TWN-4 C-0 C
Bo-An Chen

IChO
General instructions
Cover sheet

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

G0-1

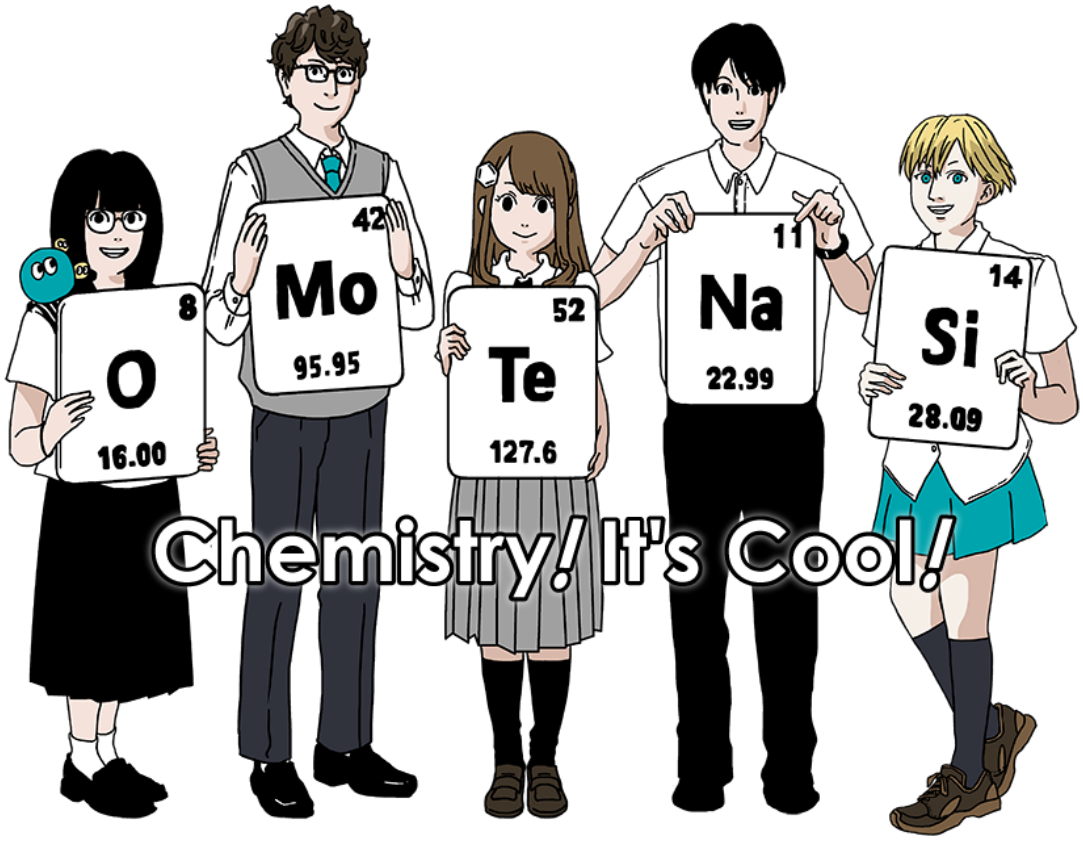
English (Official)

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

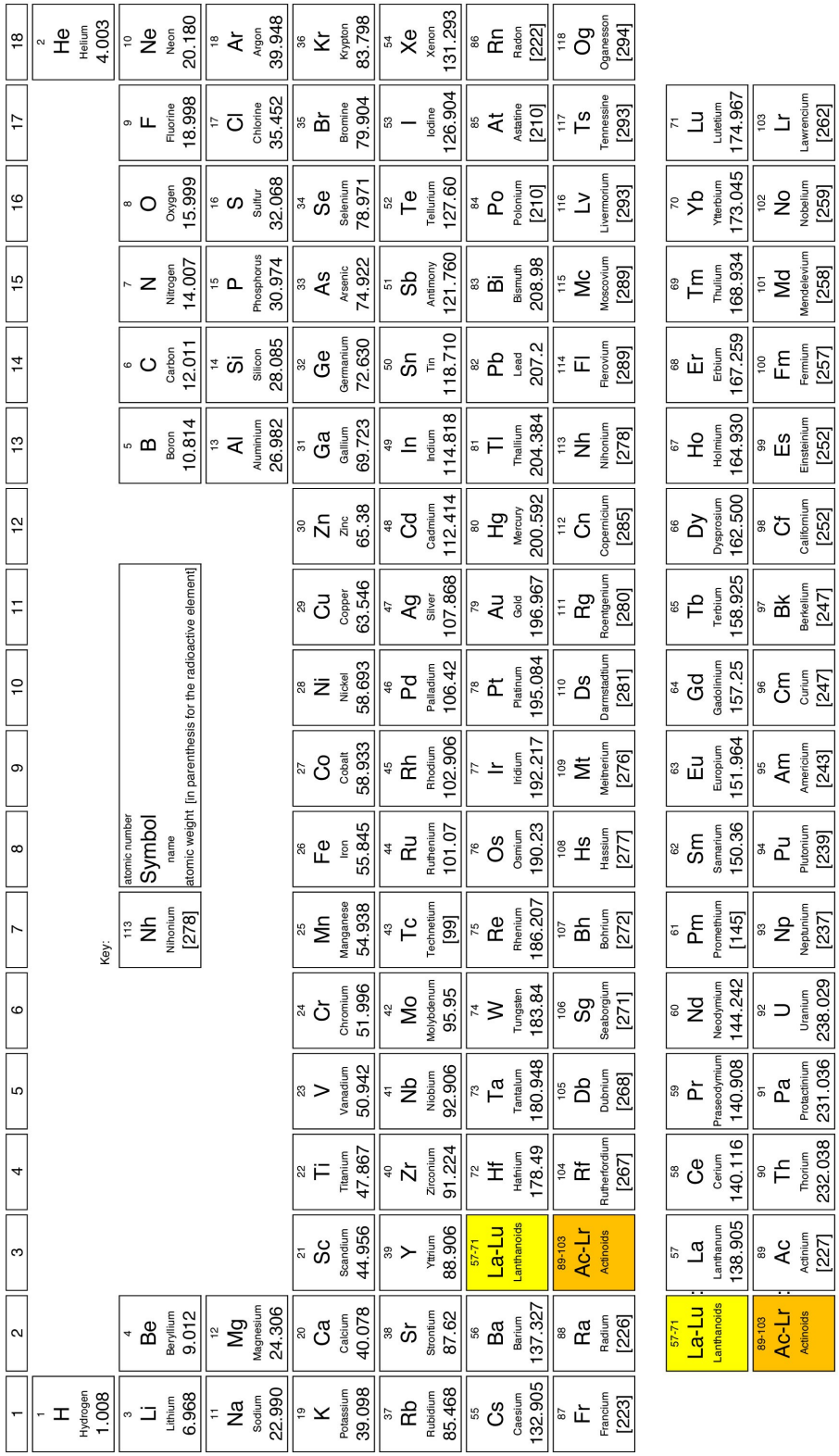
Speed of light in vacuum	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Planck constant	$h = 6.62607015 \times 10^{-34}\ \mathrm{J\ s}$
Elementary charge	$e = 1.602176634 \times 10^{-19}\ \mathrm{C}$
Electron mass	$m_{\mathrm{e}} = 9.10938370 \times 10^{-31}\ \mathrm{kg}$
Electric constant (permittivity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

Equations

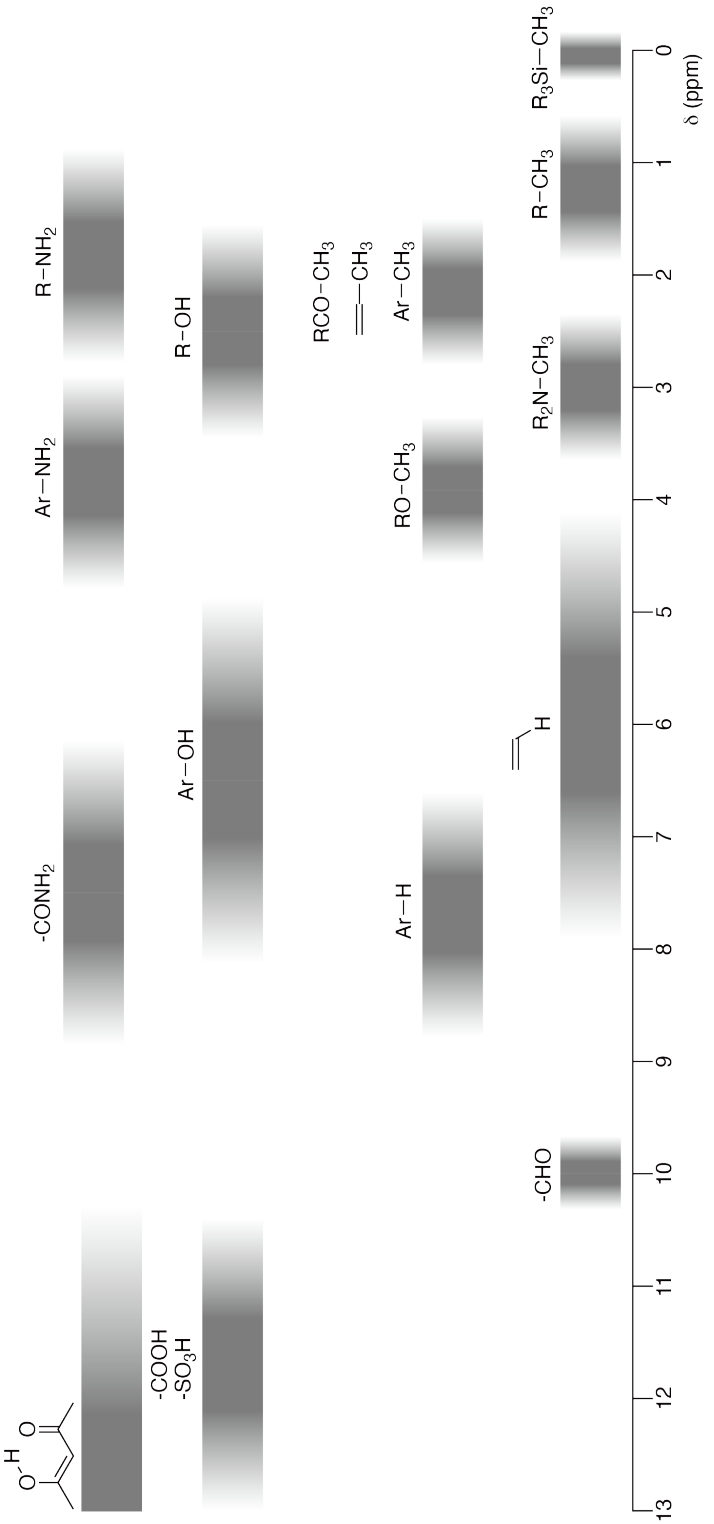
The ideal gas law	$PV = nRT$, where P is the pressure, V is the volume, n is the amount of substance, T is the absolute temperature of ideal gas.
Coulomb's law	$F = k_{\mathrm{e}} \frac{q_1 q_2}{r^2}$, where F is the electrostatic force, $k_{\mathrm{e}} (\simeq 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}})$ 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}H NMR Chemical Shifts

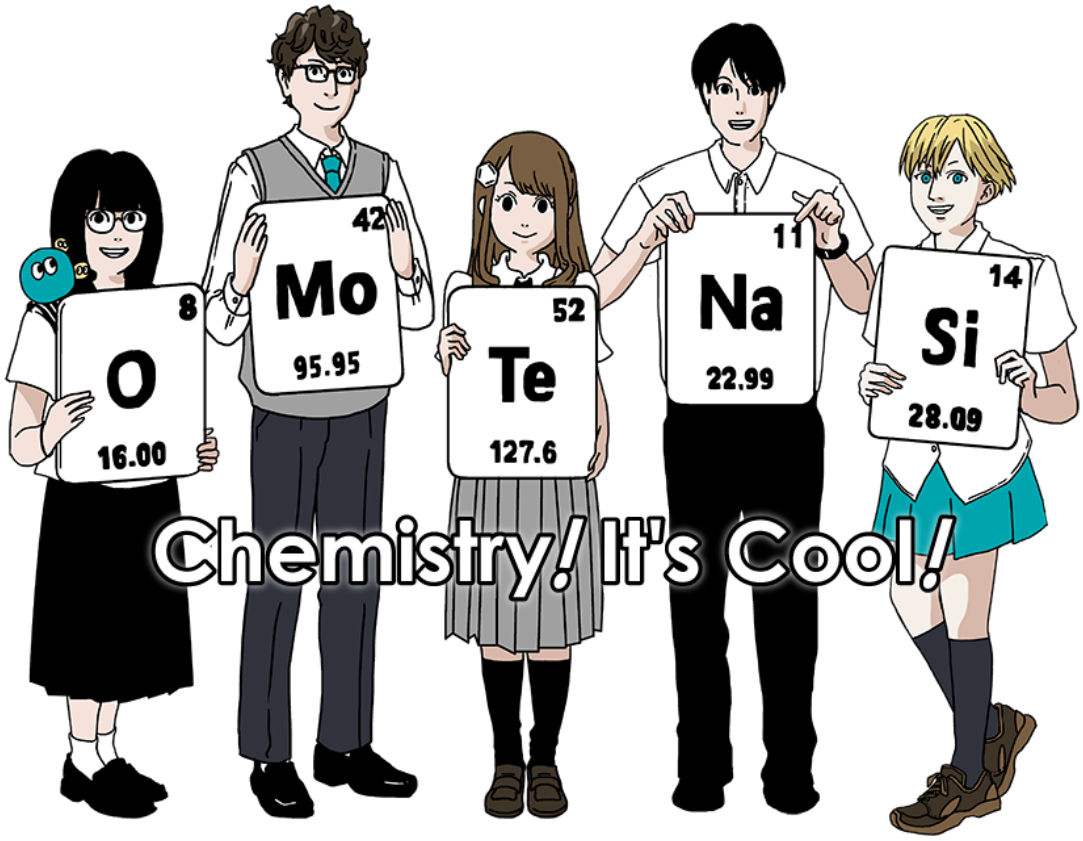


$\Delta\delta$ for one alkyl group-substitution: *ca.* +0.4 ppm

G0-1

Chinese Taipei (Chinese Taipei)

國際化學奧林匹亞 2021 日本



G0-2

Chinese Taipei (Chinese Taipei)

一般說明

- 你只能使用筆 (非鉛筆) 來寫答案。
- 你的計算器必須不可編寫程式。
- 本次考試有 **9** 題。
- 你將有 **5** 個小時的時間來完成所有考試。
- 只有在發出 START 命令後才能開始工作。
- 所有結果必須用筆在答卷上寫在相應的答題框內。如果你需要計算紙，可用考試卷的背面。記住，寫在答案框之外的答案將不計分。
- 所有需要計算的答案，都要有計算過程，在適當的方框中寫下相關的計算。只有含過程的正確答案，才會得滿分。
- 監考人員會在結束前 30 分鐘提醒。
- 聽到停止後，你必須立刻停止。不停止寫答，會導致你的考試被取消。
- 本考試的官方英文版本可應要求提供，僅供說明之用。
- 未經許可，不得離開考試場所。如果你需要任何幫助（損壞的計算器、需要去洗手間等），請舉手，等待監考人員到達。

祝你好運！

題目及配分

	題目名稱	滿分	百分配分
1	金屬表面的氫	**24**	**11**
2	同位素時間膠囊	**35**	**11**
3	朗伯－比爾定律？	**22**	**8**
4	鋅的氧化還原化學	**32**	**11**
5	神秘的矽	**60**	**12**
6	過渡金屬的固態化學	**45**	**13**
7	玩轉非苯類芳香性	**36**	**13**
8	動態有機分子與其掌性	**26**	**11**
9	膠囊的喜好	**23**	**10**
		總分	**100**

物理常數與公式

常數

光速 (真空)	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$
普朗克常數	$h = 6.62607015 \times 10^{-34}\ \mathrm{J\ s}$
基本電荷	$e = 1.602176634 \times 10^{-19}\ \mathrm{C}$
電子質量	$m_{\mathrm{e}} = 9.10938370 \times 10^{-31}\ \mathrm{kg}$
電常數 (真空介電常數)	$\varepsilon_0 = 8.85418781 \times 10^{-12}\ \mathrm{F\ m^{-1}}$
亞佛加厥常數	$N_{\mathrm{A}} = 6.02214076 \times 10^{23}\ \mathrm{mol^{-1}}$
波茲曼常數	$k_{\mathrm{B}} = 1.380649 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
法拉第常數	$F = N_{\mathrm{A}} \times e = 9.64853321233100184 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
理想氣體常數	$R = N_{\mathrm{A}} \times k_{\mathrm{B}} = 8.31446261815324\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $= 8.2057366081 \times 10^{-2}\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
原子質量單位	$u = 1\ \mathrm{Da} = 1.66053907 \times 10^{-27}\ \mathrm{kg}$
標準壓力	$p = 1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$
大氣壓力	$p_{\mathrm{atm}} = 1.01325 \times 10^{5}\ \mathrm{Pa}$
攝氏零度	$0\ ^{\circ}\mathrm{C} = 273.15\ \mathrm{K}$
埃	$1\ \text{Å} = 10^{-10}\ \mathrm{m}$
皮米	$1\ \mathrm{pm} = 10^{-12}\ \mathrm{m}$
電子伏特	$1\ \mathrm{eV} = 1.602176634 \times 10^{-19}\ \mathrm{J}$
百萬分點	$1\ \mathrm{ppm} = 10^{-6}$
十億分點	$1\ \mathrm{ppb} = 10^{-9}$
兆分點	$1\ \mathrm{ppt} = 10^{-12}$
pi, π	$\pi = 3.141592653589793$
自然對數底 (Euler's number)	$e = 2.718281828459045$

公式

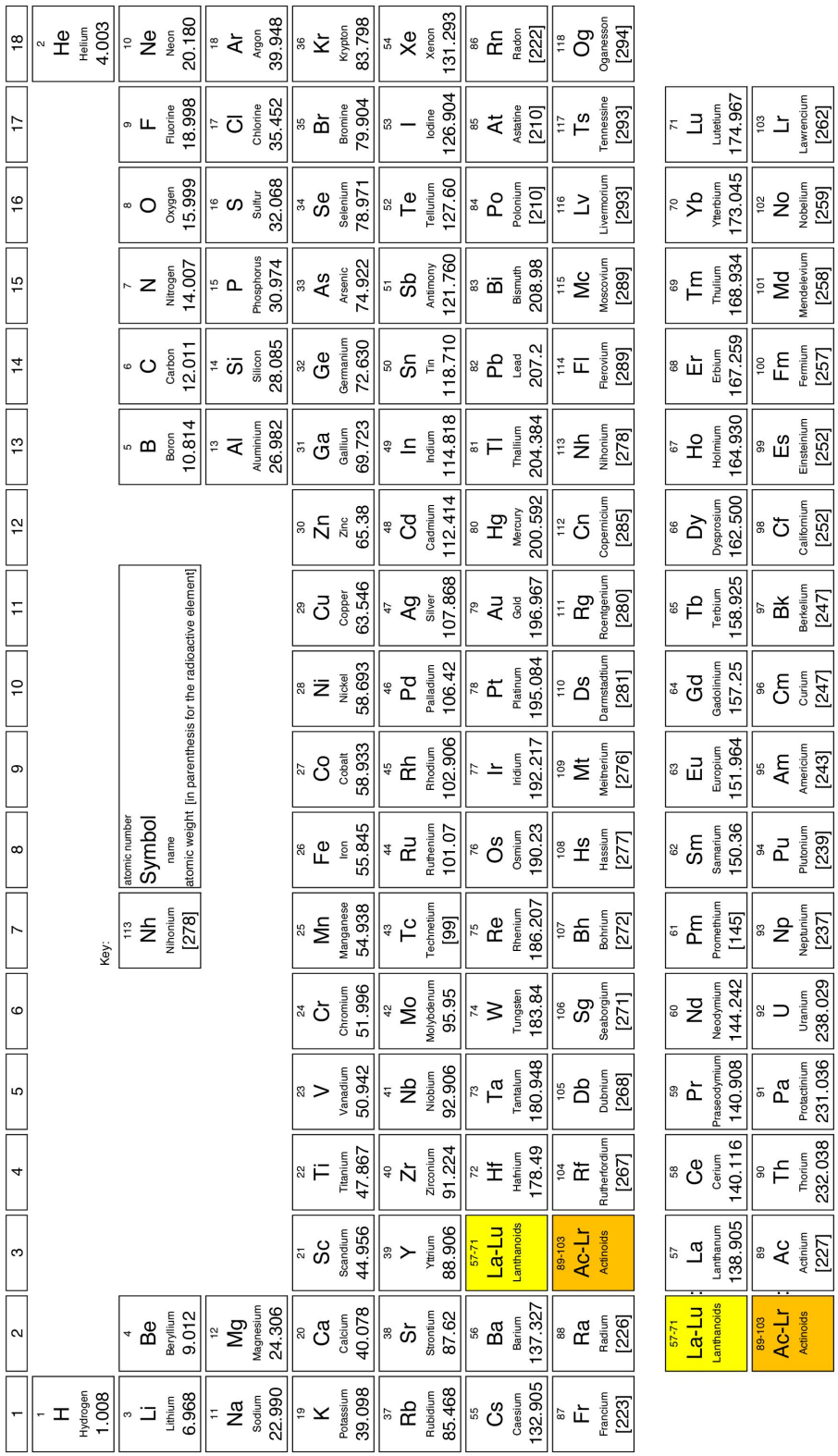
理想氣體方程式：	*PV* = *nRT* 其中 *P* 是壓力，*V* 是體積，*n* 是物質的莫耳數，*T* 是理想氣體的絕對溫度。
庫倫定律	$F = k_\mathrm{e}\frac{q_1 q_2}{r^2}$ 其中 F 是靜電力, $k_\mathrm{e}(\simeq 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}})$ 是庫倫常數, q_1 和 q_2 是電荷量的大小, 和 r 是兩電荷間的距離。
熱力學第一定律：	Δ*U* = *q* + *w* 其中 Δ*U* 是內能的變化，*q* 是提供的熱量，*w* 是所做的功。
焓 H	$H = U + PV$
熵 (波茲曼原理) *S*	$S = k_\mathrm{B}\ln W$ 其中 W 是微觀狀態的數量
熵變化 ΔS	$\Delta S = \frac{q_\mathrm{rev}}{T}$ 其中 q_rev 是可逆過程的熱量
Gibbs 自由能 G	$G = H - TS$ $\Delta_\mathrm{r}G^\circ = -RT\ln K = -zFE^\circ$ 其中 K 是平衡常數，z 是電子數，E° 是標準電位
反應商 *Q*	$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\circ + RT\ln Q$ 對一反應 $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$ $Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$ 其中 [A] 是反應物 A 的濃度

