pt)

(i)	(ii)	(iii)

A.2 (4 pt)

(i)	(ii)



CHE-4 C-1 A-2

A1-2

English (Switzerland)

Part B

B.1 (5 pt)

$C =$ _____

B.2 (3 pt)

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



CHE-4 C-1 A-3

A1-3

English (Switzerland)

B.3 (3 pt)

$k_3 =$ _____ s^{-1}

B.4 (3 pt)

CHE-4 C-2 C-1

CHE-4 C-2 C
Anastasia Sandamirskaya

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:



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

$$S = k_{\text{B}} \ln W \quad (2)$$

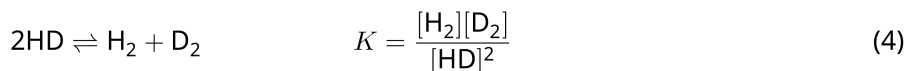
$W = 1$ for $^{12}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}_2$. In contrast, $W = 2$ for a $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}\text{C}^{16}\text{O}^{18}\text{O}$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

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



Calculate the equilibrium constants, K , for eq. 3 at very low (think of $T \rightarrow 0$) and very high (think of $T \rightarrow +\infty$) temperatures. Assume that the reaction remains unchanged at these temperatures and that ΔH converges to a constant value for high temperatures.

The ΔH of the following process can be explained by molecular vibrations.



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} .



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 .

$$\Delta_{\text{D}_2} = \frac{R_{\text{D}_2}}{R_{\text{D}_2}^*} - 1 \quad (9)$$

Here, R_{D_2} refers to $\frac{[\text{D}_2]}{[\text{H}_2]}$ in the sample and $R_{\text{D}_2}^*$ to $\frac{[\text{D}_2]}{[\text{H}_2]}$ at $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

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 $\text{CO}_2[44]$ and $\text{CO}_2[47]$ below. The quantity Δ_{47} is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \quad (10)$$

R_{47} refers to $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ in the sample and R_{47}^* to $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ at $T \rightarrow +\infty$. 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:

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

- 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 $\text{CO}_2[47]$ for the calculation. 9pt

Isotope Time Capsule

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



Molecules that differ only in isotopic composition, such as CH_4 and CH_3D , are called isotopologues. Isotopologues are widely considered to have the same chemical characteristics. In fact, however, there is a slight difference.

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

Consider the following equilibrium:



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

$$S = k_{\text{B}} \ln W \quad (2)$$

$W = 1$ for $^{12}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}_2$.

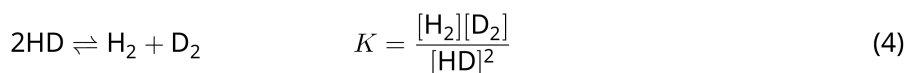
In contrast, $W = 2$ for a $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecule because the oxygen atoms in this molecule are distinguishable. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecules, $W = 2^2 = 4$.

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



Calculate the equilibrium constant, K , for eq. 3 at very low temperatures (as $T \rightarrow 0$) and at very high temperatures (as $T \rightarrow +\infty$). Assume that the reaction remains unchanged at these temperatures and that ΔH converges to a constant value for high temperatures.

The ΔH of the following process can be explained by considering molecular vibrations.



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

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A.2 The vibration of H_2 is at 4161.0 cm^{-1} . 8pt

Calculate ΔH of the following equation at $T = 0$ K in units of J mol^{-1} .



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 is 1 Da and the mass of D is 2 Da.

In a system in equilibrium, the molar ratios among H_2 , HD, and D_2 depend on the temperature. We define Δ_{D_2} as the change of the molar ratio of D_2 .

$$\Delta_{\text{D}_2} = \frac{R_{\text{D}_2}}{R_{\text{D}_2}^*} - 1 \quad (9)$$

Here, R_{D_2} refers to $\frac{[\text{D}_2]}{[\text{H}_2]}$ in the sample and $R_{\text{D}_2}^*$ to $\frac{[\text{D}_2]}{[\text{H}_2]}$ at $T \rightarrow +\infty$.

It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

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

A doubly substituted isotopologue contains two heavy isotope atoms in one molecule.

The molar ratio of the doubly substituted isotopologue increases with decreasing temperature.

Consider the molar ratio of CO_2 molecules with molecular weights of 44 and 47, which are described as $\text{CO}_2[44]$ and $\text{CO}_2[47]$ below. The quantity Δ_{47} is defined as:

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

- A.4** The R_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-5} . 9pt
Determine the temperature using this R_{47} .
 This temperature corresponds to the air temperature during the era in which the plankton lived.
 Consider only the most common isotopologue of $\text{CO}_2[47]$ for the calculation.



CHE-4 C-2 A-1

A2-1
English (Switzerland)

Isotope Time Capsule

A.1 (8 pt)

$\underline{T \rightarrow 0 : K =}$ _____ , $\underline{T \rightarrow +\infty : K =}$ _____



CHE-4 C-2 A-2

A2-2

English (Switzerland)

A.2 (8 pt)

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



CHE-4 C-2 A-3

A2-3

English (Switzerland)

A.3 (10 pt)

$\Delta_{D_2} =$ _____



CHE-4 C-2 A-4

A2-4

English (Switzerland)

A.4 (9 pt)

$T =$ _____ K

CHE-4 C-3 C-1

CHE-4 C-3 C
Anastasia Sandamirskaya

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 $1.00 \times 10^{-2} \text{ mol L}^{-1}$, $1.00 \times 10^{-3} \text{ mol L}^{-1}$, and $1.00 \times 10^{-4} \text{ mol L}^{-1}$, respectively, which are correlated via the following acid-base equilibrium:



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.



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 $\varepsilon_D/\varepsilon_M$ 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 $\varepsilon_D/\varepsilon_M$ at λ_{B2} . 6pt

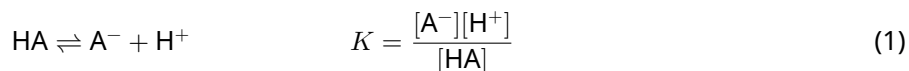
Lambert-Beer Law

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 $1.00 \times 10^{-2} \text{ mol L}^{-1}$, $1.00 \times 10^{-3} \text{ mol L}^{-1}$, and $1.00 \times 10^{-4} \text{ mol L}^{-1}$, respectively, which are correlated via the following acid-base equilibrium:



In Part A, the optical path length is l . 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 .
Solution **X** was then diluted to twice its initial volume using hydrochloric acid with a pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1 .
10pt
- Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-} represent the absorption coefficients (at λ_1) of HA and A^- , respectively.

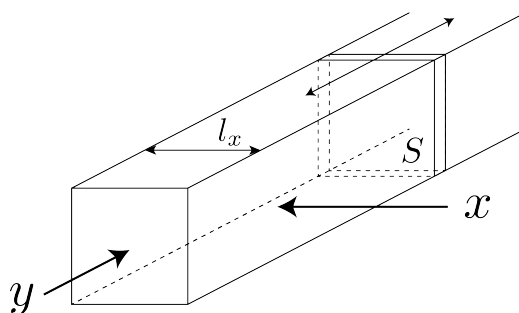
Part B

Consider the following equilibrium in the gas phase.



A cuboidal container has a transparent movable wall with a cross-section of S (see the figure below). The container is filled with pure gas D at a pressure P , and equilibrium is established while the total pressure is maintained at P .

The absorbance of the gas is $A = \varepsilon(n/V)l$, where ε is the absorption coefficient, n the amount of the gas in moles, V the volume of the gas, and l the optical path length. 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 in direction x (i.e. $l = l_x$) was A_{B1} both at the initial state and after the equilibrium. 6pt

Determine the ratio $\varepsilon_D/\varepsilon_M$ at λ_{B1} , where ε_D and ε_M represent the absorption coefficients of D and of M, respectively.

- B.2** The absorbance of the gas at λ_{B2} measured in direction y was A_{B2} both at the initial state (where $l = l_{y0}$) and after the equilibrium (where $l = l_y$). 6pt

Determine the ratio $\varepsilon_D/\varepsilon_M$ at λ_{B2} .



CHE-4 C-3 A-1

A3-1
English (Switzerland)

Lambert-Beer Law

Part A

A.1 (10 pt)

(Continued on the next page)



CHE-4 C-3 A-2

A3-2

English (Switzerland)

A.1 (cont.)

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



CHE-4 C-3 A-3

A3-3

English (Switzerland)

Part B

B.1 (6 pt)

$$\varepsilon_D/\varepsilon_M =$$



CHE-4 C-3 A-4

A3-4

English (Switzerland)

B.2 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

CHE-4 C-4 C-1

CHE-4 C-4 C
Anastasia Sandamirskaya

ICHO Problem 4

Cover sheet

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

The Redox Chemistry of Zinc

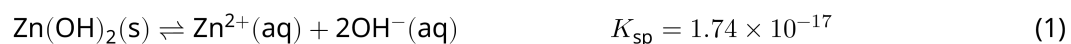
11 % of the total							
Question	A.1	A.2	B.1	B.2	B.3	B.4	Total
Points	6	5	4	3	5	9	32
Score							



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



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

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

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

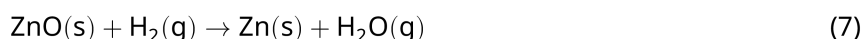
A.2 A saturated aqueous solution of $\text{Zn}(\text{OH})_2(\text{s})$ with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. **Calculate** the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature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

Part B

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

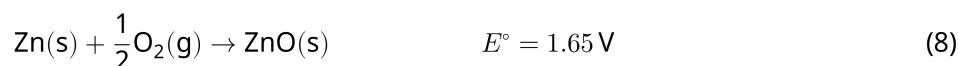


The zinc oxide is then reduced to metallic zinc by reaction with hydrogen:



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 $\Delta G_{\text{ZnO}}(300^\circ\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{H}_2\text{O}}(300^\circ\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$, respectively. 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° .



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



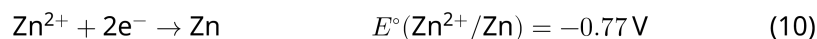
Mt. Fuji

- 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°C (February) and 3776 m, respectively. The atmospheric pressure is represented by 5pt

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

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

- B.4** **Calculate** the Gibbs energy change for reaction (6) at 25°C . Note that the standard reduction potentials, $E^{\circ}(\text{Zn}^{2+}/\text{Zn})$ and $E^{\circ}(\text{O}_2/\text{H}_2\text{O})$ at 25°C and 1 bar are given as (10) and (11), respectively. 9pt



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 in alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to purify the water. The precipitate is reduced to recover metallic zinc.

Part A

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



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

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

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

A.2 A saturated aqueous solution of $\text{Zn}(\text{OH})_2(\text{s})$ with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. 5pt

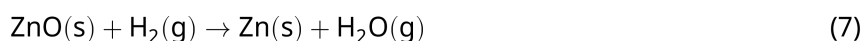
Calculate the molar percentage of zinc that precipitates when the pH is increased from 7.00 to 12.00.
Ignore the volume and temperature changes.

Part B

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



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



B.1 It is necessary to reduce the partial pressure of the water vapour formed, so reaction (7) can proceed at a constant hydrogen pressure of 1 bar. 4pt

Calculate the upper limit for the partial pressure of water vapour to allow reaction (7) to proceed at 300 °C.

Gibbs free energies of formation at 300 °C and 1 bar for all gaseous species are:

$$\Delta G_{\text{ZnO}}(300^\circ\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{H}_2\text{O}}(300^\circ\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$$

Metallic zinc is used as a negative electrode (anode) material for metal-air batteries. The electrode consists of Zn and ZnO.

At 25 °C and pressure of 1 bar, the following redox reaction generates electricity with the electromotive force (e.m.f.), E° .



B.2 A zinc-air battery was discharged at 20 mA for 24 hours. 3pt

Calculate the change in mass of the negative electrode (anode) of the battery.



Mt. Fuji

B.3 Consider the change in e.m.f. of a zinc-air battery due to the environment. 5pt

Calculate the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are -38°C (February) and 3776 m, respectively.

The atmospheric pressure is represented by

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

at altitude h [m] and temperature T [$^\circ\text{C}$].

The molar proportion of oxygen in the atmosphere is 21%.

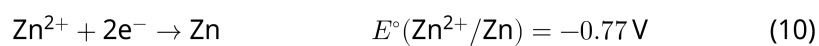
The Gibbs free energy change of reaction (8) at -38°C and 1 bar is

$$\Delta G_{\text{ZnO}}(-38^\circ\text{C}) = -3.26 \times 10^2 \text{ kJ mol}^{-1}.$$

B.4 Calculate the Gibbs free energy change for reaction (6) at 25 °C.

9pt

The standard reduction potentials at 25 °C and 1 bar, $E^\circ(\text{Zn}^{2+}/\text{Zn})$ and $E^\circ(\text{O}_2/\text{H}_2\text{O})$ are given as (10) and (11).





CHE-4 C-4 A-1

A4-1
English (Switzerland)

The Redox Chemistry of Zinc

Part A

A.1 (6 pt)

_____ < pH < _____



CHE-4 C-4 A-2

A4-2

English (Switzerland)

A.2 (5 pt)

%



CHE-4 C-4 A-3

A4-3

English (Switzerland)

Part B

B.1 (4 pt)

$p_{\text{H}_2\text{O}} =$ _____ bar

B.2 (3 pt)

_____ g



CHE-4 C-4 A-4

A4-4
English (Switzerland)

B.3 (5 pt)

_____ V



CHE-4 C-4 A-5

A4-5

English (Switzerland)

B.4 (9 pt)

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

CHE-4 C-5 C-1

CHE-4 C-5 C
Anastasia Sandamirskaya

ICHO

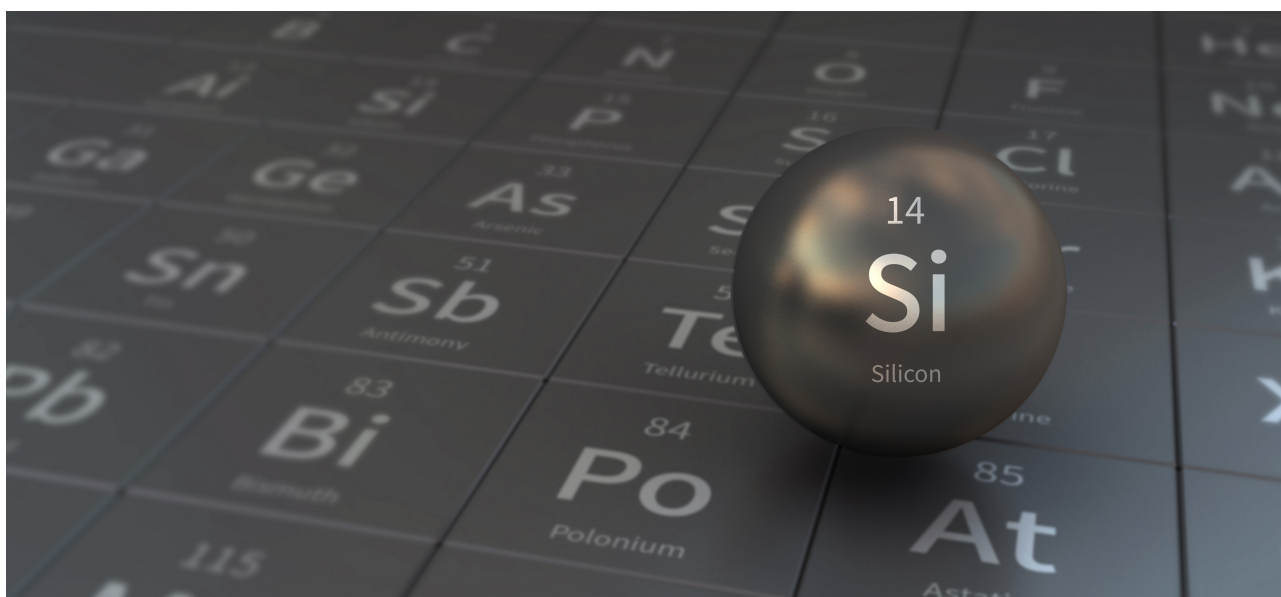
Problem 5

Cover sheet

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

Mysterious Silicon

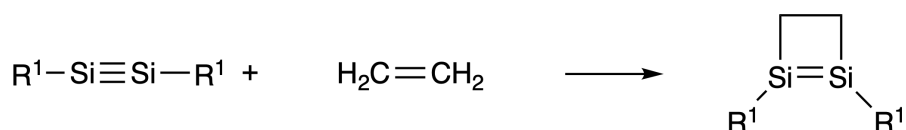
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	Total
Points	9	7	6	10	5	15	8	60
Score								



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 $R^1-Si \equiv Si-R^1$ (R : organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.



