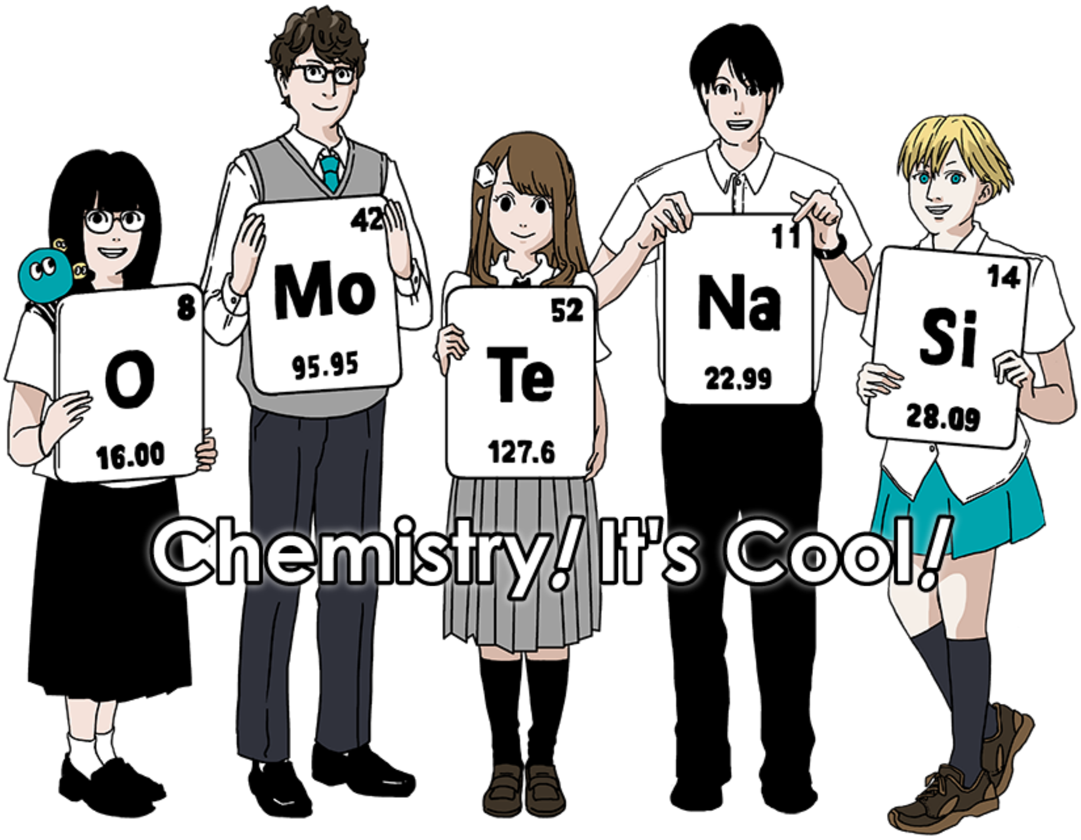
IChO
General instructions

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	**100**

Physical Constants and Equations

Constants

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

Equations

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

Heat change Δq	$\Delta q = n c_{\mathrm{m}} \Delta T$, where c_{m} is the temperature-independent molar heat capacity.
Nernst equation for redox reaction	$E = E^{\circ} + \frac{RT}{zF} \ln \frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}$, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration of reduced substance.
Arrhenius equation	$k = A \exp\left(-\frac{E_a}{RT}\right)$, 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	$A = \varepsilon l c$, where A is the absorbance, ε is the molar absorption coefficient, l is the optical path length, c is the concentration of the solution.
Henderson–Hasselbalch equation	For an equilibrium $\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$, where equilibrium constant is K_{a}, $\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
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 $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$
Approximation equation that can be used to solve problems	When $x \ll 1$, $\frac{1}{1 - x} \simeq 1 + x$

Periodic Table

Key:

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

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											5 B Boron 10.814	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.306											13 Al Aluminium 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.068	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]
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Ac-Lr Actinoids	104 Rf Rutherfordium [267]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [272]	108 Hs Hassium [277]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [278]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [293]	118 Og Oganesson [294]

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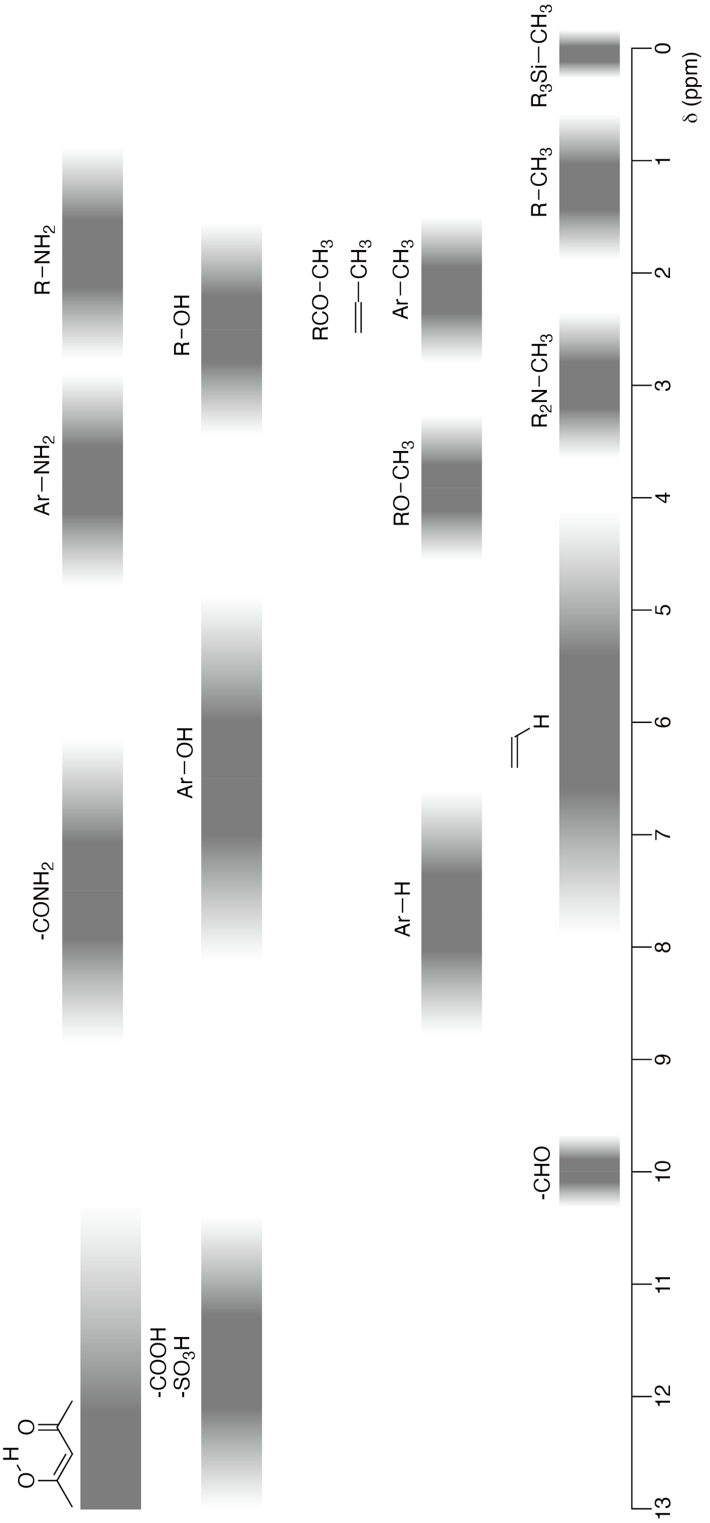
89-103 Ac-Lr Actinoids :	89 Ac Actinium [227]	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [239]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [252]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]

^{1}H NMR Chemical Shifts



Δδ for one alkyl group-substitution: *ca.* +0.4 ppm

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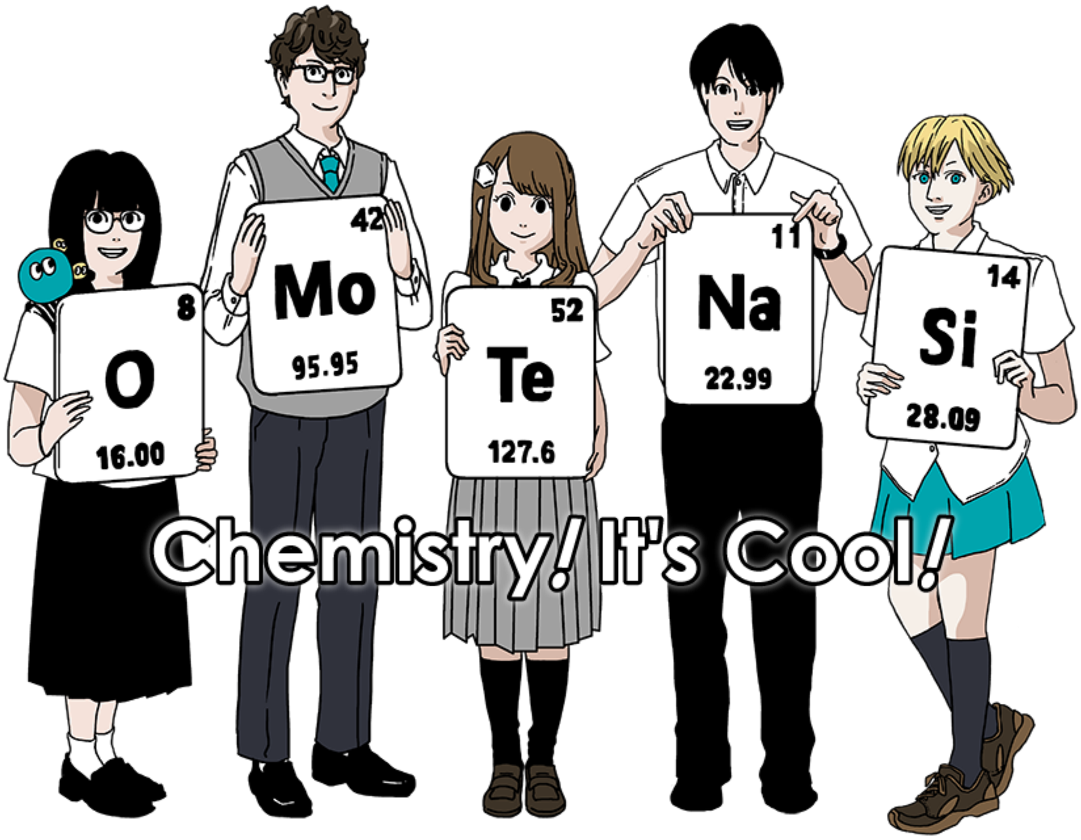

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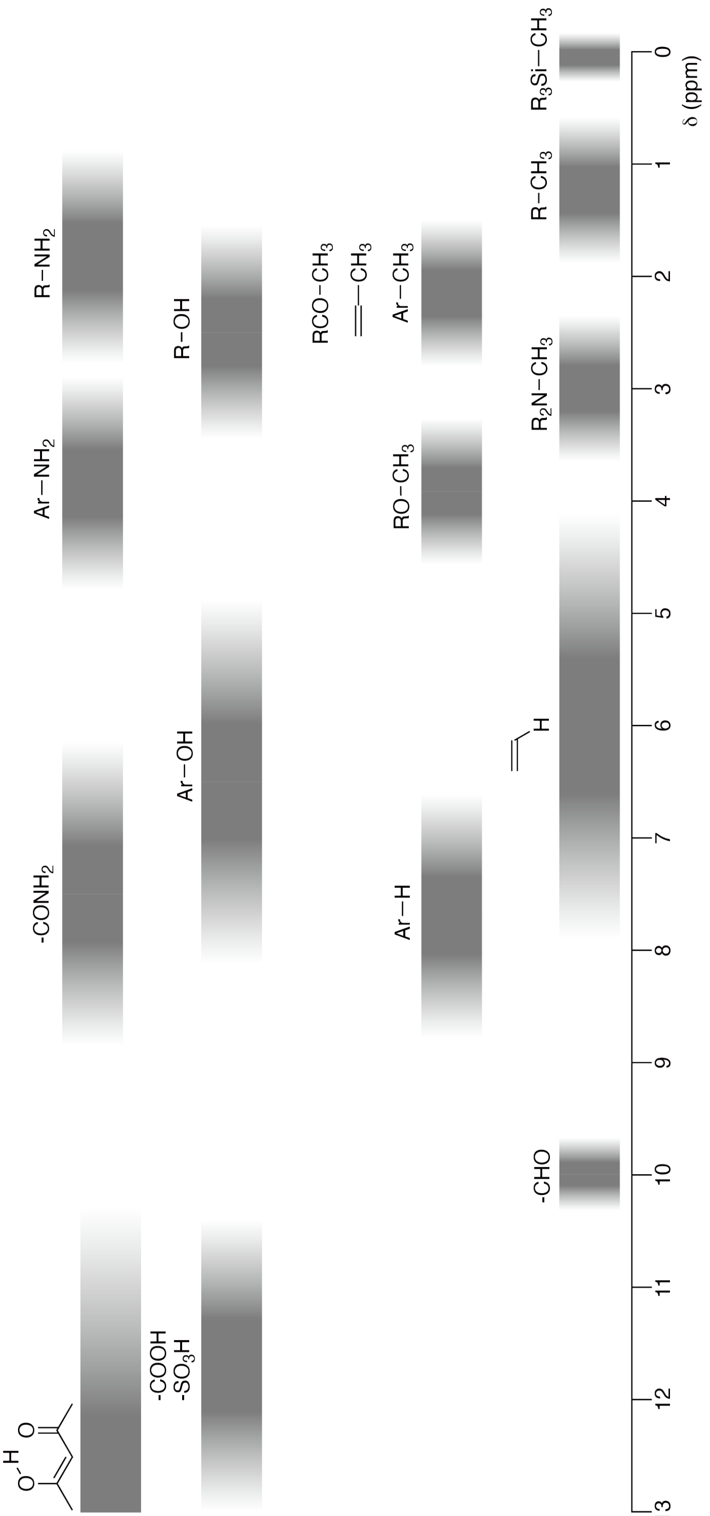


$\Delta\delta$ for one alkyl group-substitution: *ca.* +0.4 ppm

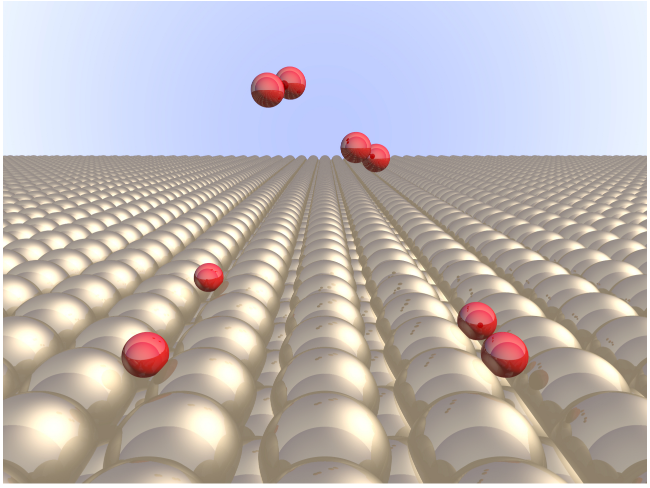
IChO
Problem 1

Cover sheet

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

Hydrogen at a Metal Surface

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



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

Part A

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

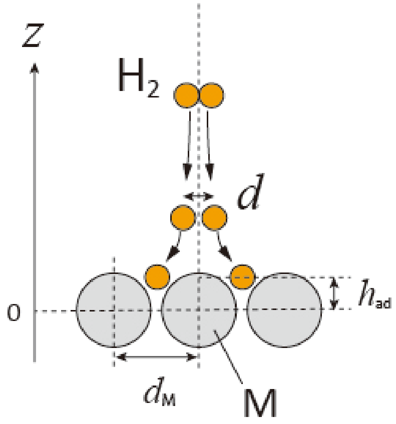


Fig.1 Definition of variables. Drawing is not in scale.

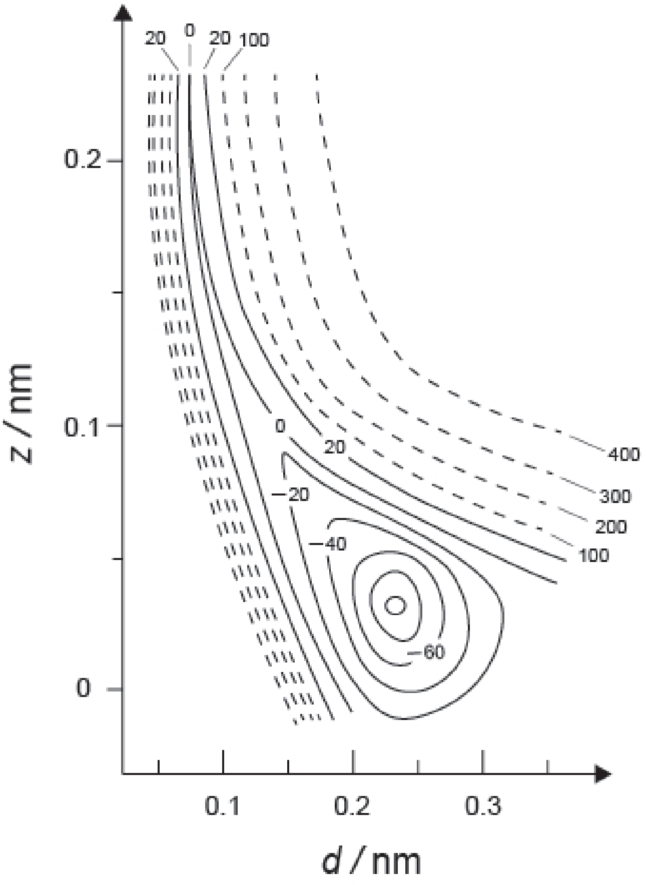


Fig.2

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

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

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

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

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

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

Part B

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

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

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

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

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

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

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

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

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

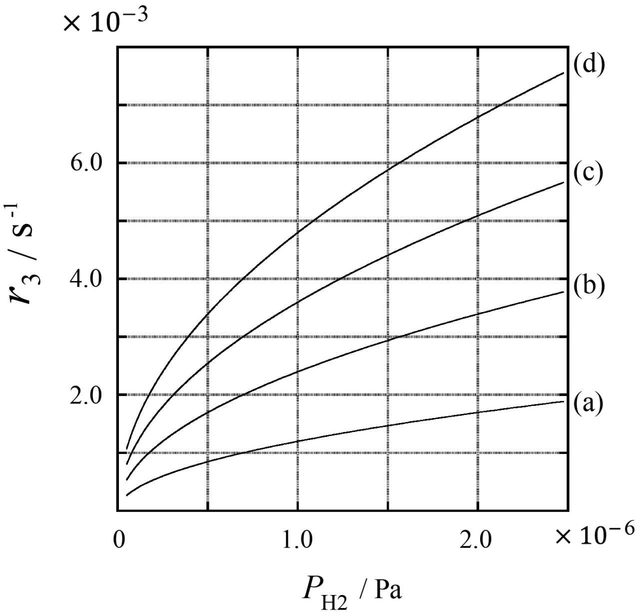
Express C using k_1 and k_2.