熱變化 Δq	$\Delta q = nc_{\mathrm{m}}\Delta T$ 其中 c_{m} 是莫耳熱含量 (與溫度無關)
能斯特氧化還原式：	$E = E^{\circ} + \frac{RT}{zF}\ln\frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}$, where C_{ox} 是氧化物的濃度，C_{red} 是還原物的濃度，
阿瑞尼斯公式：	$k = A\exp\left(-\frac{E_a}{RT}\right)$ 其中 k 是反應速率常數，A i 是前因子，E_a 是活化能。 $\exp(x) = e^x$
比爾定律	$A = \varepsilon lc$ 其中 A 是吸收度，ε 是莫耳吸收係數，l 是光徑長度，c 是溶液的濃度。
Henderson–Hasselbalch equation	對一平衡反應 $\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$ ，其平衡常數是 K_{a}, $\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
光子能量	$E = h\nu = h\frac{c}{\lambda}$ 其中 ν 是光的頻率，λ 是光的波長。
幾何級數之和	當 $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$
近似方程式 (可用於解問題)	當 $x \ll 1$, $\frac{1}{1-x} \simeq 1 + x$

G0-6

Chinese Taipei (Chinese Taipei)

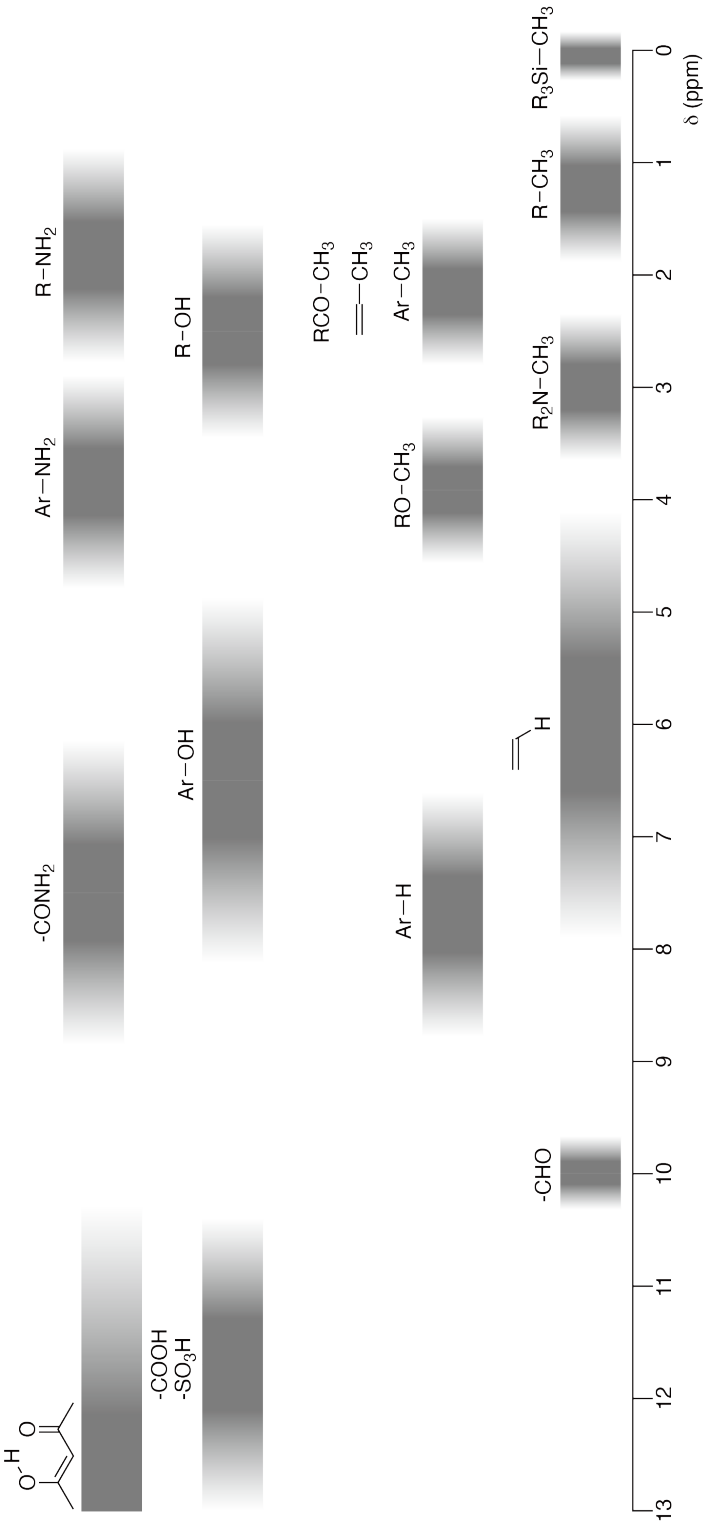
週期表



G0-7

Chinese Taipei (Chinese Taipei)

^{1}H NMR Chemical Shifts



每個 -CH3 取代基會造成位移 $\Delta\delta$ 的改變：約 +0.4 ppm

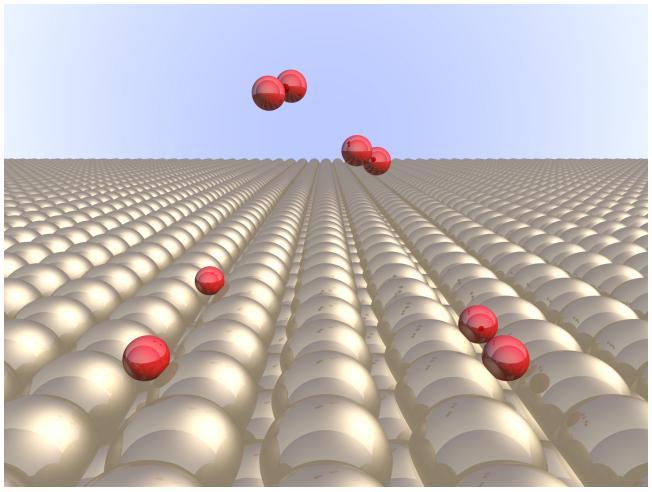
TWN-4 C-1 C
Bo-An Chen

IChO
Problem 1
Cover sheet

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

Hydrogen at a Metal Surface

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



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

Part A

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

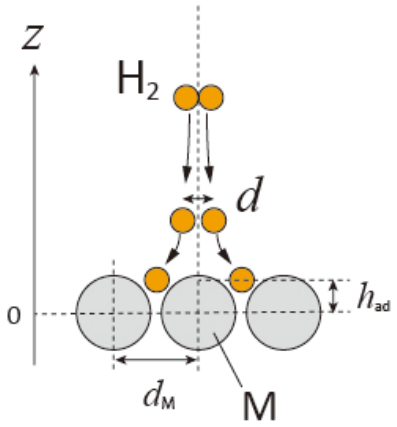


Fig.1 Definition of variables. Drawing is not in scale.

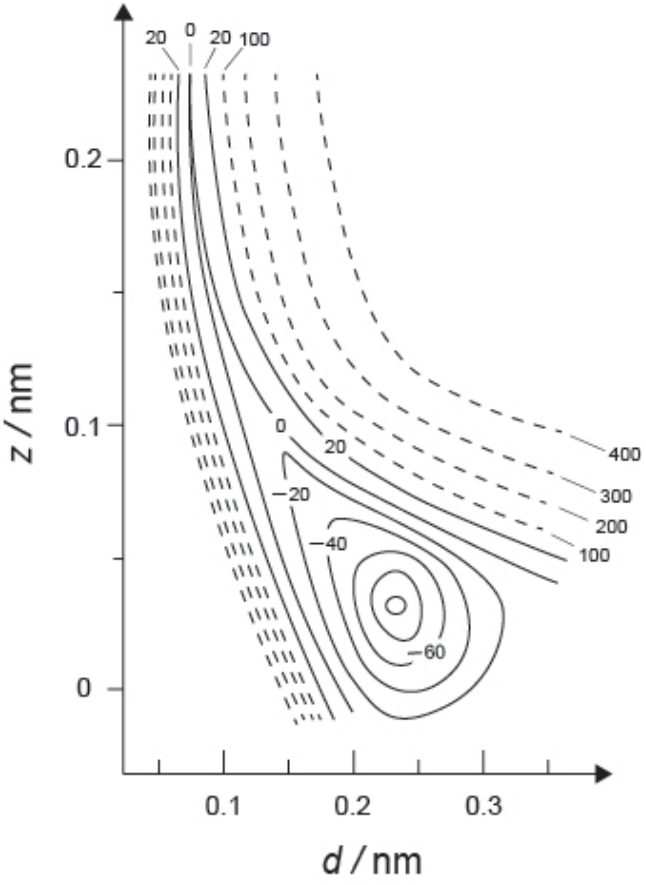


Fig.2

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

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

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

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

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

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

Part B

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

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

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

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

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

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

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

where $k_1\,[\mathrm{s^{-1}\ Pa^{-1}}], k_2\,[\mathrm{s^{-1}}]$ and $k_3\,[\mathrm{s^{-1}}]$ are the reaction rate constants and $P_{\mathrm{H_2}}$ is the pressure of $\mathrm{H_2}$. Among the sites available on the surface, θ ($0 \le \theta \le 1$) 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

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

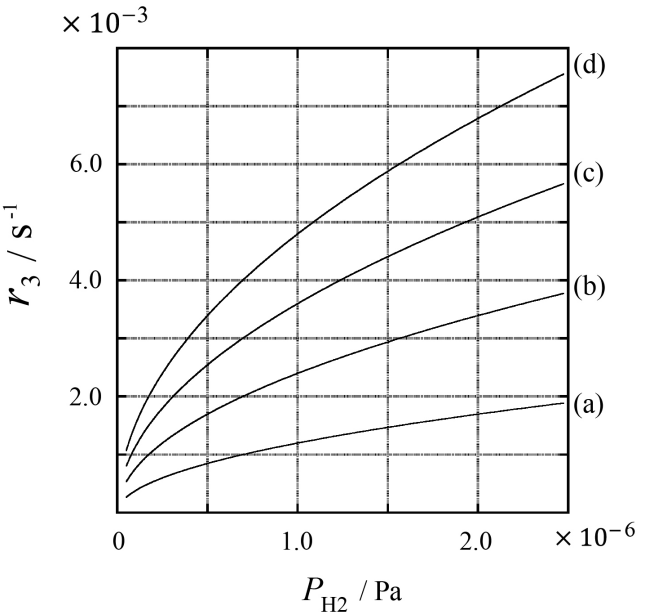
Express C using k_1 and k_2.

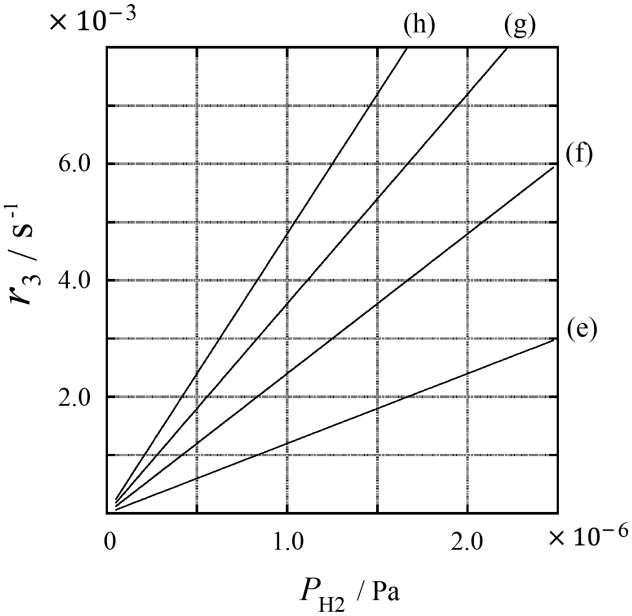
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m^2 was placed in a container (1L = 1.0×10^{-3} m^3) with H_2 ($P_{H_2} = 1.0 \times 10^2$ Pa). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m^{-2}. The surface temperature was kept at $T = 400$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

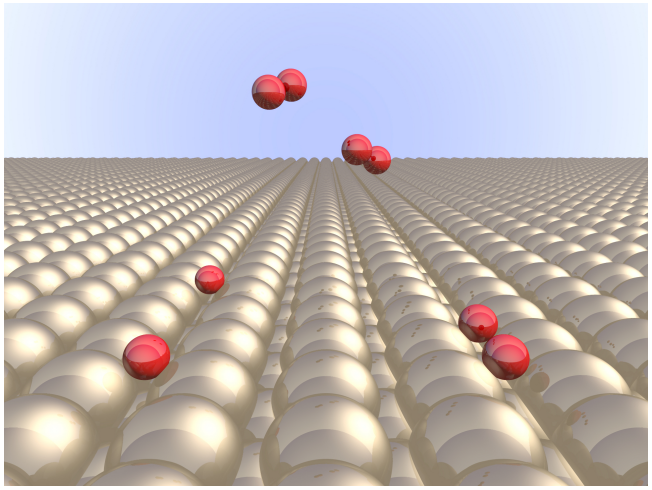
B.4 At a different T, $C = 2.5 \times 10^3$ Pa^{-1} and $k_3 = 4.8 \times 10^{-2}$ s^{-1} are given. For r_3 as a function of P_{H_2} at this temperature, **select** the correct plot from (a)–(h). 3pt





金屬表面的氫

佔總分比例 11 %							
小題	A.1	A.2	B.1	B.2	B.3	B.4	**Total**
配分	6	4	5	3	3	3	**24**
得分							



氫氣是非化石燃料的未來能源。此題考慮氫氣儲存於金屬的過程，這和氫氣運輸與儲存的技術有關。

A 部分

當氫氣要通過金屬表面進入內部時，首先需考慮氫氣於金屬表面的吸附過程。氫氣分子 (H_2) 抵達金屬表面 (M) 時，會分解成氫原子，並吸附於金屬表面，反應式為 $H_2(g) \rightarrow 2H(ad)$，其中 (g) 和 (ad) 分別表示氫的氣態與吸附態。假設分解的過程中，H_2 的長軸與金屬表面保持平行，如圖 1，且氫分子的重心維持在圖 1 中垂直的虛線上。

吸附過程中，氫分子的位能曲面包含兩個變數：一個是 H_2 的原子間距離 d，另一個是氫原子和表面金屬原子的距離 z，如下圖 2。圖 2 上的數字是氫分子的能量，單位是 kJ mol^{-1}。其中，實線的能量間距為 20 kJ mol^{-1}，虛線的間距是 100 kJ mol^{-1}，相鄰的實線與虛線間距是 80 kJ mol^{-1}。此處不考慮氫分子的振動零點能。

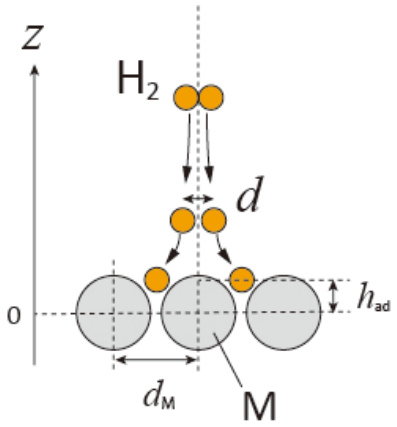


圖 1　各變數之定義圖示，注意：此圖未按比例繪製。

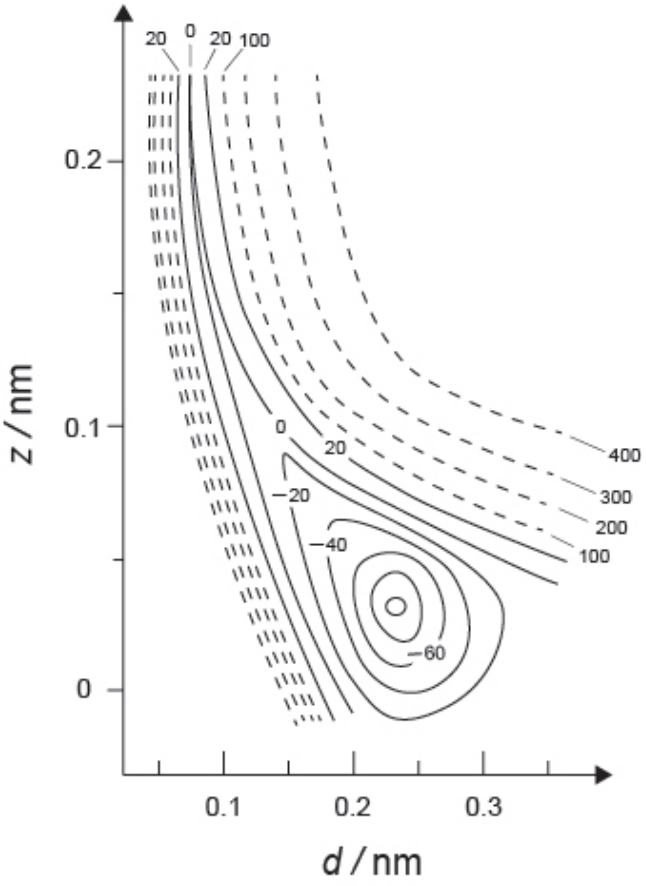


圖 2

A.1 對於 (i)-(iii) 小題，從 A-G 選項中 **選出** 最接近的答案。 6pt

(i) 氣態 H_2 分子的原子間距離

(ii) 金屬表面原子的原子間距離（即圖 1 中的 d_M）

(iii) 金屬表面原子與吸附的氫原子之間的距離（即圖 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 對於 (i)-(ii) 小題，從 A-H 選項中 **選出** 最接近的答案。 4pt

(i) 氣態 H_2 分子分解為氣態 H 原子所需的能量。[$H_2(g) \rightarrow 2H(g)$]

(ii) 氣態 H_2 分子吸附於金屬表面過程中放出的能量。[$H_2(g) \rightarrow 2H(ad)$]

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

氫氣吸附於金屬表面後，氫原子可能被金屬吸收，進入金屬內部，也可能再度從金屬表面脫附，重新結合為氣態氫分子，如反應 (1a) 及 (1b) 所示。其中，H(ab) 代表被金屬吸收進入金屬內部的氫原子。

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

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

表面上單一活性位置的吸附、脫附和吸收的反應速率分別是 $r_1[\mathrm{s}^{-1}], r_2[\mathrm{s}^{-1}]$ 和 $r_3[\mathrm{s}^{-1}]$。它們的反應速率式分別表示如下：

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

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

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

其中，$k_1\,[\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}], k_2\,[\mathrm{s}^{-1}]$ 和 $k_3\,[\mathrm{s}^{-1}]$ 是反應速率常數，$P_{\mathrm{H_2}}$ 是氫氣的壓力，θ $(0 \le \theta \le 1)$ 是表面上活性位置被氫原子所佔據的比例。假設吸附和脫附的反應速率都比吸收快很多 $(r_1, r_2 \gg r_3)$，且 θ 會維持定值。