When $R^1-Si \equiv Si-R^1$ is treated with an alkyne ($R^2-C \equiv C-R^2$), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of $R^2-C \equiv C-R^2$ 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 $(R^1-Si)_2(R^2-C)_4$.



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 $\text{R}^1 = \text{R}^2 = \text{H}$) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1). 7pt

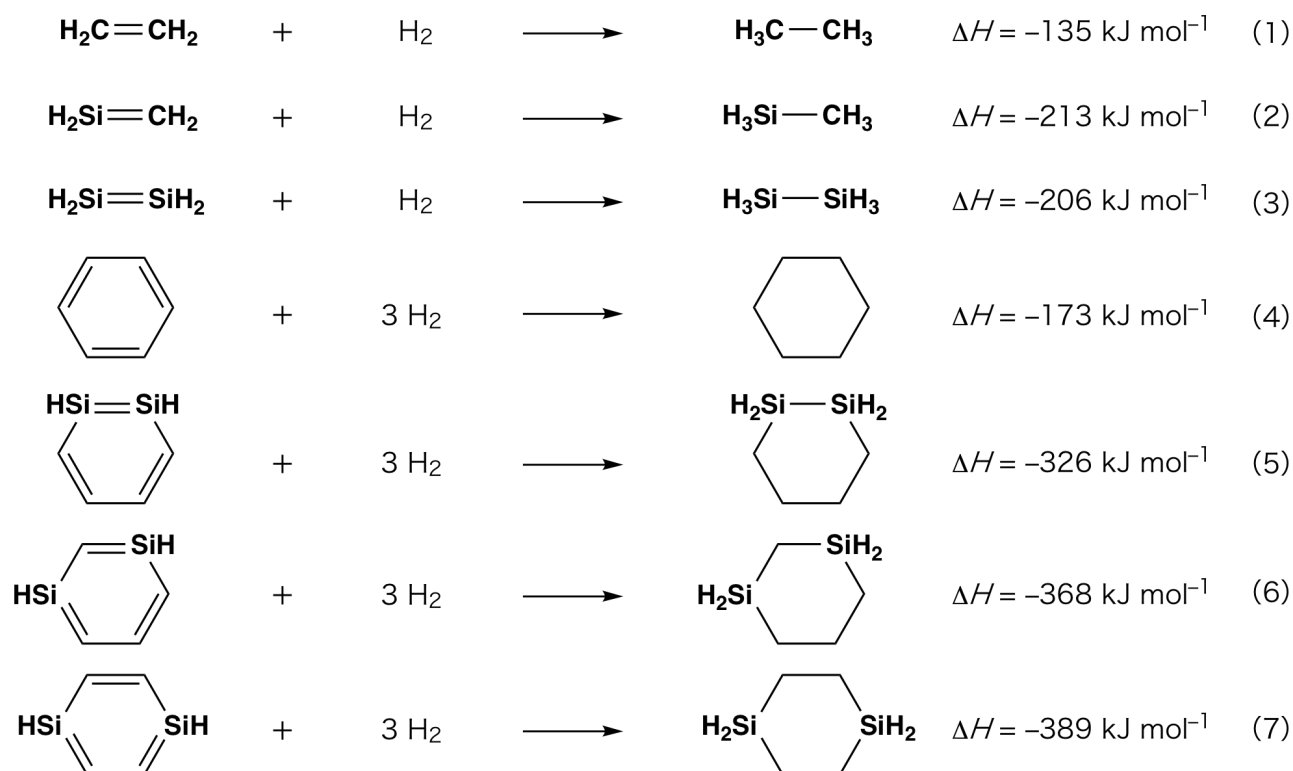


Fig. 1

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 ($188.053 \text{ g mol}^{-1}$) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $\text{Ce}_2(\text{SO}_4)_3$ ($568.424 \text{ g mol}^{-1}$) 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 $\text{Si}(\text{OH})_4$.

B.1 Write the balanced equation for the reaction of Na_2SiF_6 with $\text{Ce}_2(\text{SO}_4)_3$. 5pt

• Reaction of CCl_4 with Na_2SiF_6 :

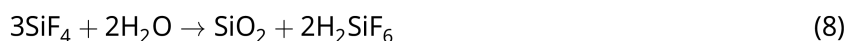
(Substance losses by e.g. evaporation are negligible during the following operations.)

Na_2SiF_6 ($x \text{ [g]}$) 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:



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.

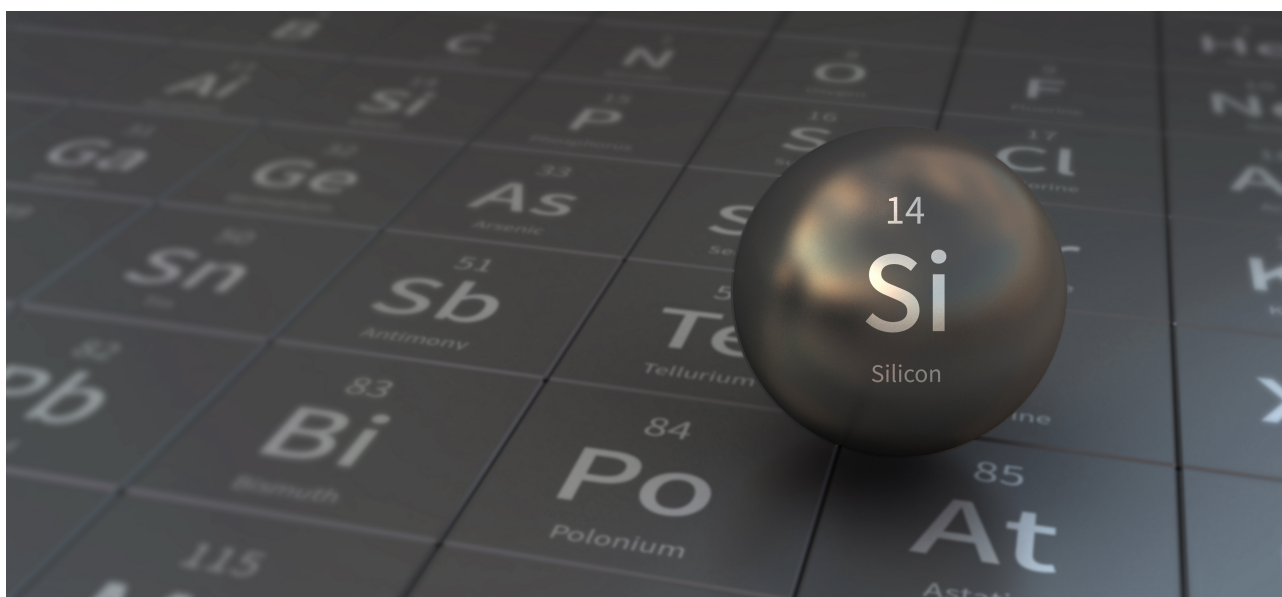
It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

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

Mysterious Silicon

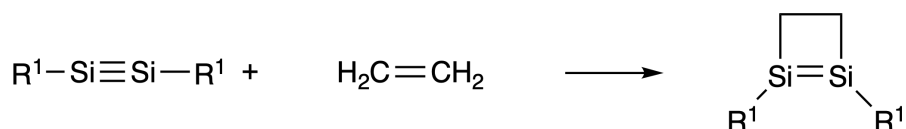
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	Total
Points	9	7	6	10	5	15	8	60
Score								



The group 14 elements carbon and silicon differ significantly in their properties.

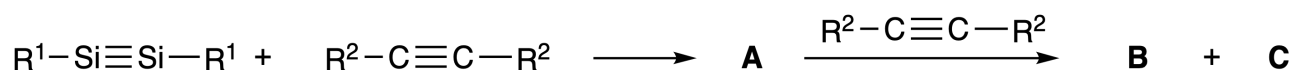
Part A

Unlike the carbon-carbon triple bond, the silicon-silicon triple bond, $R^1-Si \equiv Si-R^1$ (R: organic substituent), is extremely reactive. For example, it reacts with ethene to form a four-membered ring.



When $R^1-Si \equiv Si-R^1$ is treated with an alkyne ($R^2-C \equiv C-R^2$), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of **A** with another molecule of $R^2-C \equiv C-R^2$ gives isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures.

These so-called 'disilabenzenes' contain a six-membered ring and can be formulated as $(R^1-Si)_2(R^2-C)_4$.



^{13}C NMR analysis of the corresponding Si_2C_4 six-membered ring skeletons 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, as one of the possible resonance structures. 9pt

A.2 Calculate the aromatic stabilisation energy (ASE) for benzene and **C** (in the case of $\text{R}^1 = \text{R}^2 = \text{H}$) as positive values, given the enthalpy change of some hydrogenation reactions of unsaturated systems shown below (Fig. 1). 7pt

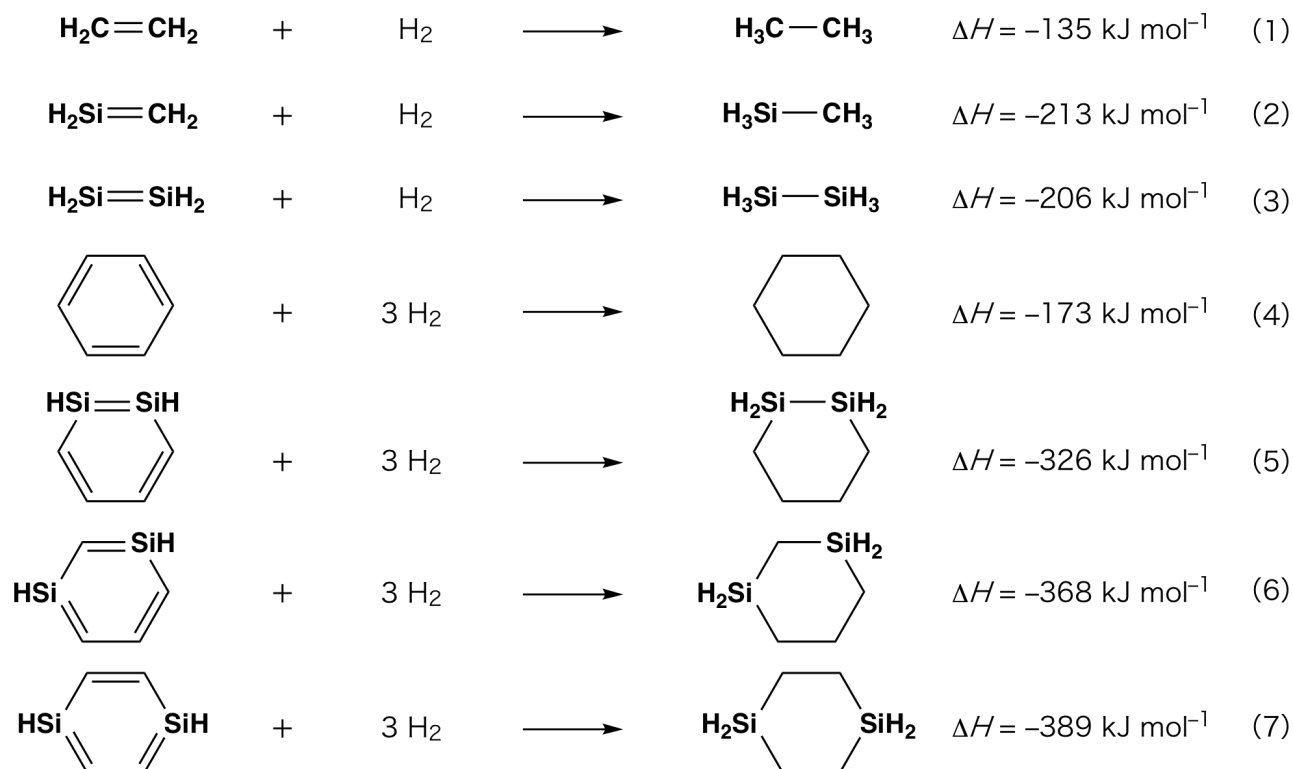


Fig. 1

When a xylene solution of **C** is heated, it undergoes isomerisation 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 isomerisation from **C** to **D** and to **E** proceeds via transformations of π -bonds into σ -bonds without breaking any σ -bonds. ^{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 (more than four substituents) with electronegative elements such as fluorine. Like metal fluorides, highly coordinated silicon fluorides can also act as fluorination reagents.

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

• Standardisation of Na_2SiF_6 solution :

• Preparation

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

Aqueous solution **G**: 6.86 g of $\text{Ce}_2(\text{SO}_4)_3$ ($568.424 \text{ g mol}^{-1}$) dissolved in water (total volume: 200 mL).

• Precipitation Titration Procedure

Solution **F** (50.0 mL) was titrated with solution **G** in the presence of xlenol orange, an indicator which coordinates to Ce^{3+} . After adding 18.8 mL of solution **G**, the colour of the solution changed from yellow to magenta. The precipitate formed is a binary compound that contains Ce^{3+} , and the only resulting silicon compound is $\text{Si}(\text{OH})_4$.

B.1 Write the balanced equation for the reaction of Na_2SiF_6 with $\text{Ce}_2(\text{SO}_4)_3$.

5pt

• Reaction of CCl_4 with Na_2SiF_6 :

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

Na_2SiF_6 ($x \text{ [g]}$) was added to CCl_4 (500.0 g) and heated to 300 °C in a sealed vessel.

The unreacted Na_2SiF_6 and NaCl produced 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 integrals in the ^{19}F NMR spectrum are proportional to the number of fluorine nuclei.

Table 1

¹⁹ F NMR data	CFCl ₃	CF ₂ Cl ₂	CF ₃ Cl	CF ₄
Integral	45.0	65.0	18.0	2.0

SiF₄ is hydrolysed to form H₂SiF₆ according to the following eq. 8:



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

The precipitate of unreacted Na₂SiF₆ and NaCl, which was removed by filtration in the initial step (previously 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 the entire amount of solution **J**: 61.6 mL.