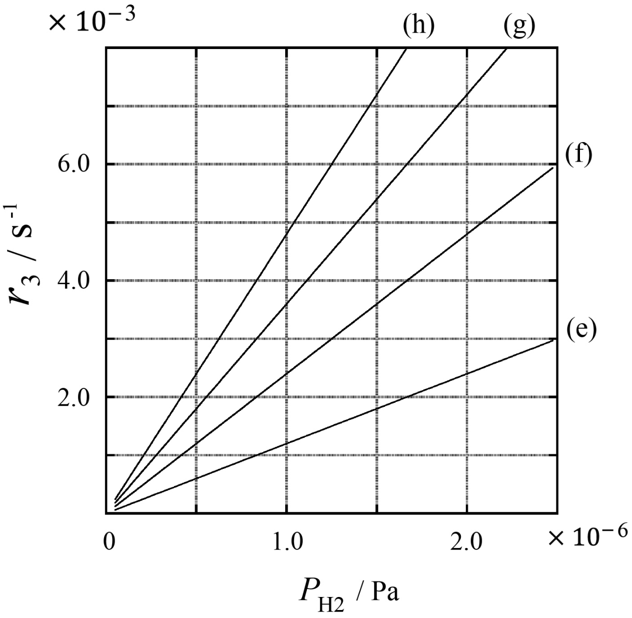
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m^2 was placed in a container (1L = 1.0×10^{-3} m^3) with H_2 ($P_{H_2} = 1.0 \times 10^2$ Pa). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m^{-2}. The surface temperature was kept at $T = 400$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

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

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

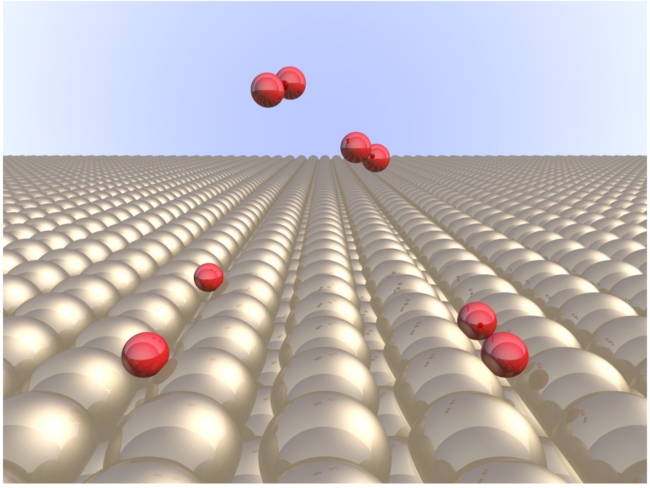
B.4	At a different T, $C = 2.5 \times 10^3$ Pa^{-1} and $k_3 = 4.8 \times 10^{-2}$ s^{-1}are given. For r_3 as a function of P_{H_2}at this temperature, **select** the correct plot from (a)–(h).	3pt





Vetni á yfirborði málms

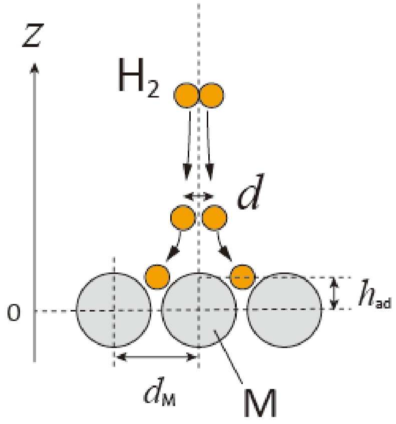
11 % of the total							
Question	A.1	A.2	B.1	B.2	B.3	B.4	**Total**
Points	6	4	5	3	3	3	**24**
Score							



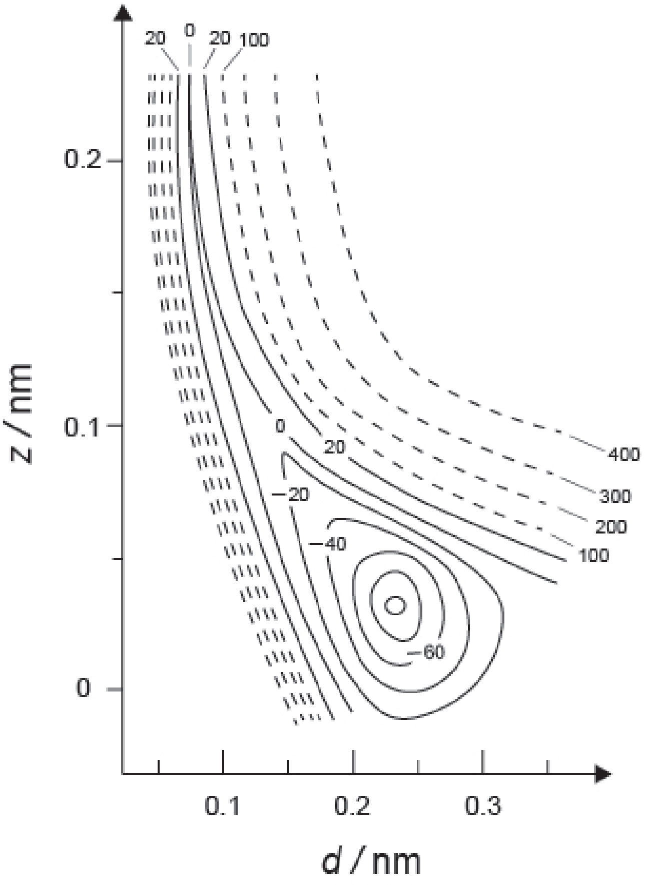
Talið er að vetni verði sá orkugjafi framtíðarinnar sem ekki er háður jarðefnaeldsneyti. Í þessu dæmi er fjallað um geymsluferli vetnis í málmi en það er skylt flutnings- og geymslutækni fyrir vetni.

Hluti A

Þegar vetni ísogast (absorbs) inn í málm gegnum yfirborð hans, þá þarf fyrst að huga að ásogsferli (adsorption process) vetnis á málmyfirborðið, $H_2(g) \rightarrow 2H(ad)$, þar sem gasástand er táknað með (g) og ásogað ástand með (ad). Vetnissameindir (H_2) sem koma að málmyfirborði (M) klofna þar og ásogast sem H atóm (mynd 1). Mættisorka (potential energy) H_2 er sýnd sem fall af tveimur breytistærðum: fjarlægðinni á milli atómanna, d, og hæð þeirra frá málmatómi á yfirborði, z. Gert er ráð fyrir að ásinn milli H atómanna tveggja sé samsíða yfirborðinu og að massamiðja þeirra sé ávallt á lóðréttu punktalínunni á mynd 1. Mynd 2 sýnir hæðarlínur mættisorkunnar fyrir klofnunina á yfirborðinu. Tölugildin sýna mættisorkuna í einingunni kJ per mól af H_2. Bil milli heillína er 20 kJ mol^{-1}, bil milli punktastrikaðra lína er 100 kJ mol^{-1} og bil milli heillína og punktastrikaðra lína er 80 kJ mol^{-1}. Ekki þarf að taka tillit til núllstigsorku titrings (zero-point vibration energy).



Mynd 1 Skilgreiningar á breytistærðum. Teikningin er ekki í réttum hlutföllum.



Mynd 2

A.1 **Veldu** það gildi af A-G sem kemst næst eftirfarandi stærðum (i)–(iii). 6pt

(i) Fjarlægðin milli atóma í H_2 gassameind
(ii) Fjarlægðin milli málmatóma (d_{M} á mynd 1)
(iii) Fjarlægð ásogaðs H atóms frá yfirborðinu (h_{ad} á mynd 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 **Veldu** það gildi A-H sem kemst næst eftirfarandi stærðum (i)–(ii). 4pt

(i) orkan sem þarf fyrir klofnun H_2 í gasfasa í H atóm í gasfasa
[$H_2(g) \rightarrow 2H(g)$]
(ii) orkan sem losnar við ásog H_2 gass
[$H_2(g) \rightarrow 2H(ad)$]

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

Hluti B

Ásoguð vetnisatóm geta annaðhvort ísogast inn í málminn eða þau tengjast saman aftur og frásogast (desorb) til baka í gasfasa, eins og sýnt er í efnahvörfum (1a) og (1b). H(ab) táknar vetnisatóm sem hefur ísogast inn í málminn.

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

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

Hvarfhraðar á hvern ásogsstað yfirborðsins fyrir ásog, frásog og ísog (í sömu röð) eru $r_1[\mathrm{s}^{-1}], r_2[\mathrm{s}^{-1}]$ og $r_3[\mathrm{s}^{-1}]$. Jöfnurnar fyrir hvarfhraðana eru:

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

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

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

þar sem k_1 [s^{-1} Pa^{-1}]$,$ k_2 [s^{-1}] og k_3 [s^{-1}] eru hraðafastarnir og $P_{\mathrm{H_2}}$ er þrýstingur $\mathrm{H_2}$.

Fyrir ásogsstaðina á yfirborðinu þá er θ ($0 \leq \theta \leq 1$) sá hluti þeirra sem er setinn H atómum. Gert er ráð fyrir að ásog og frásog gerist hratt miðað við ísog ($r_1, r_2 \gg r_3$) og að θ sé fasti.

B.1 r_3 er hægt að lýsa með jöfnunni: 5pt

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

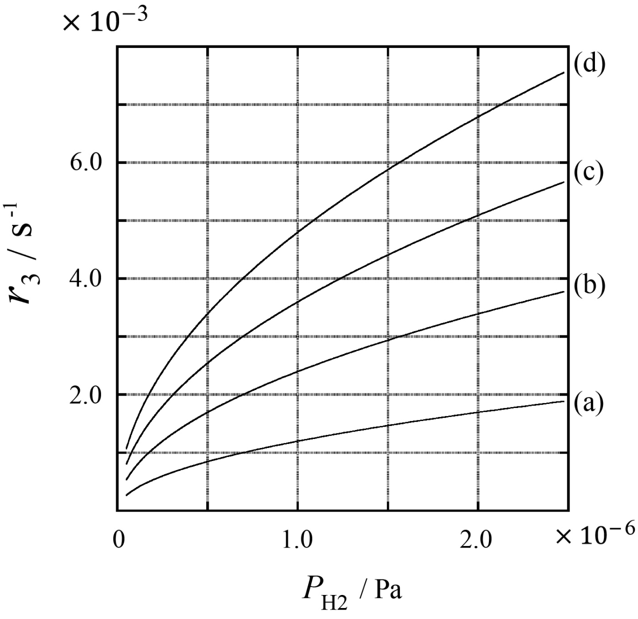
Sýndu jöfnu fyrir C sem fall k_1 og k_2.

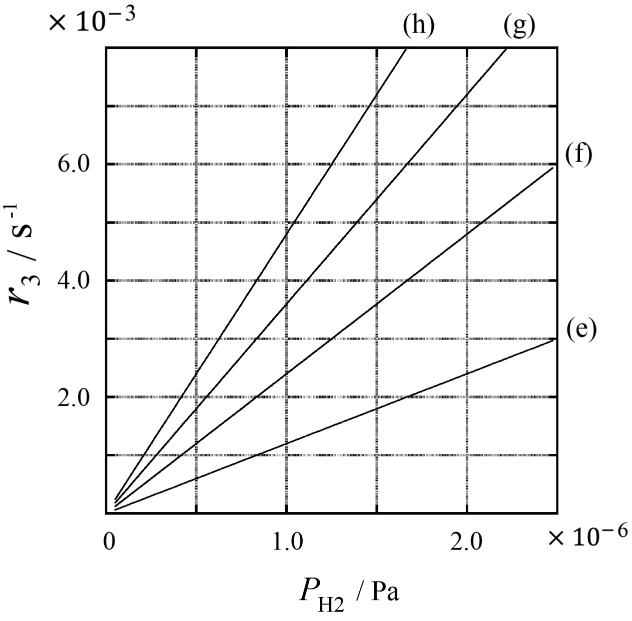
Málmsýni með yfirborðsflatarmál$S = 1,0 \times 10^{-3}$ m^2 var sett í hylki (1L = $1,0 \times 10^{-3}$ m^3) sem innihélt H_2 ($P_{H_2} = 1,0 \times 10^2$ Pa). Þéttleiki ásogsstaða vetnisatóma á yfirborðinufyrir var $N = 1,3 \times 10^{18}$ m^{-2}. Hitastiginu á yfirborðinu var haldið við $T = 400$ K. Eftir því sem hvarfi (1) miðaði áfram lækkaði P_{H_2} með jöfnum hraða, $v = 4,0 \times 10^{-4}$ Pa s^{-1}. Gera má ráð fyrir að H_2 sé kjörgas og að rúmmál málmsýnisins sé óverulegt.

B.2 **Reiknaðu** mólfjölda ásogaðra H atóma á flatarmálseiningu á tímaeiningu, $A\,[\text{mol s}^{-1}\text{ m}^{-2}]$. 3pt

B.3 Við $T = 400$ K, er gildi C $1,0 \times 10^2$ Pa^{-1}. **Reiknaðu** gildi k_3 við 400 K. Ef þú gast ekki reiknað svarið í **B.2**, notaðu þá gildið $A = 3,6 \times 10^{-7}$ mol s^{-1} m^{-2}. 3pt

B.4 Við annað hitastig T, eru gildi $C = 2,5 \times 10^3$ Pa^{-1} og $k_3 = 4,8 \times 10^{-2}$ s^{-1}. **Veldu** þann feril af (a)–(h) sem sýnir r_3 sem fall af P_{H_2}við þetta hitastig. 3pt





Vetni á yfirborði málms

Hluti A

A.1 (6 pt)

(i)	(ii)	(iii)

A.2 (4 pt)

(i)	(ii)

Hluti B

B.1 (5 pt)

$C =$ ____________________

B.2 (3 pt)

$A =$ ____________________ mol s^{-1} m^{-2}

B.3 (3 pt)

$k_3 =$ ____________________ s^{-1}

B.4 (3 pt)

____

IChO
Problem 2

Cover sheet

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

Isotope Time Capsule

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

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

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

Let us consider the following equilibrium:

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

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

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

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

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

$$\mathrm{H_2 + DI \rightleftharpoons HD + HI} \tag{3}$$

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

$$\mathrm{2HD \rightleftharpoons H_2 + D_2} \qquad K = \frac{[\mathrm{H_2}][\mathrm{D_2}]}{[\mathrm{HD}]^2} \tag{4}$$

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

$$E = \frac{1}{2}h\nu \tag{5}$$

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

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:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7}$$

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

$$\mathrm{2HD \rightarrow H_2 + D_2} \tag{8}$$

Assume that:

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

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

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

Here, R_{D_2} refers to $\frac{[D_2]}{[H_2]}$ in the sample and $R^*_{D_2}$ to $\frac{[D_2]}{[H_2]}$ at $T \rightarrow +\infty$. 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 $CO_2[44]$ and $CO_2[47]$ below. The quantity Δ_{47} is defined as:

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

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

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

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

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

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

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

Samsætutímaglas

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

Sameindir sem eru ólíkar að því eina leyti að hafa mismunandi samsetningar samsæta, eins og CH_4 og CH_3D, eru kallaðar samsætuhverfur (isotopologues). Samsætuhverfur teljast hafa sömu efnaeiginleika en í raun er á þeim smá munur.

Gerðu ráð fyrir að öll efnin í þessu dæmi séu í gasfasa.

Athugum eftirfarandi efnajafnvægi:

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

Óreiðan, S, eykst með auknum fjölda mögulegra örástanda kerfis, W:

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

$W = 1$ fyrir $^{12}C^{16}O_2$ og $^{12}C^{18}O_2$. Hins vegar er $W = 2$ fyrir $^{12}C^{16}O^{18}O$ sameind því að hægt er að greina á milli súrefnisatómanna þeirri sameind.

Hægra megin í jafnvæginu (sjá jöfnu 1) eru tvær $^{12}C^{16}O^{18}O$ sameindir og þar er því $W = 2^2 = 4$.

A.1 Vermibreytingin, ΔH, í efnajöfnu 3 er jákvæð við öll hitastig. 8pt

$$\mathrm{H_2 + DI \rightleftharpoons HD + HI} \tag{3}$$

Reiknaðu jafnvægisfastann, K, fyrir efnajafnvægi 3 við mjög lág hitastig (þegar $T \to 0$) og við mjög há hitastig (þegar $T \to +\infty$). Gerðu ráð fyrir að hvarfið breytist ekki við þessi hitastig og að ΔH nái föstu gildi við há hitastig.

Finna má gildi Δ*H* fyrir eftirfarandi hvarf út frá sameindatitringum.

$$\mathrm{2HD \rightleftharpoons H_2 + D_2} \qquad K = \frac{[\mathrm{H_2}][\mathrm{D_2}]}{[\mathrm{HD}]^2} \tag{4}$$

Við T = 0 K, má lýsa titringsorku tvíatóma sameindar, sem hefur titringstíðnina ν [$\mathrm{s^{-1}}$], með eftirfarandi jöfnu:

$$E = \frac{1}{2}h\nu \tag{5}$$

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

Hér er *k* kraftstuðullinn (force constant) og μ er skerti massinn (reduced mass), en hann er samsettur úr massa atómanna í tvíatóma sameind, m_1 og m_2, eins og eftirfarandi jafna sýnir:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7}$$

A.2 Titringur $\mathrm{H_2}$ er við 4161,0 $\mathrm{cm^{-1}}$ (þegar gildið er gefið á formi bylgjutölu (wavenumber)). 8pt
Reiknaðu ΔH fyrir eftirfarandi efnajöfnu við T = 0 K í einingunum J $\mathrm{mol^{-1}}$.

$$\mathrm{2HD \rightarrow H_2 + D_2} \tag{8}$$

Gerðu ráð fyrir eftirfarandi:
- ΔH er aðeins háð titringsorku
- gildi k fyrir $\mathrm{H_2}$, HD, og $\mathrm{D_2}$ eru þau sömu.
- massi H er 1 Da og massi D er 2 Da.

Í kerfi sem er við jafnvægi eru mólhlutföll H_2, HD og D_2 háð hitastigi. Hér er Δ_{D_2} skilgreint sem breytingin á mólhlutfalli D_2.

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

Hér vísar R_{D_2} til $\frac{[D_2]}{[H_2]}$ í sýninu og $R^*_{D_2}$ til $\frac{[D_2]}{[H_2]}$ þegar $T \to +\infty$.

Bent skal á að dreifing samsæta er handahófskennd (random) þegar $T \to +\infty$.

A.3	**Reiknaðu** Δ_{D_2} þegar samsætuskiptin eru í jafnvægi, við það hitastig þegar *K* í jöfnu 4 er 0,300. Gerðu ráð fyrir að náttúrulegt samsætuhlutfall D sé $1,5576 \times 10^{-4}$ og náttúrulegt samsætuhlutfall H sé $1 - 1,5576 \times 10^{-4}$.	10pt

Tvísetin samsætuhverfa (doubly substituted isotopologue) inniheldur tvö þung samsætuatóm í einni sameind. Almennt eykst mólhlutfall tvísetinna samsætuhverfa með lækkandi hitastigi.

Skoðum mólhlutfall CO_2 sameinda sem hafa mólmassana 44 og 47, og sem táknuð eru sem $CO_2[44]$ og $CO_2[47]$. Stærðin Δ_{47} er skilgreind á eftirfarandi hátt:

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

Hér vísar R_{47} til $\frac{[CO_2[47]]}{[CO_2[44]]}$ í sýninu og R^*_{47} til $\frac{[CO_2[47]]}{[CO_2[44]]}$ þegar $T \to +\infty$.

Náttúrulegt samsætuhlutfall kolefnis- og súrefnisatóma er sýnt hér að neðan; ekki þarf að taka tillit til annarra samsæta.

	^{12}C	^{13}C
náttúrulegt samsætuhlutfall	0,988888	0,011112

	^{16}O	^{17}O	^{18}O
náttúrulegt samsætuhlutfall	0,997621	0,0003790	0,0020000

Hvernig Δ_{47} er háð hitastigi er gefið með jöfnunni hér að neðan, þar sem hitastigið *T* er gefið með einingunni K:

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

A.4 Gildi R_{47} í steingervingi svifjurtar frá hafsbotni við Suðurskautslandið er $4,50865 \times 10^{-5}$.
Notaðu þetta gildi á R_{47} til að **<u>áætla</u>** hitastigið þegar svifjurtin var á lífi. Þetta hitastig er talið vera lofthitinn á þeim tíma þegar svifjurtin var uppi. Í útreikningunum þarf aðeins að nota algengustu samsætuhverfu $CO_2[47]$.

