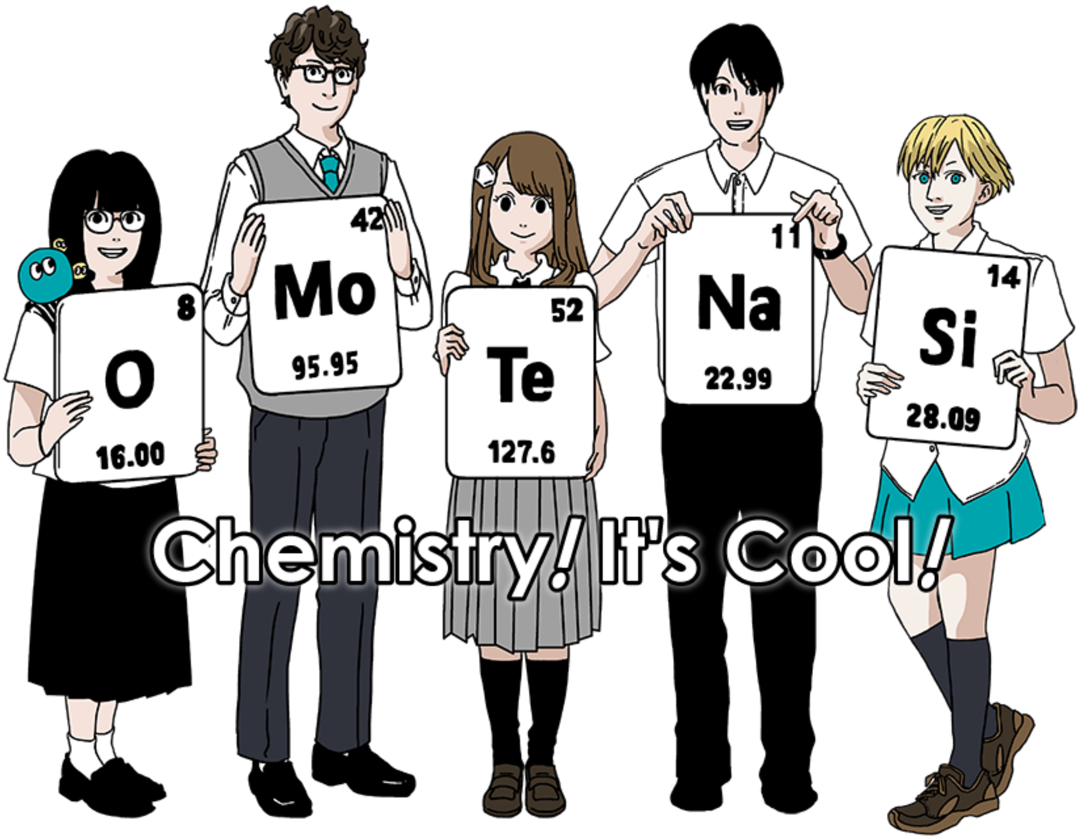
IChO
General instructions

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



General Instruction

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

GOOD LUCK!

Problems and Grading Information

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

Physical Constants and Equations

Constants

Speed of light in vacuum	$c = 2.99792458 \times 10^{8}$ 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.

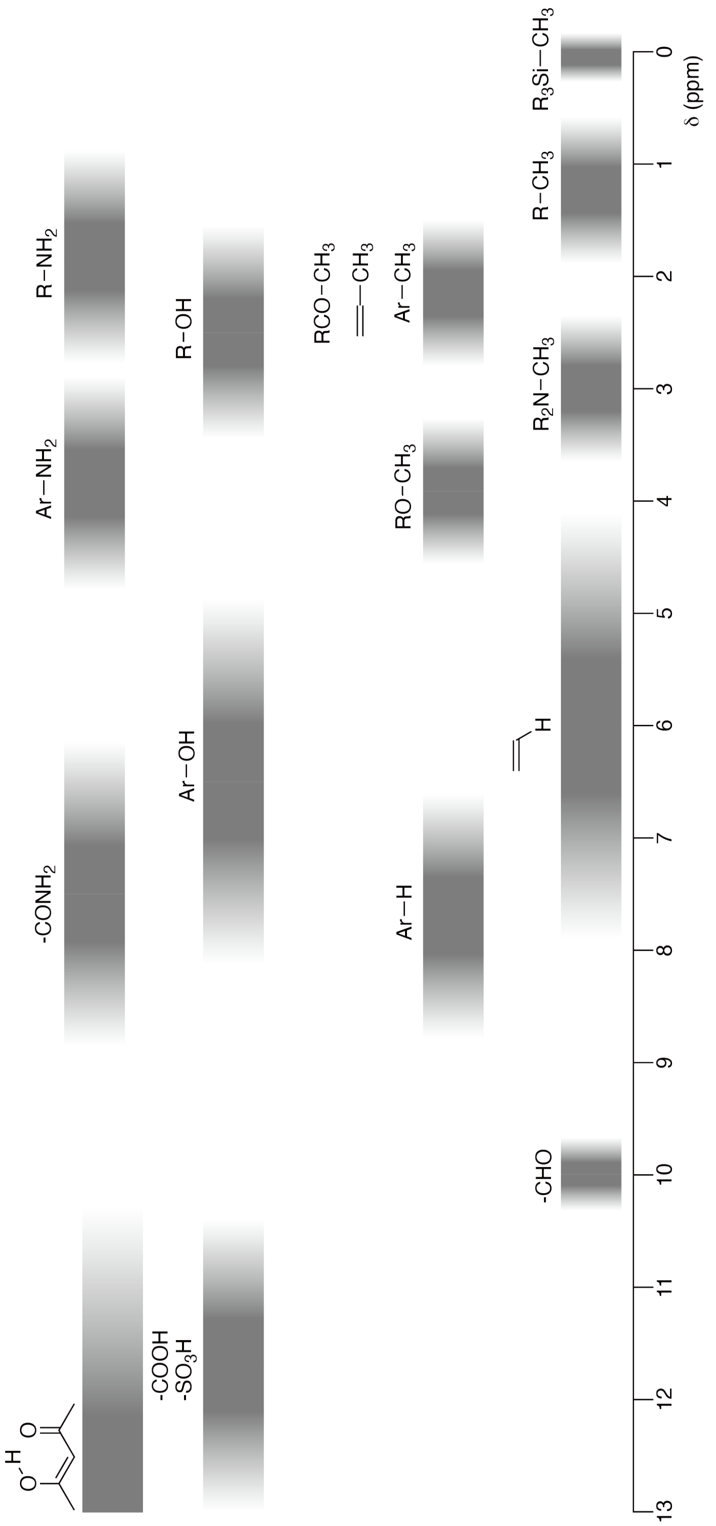
Heat change Δq	$\Delta q = nc_{\mathrm{m}}\Delta T$, where c_{m} is the temperature-independent molar heat capacity.
Nernst equation for redox reaction	$E = E^{\circ} + \frac{RT}{zF}\ln\frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}$, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration 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	$A = \varepsilon lc$, where A is the absorbance, ε is the molar absorption coefficient, l is the optical path length, c is the concentration of the solution.
Henderson–Hasselbalch equation	For an equilibrium $\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$, 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

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.008						Key:											2 He Helium 4.003
3 Li Lithium 6.968	4 Be Beryllium 9.012					113 Nh Nihonium [278]	atomic number Symbol name atomic weight [in parenthesis for the radioactive element]					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]

57-71 La-Lu Lanthanoids :	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.967
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



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

2021 国际化学奥林匹克 日本

第 53 届 IChO2021 日本

2021 年 7 月 25 日-8 月 2 日

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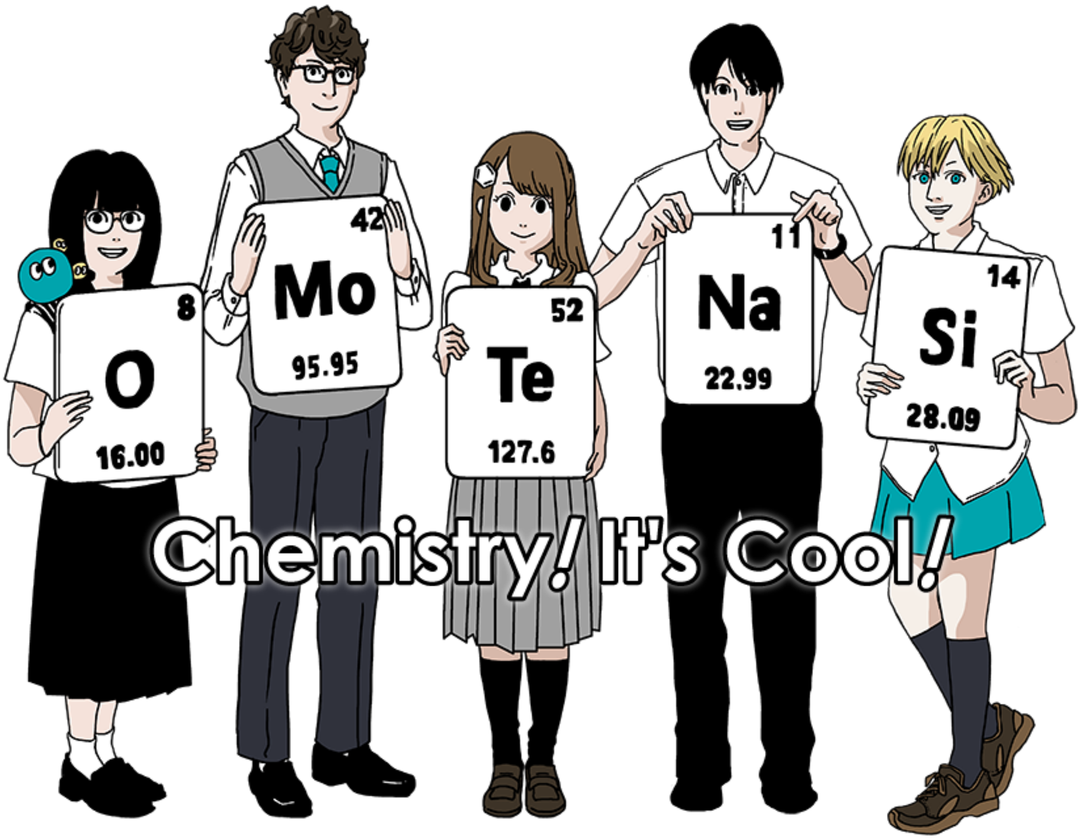

通则

- 只能用墨水笔回答问题。
- 只能使用非编程计算器。
- 一共有 **9 道题**。
- 你可以按照任何顺序回答问题。
- 考试时间 **5 小时**。
- 只有在**开始**（**START**）指令发出后，才可以**开始**（**Begin**）答题。
- 所有结果必须用墨水笔书写在**答题纸**指定的相应答题框中。可以在试卷的背面打草稿。谨记写在答题框外的答案不予评判。
- 相关的计算须写在指定的答题框中。只有写出过程且得出正确答案的才能得满分。
- 在**停止**（**STOP**）命令发出前 **30 分钟**，监考人员将给予提醒。
- 当**停止**（**STOP**）命令发出后，必须立即停止答题。若不停止书写，将导致你的考试无效。
- 为准确理解题意，可向监考老师索要英文原版试卷。
- 未经允许，不许离开座位。如果需要帮助（如计算器有问题，需要去洗手间，等等），请举手，待监考老师过来。

祝好运！

考题和评判信息。

	题目	分数	百分比
1	金属表面的氢	24	11
2	同位素时光胶囊	35	11
3	朗伯—比尔定律	22	8
4	锌的氧化还原化学	32	11
5	神秘的硅元素	60	12
6	过渡金属的固体化学	45	13
7	趣玩非苯芳香性	36	13
8	动态有机分子及其手性	26	11
9	胶囊的好与恶	23	10
		总分	100

物理常数和公式

常数

真空中的光速	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$
普朗克常数	$h = 6.62607015 \times 10^{-34}\ \mathrm{J\ s}$
元电荷	$e = 1.602176634 \times 10^{-19}\ \mathrm{C}$
电子质量	$m_\mathrm{e} = 9.10938370 \times 10^{-31}\ \mathrm{kg}$
电常数（真空介电常数）	$\varepsilon_0 = 8.85418781 \times 10^{-12}\ \mathrm{F\ m^{-1}}$
阿伏加德罗常数	$N_\mathrm{A} = 6.02214076 \times 10^{23}\ \mathrm{mol^{-1}}$
玻尔兹曼常数	$k_\mathrm{B} = 1.380649 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
法拉第常数	$F = N_\mathrm{A} \times e = 9.64853321233100184 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
气体常数	$R = N_\mathrm{A} \times k_\mathrm{B} = 8.31446261815324\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $= 8.2057366081 \times 10^{-2}\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
统一的原子质量单位	$u = 1\ \mathrm{Da} = 1.66053907 \times 10^{-27}\ \mathrm{kg}$
标准压力	$p = 1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$
大气压	$p_\mathrm{atm} = 1.01325 \times 10^{5}\ \mathrm{Pa}$
零摄氏度	$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$
埃	$1\ \text{Å} = 10^{-10}\ \mathrm{m}$
皮米	$1\ \mathrm{pm} = 10^{-12}\ \mathrm{m}$
电子伏特	$1\ \mathrm{eV} = 1.602176634 \times 10^{-19}\ \mathrm{J}$
百万分之一	$1\ \mathrm{ppm} = 10^{-6}$
十亿分之一	$1\ \mathrm{ppb} = 10^{-9}$
万亿分之一	$1\ \mathrm{ppt} = 10^{-12}$
圆周率	$\pi = 3.141592653589793$
自然对数的底数（欧拉数）	$e = 2.718281828459045$

公式

理想气体方程	$PV = nRT$，P 是压力，V 是体积，n 是物质的量, T 是理想气体的绝对温度。
库仑定律	$F = k_\mathrm{e}\frac{q_1 q_2}{r^2}$， F 是静电力，$k_\mathrm{e}(\simeq 9.0\times 10^9\ \mathrm{N\,m^2\,C^{-2}})$ 是库伦常数，q_1 和 q_2 是电荷电量，r 是电荷间距离。
热力学第一定律	$\Delta U = q + w$，ΔU 是内能变，q 是热，w 是功。
焓 H	$H = U + PV$
基于玻尔兹曼原理的熵 S	$S = k_\mathrm{B}\ln W$，W 是微观状态数。
熵变 ΔS	$\Delta S = \frac{q_\mathrm{rev}}{T}$，$q_\mathrm{rev}$ 是可逆过程的热量。
吉布斯自由能 G	$G = H - TS$ $\Delta_\mathrm{r}G^\circ = -RT\ln K = -zFE^\circ$，$K$ 是平衡常数，z 是电子数，E° 是标准电极电势。
反应商 Q	$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\circ + RT\ln Q$ 对于如下反应 $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$ $Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$，[A] 是 A 的浓度。

热交换 Δq	$\Delta q = nc_\mathrm{m}\Delta T$，$c_\mathrm{m}$ 为与温度无关的摩尔热容。
氧化还原反应的能斯特方程	$E = E^\circ + \frac{RT}{zF}\ln\frac{C_\mathrm{ox}}{C_\mathrm{red}}$，$C_\mathrm{ox}$ 为氧化态物质的浓度，C_red 为还原态物质的浓度。
阿伦尼乌斯方程	$k = A\exp\left(-\frac{E_a}{RT}\right)$，$k$ 是速率常数，A 是指前因子，E_a 是活化能。 $\exp(x) = e^x$
朗伯—比尔定律	$A = \varepsilon lc$，A 是吸光度，ε 是摩尔吸收系数，l 是光程，c 是溶液浓度。
亨德森—哈塞尔巴尔赫方程	对于如下平衡 $\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$，$K_\mathrm{a}$ 为平衡常数， $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
光子的能量	$E = h\nu = h\frac{c}{\lambda}$，$\nu$ 是光的频率，λ 是光的波长。
几何级数的和	当 $x \neq 1$ 时，$1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1-x^{n+1}}{1-x}$
解题可能用到的近似方程	当 $x \ll 1$ 时，$\frac{1}{1-x} \simeq 1 + x$

元素周期表

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
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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
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57-71 La-Lu Lanthanoids :	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.967
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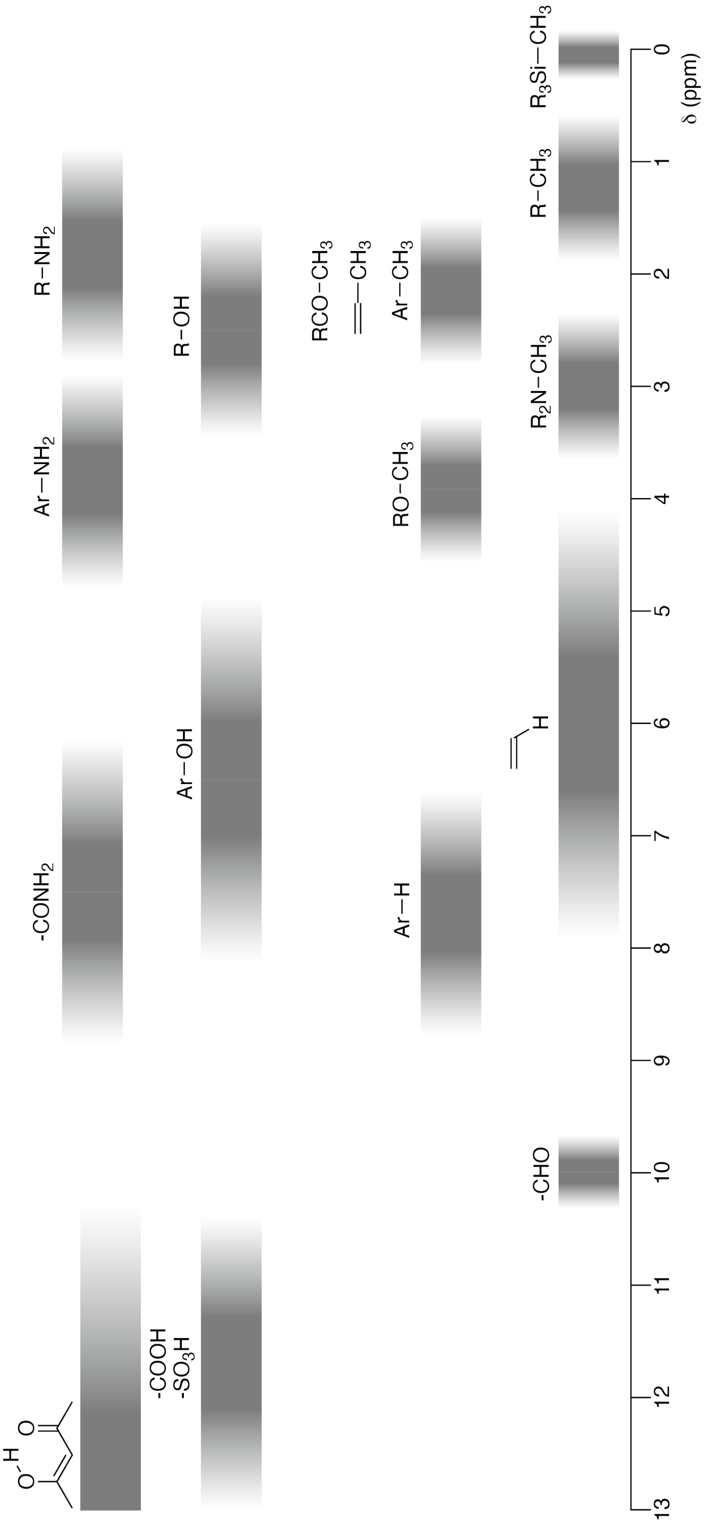
^{1}H NMR 化学位移


R_3Si-CH_3
$R-CH_3$
R_2N-CH_3
H
-CHO
δ (ppm)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
$RCO-CH_3$
$\equiv-CH_3$
$Ar-CH_3$
$RO-CH_3$
Ar−H
R−OH
Ar−OH
-COOH
$-SO_3H$
$R-NH_2$
$Ar-NH_2$
$-CONH_2$
O
H
O

每一个烷基取代，$\Delta\delta$ 大约为 +0.4 ppm

CHN-2 C-1 C-1

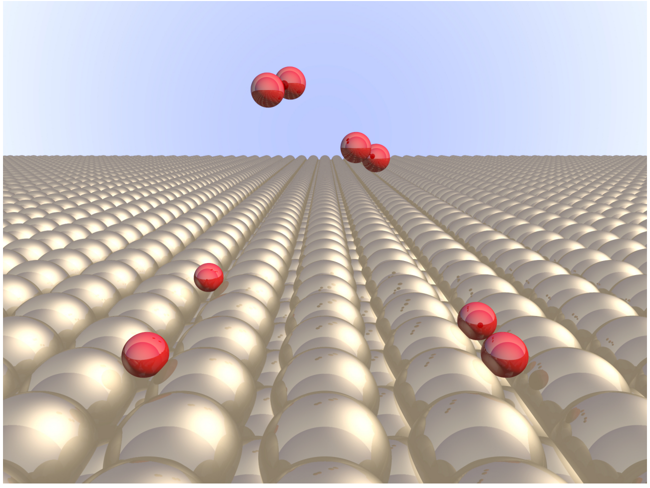
IChO
Problem 1

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.