B.1 r_3 可以表示為 5pt

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

將 C 以 k_1 和 k_2 來 **表示** 。

Q1-5

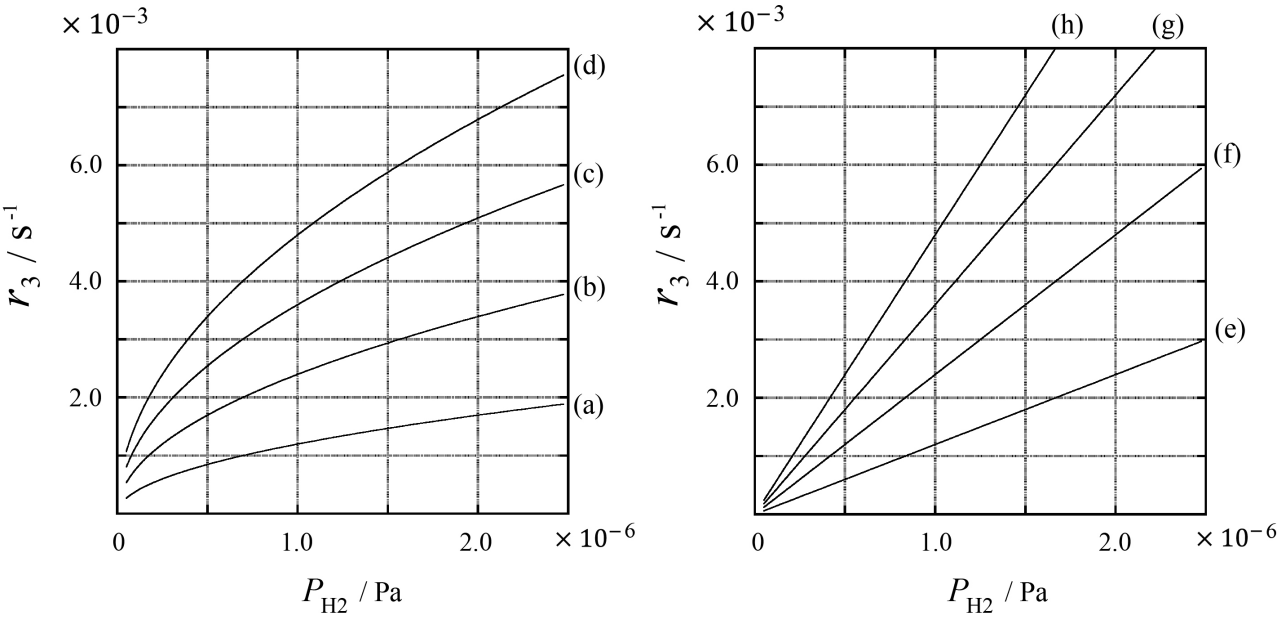
Chinese Taipei (Chinese Taipei)

在 1.0×10^{-3} m^3 的容器中裝了氫氣 ($P_{H_2} = 1.0 \times 10^2$ Pa) 和一塊金屬樣品，表面積為 $S = 1.0 \times 10^{-3}$ m^2，金屬表面可吸附氫原子的活性位置之密度為 $N = 1.3 \times 10^{18}$ m^{-2}，表面的溫度維持在 $T = 400$ K。當反應 (1) 發生時，氫氣的分壓會以等速下降，下降的速率為 $v = 4.0 \times 10^{-4}$ Pa s^{-1}。此處假設氫氣是理想氣體，且金屬體積可忽略不計。

B.2 **計算** 每單位時間內，由每單位金屬表面吸入內部的氫原子莫耳數：A [mol s^{-1} m^{-2}] 3pt

B.3 在 $T = 400$ K 時，C 值為 1.0×10^2 Pa^{-1}。**計算** 此溫度下的 k_3。(如果你沒有算出 **B.2** 小題的答案，則可使用右側數值計算：$A = 3.6 \times 10^{-7}$ mol s^{-1} m^{-2}。) 3pt

B.4 在另一個不同的溫度下，已知 $C = 2.5 \times 10^3$ Pa^{-1}，$k_3 = 4.8 \times 10^{-2}$ s^{-1}。此時 r_3 與 P_{H_2} 的關係符合下列圖片中 (a) 到 (h) 的哪一條？**選出** 正確的答案。 3pt



金屬表面的氫

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)

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

B.3 (3 pt)

$k_3 =$ _____ s^{-1}

B.4 (3 pt)

_____

TWN-4 C-2 C
Bo-An Chen

IChO
Problem 2
Cover sheet

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

Isotope Time Capsule

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



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

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

Let us consider the following equilibrium:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

同位素時間膠囊

佔總分比例 11 %					
小題	A.1	A.2	A.3	A.4	**Total**
配分	8	8	10	9	**35**
得分					



由不同的同位素組成的分子，例如 CH_4 和 CH_3D，稱為同位素體（isotopologues）。同位素體有相同的化學特性。然而，在自然界中，它們仍有細微的差異。

假設本題中的所有物質均為氣態。

考慮以下的平衡：

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

已知熵 S 會隨系統可能的微觀狀態數目 W 增加而增加：

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

$^{12}C^{16}O_2$ 和 $^{12}C^{18}O_2$ 的 $W = 1$，而 $^{12}C^{16}O^{18}O$ 中的兩個氧原子是可區別的，所以 $^{12}C^{16}O^{18}O$ 的 $W = 2$。反應式 (1) 之右側有兩個 $^{12}C^{16}O^{18}O$ 分子，因此反應式右側的 $W = 2^2 = 4$。

A.1 反應式 (3) 的焓變化 ΔH 在所有溫度下皆為正值。 8pt

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

分別 **計算** 反應式 (3) 在極低溫 ($T \to 0$) 與極高溫 ($T \to +\infty$) 的平衡常數 K。假設在這些溫度下，反應均保持不變，且 ΔH 於 $T \to +\infty$ 收斂到一常數值。

下述反應的 ΔH 可以用分子振動來解釋。

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

在 T = 0 K 時，振動頻率為 ν [s^{-1}] 的雙原子分子之振動能可以表示為：

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

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

其中 k 是力常數，μ 為約化質量。μ 與雙原子分子中兩個原子的質量 m_1 和 m_2 之關係為

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

A.2 H_2 的振動頻率 ν（以波數表示）為 4161.0 cm^{-1}。 8pt
計算 下列反應式在 T = 0 K 的 ΔH ，單位使用 J mol^{-1}。

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

假設：
- 只要考慮振動能對 ΔH 有貢獻
- H_2、HD 和 D_2 的 k 相同
- H 的原子質量為 1 Da，D 的原子質量為 2 Da。

平衡系統中的 H_2、HD 和 D_2 之莫耳比與溫度有關。這裡 Δ_{D_2} 定義為 D_2 對 H_2 之莫耳比的變化。

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

上式中的 R_{D_2} 是樣品中的 $\frac{[D_2]}{[H_2]}$ ，而 $R^*_{D_2}$ 是 $T \to +\infty$ 時的 $\frac{[D_2]}{[H_2]}$。注意：在 $T \to +\infty$ 時，分子內的同位素會變成隨機分布。

A.3 在某一溫度，同位素交換反應 (式 8) 的平衡常數 $K = 0.300$。用 D 的天然豐度 **計算** Δ_{D_2}。假設 D 和 H 的天然豐度分別為 1.5576×10^{-4} 和 $(1 - 1.5576 \times 10^{-4})$。 10pt

雙取代的同位素體包含兩個重同位素原子，它的莫耳比會隨溫度的降低而增加。考慮分子量分別為 44 和 47 的 CO_2 分子，分別寫為 $CO_2[44]$ 和 $CO_2[47]$。它們的莫耳比變化 Δ_{47} 的定義如下：

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

R_{47} 是樣品中的 $\frac{[CO_2[47]]}{[CO_2[44]]}$，$R_{47}^*$ 是在 $T \to +\infty$ 時的 $\frac{[CO_2[47]]}{[CO_2[44]]}$。碳與氧原子的天然豐度如下表所示；此處未顯示的同位素可忽略。

	^{12}C	^{13}C
天然豐度	0.988888	0.011112

	^{16}O	^{17}O	^{18}O
天然豐度	0.997621	0.0003790	0.0020000

Δ_{47} 與溫度的關係如下，其中 T 為絕對溫度（單位為 K）：

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

A.4 從南極海床獲得的浮游生物化石的 R_{47} 為 4.50865×10^{-5}。使用這個 R_{47} 值 **估算** 溫度 (T)，此溫度可視為浮游生物生存時代的氣溫。計算時，只要考慮 $CO_2[47]$ 當中最常見的同位素體。 9pt

同位素時間膠囊

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)

$\Delta_{D_2} =$ _____

A.4 (9 pt)

$T =$ _____ K

TWN-4 C-3 C
Bo-An Chen

IChO
Problem 3
Cover sheet

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

Lambert–Beer Law?

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

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

Part A

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

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

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

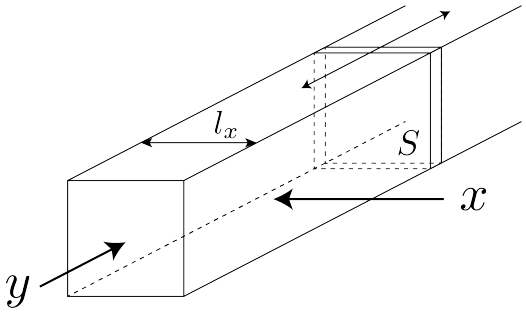
A.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. **Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-}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

Part B

Let us consider the following equilibrium in the gas phase.

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

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



Use the following definitions if necessary.

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

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

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

Q3-1

Chinese Taipei (Chinese Taipei)

朗伯-比爾定律？

佔總分比例 8%				
小題	A.1	B.1	B.2	**Total**
配分	10	6	6	**22**
得分				

在這個問題中，忽略比色槽和溶劑的吸收。所有溶液和氣體的溫度都維持在 25 °C 。

A 部分

使用 HA 和 NaA 製備水溶液 X。基於下列酸鹼平衡式，溶液 X 中的 $[A^-]$、$[HA]$ 和 $[H^+]$ 分別為 1.00×10^{-2} mol L^{-1}、1.00×10^{-3} mol L^{-1} 和 1.00×10^{-4} mol L^{-1}。

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

A 部分中比色槽的光徑長度為 l。忽略稀釋時的密度變化。假設除了反應式 (1) 以外，沒有其他任何化學反應發生。

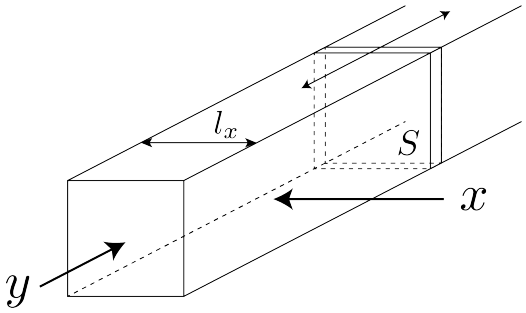
A.1 在波長 λ_1 處溶液 X 的吸收度為 A_1。然後，使用 pH = 2.500 的鹽酸將溶液 X 稀釋至初始體積的兩倍。稀釋後，吸收度在 λ_1 處仍為 A_1。**推導** $\varepsilon_{HA}/\varepsilon_{A^-}$ 的比值，其中 ε_{HA} 和 ε_{A^-} 分別表示在波長 λ_1 時，HA 和 A^- 的吸收係數。 10pt

B 部分

考慮以下氣態平衡：

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

在壓力 P 下，將純氣體 D 填充到具有橫截面為 S 的透明活動壁（見下圖）之長方體容器中，並在壓力保持 P 的恆定情況下建立平衡。氣體的吸收度為 $A = \varepsilon(n/V)l$，其中 ε、n、V 和 l 分別是吸收係數、氣體莫耳數、氣體體積和光徑長度。假設氣體混合物的所有成分都視為理想氣體。



如有必要，請使用以下定義。

	起始狀態		平衡後	
	D	M	D	M
分壓	P	0	p_D	p_M
莫耳數	n_0	0	n_D	n_M
體積	V_0		V	

B.1 在波長 λ_{B1} 處，從方向 x ($l = l_x$) 測量氣體的吸收度，初始狀態和平衡後均為 A_{B1}。 6pt
推導 在 λ_{B1} 處，$\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ 的比值。其中，ε_D 和 ε_M 分別代表 D 和 M 的吸收係數。

B.2 在波長 λ_{B2} 處，從方向 y 測量氣體的吸收度，在初始狀態 ($l = l_{y0}$) 和平衡後 ($l = l_y$)， 6pt
均為 A_{B2}。**推導** 在波長 λ_{B2} 處，$\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ 的比值。

朗伯-比爾定律？

A 部分

A.1 (10 pt)

(接續下一頁)

A.1 (cont.)

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

B 部分

B.1 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

B.2 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

TWN-4 C-4 C
Bo-An Chen

IChO
Problem 4
Cover sheet

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

The Redox Chemistry of Zinc

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



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

Part A

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

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

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

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

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

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

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

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

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

Part B

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

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

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

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

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

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

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

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



Mt. Fuji

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

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

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

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

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

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

鋅的氧化還原化學

佔總分比例 11%							
小題	A.1	A.2	B.1	B.2	B.3	B.4	**Total**
配分	6	5	4	3	5	9	**32**
得分							



長期以來，鋅一直被用作黃銅和鋼材的合金。工業廢水中所含的鋅可利用沉澱分離，使水的毒性降低，所得到的沉澱物經還原回收，可作為金屬鋅再利用。

A 部分

在 25 °C 時，$Zn(OH)_2(s)$ 的溶解平衡與相關平衡常數如反應式 (1)–(4) 所示。

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

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

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

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

鋅的溶解度 S（飽和水溶液中鋅的濃度）如反應式 (5) 所示：

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

A.1	當反應式 (1)–(4) 達成平衡，**計算** 在哪一段 pH 值的範圍中 $[\mathrm{Zn(OH)_2(aq)}]$ 是 $[\mathrm{Zn^{2+}(aq)}]$、$[\mathrm{Zn(OH)_2(aq)}]$ 與 $[\mathrm{Zn(OH)_4^{2-}(aq)}]$ 之中最大者。	6pt

A.2	配製 pH = 7.00 的 $\mathrm{Zn(OH)_2(s)}$ 飽和水溶液並過濾之。然後在該濾液中加入 NaOH 使其 pH 值提高至 12.00。當 pH 值由 7.00 上升至 12.00 時，**計算** 所沉澱的鋅之莫耳百分比，忽略體積與溫度變化。	5pt

B 部分

接著，依以下反應，將回收的氫氧化鋅加熱得到氧化鋅：

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

然後氧化鋅與氫氣反應還原為金屬鋅：

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

B.1	為了使反應式 (7) 可維持氫氣壓力在 1 bar 下進行，必須降低所產生的水蒸氣分壓。**計算** 在 300 °C 時，使反應式 (7) 仍可進行的水蒸氣分壓上限。在 300 °C 和所有氣體皆為 1 bar 時，氧化鋅和水的吉布斯生成能分別是 $\Delta G_{\mathrm{ZnO}}(300^\circ\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ 與 $\Delta G_{\mathrm{H_2O}}(300^\circ\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\,mol^{-1}}$。	4pt

金屬鋅被當作金屬-空氣電池的負極 (陽極) 材料。電極包括鋅與氧化鋅，利用以下氧化還原反應發電，在 25 °C 與 1 bar 下，其電動勢 E° 如下：

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

B.2	鋅-空氣電池以 20 mA 放電 24 小時後，**計算** 電池負極 (陽極) 的質量變化。	3pt



富士山

B.3 考慮鋅-空氣電池的電動勢會因所在環境而改變。**計算** 在富士山頂的電動勢，其溫度和海拔分別為 $-38\,^{\circ}\mathrm{C}$（二月）和 3776 m。其大氣壓如下式： 5pt

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

在高度為 $h\,[\mathrm{m}]$ 且溫度為$T\,[^{\circ}\mathrm{C}]$，氧氣在空氣中的莫耳比為 21%。在 $-38\,^{\circ}\mathrm{C}$ 與 1 bar 時，反應式 (8) 的吉布斯能 $\Delta G_{\mathrm{ZnO}}(-38^{\circ}\mathrm{C}) = -3.26 \times 10^{2}\ \mathrm{kJ\,mol^{-1}}$

B.4 **計算** 反應式 (6) 在 $25\,^{\circ}\mathrm{C}$ 時的吉布斯能。注意：在 $25\,^{\circ}\mathrm{C}$ 和 1 bar 下，標準還原電位 $E^{\circ}(\mathrm{Zn^{2+}/Zn})$ 和 $E^{\circ}(\mathrm{O_2/H_2O})$ 如反應式 (10) 和 (11) 所示。 9pt

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

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

鋅的氧化還原化學

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)

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

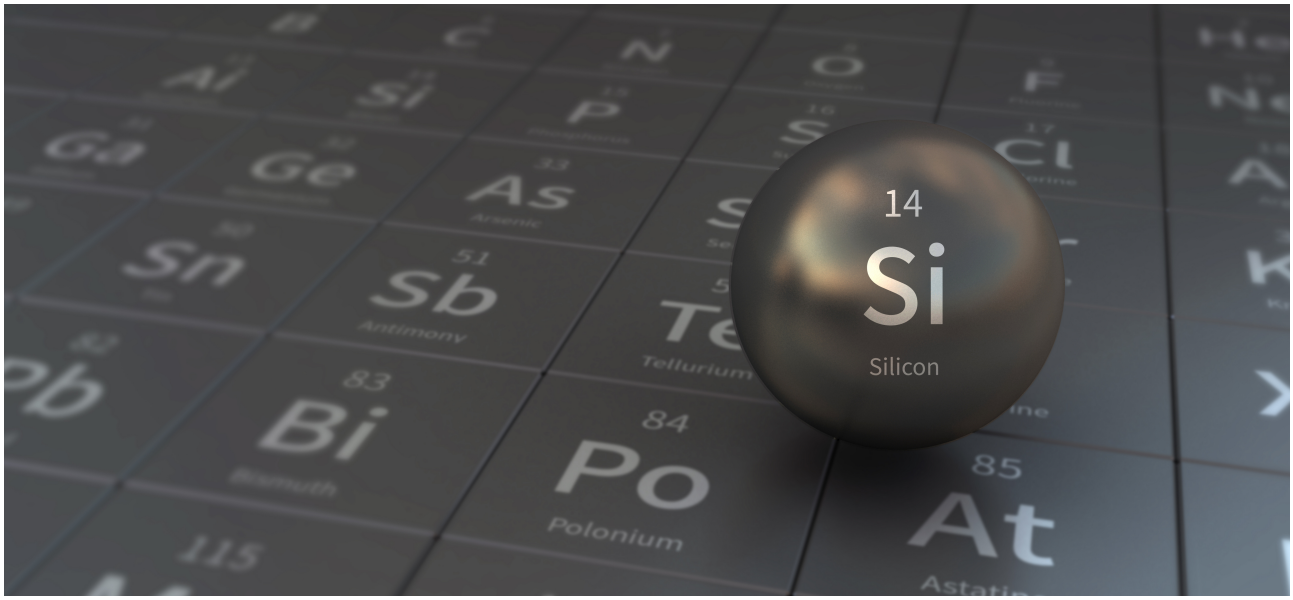
TWN-4 C-5 C
Bo-An Chen

IChO
Problem 5
Cover sheet

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

Mysterious Silicon

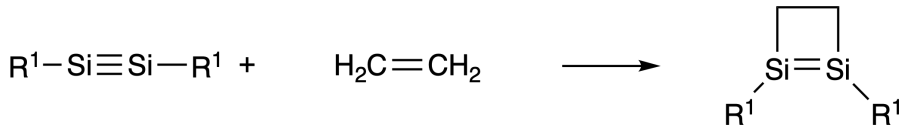
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



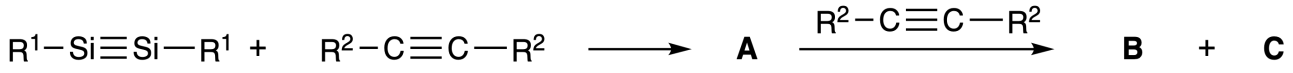
Although silicon is also a group 14 element like carbon, their properties differ significantly.