9pt

Samsætutímaglas

A.1 (8 pt)

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

A.2 (8 pt)

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

A.3 (10 pt)

Δ_{D_2} = ______________________

A.4 (9 pt)

$T =$ ______________ K

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 $[\mathrm{A^-}]$, $[\mathrm{HA}]$, and $[\mathrm{H^+}]$ in solution **X** are 1.00×10^{-2} mol $\mathrm{L^{-1}}$, 1.00×10^{-3} mol $\mathrm{L^{-1}}$, and 1.00×10^{-4} mol $\mathrm{L^{-1}}$, respectively, which are correlated via the following acid-base equilibrium:

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

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

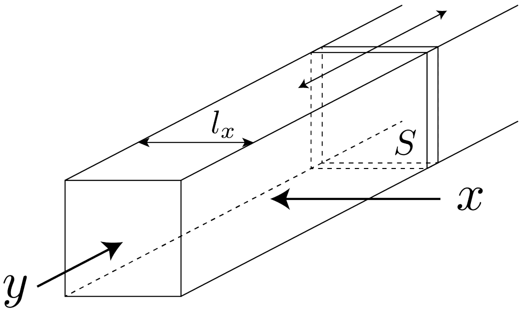
A.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. **Determine** the ratio $\varepsilon_{\mathrm{HA}}/\varepsilon_{\mathrm{A^-}}$, where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

Part B

Let us consider the following equilibrium in the gas phase.

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

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



Use the following definitions if necessary.

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

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

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

Lambert–Beer lögmál?

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

Í þessu verkefni skaltu hunsa gleypni kúvettunnar og leysisins. Hitastigi allra lausna og gastegunda er haldið föstu við 25 °C.

Hluti A

Vatnslausn **X** var útbúin með HA og NaA. Styrkir $[\mathrm{A^-}]$, $[\mathrm{HA}]$, og $[\mathrm{H^+}]$ í lausninni eru $1{,}00 \times 10^{-2}$ mol L^{-1}, $1{,}00 \times 10^{-3}$ mol L^{-1}, og $1{,}00 \times 10^{-4}$ mol L^{-1}, (talið upp í sömu röð) og um samband styrkjanna gildir eftirfarandi sýru-basa jafnvægi:

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

Lengd geisla í mælilausn (optical path length) er l í hluta A. Hunsaðu eðlismassabreytingu sem kann að verða við þynningu og gerðu ráð fyrir að jafna 1 sé eina efnahvarfið sem á sér stað.

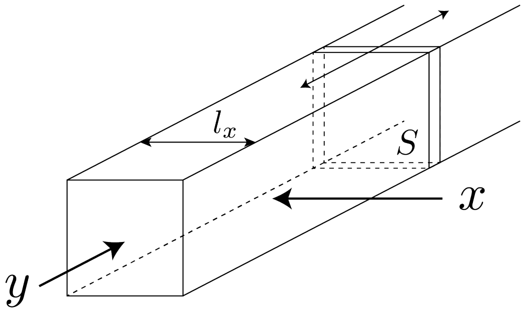
A.1 Gleypni **X** var A_1 við bylgjulengd λ_1. Síðan var lausn **X** þynnt að tvöföldu upphaflegu rúmmáli lausnarinnar með saltsýru (hydrochloric acid) sem hafði pH = 2,500. Eftir þynningu var gleypnin ennþá A_1 við λ_1. **Ákvarðaðu** hlutfallið $\varepsilon_{\mathrm{HA}}/\varepsilon_{\mathrm{A^-}}$, þar sem $\varepsilon_{\mathrm{HA}}$ og $\varepsilon_{\mathrm{A^-}}$ eru gleypnistuðlar (absorption coefficients) HA og A$^-$, við λ_1. 10pt

Hluti B

Skoðum eftirfarandi efnajafnvægi í gasfasa.

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

Hreinu gasi D er komið fyrir við þrýsting P í ferstrendingslaga íláti sem hefur gegnsæja og færanlega hlið með þversnið S (sjá mynd að neðan). Jafnvægi er komið á meðan heildarþrýstingnum er haldið föstum við P. Gleypni gassins er $A = \varepsilon(n/V)l$, þar sem ε er gleypnistuðullinn, n er mólfjöldi gass, V er rúmmál gassins og l er lengd geisla. Gerðu ráð fyrir að allir hlutar gasblöndunnar hegði sér sem kjörgas.



Notaðu eftirfarandi skilgreiningar eftir þörfum:

	Upphafsástand		Við jafnvægi	
	D	M	D	M
Hlutþrýstingur	P	0	p_D	p_M
Mólfjöldi	n_0	0	n_D	n_M
Rúmmál	V_0		V	

B.1	Gleypni gassins við λ_B1 þegar mæld eftir stefnu x ($l = l_x$) var A_B1, bæði við upphafsástand og við jafnvægi. **Ákvarðaðu** hlutfallið $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ við λ_B1, þar sem ε_D og ε_M eru gleypnistuðlar D og M.	6pt

B.2	Gleypni gassins við λ_B2 þegar mæld eftir stefnu y var A_B2, bæði við upphafsástand ($l = l_{y0}$) og við jafnvægi ($l = l_y$). **Ákvarðaðu** hlutfallið $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ við λ_B2.	6pt

Lambert–Beer Lögmál?

Hluti A

A.1 (10 pt)

(Framhald á næstu síðu)

A.1 (cont.)

$\varepsilon_{\mathrm{HA}}/\varepsilon_{\mathrm{A^-}} =$ ______________________

Hluti B

B.1 (6 pt)

$\varepsilon_{\mathsf{D}}/\varepsilon_{\mathsf{M}} =$ ____________________

B.2 (6 pt)

$\varepsilon_D/\varepsilon_M =$ ______________________

IChO
Problem 4

Cover sheet

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

The Redox Chemistry of Zinc

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

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

Part A

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

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

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

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

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

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

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

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

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

Part B

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

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

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

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

B.1	In order for reaction (7) to proceed at a hydrogen pressure kept at 1 bar, it is necessary to reduce the partial pressure of the generated water vapor. **Calculate** the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 °C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are $\Delta G_{\mathrm{ZnO}}(300^\circ\mathrm{C}) = -2.90 \times 10^2$ kJ mol^{-1} and $\Delta G_{\mathrm{H_2O}}(300^\circ\mathrm{C}) = -2.20 \times 10^2$ kJ mol^{-1}, respectively.	4pt

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

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

B.2	A zinc–air battery was discharged at 20 mA for 24 hours. **Calculate** the change in mass of the negative electrode (anode) of the battery.	3pt

Mt. Fuji

B.3 Consider the change of e.m.f. of a zinc–air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are $-38\,^\circ$C (February) and 3776 m, respectively. The atmospheric pressure is represented by **5pt**

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

at altitude $h\,[\text{m}]$ 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 $-38\,^\circ$C and 1 bar.

B.4 **Calculate** the Gibbs energy change for reaction (6) at $25\,^\circ$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 $25\,^\circ$C and 1 bar are given as (10) and (11), respectively. **9pt**

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

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

Redox efnafræði sinks

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							

Sink hefur löngum verið notað í málmblöndur. Sink sem finna má í úrgangsvatni frá iðnaði er aðskilið frá vatninu með fellingu (precipitation), til að afeitra vatnið. Fellingin sem fæst er afoxuð svo að hægt sé að endurheimta sinkið og að lokum endurnýta það sem sinkmálm.

Hluti A

Leysnijafnvægi sinkhýdroxíðs $Zn(OH)_2(s)$ við 25 °C og tilheyrandi jafnvægisfastar er gefið í jöfnum 1-4.

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

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

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

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

Leysni, S, sinks (þ.e. styrkur sinks í mettaðri vatnslausn) er gefin með jöfnu 5.

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

A.1	Þegar jafnvægjum 1-4 er náð, **reiknaðu** á hvaða pH bili styrkur $[\text{Zn(OH)}_2(\text{aq})]$ er hæstur af styrkjum $[\text{Zn}^{2+}(\text{aq})]$, $[\text{Zn(OH)}_2(\text{aq})]$ og $[\text{Zn(OH)}_4^{2-}(\text{aq})]$.	6pt

A.2	Mettuð $\text{Zn(OH)}_2(\text{s})$ vatnslausn með pH = 7,00 var útbúin og síuð. NaOH var bætt við síuvökvann til að hækka pH hans upp í 12,00. **Reiknaðu** mólprósentu sinks sem fellur út þegar pH er hækkað úr 7,00 í 12,00. Hunsaðu rúmmáls- og hitastigsbreytingar.	5pt

Hluti B

Næst var hið endurheimta sinkhýdroxíð hitað og umbreytt í sinkoxíð samkvæmt hvarfinu hér að neðan:

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

Svo var sinkoxíðið afoxað í sinkmálm, með því að hvarfa það við vetni:

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

B.1	Til þess að hvarf (7) geti gengið við fastan 1 bar þrýsting vetnis, þá er nauðsynlegt að minnka hlutþrýsting vatnsgufunnar sem myndast. **Reiknaðu** efri mörk hlutþrýstings vatnsgufu ef hvarf (7) á að geta gengið við 300 °C. Hér er Gibbs myndunarfríorka sinkoxíðs og vatnsgufu við 300 °C og 1 bar (fyrir öll efni á gasfasa) $\Delta G_{\text{ZnO}}(300°\text{C}) = -2,90 \times 10^2$ kJ mol^{-1} og $\Delta G_{\text{H}_2\text{O}}(300°\text{C}) = -2,20 \times 10^2$ kJ mol^{-1}.	4pt

Sinkmálmur er notaður sem efniviður í neikvætt rafskaut (anóðu) í málm-loft rafhlöðum. Rafskautið samanstendur af Zn og ZnO. Það notar eftirfarandi oxunar-afoxunarhvarf til að framkalla rafstraum með íspennu (electromotive force, e.m.f.) $E°$ við 25 °C og 1 bar.

$$\text{Zn(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{ZnO(s)} \qquad E° = 1.65\,\text{V} \tag{8}$$

B.2	Sink-loft rafhlaða var afhlaðin við 20 mA í 24 klst. **Reiknaðu** massabreytingu neikvæða rafskautsins (anóðunnar) í rafhlöðunni.	3pt

Mt. Fuji

B.3 Skoðum nú hvernig breyting íspennu í sink-loft rafhlöðu er háð aðstæðum. **Reiknaðu** íspennuna á tindi Mt. Fuji, þar sem hitastig er $-38\,^{\circ}$C (í febrúar) og hæð fjallsins er 3776 m. Loftþrýstingur er gefinn með 5pt

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

við hæð $h\,[\text{m}]$ og hitastig $T\,[^{\circ}\text{C}]$. Mólhlutfall súrefnis í andrúmslofti er 21%. Gibbs fríorkubreyting hvarfs (8) er $\Delta G_{\text{ZnO}}(-38^{\circ}\text{C}) = -3,26 \times 10^{2}$ kJ mol^{-1} við $-38\,^{\circ}$C og 1 bar.

B.4 **Reiknaðu** Gibbs fríorkubreytingu hvarfs (6) við $25\,^{\circ}$C. Staðalafoxunaríspennur, $E^{\circ}(\text{Zn}^{2+}/\text{Zn})$ og $E^{\circ}(\text{O}_2/\text{H}_2\text{O})$ við $25\,^{\circ}$C og 1 bar eru gefnar í jöfnum (10) og (11). 9pt

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

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

Redox efnafræði sinks

Hluti A

A.1 (6 pt)

______ < pH < ______

A.2 (5 pt)

______________ %

Hluti B

B.1 (4 pt)

$p_{H_2O}=$ ________________ bar

B.2 (3 pt)

________________ g

B.3 (5 pt)

________________ V

B.4 (9 pt)

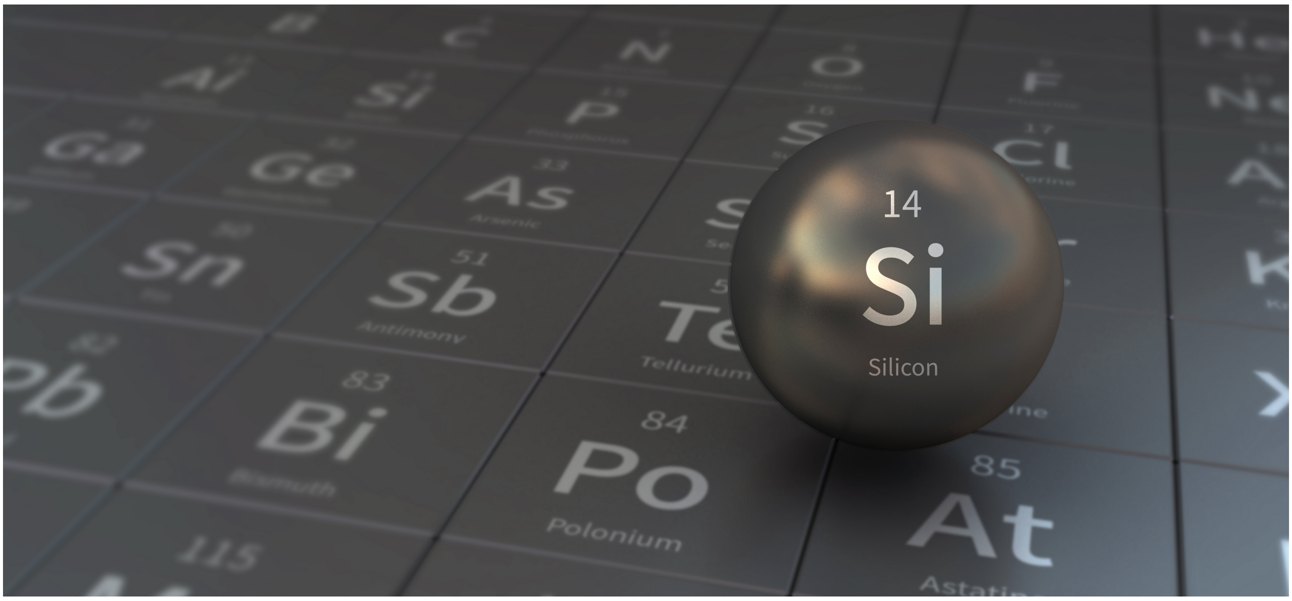
$\Delta G^{\circ} =$ ________________ J mol^{-1}

IChO
Problem 5
Cover sheet

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

Mysterious Silicon

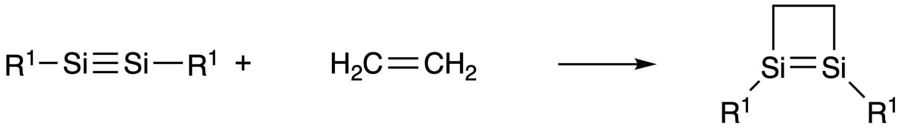
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



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 $(R^1{-}Si)_2(R^2{-}C)_4$.

$$R^1-Si\equiv Si-R^1 + R^2-C\equiv C-R^2 \longrightarrow \mathbf{A} \xrightarrow{R^2-C\equiv C-R^2} \mathbf{B} + \mathbf{C}$$

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

A.1 **Draw** the structural formulae of **A**, **B**, and **C** using R^1, R^2, Si, and C, with one of the possible resonance structures. 9pt

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

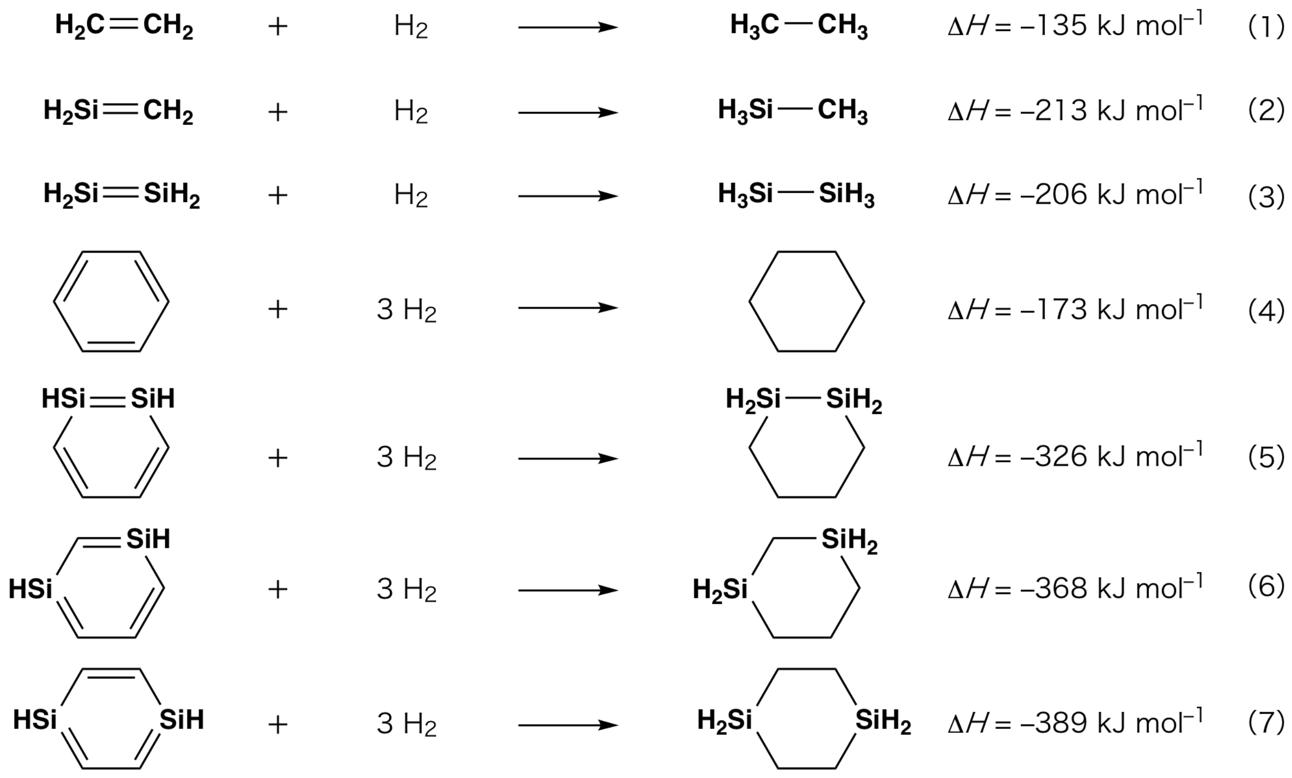


Fig. 1

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

A.3	**Calculate** ΔH for the transformation of **D** to **E**. Assume that ΔH does not depend on temperature.	6pt

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

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

Part B

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

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

- **Standardization of Na_2SiF_6 solution** :

· Preparation

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

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

· Procedure

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

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

- **Reaction of CCl_4 with Na_2SiF_6:**

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

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

Table 1

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

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

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

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.

