IChO
General instructions

Cover sheet

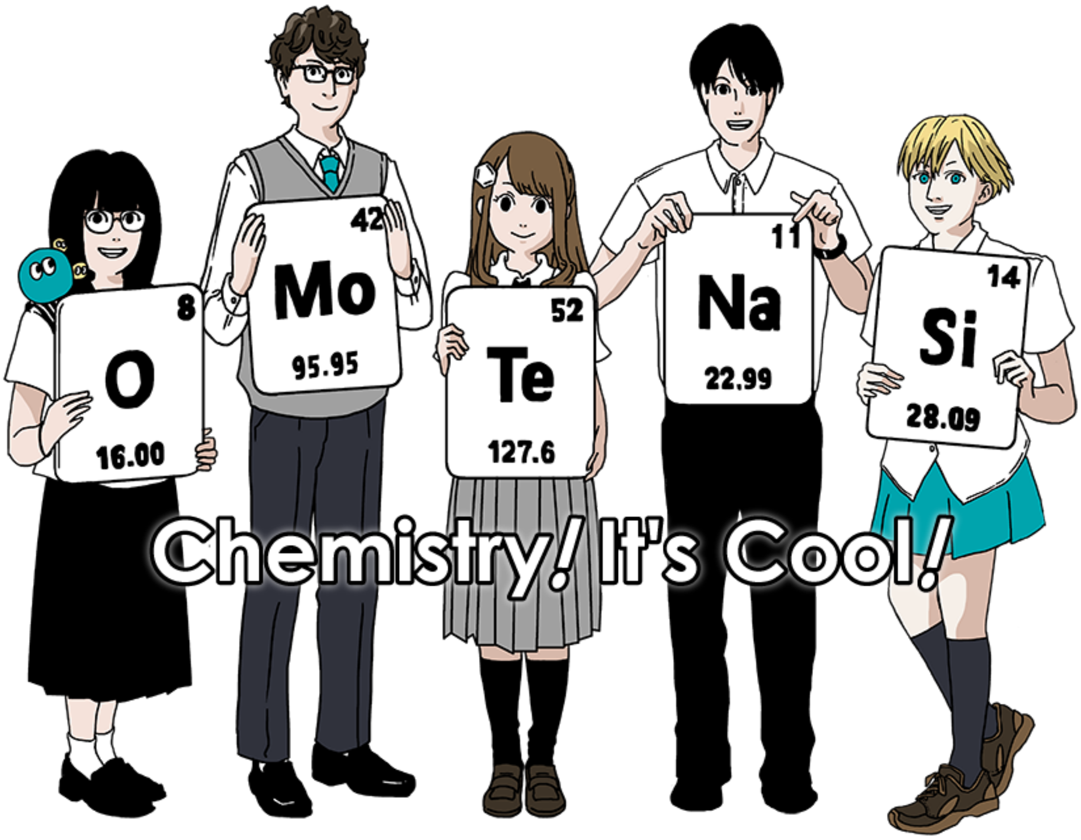
Please return this cover sheet together with all the related question sheets.

International Chemistry Olympiad 2021 Japan

53rd IChO2021 Japan

25th July – 2nd August, 2021

https://www.icho2021.org



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GOOD LUCK!

Problems and Grading Information

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

Physical Constants and Equations

Constants

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

Equations

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

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

Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.008						Key:											2 He Helium 4.003
3 Li Lithium 6.968	4 Be Beryllium 9.012					113 Nh Nihonium [278]	atomic number Symbol name atomic weight [in parenthesis for the radioactive element]					5 B Boron 10.814	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.306											13 Al Aluminium 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.068	17 Cl Chlorine 35.452	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium [99]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.293
55 Cs Caesium 132.905	56 Ba Barium 137.327	57-71 La-Lu Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.384	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium [210]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Ac-Lr Actinoids	104 Rf Rutherfordium [267]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [272]	108 Hs Hassium [277]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [278]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [293]	118 Og Oganesson [294]

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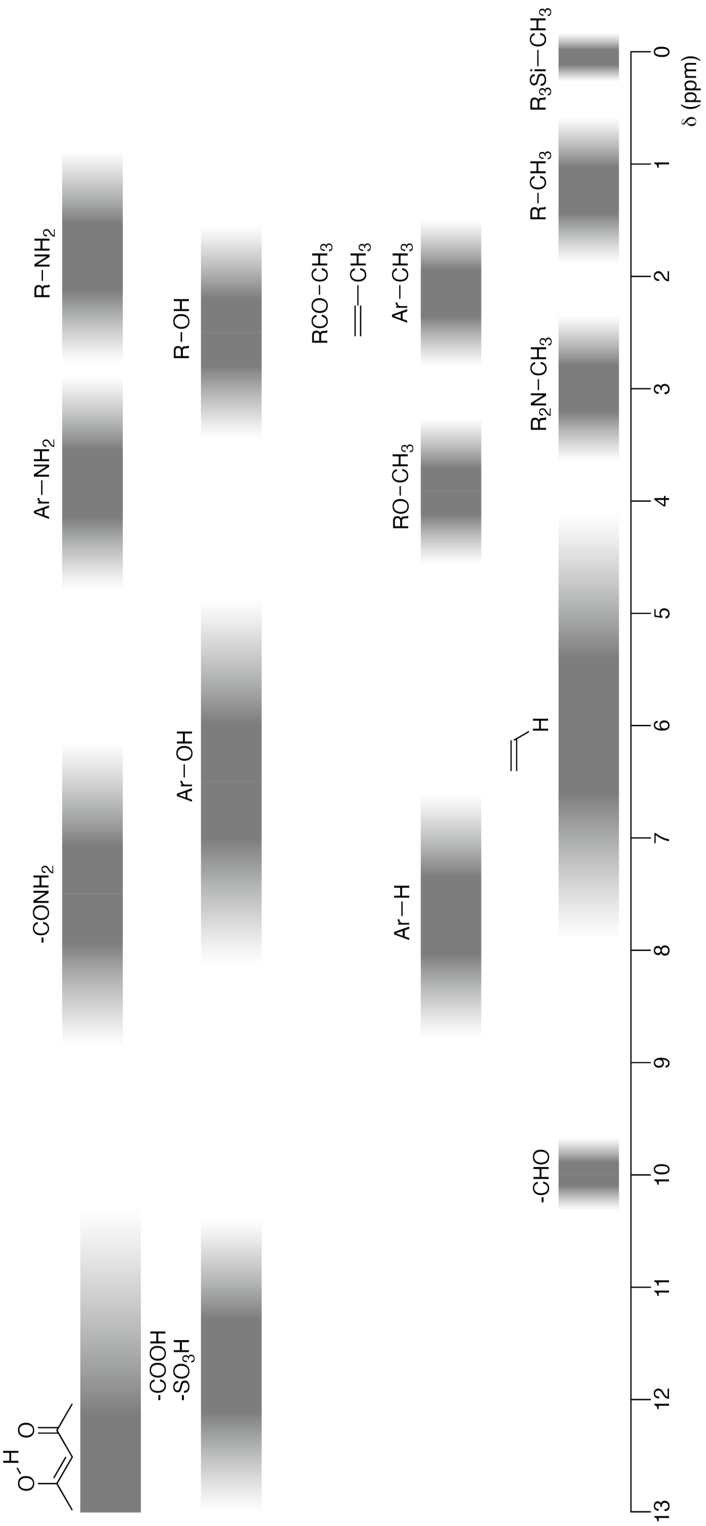
89-103 Ac-Lr Actinoids :	89 Ac Actinium [227]	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [239]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [252]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium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