Part A

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



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



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

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

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

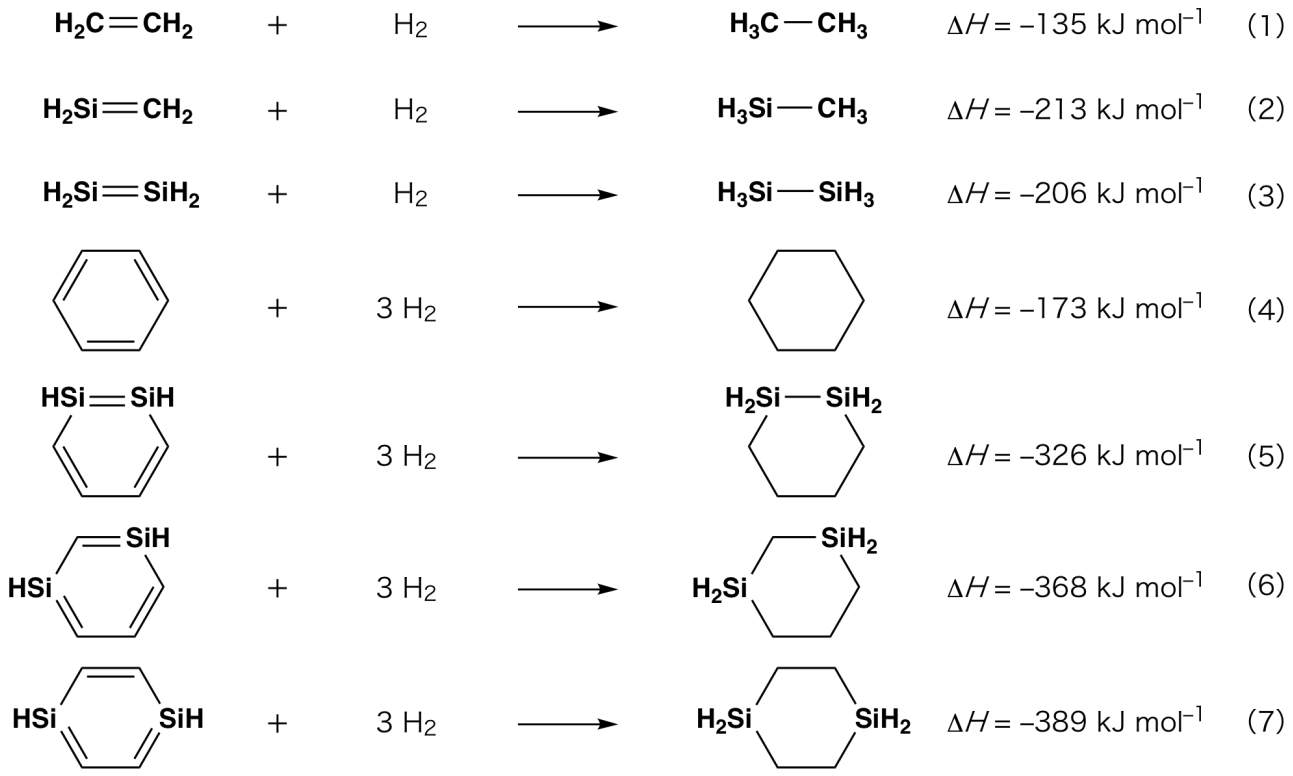


Fig. 1

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

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

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

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

Part B

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

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

- **Standardization of Na_2SiF_6 solution** :

· Preparation

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

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

· Procedure

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

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

- **Reaction of CCl_4 with Na_2SiF_6:**

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

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

Table 1

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

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

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

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

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

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

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

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

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

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

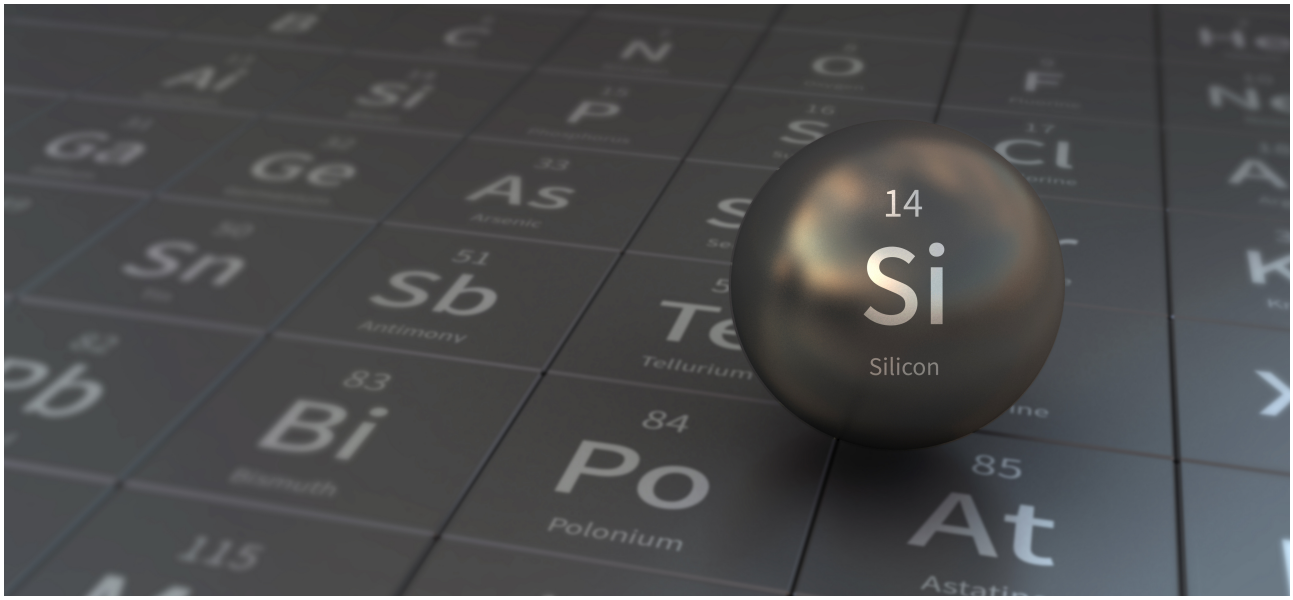
B.3	77.8% of the CCl_4 used as a starting material was unreacted. **Calculate** the mass of CF_3Cl generated.	8pt

Q5-1

Chinese Taipei (Chinese Taipei)

神秘的矽

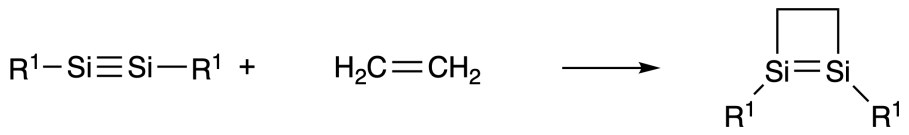
佔總分比例 12 %								
小題	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
配分	9	7	6	10	5	15	8	**60**
得分								



矽和碳都是第 14 族的元素，但是它們的性質卻大不相同。

A 部份

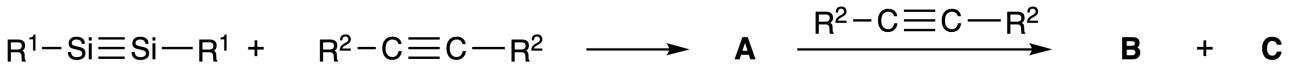
不同於碳-碳三鍵，化合物中的矽-矽三鍵（分子式可寫為 $R^1–Si \equiv Si–R^1$，R 為有機取代基）具有極強的反應活性。例如：它與乙烯反應可生成含有四員環的環狀產物。



Q5-2

Chinese Taipei (Chinese Taipei)

將 $R^1–Si\equiv Si–R^1$ 和炔類 $R^2–C\equiv C–R^2$ 反應，會形成四員環化合物 **A** 的初始中間體。若再有另一個 $R^2–C\equiv C–R^2$ 分子與 **A** 進一步反應可得到異構物 **B** 和 **C**，它們都具有類似苯的六員環狀共軛結構，即所謂的「二矽苯」，分子式可寫為 $(R^1–Si)_2(R^2–C)_4$。



六員環產物 Si_2C_4 的 ^{13}C NMR 光譜顯示，**B** 有兩個訊號峰，而 **C** 僅有一個訊號峰。

A.1	使用 R^1、R^2、Si 和 C **畫出** **A**、**B** 和 **C** 的結構（若有共振結構，畫出其中一種）。	9pt

A.2	使用下列之不飽和系統氫化反應的反應焓（圖 1），分別 **計算** 苯和產物 **C** 的芳香性穩定能（aromatic stabilization energy，在 $R^1 = R^2 = H$ 的情況下），以正值表示。	7pt

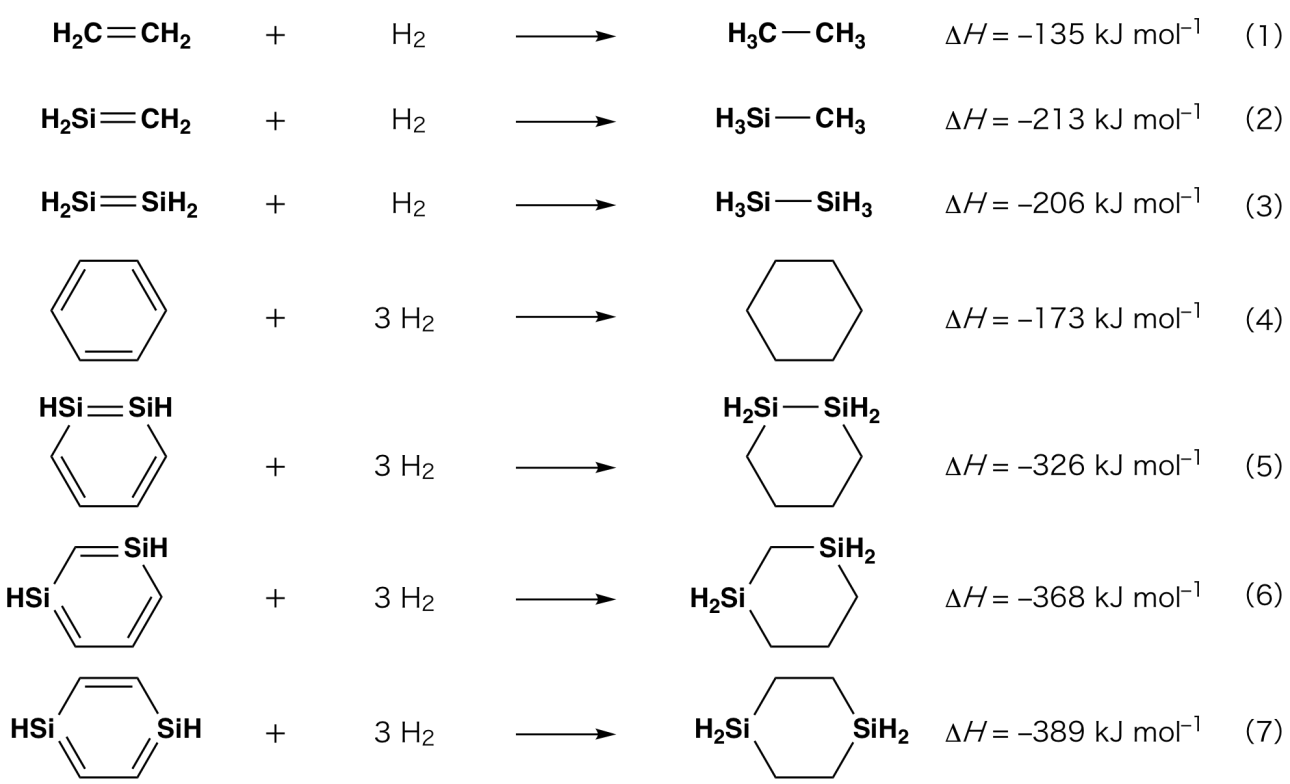


圖 1

將溶於二甲苯的 **C** 加熱，會發生異構化，可得到化合物 **D** 和 **E** 的平衡混合物。在 50.0 °C 下，**D** 和 **E** 的莫耳比為 1 : 40.0，在 120.0 °C 下，**D** 和 **E** 的莫耳比為 1 : 20.0。

A.3	**計算** **D** 轉化到 **E** 的 ΔH，假設 ΔH 不會隨溫度改變。	6pt

從 **C** 到 **D** 和 **E** 的異構化，是經由將 π 鍵轉換為 σ 鍵，而不破壞任何 σ 鍵來進行。^{13}C NMR 的分析顯示 **D** 的 Si_2C_4 骨架具有一個訊號峰，而 **E** 具有兩個訊號峰。**D** 的骨架不包含任何三員環，而 **E** 的骨架有兩個三員環共用一棱邊。

A.4	使用 R^1、R^2、Si 和 C **畫出** **D** 和 **E** 的結構。	10pt

B 部份

矽能夠與帶負電的元素（例如氟）形成高配位的化合物（大於四配位）。由於金屬氟化物通常用作氟化試劑，因此高配位的氟化矽也可當作氟化試劑。

使用 Na_2SiF_6 將 CCl_4 進行氟化反應的步驟如下：

Na_2SiF_6 溶液的標準化：

· 製備

水溶液 **F**：0.855 g Na_2SiF_6（188.053 $g\,mol^{-1}$）溶於水（總體積：200 mL）。

水溶液 **G**：6.86 g $Ce_2(SO_4)_3$（568.424 $g\,mol^{-1}$）溶於水（總體積：200 mL）。

· 步驟

加入指示劑二甲苯酚橙（會和 Ce^{3+} 離子配位）後，將溶液 **G** 逐滴加入溶液 **F**（50.0 mL）進行沉澱滴定。加入 18.8 mL 溶液 **G** 後，溶液的顏色由黃色變為洋紅色。生成的沉澱是含 Ce^{3+} 的二元化合物，唯一生成的矽化合物是 $Si(OH)_4$。

B.1	**寫出** Na_2SiF_6 與 $Ce_2(SO_4)_3$ 反應的平衡反應式。	5pt

CCl_4 與 Na_2SiF_6 的反應：

(在以下實驗過程中，會蒸發的物質損失可以忽略不計。)

將 Na_2SiF_6（x g）加入 CCl_4（500.0 g），並在密封的耐壓反應容器中加熱至 300 °C。過濾移除未反應的 Na_2SiF_6 和生成的 NaCl。以 CCl_4 將濾液稀釋至總體積為 1.00 L（溶液 **H**）。溶液 **H** 的 ^{29}Si 和 ^{19}F NMR 光譜顯示 SiF_4 為唯一的矽化合物。在 ^{19}F NMR 光譜中，除了 SiF_4 之外，還觀察到了對應於 $CFCl_3$、CF_2Cl_2、CF_3Cl 和 CF_4 的訊號峰（參見表 1）。^{19}F NMR 光譜中的積分比與氟的個數成正比。

表 1

^{19}F NMR 數據	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
積分比	45.0	65.0	18.0	2.0

SiF_4 可依據反應式 (8) 水解成 H_2SiF_6：

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

將溶液 **H**（10 mL）加入過量的水中，導致 SiF_4 完全水解。分離後，水溶液中水解產生的 H_2SiF_6 被中和，並完全轉化為 Na_2SiF_6（水溶液 **J**）。

將初反應中過濾移除之未反應的 Na_2SiF_6 和 NaCl 沉澱物（有底線的部分）完全溶解在水中，得到水溶液（溶液 **K**，10.0 L）。

再使用溶液 **G** 進行更多的沉澱滴定，其滴定終點之使用量如下：

- 全部的溶液 **J**：61.6 mL。
- 100 mL 的溶液 **K**：44.4 mL。

B.2	**計算** 反應中所產生 NaCl 的質量（有底線的部分），並 **計算** 一開始反應物 Na_2SiF_6 的質量（x g）。	15pt

B.3	當作起始反應物的 CCl_4 有 77.8 % 未反應。**計算** CF_3Cl 生成的質量。	8pt

神秘的矽

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)

(接續下一頁)

B.2 (cont.)

NaCl : _____ g, Na_2SiF_6 : _____ g

B.3 (8 pt)

CF_3Cl : _____ g

TWN-4 C-6 C
Bo-An Chen

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:

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

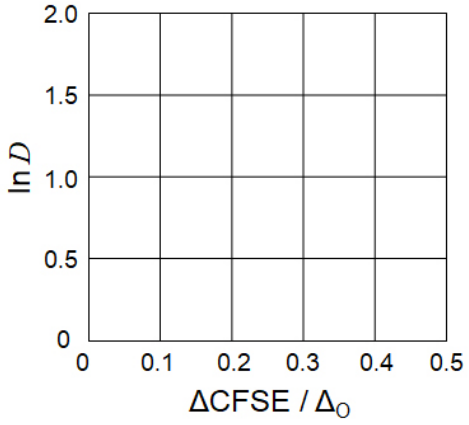
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

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

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

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

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



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

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

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

Part B

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

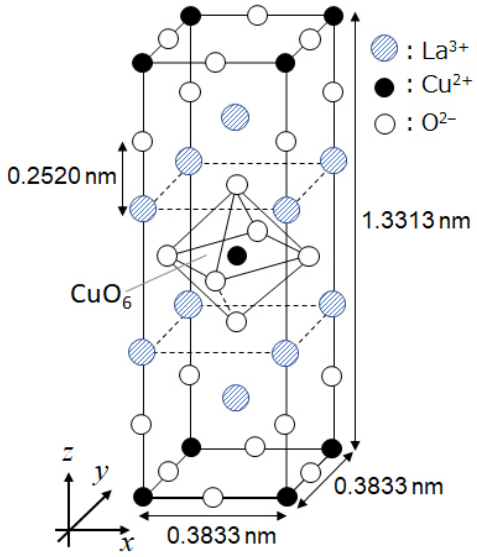


Fig. 1

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

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

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

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

Part C

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

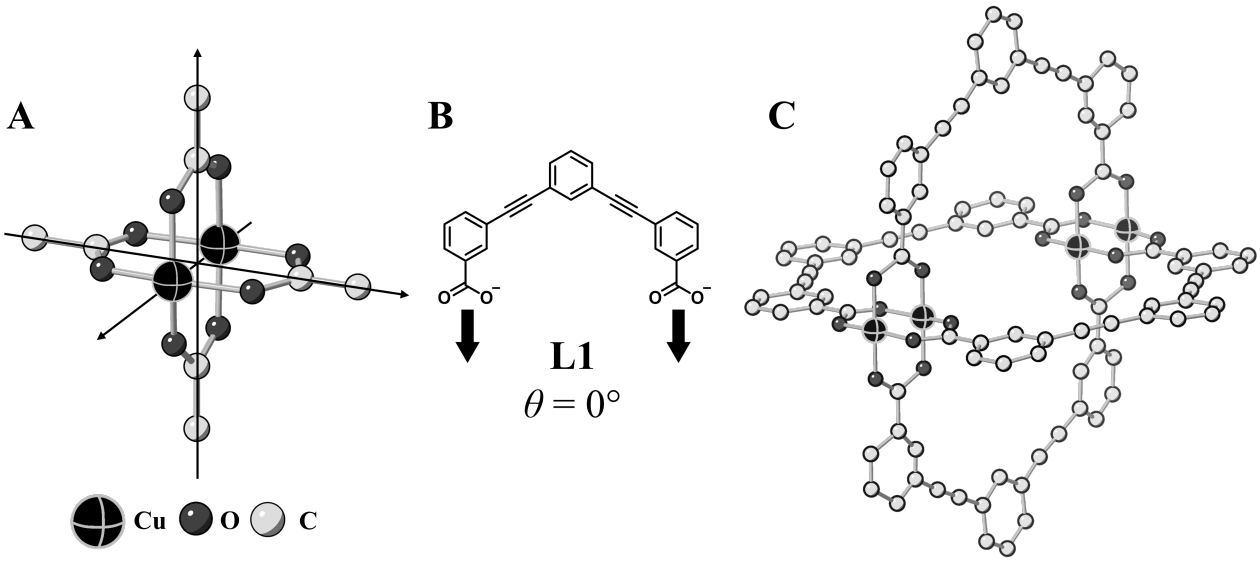
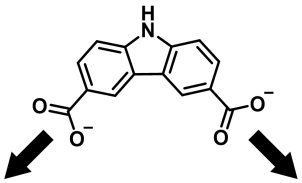


Fig. 2

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



L2

$\theta = 90°$

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

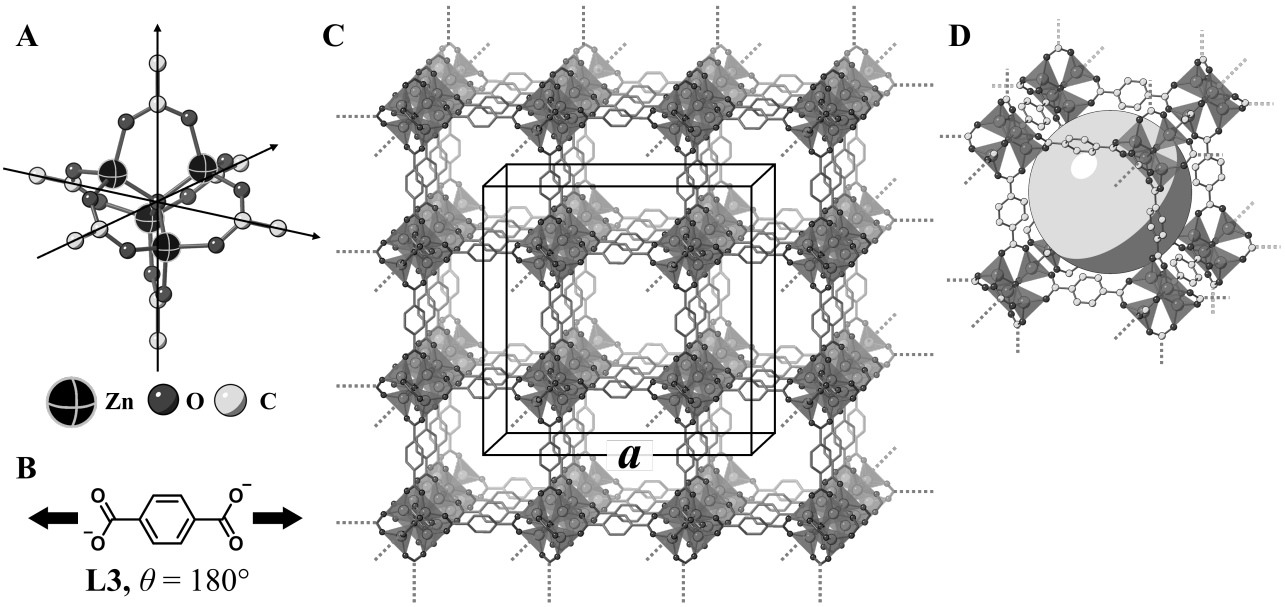


Fig. 3

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

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

Q6-1

Chinese Taipei (Chinese Taipei)

過渡金屬的固態化學

佔總分比例 13 %											
小題	A.1	A.2	A.3	B.1	B.2	B.3	B.4	C.1	C.2	C.3	**Total**
配分	6	3	3	6	4	4	4	5	5	5	**45**
得分											