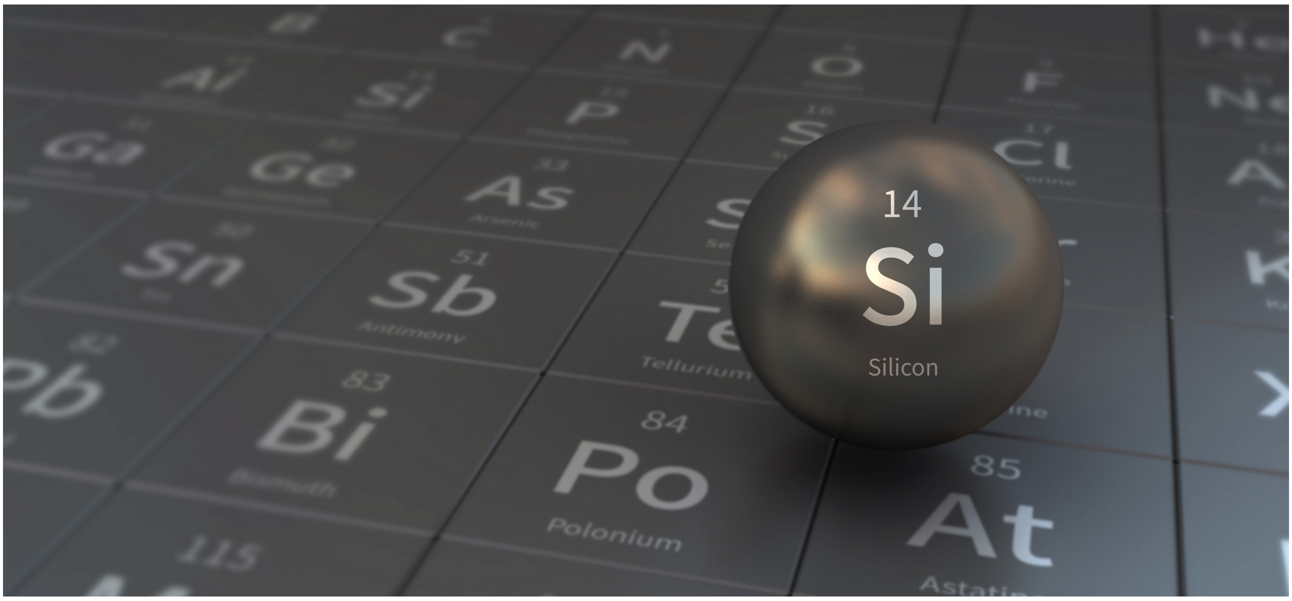
It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

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

Hinn dularfulli kísill

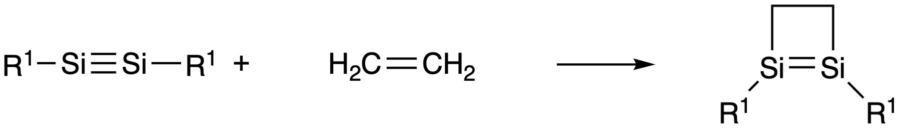
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



Þótt kísill sé frumefni í flokki 14, eins og kolefni, þá er verulegur munur á eiginleikum þessara efna.

Hluti A

Ólíkt kolefnis-kolefnis þrítengi, þá er kísil-kísil þrítengi í efnasambandi (táknað með $R^1{-}Si \equiv Si{-}R^1$ (R: lífrænn sethópur)), gríðarlega hvarfgjarnt. Til dæmis hvarfast það við etýlen svo það myndast hringlaga myndefni sem inniheldur fjórhring.



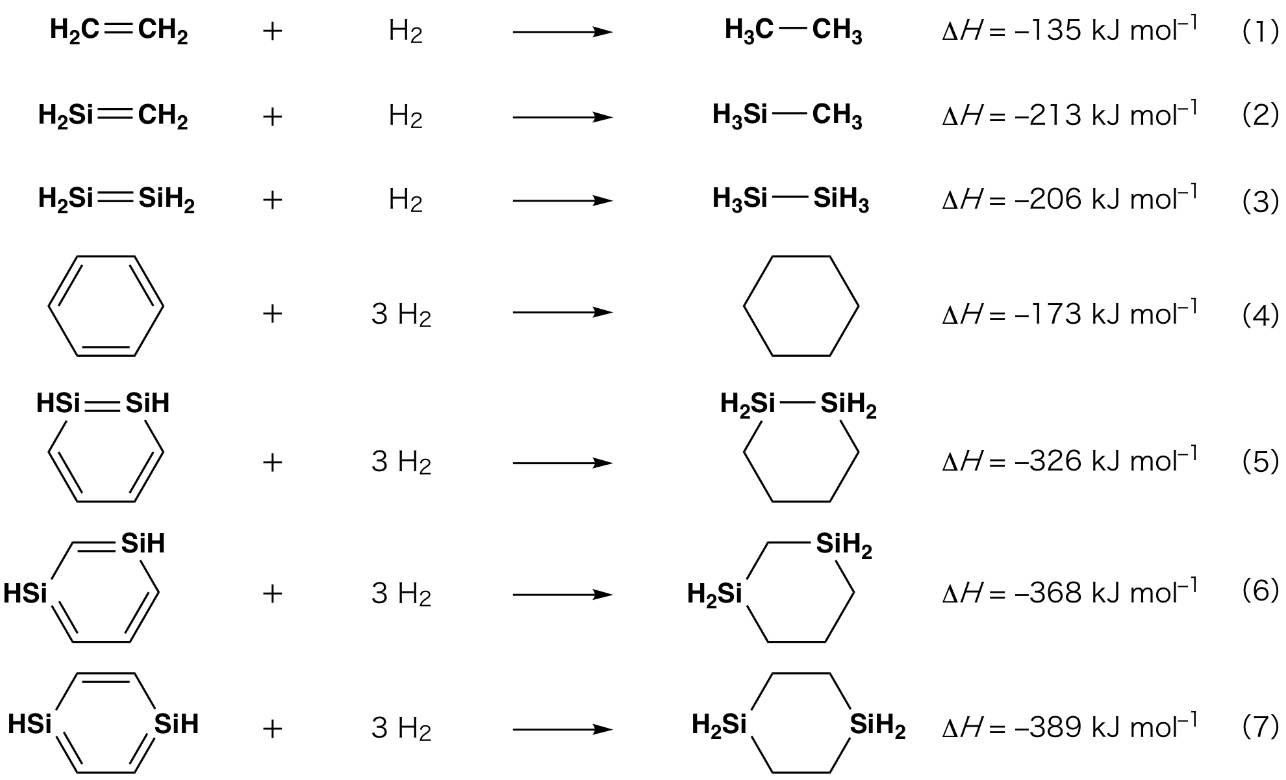
Þegar $R^1{-}Si \equiv Si{-}R^1$ er meðhöndlað með alkýn ($R^2{-}C \equiv C{-}R^2$), myndast fyrst milliefnið **A**, sem er fjórhringur. **A** hvarfast áfram við aðra $R^2{-}C \equiv C{-}R^2$ sameind og það leiðir til myndunar á ísómerum **B** og **C**, en þær hafa báðar bensen-líka (arómatíska) byggingu. **B** og **C** eru svokölluð dísílabensen sem innihalda sexhring og þau má tákna með $(R^1{-}Si)_2(R^2{-}C)_4$.

$$R^1-Si\equiv Si-R^1 + R^2-C\equiv C-R^2 \longrightarrow \mathbf{A} \xrightarrow{R^2-C\equiv C-R^2} \mathbf{B} + \mathbf{C}$$

^{13}C NMR greining á byggingum sexhringjanna Si_2C_4 sýnir tvö merki (signals) fyrir **B** og eitt merki fyrir **C**.

A.1 **Teiknaðu** byggingar **A**, **B** og **C**, með því að nota R^1, R^2, Si, og C. Það nægir að teikna eina vokmynd hvers efnis. 9pt

A.2 **Reiknaðu** arómatíska stöðgunarorku (aromatic stabilization energy (ASE)) fyrir bensen og fyrir **C** (fyrir tilfellið $R^1 = R^2 = H$) sem jákvætt gildi. Notaðu vermibreytingu sumra vetnunarhvarfanna á ómettuðum efnum, sem sýnd eru að neðan á mynd 1. 7pt



Mynd 1

Þegar xýlen (xylene) lausn efnis **C** er hituð, ísómerast efnið og fæst þá jafnvægisblanda af efnasamböndum **D** og **E**. Mólhlutfallið er **D** : **E** = 1 : 40,0 við 50,0 ˚C og **D** : **E** = 1 : 20,0 við 120,0 ˚C.

A.3 **Reiknaðu** ΔH fyrir umbreytinguna úr **D** í **E**. Gerðu ráð fyrir að ΔH sé *ekki* háð hitastigi. 6pt

Ísómerunin úr **C** í **D** og **E** verður vegna umbreytinga π-tengja yfir í σ-tengi án þess að nokkur σ-tengi rofni. ^{13}C NMR greining sýndi eitt merki fyrir Si_2C_4 hringinn í **D** og tvö merki í **E**. Byggingargrind hrings **D** inniheldur enga þríhringi, en byggingargrind hrings **E** inniheldur tvo þríhringi sem hafa sameiginlegt tengi.

A.4 **Teiknaðu** byggingu efna **D** og **E** með því að nota R^1, R^2, Si, og C. 10pt

Hluti B

Í efnasamböndum hefur kísill mikla tengigetu með rafneikvæðum (electronegative) frumefnum eins og flúori (getur tengst fleiri en fjórum atómum). Nú eru málmflúoríð gjarnan notuð sem flúorunar-hvarfefni. Kísilflúoríð má einnig nota sem flúorunarefni þegar kísillinn tengist mörgum tengihópum.

Na_2SiF_6 var notað í flúorunarhvarf CCl_4 sem framkvæmt var á eftirfarandi hátt:

- **Stöðlun Na_2SiF_6 lausnar** :

· Undirbúningar

Vatnslausn **F**: 0,855 g af Na_2SiF_6 (188,053 g mol^{-1}) leyst upp í vatni (heildarrúmmál 200 mL).

Vatnslausn **G**: 6,86 g af $Ce_2(SO_4)_3$ (568,424 g mol^{-1}) leyst upp í vatni (heildarrúmmál 200 mL).

· Framkvæmd

Fellitítrun (precipitation titration) á lausn **F** (50,0 mL) með því að bæta lausn **G** út í í dropatali, í viðurvist xylenol orange efnavita, sem bindst Ce^{3+}. Eftir viðbót 18,8 mL af lausn **G**, breyttist litur lausnarinnar úr gulum yfir í fjólubleikan. Botnfallið sem myndaðist er tvíefni (binary compound) sem inniheldur Ce^{3+}, og eina kísil-efnasambandið sem myndaðist er $Si(OH)_4$.

B.1 **Skrifaðu** stillta efnajöfnu fyrir hvarf Na_2SiF_6 með $Ce_2(SO_4)_3$. 5pt

- **Hvarf CCl_4með Na_2SiF_6:**

(Magn þess efnis sem kann að tapast t.d. vegna uppgufunar er hverfandi í eftirfarandi framkvæmd.)

Na_2SiF_6(x [g]) var bætt út í CCl_4 (500,0 g) og hitað að 300˚C í lokuðu þrýstiþolnu hvarfhylki. Óhvarfað Na_2SiF_6 og NaCl sem myndaðist var síað frá. Síuvökvinn var þynntur að heildarrúmmáli 1,00 L með CCl_4 (lausn **H**). ^{29}Si og ^{19}F NMR róf af lausn **H** sýndu að SiF_4 var eina kísil-efnasambandið. Í ^{19}F NMR rófinu sást, að auk SiF_4 voru merki sem svara til $CFCl_3$, CF_2Cl_2, CF_3Cl, og CF_4 (Tafla 1). Heildunarhlutföll (integration ratio) í ^{19}F NMR rófinu eru í réttu hlutfalli við fjölda flúorkjarna.

Tafla 1

^{19}F NMR	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
Heildunarhlutfall	45,0	65,0	18,0	2,0

SiF_4 er vatnað svo það myndast H_2SiF_6 samkvæmt efnajöfnu 8:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \tag{8}$$

Þegar lausn **H** (10 mL) var bætt út í yfirmagn vatns, vatnaðist SiF_4 að fullu. Það H_2SiF_6 sem myndaðist við hvarfið var aðskilið frá lausninni. Það var hlutleyst og umbreytt að fullu í Na_2SiF_6 (vatnslausn **J**).

Botnfallið sem innihélt hið óhvarfaða Na_2SiF_6 og NaCl, sem var síað frá í upphafsskrefinu (undirstrikað í texta) var leyst upp að fullu í vatni, og fékkst þá vatnslausn **K** (10,0 L)

Næst voru framkvæmdar fellitítranir með lausn **G**. Endapunktar þessara títrana voru eftirfarandi:

· Fyrir lausn **J** (öll lausnin) þurfti 61,6 mL af lausn **G**

· Fyrir 100 mL af lausn **K** þurfti 44,4 mL af lausn **G**

Vert er að taka fram að NaCl og SiO_2 hafa engin áhrif á fellitítrunina.

B.2	**Reiknaðu** massa NaCl sem myndaðist í hvarfhylkinu (undirstrikað í texta), og **reiknaðu** massa (x [g]) af Na_2SiF_6 sem var notað sem upphafsefni.	15pt

B.3	77,8% af því CCl_4 sem var notað sem upphafsefni, var óhvarfað. **Reiknaðu** massa CF_3Cl sem myndaðist.	8pt

Hinn dularfulli kísill

Hluti A

A.1 (9 pt)

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

A.2 (7 pt)

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

A.3 (6 pt)

ΔH = kJ mol^{-1}

A.4 (10 pt)

D (5 pt)	**E** (5 pt)

Hluti B

B.1 (5 pt)

B.2 (15 pt)

(Framhald á næstu síðu)

B.2 (cont.)

NaCl ： g, Na_2SiF_6 ： g

B.3 (8 pt)

CF_3Cl : ____________________ g

IChO
Problem 6
Cover sheet

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

The Solid-State Chemistry of Transition Metals

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

Volcano at Sakurajima island

Part A

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

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

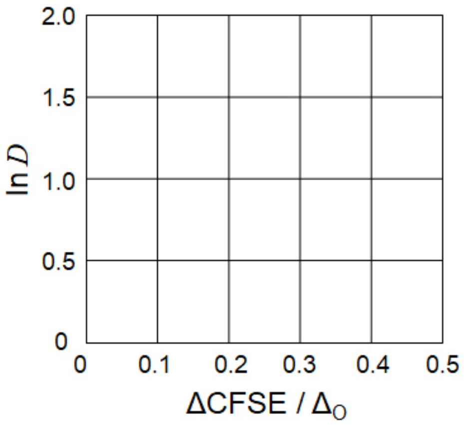
where $[\mathrm{M}]_\mathrm{s}$ and $[\mathrm{M}]_\mathrm{l}$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of $Cr^{2+}$and Mn^{2+} as examples.

	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.
Estimate D for Co^{2+}. 3pt



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

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

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

Part B

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

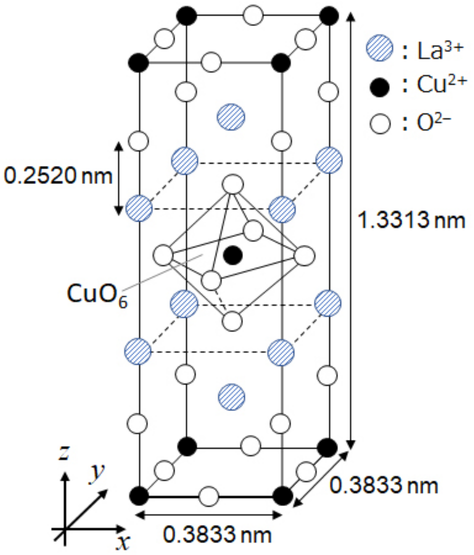


Fig. 1

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

B.1	**Write** the chemical formulae for **A** and **B**.	6pt
B.2	**Calculate** l_x and l_z using Fig. 1.	4pt
B.3	For Cu^{2+} in the distorted $[CuO_6]$ octahedron in **A** of Fig. 1, **write** the names of the split e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) in (i) and (ii), and **draw** the electron configuration in the dotted box in your answer sheet.	4pt

A is an insulator. When one La^{3+} is substituted with one Sr^{2+}, one hole is generated in the crystal lattice that can conduct electricity. As a result, the Sr^{2+}-doped **A** shows superconductivity below 38 K. When a substitution reaction took place for **A**, 2.05×10^{27} holes m^{-3} were generated.

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

Part C

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

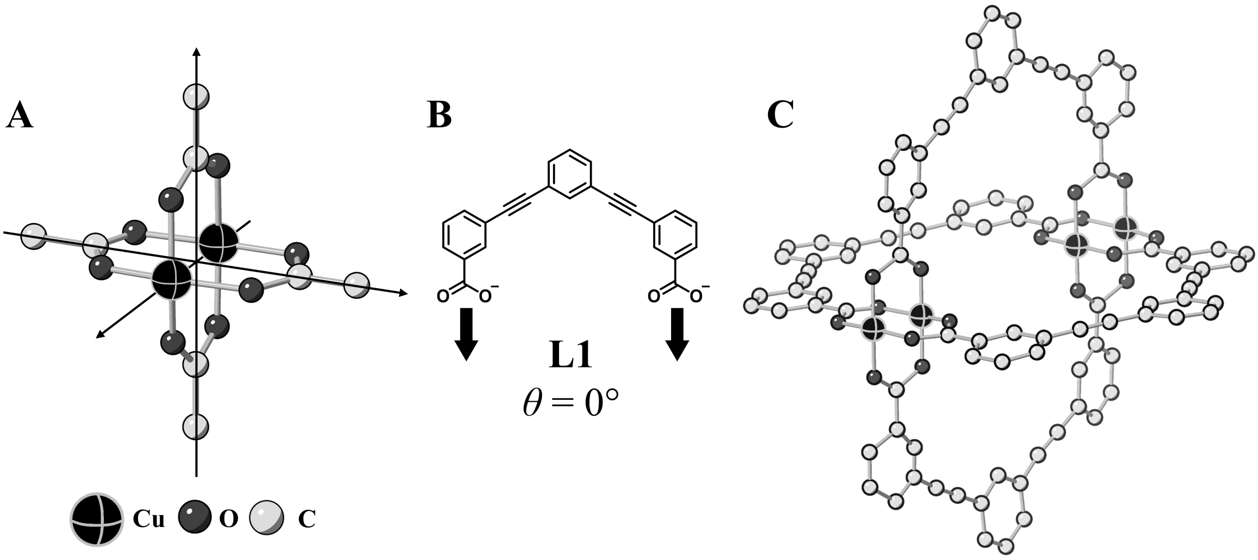
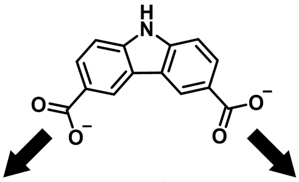


Fig. 2

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



L2

$\theta = 90°$

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

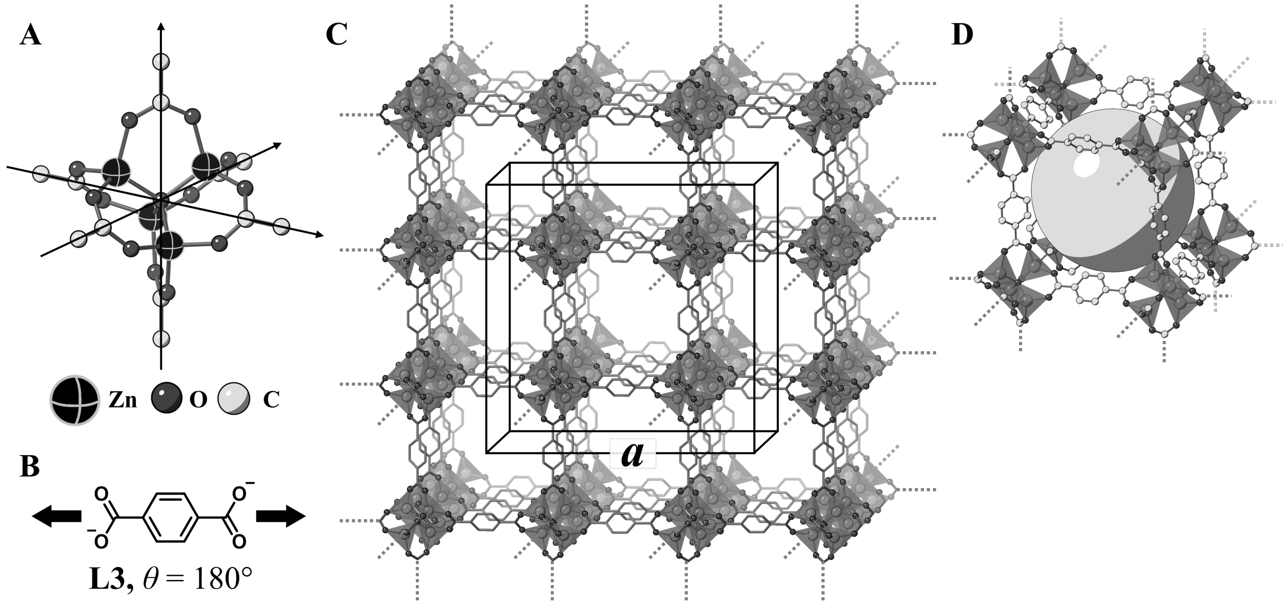


Fig. 3

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

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

Efnafræði fastra efnasambanda hliðarmálma

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											

Eldfjall á Sakurajima eyju

Part A

Japan er eitt þeirra landa í heiminum sem hefur flest eldfjöll. Þegar silíkatasteindir kristallast frá hraunkviku þá fer hluti af hliðarmálmjónum (M^{n+}) úr hraunkvikunni í silikatsteindirnar. Í þessu dæmi eru M^{n+} jónir girtar (coordinated) oxíðjónum (O^{2-}) með fjórtengdri tetrahedral (T_d) byggingu í hraunkvikunni og sextengdri oktahedral (O_h) byggingu í silíkatsteindum. Í bæði $T_d$og O_h byggingum hafa M^{n+} jónirnar háspuna rafeindaskipan. Dreifingarstuðullinn fyrir M^{n+} milli silíkatsteinda og kvikubráðar, D, er gefinn með eftirfarandi jöfnu:

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

þar sem $[M]_s$ styrkur M^{n+} í silíkatsteindum og $[M]_l$ er styrkur M^{n+} í hraunkvikunni. Í töflunni hér að neðan eru gefin dæmi um gildi D fyrir Cr^{2+}og Mn^{2+}.