^{1}H NMR Chemical Shifts



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

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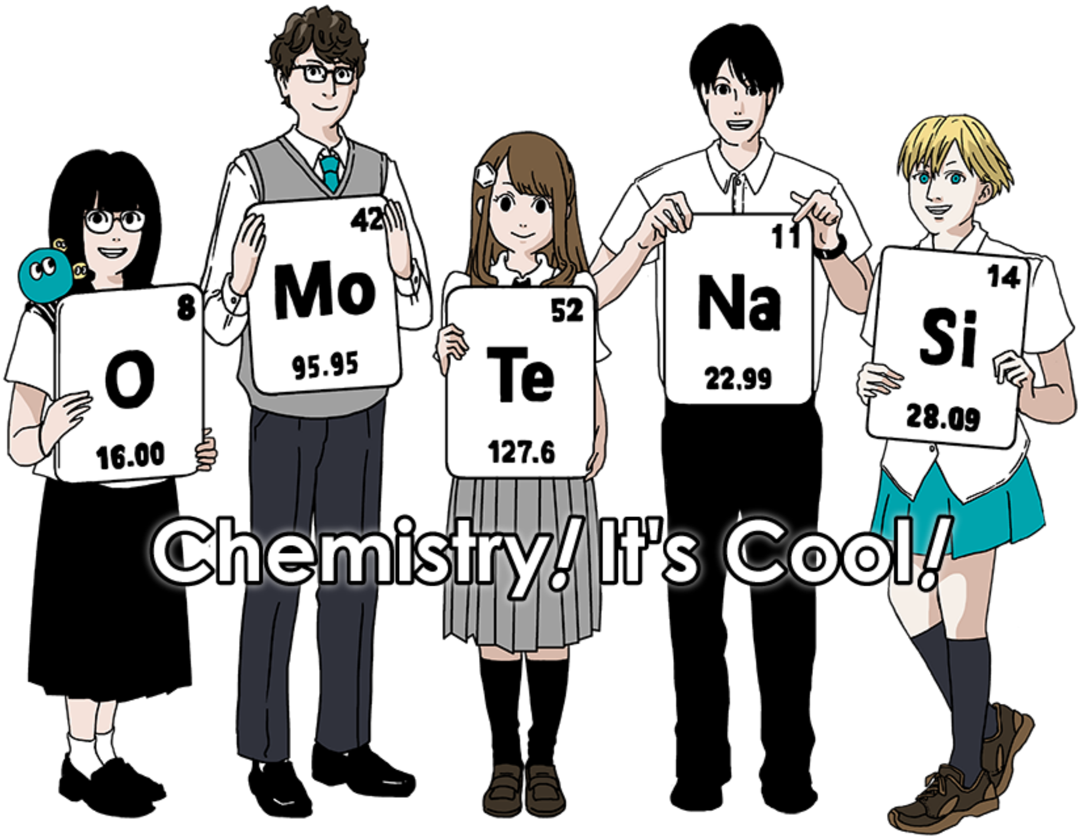

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Key:

113
Nh
Nihonium
[278]

atomic number
Symbol
name
atomic weight [in parenthesis for the radioactive element]