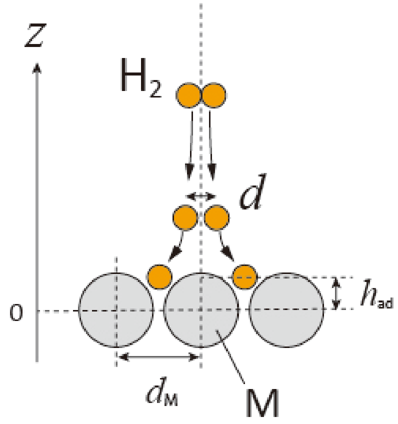


Fig.1 Definition of variables. Drawing is not in scale.

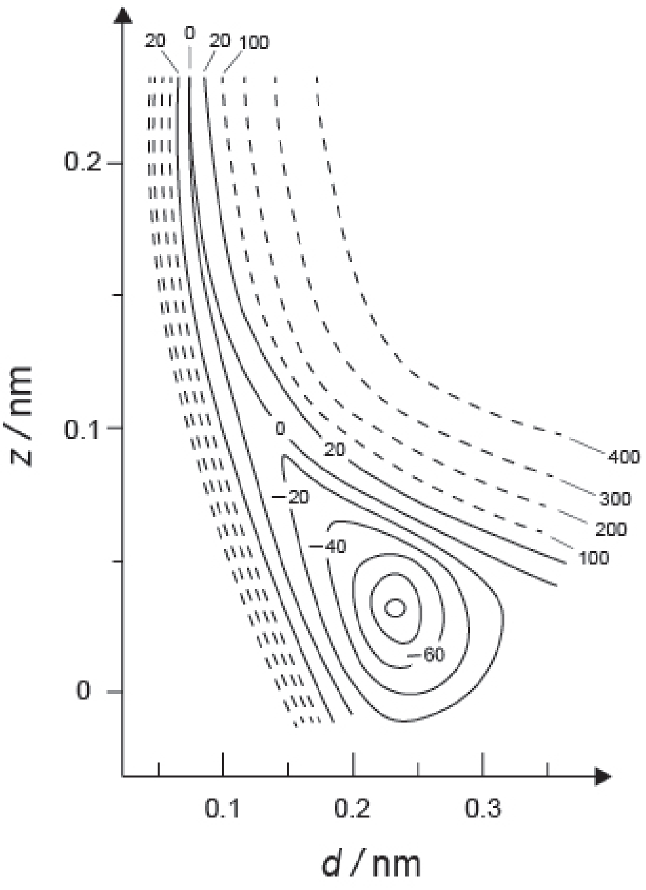


Fig.2

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

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

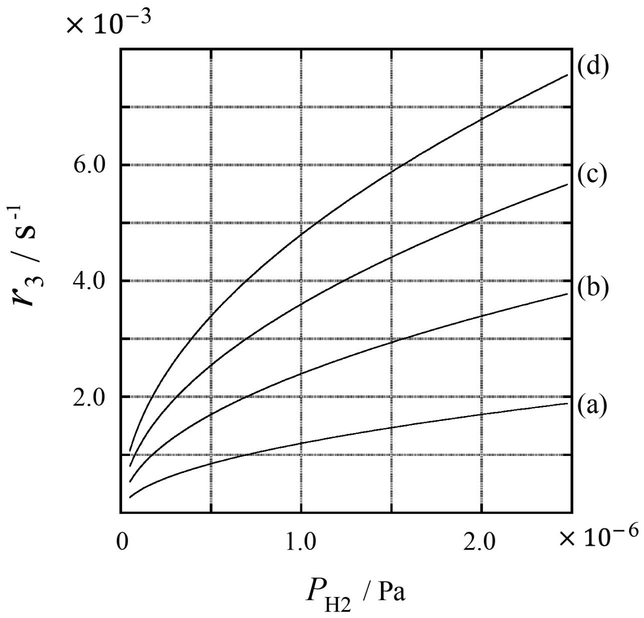
Express C using k_1 and k_2.

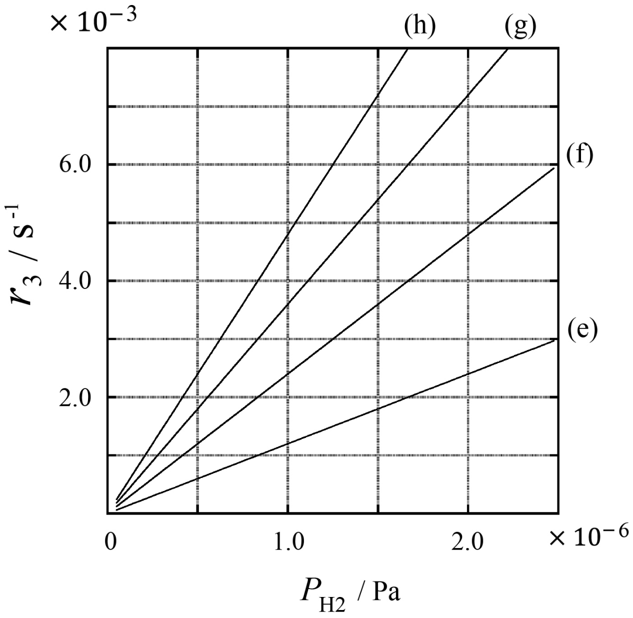
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m^2 was placed in a container (1L = 1.0×10^{-3} m^3) with H$_2$ ($P_{H_2} = 1.0 \times 10^2$ Pa). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m^{-2}. The surface temperature was kept at $T = 400$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

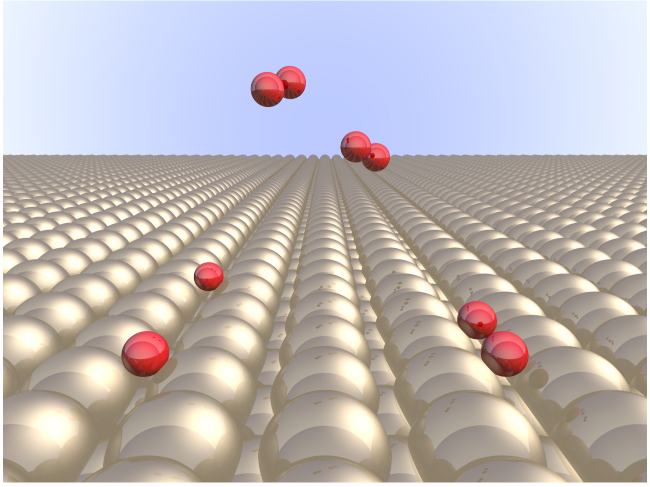
B.4 At a different T, $C = 2.5 \times 10^3$ Pa^{-1} and $k_3 = 4.8 \times 10^{-2}$ s^{-1}are given. For r_3 as a function of P_{H_2}at this temperature, **select** the correct plot from (a)–(h). 3pt





金属表面的氢

占总分 11 %							
题目	A.1	A.2	B.1	B.2	B.3	B.4	**小计**
分值	6	4	5	3	3	3	**24**
得分							



不依赖于化石燃料的氢气是未来可指望的能源。在此，我们讨论氢气在金属中的储存过程，这一过程与氢气输运和储存技术相关。

A 部分

鉴于氢经由表面而吸收到金属体相，就让我们首先考虑氢在金属表面的吸附过程：$H_2(g) \rightarrow 2H(ad)$，此处，氢的气态和吸附态分别表示为 (g) 和 (ad)。到达金属表面（M）的氢分子 (H_2) 在表面解离并以 H 原子的方式被吸附（图 1）。这里，H_2 的势能由两个变量表示: 原子间距 d、相对于金属原子表面的高度 z。假设两个 H 原子之间连线的轴平行于表面且连线中心始终处在垂直虚线上，如图 1 所示。图 2 示出氢在金属表面解离过程势能变化的等高线图。图中所示势能数值的单位是 kJ 每摩尔 H_2。实线间距为 20 kJ mol^{-1}, 虚线间距为 100 kJ mol^{-1}, 实线和虚线间距为 80 kJ mol^{-1}。忽略振动零点能。

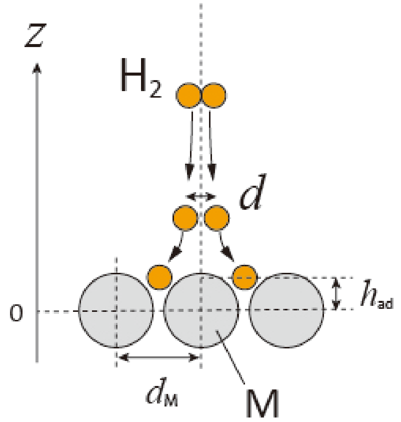


图 1：参数的物理意义。未全按比例示出。

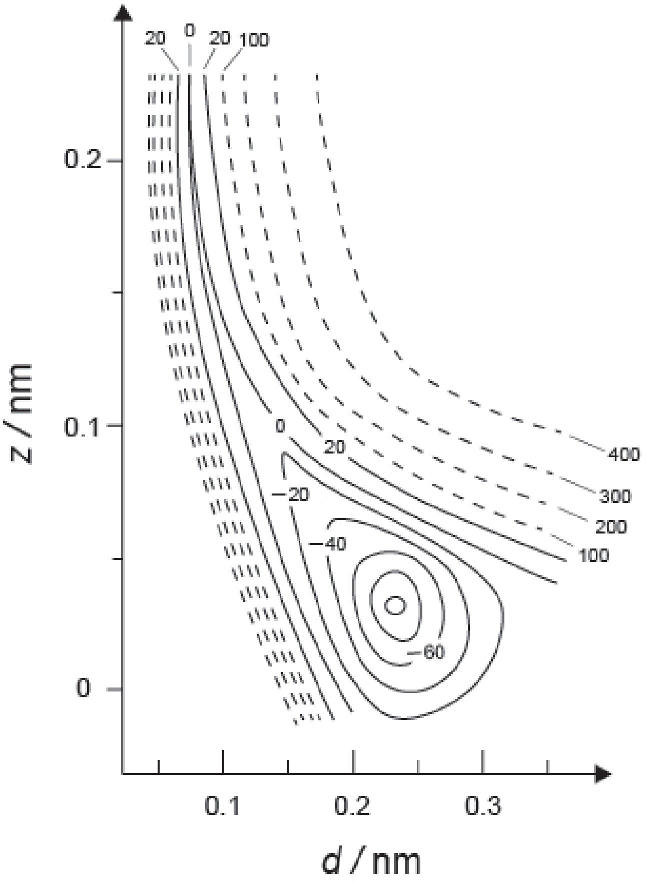


图 2

A.1 对如下 (i)–(iii) 项, 从 A–G 中 **选择** 最接近的值。 6pt

(i) 气态 H_2 分子中的原子间距
(ii) 金属原子之间的距离（图 1 中的 d_{M})
(iii) 被吸附的 H 原子距表面的距离 (图 1 中的 h_{ad})

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 对如下 (i)–(ii) 项, 从 A–H 中 **选择** 最接近的值。 4pt

(i) 将气态 H_2 解离为气态 H 所需的能量 [$H_2(g) \rightarrow 2H(g)$]
(ii) 气态 H_2 吸附过程中释放的能量 [$H_2(g) \rightarrow 2H(ad)$]

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}

B 部分

随后，吸附的氢原子或者被吸收到体相中，或者重新结合并解吸而返回气相，如反应（1a）和（1b）所示。H(ab) 表示被吸收到体相中的氢原子。

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

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

表面单位位点的吸附、解吸和吸收的反应速率分别为 $r_1[\mathrm{s}^{-1}], r_2[\mathrm{s}^{-1}]$ 和 $r_3[\mathrm{s}^{-1}]$ 。其表达式如下：

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

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

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

这里，k_1 [s^{-1} Pa^{-1}], k_2 [s^{-1}] 和 k_3 [s^{-1}] 为反应速率常数，$P_{\mathrm{H_2}}$ 是 $\mathrm{H_2}$ 的分压，θ $(0 \leq \theta \leq 1)$ 表示表面可用位点被 H 原子占据的分数。假设与吸收相比，吸附和解吸速率要快得多 $(r_1, r_2 \gg r_3)$ 且 θ 保持恒定。

B.1 将 r_3 表示为: 5pt

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

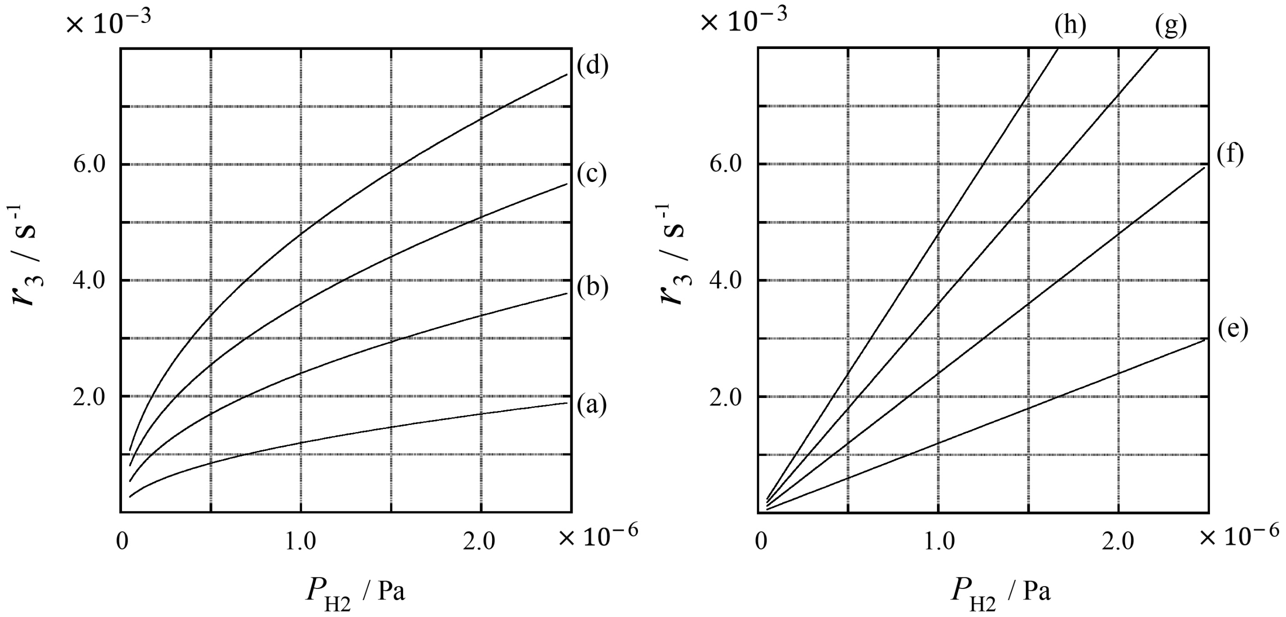
推出采用 k_1 和 k_2**表示** 的 C 的表达式

将表面积 $S = 1.0 \times 10^{-3}$ m^2 的金属样品置于充有 H_2 ($P_{H_2} = 1.0 \times 10^2$ Pa) 的容器 (1 L = 1.0×10^{-3} m^3) 中。氢原子在该表面吸附位点的密度为 $N = 1.3 \times 10^{18}$ m^{-2}。表面温度维持在 $T = 400$ K。随着反应（1）的进行，氢气分压 P_{H_2} 以恒定的速率 $v = 4.0 \times 10^{-4}$ Pa s^{-1} 降低。假设 H_2 是理想气体，并且金属样品的体积可忽略不计。

B.2 **计算** 金属表面上单位时间单位面积吸收的 H 原子的物质的量 A [mol s^{-1} m^{-2}]. 3pt

B.3 在 $T = 400$ K, C 等于 1.0×10^2 Pa^{-1}。**计算** 400K 时的 k_3 。如果 **B.2** 中没有得到答案，采用 $A = 3.6 \times 10^{-7}$ mol s^{-1} m^{-2} 进行处理。 3pt

B.4 在另一不同温度 T 时, $C = 2.5 \times 10^3$ Pa^{-1} 且 $k_3 = 4.8 \times 10^{-2}$ s^{-1}。从如下所给图示的 (a)–(h) 中，**选出** 该温度下，r_3 随 P_{H_2} 变化的关系。 3pt



金属表面的氢

A 部分

A.1 (6 pt)

(i)	(ii)	(iii)

A.2 (4 pt)

(i)	(ii)

B 部分

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)

____

CHN-2 C-2 C
Bangsen ZHAO

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 $T \to 0$) and very high (think of $T \to +\infty$) temperatures. Assume that the reaction remains unchanged at these temperatures and that ΔH converges to a constant value for high temperatures.

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

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

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

A.3	<u>**Calculate**</u> 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

同位素时光胶囊

占总分 11 %					
题目	A.1	A.2	A.3	A.4	**小计**
分值	8	8	10	9	**35**
得分					

仅同位素组成不同的分子实体称为同位素异素体, 例如 CH_4 和 CH_3D。通常认为同位素异素体具有相同的化学特性。然而，其在本质上仍略有差异。

假设本题中所有的物种均以气态存在。

让我们考虑如下平衡：

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

熵（S）随着体系可能的微观状态数（W）增加而增加:

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

对 $^{12}C^{16}O_2$ 和 $^{12}C^{18}O_2$，$W = 1$；而对 一个 $^{12}C^{16}O^{18}O$ 分子，$W = 2$，这是因为此分子中氧原子不同。在 方程式（1）所示平衡的右侧，有两个 $^{12}C^{16}O^{18}O$ 分子, $W = 2^2 = 4$ 。

A.1 对方程（3）所示的反应，在任意温度，焓变（ΔH）均为正值。 8pt

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

计算 在极低温度（可设想 $T \to 0$）和极高温度（可设想 $T \to +\infty$）时方程（3）的平衡常数 K。假设在这些温度下反应保持且其 ΔH 在高温时趋于定值。

如下过程的 ΔH 可以通过分子振动得以解释。

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

在 T = 0 K, 振动频率为 $\nu[\mathrm{s}^{-1}]$ 的双原子分子的振动能量表达式为:

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

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

其中，k 是力常数，μ 为折合质量，在双原子分子中，两个原子（质量分别为 m_1 和 m_2 ）的折合质量可按下式求出:

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

A.2 以波数计，H_2 的振动为 4161.0 cm^{-1}。**计算** 如下反应在 T= 0 K 的 ΔH ，单位为 J mol^{-1}。 8pt

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

假设:

- 只有振动能对 ΔH 有贡献
- H_2, HD, 和 D_2 的 k 值相同
- H 的质量为 1 Da ，D 的质量为 2 Da

达平衡时，体系中 H_2, HD 和 D_2 的摩尔比取决于温度。此处，Δ_{D_2} 定义为 D_2 的摩尔比的变化：

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

其中, R_{D_2} 表示样品中的 $\frac{[D_2]}{[H_2]}$ ，$R^*_{D_2}$ 表示 $T \to +\infty$ 时的 $\frac{[D_2]}{[H_2]}$ 。需要指出的是，在 $T \to +\infty$ 时同位素随机分布。

A.3	利用 D 的天然丰度，**计算** 方程式 4 所示反应同位素交换达平衡时的 Δ_{D_2} ，已知此温度时 K 为 0.300。假设 D 和 H 的天然丰度分别为 1.5576×10^{-4} 和 $1 - 1.5576 \times 10^{-4}$。	10pt

通常，一个分子中含有两个重同位素原子的双取代异素体的摩尔比随着温度的降低而增加。让我们考虑分子量分别为 44 和 47 的 CO_2 分子（以下分别简写为 $CO_2[44]$ 和 $CO_2[47]$）的摩尔比，Δ_{47} 参量的定义如下：

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

R_{47} 代表样品中的 $\frac{[CO_2[47]]}{[CO_2[44]]}$，$R^*_{47}$ 代表 $T \to +\infty$ 时的 $\frac{[CO_2[47]]}{[CO_2[44]]}$。碳和氧原子的天然丰度在下表给出，表中未示出的同位素不用考虑。

	^{12}C	^{13}C
天然丰度	0.988888	0.011112

	^{16}O	^{17}O	^{18}O
天然丰度	0.997621	0.0003790	0.0020000

Δ_{47} 随温度的变化由下式确定，其中 T 是绝对温度，单位 为 K:

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

A.4 从南极海底获得的一种浮游生物化石的 R_{47} 为 4.50865×10^{-5}。利用此 R_{47} **估算** 温度，该温度是指浮游生物生存期间的空气温度。计算中只需考虑 $CO_2[47]$ 最常见的同位素异素体。 9pt

同位素时光胶囊

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

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

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.