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

Látum Δ_O vera orkumun d-svigrúma M^{n+} og $CFSE^O$ vera kristalsviðsorkuna (the crystal-field stabilization energy) í O_h sviði. Látum Δ_T og $CFSE^T$ vera samsvarandi stærðir fyrir T_d svið.

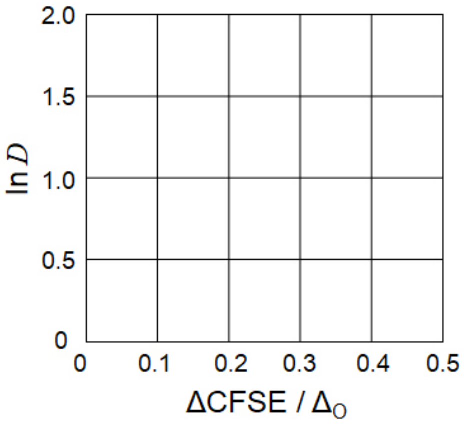
A.1 6pt

Reiknaðu $|CFSE^O - CFSE^T| = \Delta CFSE$ miðað við Δ_O fyrir Cr^{2+}, Mn^{2+}og Co^{2+}; gerðu ráð fyrir að $\Delta_T = 4/9\Delta_O$.

A.2 3pt

Línulegt samband kemur fram á grafi þegar ln$D$ er teiknað á móti $\Delta CFSE / \Delta_O$ í hnitakerfinu hér fyrir neðan.

Reiknaðu gildi D fyrir Co^{2+}.



Málmoxíð MO (M: Ca, Ti, V, Mn eða Co) hafa samskonar kristalbyggingu og matarsalt þar sem M^{n+} er í O_h umhverfi og með háspuna rafeindaskipan. Grindarorka þessara oxíða er aðalega vegna Coulombkrafta á milli jóna, en þeir ráðast af radíus og hleðslu jónanna, auk dálítils framlags frá CFSE fyrir M^{n+} í O_h sviði.

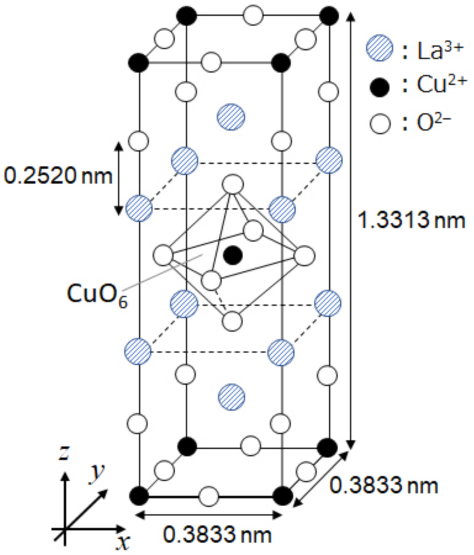
A.3 3pt

Veldu viðeigandi röð (a) til (f) fyrir grindarorku [kJ mol^{-1}] málmoxíðanna.

	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

Blandað oxíð **A**, sem inniheldur La^{3+} og Cu^{2+}, kirstallast með tetragonal grindareiningu eins og sýnt er á mynd 1. Í $[\mathrm{CuO_6}]$ oktahedroninum er Cu–O lengdin eftir *z*-ásnum (l_z) lengri en sú sem er á *x*-ásnum (l_x). $[\mathrm{CuO_6}]$ er því bjagað frá reglulegri O_h byggingu og hverfur þá margfeldni (degeneracy) $\mathrm{e_g}$ svigrúmanna ($\mathrm{d}_{x^2-y^2}$ og d_{z^2}).



Mynd 1

A er búið til með því að hitarjúfa (pyrolysis) komplex **B.** **B** er búið til með því að blanda saman málmklóríðum í þynntri ammoníks vantslausn sem inniheldur squariksýru $C_4H_2O_4$, en hún er tvísýra. Þegar **B** er hitað upp í 200 °C í þurru lofti tapar það 29,1% af massa sínum vegna uppgufunar kristalvatns (crystallization water), og ef það er hitað áfram upp í 700 °C þá rofnar CO_2 frá efninu. Heildarmassatapið við myndun **A** frá **B** er 63,6%. Bent skal á að aðeins vatn og CO_2 rjúka burt við hitarofshvarfið.

B.1 6pt

Ritaðu efnaformúlur **A** og **B**.

B.2 4pt

Reiknaðu l_x og l_z frá mynd 1.

B.3 4pt

Ritaðu nöfn klofnu $\mathrm{e_g}$ svigrúmanna ($\mathrm{d}_{x^2-y^2}$ og d_{z^2}) í (i) og (ii) fyrir Cu^{2+} bjagaða $[\mathrm{CuO_6}]$ oktahedroninn í **A** á mynd 1 og **teiknaðu** rafeindaskipanina í punktsrikuðu reitina á svarblaðinu þínu.

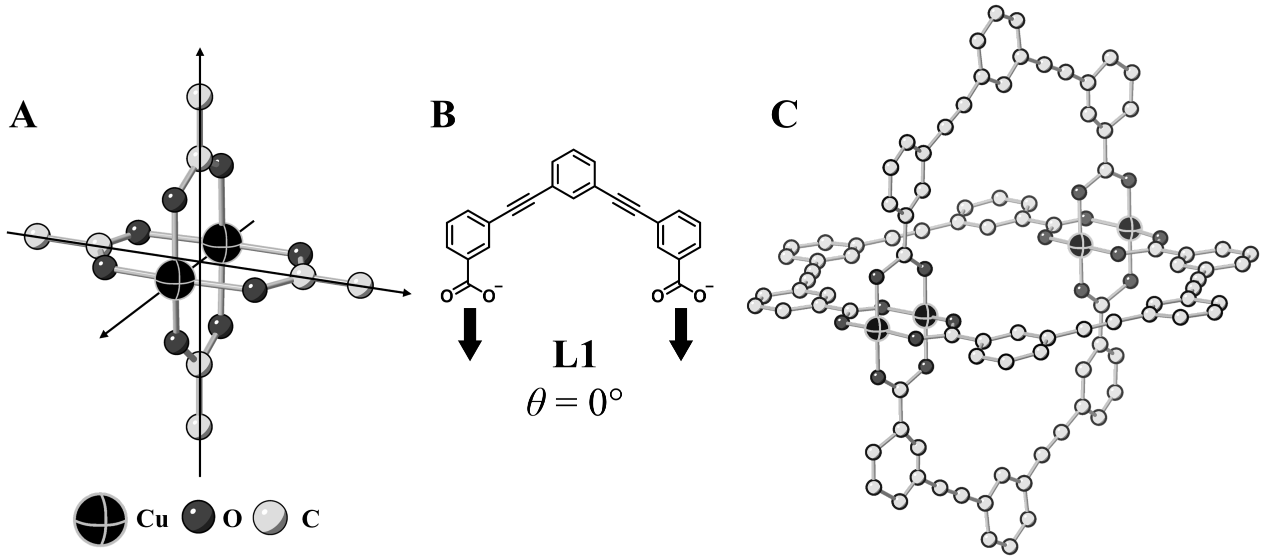
A er rafeinangrandi efni. Þegar einu La^{3+} er skipt út fyrir eitt Sr^{2+}, þá myndast ein hola í kristagrindinni sem getur leitt rafmagn. **A** sem íbætt (doped) er með Sr^{2+} verður þá ofurleiðandi fyrir neðan 38 K. Þegar slíkt skiptihvarf var framkvæmt fyrir **A** þá mynduðust $2,05 \times 10^{27}$ holur á m^3.

B.4 4pt

Reiknaðu prósentuna af Sr^{2+} sem skipt var út fyrir La^{3+} frá mólhlutfallinu í skiptihvarfinu. Athugaðu að hleðsla jónanna og kristalbyggingin breytast ekki við skiptihvarfið.

Hluti C

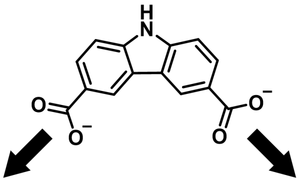
$Cu_2(CH_3CO_2)_4$ er samsett úr $CH_3CO_2{}^-$ sem tengjast tveimur Cu^{2+} (mynd 2A). Bygging $Cu_2(CH_3CO_2)_4$ hefur mikla samhverfu (symmetry) þar sem tveir ásar fara í gegnum kolefnisatóm fjögurra $CH_3CO_2{}^-$ auk áss sem fer í gegnum tvö Cu^{2+}, en ásarnir þrír eru hornréttir hver á annan. Þegar díkarboxýlat tengill (ligand) er notaður í stað $CH_3CO_2{}^-$, myndast ”búrkomplex” (“cage complex”) . Búrkomplexinn $Cu_4(\mathbf{L1})_4$ er samsettur úr flötu díkarboxýlati **L1** (mynd 2B) og Cu^{2+} (mynd 2C). Bygging búrkomplexins ákvaðast af horninu θ milli girðistefnu (coordination directions) karboxýlathópanna tveggja, en θ-hornið sem er sýnt með örvunum á mynd 2B. Gildi θ er 0° fyrir **L1**. Athugaðu að vetnisatómin eru ekki sýnd á mynd 2.



Mynd 2

C.1 5pt

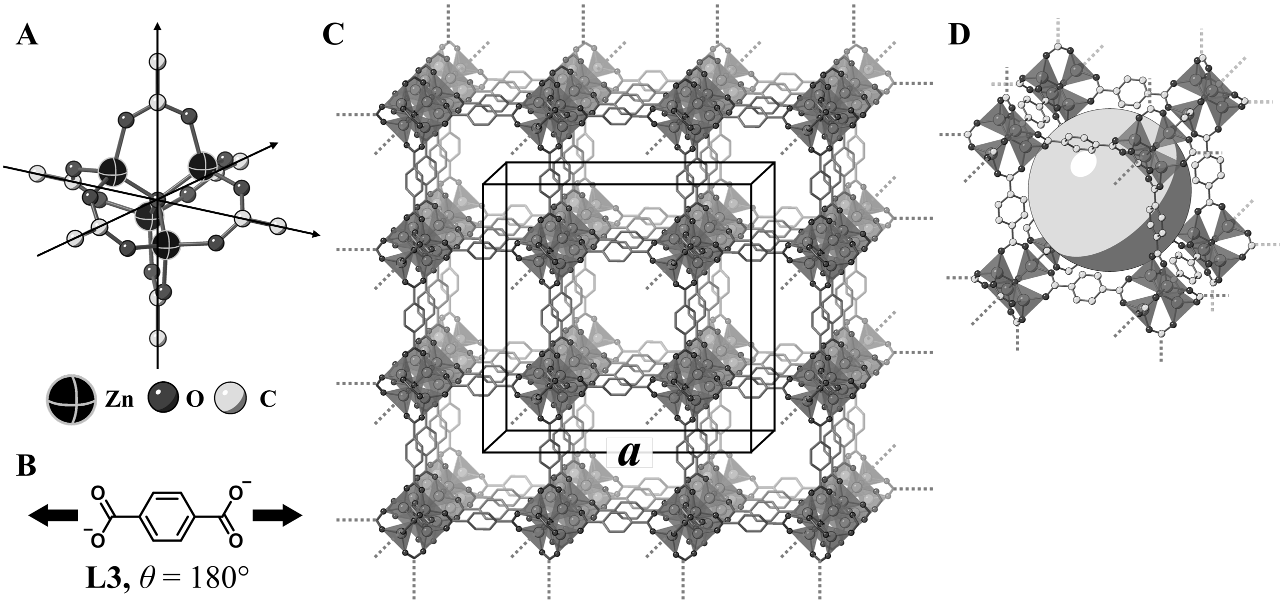
Hornið θ fyrir flata díkarboxýlatið **L2** hér að neðan helst fast við 90˚. **Ákvaðaðu** minnstu gildin fyrir *n* og *m* ef samsetning búrkomplexins sem myndast frá **L2** og Cu^{2+}er $Cu_n(\mathbf{L2})_m$. Gerðu ráð fyrir að aðeins CO_2^- hópar **L2** tengist Cu^{2+} jónum.



L2

$\theta = 90°$

Zinkkomplex, $Zn_4O(CH_3CO_2)_6$, inniheldur fjögur Zn^{2+} sem mynda tetrahedral-laga klasa, ásamt sex $CH_3CO_2^-$og einu O^{2-} (mynd 3A). Í $Zn_4O(CH_3CO_2)_6$ er O^{2-} í miðjunni og þrír ásar fara í gegnum kolefnisatóm $CH_3CO_2^-$ og eru þeir hornréttir hver á annan. Þegar *p*-benzenedíkarboxýlat (mynd 3B, **L3**, *θ* = 180°) er notað í stað $CH_3CO_2^-$, tengjast Zn^{2+} klasarnir sama í kristallað fast efni (**X**) sem kallast ”gljúp girðifjölliða” (“porous coordination polymer”, mynd 3C). Samsetning **X** er $[Zn_4O(\mathbf{L3})_3]_n$, og hefur efnið teningslaga kristalbyggingu með holur af nanóstærð. Ein slík nanóhola er sýnd sem kúla á mynd 3D og er hver tetrahedral-laga Zn^{2+} klasi táknaður sem dökkgrár fjölflötungur á myndum 3C og 3D. Athugaðu að vetnisatómin eru ekki sýnd á mynd 3.



Mynd 3

C.2 5pt

X hefur teningslaga grindareiningu með kantlengdina *a* (mynd 3C) og eðlismassann 0,592 g cm^{-3}. **Reiknaðu** gildi *a* í [cm].

C.3 5pt

X inniheldur aragrúa fjölda nanóhola og 1 g af **X** getur hýst $3,0 \times 10^2$ mL af CO_2 sem er við 1 bar og 25 °C. **Reiknaðu** meðalfjölda CO_2 sameinda sem eru í hverri nanóholu.

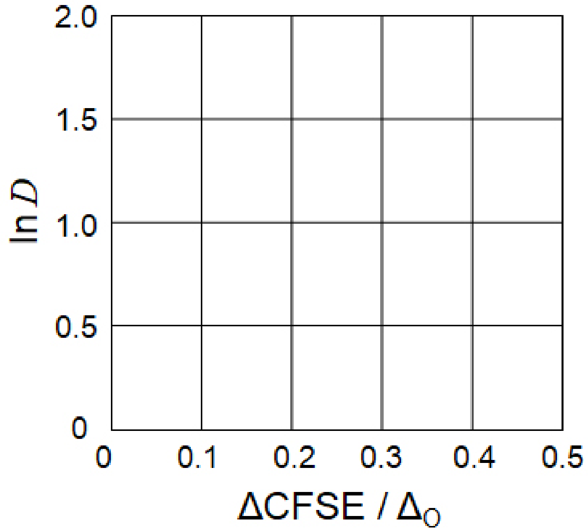
Efnafræði fastra efnasambanda hliðarmálma

Hluti 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)

____

Part B

B.1 (6 pt)

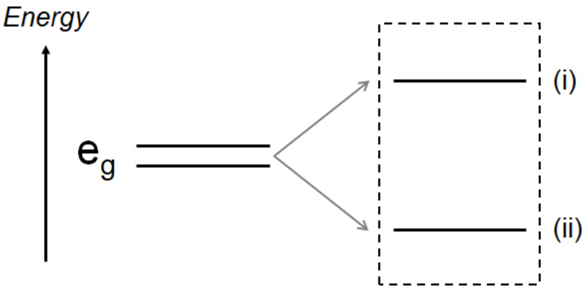
A : ______________________________, B : ______________________________

B.2 (4 pt)

$l_x =$ ________________________ nm, $l_z =$ ________________________ nm

B.3 (4 pt)

(i) : ________________________, (ii) : ________________________



B.4 (4 pt)

____________________ %

Hluti C

C.1 (5 pt)

$n =$ ____________________, $m =$ ____________________

C.2 (5 pt)

$a =$ ____________________ cm

C.3 (5 pt)

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					

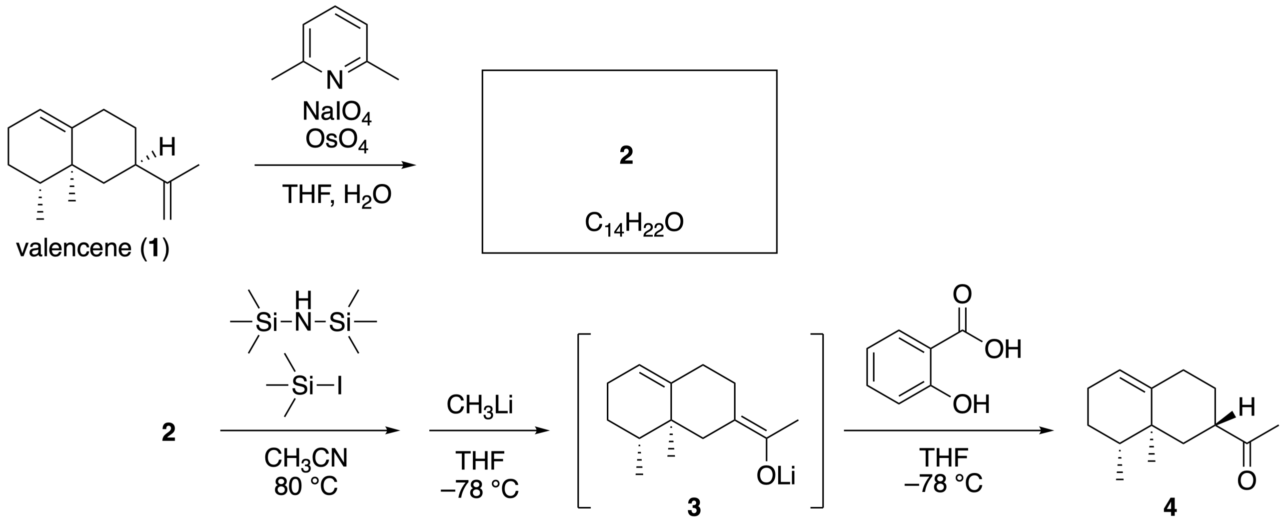
Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

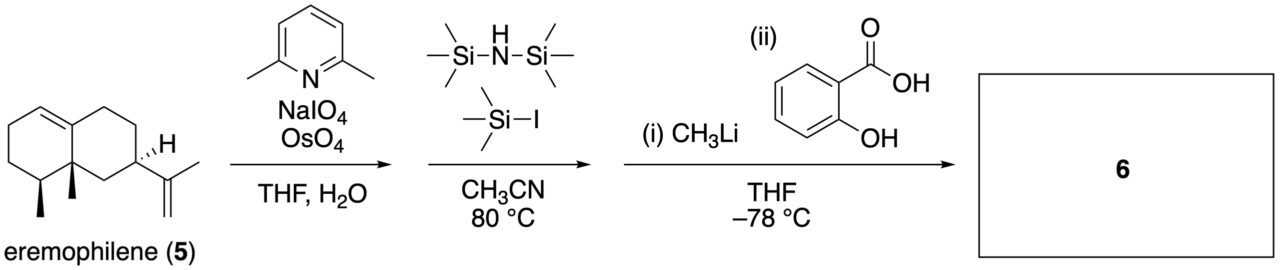
Photo courtesy: Tohoku Univ.