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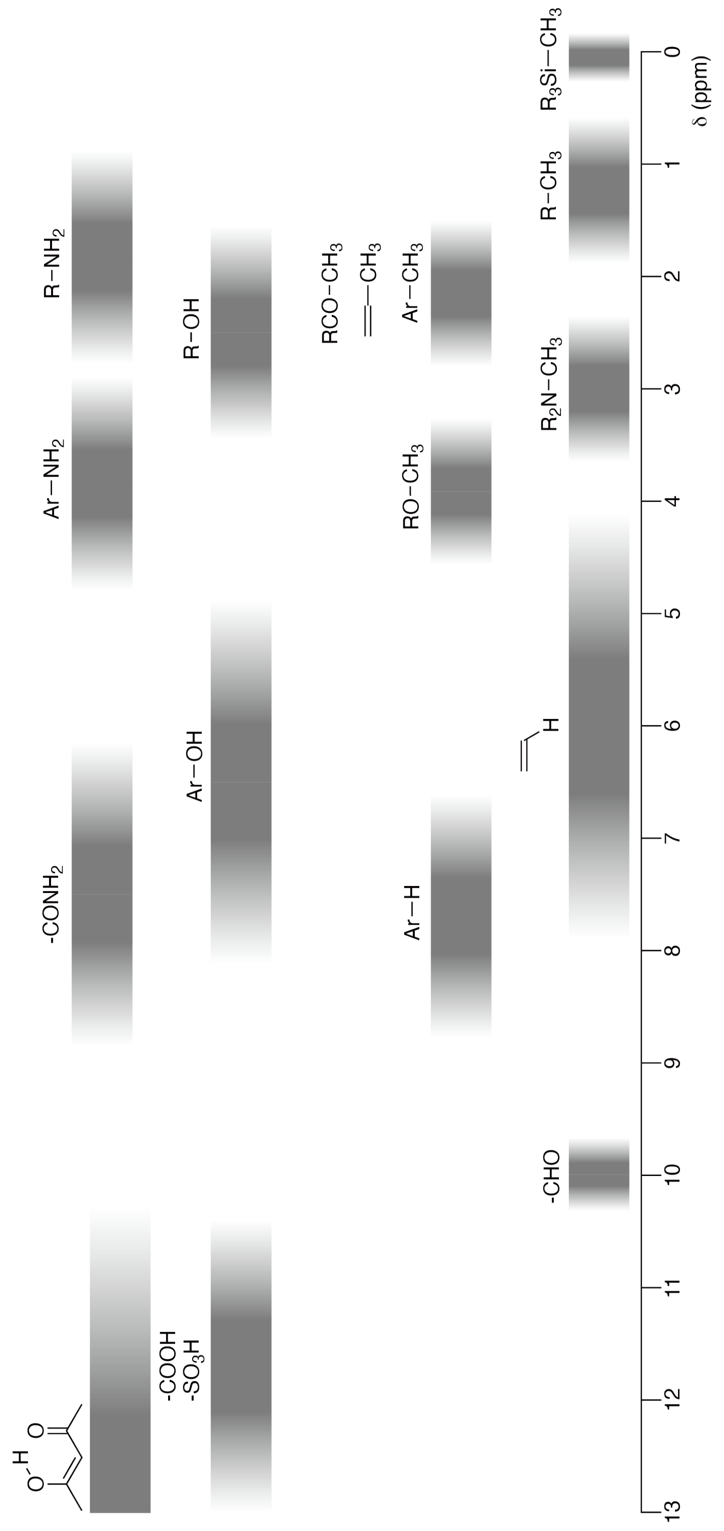


Δ*δ* for one alkyl group-substitution: *ca.* +0.4 ppm

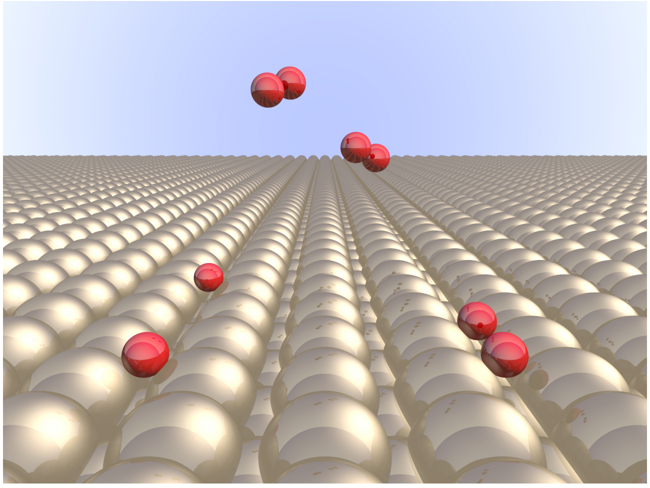
SAU-1 C-1 C-1

IChO
Problem 1
Cover sheet

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

Hydrogen at a Metal Surface

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



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

Part A

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

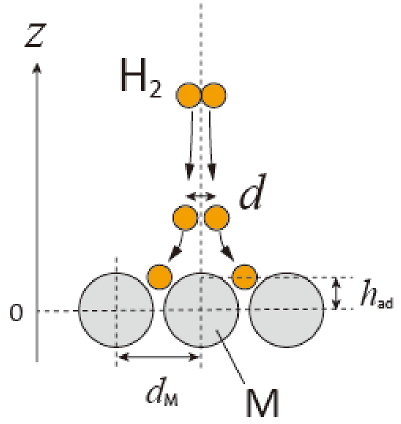


Fig.1 Definition of variables. Drawing is not in scale.