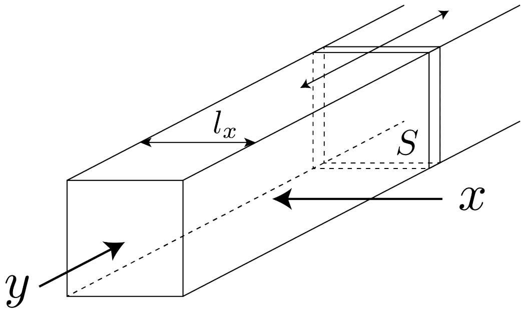
A.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. **Determine** the ratio $\varepsilon_{\mathrm{HA}}/\varepsilon_{\mathrm{A^-}}$, where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

朗伯—比尔定律

占总分 8 %				
题目	A.1	B.1	B.2	**小计**
分值	10	6	6	**22**
得分				

本题中忽略容器和溶剂的吸收，所有溶液和气体的温度都保持 25 °C 不变。

A 部分

用 HA 和 NaA 配制水溶液 **X**。在溶液 **X** 中，浓度 $[\text{A}^-]$, $[\text{HA}]$ 和 $[\text{H}^+]$ 分别为 1.00×10^{-2} mol L^{-1}, 1.00×10^{-3} mol L^{-1} 和 1.00×10^{-4} mol L^{-1}，相关酸碱平衡如下：

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

在 A 部分中，光程为l。稀释过程中忽略溶液密度的变化。除了方程 1，假设不发生其他化学反应。

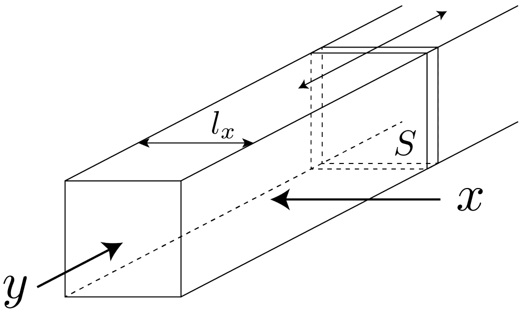
A.1	在波长 λ_1 处，溶液 **X** 的吸光度为 A_1。溶液 **X** 用 pH=2.500 的盐酸稀释，至其起始体积的 2 倍。稀释后，波长 λ_1 处溶液的吸光度仍为 A_1。分别用 ε_{HA} 和 ε_{A^-} 表示 HA 和 A⁻ 的吸光系数，**计算** 在 λ_1 处的 $\varepsilon_{\text{HA}}/\varepsilon_{\text{A}^-}$ 比值。	10pt

B 部分

让我们考虑在气相中存在如下平衡：

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

在压力为 P 下，将纯气体 D 充入一个横截面为 S、带有透明可移动壁的长方体容器（见下图）中。保持总压力 P 恒定，达到平衡。气体的吸光度为 $A = \varepsilon(n/V)l$，其中 ε，n，V 和 l 分别为吸光系数，气体的量（摩尔），气体体积和光程。假设气体混合物中的各组分都可看作理想气体。



如果有必要，可使用下列符号：

	起始状态		平衡后	
	D	M	D	M
分压	P	0	p_{D}	p_{M}
物质的量（摩尔）	n_0	0	n_{D}	n_{M}
体积	V_0		V	

B.1 沿着 x 方向（$l = l_x$），气体在起始状态和达到平衡后，波长 λ_{B1} 处测得的吸光度均为 A_{B1}。分别用 ε_{D} 和 ε_{M} 表示 D 和 M 的吸光系数，**计算** 在λ_{B1} 处的 $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ 比值。 6pt

B.2 沿着 y 方向，气体在起始状态（$l = l_{y0}$）和达到平衡后（$l = l_y$），波长 λ_{B2} 处测得的吸光度均为 A_{B2}。**计算** 在 λ_{B2} 处的$\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ 比值。 6pt

朗伯-比尔定律

A 部分

A.1 (10 pt)

(续后页)

A.1 (cont.)

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

B 部分

B.1 (6 pt)

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

B.2 (6 pt)

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

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.

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

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

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

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

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

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

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

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

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

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

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

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

锌的氧化还原化学

占总分 11 %							
题目	A.1	A.2	B.1	B.2	B.3	B.4	**小计**
分值	6	5	4	3	5	9	**32**
得分							

长期以来，锌被用于合金如黄铜和钢铁中。工业废水中的锌用沉淀法分离使水净化，且还原所得沉淀物后可回收金属锌并重新利用。

A 部分

25 °C 时，氢氧化锌 $Zn(OH)_2(s)$ 的溶解平衡及其相关的平衡常数如方程 1–4 所示：

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

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

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

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

锌的溶解度 S（饱和水溶液中锌的浓度）如方程 5 所示：

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

A.1	当方程 1–4 达到平衡，$[\mathrm{Zn(OH)_2(aq)}]$ 在 $[\mathrm{Zn^{2+}(aq)}]$，$[\mathrm{Zn(OH)_2(aq)}]$ 和 $[\mathrm{Zn(OH)_4^{2-}(aq)}]$ 三者中 为最大时，**计算** 溶液的 pH 范围。	6pt

A.2	pH = 7.00 时制备 $\mathrm{Zn(OH)_2(s)}$ 的饱和水溶液，过滤。往滤液中加入 NaOH，使溶液的 pH 升高至 12.00。**计算** 当溶液 pH 由 7.00 提升至 12.00 时，沉淀出锌的摩尔百分比。忽略体积和温度的变化。	5pt

B 部分

接下来，根据如下反应，将回收的氢氧化锌加热得到氧化锌：

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

然后，氧化锌与氢气反应被还原成金属锌：

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

B.1	保持氢气的压力为 1bar，为了能使反应 (7) 进行，必须降低生成的水蒸气的分压。**计算** 能使反应 (7) 在 300 °C 条件下进行的水蒸气分压的上限值。这里，在 300 °C，所有气体物种均为 1 bar 时，氧化锌和水蒸气的吉布斯生成自由能分别为 $\Delta G_{\mathrm{ZnO}}(300^\circ\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ 和 $\Delta G_{\mathrm{H_2O}}(300^\circ\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\,mol^{-1}}$。	4pt

金属锌可用作金属-空气电池中的负极材料。该电极由 Zn 和 ZnO 组成。利用如下的氧化还原反应产生电能，在 25°C，1 bar 压力时的电动势（e.m.f.）为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	锌-空气电池在 20 mA 下放电 24 小时，**计算** 电池负极的质量变化值。	3pt

富士山

B.3 考虑锌-空气电池的电动势（e.m.f.）随环境而变化。**计算** 在温度和海拔分别为 $-38\,^\circ$C（二月）、3776 米的富士山顶上锌-空气电池的电动势（e.m.f.）。在海拔为 h [m]，温度为 T [°C] 时，大气压的表达式如下： 5pt

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

大气中氧气的摩尔分数为 21%。在 $-38\,^\circ$C 和 1 bar 下，反应 (8) 的吉布斯自由能变为 $\Delta G_{\text{ZnO}}(-38^\circ\text{C}) = -3.26 \times 10^2\ \text{kJ mol}^{-1}$。

B.4 **计算** $25\,^\circ$C 时反应 (6) 的吉布斯自由能变。注意：在 $25\,^\circ$C，1 bar 时，标准电极电势 $E^\circ(\text{Zn}^{2+}/\text{Zn})$ 和 $E^\circ(\text{O}_2/\text{H}_2\text{O})$ 分别如方程（10）和（11）所示。 9pt

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

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

锌的氧化还原化学

A 部分

A.1 (6 pt)

________________ $<$ pH $<$ ________________

A.2 (5 pt)

_____________ %

B 部分

B.1 (4 pt)

p_{H_2O}= ______________ bar

B.2 (3 pt)

______________ g

B.3 (5 pt)

________________ V

B.4 (9 pt)

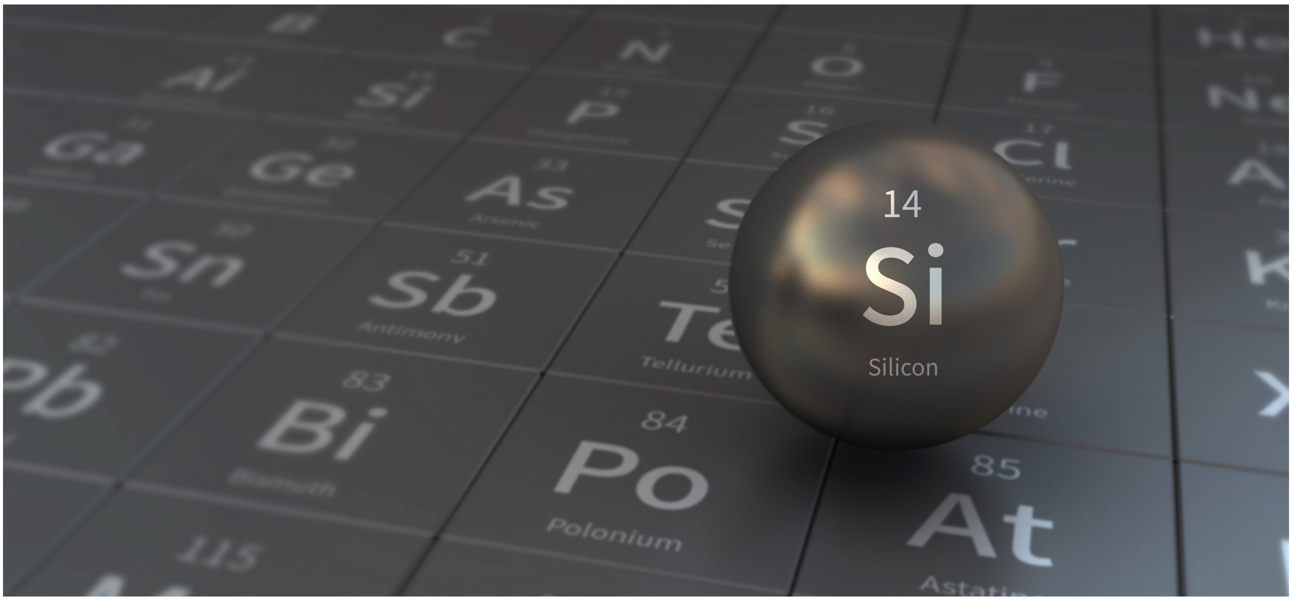
$\Delta G^\circ =$ ______________ J mol^{-1}

IChO
Problem 5
Cover sheet

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

Mysterious Silicon

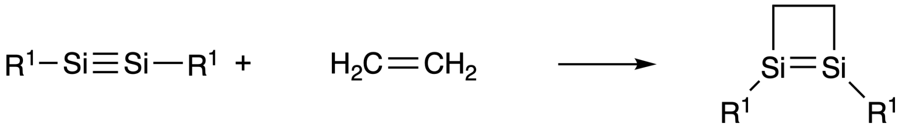
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



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

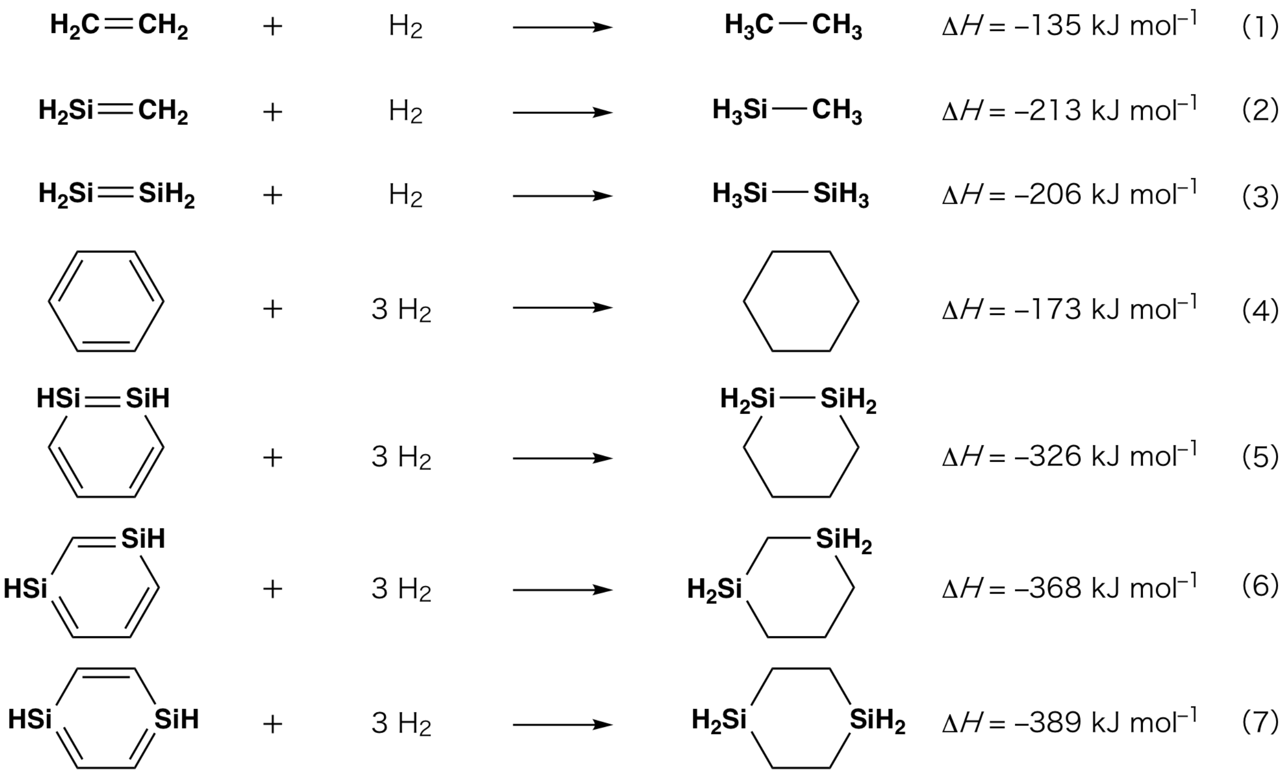


Fig. 1

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	<u>**Calculate**</u> 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	<u>**Draw**</u> 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	<u>**Write**</u> 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. <u>The unreacted Na_2SiF_6 and generated NaCl</u> 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:

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

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.

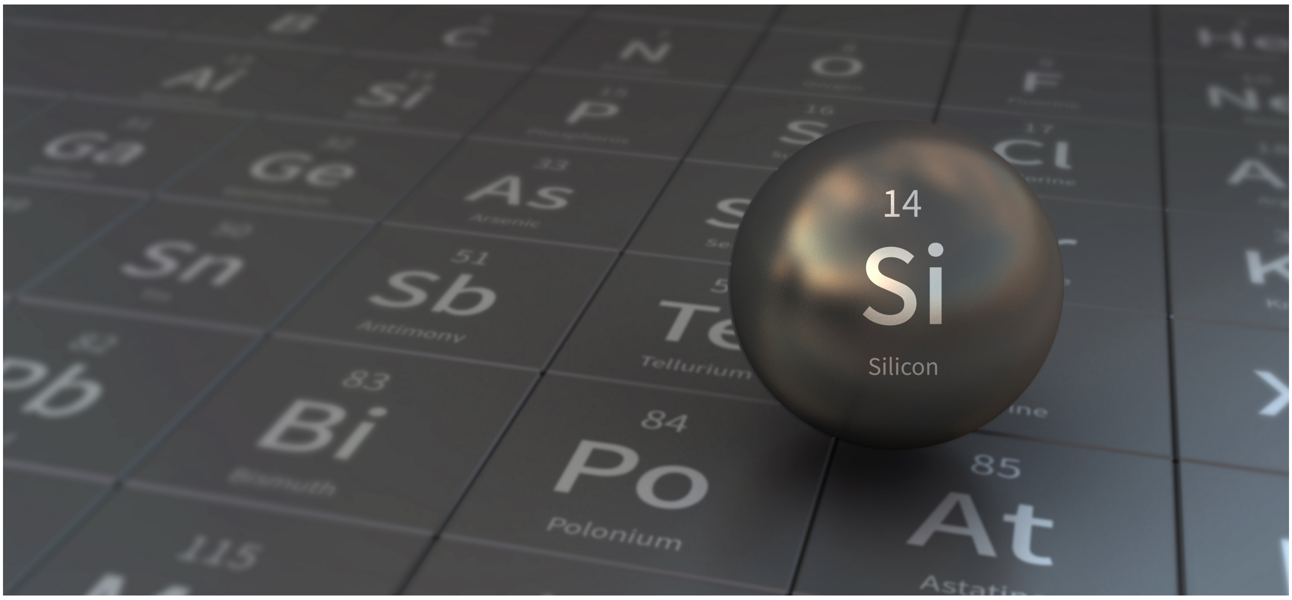
It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

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

神秘的硅元素

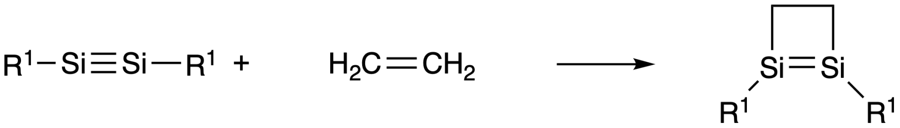
占总分 12%								
题目	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**小计**
分值	9	7	6	10	5	15	8	**60**
得分								



尽管硅和碳同为 14 族元素，但它们的性质却有很大的不同。

A 部分

不同于碳碳三键，在化合物中以 $R^1–Si\equiv Si–R^1$(R: 有机取代基) 形式出现的硅硅三键非常活泼。例如，它和乙烯反应生成四元环产物。



当 $R^1–Si\equiv Si–R^1$ 与一分子炔 $(R^2–C\equiv C–R^2)$ 反应时，先生成四元环化合物中间体 **A** 。进一步与另一分子 $R^2–C\equiv C–R^2$ 反应，产生同分异构体 **B** 和 **C**，它们都有与苯类似的环共轭结构，也就是所谓的“二硅苯”，可以表示为 $(R^1–Si)_2(R^2–C)_4$。