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

The presence of NaCl or SiO₂ has no effect on the precipitation titration.

B.2 Calculate the mass of NaCl produced in the reaction vessel (information previously underlined), and calculate the mass (x [g]) of the Na₂SiF₆ used as starting material. 15pt

B.3 77.8% of the CCl₄ used as a starting material did not react. Calculate the mass of CF₃Cl generated. 8pt



CHE-4 C-5 A-1

A5-1
English (Switzerland)

Mysterious Silicon

Part 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}



CHE-4 C-5 A-2

A5-2

English (Switzerland)

A.3 (6 pt)

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

A.4 (10 pt)

D (5 pt)

E (5 pt)



CHE-4 C-5 A-3

A5-3

English (Switzerland)

Part B

B.1 (5 pt)

B.2 (15 pt)

(Continued on the next page)



CHE-4 C-5 A-4

A5-4
English (Switzerland)

B.2 (cont.)

NaCl : _____ g, Na₂SiF₆ : _____ g



CHE-4 C-5 A-5

A5-5

English (Switzerland)

B.3 (8 pt)

CF_3Cl : _____ g

CHE-4 C-6 C-1

CHE-4 C-6 C
Anastasia Sandamirskaya

ICHO

Problem 6

Cover sheet

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

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:

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

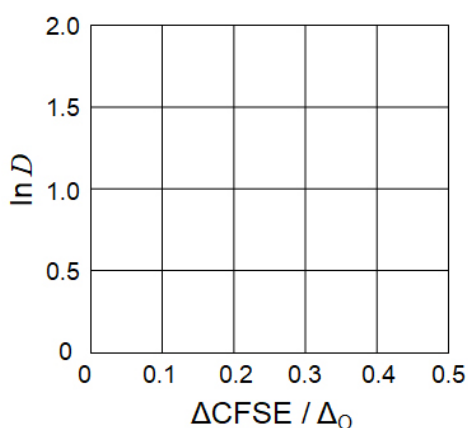
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

	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** $|\text{CFSE}^O - \text{CFSE}^T| = \Delta\text{CFSE}$ 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 $\Delta\text{CFSE} / \Delta_o$ 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 $[\text{CuO}_6]$ octahedron, the Cu–O length along the z-axis (l_z) is longer than that of the x-axis (l_x), and $[\text{CuO}_6]$ 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}).

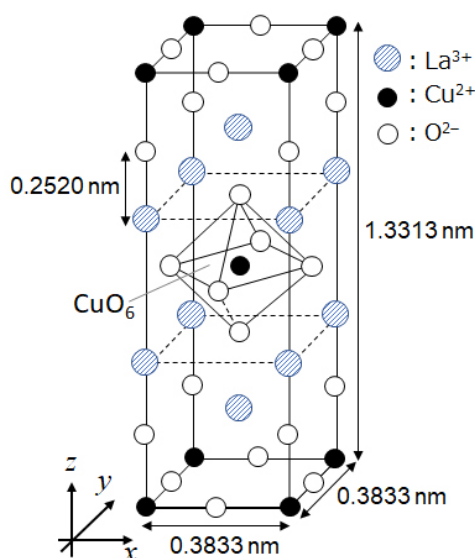


Fig. 1

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 $\text{C}_4\text{H}_2\text{O}_4$, 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 $[\text{CuO}_6]$ 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

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ is composed of four CH_3CO_2^- coordinated to two Cu^{2+} (Fig. 2A). $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ 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 $\text{Cu}_4(\text{L1})_4$ 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.

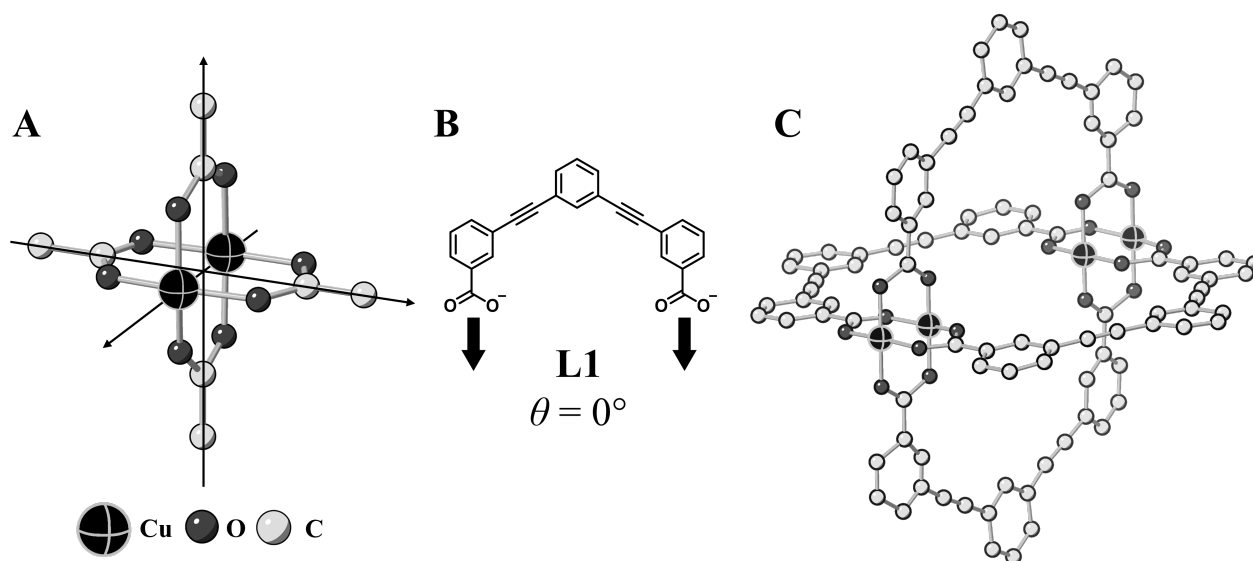
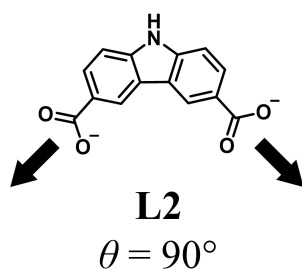


Fig. 2

- 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 $\text{Cu}_n(\text{L2})_m$, 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



A zinc complex, $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$, contains four tetrahedral Zn^{2+} , six CH_3CO_2^- , and one O^{2-} (Fig. 3A). In $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$, 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**, $\theta = 180^\circ$) 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 $[\text{Zn}_4\text{O}(\text{L3})_3]_n$, 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.

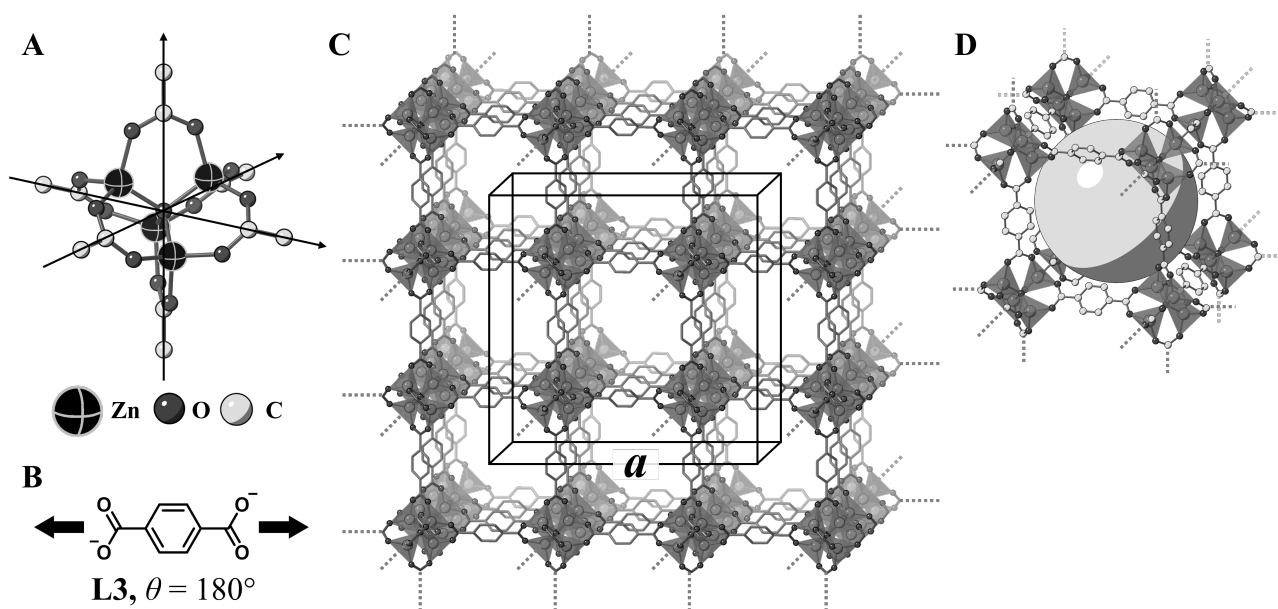


Fig. 3

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 $3.0 \times 10^2 \text{ mL}$ of CO_2 gas in the pores at 1 bar and 25°C . **Calculate** the average number of CO_2 molecules per pore. 5pt

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 has many volcanoes. When silicate minerals crystallize from magma, some transition-metal ions (M^{n+}) in the magma are incorporated into the silicate minerals.

The M^{n+} studied in this problem are coordinated by oxide ions (O^{2-}). They adopt a four-coordinate tetrahedral (T_d) geometry in the magma and a six-coordinate octahedral (O_h) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration.

The distribution coefficient of M^{n+} between the silicate minerals and magma, D , can be expressed by:

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

where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively.

The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

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

In an O_h field, Δ_o is the energy separation of the d-orbitals of M^{n+} and CFSE^O is the crystal-field stabilization energy.

Δ_T and CFSE^T are the equivalents in a T_d field.

A.1 ΔCFSE is defined as:

6pt

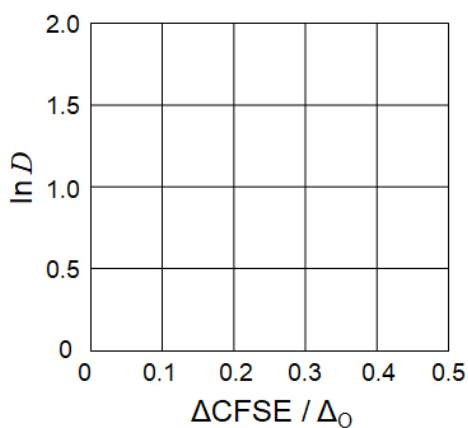
$$\Delta\text{CFSE} = |\text{CFSE}^O - \text{CFSE}^T|$$

Calculate ΔCFSE in terms of Δ_o for Cr^{2+} , Mn^{2+} , and Co^{2+} .

Assume $\Delta_T = 4/9\Delta_o$.

A.2 A linear relationship is observed by plotting $\ln D$ against $\Delta\text{CFSE} / \Delta_o$ as shown below. 3pt

Determine D for Co^{2+} .



Metal oxides, MO (where M is Ca, Ti, V, Mn, or Co), crystallise 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+} , crystallises in a tetragonal unit cell shown in Fig.1.

The $[\text{CuO}_6]$ octahedron is distorted from the regular O_h geometry: the Cu-O length along the z -axis (l_z) is longer than that of the x -axis (l_x).

This distortion removes the degeneracy of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}).

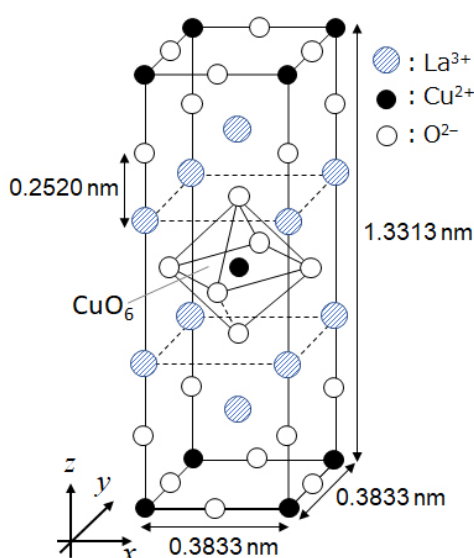


Fig. 1

A can be synthesised by thermal decomposition of complex **B**. **B** is formed by mixing metal chlorides in dilute aqueous ammonia solution containing the diacid, squaric acid $\text{C}_4\text{H}_2\text{O}_4$.

The thermal decomposition of **B** in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallisation 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%. Only water and CO_2 are released in the thermal decomposition 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 Complete the diagram in your answer sheet for Cu^{2+} in the distorted $[\text{CuO}_6]$ 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).
- Draw the electron configuration in the dotted box.

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 La^{3+} substituted by Sr^{2+} based on the mole ratio 4pt
in the substitution reaction.
Note that the valence of the constituent ions and the crystal structure are not altered by the substitution reaction.

Part C

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ is composed of four CH_3CO_2^- ions coordinated to two Cu^{2+} ions (Fig. 2A).

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ 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.

A “cage complex” is formed if a dicarboxylate ligand is used instead of CH_3CO_2^- .

The cage complex $\text{Cu}_4(\text{L1})_4$ 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.

For **L1** $\theta = 0^\circ$.

Note that hydrogen atoms are not shown in Fig. 2.

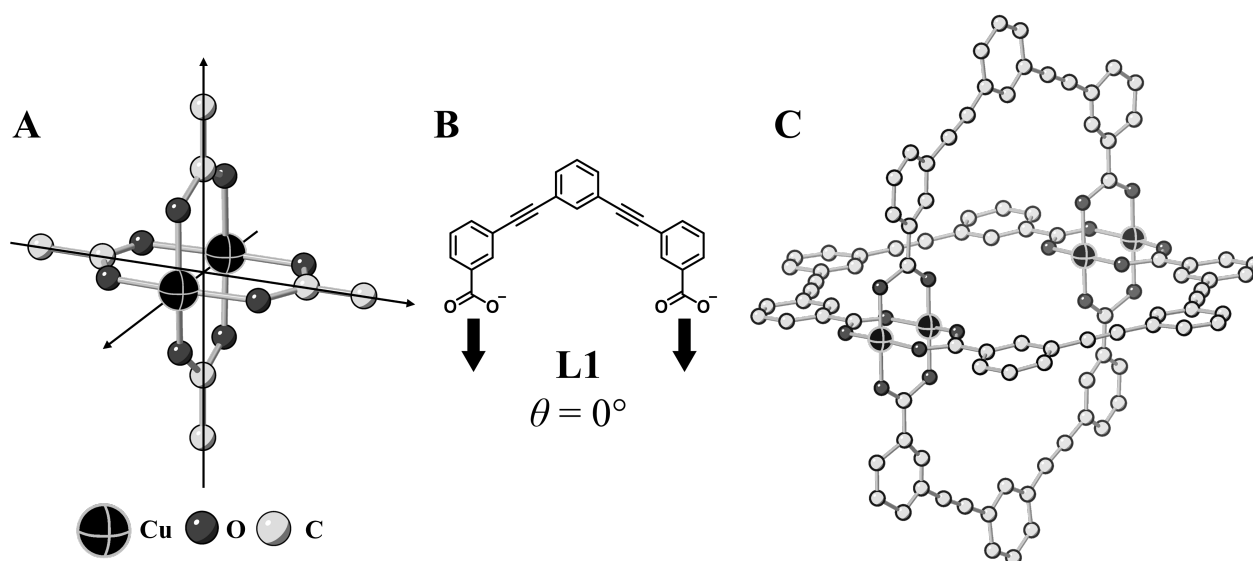
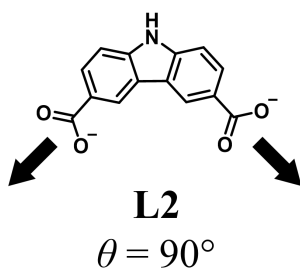


Fig. 2

- C.1** The θ of the planar dicarboxylate **L2** below is fixed to 90° .
 The cage complex formed from **L2** and Cu^{2+} is $\text{Cu}_n(\text{L2})_m$.