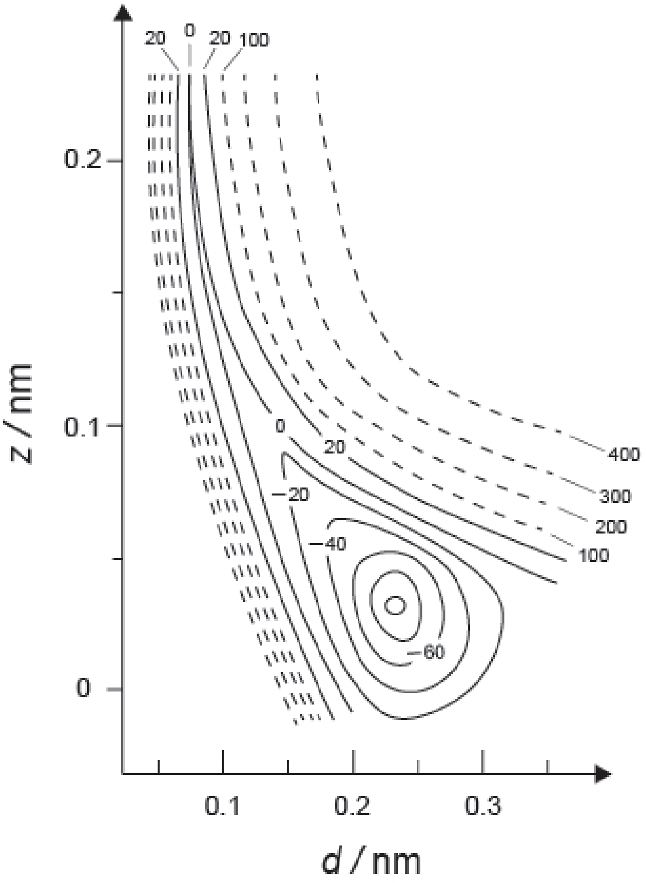


Fig.2

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

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

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

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

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

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

Part B

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

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

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

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

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

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

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

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

B.1 r_3 can be expressed as: 5pt

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

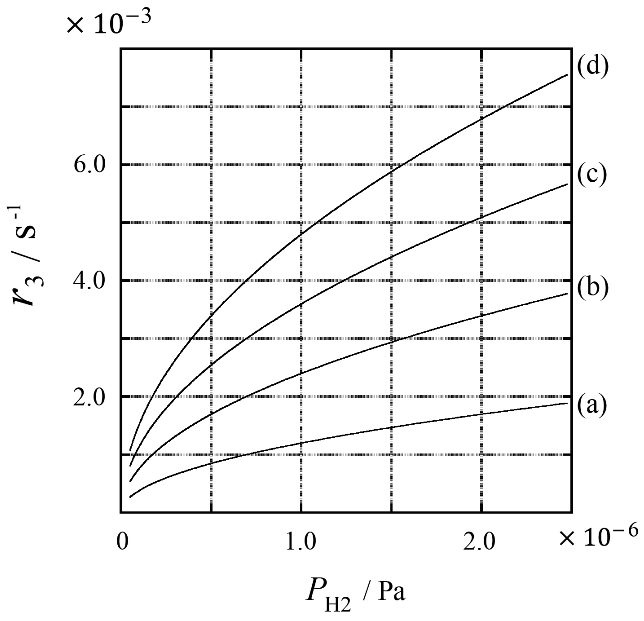
Express C using k_1 and k_2.

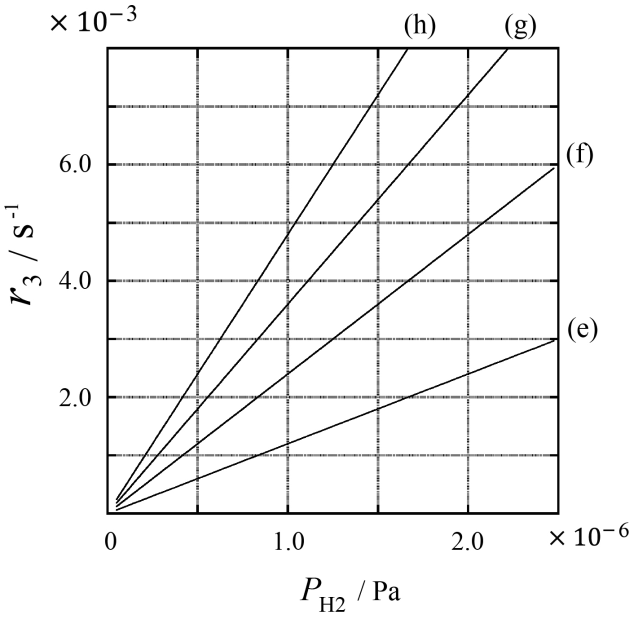
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m^2 was placed in a container (1L = 1.0×10^{-3} m^3) with H$_2$ ($P_{H_2} = 1.0 \times 10^2$ Pa). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m^{-2}. The surface temperature was kept at $T = 400$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

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

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

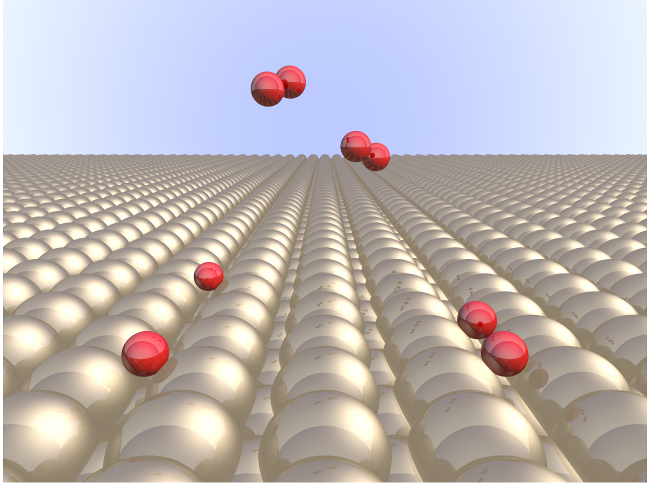
B.4 At a different T, $C = 2.5 \times 10^3$ Pa^{-1} and $k_3 = 4.8 \times 10^{-2}$ s^{-1} are given. For r_3 as a function of P_{H_2} at this temperature, **select** the correct plot from (a)–(h). 3pt





الهيدروجين على سطح معدني

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.