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

六元环骨架 Si_2C_4 的 ^{13}C NMR 分析显示，**B** 有两个信号，**C** 有一个信号。

A.1 采用 R^1, R^2, Si 和 C，**画出** 化合物 **A**，**B 和 C 的**结构，给出对应的一个合理的共振结构式即可。 9pt

A.2 分别**计算** 苯和 **C** 的芳香稳定化能 ASE (取正值，设 $R^1 = R^2 =$ H)，一些不饱和体系的氢化反应的焓变如下 (图 1)。 7pt

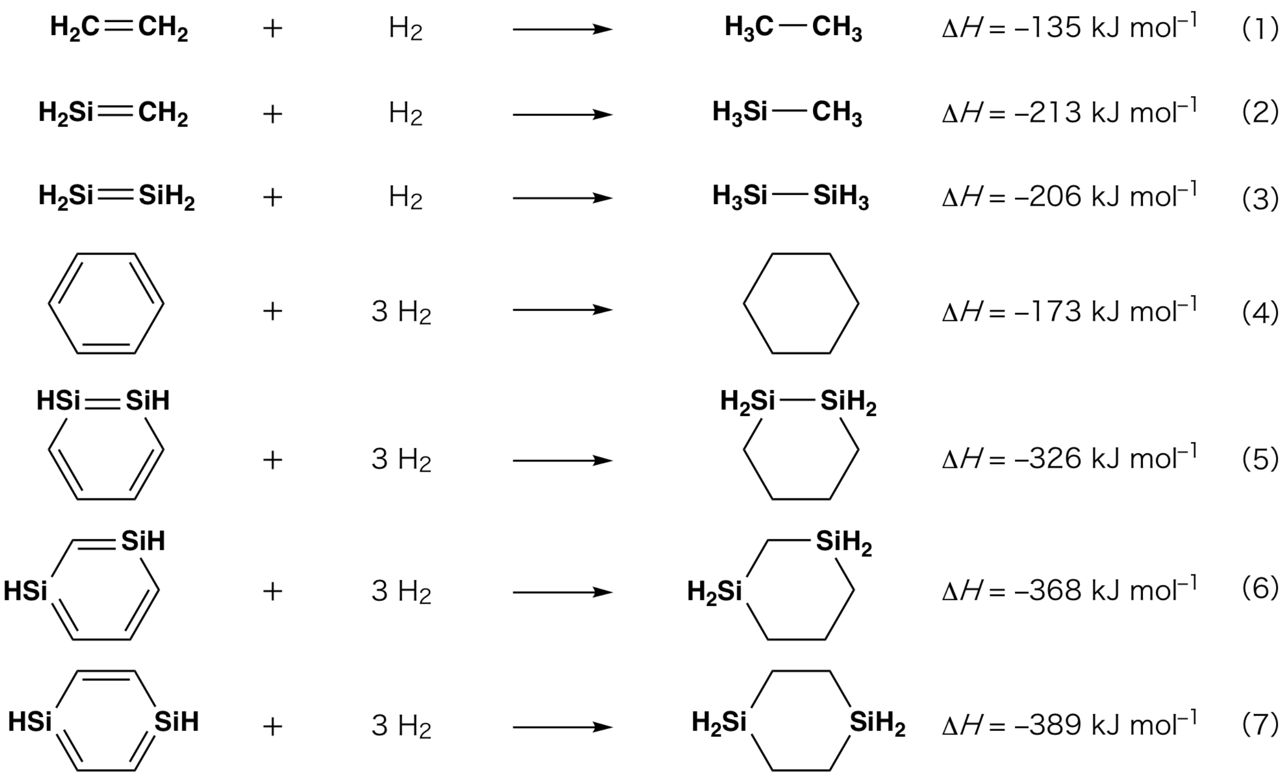


图 1

当加热 **C** 的二甲苯溶液，**C** 发生异构化，得到处于平衡的混合物 **D** 和 **E**，在 50.0 °C 时，**D** : **E** = 1 : 40.0 (摩尔比)，在 120.0 °C 时，**D** : **E** = 1 : 20.0 (摩尔比)。

A.3	**计算** **D** 转变为 **E** 的 ΔH。假设 ΔH 不随温度变化。	6pt

从 **C** 到 **D** 和从 **C** 到 **E** 的异构化反应经历了 π 键向 σ 键的转变，该过程中没有 σ 键的断裂。^{13}C NMR 显示，**D** 中的 Si_2C_4 骨架给出一个信号而 **E** 中的 Si_2C_4 骨架给出两个信号。**D** 的分子骨架中不包含任何三元环结构，而 **E** 的分子骨架中含有两个三元环并且共用一条边。

A.4	采用 R^1, R^2, Si 和 C，**画出** **D** 和 **E** 的结构。	10pt

B 部分

硅与氟等电负性强的元素可形成高配位化合物 (> 四个连接基团)。像金属氟化物常被用作氟化试剂一样，硅的高配位氟化物也充当氟化试剂。

用 Na_2SiF_6 对 CCl_4 进行的氟化反应操作如下。

- **Na_2SiF_6 溶液的标定**：

· 准备

水溶液 **F**: 0.855 g Na_2SiF_6 (188.053 g mol^{-1}) 溶于水 (总体积 200 mL)。

水溶液 **G**: 6.86 g $Ce_2(SO_4)_3$ (568.424 g mol^{-1}) 溶于水 (总体积 200 mL)。

· 步骤

以可与 Ce^{3+} 配位的二甲酚橙为指示剂，向溶液 **F** (50.0 mL) 中逐滴加入溶液 **G**，进行沉淀滴定。加入 18.8 mL 溶液 **G** 后，溶液颜色由黄色变为品红色。生成的沉淀物是一种含有 Ce^{3+} 的二元化合物，唯一生成的含硅化合物是 $Si(OH)_4$。

B.1	**写出** Na_2SiF_6 和 $Ce_2(SO_4)_3$ 反应的配平的方程式。	5pt

- **CCl_4 和 Na_2SiF_6 的反应:**

(以下操作中，蒸发等造成的物质损失忽略不计。)

将 Na_2SiF_6(x [g]) 加入到 CCl_4(500.0 g) 中，在密封的耐压反应釜中加热至 300 °C。过滤移去未反应的 Na_2SiF_6 和所生成的 NaCl。用 CCl_4 稀释滤液至总体积为 1.00 L (**H** 溶液), **H** 溶液的 ^{29}Si NMR 和 ^{19}F NMR 显示，SiF_4 为唯一的含硅化合物。在 ^{19}F NMR 中，除 SiF_4 外，还观察到 $CFCl_3$，CF_2Cl_2，CF_3Cl 和 CF_4 对应的信号 (见表 1)。^{19}F NMR 谱中的积分面积与氟核的数目成正比。

表 1

^{19}F NMR 数据	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
积分面积	45.0	65.0	18.0	2.0

SiF_4 水解生成 H_2SiF_6，反应式如下 (式 8):

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

将溶液 **H** (10 mL) 加入过量的水中，使 SiF_4 完全水解。分离后，中和溶液中水解生成的 H_2SiF_6 使之全部转化为 Na_2SiF_6 (水溶液 **J**)。

将前面滤出的未反应的 Na_2SiF_6 和 NaCl 的沉淀 (下划线部分) 完全溶解在水中，得到水溶液 (溶液 **K**; 10.0 L)。

然后, 用 **G** 溶液进行进一步的沉淀滴定，滴定终点如下：

·溶液 **J** (全部)：61.6 mL。

·溶液 **K** (取 100 mL)：44.4 mL。

提示：共存的 NaCl 或 SiO_2 对沉淀滴定没有影响。

B.2	**计算** 反应釜中产生的 NaCl 的质量 (下划线部分)，并**计算** 作为起始原料的 Na_2SiF_6 的质量 (x [g])。	15pt

B.3	初始原料中 77.8% 的 CCl_4 未反应，**计算** 所生成的 CF_3Cl 的质量。	8pt

神秘的硅元素

A 部分

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)

B 部分

B.1 (5 pt)

B.2 (15 pt)

(续后页)

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:

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

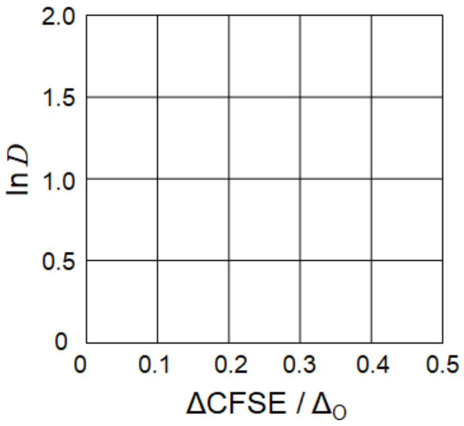
where $[\mathrm{M}]_\mathrm{s}$ and $[\mathrm{M}]_\mathrm{l}$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of $Cr^{2+}$and Mn^{2+} as examples.

	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}).

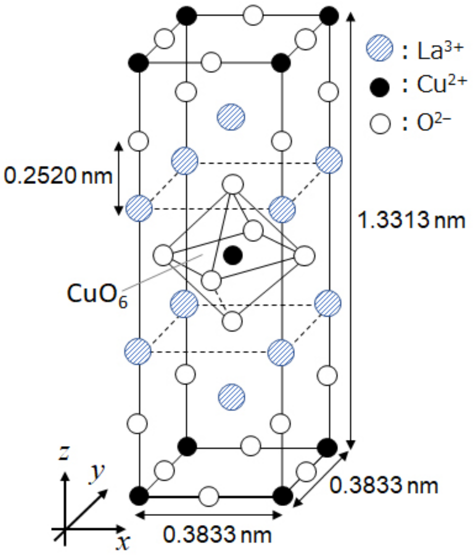


Fig. 1

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.

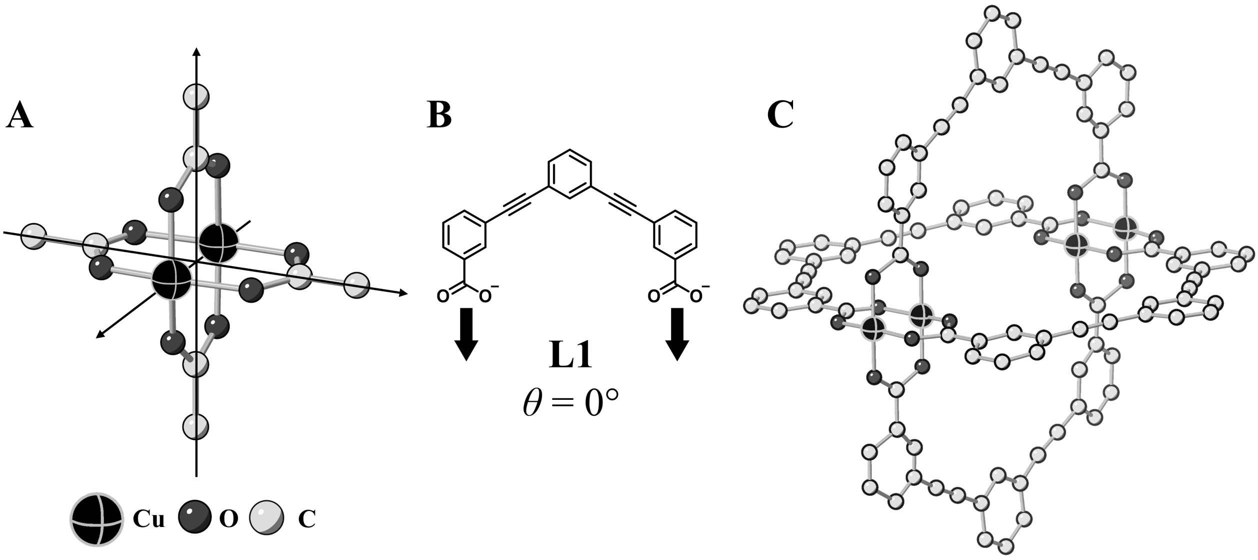
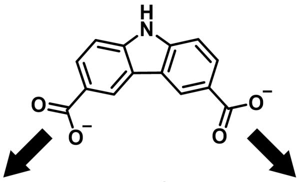


Fig. 2

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

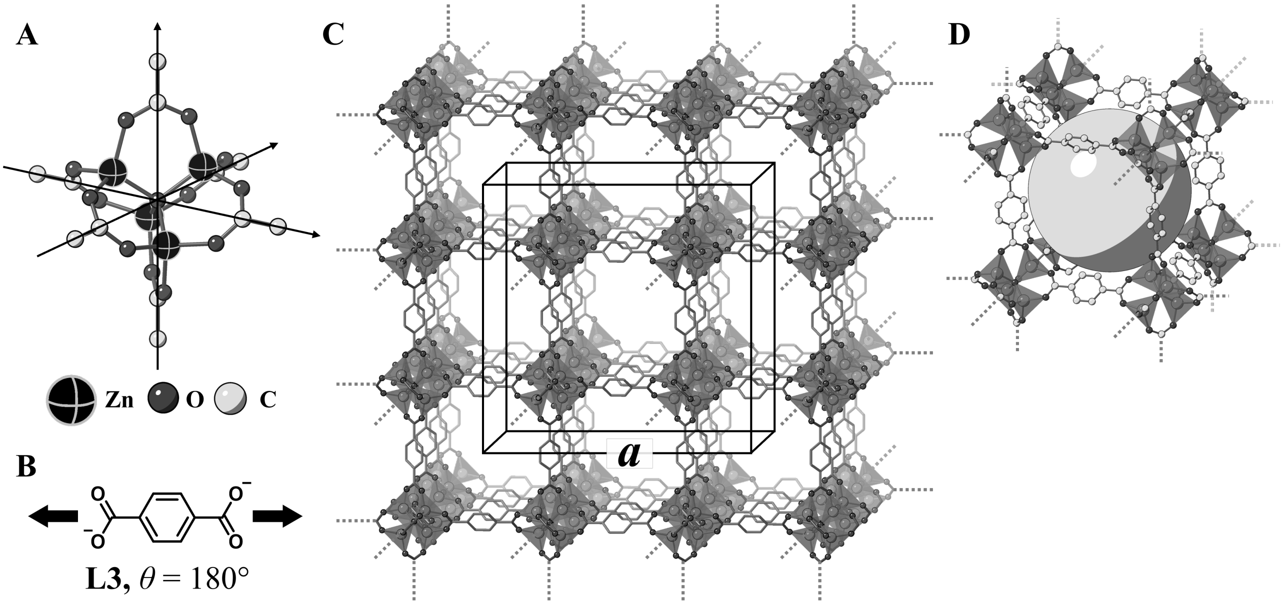


Fig. 3

C.2 **X** has a cubic unit cell with a side length of a (Fig. 3C) and a density of 0.592 $\mathrm{g\,cm^{-3}}$. **<u>Calculate</u>** 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 $\mathrm{CO_2}$ gas in the pores at 1 bar and 25 °C. **<u>Calculate</u>** the average number of $\mathrm{CO_2}$ molecules per pore. 5pt

过渡金属的固体化学

占总分 13%										
题目	A.1	A.2	A.3	B.1	B.2	B.3	B.4	C.1	C.2	C.3	**小计**
分值	6	3	3	6	4	4	4	5	5	5	**45**
得分											

樱岛火山

A 部分

日本是世界上火山数量最多的国家之一。当硅酸盐矿物从岩浆中结晶时，岩浆中的一部分过渡金属离子 (M^{n+}) 被引入硅酸盐矿物中。本题研究的 M^{n+} 由氧离子 (O^{2-}) 配位，在岩浆中采用四配位的四面体 (T_d) 几何，在硅酸盐矿物中采用六配位的八面体 (O_h) 几何，均表现为高自旋电子构型。M^{n+} 在硅酸盐矿物与岩浆之间的分配系数 D 可表示为：

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

其中，$[\mathrm{M}]_\mathrm{s}$ 和 $[\mathrm{M}]_\mathrm{l}$ 分别为 M^{n+} 在硅酸盐矿物和岩浆中的浓度。下表示出了 Cr^{2+} 和 Mn^{2+} 的 D 值。

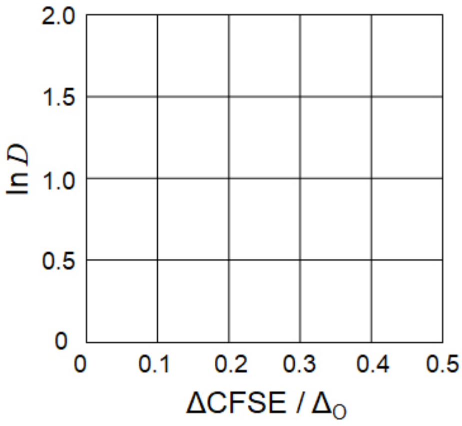
	Cr^{2+}	Mn^{2+}
D	7.2	1.1

设 Δ_O 和 CFSE^O 分别为 O_h 场中 M^{n+} 的 d 轨道的分裂能和晶体场稳定能，Δ_T 和 CFSE^T 分别为 T_d 场中 M^{n+} 的 d 轨道的分裂能和晶体场稳定能。

A.1 $|\mathrm{CFSE}^{\mathrm{O}}-\mathrm{CFSE}^{\mathrm{T}}|=\Delta\mathrm{CFSE}$，**计算**$Cr^{2+}$, Mn^{2+} 和 Co^{2+} 的 ΔCFSE，以 Δ_O 为单位。假设 $\Delta_T = 4/9\Delta_O$。 6pt

A.2 在如下所示的直角坐标系中，以 ln$D$ 对 $\Delta\mathrm{CFSE}/\Delta_O$ 画图，观察到二者之间存在线性关系。 3pt

估算 Co^{2+} 的 D 。



金属氧化物 MO (M: Ca, Ti, V, Mn 或 Co) 均结晶为岩盐结构，其中 M^{n+} 采用 O_h 几何构型且为高自旋电子组态。这些氧化物的晶格焓主要由基于离子半径和电荷的库仑相互作用以及 O_h 场中 M^{n+} 的 CFSE 的贡献所决定。

A.3 从 (a) 到 (f) 中**选出** 一套合理的晶格焓 [kJ mol^{-1}] 数据。 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

B 部分

复合氧化物 **A** 结晶形成四方晶胞，其中含有 La^{3+} 和 Cu^{2+}，如图 1 所示。在 $[CuO_6]$ 八面体中，Cu-O 之间沿 z 轴的距离 (l_z) 比其沿 x 轴的距离 (l_x) 长，$[CuO_6]$ 从规则的 O_h 几何构型发生变形。这种畸变消除了 e_g 轨道（$d_{x^2-y^2}$ 和 d_{z^2}）的简并。

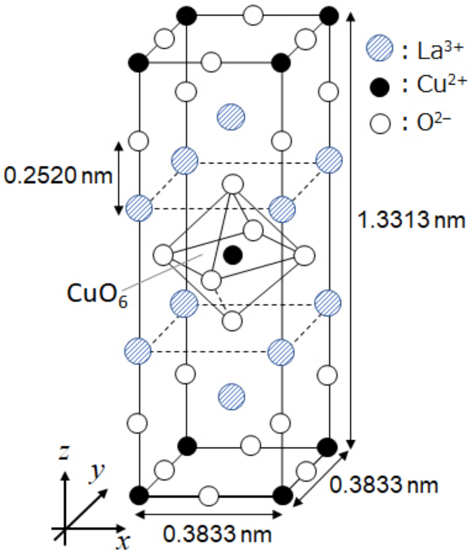


图 1

A 可以通过配合物 **B** 的热分解 (热解) 得到，**B** 可以由金属氯化物加入含有方酸 $C_4H_2O_4$(二元酸) 的稀氨水溶液中混合得到。在干燥的空气中，**B** 受热分解，至 200°C 失重 29.1%，对应于结晶水的失去；随后，继续失重至 700°C，对应于二氧化碳的放出。从 **B** 到 **A** 的总失重为 63.6%。需要注意的是，在热解反应中只释放出水和 CO_2。

B.1	**写出** **A** 和 **B** 的化学式。	6pt
B.2	参照图 1，**计算** l_x 和 l_z。	4pt
B.3	图 1 中，Cu^{2+} 位于畸变的 $[CuO_6]$ 八面体场中。在 (i) 和 (ii) 上**写出** 其分裂的 e_g 轨道的名称 ($d_{x^2-y^2}$ 和 d_{z^2})，在答题纸上的虚线框中**画出** 电子结构。	4pt