5pt

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.



A zinc complex, $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$, contains four tetrahedral Zn^{2+} , six CH_3CO_2^- , and one O^{2-} (Fig. 3A). In $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$, 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**, $\theta = 180^\circ$) 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 $[\text{Zn}_4\text{O}(\text{L3})_3]_n$, 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 grey polyhedron in Fig. 3C and 3D. *Note that hydrogen atoms are not shown in Fig. 3.*

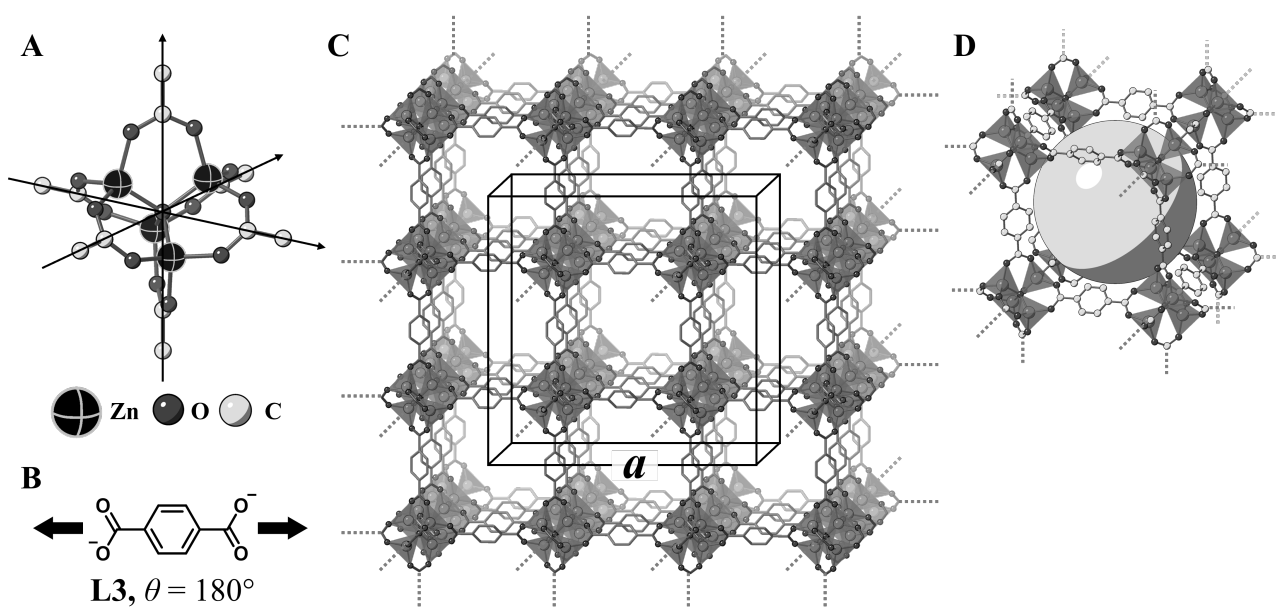


Fig. 3

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

Calculate a in [cm].

C.3 **X** contains a considerable number of pores. 5pt
1 g of **X** can accommodate $3.0 \times 10^2 \text{ mL}$ of CO_2 gas in the pores at 1 bar and 25°C .

Calculate the average number of CO_2 molecules per pore.



CHE-4 C-6 A-1

A6-1
English (Switzerland)

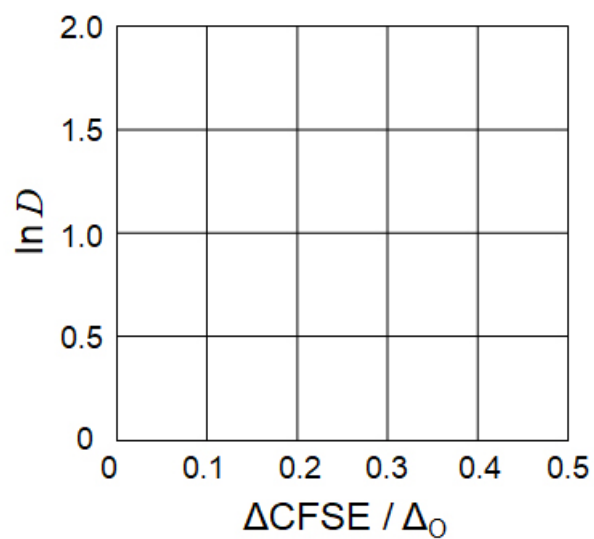
The Solid-State Chemistry of Transition Metals

Part A

A.1 (6 pt)

Cr^{2+} : _____ Δ_{O} , Mn^{2+} : _____ Δ_{O} , Co^{2+} : _____ Δ_{O}

A.2 (3 pt)



D : _____

A.3 (3 pt)



CHE-4 C-6 A-3

A6-3

English (Switzerland)

Part B

B.1 (6 pt)

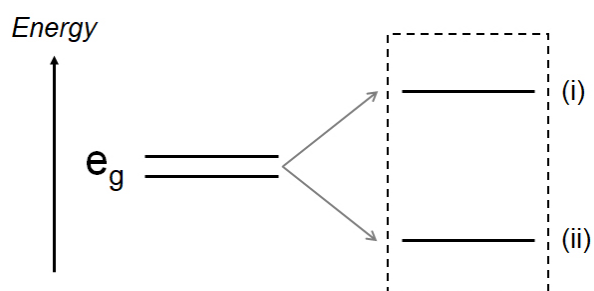
A : _____, B : _____

B.2 (4 pt)

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

B.3 (4 pt)

(i) : _____, (ii) : _____



B.4 (4 pt)

_____ %



CHE-4 C-6 A-5

A6-5

English (Switzerland)

Part C

C.1 (5 pt)

$n =$ _____, $m =$ _____

C.2 (5 pt)

$a =$ _____ cm



CHE-4 C-6 A-6

A6-6

English (Switzerland)

C.3 (5 pt)

CHE-4 C-7 C-1

CHE-4 C-7 C
Anastasia Sandamirskaya

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.



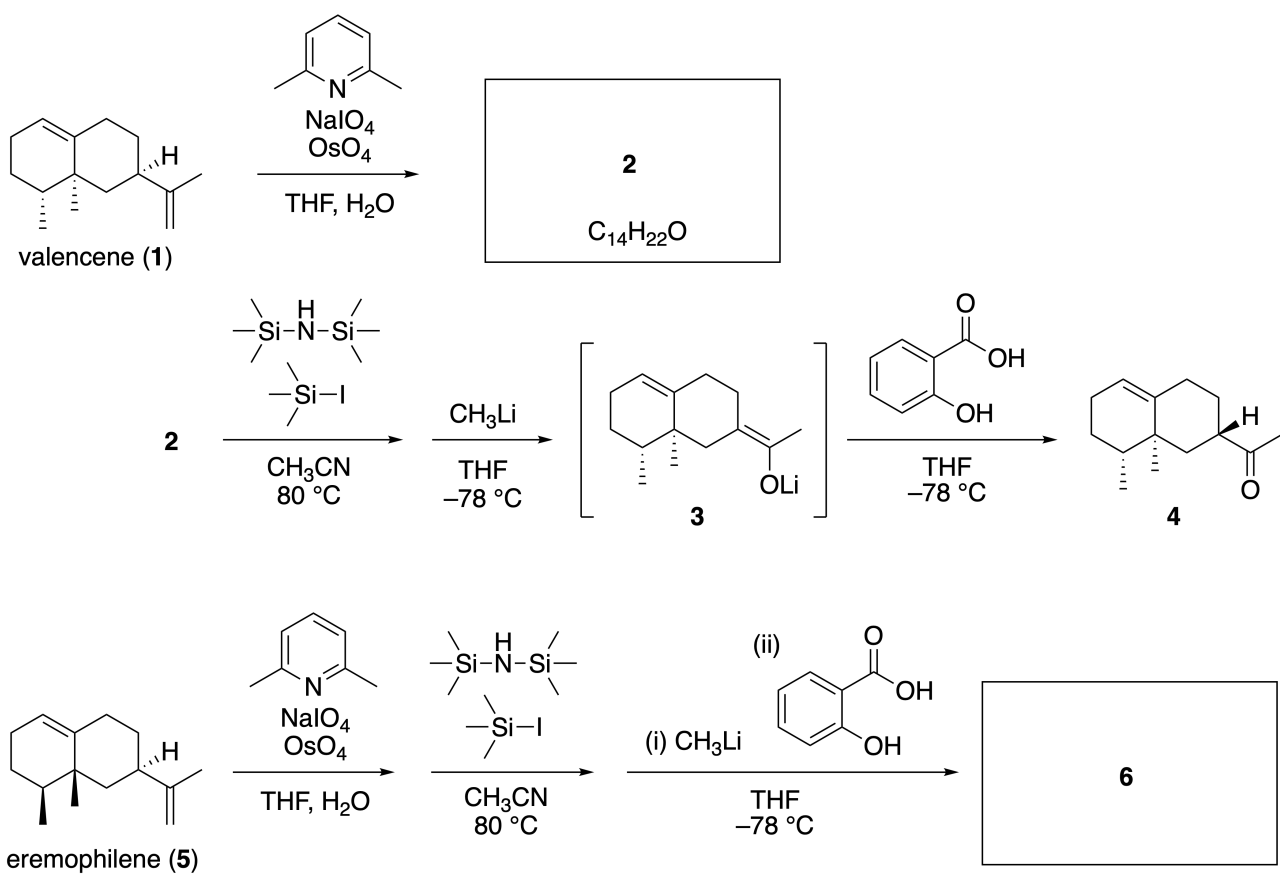
Photo courtesy: Tohoku Univ.

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.



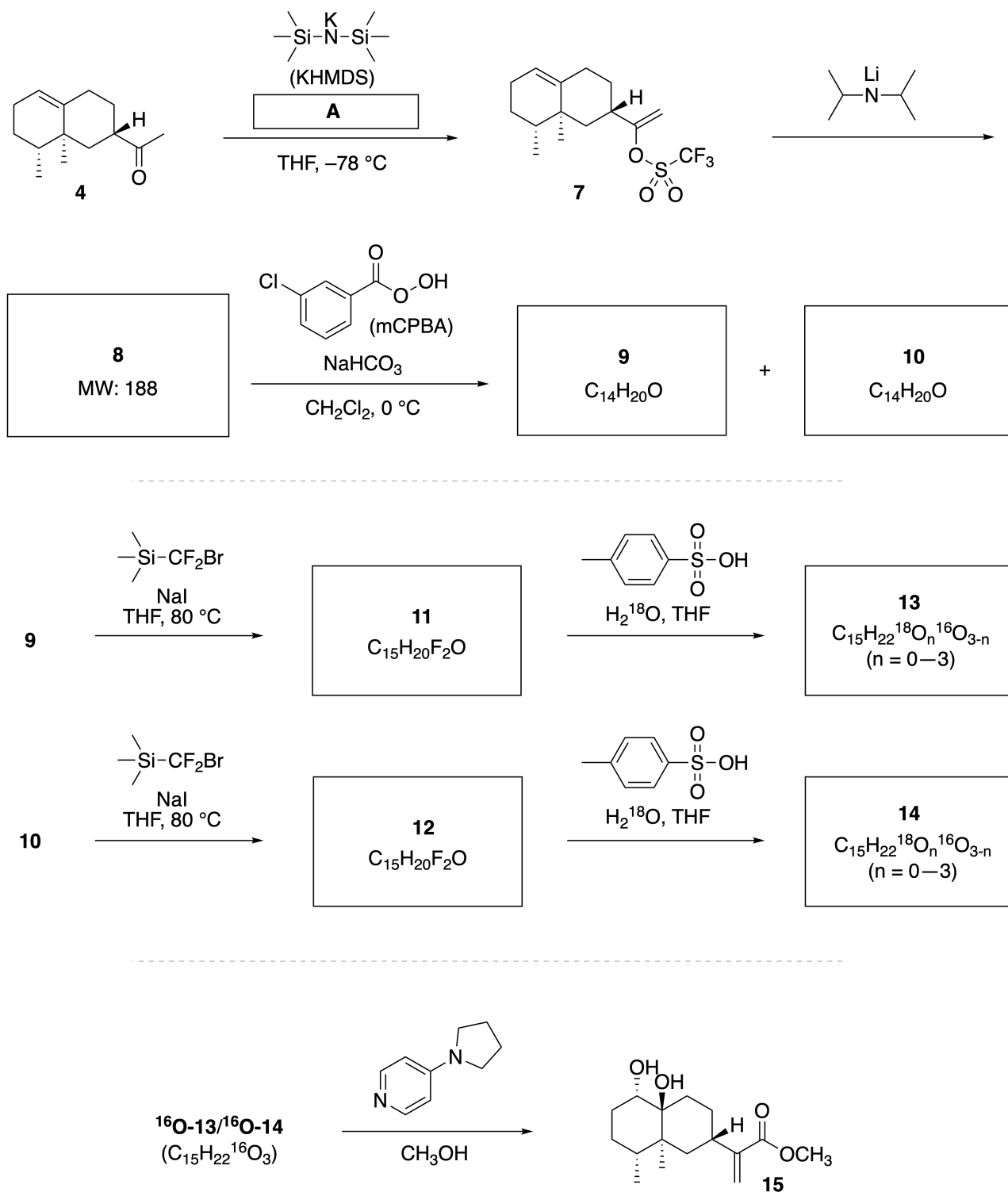
Inula linariifolia



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

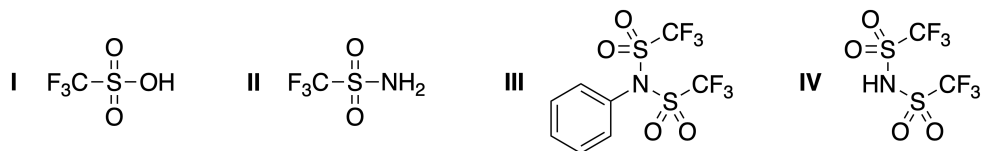
Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume

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.



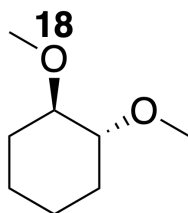
A.2 Choose the appropriate structure for **A**.