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.

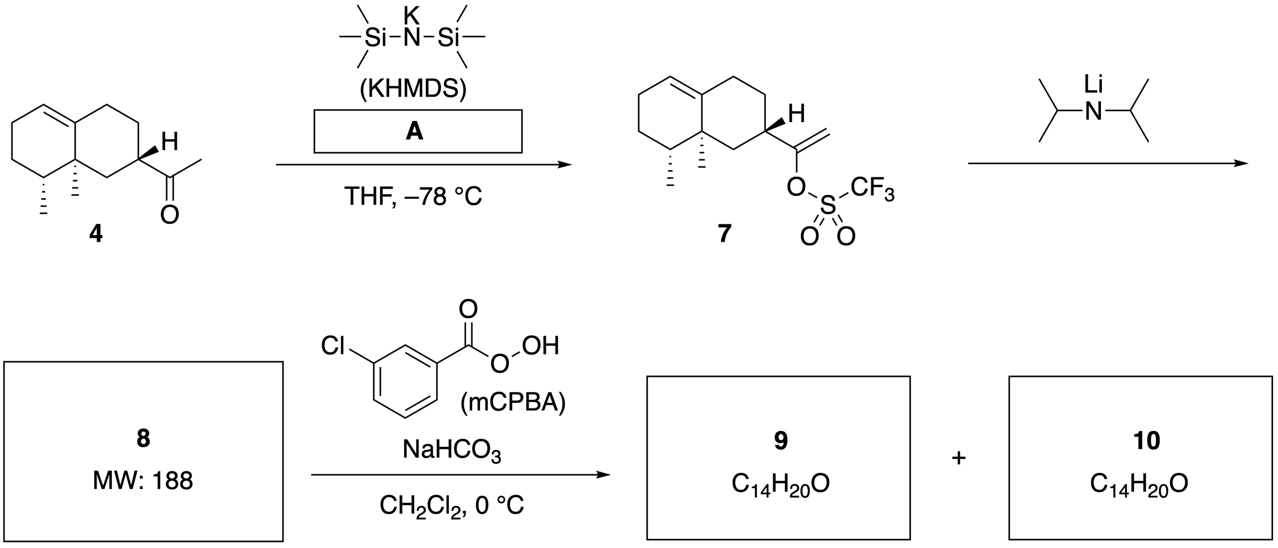
Inula linariifolia

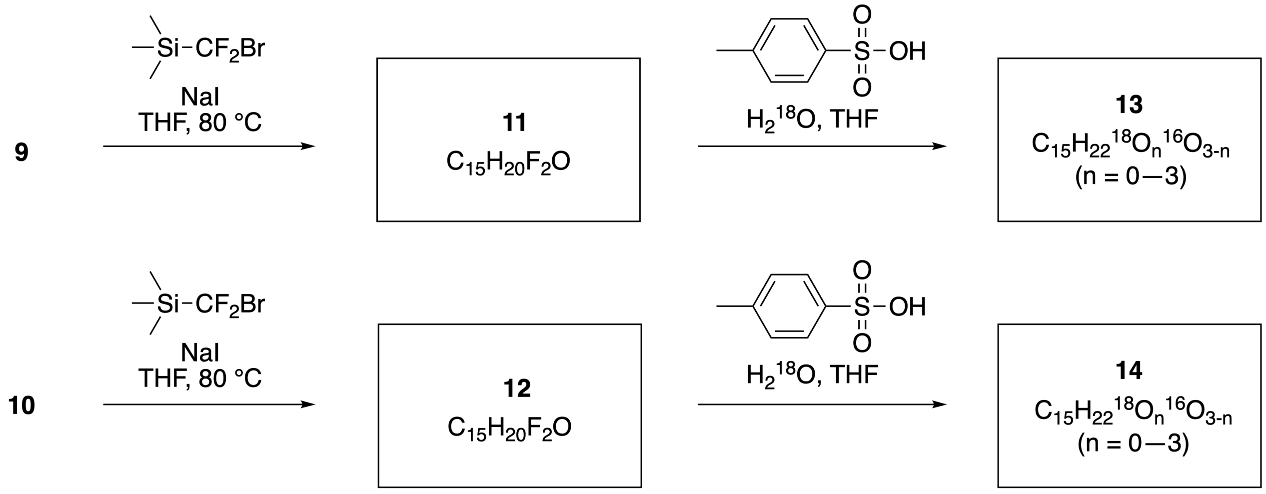


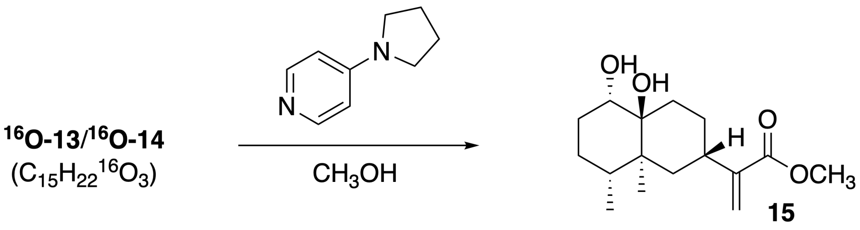


A.1	**Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary.	5pt

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-lineariifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.

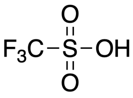






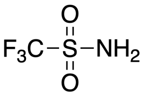
A.2 **Choose** the appropriate structure for **A**. 2pt

I



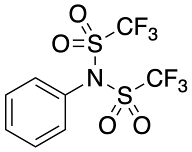
$F_3C-S(=O)_2-OH$

II

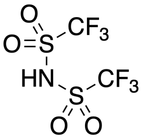


$F_3C-S(=O)_2-NH_2$

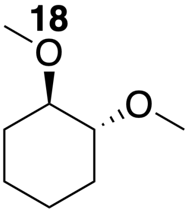
III



IV

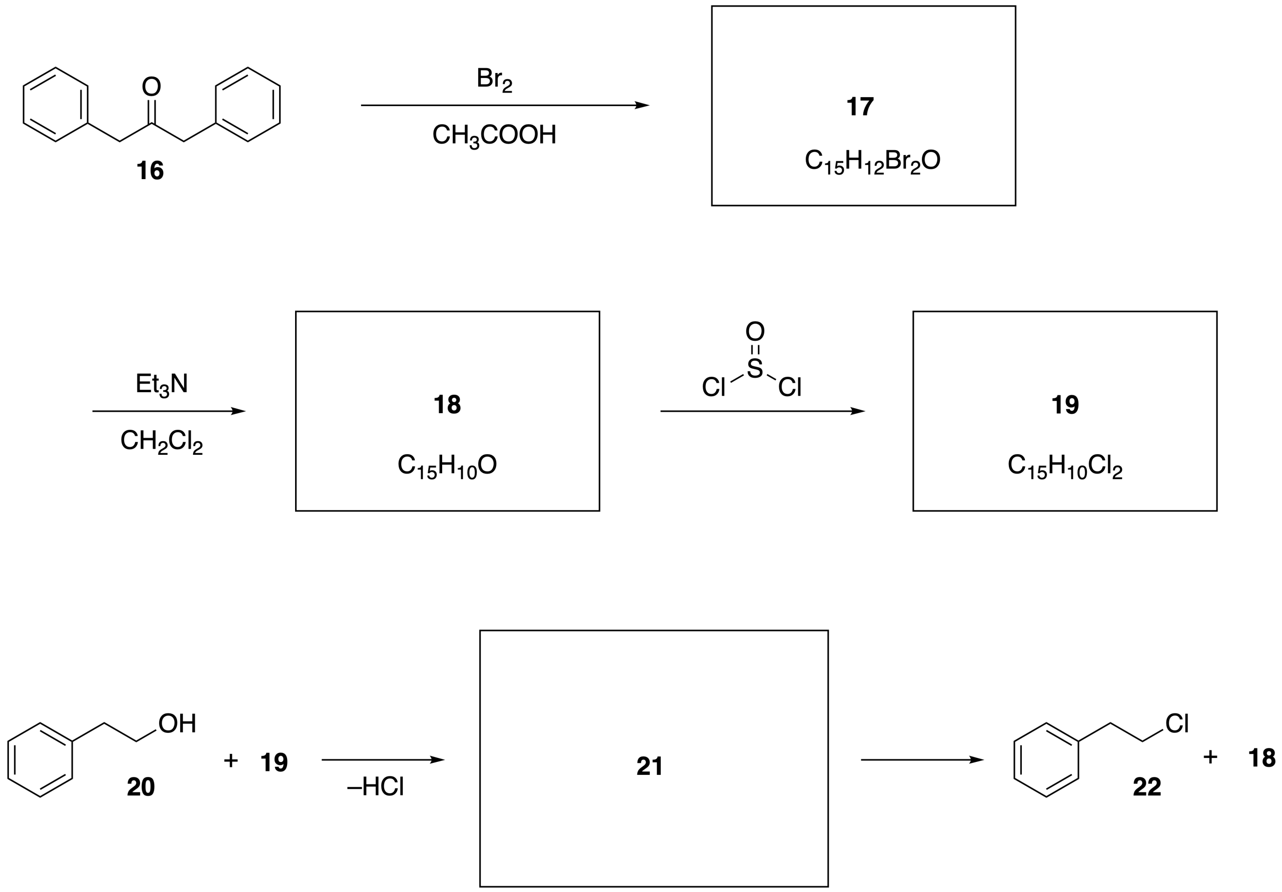


A.3 **Draw** the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, **indicate** the introduced ^{18}O atoms for **13** and **14** as shown in the example below. 19pt



Part B

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



^{1}H NMR (CD$_3$CN, 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	<u>**Draw**</u> 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					

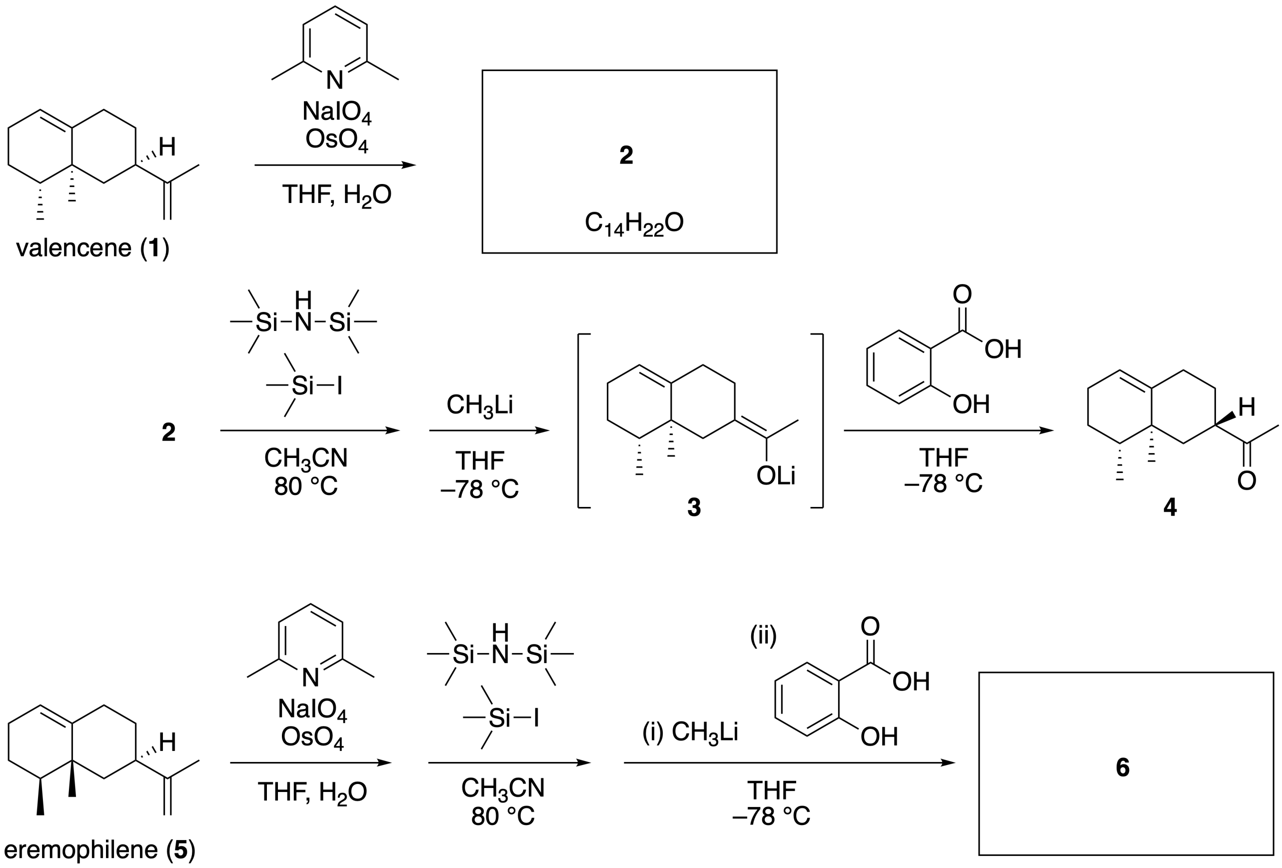
Prof. Nozoe (1902–1996) founded the research field of non-benzenoid aromatic compounds.

Photo credit: Tohoku Univ.

Part A

Leariifolianone 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

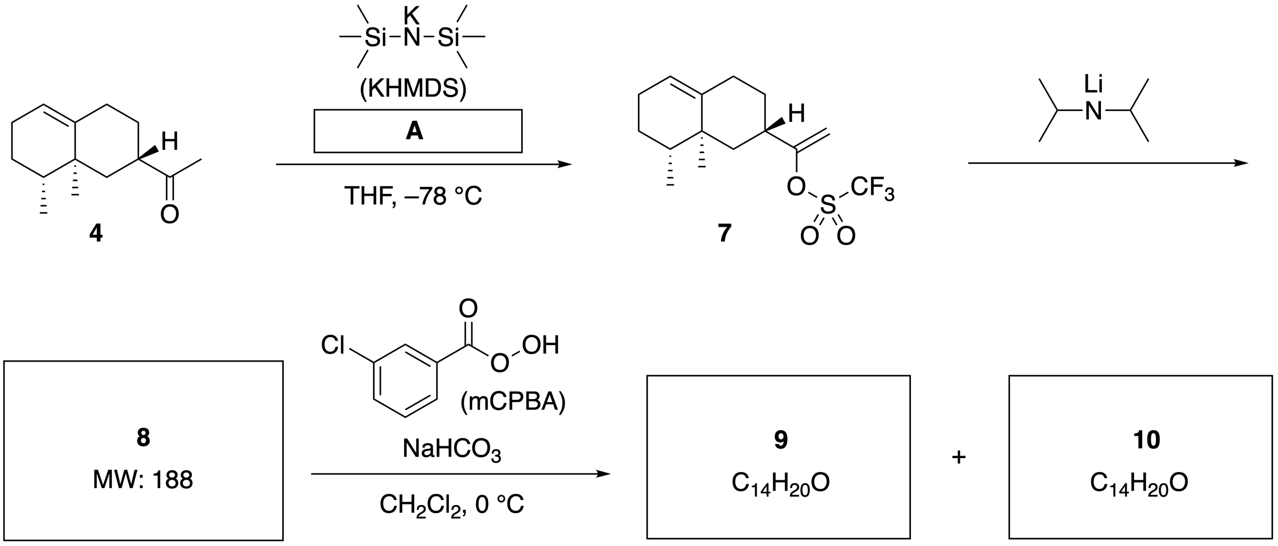


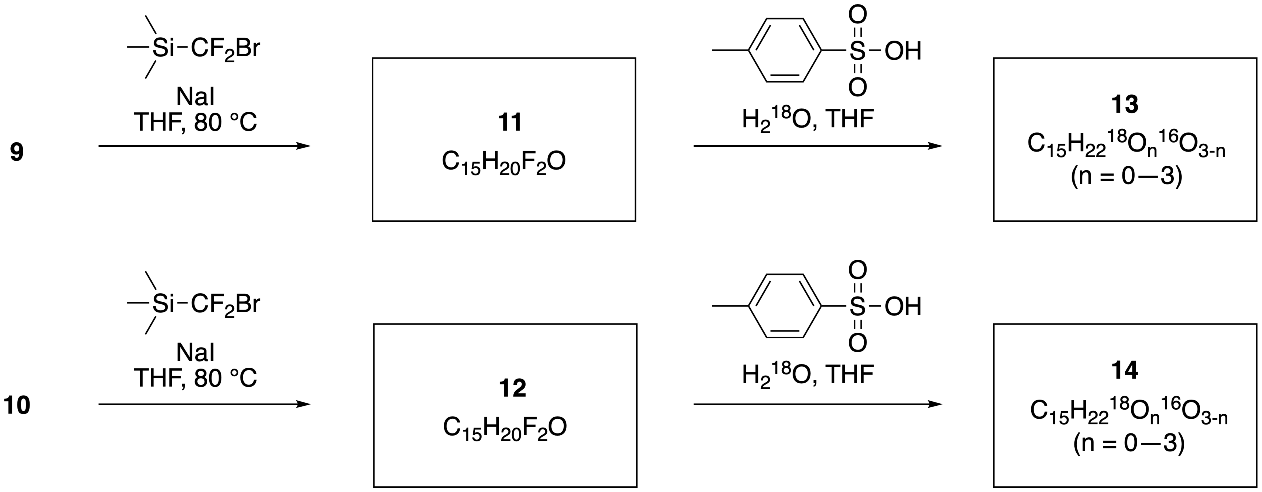
A.1	<u>**Draw**</u> the structures of **2** and **6** and clearly identify the stereochemistry where necessary.	5pt

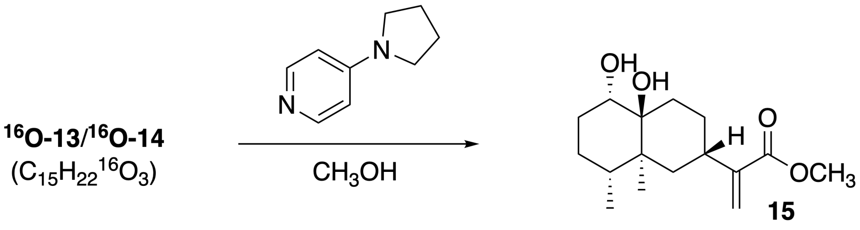
Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocentres in **7**. Compounds **9** and **10** have five stereocentres and no carbon-carbon double bonds.

Assume that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-lineariifolianones **13** and **14** from **11** and **12**, respectively.