A 是绝缘体。当一个 La^{3+} 被一个 Sr^{2+} 取代时，晶格中会产生一个可以导电的空穴。因此，掺杂 Sr^{2+} 的 **A** 在温度低于 38 K 时 具有超导电性。当 **A** 发生取代反应后，每立方米产生空穴数 2.05×10^{27} 个。

B.4	基于取代反应的摩尔比，**计算**Sr^{2+} 取代 La^{3+} 的百分率。提示，组成离子的价态和晶体结构不会因取代反应而改变。	4pt

C 部分

$Cu_2(CH_3CO_2)_4$ 由四个 $CH_3CO_2^-$ 和两个 Cu^{2+} 配位组成 (图 2A)。$Cu_2(CH_3CO_2)_4$ 具有高度的结构对称性，两个轴穿过四个 $CH_3CO_2^-$ 中的碳原子，一个轴穿过两个 Cu^{2+}，所有这些轴交于一点且互相垂直。当用二羧酸配体代替 $CH_3CO_2^-$ 时，就形成了 “笼状配合物”。笼状配合物 $Cu_4(\mathbf{L1})_4$ 由平面二羧酸 **L1**(图 2B) 和 Cu^{2+} 组成 (图 2C)。图 2B 中箭头所示的两个羧酸配位方向之间的夹角 θ 决定了笼状配合物的结构。**L1** 的 θ 为 0°。注意，图 2 中未示出氢原子。

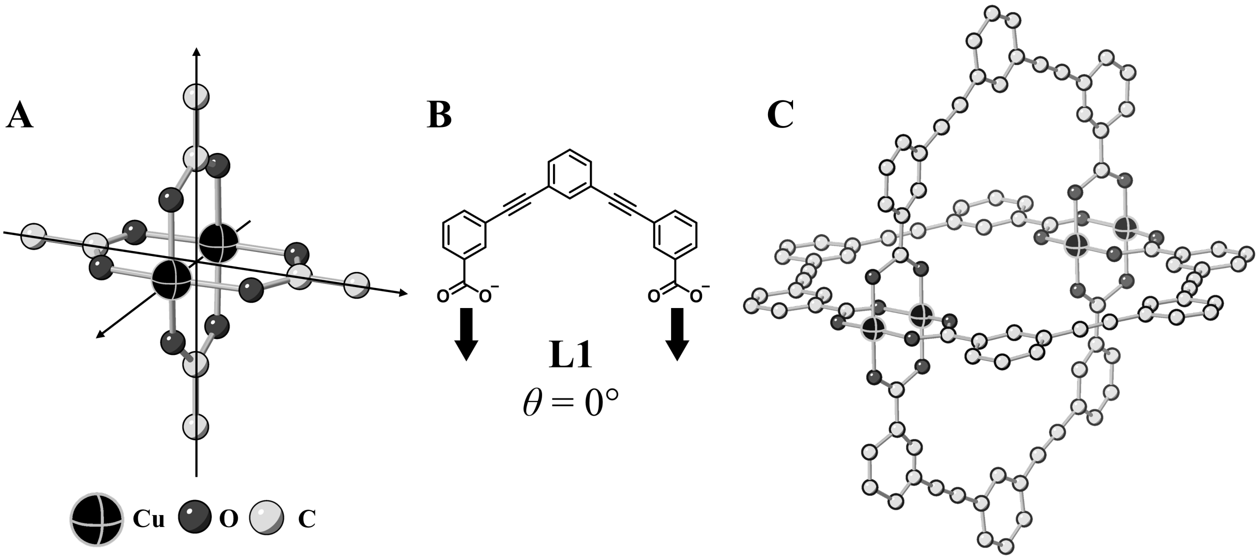
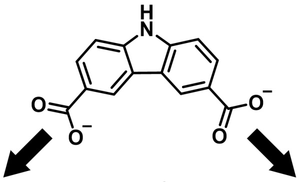


图 2

C.1 平面二羧酸盐 **L2** 的 θ 为 90°。如果 **L2** 和 Cu^{2+} 形成的笼形配合物的组成为 $Cu_n(\mathbf{L2})_m$，<u>**给出**</u> n 和 m 取最小整数的组合。假设 **L2** 中只有 CO_2^- 基团与 Cu^{2+} 形成配位键。 5pt



L2

$\theta = 90°$

一种锌的配合物 $Zn_4O(CH_3CO_2)_6$ 中，含有四个呈四面体分布的 Zn^{2+}，六个 $CH_3CO_2^-$ 和一个 O^{2-}(图 3A)。在 $Zn_4O(CH_3CO_2)_6$ 中，O^{2-} 位于原点，且穿过 $CH_3CO_2^-$ 的碳原子的三个轴彼此垂直相交。当采用对苯二甲酸酯 (图 3B，**L3**，$\theta = 180°$) 替换 $CH_3CO_2^-$ 后，Zn^{2+} 团簇相互连接形成的晶体 (**X**) 称为“多孔配位聚合物”(图 3C)。**X** 的组成为 $[Zn_4O(\mathbf{L3})_3]_n$，形成包含纳米孔隙的立方晶体结构，在图 3D 中，用大球表示孔隙；在图 3C 和图 3D 中每个四面体 Zn^{2+} 团簇表示为灰色多面体。请注意，图 3 中未示出氢原子。

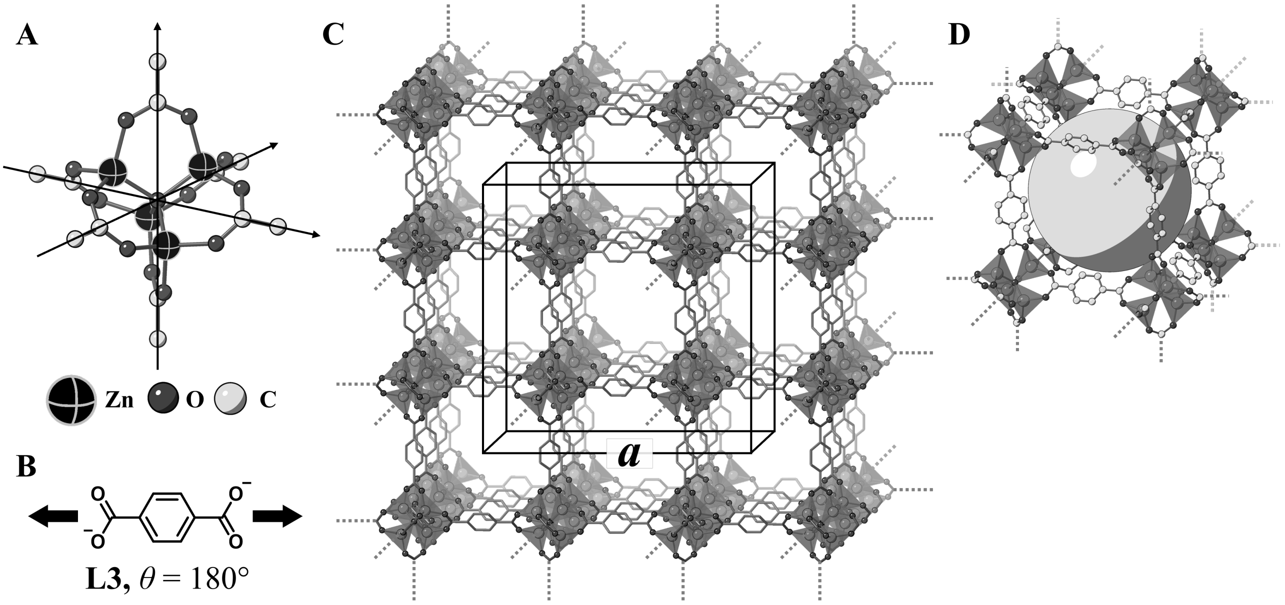


图 3

C.2	**X** 的密度为 0.592 g cm^{-3}，立方晶胞边长为 a (图 3C)。**计算** a，单位用 [cm]。	5pt
C.3	**X** 含有大量的孔隙，在 1bar 和 25°C 条件下，1g **X** 可容纳 3.0×10^2 mL 的 CO_2 气体。**计算** 每个孔隙中容纳 CO_2 分子的平均个数。	5pt

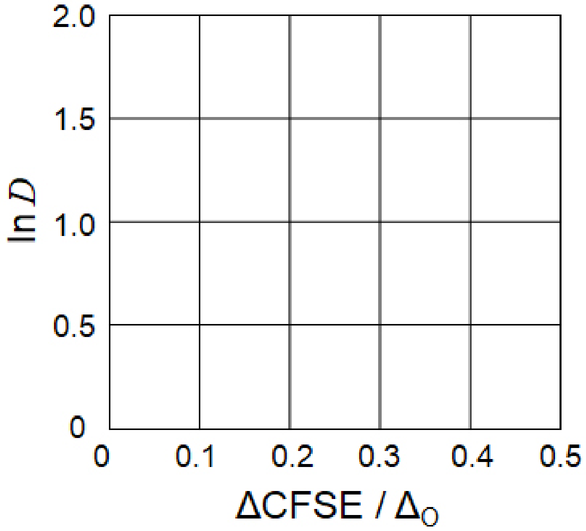
过渡金属的固体化学

A 部分

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)

____

B 部分

B.1 (6 pt)

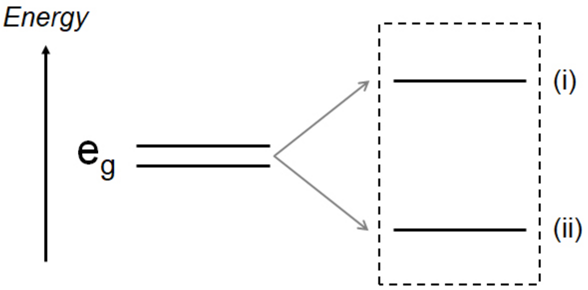
A : ______________________, B : ______________________

B.2 (4 pt)

$l_x =$ ______________________ nm, $l_z =$ ______________________ nm

B.3 (4 pt)

(i) : ______________________ , (ii) : ______________________



B.4 (4 pt)

______________________ %

C 部分

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					

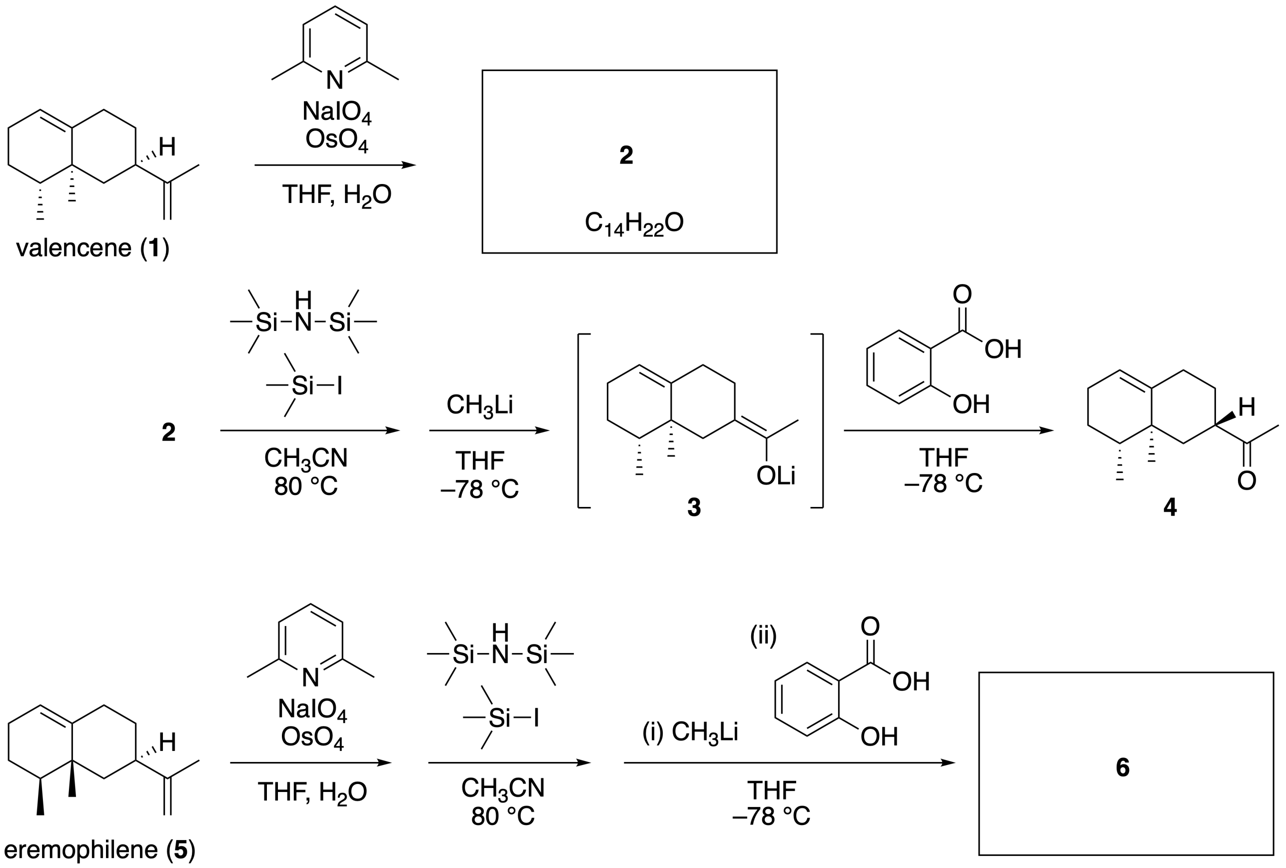
Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

Photo courtesy: Tohoku Univ.

Part A

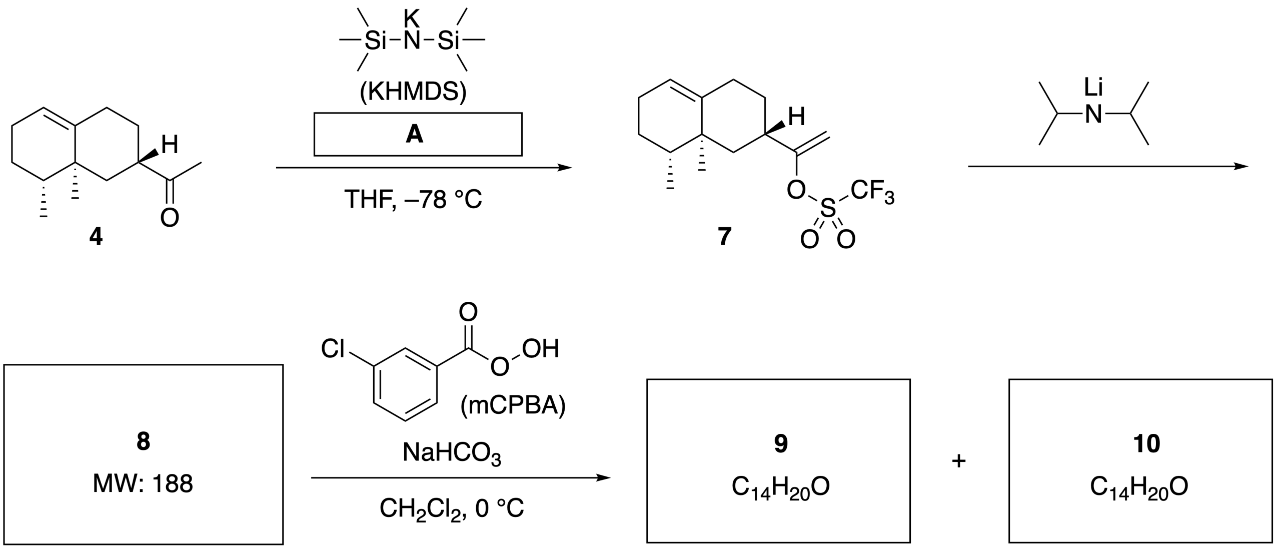
Leariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (**1**), a one-step conversion yields **2**, before a three-step conversion via **3** yields ketone **4**. Eremophilene (**5**) is converted into **6** by performing the same four-step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

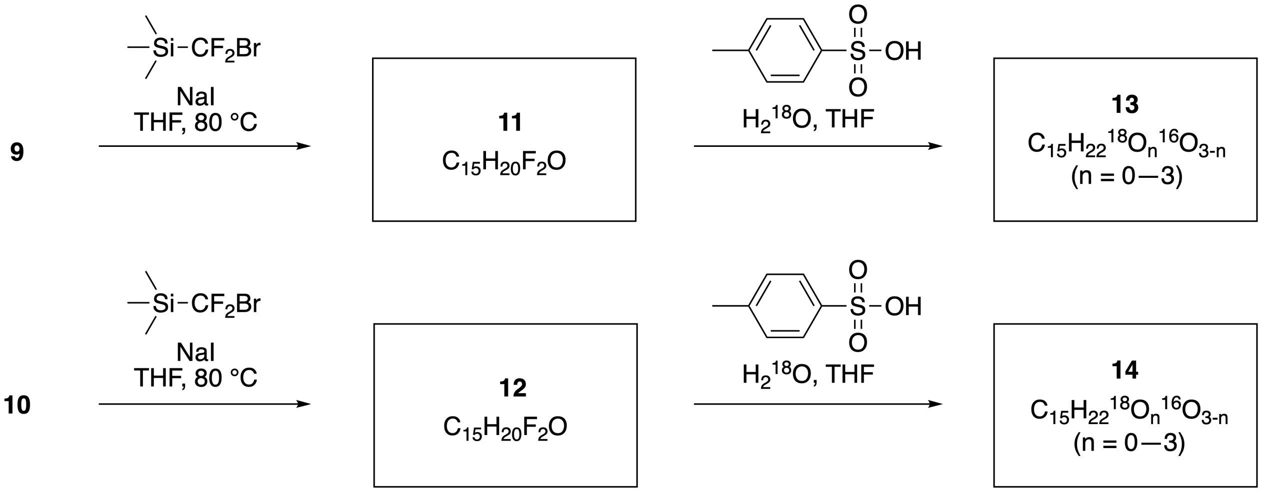
Inula linariifolia

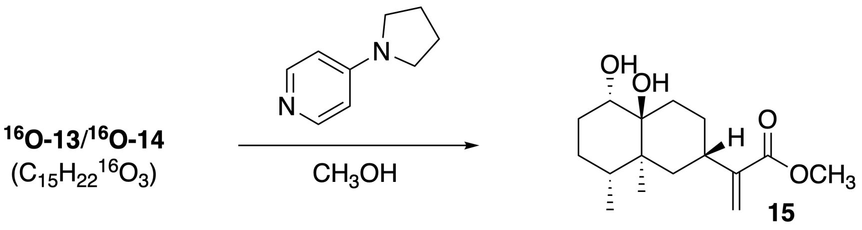


A.1	**Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary.	5pt

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.