2pt



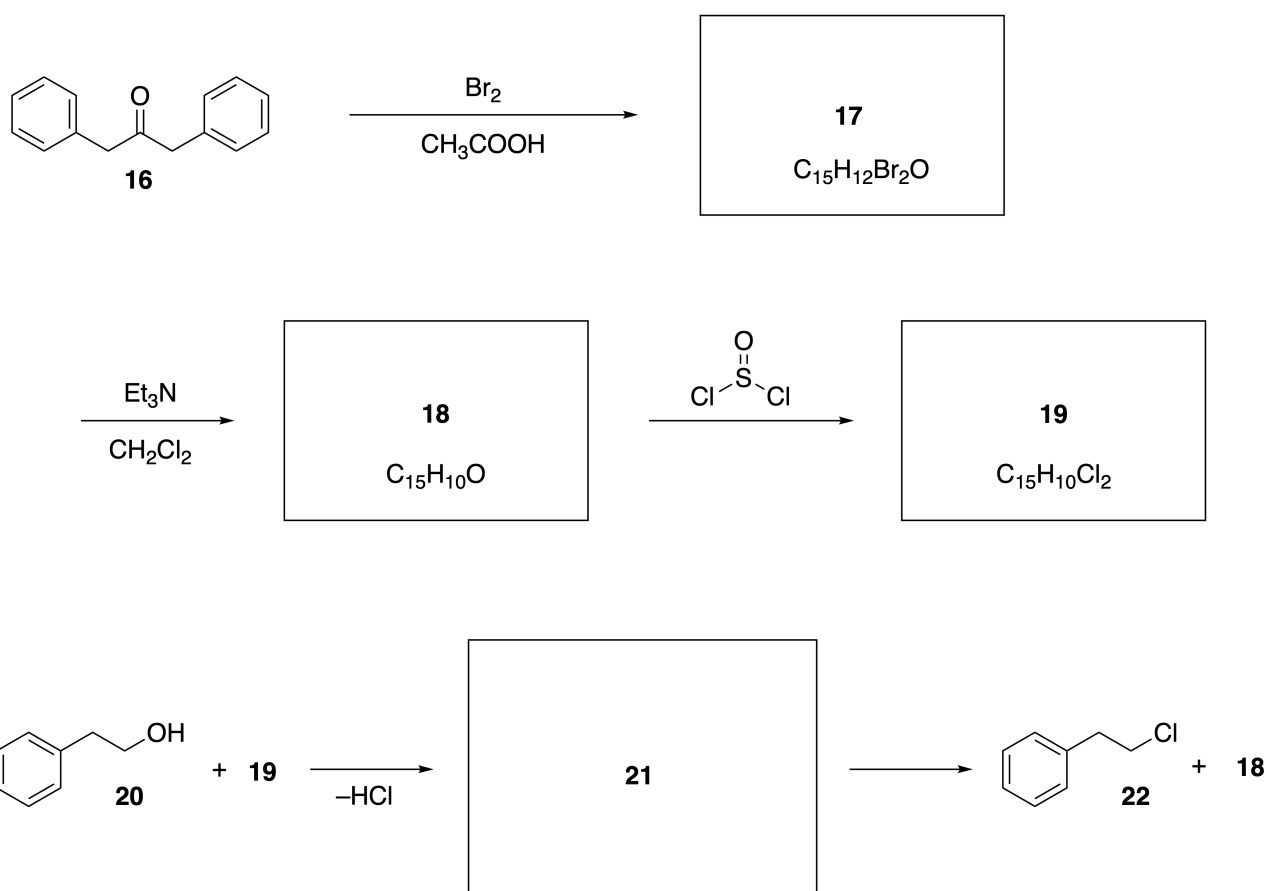
A.3 Draw the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, indicate the introduced ^{18}O atoms for **13** and **14** as shown in the example below.

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**.



^1H 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

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) founded the research field of non-benzenoid aromatic compounds.



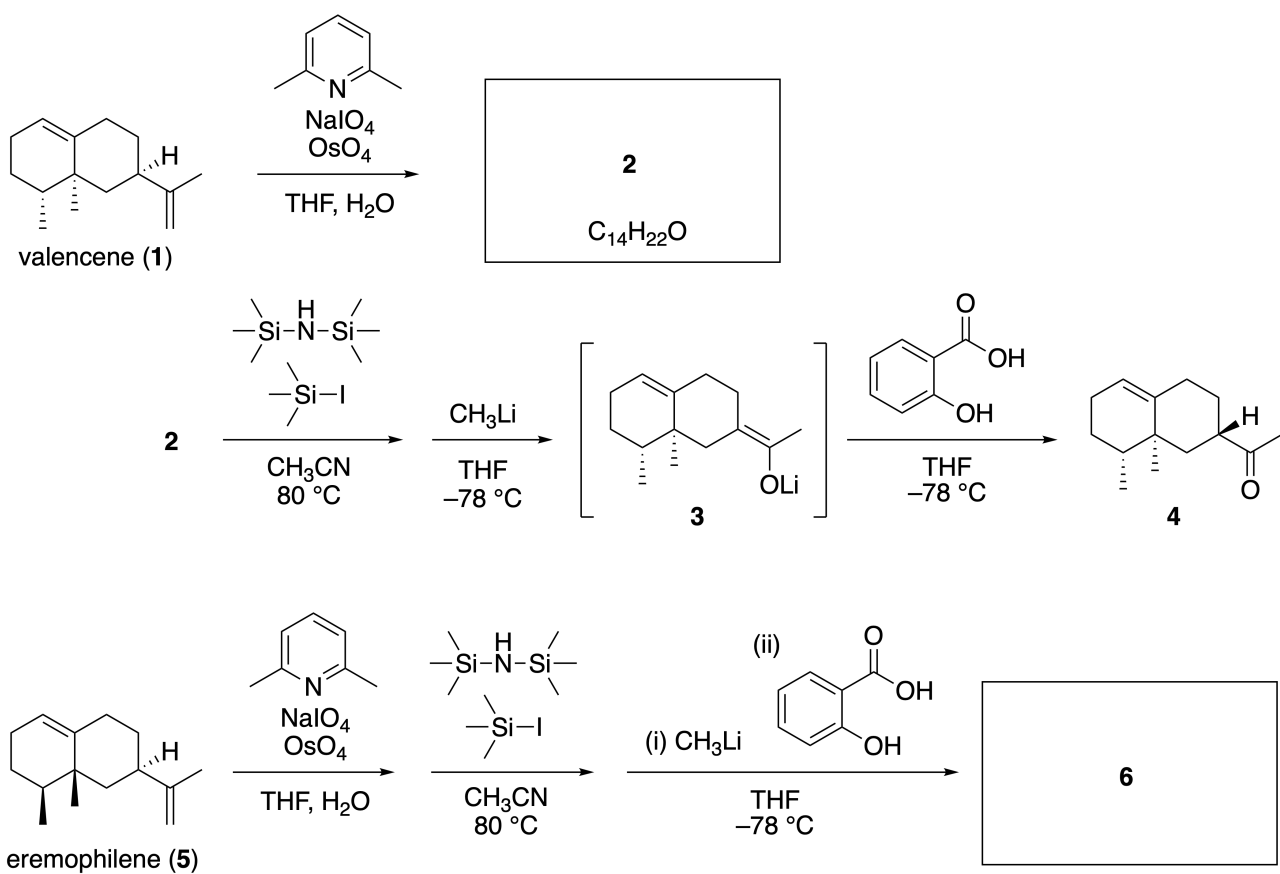
Photo credit: Tohoku Univ.

Part A

Lineariifolianone is a natural product 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



CHE-4 C-7 Q-3

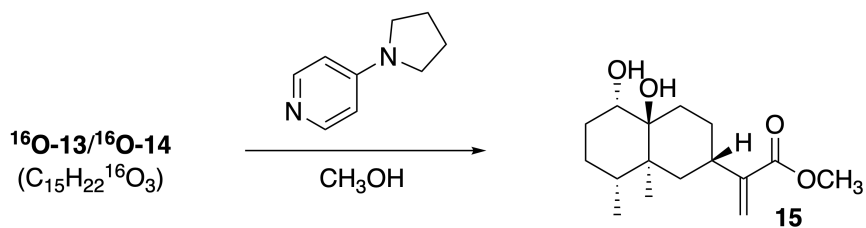
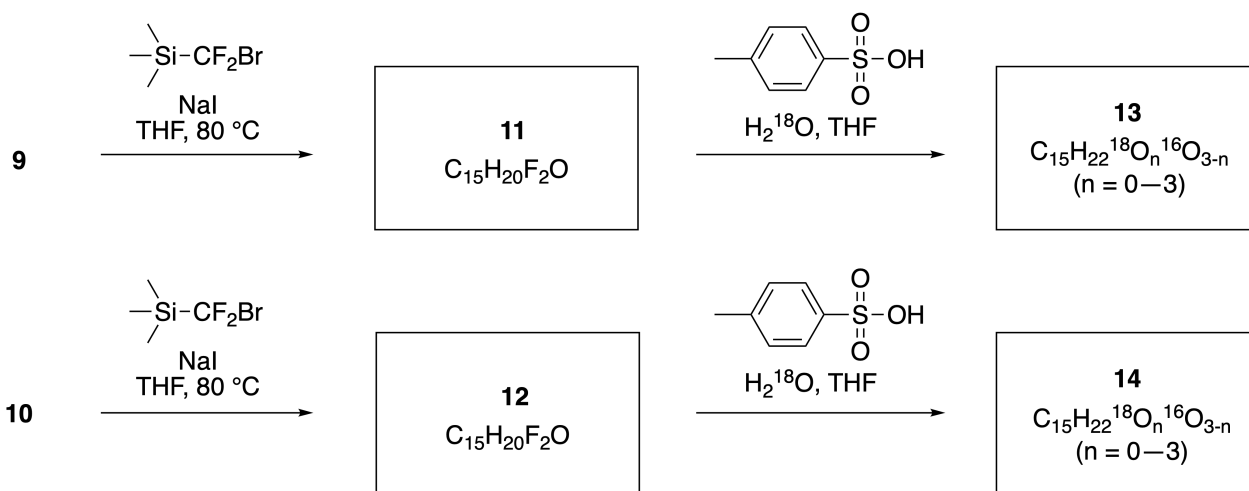
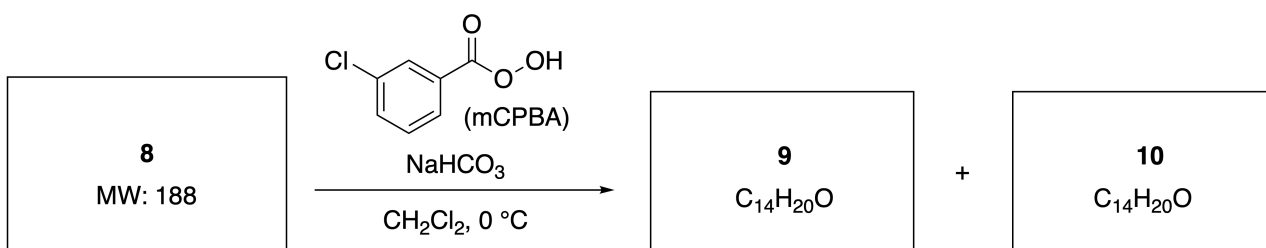
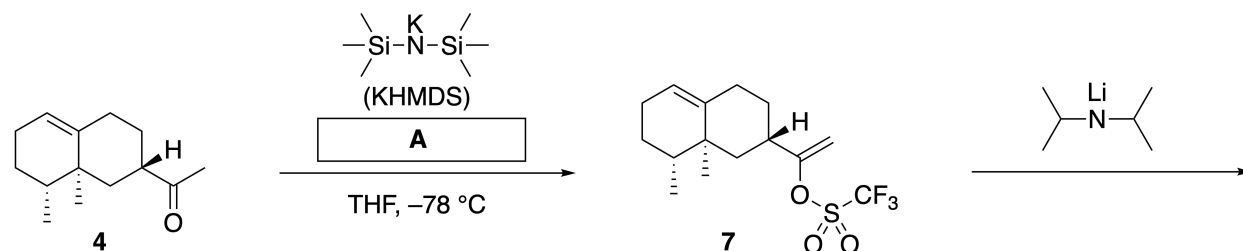
Q7-3

English (Switzerland)

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

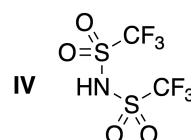
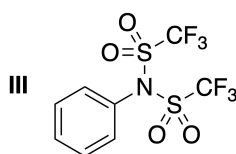
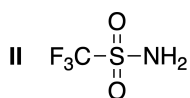
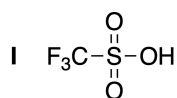
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Compounds **13** and **14** are ^{18}O -labelled isotopomers. Both **13** and **14** provide the same product **15** with identical stereochemistry ignoring isotopic labelling.



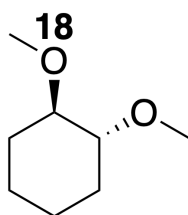
A.2 Choose the appropriate structure for **A**.

2pt



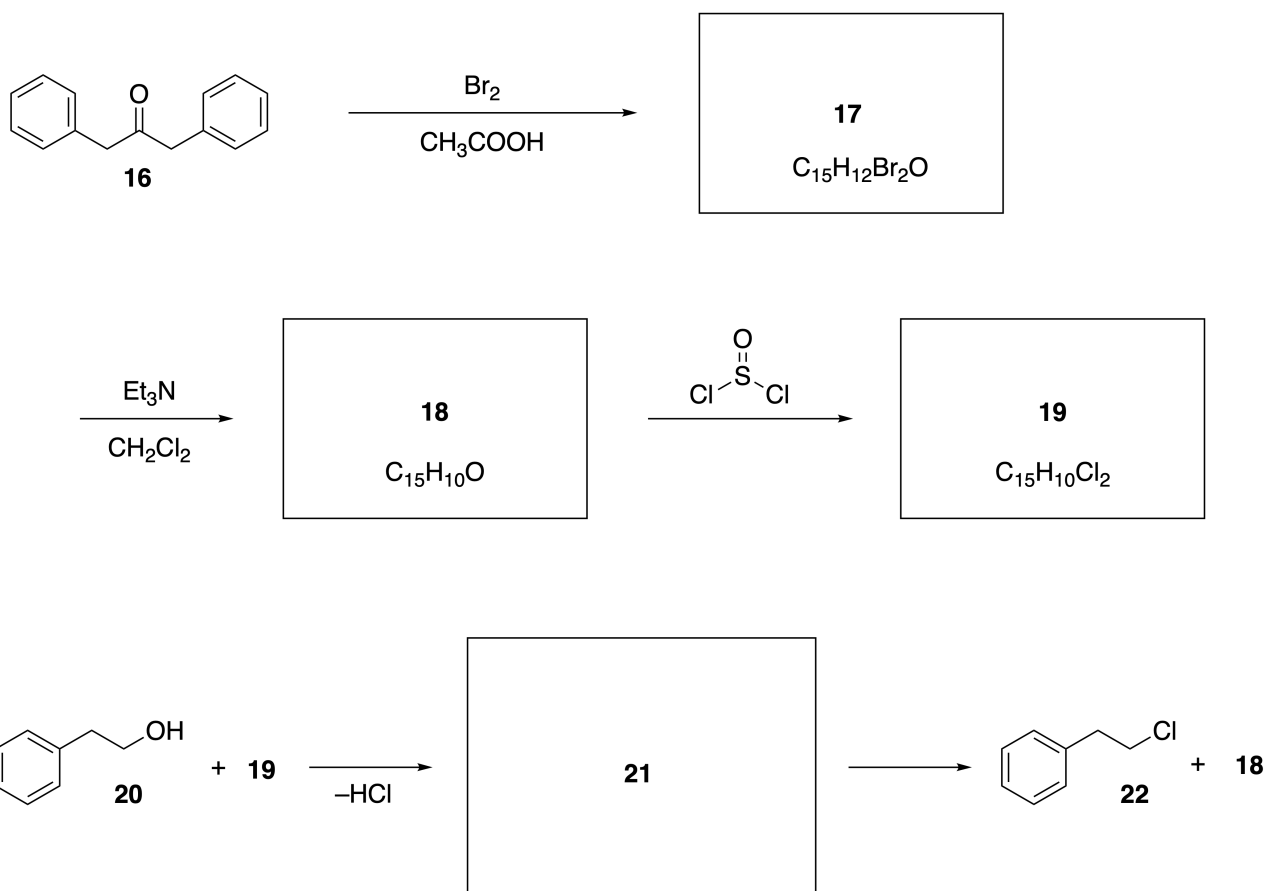
A.3 Draw the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, indicate the introduced ^{18}O atoms for **13** and **14** as shown in the example below.