櫻島火山

A 部份

日本是世界上火山數量最多的國家之一。當矽酸鹽礦物從岩漿中結晶出來時，岩漿中的一些過渡金屬離子 (M^{n+}) 會結合到矽酸鹽礦物中。本題所討論之 M^{n+} 和氧離子 (O^{2-}) 配位，在岩漿中形成四配位的四面體 (T_d) 結構，在矽酸鹽礦物中則形成六配位的八面體 (O_h) 結構，兩者都是高自旋的電子組態。M^{n+} 在矽酸鹽礦物與岩漿之間的分佈係數 D 表示如下：

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

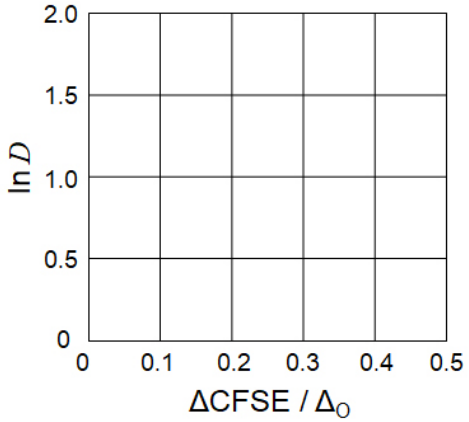
其中 $[M]_s$ 和 $[M]_l$ 分別是 M^{n+} 在矽酸鹽礦物和岩漿中的濃度。下表列出 Cr^{2+} 和 Mn^{2+} 的 D 值

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

用 Δ_O 和 $CFSE^O$ 分別代表 M^{n+} 的 d 軌域在八面體晶場（O_h）中之能量分裂和晶場穩定能，Δ_T 和 $CFSE^T$ 則分別代表在四面體晶場（T_d）中的能量分裂和晶場穩定能。

A.1 以 Δ_O 為單位，**計算** Cr^{2+}、Mn^{2+} 和 Co^{2+} 的 $|CFSE^O - CFSE^T| = \Delta CFSE$，並假設 $\Delta_T = 4/9\Delta_O$。 6pt

A.2 在下圖的直角坐標系中，以 ln$D$ 對 ΔCFSE /Δ_O 作圖，可發現二者間具有線性關係。依此 **估計** Co^{2+} 的 D 值 3pt



金屬氧化物 MO (M: Ca, Ti, V, Mn, Co) 的結晶為岩鹽結構，其中 M^{n+} 為具有高自旋電子組態的 O_h 結構。這些氧化物的晶格能主要來自離子之間的庫侖作用力 (受離子半徑和電荷影響)，以及 M^{n+} 在 O_h 中晶場穩定能的些許貢獻。

A.3 從選項 **(a)** 到 **(f)** 中 **選出** 最適合的一組晶格能 [kJ mol^{-1}] 3pt

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

Q6-3

Chinese Taipei (Chinese Taipei)

B 部份

混合氧化物 **A** 含有 La^{3+} 和 Cu^{2+}，結晶形成長方體的單位晶格如圖 1 所示。在 $[CuO_6]$ 的八面體中，*z* 軸方向 Cu-O 的距離（l_z）比在 *x* 軸方向的距離（l_x）略長，造成 $[CuO_6]$ 些微變形，不是標準正八面體，此變形造成 Cu^{2+} 的 e_g 軌域（$d_{x^2-y^2}$ 和 d_{z^2}）能量分裂，不再為簡併能階。

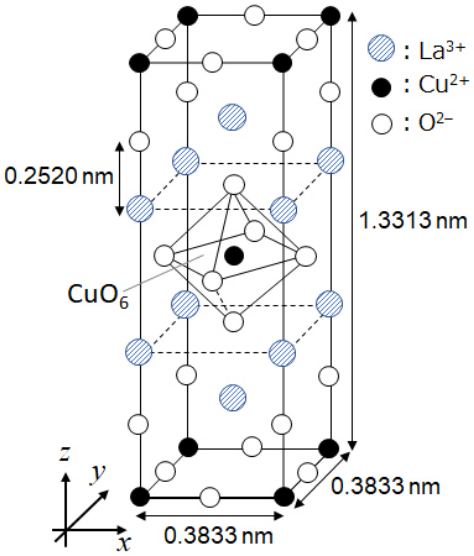


圖 1.

A 可由加熱分解錯合物 **B** 而生成。**B** 則是由金屬氯化物和含有方酸 $C_4H_2O_4$（一種二質子酸）的稀氨水溶液混合而成。**B** 在乾燥空氣中加熱分解，在 200 °C 時因失去結晶水，導致 29.1 % 的重量損失，溫度昇到 700 °C 時，則因放出 CO_2 而再次損失重量。從**B**形成 **A** 的總重量損失為 63.6 %。注意：在加熱分解反應中只釋放出水和 CO_2。

B.1	**寫出** **A** 和 **B** 的化學式	6pt
B.2	利用 圖 1 **計算** l_x 和 l_z。	4pt
B.3	考慮圖 1 的**A**中，些微變形的 $[CuO_6]$ 內之 Cu^{2+} 離子，在答案卷 (i)、(ii) 處分別 **寫出** e_g 軌域（$d_{x^2-y^2}$ 和 d_{z^2}）分裂後的相對應軌域名稱，並在虛線框內**畫出** 電子組態。	4pt

A 是絕緣體。但當一個 La^{3+} 被一個 Sr^{2+} 取代時，會在結晶格內產生一個電洞，使其可導電。摻雜 Sr^{2+} 的 **A** 在低於 38 K 時，具有超導性質。某次取代反應後，每立方公尺的 **A** 含有 2.05×10^{27} 個電洞。

B.4	根據取代反應中的莫耳比，**計算** Sr^{2+} 取代 La^{3+} 的百分比（%）。注意：組成離子的價數和取代反應不會改變晶體結構。	4pt

C 部份

$Cu_2(CH_3CO_2)_4$ 由四個 $CH_3CO_2^-$ 配位兩個 Cu^{2+} 所組成（圖 2A）。$Cu_2(CH_3CO_2)_4$ 之結構具有高度對稱性，兩個軸穿過四個 $CH_3CO_2^-$ 的碳原子，一個軸穿過兩個 Cu^{2+}，這些軸都互相垂直。當使用二羧酸根配位基取代 $CH_3CO_2^-$ 時，會形成“籠狀錯合物”。籠狀錯合物 $Cu_4(\mathbf{L1})_4$ 由平面二酸根 **L1**（圖 2B）和 Cu^{2+} 組成（圖 2C）。由圖 2B 中的箭頭表示兩個羧酸根的配位方向，其夾角 θ 決定籠狀錯合物的結構，**L1** 的 θ 為 0°。注意：圖 2 未顯示氫原子。

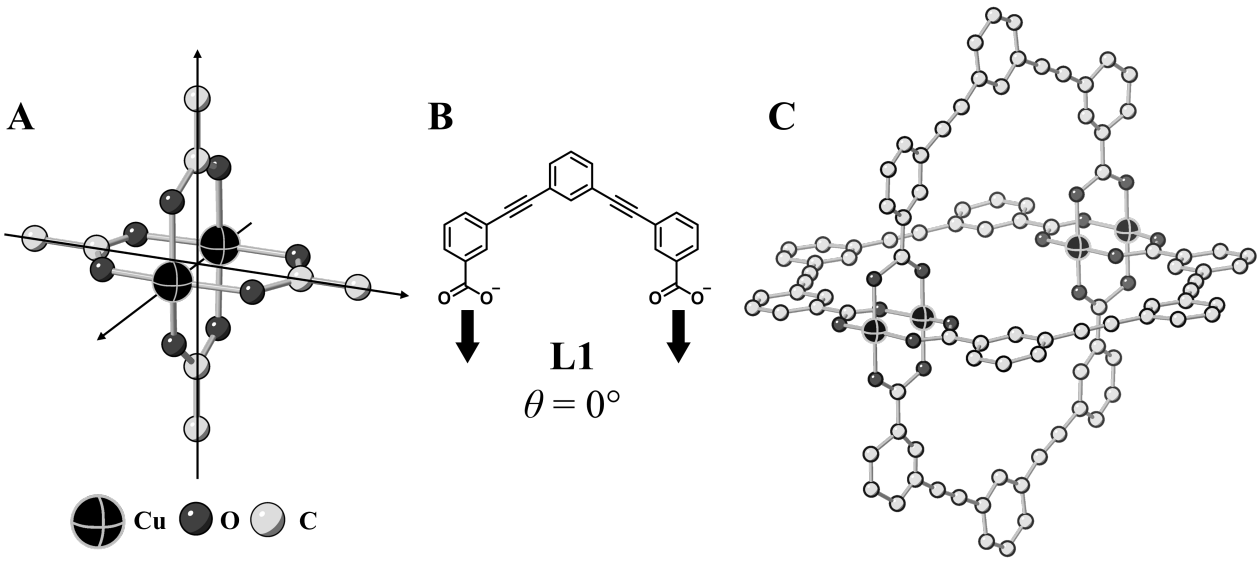
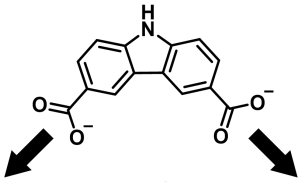


圖 2.

Q6-5

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C.1 平面二羧酸根 **L2** 的 θ 固定為 90˚。由 **L2** 和 Cu^{2+} 所形成的籠狀錯合物之組成為 $Cu_n(\mathbf{L2})_m$，**寫出** n 和 m 的最小整數組合。假設只有 **L2** 的 CO_2^- 基團與 Cu^{2+} 配位。 5pt



L2

$\theta = 90°$

Q6-6

Chinese Taipei (Chinese Taipei)

鋅錯合物 $Zn_4O(CH_3CO_2)_6$，包含四個四面體結構的 Zn^{2+} 、六個 $CH_3CO_2^-$ 和一個 O^{2-}（圖 3A）。在 $Zn_4O(CH_3CO_2)_6$ 結構中，O^{2-} 位於原點，三個軸穿過 $CH_3CO_2^-$ 的碳原子並互相垂直。當使用對苯二羧酸根（圖 3B，**L3**，$\theta = 180°$）代替 $CH_3CO_2^-$ 時，四面體 Zn^{2+} 團簇相互連接形成晶體固體（**X**），稱為“多孔配位聚合物”（圖 3C）。**X** 的組成為 $[Zn_4O(\mathbf{L3})_3]_n$，具有立方晶體結構，並有奈米級孔洞。圖 3D 顯示一個孔洞（用圓球表示），其中四面體 Zn^{2+} 團簇以深灰色顯示（圖 3C 中亦同）。注意：圖 3 中未顯示氫原子。

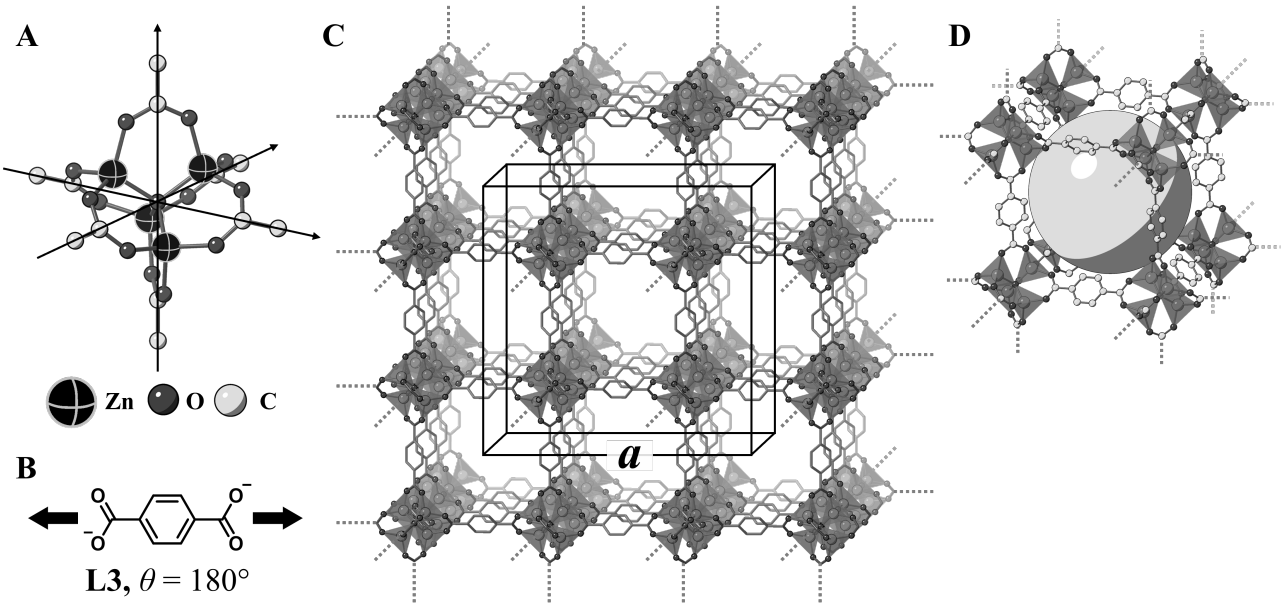


圖 3.

C.2	**X** 由邊長為 a 的立方單位晶格組成（圖 3C），密度為 0.592 g cm^{-3}。以 [cm] 為單位 **計算** 邊長 a 。	5pt

C.3	**X** 含有相當多的孔洞，在 1 bar 和 25 °C 條件下，1 g 的 **X** 可吸附 3.0×10^2 mL 的 CO_2 氣體。**計算** 平均每個孔洞吸附 CO_2 的分子數。	5pt

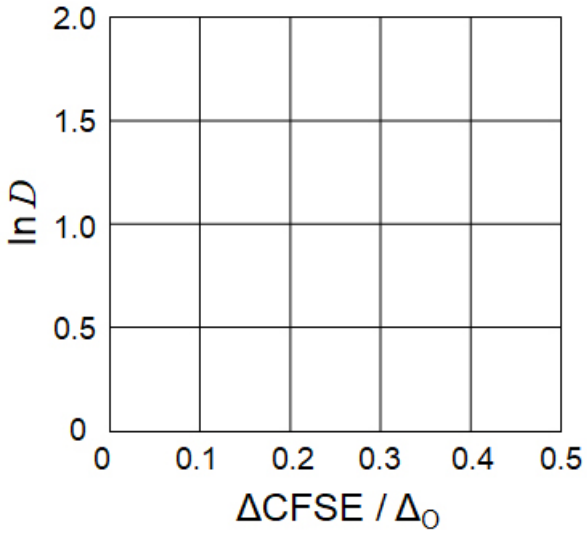
過渡金屬的固態化學

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)

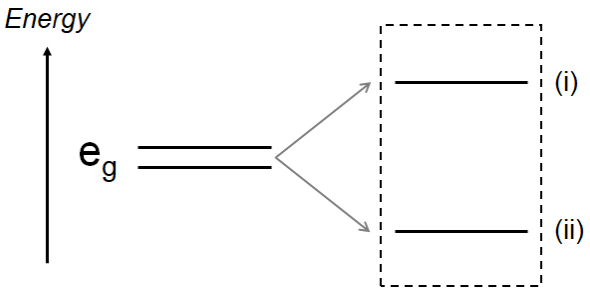
A : _____ , B : _____

B.2 (4 pt)

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

B.3 (4 pt)

(i) : _____ , (ii) : _____



B.4 (4 pt)

_____ %

Part C

C.1 (5 pt)

$n =$ _____, $m =$ _____

C.2 (5 pt)

$a =$ _____ cm

C.3 (5 pt)

TWN-4 C-7 C
Bo-An Chen

IChO
Problem 7
Cover sheet

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

Playing with Non-benzenoid Aromaticity

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

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



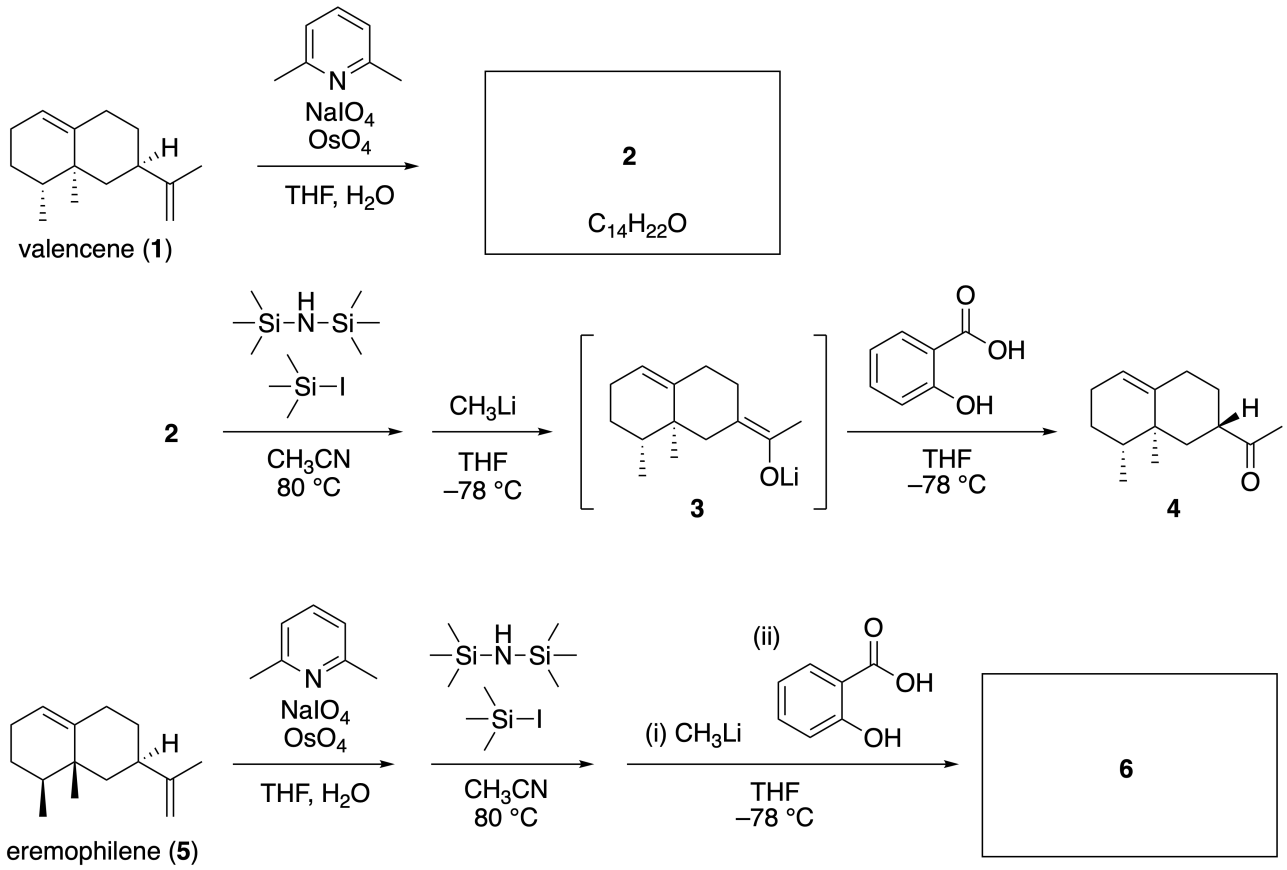
Photo courtesy: Tohoku Univ.