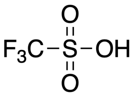






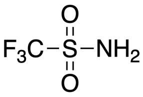
A.2 **Choose** the appropriate structure for **A**. 2pt

I



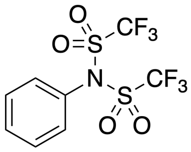
$F_3C-S(=O)_2-OH$

II

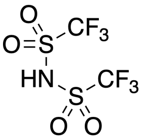


$F_3C-S(=O)_2-NH_2$

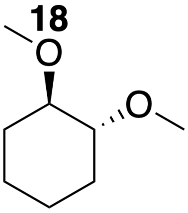
III



IV

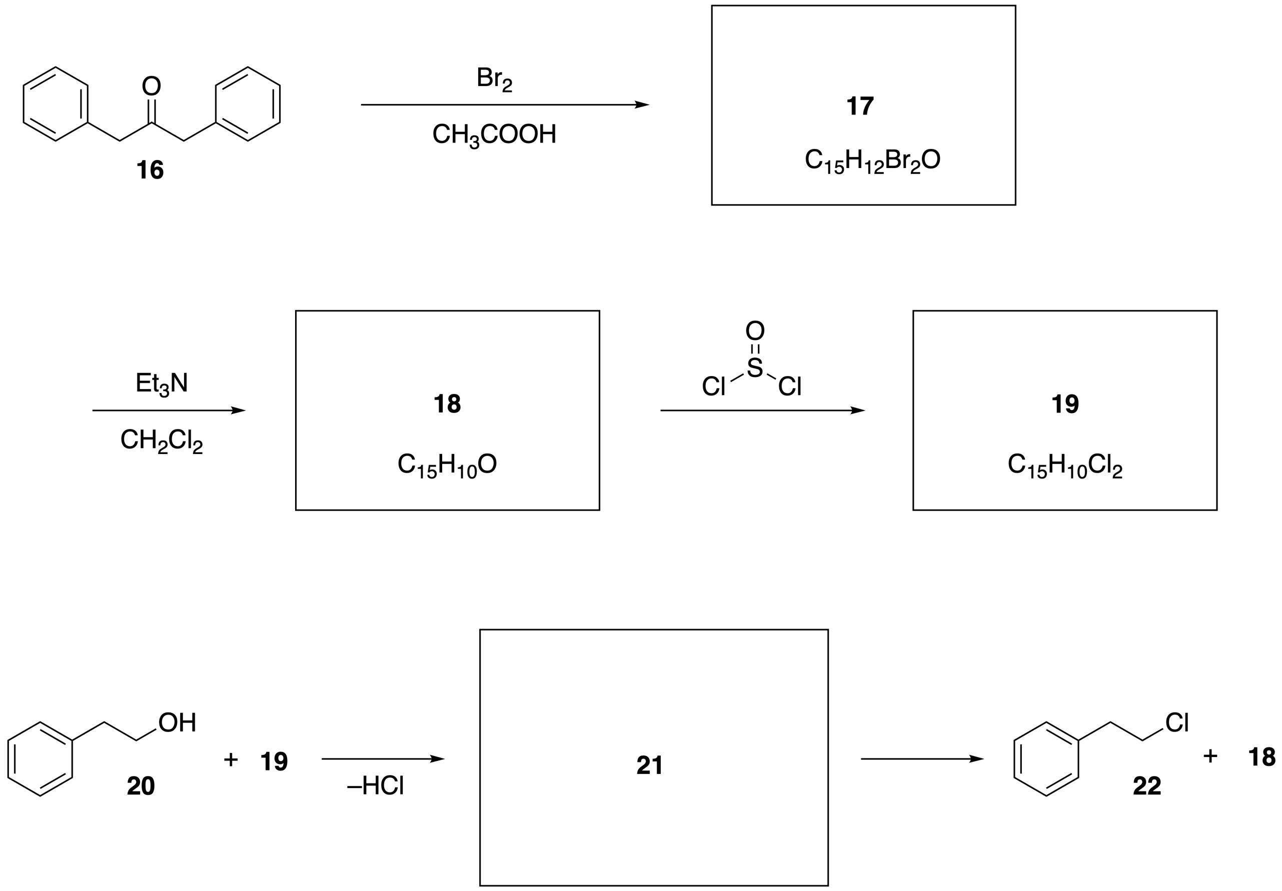


A.3 **Draw** the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, **indicate** the introduced ^{18}O atoms for **13** and **14** as shown in the example below. 19pt



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_3CN, ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)

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

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

趣玩非苯芳香性

占总分 13 %					
题目	A.1	A.2	A.3	B.1	**小计**
分值	5	2	19	10	**36**
得分					

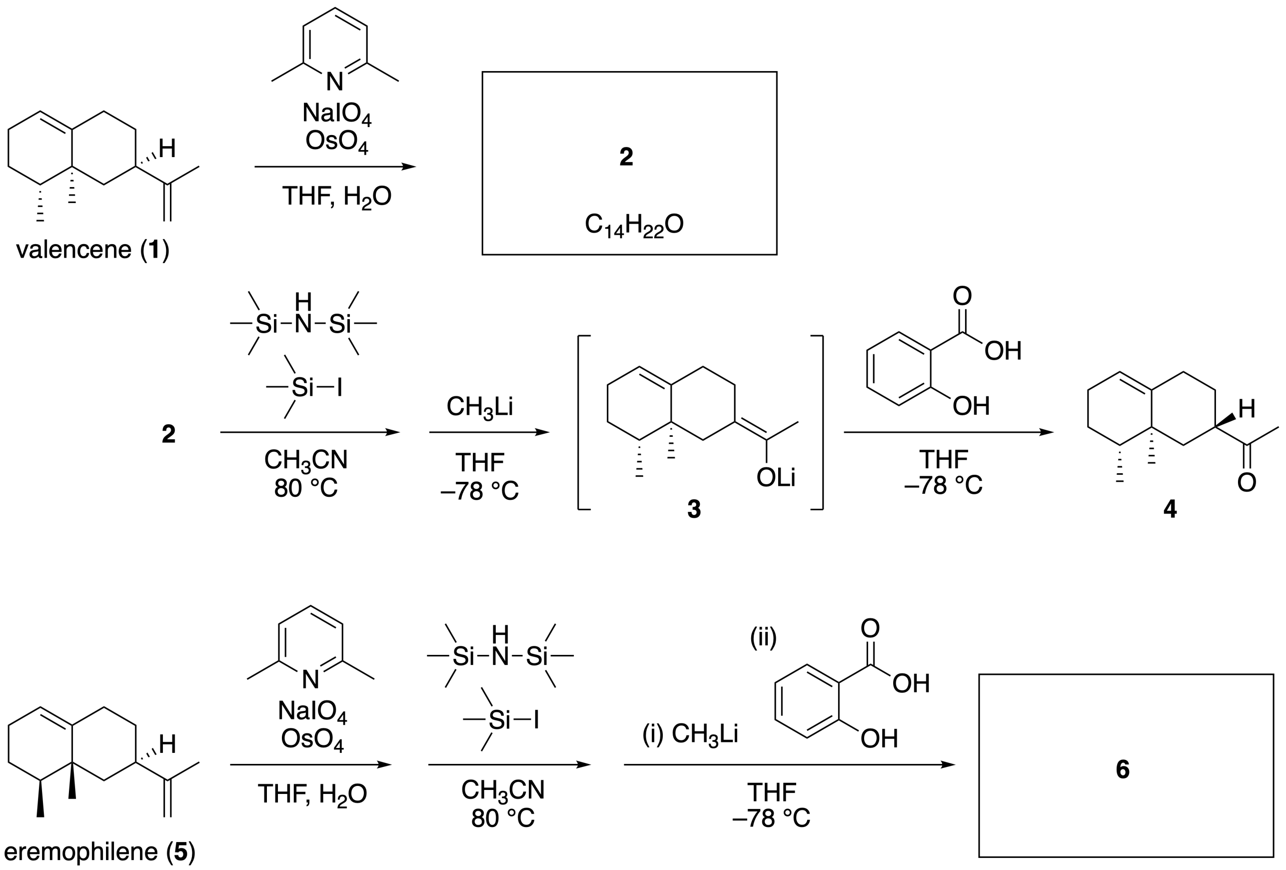
Nozoe 教授 (1902-1996) 开创了非苯芳香化合物研究领域，这些化合物在有机化学中普遍存在。

图片提供：东北大学（日本）

A 部分

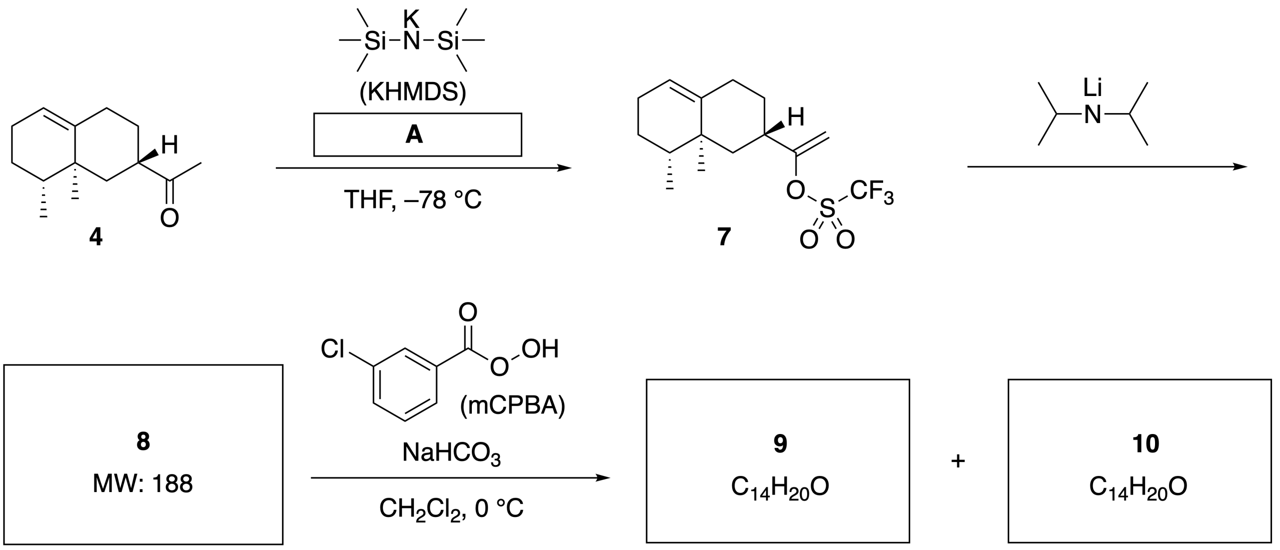
Leariifolianone 是一类结构独特的天然产物，从菊苣（Inula linariifolia）中分离得到。从 valencene (**1**) 出发，一步转化形成 **2**，通过 **3** 经三步转化生成酮 **4**。通过同样的四步转化，Eremophilene (**5**) 可以转化成 **6** 。

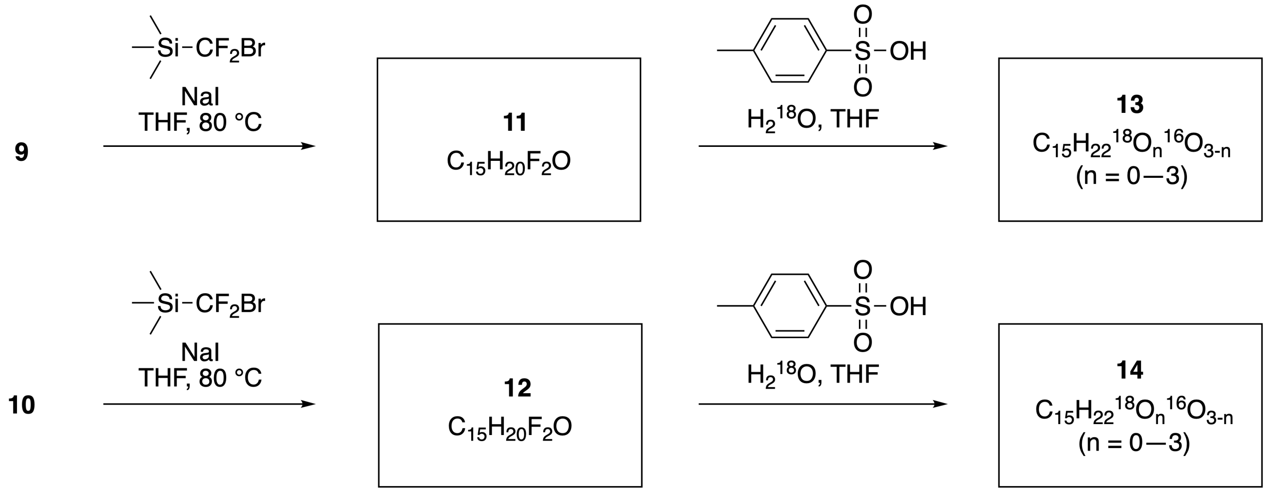
菊苣（Inula linariifolia）

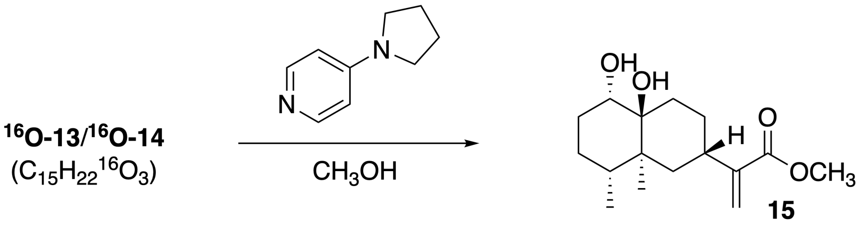


A.1 **画出** **2** 和 **6** 的结构，必要时，明确立体化学。 5pt

然后，酮 **4** 可以转化成酯 **15**。化合物 **8**（分子量：188）保留化合物 **7** 中所有手性中心，化合物 **9** 和化合物 **10** 各含有 5 个手性中心，不含碳碳双键。用 $H_2{}^{18}O$ 代替 $H_2{}^{16}O$，可以分别从 **11** 和 **12** 合成 ^{18}O-标记的 Lineariifolianones（**13** 和 **14**），化合物 **13** 和 **14** 是 ^{18}O-标记的同位素异素体。忽略同位素标记，化合物 **13** 和 **14** 可生成立体化学相同的同一化合物 **15**。

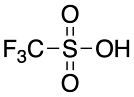

4
(KHMDS)
A
THF, –78 °C
7
8
MW: 188
(mCPBA)
NaHCO$_3$
CH$_2$Cl$_2$, 0 °C
9
$C_{14}H_{20}O$
+
10
$C_{14}H_{20}O$


9
NaI
THF, 80 °C
11
$C_{15}H_{20}F_2O$
$H_2{}^{18}O$, THF
13
$C_{15}H_{22}{}^{18}O_n{}^{16}O_{3-n}$
(n = 0—3)
10
NaI
THF, 80 °C
12
$C_{15}H_{20}F_2O$
$H_2{}^{18}O$, THF
14
$C_{15}H_{22}{}^{18}O_n{}^{16}O_{3-n}$
(n = 0—3)


^{16}O-13/^{16}O-14
($C_{15}H_{22}{}^{16}O_3$)
CH$_3$OH
15

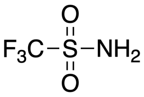
A.2 **选择 A** 的合适结构. 2pt

I



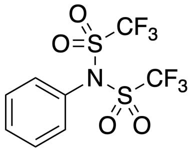
$F_3C-\overset{O}{\underset{O}{S}}-OH$

II

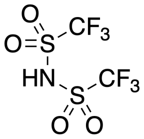


$F_3C-\overset{O}{\underset{O}{S}}-NH_2$

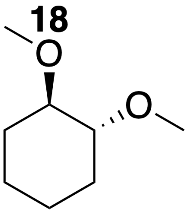
III



IV

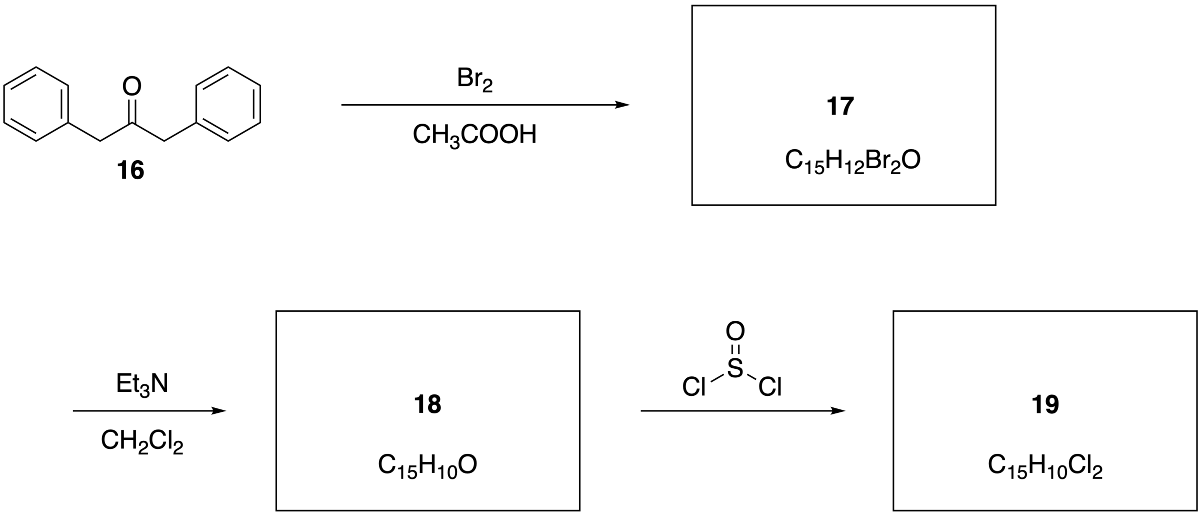


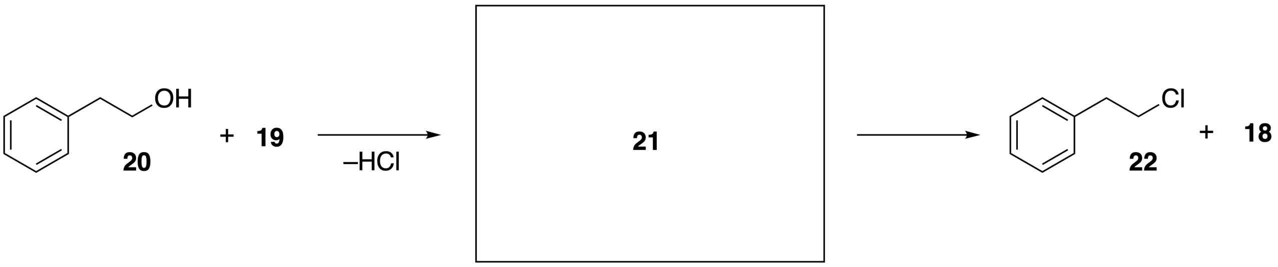
A.3 **画出 8-14** 的结构式，必要时，明确立体化学。并按如下所示的方法，**标记 13** 和 **14** 中引入的 ^{18}O . 19pt



B 部分

化合物 **19** 可以按如下所示的方法合成。和非苯芳香性相关，**19** 可以用作醇的活化剂，**20** 可以通过离子对中间体 **21** 转化成 **22**。尽管可以用核磁观察到 **21** 的形成，但 **21** 可逐渐分解生成 **18** 和 **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 **画出** **17-19** 及 **21** 的结构式，不要求立体化学。 10pt

趣玩非苯芳香性

A 部分

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)

B 部分

B.1 (10 pt)

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

IChO
Problem 8
Cover sheet

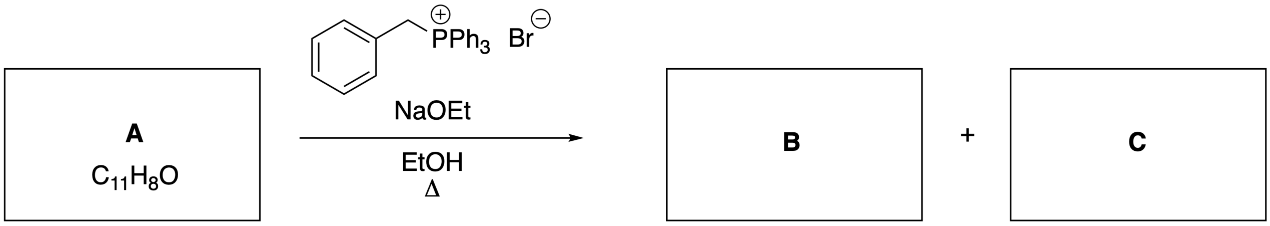
Please return this cover sheet together with all the related question sheets.