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

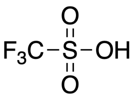

K
Si
N
Si
(KHMDS)
A
THF, –78 °C
H
O
4
H
O
S
CF3
O O
7
Li
N
8
MW: 188
Cl
O
O
OH
(mCPBA)
NaHCO3
CH2Cl2, 0 °C
9
C14H20O
+
10
C14H20O


9
Si–CF2Br
NaI
THF, 80 °C
11
C15H20F2O
O
S–OH
O
H2 18O, THF
13
C15H22 18On 16O3-n
(n = 0—3)
10
Si–CF2Br
NaI
THF, 80 °C
12
C15H20F2O
O
S–OH
O
H2 18O, THF
14
C15H22 18On 16O3-n
(n = 0—3)


16O-13/16O-14
(C15H22 16O3)
N
N
CH3OH
OH
OH
H
O
OCH3
15

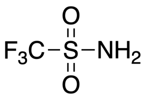
A.2 **Choose** the appropriate structure for **A**. 2pt

I



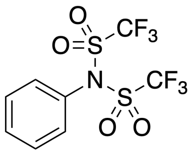
$F_3C-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-OH$

II

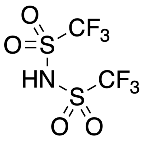


$F_3C-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-NH_2$

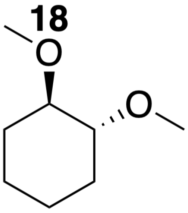
III



IV

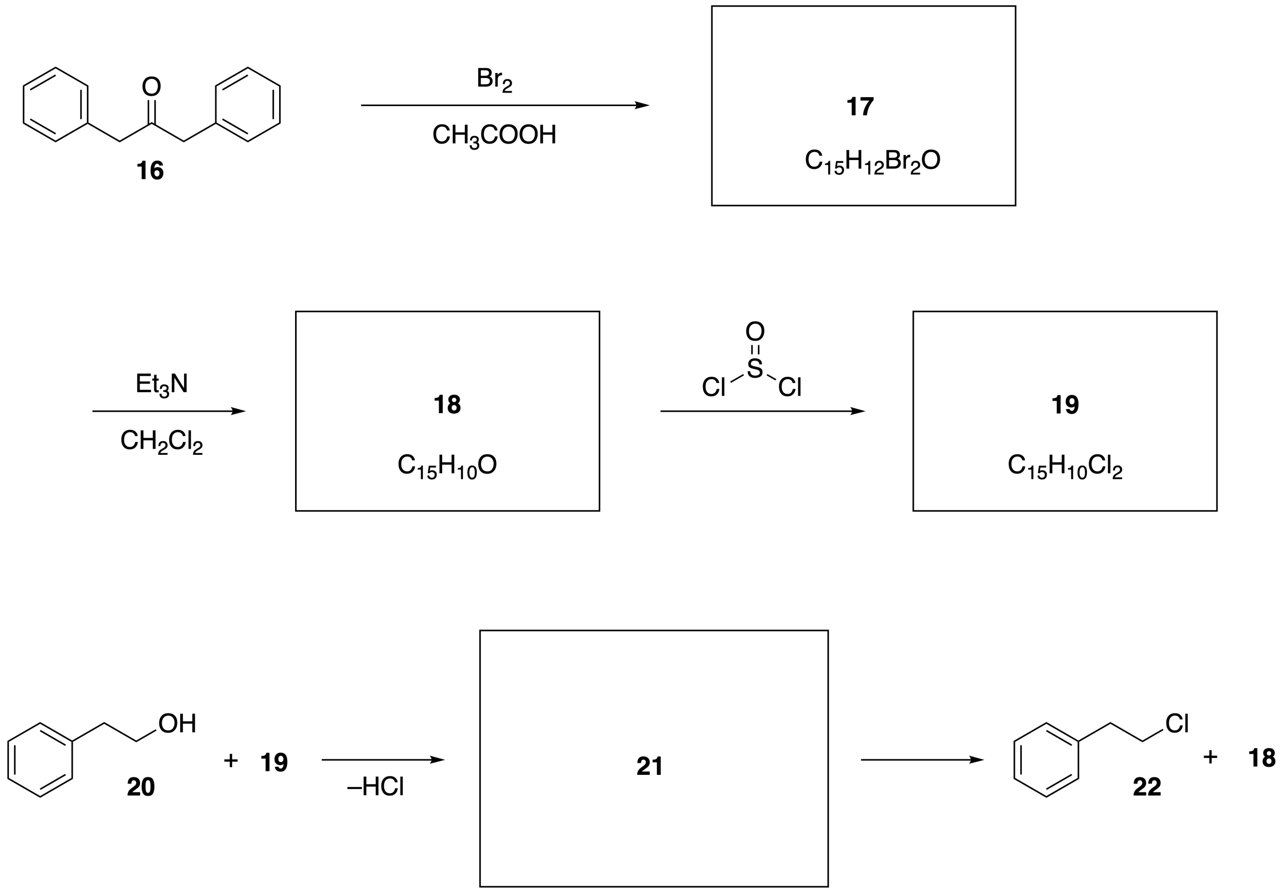


A.3 **Draw** the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, **indicate** the introduced ^{18}O atoms for **13** and **14** as shown in the example below. 19pt



Part B

Compound **19** is 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**.



^{1}H NMR (CD_3CN, ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)

21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

B.1 <u>**Draw**</u> the structures of **17–19** and **21**. Stereochemistry is not required. 10pt

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)

Part B

B.1 (10 pt)

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

IChO
Problem 8

Cover sheet

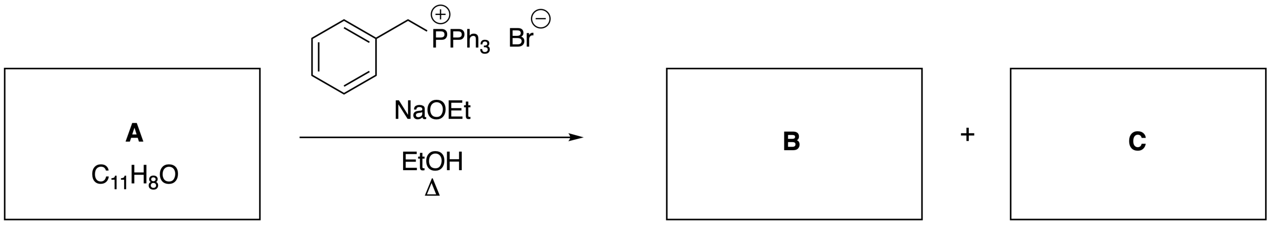
Please return this cover sheet together with all the related question sheets.

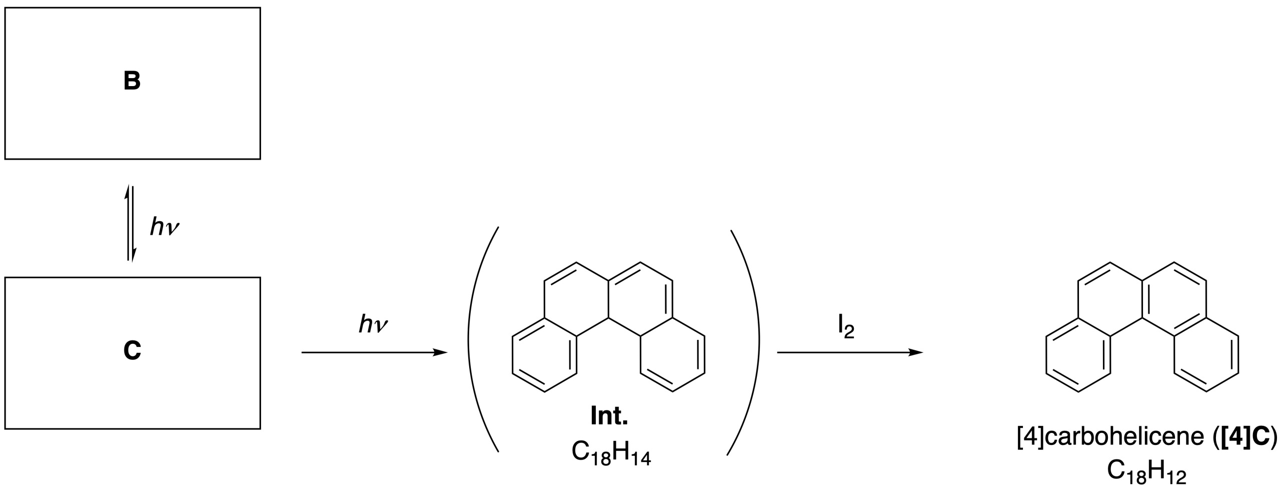
Dynamic Organic Molecules and Their Chirality

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

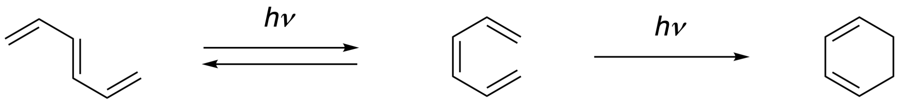
Part A

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.

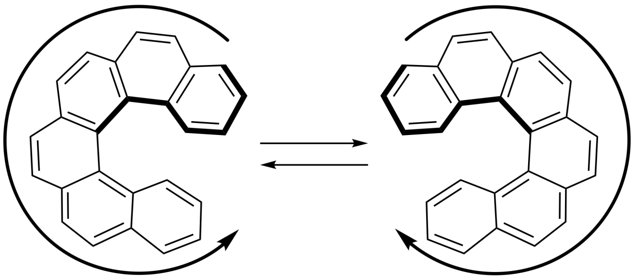


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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 ^{1}H NMR chemical shifts of **D** are listed below. **Draw** the structure of **D**. **[D** (δ, ppm in CS_2, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)**]**	3pt

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



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

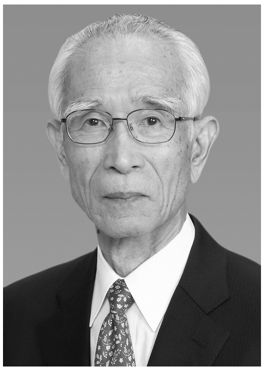
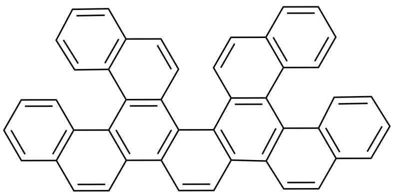
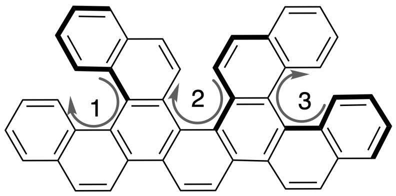


Photo courtesy: The Japan Prize Foundation

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.

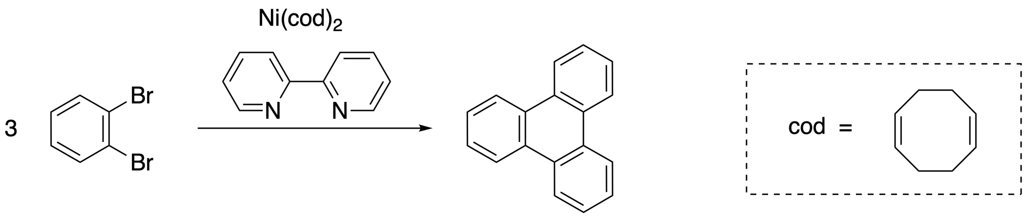


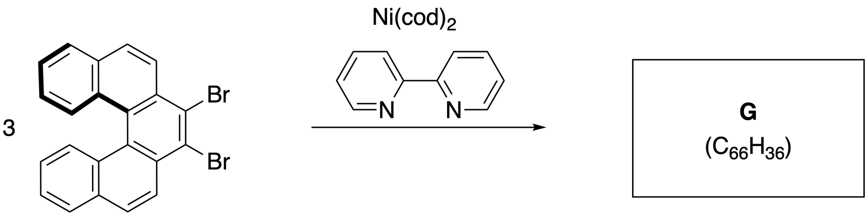
E



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

A.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify all** the possible stereoisomers of **G** formed in this process, without duplication. As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and *M* and *P* labels according to the same numbering. For instance, the other stereoisomers of **E** should be listed as (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *M*, *P*), (*M*, *P*, *P*), and (*M*, *P*, *M*). 7pt

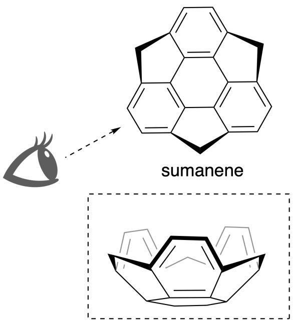




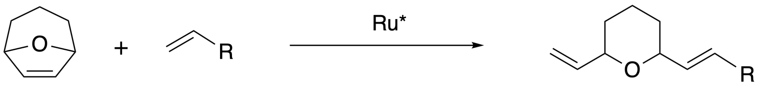
(*P*)-**F**

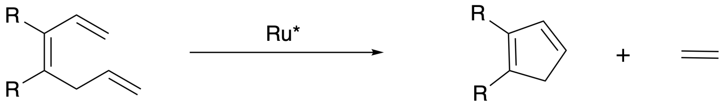
Part B

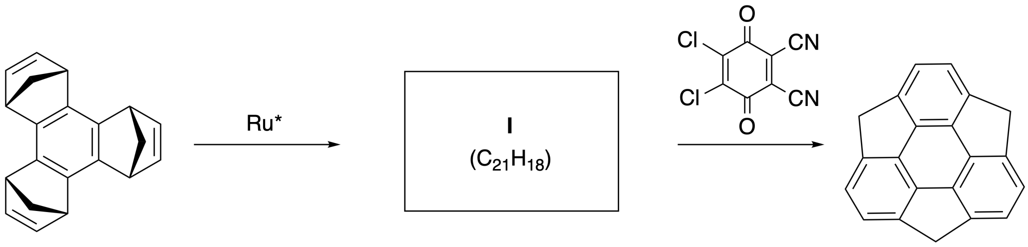
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



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

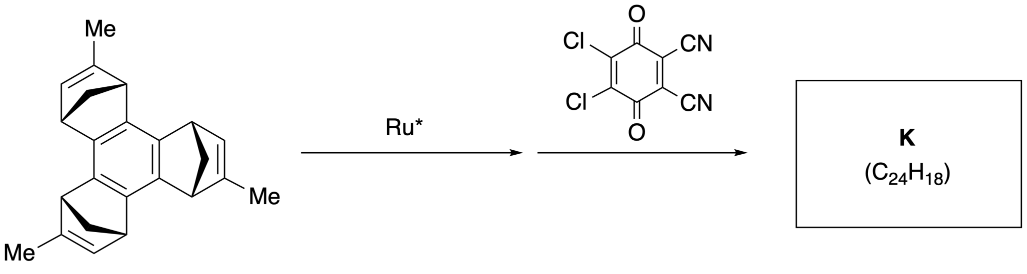






H

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



J

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

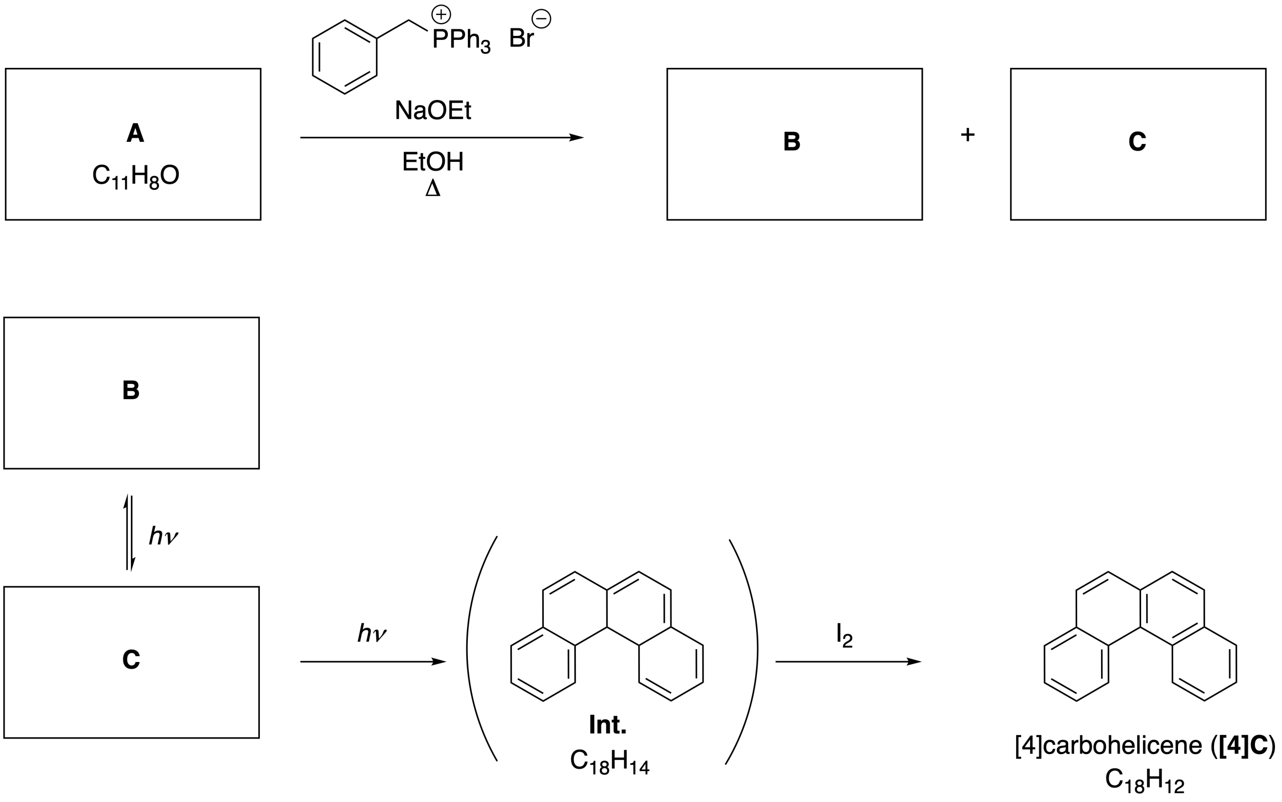
Dynamic Organic Molecules and Their Chirality

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

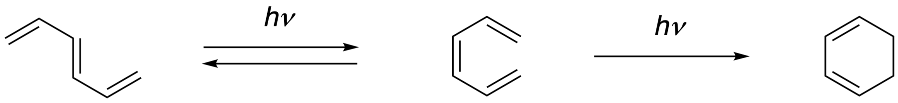
Part A

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.

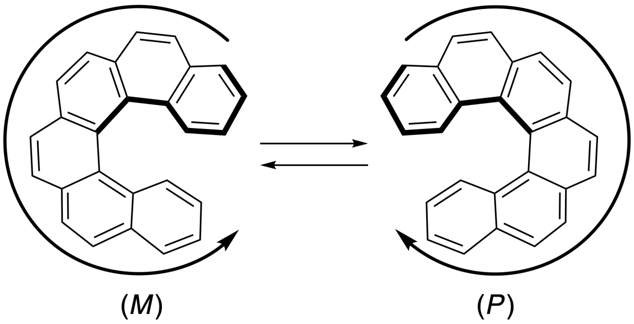


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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. **Draw** the structure of **D**. The ^{1}H NMR chemical shifts of **D** are listed below. **[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 very slow at room temperature. The chirality of [n]carbohelicenes is defined as (*M*) or (*P*) as shown below.

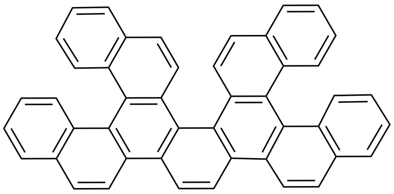


[n]Carbohelicenes with n larger than 4 can be enantiomerically separated by chiral column chromatography, which was developed by Prof. Yoshio Okamoto.

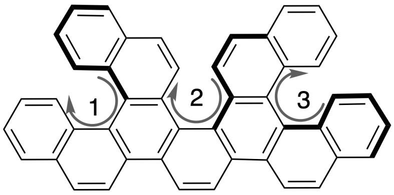
Photo credit: The Japan Prize Foundation

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.