Part A

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



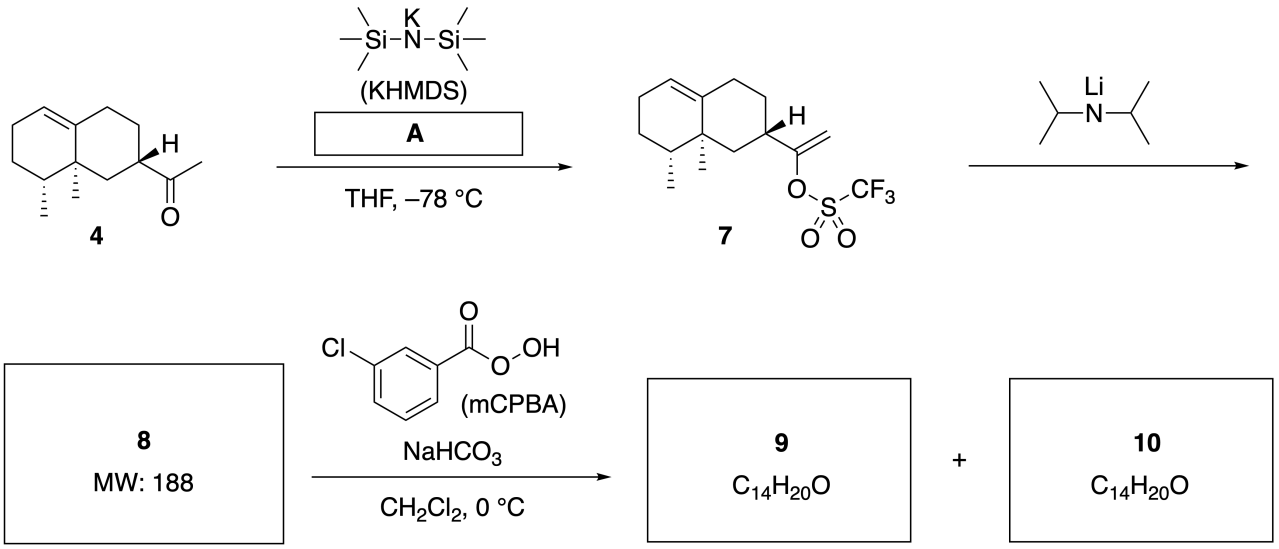
Inula linariifolia

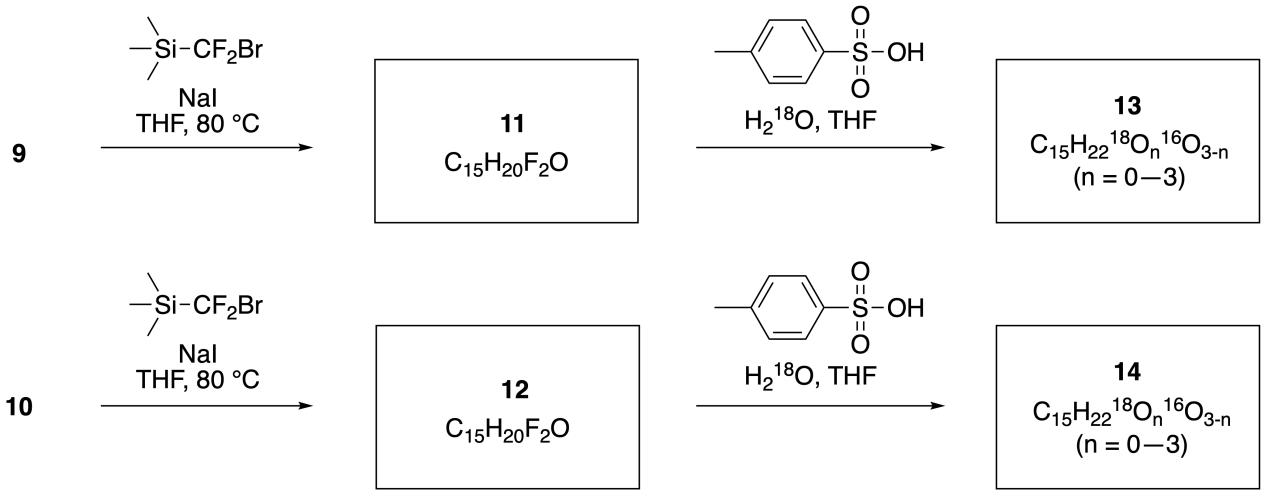


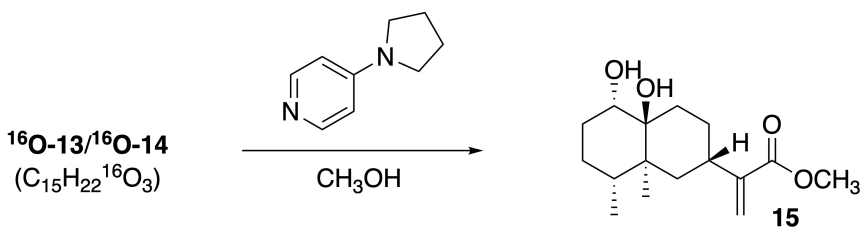
A.1 **Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary. 5pt

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

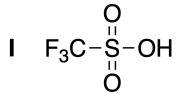
that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product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

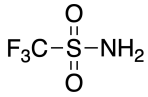


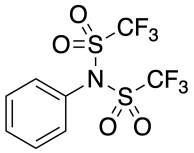


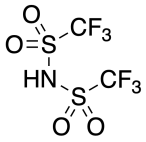


A.2 **Choose** the appropriate structure for **A**. 2pt

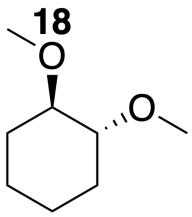
I 

II 

III 

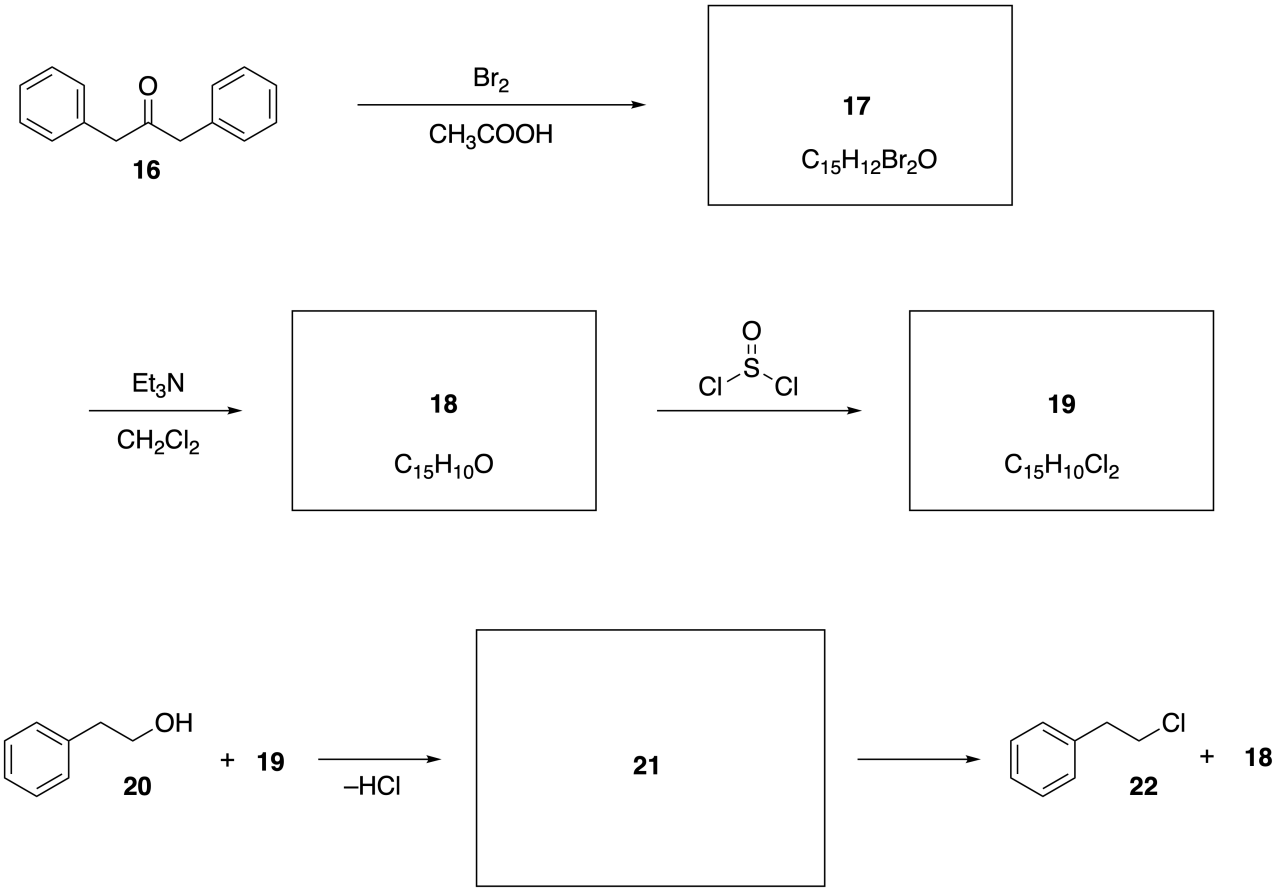
IV 

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



Part B

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



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

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

玩轉非苯類芳香性

佔總分比例 13%					
小題	A.1	A.2	A.3	B.1	**Total**
配分	5	2	19	10	**36**
得分					

野副 (Nozoe) 教授 (1902–1996) 開啟了現在有機化學研究領域中無處不在的非苯類芳香族化合物



照片提供：東北大學

A 部分

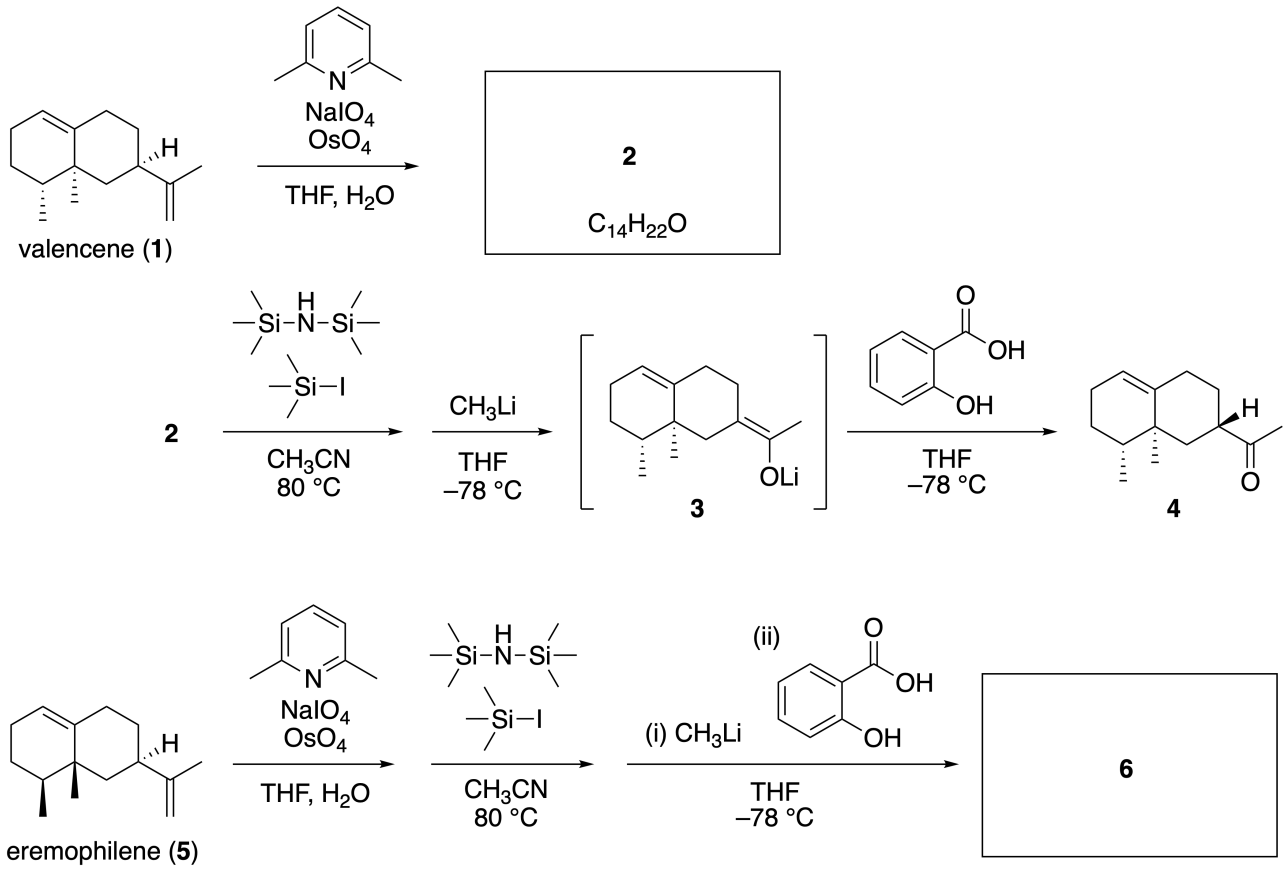
Lineariifolianone 是一種結構獨特的天然產物，可從植物 *Inula linariifolia* 中分離出來。從 valencene (**1**) 開始，一步反應生成化合物 **2**，然後再進行三步反應，生成化合物 **3** 後轉化產生酮類化合物 **4**。而從 eremophilene (**5**)，執行相同的四步反應可得到化合物 **6**。

Q7-2

Chinese Taipei (Chinese Taipei)



Inula linariifolia

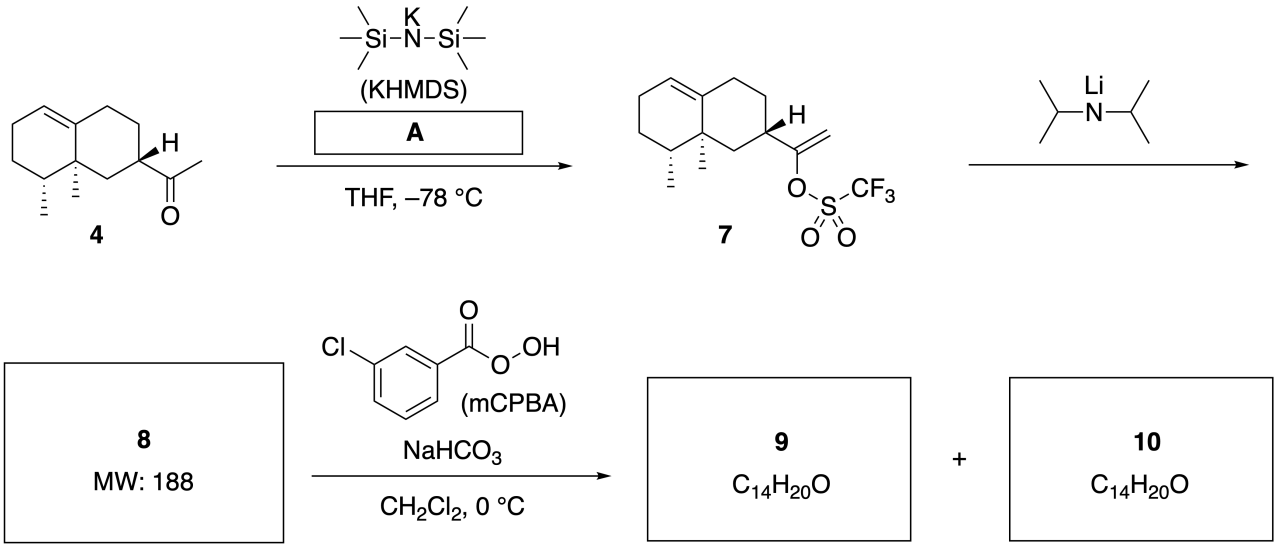


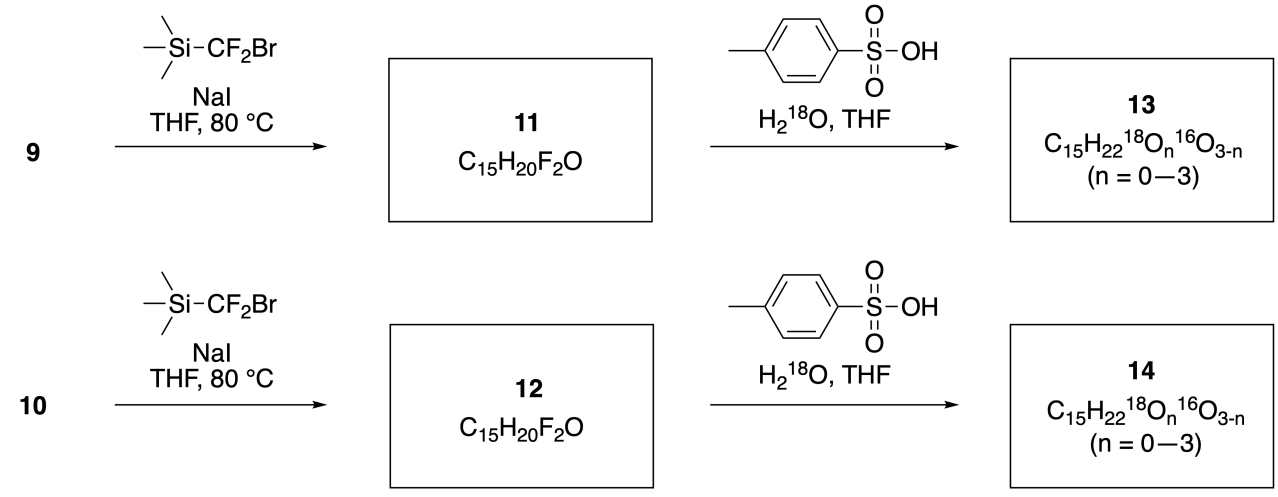
A.1 **<u>畫出</u>** 化合物 **2** 和 **6** 的化學結構，必要時請清楚地標記其立體化學。 5pt

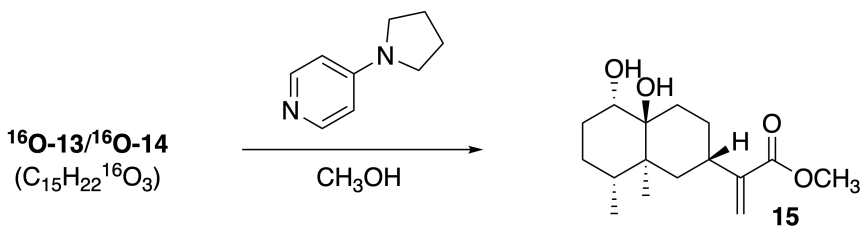
Q7-3

Chinese Taipei (Chinese Taipei)

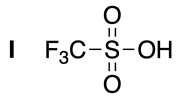
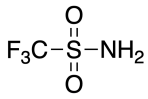
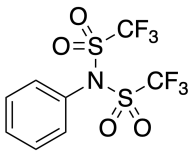
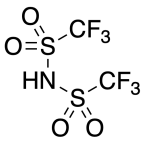
接下來，酮化合物 **4** 可經多步反應轉化為酯化合物 **15**。以下反應流程中，化合物 **8**（分子量：188）保留所有與化合物 **7** 相同的立體中心。化合物 **9** 和 **10** 各別有五個立體中心，且結構當中沒有碳-碳雙鍵的存在。若用 $H_2{}^{18}O$ 代替 $H_2{}^{16}O$ 和化合物 **11** 與 **12** 分別合成含 ^{18}O 標記的化合物 **13** 和 **14**。若忽略同位素標記，將化合物 **13** 和 **14** 進行相同反應，可以得到相同的產物 **15**，且具同樣的立體化學。



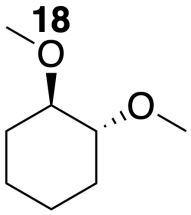




A.2 **選出 A** 合適的化學結構 2pt

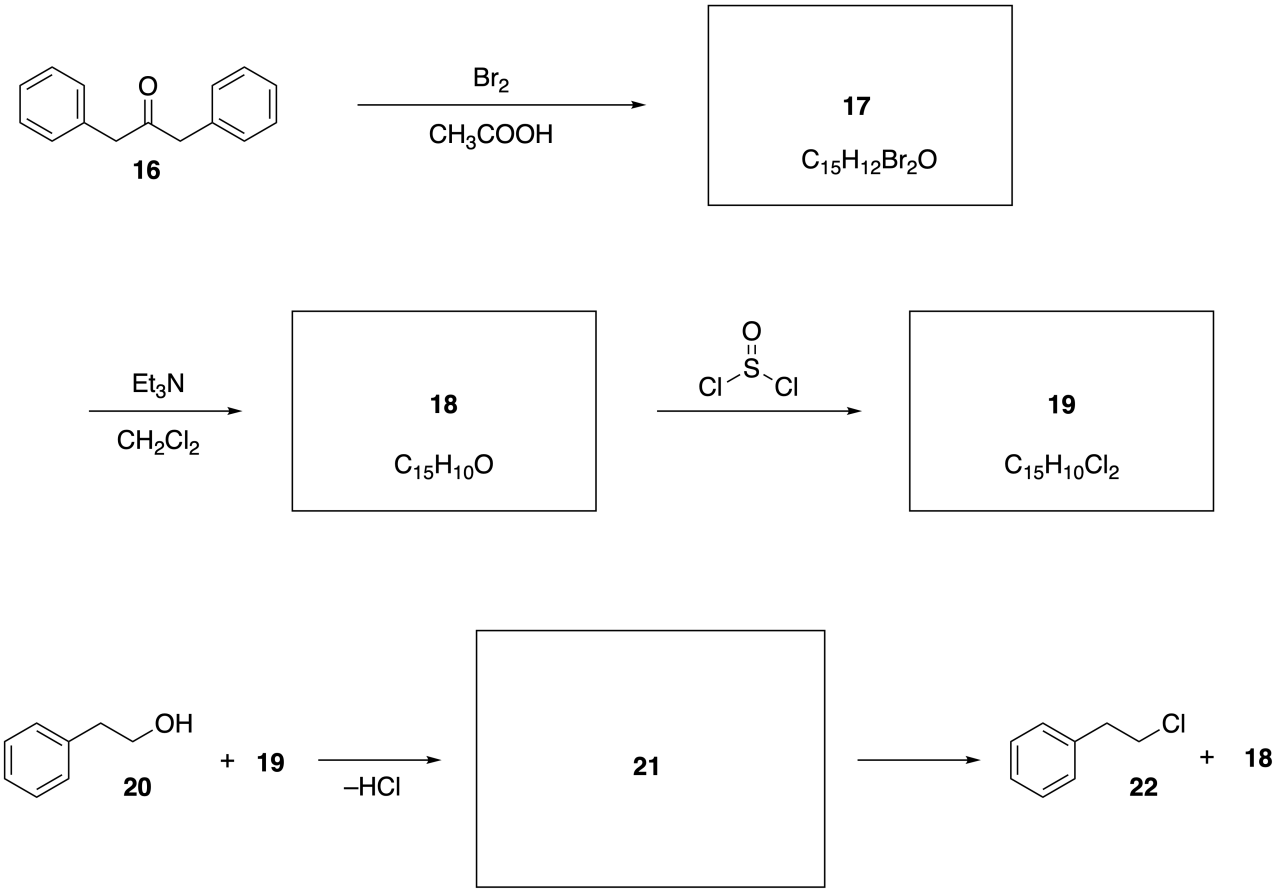
I  **II**  **III**  **IV** 

A.3 **畫出** 化合物 **8**-**14** 的結構，並在必要時清楚地標示其立體化學。此外，請明確 **標出** 化合物 **13** 和 **14** 中 ^{18}O 原子的位置，如下面圖例所示。 19pt