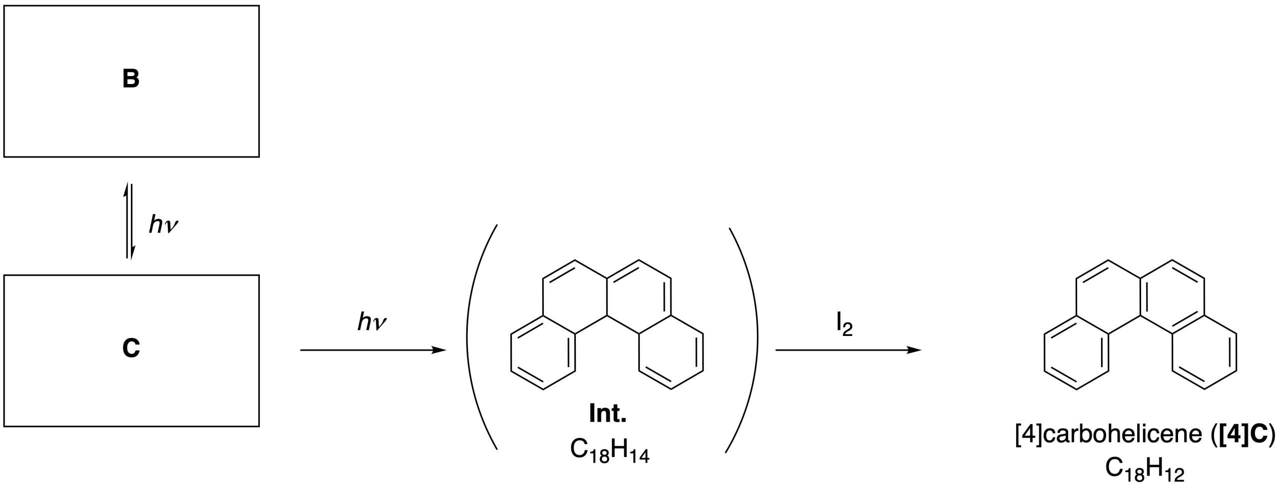
Dynamic Organic Molecules and Their Chirality

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

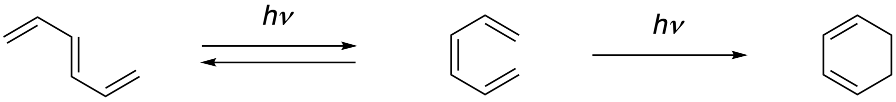
Part A

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.

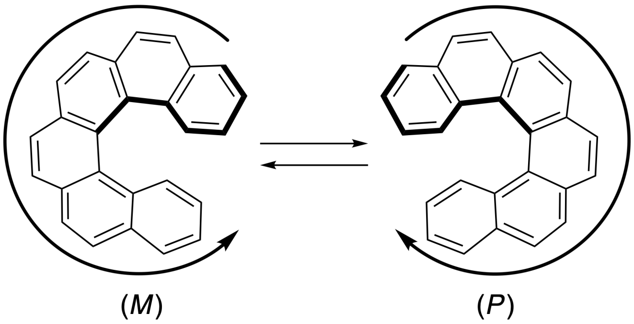


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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.

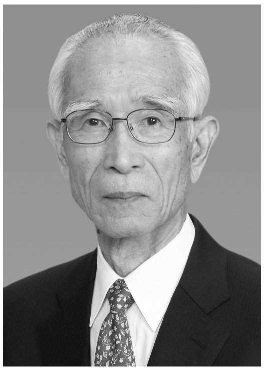
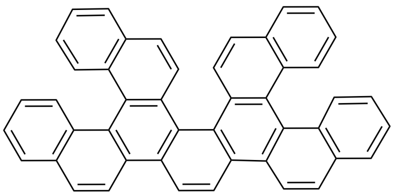
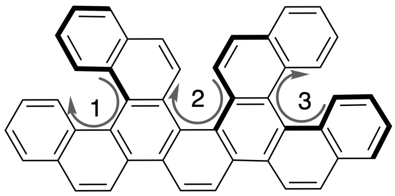


Photo courtesy: The Japan Prize Foundation

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.

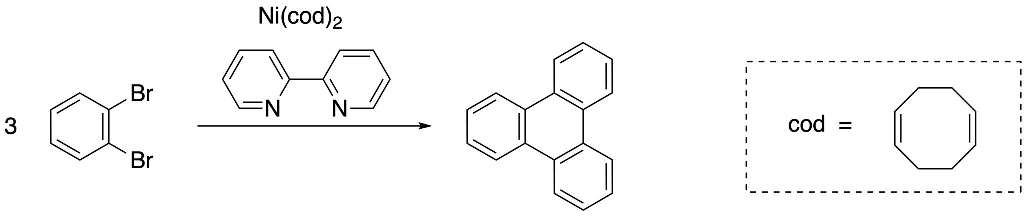


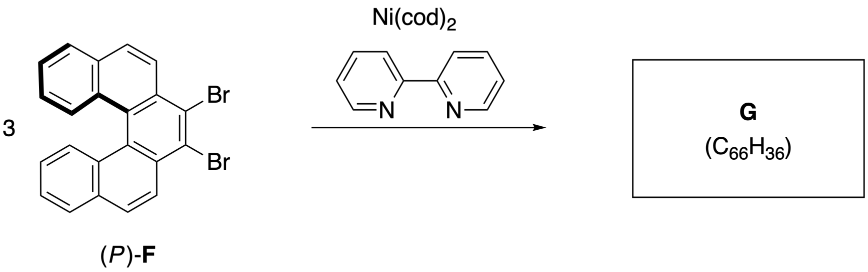
E



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

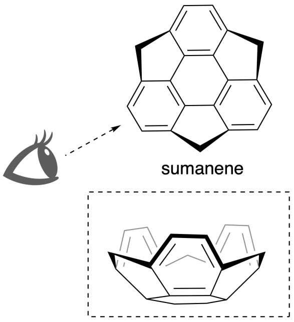
A.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify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



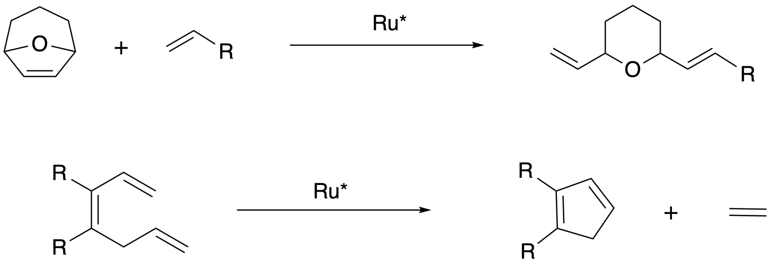


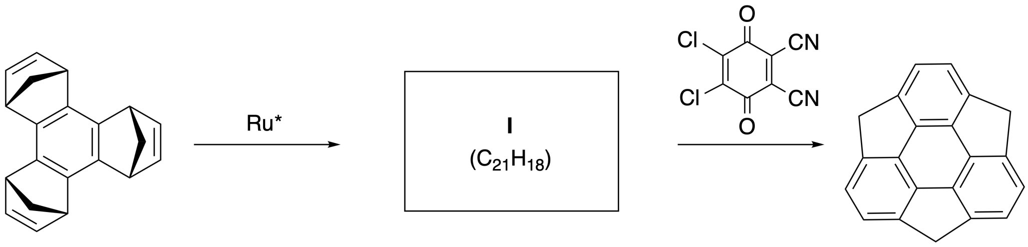
Part B

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.



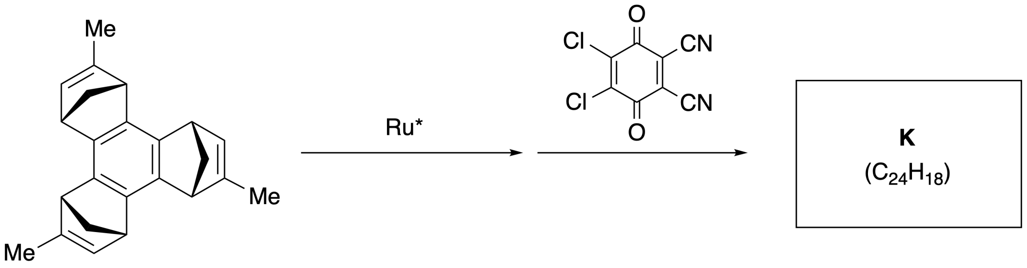
Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.





H

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



J

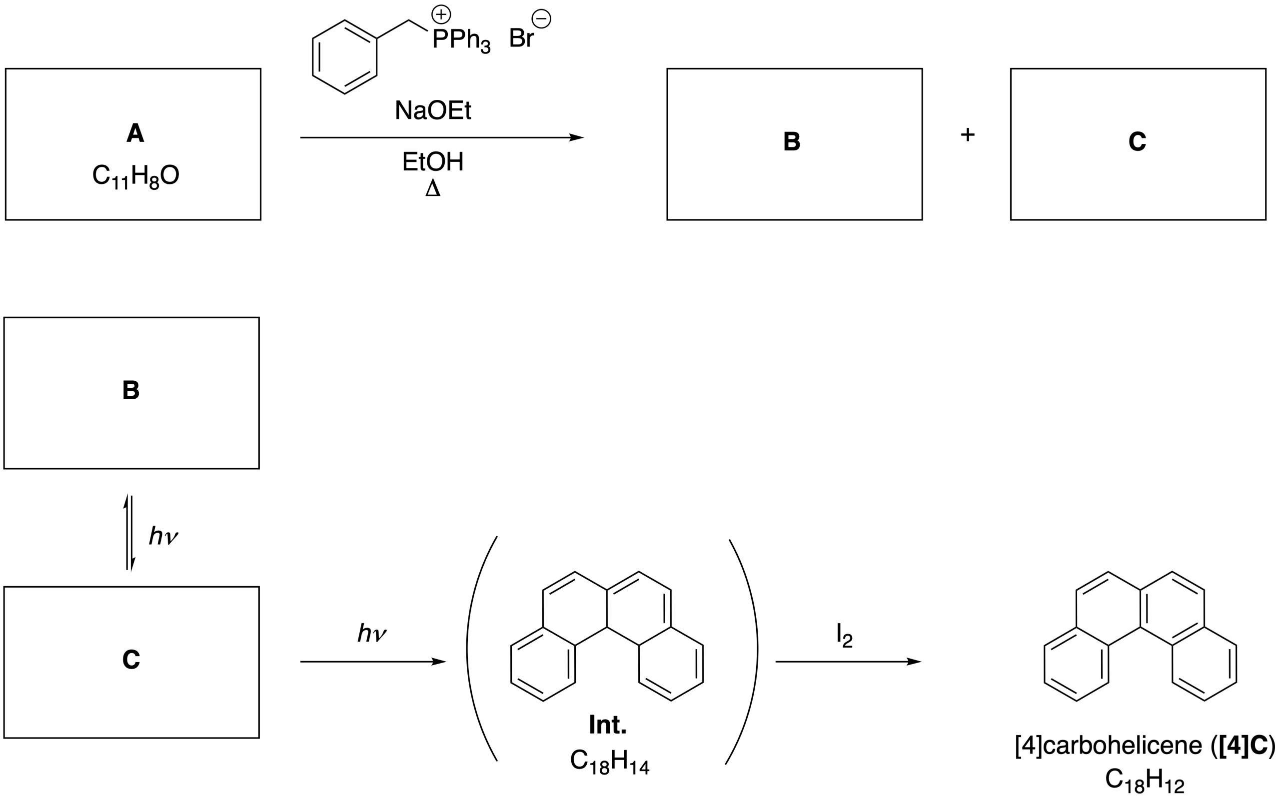
B.2 Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. **Draw** the structure of **K** with the appropriate stereochemistry. 4pt

动态有机分子及其手性

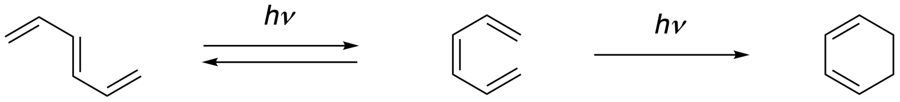
占总分 11 %						
题目	A.1	A.2	A.3	B.1	B.2	**小计**
分值	9	3	7	3	4	**26**
得分						

A 部分

经连续邻位稠合的多环芳烃称为 [n] 碳螺旋烃（n 指分子中六元环的个数）（可见如下示例）。[4] 碳螺旋烃（**[4]C**）可由如下光反应路线高效制备，反应产生的中间体（**Int.**）易被碘氧化。



其光反应过程与如下示例相类似。

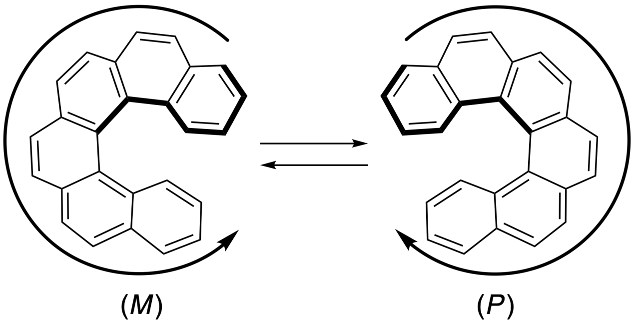


注意：在整个第 8 题的问题作答中，请参照示例，采用单双键交替的方式画碳螺旋烃。请勿使用圆圈表示共轭π体系。

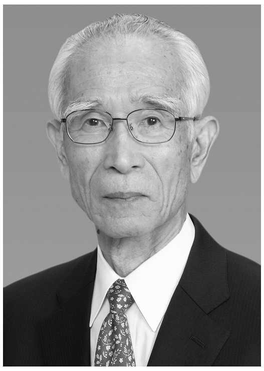
A.1	**画出A–C** 的结构。立体异构体应清晰可区分。	9pt

A.2	尝试采用相同的鏻盐及合适的起始原料来合成 [5] 碳螺旋烃，结果仅得到少量 [5] 碳螺旋烃，而主要生成产物 **D**，其分子量比 [5] 碳螺旋烃少 2 Da。化合物 **D** 的 ^{1}H NMR 数据如下。**画出D** 的结构。 **[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]-及更大的碳螺旋烃具有螺旋手性，在室温下这些螺旋烃对映异构体之间的相互转化十分缓慢。[n] 碳螺旋烃的手性按如下方式用（*M*）或（*P*）定义。

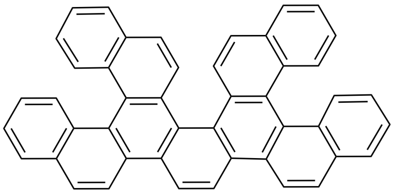


环数 n 大于 4 的 [n] 碳螺旋烃的对映异构体可通过手性柱色谱分离，Yoshio Okamoto 教授发展了这一方法。

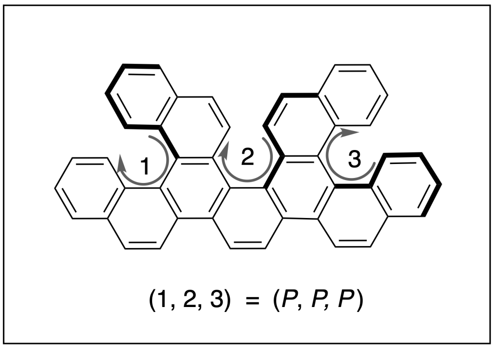


图片来源于日本奖励基金会

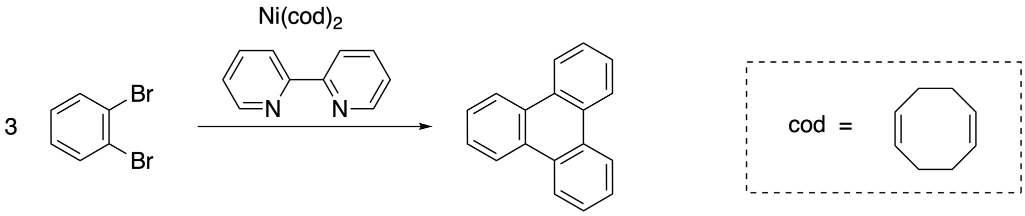
多重螺旋烃是指分子中含有 2 个或 2 个以上螺旋结构的分子。如果考虑其螺旋手性，多重螺旋烃存在多个立体异构体。例如，一分子化合物 **E** 含有 3 个类似 [5] 碳螺旋烃结构单元。如下图所示，其中一个立体异构体可描述为 (*P, P, P*) 异构体。

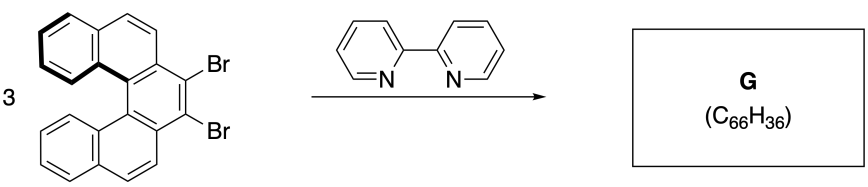


E



A.3 镍催化 1,2-二溴苯的三聚反应生成苯并菲。将螺旋烃 **F** 的对映异构体 (*P*)-**F** 在相同条件下进行反应，得到多重螺旋烃 **G** ($C_{66}H_{36}$)。已知在此反应过程中立体异构体之间不会发生相互转化，**确定** 此反应过程中可能生成的**全部** 产物 **G** 的立体异构体，不要重复给出同一个立体异构体。作为参照物，一个异构体应该按照上面示例的方式给出其包括手性和数字标识的完整结构；其他异构体应该根据相同的编号方法，采用位置编号及 *M* 和 *P* 标注的方式列出。例如，化合物 **E** 的其他立体异构体应如此列出：(1, 2, 3) = (*P, M, P*), (*P, M, M*), (*P, P, M*), (*M, M, M*), (*M, M, P*), (*M, P, P*), 和 (*M, P, M*)。 7pt



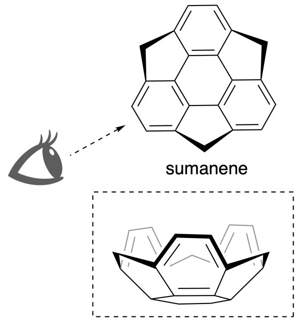


(*P*)-**F**

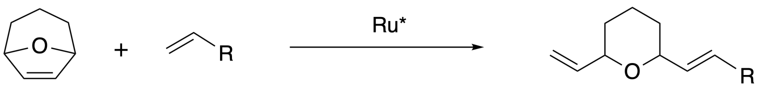
B 部分

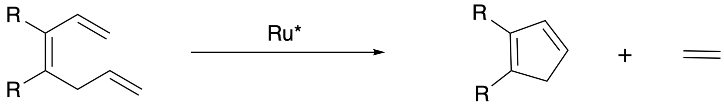
太阳花烃（Sumanene）是一种碗状烃，最先于 2003 年在日本报道。其名称由印度梵文“suman”衍生而来，意思为太阳花。

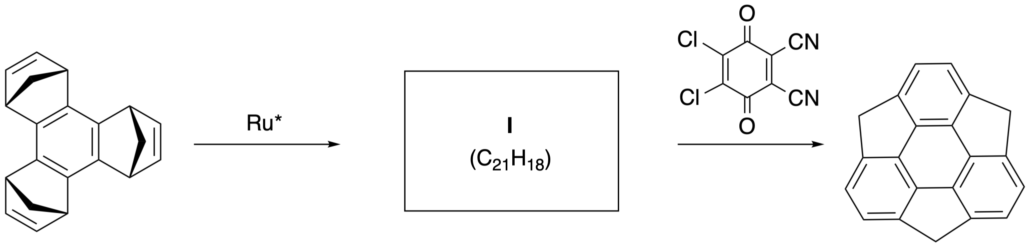
太阳花烃的合成可通过开环和关环烯烃复分解反应步骤实现。



代表性的钌催化烯烃复分解反应列举如下。

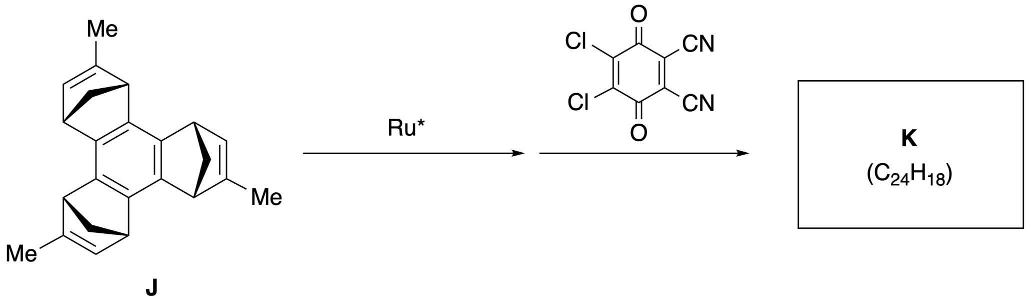






H

B.1 **画出** 中间体 **I** 的结构 (对其立体化学不作要求)。 3pt



B.2 从光学活性的前体化合物 **J** 出发, 经过相同的反应步骤，制得具有光学活性的太阳花烃衍生物 **K**。在烯烃复分解反应过程中，前体化合物 **J** 所包含的手性中心未发生构型翻转。**画出** 化合物 **K** 的结构，包括其正确的立体化学。 4pt

动态有机分子及其手性

A 部分

A.1 (9 pt)

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

A.2 (3 pt)

A.3 (7 pt)

B 部分

B.1 (3 pt)

B.2 (4 pt)

IChO
Problem 9
Cover sheet

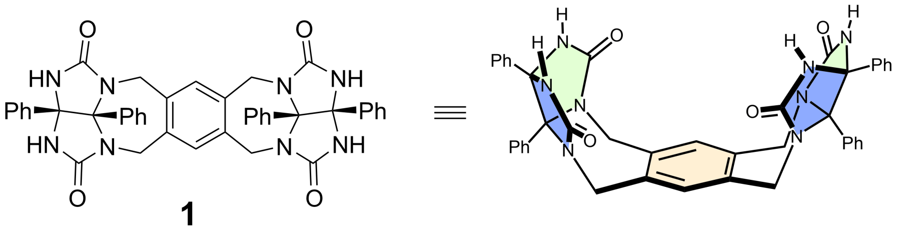
Please return this cover sheet together with all the related question sheets.