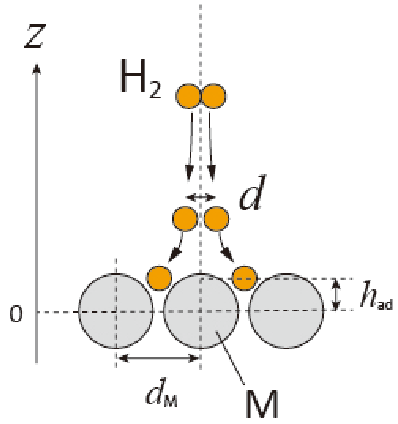
يتوقع أن يكون الهيدروجين مصدر طاقة في المستقبل لا يعتمد على الوقود الأحفوري. في هذا السؤال، سننظر إلى عملية تخزين الهدروجين في معدن، وهذا يتعلق بتقنية نقل وتخزين الهيدروجين.

A Part

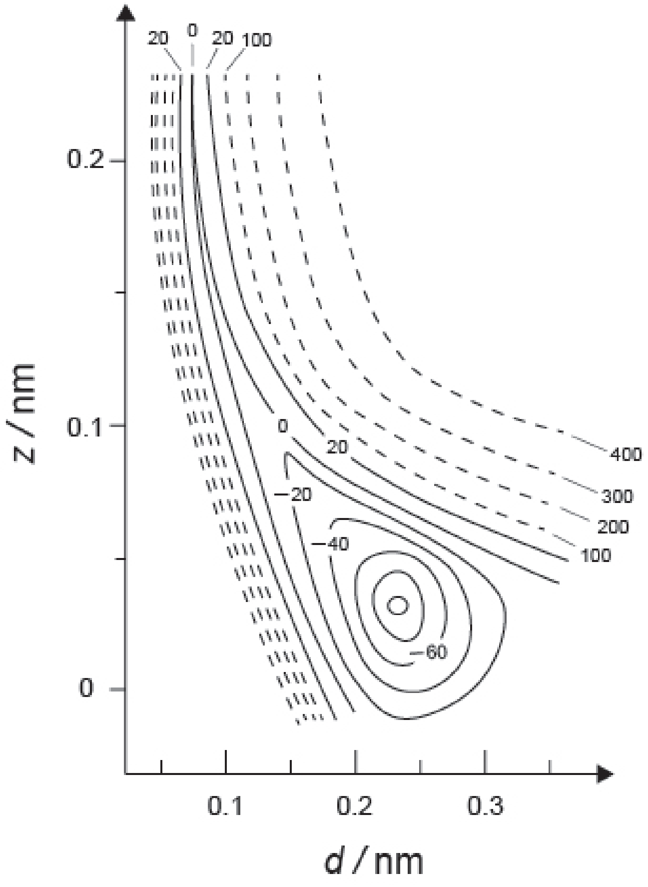
As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $H_2(g) \rightarrow 2H(ad)$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (H_2) that 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.

يُمتص الهيدروجين إلى داخل معدن ما من خلال سطحه. لننظر أولاً إلى عملية امتصاص الهيدروجين على سطح المعدن، $H_2(g) \rightarrow 2H(ad)$، حيث يرمز للحالة الغازية بـ (g) والحالة الممتصة على السطح بـ (ad) في المعادلة. عندما تصل جزيئات الهيدروجين (H_2) إلى سطح معدن (M) تتفكك على السطح وتمتص على شكل ذرات هيدروجين (شكل

1). هنا، الطاقة الكامنة لـ H_2 تتمثل بمتغيرين: المسافة بين الذرات (d) والارتفاع بالنسبة لسطح المعدن (z). يمكن افتراض أن المحور المار بذرتي الهيدروجين موازي للسطح، وأن مركز الثقل يقع دائماً على المحور العمودي المنقط الموضح في الشكل 1. في شكل 2 يظهر مخطط (contour) الطاقة الكامنة لعملية التفكك على السطح. الأرقام بوحدة kJ لكل مول من الهيدروجين. تباعد الخطوط المتصلة يمثل 20 kJ mol^{-1}، وتباعد الخطوط المنقطة يمثل 100 kJ mol^{-1}، وتباعد الخطوط المتصلة مع المنقطة يمثل 80 kJ mol^{-1}. تم إهمال الطاقة الاهتزازية للنقطة الصفرية (zero-point vibration energy).



شكل 1. تعريف المتغيرات. الرسم ليس للقياس.



شكل 2.

6pt

A.1

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

لكل من العناصر التالية (i)-(iii) **اختر** أقرب قيمة من الخيارات A-G.

(i) The interatomic distance for a gaseous H_2 molecule

(i) المسافة بين الذرات في جزيء H_2 الغازي

(ii) The interatomic distance between metal atoms (d_M in Fig. 1)

(ii) المسافة بين ذرات المعدن (d_M في شكل 1).

(iii) The distance of adsorbed H atoms from the surface (h_ad in Fig. 1)

(iii) المسافة بين ذرة هيدروجين والسطح (h_ad في شكل 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	

4pt **A.2**

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

لكل من العناصر التالية (i)-(ii) **اختر** أقرب قيمة من الخيارات A-H.

(i) the energy required for the dissociation of gaseous H_2 to gaseous H ($H_2(g) \rightarrow 2H(g)$)

(i) الطاقة اللازمة لتفكيك H_2 الغازي إلى H غازي ($H_2(g) \rightarrow 2H(g)$)

(ii) the energy released during the adsorption of a gaseous H_2 ($H_2(g) \rightarrow 2H(ad)$)

(ii) الطاقة المنبعثة خلال عملية امتصاص H_2 غازي ($H_2(g) \rightarrow 2H(ad)$)

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 Part

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.

ذرات الهيدروجين الممتصة على السطح إما أن تمتص إلى داخل المعدن، أو تتحد وتعود إلى الطور الغازي، كما هو موضح في المعادلتين (1a) و (1b). الرمز H(ab) يرمز لذرة هيدروجين ممتصة في داخل المعدن.