B 部分

化合物 **19** 可由下面的合成方法獲得。非苯類芳香性化合物 **19**，可以作為醇類的活化劑，因此化合物 **20** 先形成離子對中間體 **21**，再轉化為化合物 **22** 。雖然可藉由 1H NMR 光譜觀察到化合物 **21** 的形成，但它會逐漸分解，轉化而得到化合物 **22** 和 **18**。



^{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	**畫出** 化合物 **17**-**19** 和 **21** 的化學結構。不需要標記其立體化學。	10pt

A7-1

Chinese Taipei (Chinese Taipei)

玩轉非苯類芳香性

A 部分

A.1 (5 pt)

2 (2 分)	**6** (3 分)

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)

A7-3

Chinese Taipei (Chinese Taipei)

B 部分

B.1 (10 pt)

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

TWN-4 C-8 C
Bo-An Chen

IChO
Problem 8
Cover sheet

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

Q8-1

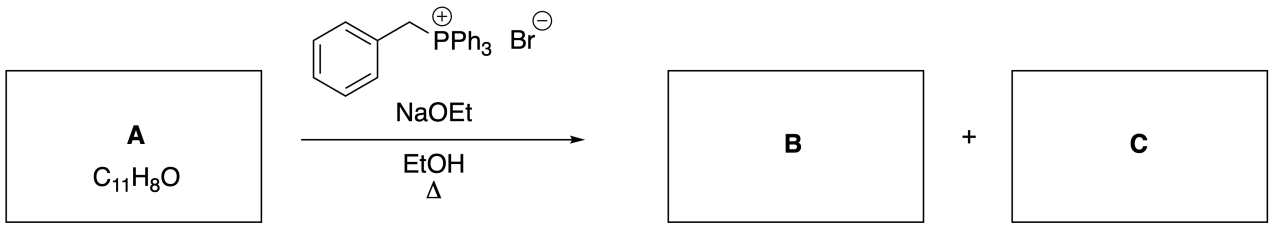
English (Official)

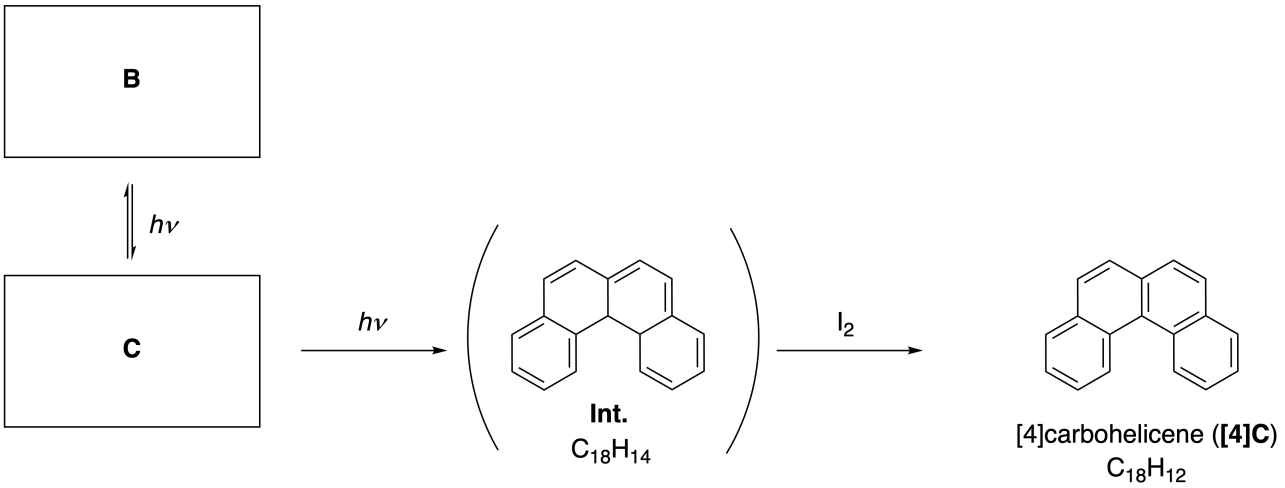
Dynamic Organic Molecules and Their Chirality

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

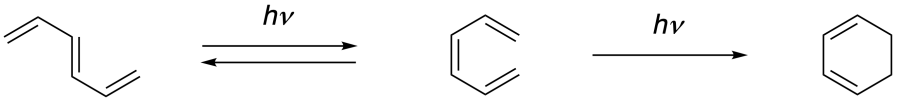
Part A

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





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

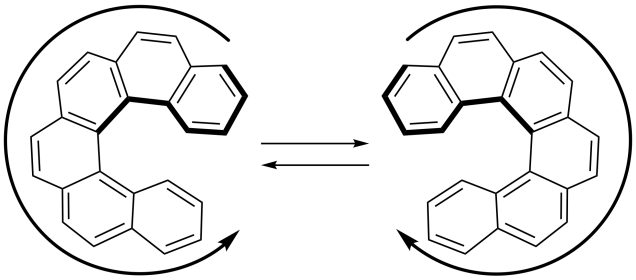


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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

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

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



(*M*) (*P*)

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

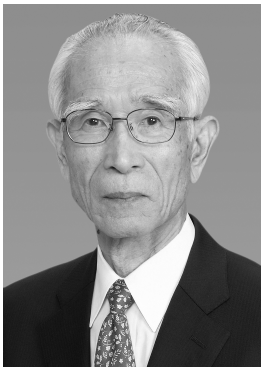
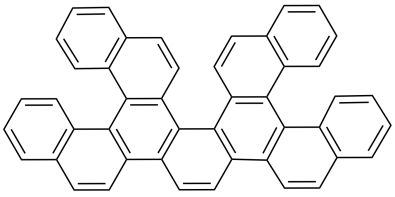


Photo courtesy: The Japan Prize Foundation

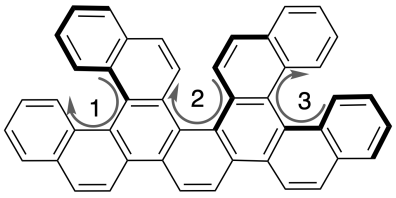
Q8-3

English (Official)

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

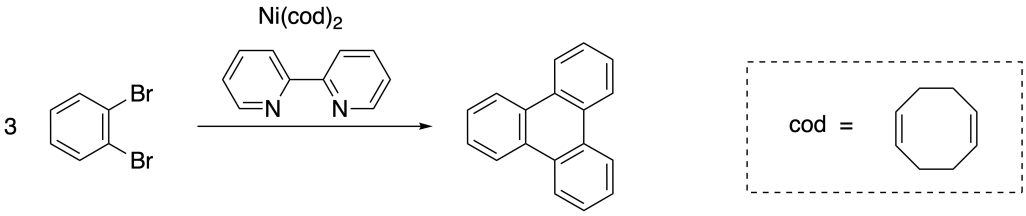


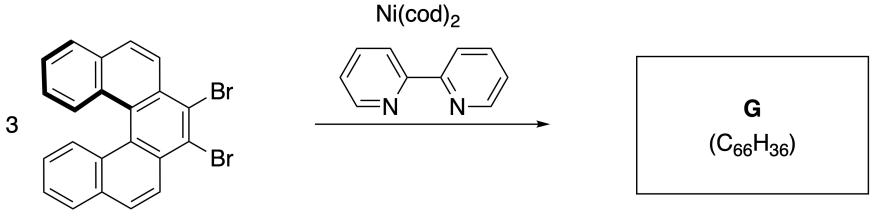
E



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

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

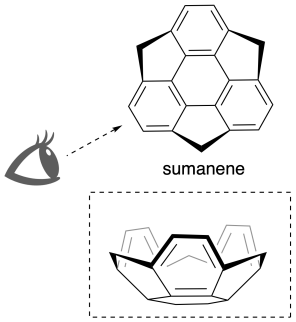




(*P*)-**F**

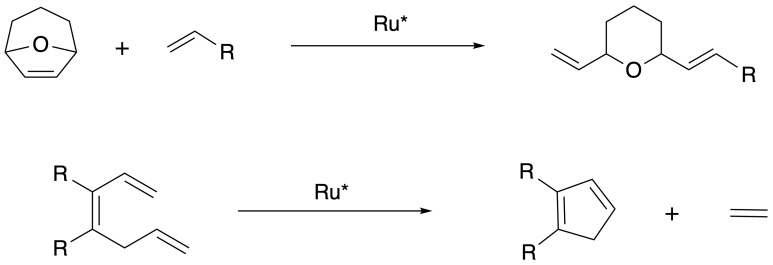
Part B

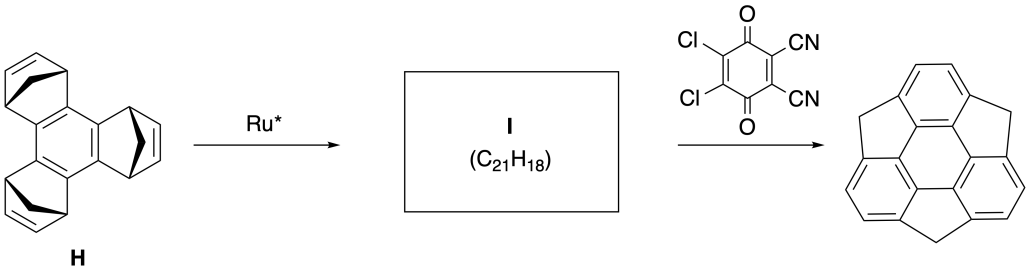
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



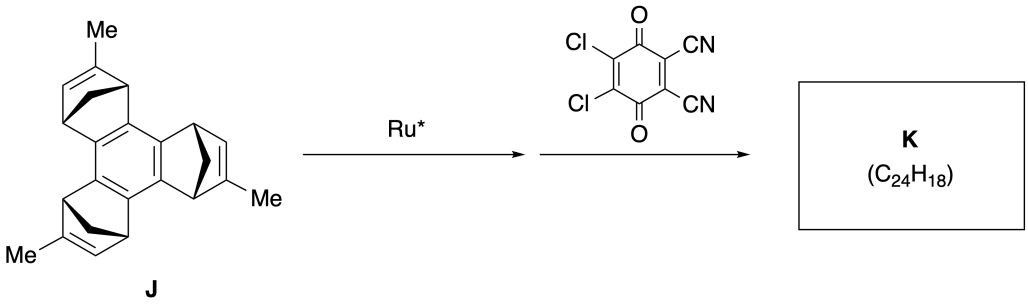


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.





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



J

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

Q8-1

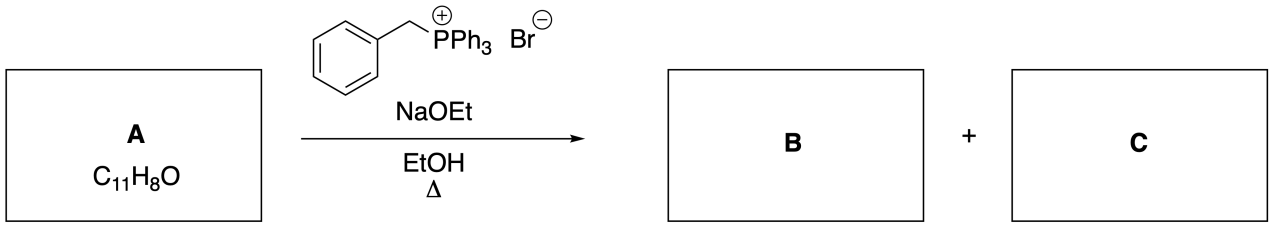
Chinese Taipei (Chinese Taipei)

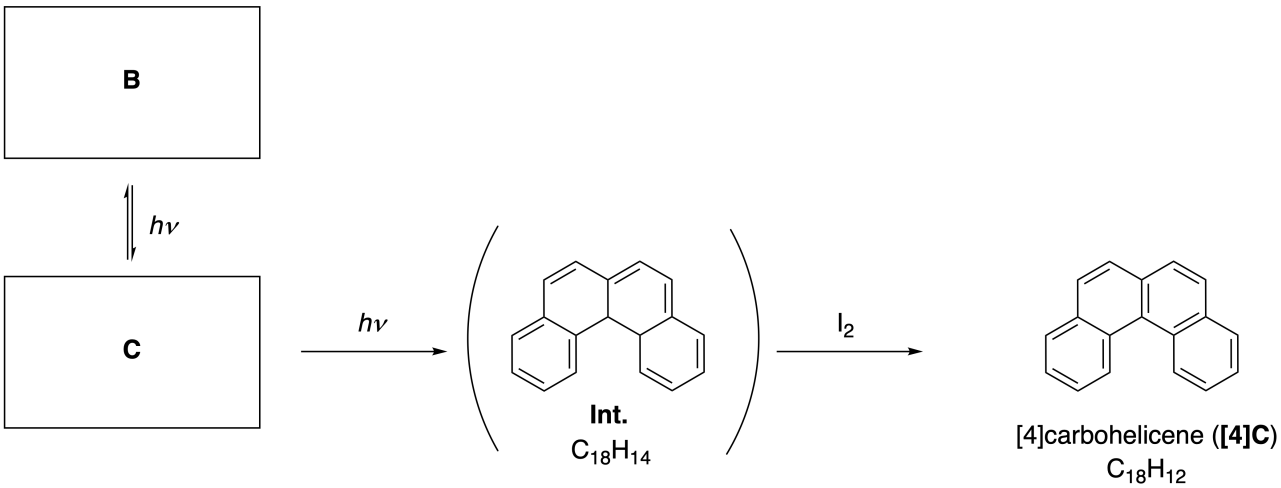
動態有機分子與其掌性

佔總分比例 11 %						
小題	A.1	A.2	A.3	B.1	B.2	**Total**
配分	9	3	7	3	4	**26**
得分						

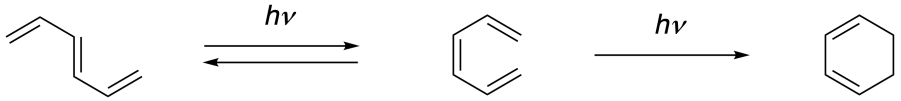
A 部分

具有連續鄰位連接的多環芳香族碳氫化合物稱為 [n] 碳螺旋烴 ([n]carbohelicene)（此處，n 表示六員環的數目）如下所示。[4] 碳螺旋烴 (**[4]C**) 可使用以下的反應途徑，利用照光反應得到中間體 (**Int.**)，再以碘分子進行氧化而得。





上述照光反應發生的反應機制與下列的例子類似。



Q8-2

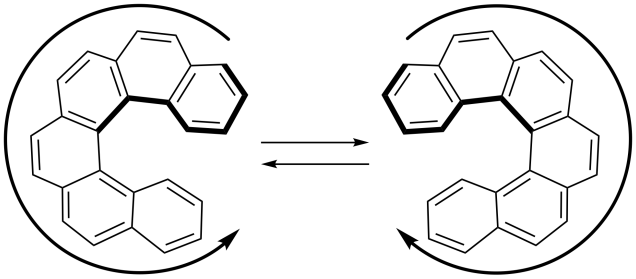
Chinese Taipei (Chinese Taipei)

注意：使用交替的單鍵和雙鍵描述共軛π 系統，而不要用圓圈畫出本題中所有的碳螺旋烴結構。

A.1	**<u>畫出</u>** 化合物 **A**–**C** 的結構 (立體異構物需要放在正確的格子內)。	9pt

A.2	嘗試以相同的鏻鹽與適當的起始物反應僅生成微量的 [5] 碳螺旋烴；卻生成比 [5] 碳螺旋烴分子量少 2 的產物 **D**。化合物 **D** 的 ^{1}H NMR 光譜化學位移如下所示。**<u>畫出</u>** 化合物 **D** 的結構。 [**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]-和更大的 [n] 碳螺旋烴具有螺旋掌性，在室溫下這些螺旋烴的鏡像異構物間的相互轉變非常緩慢。[n] 碳螺旋烴的掌性可以定義為 (*M*) 或 (*P*)，如下所示。



(*M*) (*P*)

n 大於 4 的 [n] 碳螺旋烴可以使用岡本佳男教授所開發的掌性管柱層析法，將其兩個鏡像異構物分離。

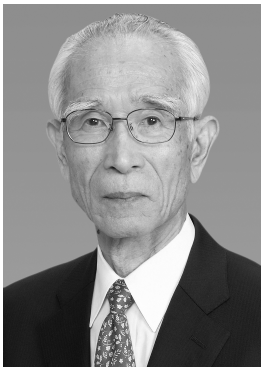
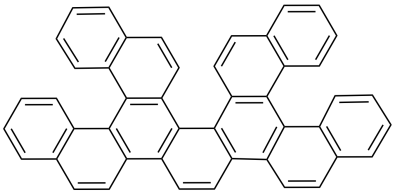


Photo courtesy: The Japan Prize Foundation

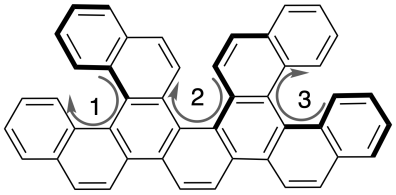
Q8-3

Chinese Taipei (Chinese Taipei)

多重螺旋烴是包含兩個或多個類螺旋烴結構的分子。如果考慮其螺旋掌性，則多重螺旋烴中存在數個立體異構物。例如，下列化合物 **E** 在一個分子中含有三個 [5] 碳螺旋烴的結構。如下所示，其中一種立體異構物可被描述為 (*P*, *P*, *P*)。

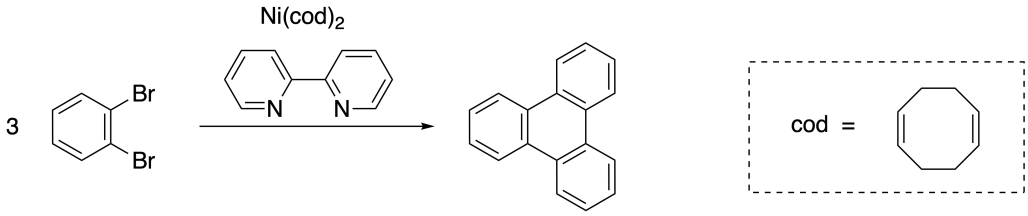


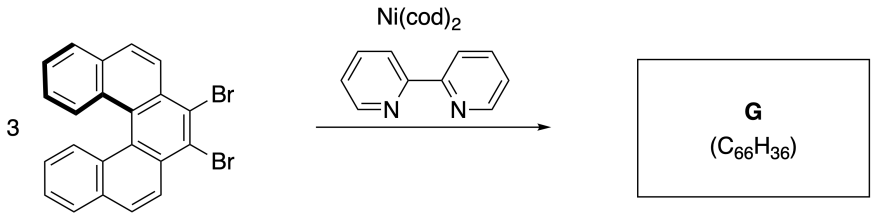
E



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

A.3 下列反應以鎳促進 1,2-二溴苯進行三聚反應可生成聯三伸苯。利用相同的反應條件於化合物 **F** 的一鏡像異構物 (*P*)-**F** 的反應中，可生成多重螺旋烴產物 **G** ($C_{66}H_{36}$)。這些立體異構物在反應過程中不會發生相互轉變。**寫出並標示** 所有可能產生的立體異構物，不得重複。如前述化合物 **E** 的例子作為答題參考標準，將產物 **G** 中的一個異構物完全畫出，給予編號，並且標示其掌性；其它異構物可只使用位置編號與相對的 *M* 和 *P* 表示。例如，化合物 **E** 的其它立體異構物可以列為 (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





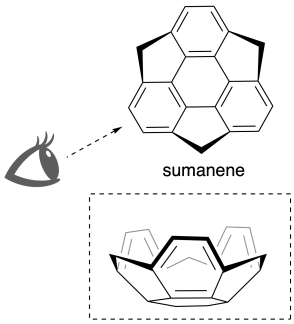
(*P*)-**F**

Q8-4

Chinese Taipei (Chinese Taipei)

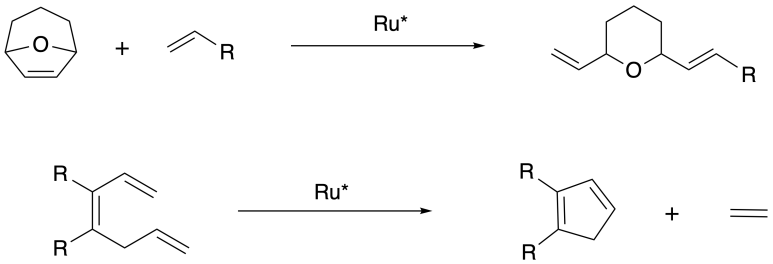
B 部分

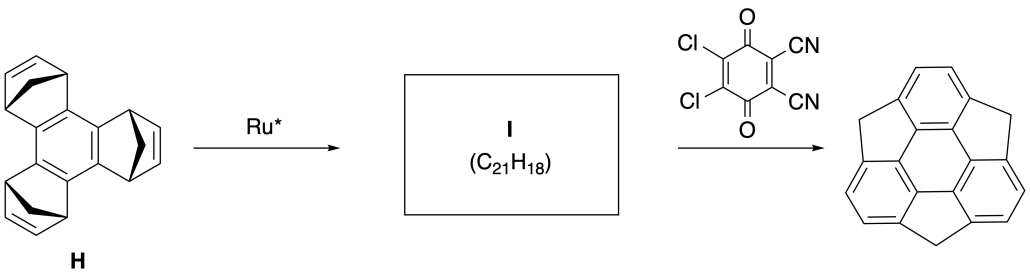
Sumanene 是一種碗狀碳氫化合物，首次於 2003 年在日本合成出來。“sumanene”這個名字源於梵文-印地語中的“suman”，意思是向日葵。合成 sumanene 可經由連續開環和閉環岐化反應途徑達成。