E



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

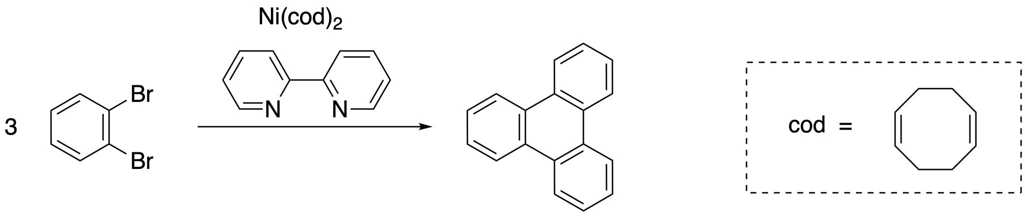
A.3 The nickel-mediated trimerisation of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple-helicene **G** ($C_{66}H_{36}$) is obtained. 7pt

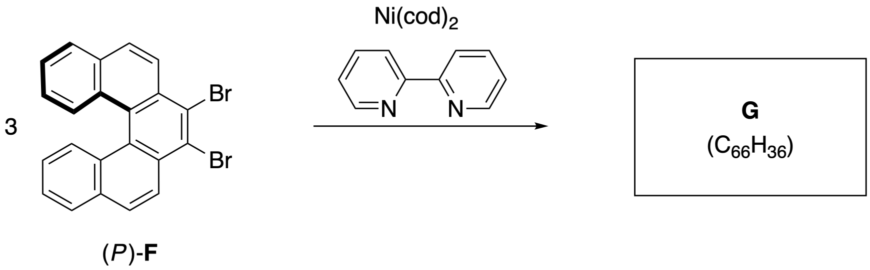
Given that interconversion between stereoisomers does not occur during the reaction, **identify all** the possible stereoisomers of **G** formed in this process, without duplicating stereoisomers.

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.

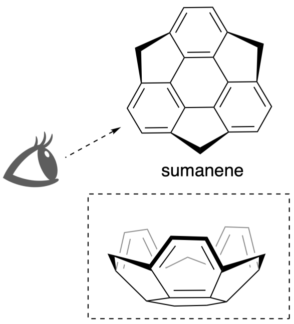
For instance, the other stereoisomers of **E** should be listed as (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *M*, *P*), (*M*, *P*, *P*), and (*M*, *P*, *M*).



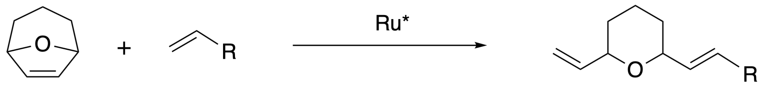


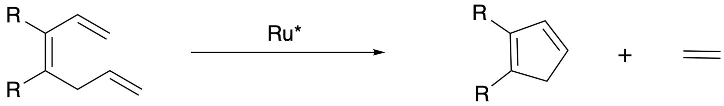
Part B

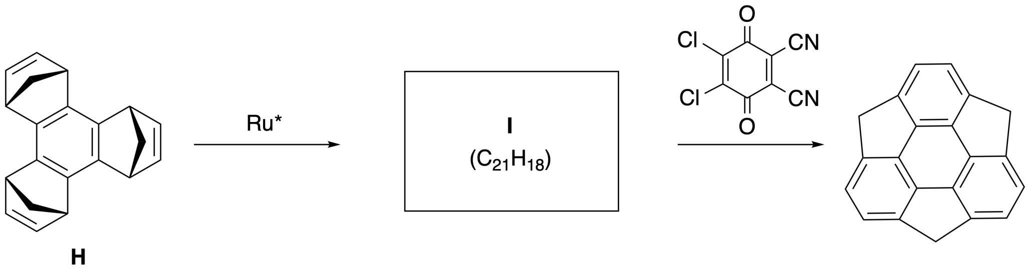
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name ”sumanene” derives from a Sanskrit-Hindi word ”suman” that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



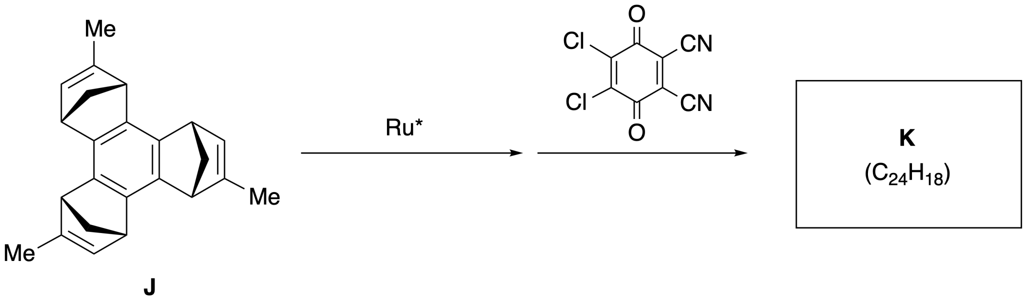
Representative metathesis reactions catalysed by a ruthenium catalyst (Ru*) are shown below.







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



J

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

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)

A.3 (7 pt)

Part B

B.1 (3 pt)

B.2 (4 pt)

IChO
Problem 9
Cover sheet

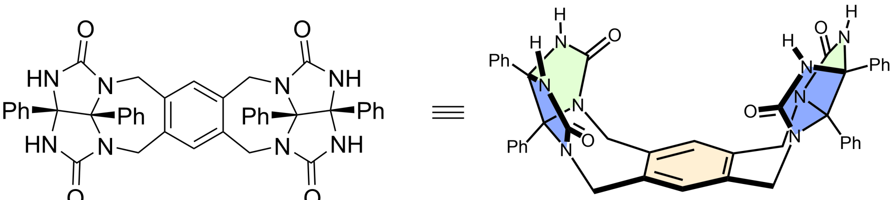
Please return this cover sheet together with all the related question sheets.

Likes and Dislikes of Capsule

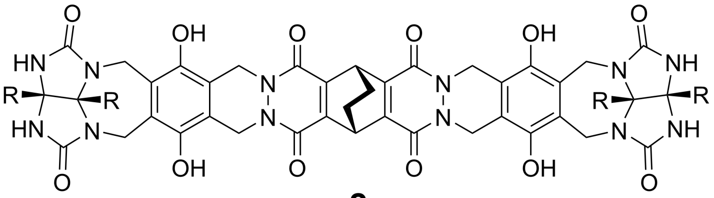
10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	**Total**
Points	13	2	2	3	3	**23**
Score						

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

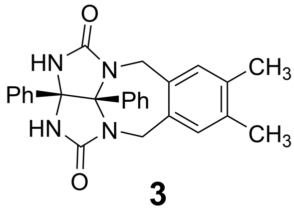
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

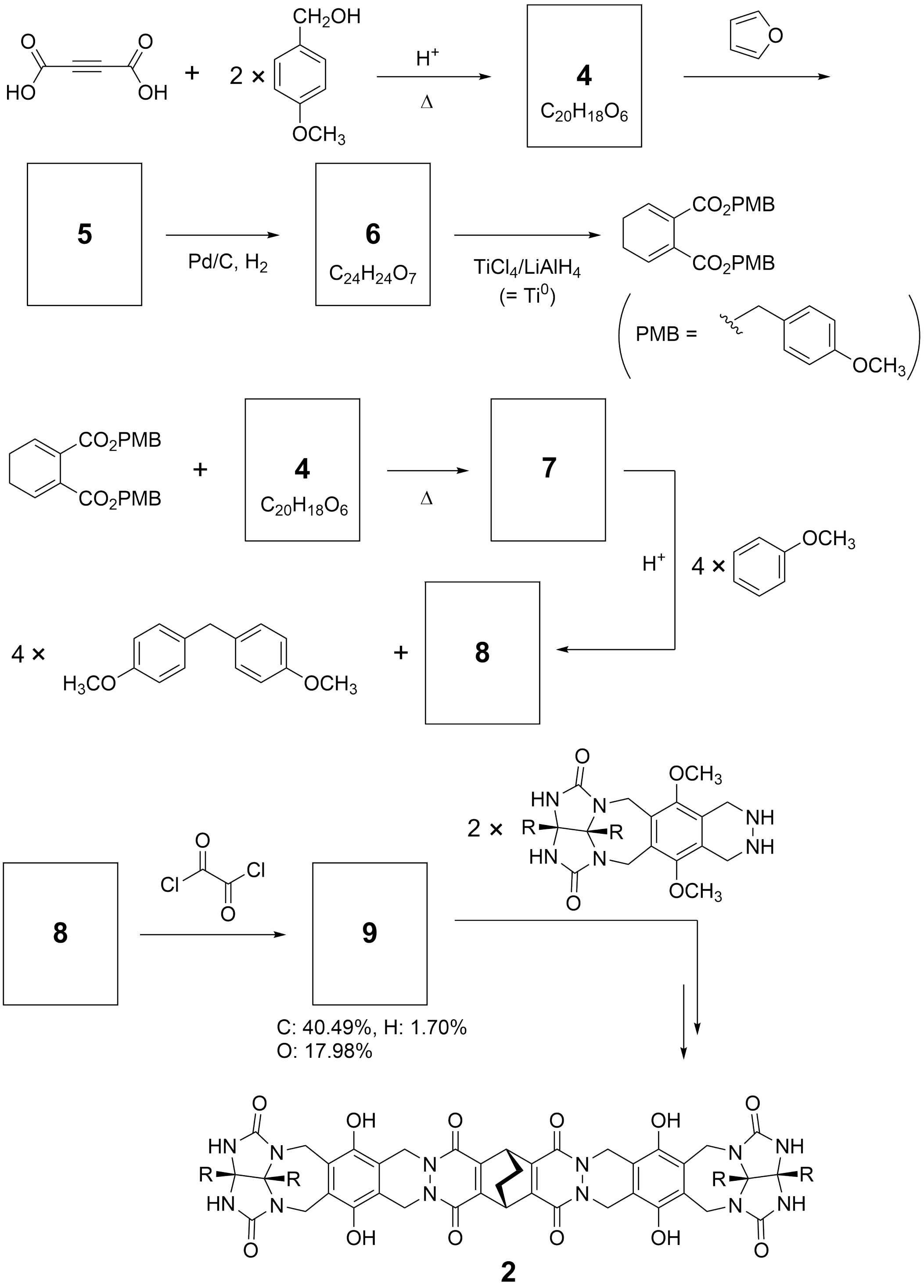


2



3

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



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

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

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

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

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

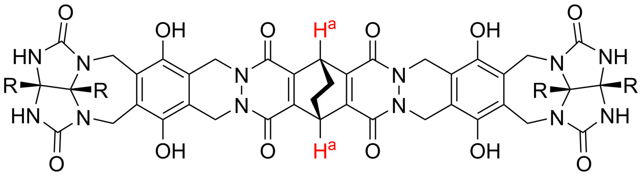
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z@}\mathbf{1}_2 \tag{1}$$

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

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

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

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



2

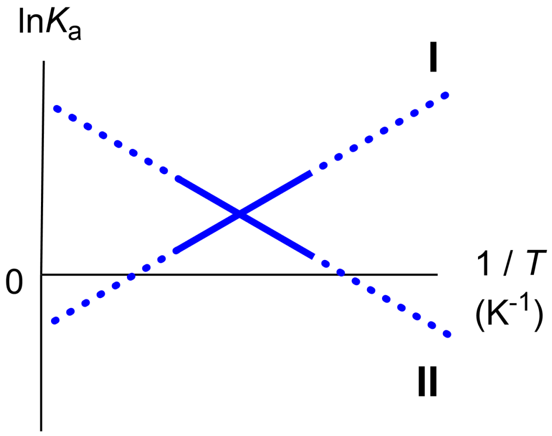
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

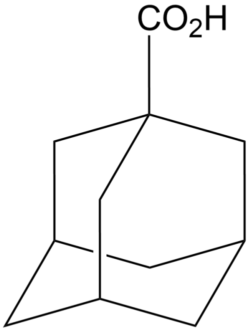
A.4 **Determine** the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2}_2$ giving each H^a signal. 3pt

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

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

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





AdA

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

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

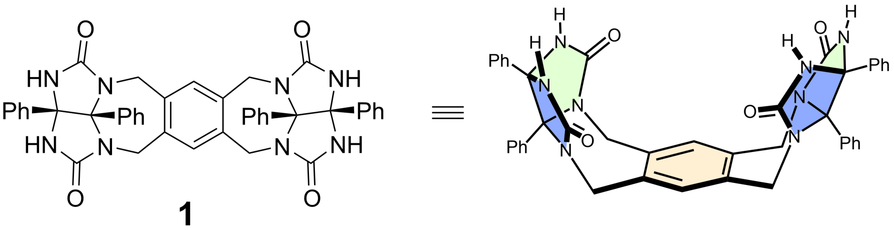
	A	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and AdA
(5)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and AdA

Likes and Dislikes of Capsule

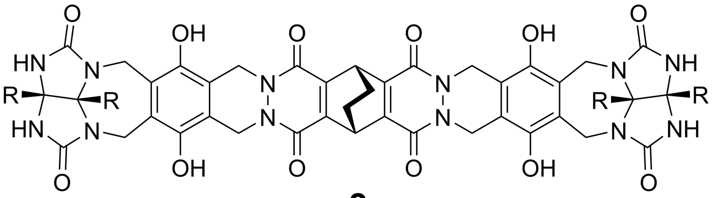
10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	**Total**
Points	13	2	2	3	3	**23**
Score						

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

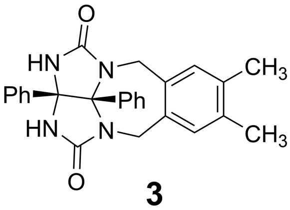
Compounds **1** and **2** are U-shaped molecules with different sizes, inspired by this idea. Compound **3** was prepared for comparison with **1** and the encapsulation behaviour of these compounds was investigated.



1



2



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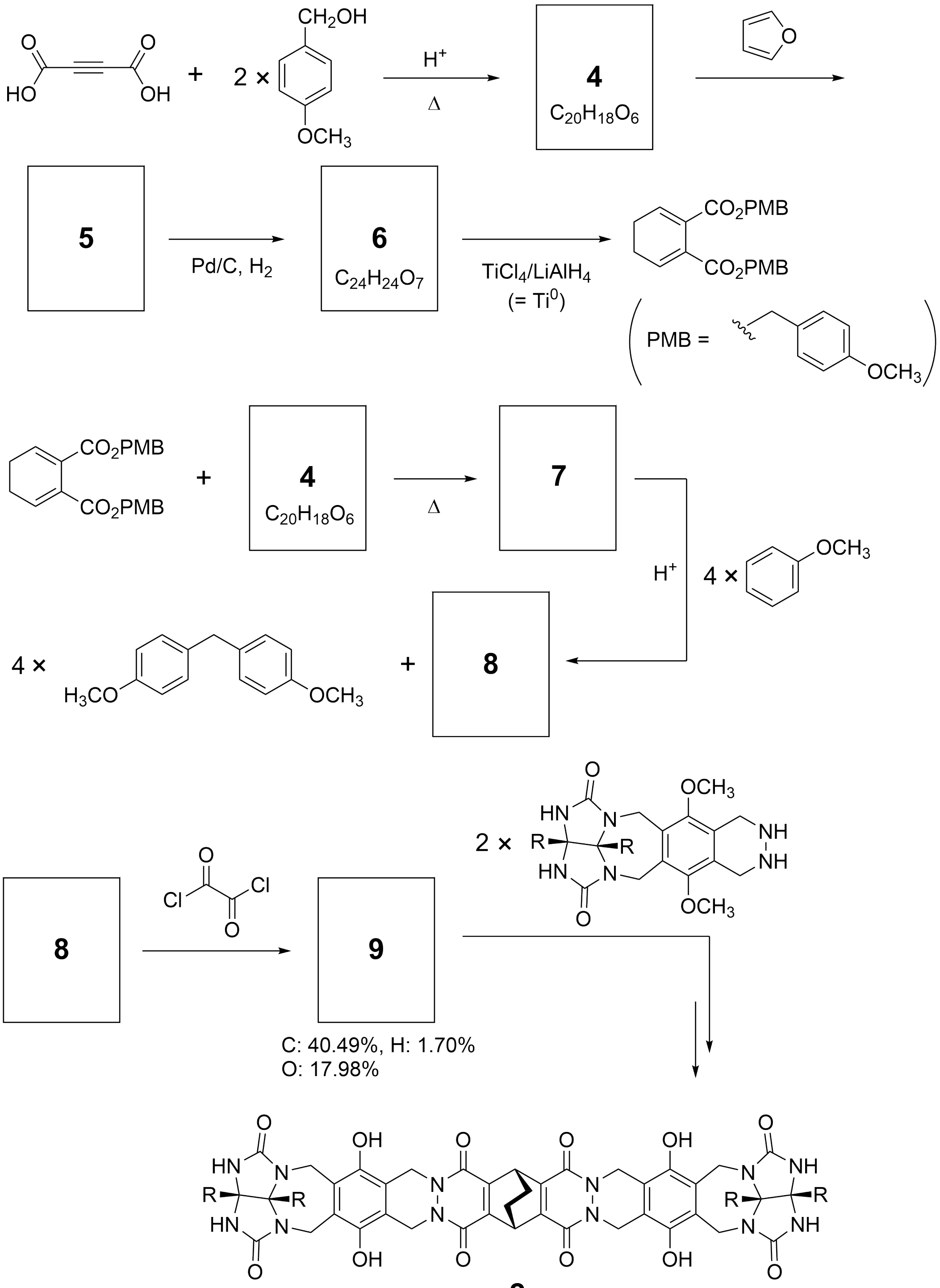

2

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

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

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

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

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

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

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

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

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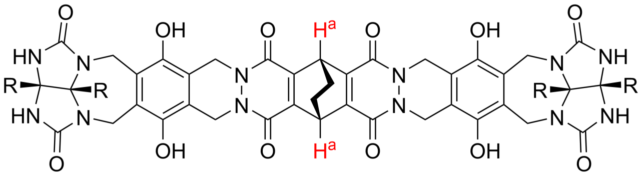

2

solvent	δ (ppm) of H^a
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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 $\mathbf{2}_2$ giving each H^a signal. 3pt

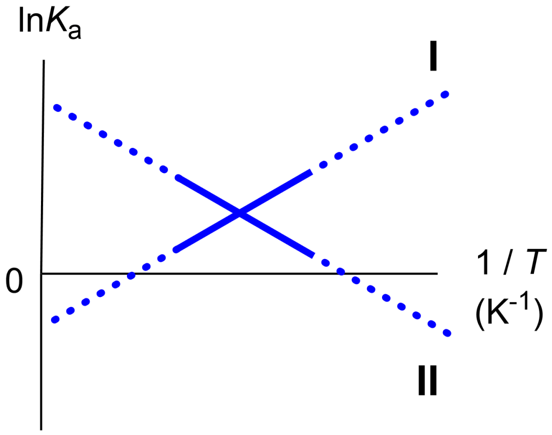
^{1}H NMR measurements in C_6D_6 revealed that $\mathbf{2}_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA).

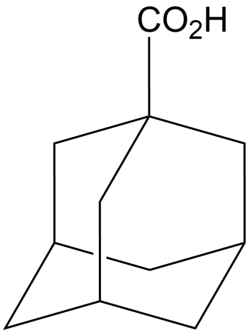
The association constants (K_a) which are expressed below were determined for various temperatures.

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

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

Similarly, the K_a values of CH_4 and $\mathbf{1}_2$ shown in eq (2) were also determined by ^{1}H 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.





AdA

No C_6D_6 is encapsulated in $\mathbf{1}_2$.

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).

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(3)	ΔS	ΔH
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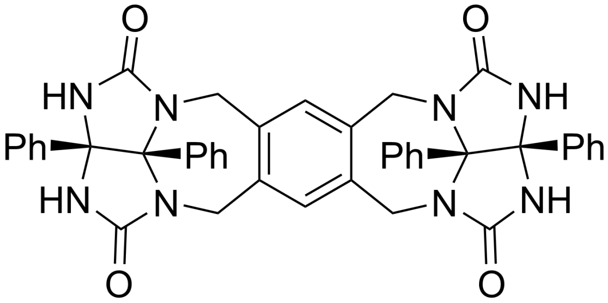
(5)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and AdA

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	numbers of C_6D_6	numbers of C_6D_5F
4.60 ppm		
4.71 ppm		
4.82 ppm		

A.5 (3 pt)

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

(4) : (5) :