19pt



Part B

Compound **19** is synthesised as shown below. Linking 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**.



^1H 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**. Stereochemistry is not required.

10pt



CHE-4 C-7 A-1

A7-1
English (Switzerland)

Playing with Non-benzenoid Aromaticity

Part A

A.1 (5 pt)

2 (2 pt)

6 (3 pt)

A.2 (2 pt)

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)



CHE-4 C-7 A-3

A7-3

English (Switzerland)

Part B

B.1 (10 pt)

17 (2 pt)

18 (2 pt)

19 (3 pt)

21 (3 pt)

CHE-4 C-8 C-1

CHE-4 C-8 C
Anastasia Sandamirskaya

IChO Problem 8

Cover sheet

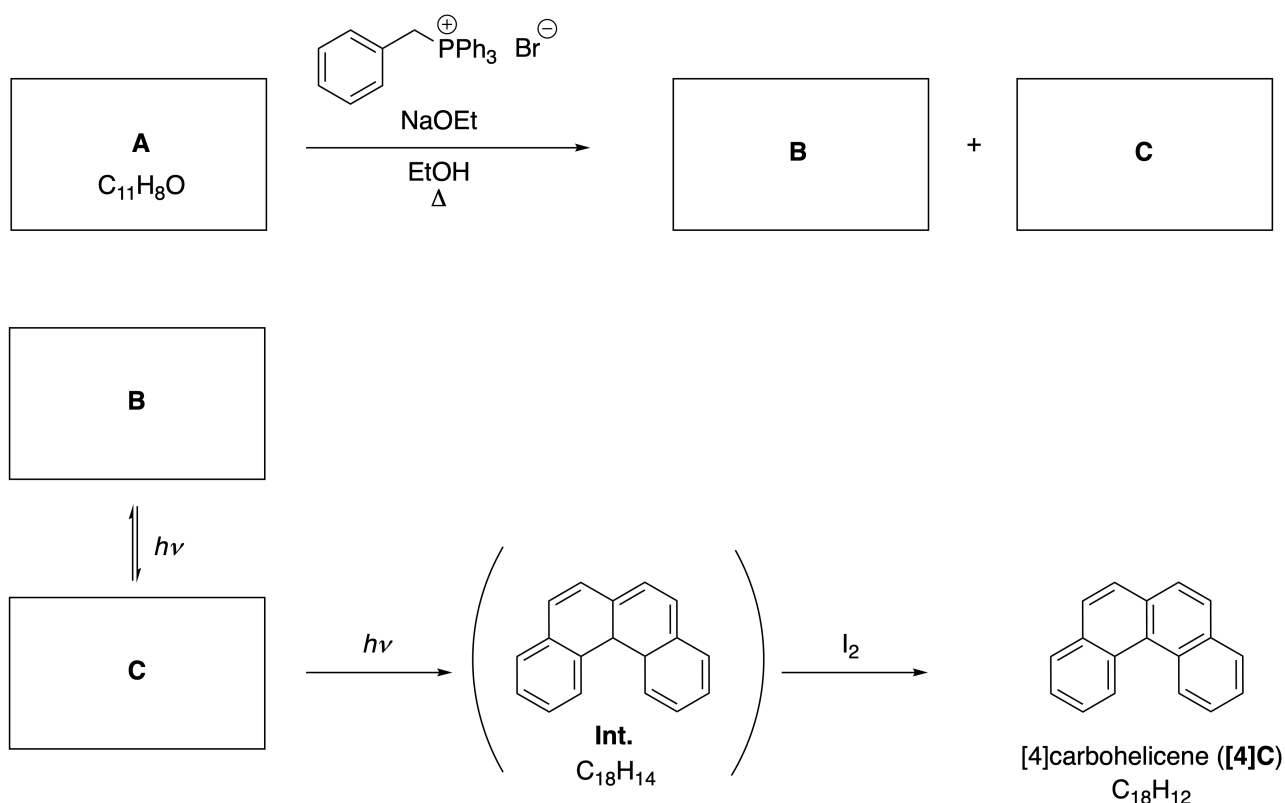
Please return this cover sheet together with all the related question sheets.

Dynamic Organic Molecules and Their Chirality

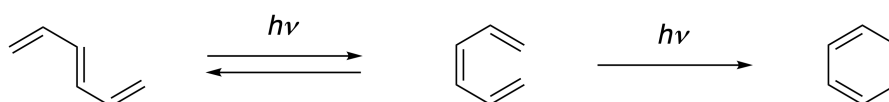
11 % of the total						
Question	A.1	A.2	A.3	B.1	B.2	Total
Points	9	3	7	3	4	26
Score						

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.

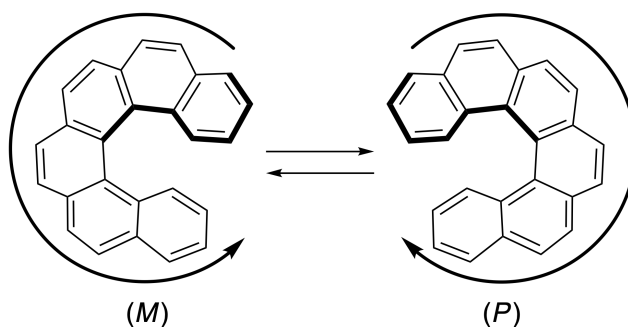


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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 ^1H 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.



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

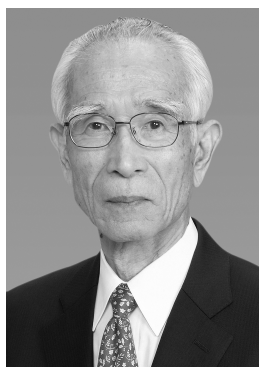
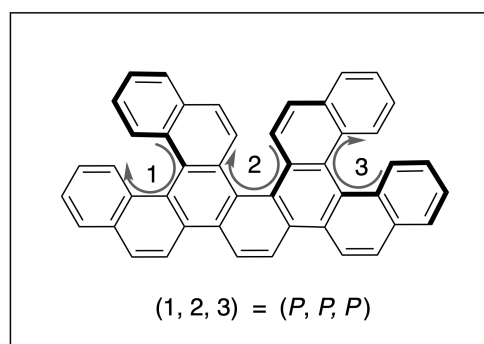
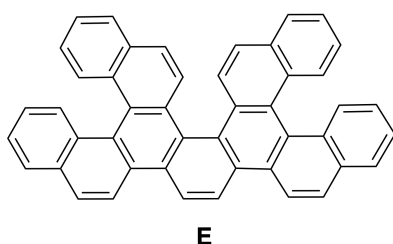
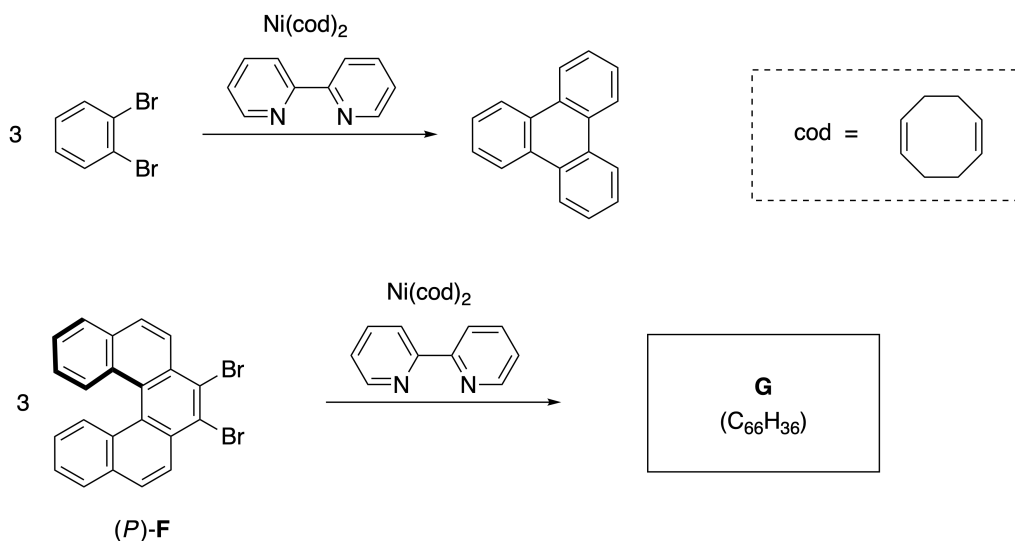


Photo courtesy: The Japan Prize Foundation

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.

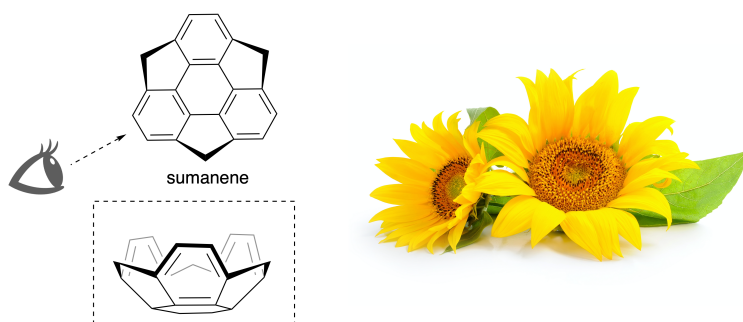


- A.3** The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **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

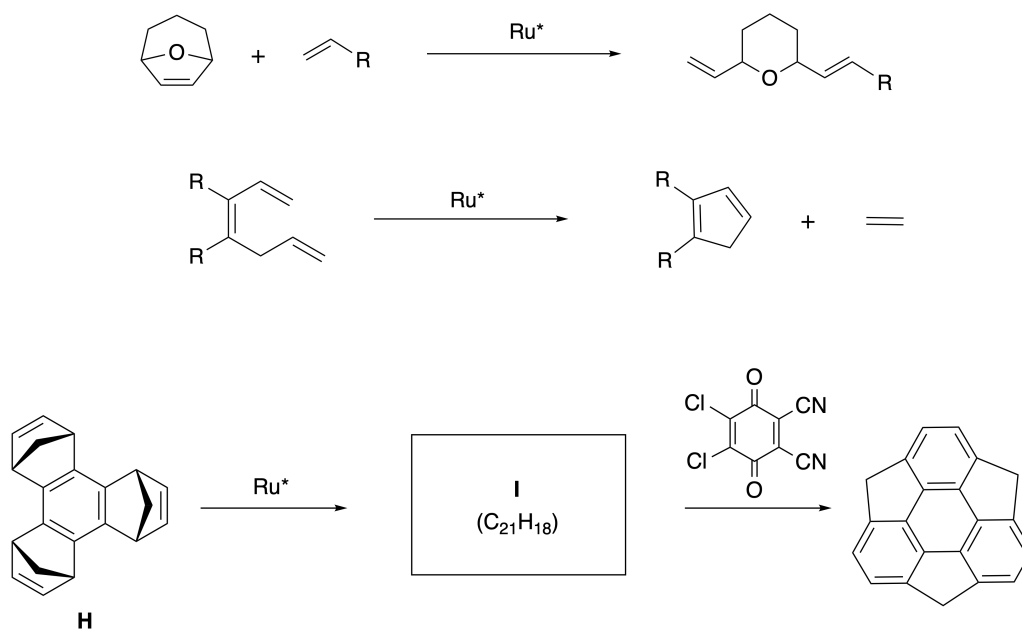


Part B

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

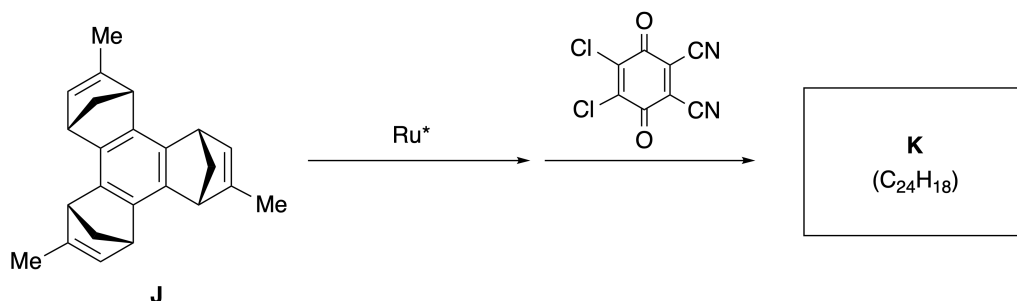


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru^*) are shown below.