Likes and Dislikes of Capsule

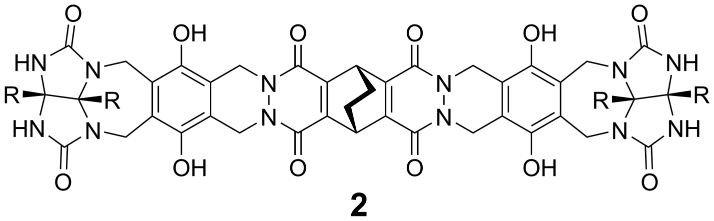
10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	**Total**
Points	13	2	2	3	3	**23**
Score						

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

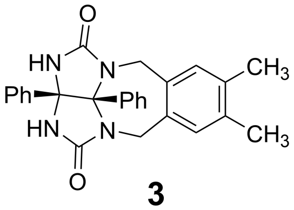
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

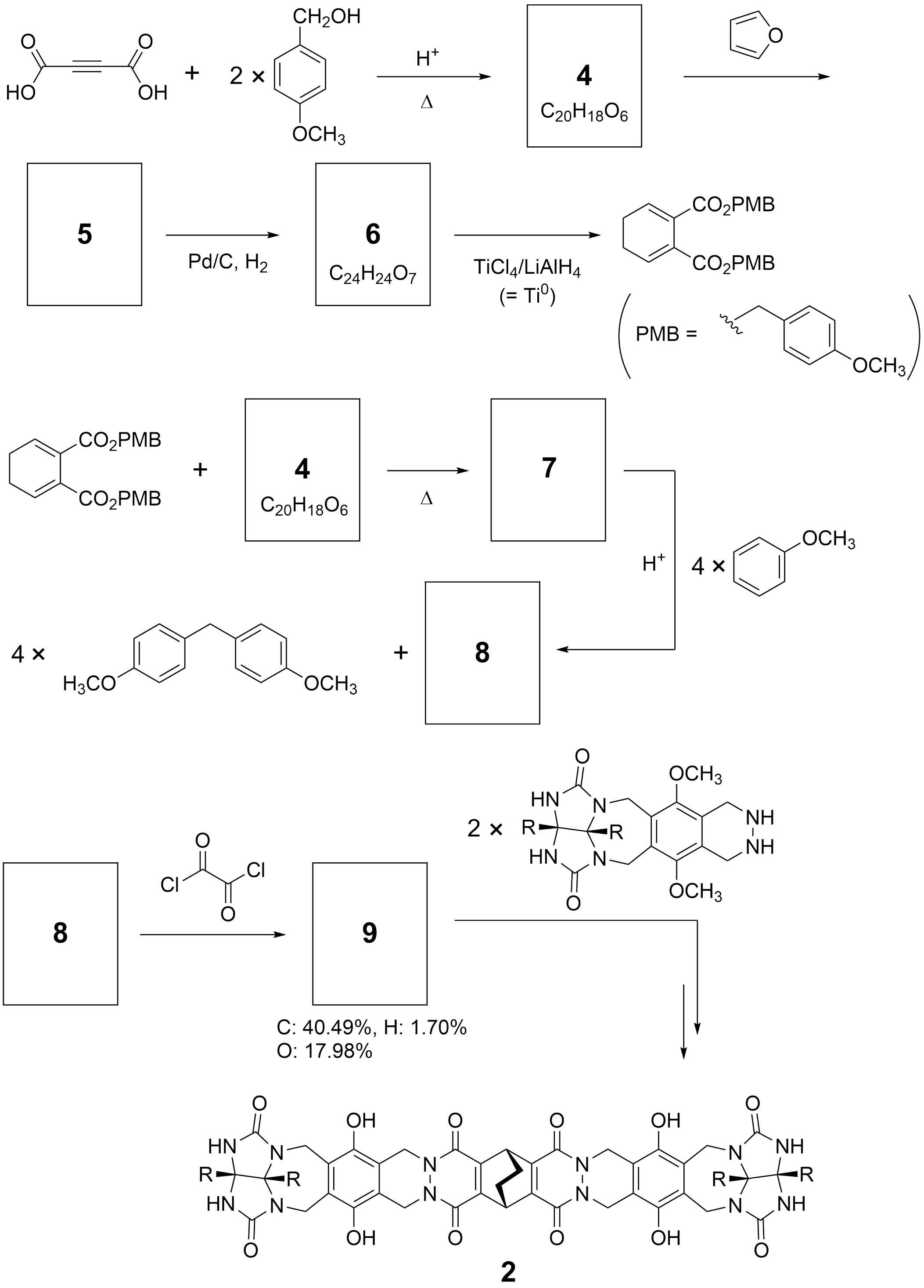


2



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:

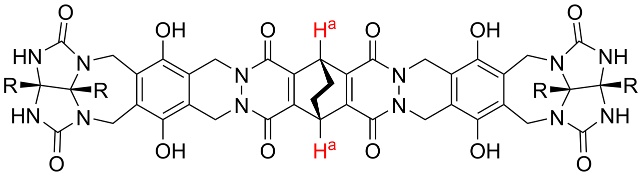
$$\text{Z} + \mathbf{1}_2 \rightarrow \text{Z@}\mathbf{1}_2 \tag{1}$$

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

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

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

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



2

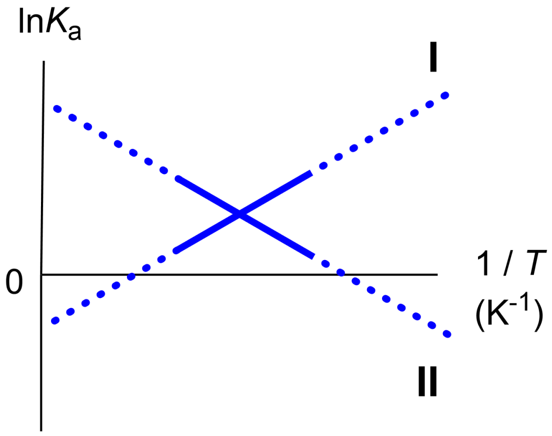
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

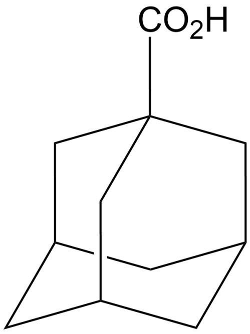
A.4 <u>**Determine**</u> the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2}_2$ giving each H^a signal. 3pt

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

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

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

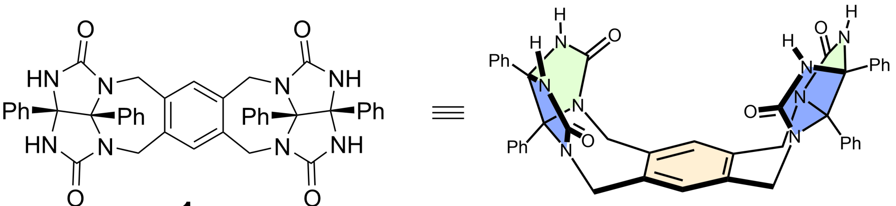
胶囊的好与恶

占总分 10 %						
题目	A.1	A.2	A.3	A.4	A.5	**小计**
分值	13	2	2	3	3	**23**
得分						

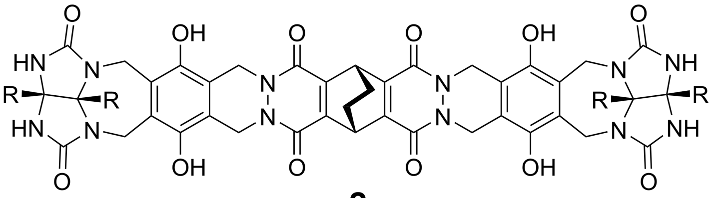
部分

如果你将网球剪开，可以将其分解成两个 U 形块。但乖孩子不会如此行事。

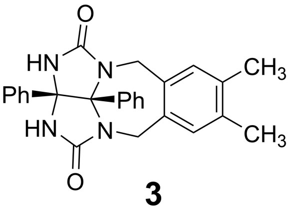
基于此想法，科学家合成了不同尺寸大小的 U 形化合物 **1** 和 **2**，同时制备了化合物 **3** 作为 **1** 的对比，并研究了这些化合物的包封行为。



1

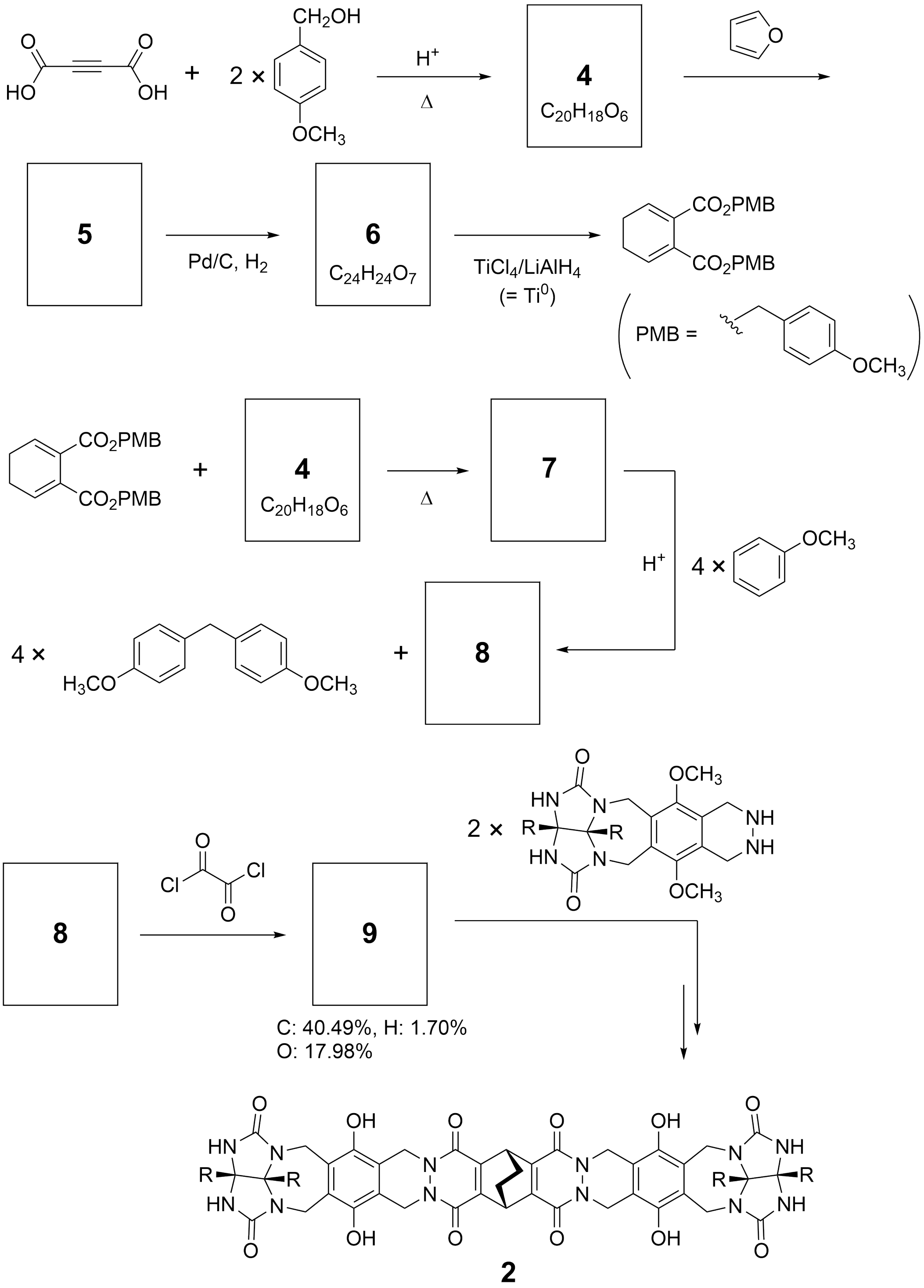


2



3

化合物 **2** 的合成路线如下图所示。化合物 **9** 中各元素的质量百分数为: C，40.49%；H，1.70%，和 O，17.98%。



A.1	**画出4–9** 的结构；可以忽略立体化学。使用“PMB”作为取代基代替上述路线图中的对-甲氧基苄基基团的整体结构。	13pt

在化合物 **1** 的质谱中，清楚地观察到与其二聚体（$\mathbf{1}_2$）对应的离子峰，而在 **3** 的质谱中没有观察到 $\mathbf{3}_2$ 的离子峰。在 $\mathbf{1}_2$ 溶液的 ^{1}H NMR 中，观察到源自 **1** 的所有 NH 质子是化学等价的，并且它们的化学位移与 **3** 中 NH 质子的化学位移存在显著差异。这些数据表明，**1** 的 NH 部分与另一个分子 **1** 中 **X** 原子之间形成了氢键，从而形成二聚体胶囊。

A.2	**圈出** 化合物 **1** 中所有合适的 **X** 原子。	2pt

A.3	**给出** 二聚体胶囊 ($\mathbf{1}_2$) 中氢键的数目。	2pt

1 的二聚体胶囊 $\mathbf{1}_2$ 具有内部空腔，可以包封合适的小分子 Z。这种现象可以用以下方程式表示：

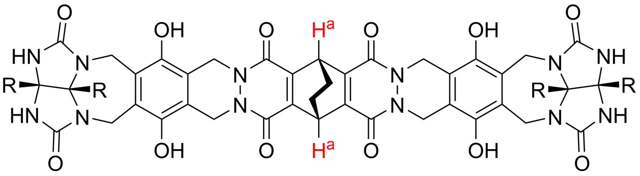
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z@}\mathbf{1}_2 \tag{1}$$

Z 包封入 $\mathbf{1}_2$ 的平衡常数如下：

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

分子包封入胶囊的过程可以通过 NMR 监测。例如，在加入 CH_4 之前和之后，$\mathbf{1}_2$ 在 C_6D_6 中的 ^{1}H NMR 具有不同的信号。

化合物 **2** 还可以形成刚性且尺寸更大的二聚体胶囊 ($\mathbf{2}_2$)。在所有其他条件保持不变的情况下，分别在 C_6D_6、C_6D_5F 和混合溶剂 C_6D_6/C_6D_5F 中测量 $\mathbf{2}_2$ 的 ^{1}H NMR。在上述溶剂中，**2** 中 H^a 质子的化学位移总结在下表中，除了所列出的之外，没有观察到来自 **2** 中 H^a 的其他信号。假设胶囊内部空间总是充满尽可能多的溶剂分子，并且每一个信号对应于已填充的胶囊的一个物种。



2

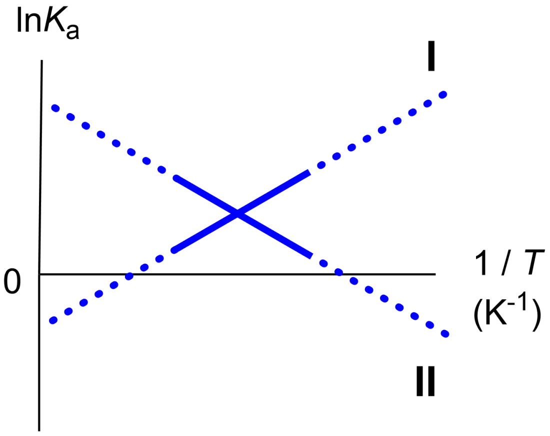
溶剂	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

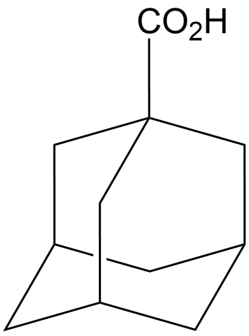
A.4	根据给出的 H^a 信号，**确定** 包封在 $\mathbf{2}_2$ 中的 C_6D_6 和 C_6D_5F 分子的数目。	3pt

C_6D_6 中的 ^{1}H NMR 测量表明，$\mathbf{2}_2$ 可以包封一分子的 1-金刚烷甲酸 (AdA)，并且在不同温度下确定了如下所示的缔合常数 (K_a)。[solvent@$\mathbf{2}_2$] 表示包含一个或多个溶剂分子的物质。

$$K_\mathrm{a} = \frac{[\mathrm{Z@}\mathbf{2}_2]}{[\mathrm{Z}][\mathrm{solvent@}\mathbf{2}_2]} \tag{3}$$

类似地，在不同温度下，在 C_6D_6 中，方程式（2）得出的 CH_4 和 $\mathbf{1}_2$ 的 K_a 值可以用 ^{1}H NMR 进行测定。两个缔合常数的图（ln K_a 与 1/T ）如下所示。





AdA

没有 C_6D_6 被包封在 $\mathbf{1}_2$ 中。在线 **II** 中，熵变 (ΔS) 为 (1)，焓变 (ΔH) 为 (2)，表明线 **II** 中包封过程的驱动力为 (3)。因此，线 **I** 对应于 (4)，线 **II** 对应于 (5)。

A.5 对应上述段落中的 (1)-(5)，从 A 和 B 中**选择** 正确选项。 3pt

	A	B
(1)	正	负
(2)	正	负
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ 和 CH_4	$\mathbf{2}_2$ 和 AdA
(5)	$\mathbf{1}_2$ 和 CH_4	$\mathbf{2}_2$ 和 AdA

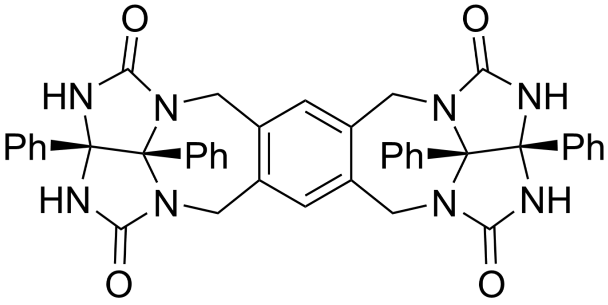
胶囊的好与恶

部分

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	C_6D_6 的数目	C_6D_5F 的数目
4.60 ppm		
4.71 ppm		
4.82 ppm		

A.5 (3 pt)

(1)：　(2)：　(3)：

(4)：　(5)：