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

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

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:

سرعة التفاعلات لكل موقع سطحي للامتصاص (adsorption)، انفصال الجسيمات من المعدن (desorption)، وامتصاص لداخل المعدن (absorption) هي $r_1[\mathrm{s^{-1}}]$، $r_2[\mathrm{s^{-1}}]$ و $r_3[\mathrm{s^{-1}}]$، على الترتيب. يمكن التعبير عنها على النحو التالي:

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

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

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

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 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.

حيث $k_1\,[\mathrm{s^{-1}\,Pa^{-1}}]$، $k_2\,[\mathrm{s^{-1}}]$، و$k_3\,[\mathrm{s^{-1}}]$ عبارة عن ثوابت سرعة التفاعلات، و $P_{\mathrm{H_2}}$ عبارة عن ضغط الهيدروجين. من بين المواقع المتاحة على السطح، يمثل θ $(0 \le \theta \le 1)$ النسبة المشغولة بذرات الهيدروجين. يمكن افتراض أن سرعة الامتصاص وانفصال الجسيمات من المعدن (desorption) كبيرة بالنسبة لعملية الامتصاص إلى داخل المادة $(r_1, r_2 \gg r_3)$ وأن θ تبقى ثابتة.

5pt **B.1**

r_3 can be expressed as:

يمكن تمثيل r_3 على النحو التالي:

$$r_3 = \frac{k_3}{1+\sqrt{\frac{1}{P_{\mathrm{H_2}}C}}} \qquad (5)$$

Express C using k_1 and k_2.

عبر عن C باستخدام k_1 و k_2.

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

وضعت عينة معدنية لها مساحة سطح $S = 1.0 \times 10^{-3}\ \mathrm{m^2}$ في وعاء بحجم 1 لتر ($1.0 \times 10^{-3}\ \mathrm{m^3}$) مع الهيدروجين ($P_{H_2} = 1.0 \times 10^2$ Pa). كثافة مواقع امتصاص ذرات الهيدروجين على السطح هي $N = 1.3 \times 10^{18}\ \mathrm{m^{-2}}$. تم الحفاظ على درجة حرارة السطح عند $T = 400$ K. عند استمرار التفاعل 1، يتناقص P_{H_2} بمعدل ثابت $v = 4.0 \times 10^{-4}\ \mathrm{Pa\ s^{-1}}$. افترض أن H_2 هو غاز مثالي وأن حجم عينة المعدن ضئيل.

3pt

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}].

احسب كمية ذرات الهيدروجين الممتصة بالمولات لكل وحدة مساحة من السطح ولكل وحدة زمنية، A [mol s^{-1} m^{-2}].

3pt

B.3

At $T = 400$ K, C equals $1.0 \times 10^2\ \mathrm{Pa^{-1}}$. **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}.

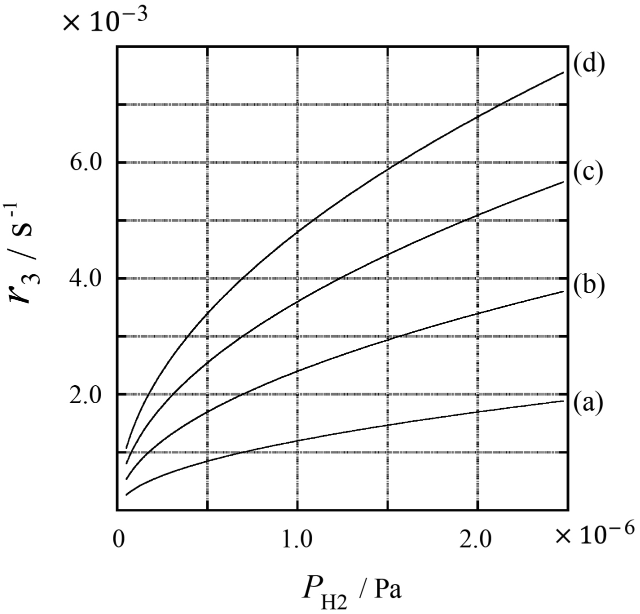
عند $T = 400$ K، تكون C مساوية لـ $1.0 \times 10^2\ \mathrm{Pa^{-1}}$. **احسب** قيمة k_3 عند 400 K. إذا لم تحصل على إجابة في الفقرة **B.2**، استخدم $A = 3.6 \times 10^{-7}$ mol s^{-1} m^{-2}.

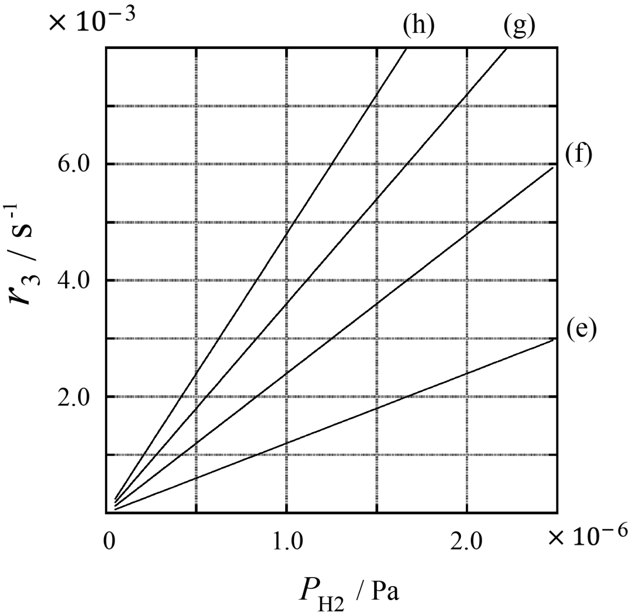
3pt

B.4

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

في درجة حرارة مختلفة، تكون $C = 2.5 \times 10^3\ \mathrm{Pa^{-1}}$ و $k_3 = 4.8 \times 10^{-2}\ \mathrm{s^{-1}}$. **اختر** شكل المنحنى من (a)–(h) لدالة r_3 بالنسبة لمتغير P_{H_2} عند هذه الدرجة من الحرارة.