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

3pt



- B.2** Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. Draw the structure of **K** with the appropriate stereochemistry. 4pt

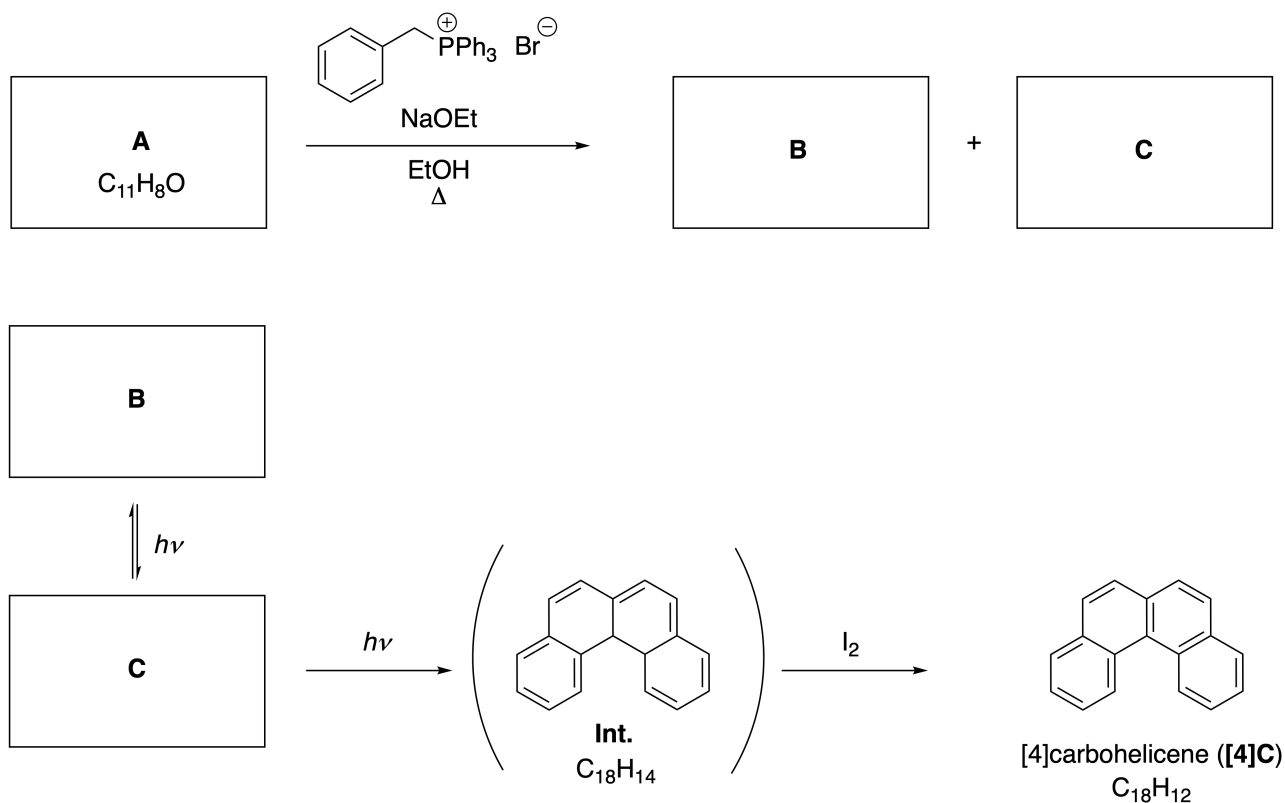
Dynamic Organic Molecules and Their Chirality

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

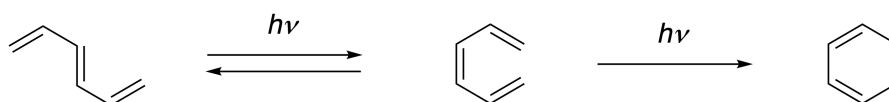
Part A

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.

3pt

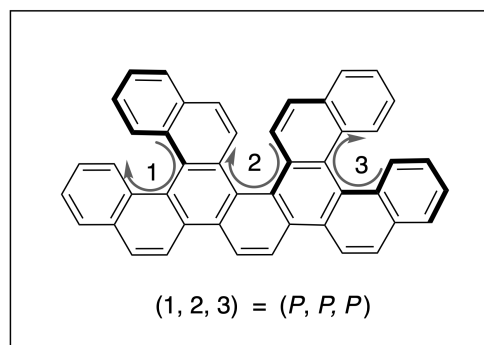
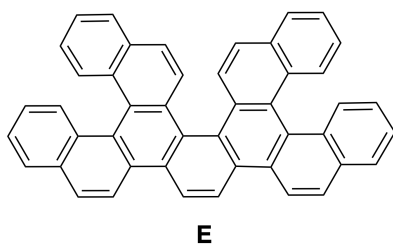
Draw the structure of **D**.

The ¹H NMR chemical shifts of **D** are listed below.

[**D** (δ , ppm in CS₂, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]

A molecule that contains two or more helicene-like structures is called a multiple-helicene. If helical chirality is considered there can be several stereoisomers of 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.



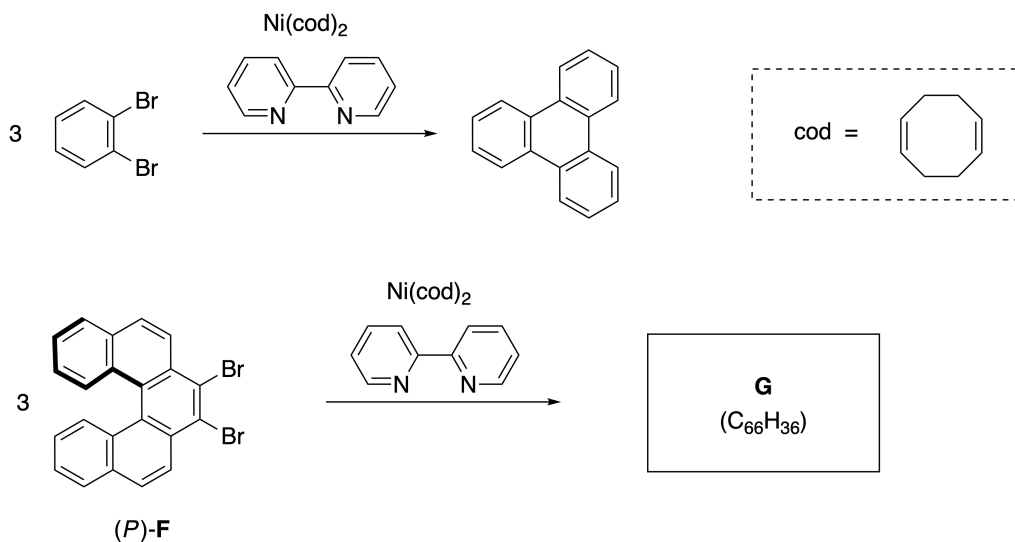
A.3 The nickel-mediated trimerisation of 1,2-dibromobenzene generates triphenylene. 7pt
When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple-helicene **G** (C₆₆H₃₆) is obtained.

Given that interconversion between stereoisomers does not occur during the reaction, **identify all** the possible stereoisomers of **G** formed in this process, without duplicating stereoisomers.

As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels.

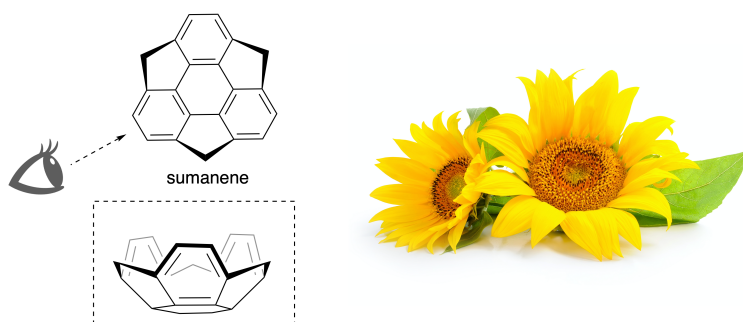
The other stereoisomers should be listed with location numbers and *M* and *P* labels according to the same numbering.

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*).

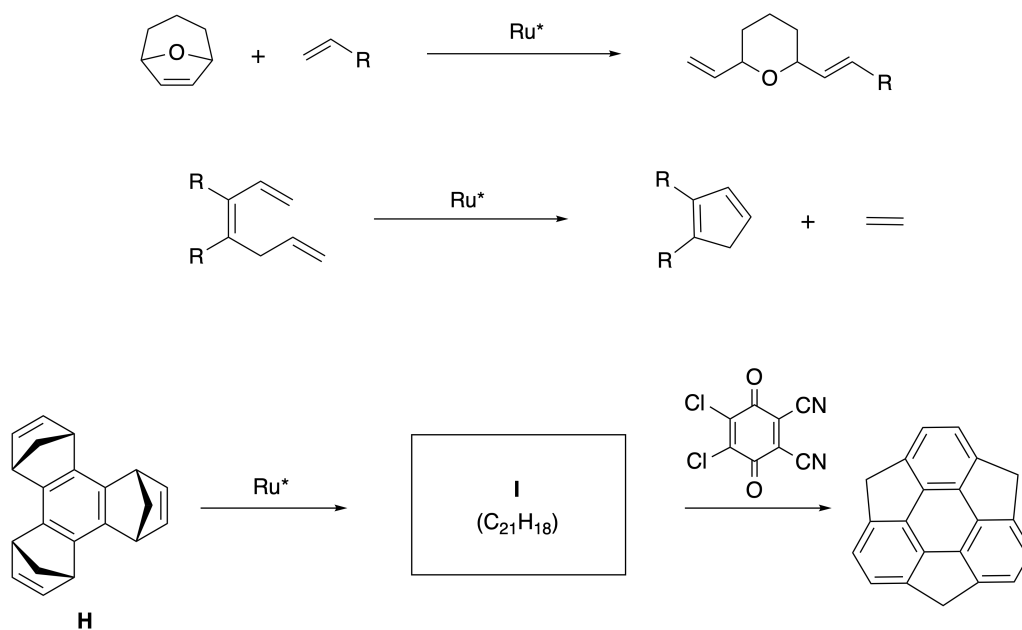


Part B

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.

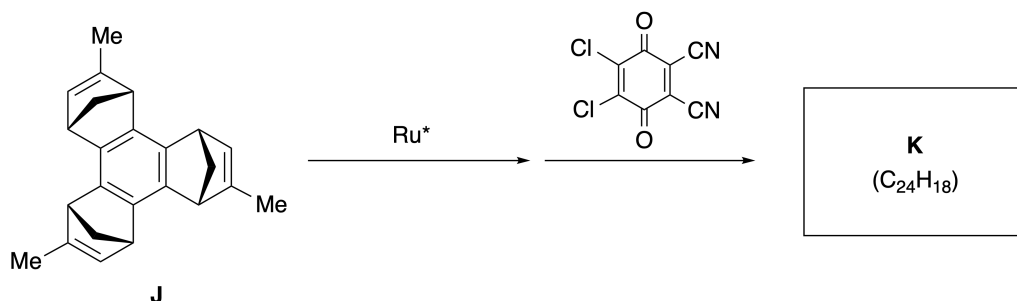


Representative metathesis reactions catalysed by a ruthenium catalyst (Ru^*) are shown below.



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

3pt



- B.2** Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K**. The stereocentres in **J** suffer no inversion during the metathesis reaction. Draw the structure of **K** with the appropriate stereochemistry. 4pt



CHE-4 C-8 A-1

A8-1
English (Switzerland)

Dynamic Organic Molecules and Their Chirality

Part A

A.1 (9 pt)

A (3 pt)

B (3 pt)

C (3 pt)

A.2 (3 pt)



CHE-4 C-8 A-2

A8-2

English (Switzerland)

A.3 (7 pt)



CHE-4 C-8 A-3

A8-3

English (Switzerland)

Part B

B.1 (3 pt)

B.2 (4 pt)

CHE-4 C-9 C-1

CHE-4 C-9 C
Anastasia Sandamirskaya

IChO

Problem 9

Cover sheet

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

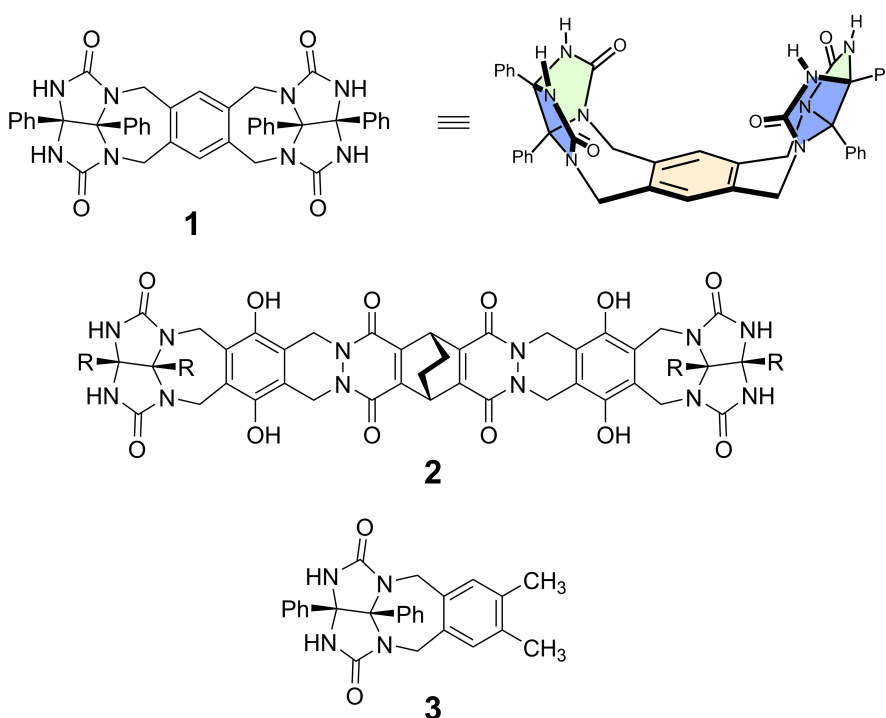
Likes and Dislikes of Capsule

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

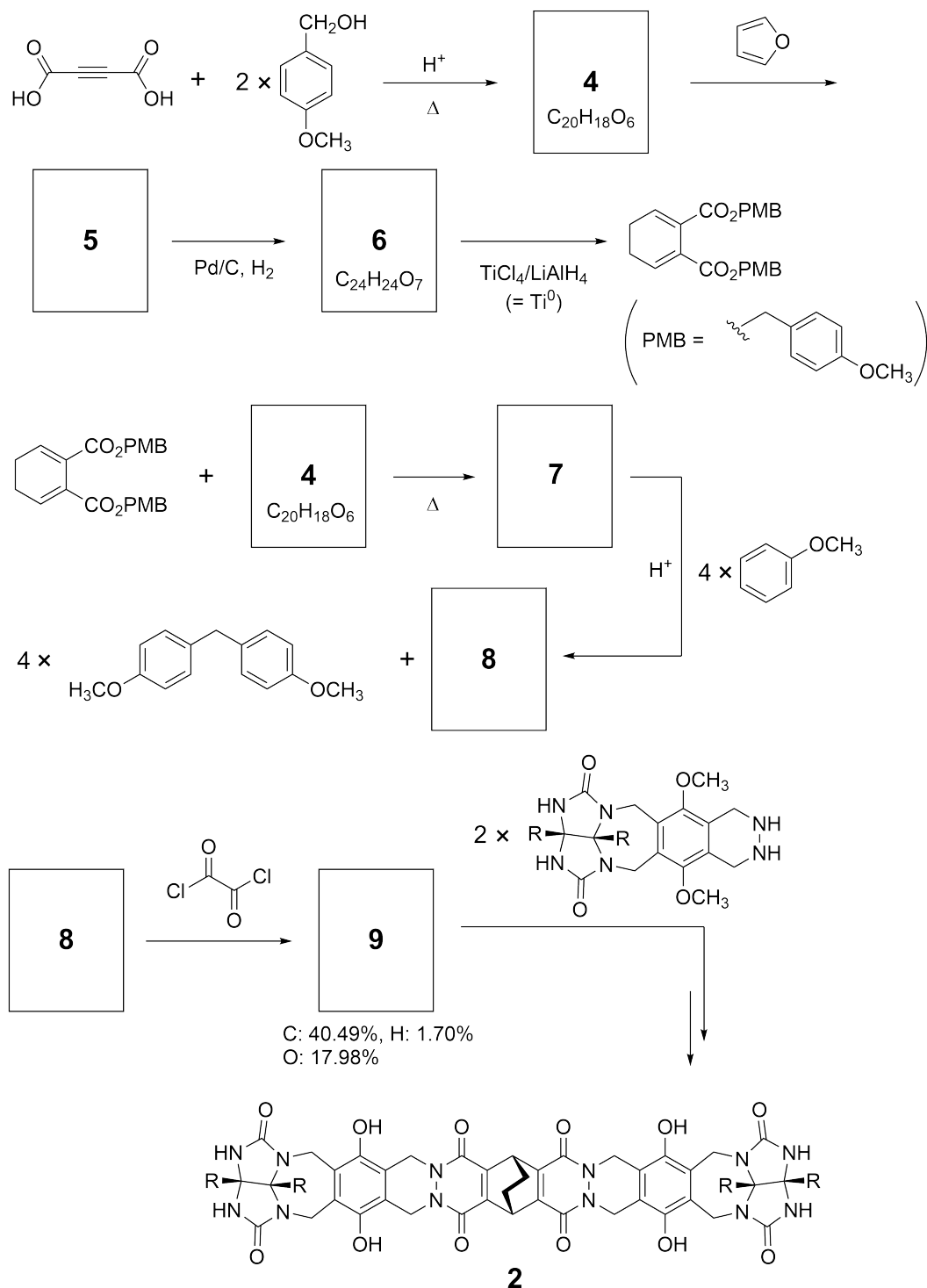
Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



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.