以釕催化劑 (Ru*) 催化岐化反應的代表反應如下所示。



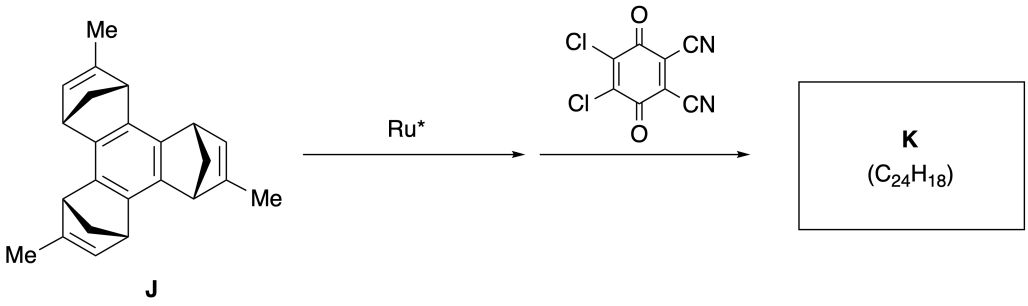


H

B.1	**畫出** 中間體 **I** 的結構（不需要表示它的立體化學）。	3pt

Q8-5

Chinese Taipei (Chinese Taipei)



B.2 從具光學活性的前驅物 **J** 開始，經由相同的反應途徑可以得到亦具光學活性的 sumanene 衍生物 **K**。在此過程中化合物 **J** 中的立體中心沒有發生反轉。**畫出** 產物 **K** 的立體化學結構。 4pt

A8-1

Chinese Taipei (Chinese Taipei)

動態有機分子與其掌性

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)

TWN-4 C-9 C
Bo-An Chen

IChO
Problem 9
Cover sheet

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

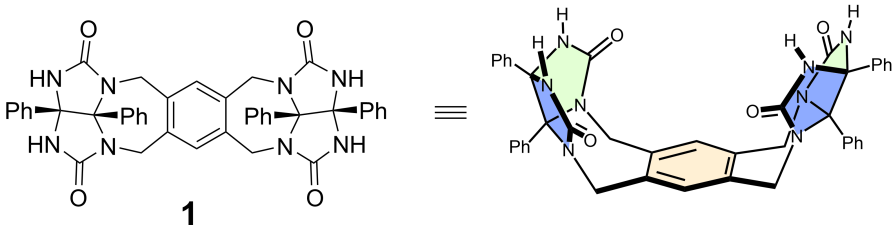
Likes and Dislikes of Capsule

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

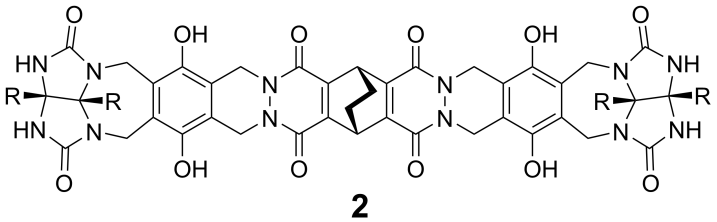
Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



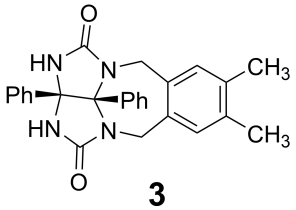
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

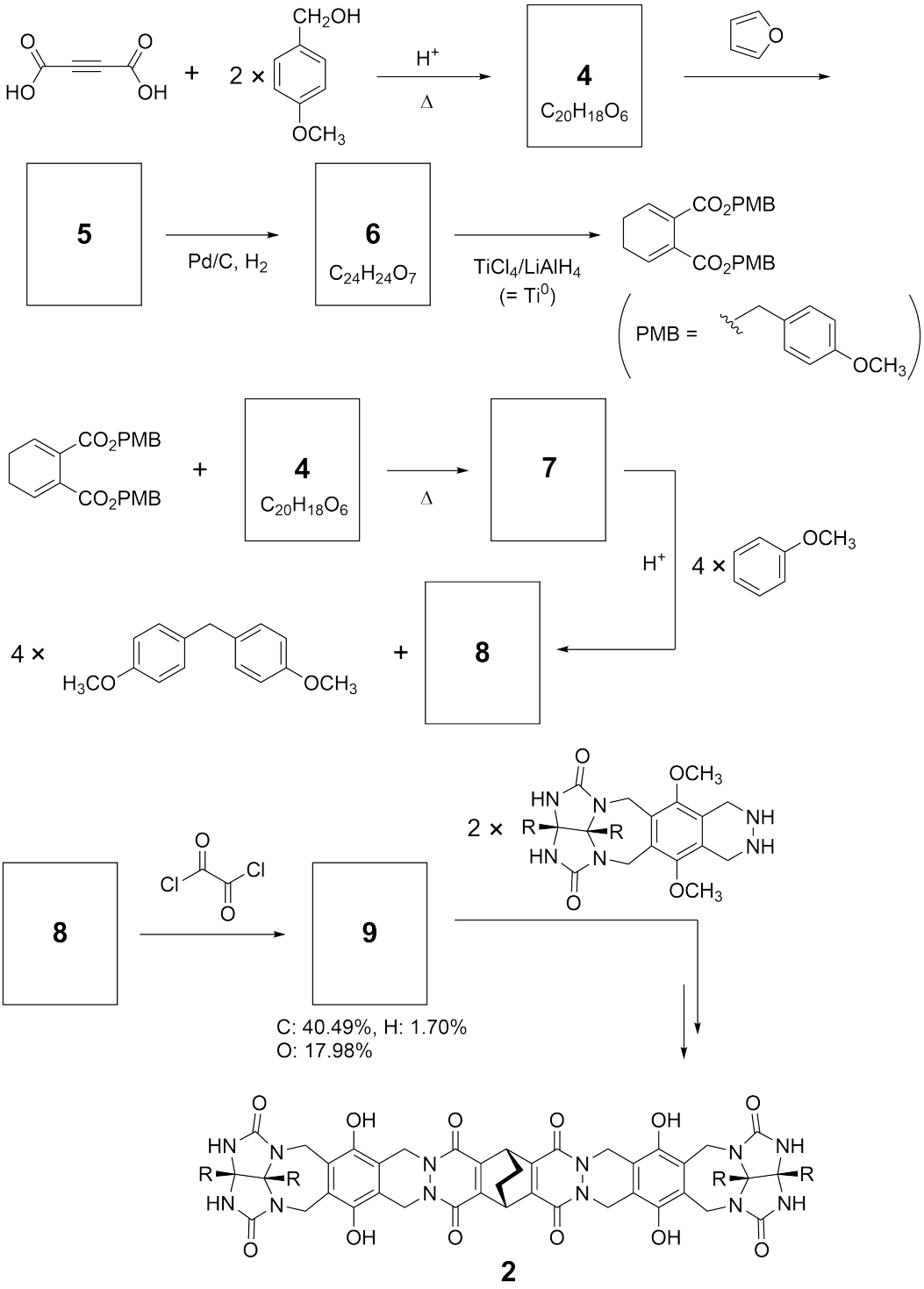


2



3

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



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

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

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

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

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

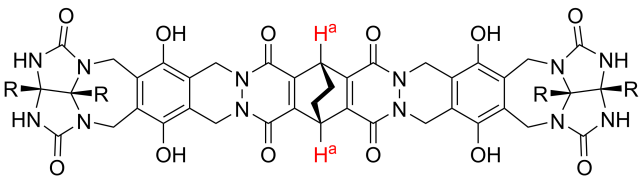
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

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

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

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

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



2

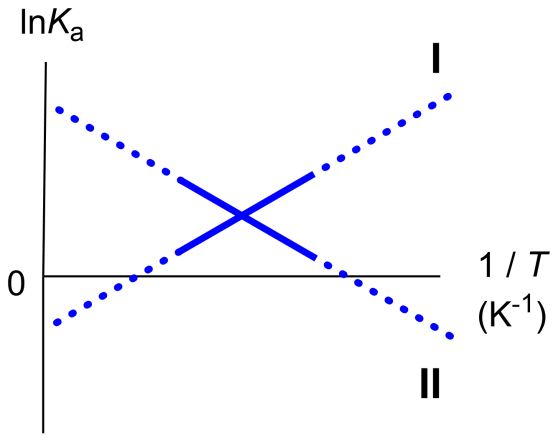
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

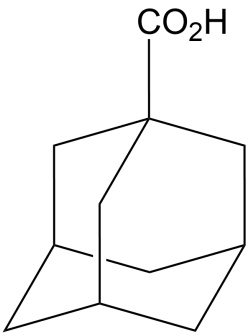
A.4 **<u>Determine</u>** the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2}_2$ giving each H^a signal. 3pt

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

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

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





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

Q9-1

Chinese Taipei (Chinese Taipei)

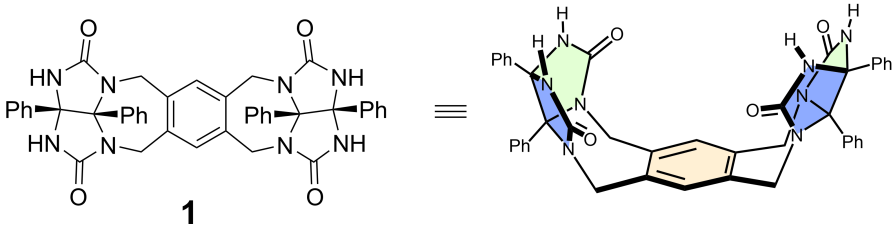
膠囊的喜好

佔總分比例 10 %						
小題	A.1	A.2	A.3	A.4	A.5	**Total**
配分	13	2	2	3	3	**23**
得分						

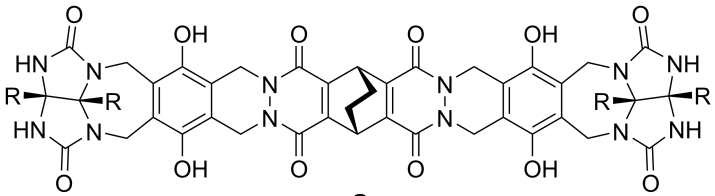
好孩子不會做這件事，但是如果你把網球拆開，你可以把它拆成兩個 U 形的物件。



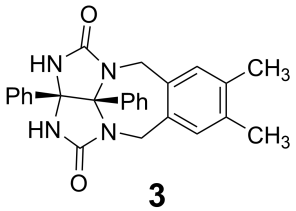
基於這個想法，化學家合成不同大小的 U 形分子，也就是化合物 **1** 和 **2**。同時也合成化合物 **3** 來作為化合物 **1** 的對照組，並研究這些化合物的包覆行為。



1



2

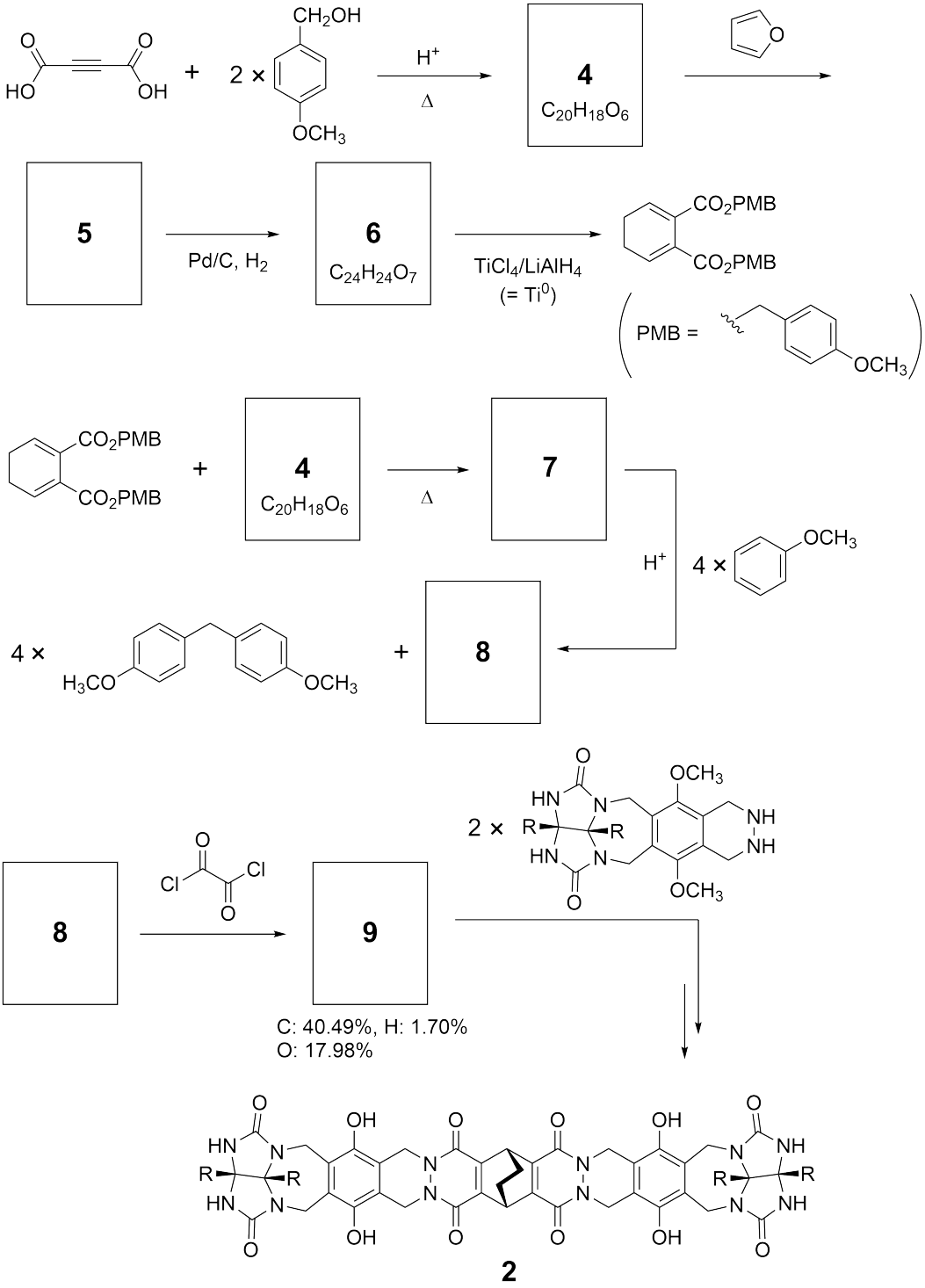


3

Q9-2

Chinese Taipei (Chinese Taipei)

化合物 **2** 的合成路徑如下所示，其中化合物 **9** 的元素重量組成：C; 40.49 %, H; 1.70 % 和 O; 17.98 % 。



Q9-3

Chinese Taipei (Chinese Taipei)

A.1	**畫出** 化合物 **4-9** 的化學結構；不需標示化合物的立體化學。結構中的對-甲氧基苄基不需畫出，而用“PMB”代替，如上圖所示。	13pt

在化合物 **1** 的質譜中，可以清楚地觀察到與其二聚體 $\mathbf{1}_2$ 相對應的離子峰，而在化合物 **3** 的質譜中則沒有觀察到 $\mathbf{3}_2$ 的離子峰。在 $\mathbf{1}_2$ 溶液的 ^{1}H NMR 光譜中，化合物 **1** 中所有 NH 的質子其化學環境均相同，但它們的化學位移和化合物 **3** NH 質子的化學位移有顯著的不同。這些數據顯示，一個分子 **1** 的 NH 與另一個分子 **1** 的某原子 **X** 之間產生氫鍵，而形成二聚體膠囊。

A.2	**圈出** 化合物 **1** 中所有符合條件的原子 **X**。	2pt

A.3	**寫出** 二聚體膠囊 ($\mathbf{1}_2$) 中氫鍵的數量。	2pt

化合物 **1** 的二聚體膠囊 ($\mathbf{1}_2$) 具有內部的空間，可以包覆大小適中的小分子 Z。這個現象可以用下面的反應式表示：

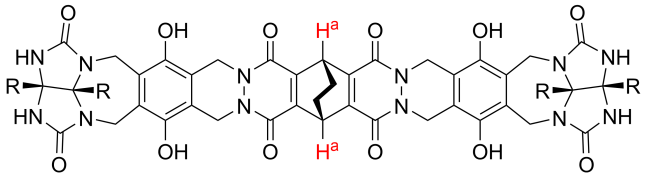
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

把小分子 Z 包覆進入 $\mathbf{1}_2$ 的平衡常數如下：

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

藉用 NMR 光譜，可以監測分子包覆到膠囊內之反應。例如，$\mathbf{1}_2$ 在 C_6D_6 中的 ^{1}H NMR 訊號，再加入 CH_4 後有明顯的不同。

化合物 **2** 也可形成比較大而且具剛性的二聚體膠囊 ($\mathbf{2}_2$)。在所有其他條件不變的前提下，測量 $\mathbf{2}_2$ 在 C_6D_6、C_6D_5F 和 C_6D_6/C_6D_5F 混合溶劑中的 ^{1}H NMR 光譜。化合物 **2** 的 H^a 質子在各溶劑中的化學位移總結如下表。除了表中所列的訊號外，沒有其他的 H^a 訊號。假設膠囊內部皆會填滿最多溶劑分子，而且每個化學位移訊號，只對應一種溶劑組合。



2

溶劑	H^a 的 δ (ppm)
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

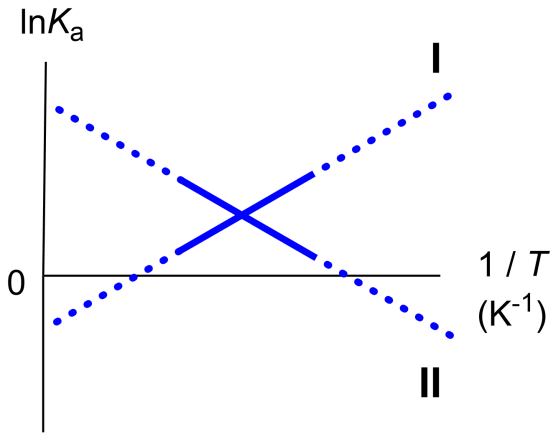
A.4	依據 H^a 訊號， **判斷** 包覆在 $\mathbf{2}_2$ 中 C_6D_6 和 C_6D_5F 分子的數量。	3pt

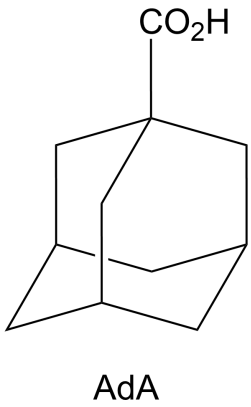
在 C_6D_6 中的 ^{1}H NMR 顯示出 $\mathbf{2}_2$ 可以包覆一個 1-金剛烷甲酸 (AdA) 分子，包覆常數 (K_a) 如下所示，並且在不同溫度下，進行包覆常數的量測。

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

其中 solvent@$\mathbf{2}_2$ 表示含有一個或多個溶劑分子的物質。

反應式 (2) 的 CH_4 和 $\mathbf{1}_2$ 在 C_6D_6 中的包覆常數 K_a，也在不同溫度下由 ^{1}H NMR 測量，將 ln K_a 對 1/T 作圖如下：





在 $\mathbf{1}_2$ 中不會包覆任何的 C_6D_6 分子，在直線 **II** 中，反應熵 (ΔS) 為 (1)，反應焓 (ΔH) 為 (2)，直線 **II** 的包覆行為之驅動力為 (3)。因此，直線 **I** 對應為 (4)，直線 **II** 對應為 (5)。

A.5 下列 (1)-(5) 的編號中，依序 **選擇** A 或 B 填入前段 (1)-(5) 空格內。 3pt

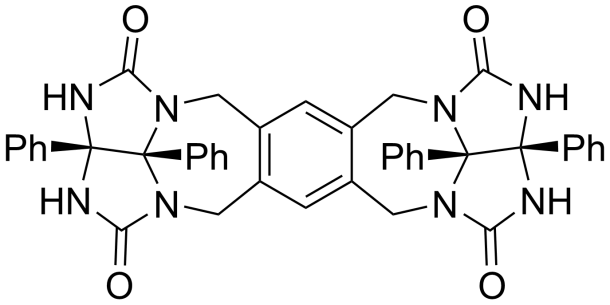
	A	B
(1)	正值	負值
(2)	正值	負值
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ 和 CH_4	$\mathbf{2}_2$ 和 AdA
(5)	$\mathbf{1}_2$ 和 CH_4	$\mathbf{2}_2$ 和 AdA

膠囊的喜好

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)

H^a 的 δ (ppm)	C_6D_6 的數目	C_6D_5F 的數目
4.60 ppm		
4.71 ppm		
4.82 ppm		

A.5 (3 pt)

(1)： (2)： (3)：

(4)： (5)：