Hydrogen at a Metal Surface

Part A

A.1 (6 pt)

(i)	(ii)	(iii)

A.2 (4 pt)

(i)	(ii)

Part B

B.1 (5 pt)

$C =$ ____________________

B.2 (3 pt)

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

B.3 (3 pt)

$k_3 =$ ______________ s^{-1}

B.4 (3 pt)

____

IChO
Problem 2
Cover sheet

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

Isotope Time Capsule

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

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

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

Let us consider the following equilibrium:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

A.3 **Calculate** $\Delta_{\mathrm{D_2}}$ 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

الكبسولة الزمنية للنظائر

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.

الكيانات الجزيئية التي تختلف فقط في التركيب النظيري، مثل CH_4 و CH_3D، تسمى isotopologues. يعتبر لهذه الجزيئات أن لها نفس الصفات الكيميائية. في الحقيقة، يوجد اختلاف طفيف.

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

افترض أن جميع المواد في هذا السؤال في الطور الغازي.

Let us consider the following equilibrium:

لننظر في تفاعل الاتزان التالي:

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

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

يزداد الإنتروبي، S، بزيادة عدد الحالات المجهرية للنظام، W:

$$S = k_\mathrm{B} \ln W \tag{2}$$

$W = 1$ 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, $W = 2^2 = 4$.

حيث $W = 1$ بالنسبة لـ $^{12}C^{16}O_2$ و $^{12}C^{18}O_2$. في المقابل، $W = 2$ لجزيء $^{12}C^{16}O^{18}O$ لأن ذرات الأكسجين متمايزة في هذا الجزيء. لأن يوجد جزيئين $^{12}C^{16}O^{18}O$ في الطرف الأيمن لمعادلة الاتزان 1، تكون $W = 2^2 = 4$.

8pt

A.1

The enthalpy change, ΔH, of eq. 3 is positive regardless of the temperature.

التغير في الإنثالبي، ΔH، للمعادلة 3 دائماً موجب بغض النظر عن درجة الحرارة.

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

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

احسب ثابت الاتزان، K، للمعادلة 3 عند درجة حرارة منخفضة جداً (فكر في $T \to 0$) وعند درجة حرارة مرتفعة جداً (فكر في $T \to +\infty$). افترض أن التفاعل لا يتغير عند درجات الحرارة هذه، وافترض أن ΔH تصبح قيمة ثابتة عند درجات الحرارة المرتفعة.

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

يمكن أن يتم تفسير ΔH لهذه العملية من خلال الاهتزازات الجزيئية.

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

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

عند درجة الحرارة 0 K، يعبر عن الطاقة الاهتزازية لجزيء ثنائي الذرة ذو التردد الاهتزازي ν [s^{-1}] بالتالي:

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

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

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

حيث k هو ثابت المرونة و μ هي الكتلة المختزلة ويمكن التعبير عنها بواسطة كتلة الذرتين في الجزيء ثنائي الذرة، m_1 و m_2، كالتالي:

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

A.2 8pt

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

يكون اهتزاز H_2 عند 4161.0 cm^{-1} عند التعبير عنه كعدد موجي. **احسب** ΔH للتفاعل التالي عند درجة حرارة 0 K بوحدة J mol^{-1}.

$$2\text{HD} \rightarrow \text{H}_2 + \text{D}_2 \tag{8}$$

Assume that:

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

افترض التالي:

- فقط الطاقة الاهتزازية تساهم في ΔH.
- قيمة k متطابقة لـ H_2، HD، و D_2.
- كتلة H هي 1 Da وكتلة D هي 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.

تعتمد النسبة المولارية لـ H_2، HD، و D_2 على درجة الحرارة للنظام عند الاتزان. هنا، تم تعريف Δ_{D_2} بالتغير في النسبة المولارية لـ D_2.

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

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 $T \to +\infty$.

حيث يمثل R_{D_2} النسبة $\frac{[D_2]}{[H_2]}$ في العينة و يمثل $R^*_{D_2}$ النسبة $\frac{[D_2]}{[H_2]}$ عند $T \to +\infty$. يجب ملاحظة أن توزيع النظائر يصبح عشوائياً عند $T \to +\infty$.

10pt

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.

احسب Δ_{D_2} من الوفرة الطبيعية لـ D عندما يكون التبادل النظيري في اتزان عند درجة حرارة تجعل ثابت الاتزان K في المعادلة 4 تساوي 0.300. افترض أن نسب الوفرة الطبيعية لـ D و H هي 1.5576×10^{-4} و $1 - 1.5576 \times 10^{-4}$، على الترتيب.

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:

بشكل عام، النسبة المولارية لـ isotopologue ذو تبديلين، أي يحتوي على ذرتين من النظائر الثقيلة في جزيء واحد، تزداد مع انخفاض درجة الحرارة. لننظر في النسبة المولارية لجزيئات CO_2 ذات الكتل الجزيئية 44 و 47، والتي موصوفة بـ $CO_2[44]$ و $CO_2[47]$ أدناه. القيمة Δ_{47} معرفة كالتالي:

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

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.

حيث يمثل R_{47} النسبة $\frac{[CO_2[47]]}{[CO_2[44]]}$ في العينة، ويمثل R^*_{47} النسبة $\frac{[CO_2[47]]}{[CO_2[44]]}$ عند $T \to +\infty$. الوفرة الطبيعية لذرات الكربون والأكسجين موضحة بالأسفل. اهمل النظائر الغير مذكورة.

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

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

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

ارتباط Δ_{47} بدرجة الحرارة موضح أدناه، حيث T عبارة عن درجة الحرارة بوحدة K:

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

9pt

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.