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



- A.1** Draw the structures of **4–9**; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above. 13pt

In the mass spectrum of **1**, the ion peak corresponding to its dimer (**1**₂) was clearly observed, whereas an ion peak for **3**₂ was not observed in the spectrum of **3**. In the ¹H NMR spectra of a solution of **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 (**1**₂). 2pt

The dimeric capsule of **1** (**1**₂) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

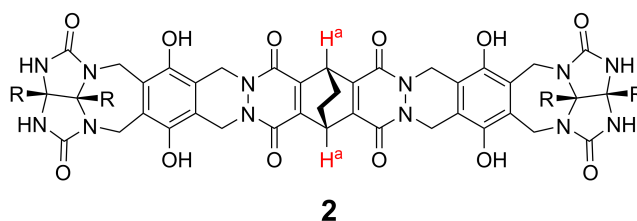


The equilibrium constant of the encapsulation of Z into **1**₂ is given as below:

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

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, **1**₂ in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

Compound **2** also forms a rigid and larger dimeric capsule (**2**₂). The ¹H NMR spectrum of **2**₂ was measured in C₆D₆, C₆D₅F, and a C₆D₆/C₆D₅F 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.



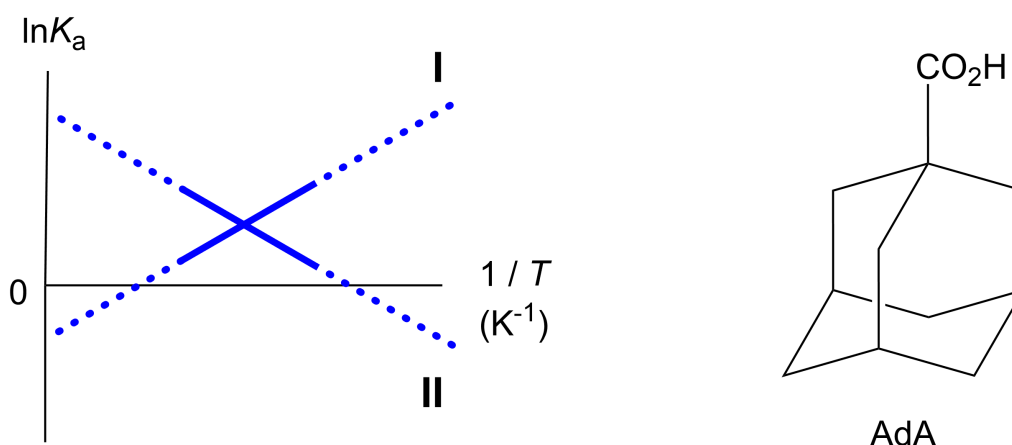
solvent	δ (ppm) of H ^a
C ₆ D ₆	4.60
C ₆ D ₅ F	4.71
C ₆ D ₆ / C ₆ D ₅ F	4.60, 4.71, 4.82

A.4 **Determine** the number of C₆D₆ and C₆D₅F molecules encapsulated in **2**₂ giving each H^a signal. 3pt

^1H NMR measurements in C_6D_6 revealed that 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. $[\text{solvent}@2_2]$ denotes a species containing one or more solvent molecules.

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

Similarly, the K_a values of CH_4 and 1_2 given as eq (2) at various temperatures in C_6D_6 were also determined by ^1H 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 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 3pt and B.

	A	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	1_2 and CH_4	2_2 and AdA
(5)	1_2 and CH_4	2_2 and AdA

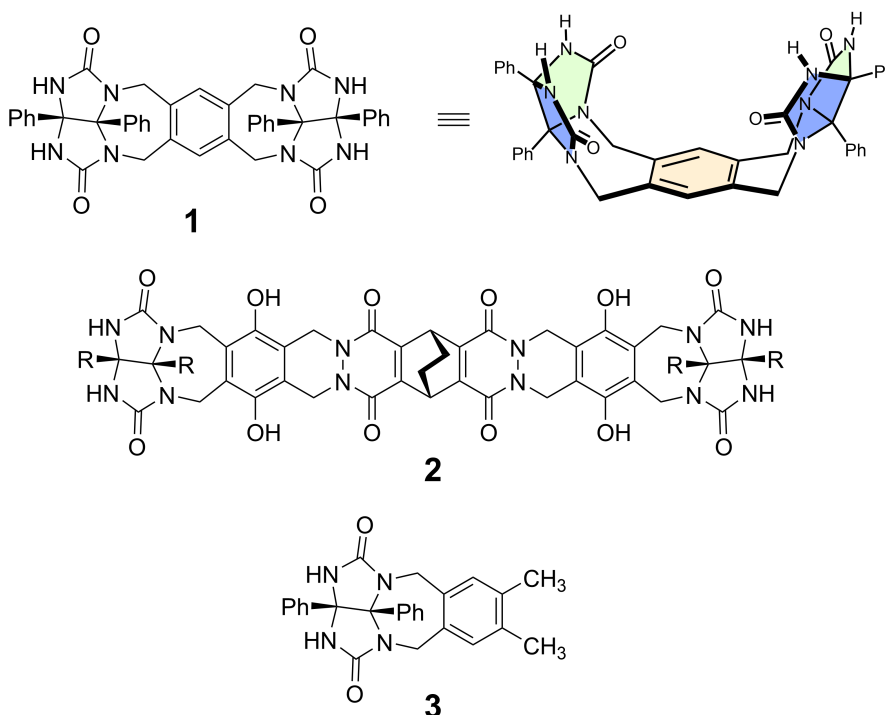
Likes and Dislikes of Capsule

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

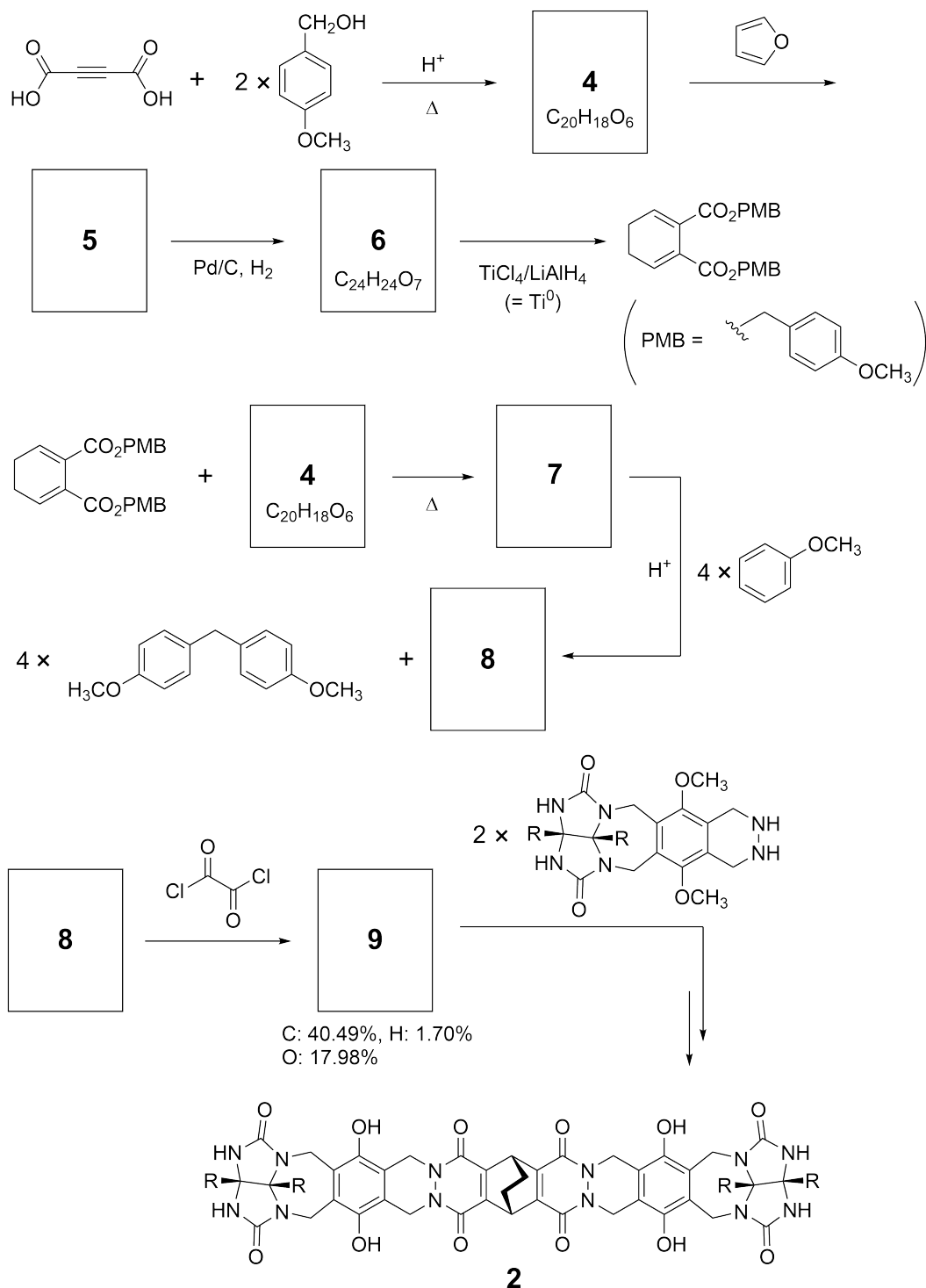
If you cut a tennis ball along the seam, you can disassemble it into two U-shaped pieces.



Compounds **1** and **2** are U-shaped molecules with different sizes, inspired by this idea. Compound **3** was prepared for comparison with **1** and the encapsulation behaviour of these compounds was investigated.



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





CHE-4 C-9 Q-3

Q9-3

English (Switzerland)

- A.1** Draw the structures of **4-9**; stereochemistry can be neglected. Use the "PMB" abbreviation 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 (**1**₂) was clearly observed, whereas an ion peak for **3**₂ was not observed in the spectrum of **3**.

In the ¹H NMR spectrum of a solution of **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 (**1**₂). 2pt

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

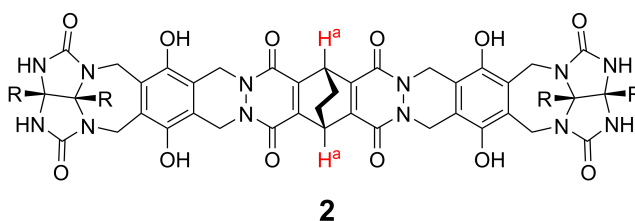


The equilibrium constant of the encapsulation of Z into 1_2 is shown below:

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

Encapsulation of a molecule into a capsule can be monitored by NMR spectroscopy. For example, 1_2 in C_6D_6 gave different signals in the 1H NMR spectra before and after addition of CH_4 .

Compound **2** also forms a larger, rigid dimeric capsule (2_2). The 1H NMR spectrum of 2_2 was measured in C_6D_6 , C_6D_5F , and a C_6D_6/C_6D_5F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H^a proton of **2** in the above solvents are summarized below, and no other signals from H^a in **2**, except for those 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 filled capsule.



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 **Determine** the number of C_6D_6 and C_6D_5F molecules encapsulated in 2_2 giving each H^a signal. 3pt

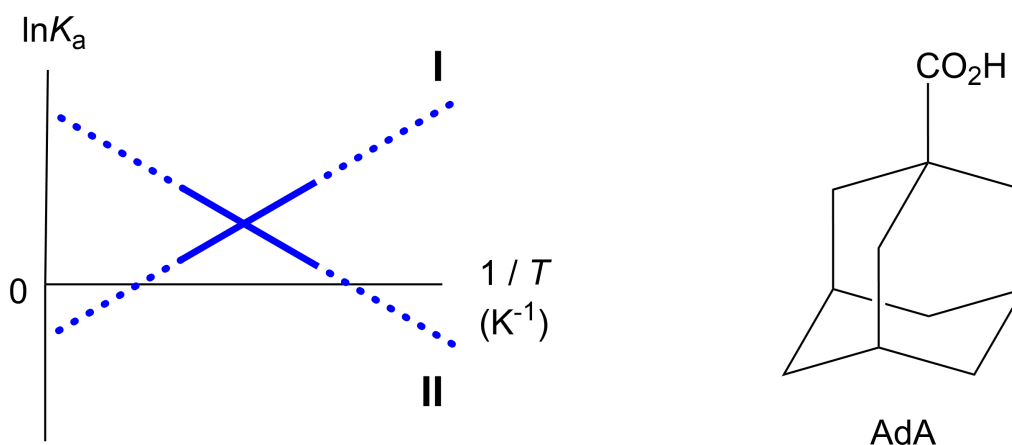
^1H NMR measurements in C_6D_6 revealed that 2_2 can incorporate one molecule of 1-adamantanecarboxylic acid (AdA).

The association constants (K_a) which are expressed below were determined for various temperatures.

$[\text{solvent}@2_2]$ denotes a species containing one or more solvent molecules.

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

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



No C_6D_6 is encapsulated in 1_2 .

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

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	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	1_2 and CH_4	2_2 and AdA
(5)	1_2 and CH_4	2_2 and AdA



CHE-4 C-9 A-1

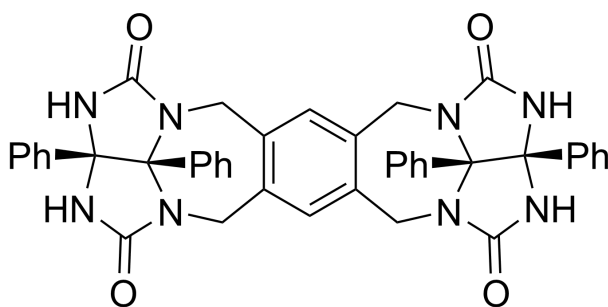
A9-1
English (Switzerland)

Likes and Dislikes of Capsule

A.1 (13 pt)

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

A.2 (2 pt)



A.3 (2 pt)

A.4 (3 pt)

δ (ppm) of H ^a	number of C ₆ D ₆	number of C ₆ D ₅ F
4.60 ppm		
4.71 ppm		
4.82 ppm		

A.5 (3 pt)

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

(4) : _____ (5) : _____