قيمة R_{47} لعالق أحفوري مأخوذ من قاع البحر في القطب الجنوبي كانت 4.50865×10^{-5}. **قدر** درجة الحرارة باستخدام قيمة R_{47}. تفسر درجة الحرارة هذه بأنها درجة حرارة الهواء خلال العصر الذي عاش فيه العالق. استخدم فقط النظير الأكثر شيوعاً لـ $CO_2[47]$ في حساباتك.

Isotope Time Capsule

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)

$\Delta_{\mathrm{D_2}} =$ ______________________

A.4 (9 pt)

$T =$ ____________________ K

IChO
Problem 3
Cover sheet

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

Lambert–Beer Law?

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

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

Part A

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

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

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

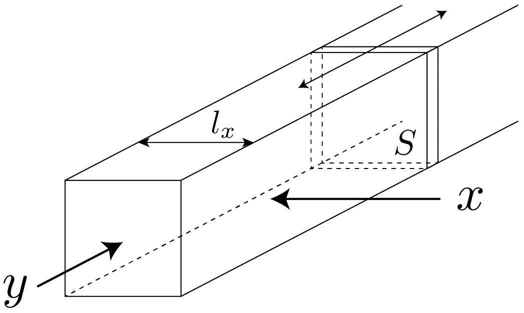
A.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. **Determine** the ratio $\varepsilon_{\mathrm{HA}}/\varepsilon_{\mathrm{A}^-}$, where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

Part B

Let us consider the following equilibrium in the gas phase.

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

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



Use the following definitions if necessary.

	Initial state		After equilibrium	
	D	M	D	M
Partial pressure	P	0	p_D	p_M
Amount in moles	n_0	0	n_D	n_M
Volume	V_0		V	

B.1 The absorbance of the gas at λ_B1 measured from direction x ($l = l_x$) was A_B1 both at the initial state and after the equilibrium. **Determine** the ratio $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ at λ_B1, where ε_D and ε_M represent the absorption coefficients of D and of M, respectively. 6pt

B.2 The absorbance of the gas at λ_B2 measured from direction y was A_B2 both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). **Determine** the ratio $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ at λ_B2. 6pt

قانون بير-لامبرت؟

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.

في هذا السؤال، اهمل امتصاص الخلية والمذيب. تم الحفاظ على درجات الحرارة لكل المحاليل والغازات عند 25 °C.

A Part

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:

تم تحضير محلول مائي **X** باستخدام HA و NaA. تراكيز $[A^-]$، $[HA]$، و $[H^+]$ في محلول **X** هي 1.00×10^{-2} mol L^{-1}، 1.00×10^{-3} mol L^{-1} و 1.00×10^{-4} mol L^{-1}، على الترتيب، والتي مرتبطة ببعضها البعض من خلال تفاعل الاتزان حمض-قاعدة التالي:

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

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.

طول المسار البصري هو l في الفقرة A من هذا السؤال. اهمل تغير الكثافة عند التخفيف. افترض عدم حدوث أي تفاعل كيميائي عدا التفاعل 1.

A.1 10pt

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.

كان امتصاص المحلول **X** هو A_1 عند الطول الموجي λ_1. بعد ذلك، تم تخفيف المحلول **X** إلى أن أصبح ضعف حجمه الابتدائي بإضافة حمض الكلور ذو الرقم الهيدروجيني pH = 2.500. بعد التخفيف، لا زال امتصاص المحلول A_1 عند λ_1. **حدد** النسبة $\varepsilon_{HA}/\varepsilon_{A^-}$، حيث يمثل ε_{HA} و ε_{A^-} معامل امتصاص HA و A^-، على الترتيب، عند λ_1.

B Part

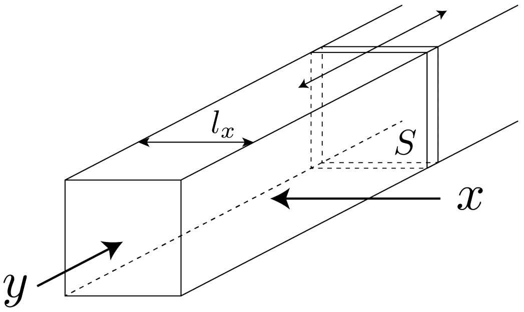
Let us consider the following equilibrium in the gas phase.

لنفكر في الاتزان التالي في الطور الغازي:

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \qquad (2)$$

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.

تم ملء غاز نقي D في وعاء متوازي مستطيلات ذو جدار متحرك شفاف بمقطع عرضي S (انظر الشكل في الأسفل) عند ضغط P، ويبقى الضغط ثابتاً عند P حتى عند الاتزان. امتصاصية الغاز هي $A = \varepsilon(n/V)l$ حيث تمثل ε معامل الامتصاص، و n كمية الغاز بالمولات، و V حجم الغاز، و l طول المسار البصري. افترض أن كل مكونات المزيج الغازي عبارة عن غازات مثالية.



Use the following definitions if necessary.

استخدم التعاريف التالية عند الحاجة.

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

6pt **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.

تم حساب امتصاصية الغاز عند λ_{B1} من اتجاه المحور x (أي $l = l_x$) وكانت A_{B1} عند الحالة الابتدائية وعند الاتزان كذلك. **حدد** النسبة $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ عند λ_{B1}، حيث تمثل ε_{D} و ε_{M} معاملات امتصاص D و M، على الترتيب.

6pt **B.2**

The absorbance of the gas at λ_{B2} measured from direction y was A_{B2} both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). **Determine** the ratio $\varepsilon_D/\varepsilon_M$ at λ_{B2}.

تم حساب امتصاصية الغاز عند λ_{B2} من اتجاه المحور y وكانت A_{B2} عند الحالة الابتدائية ($l = l_{y0}$) وكذلك بعد الاتزان ($l = l_y$). **حدد** النسبة $\varepsilon_D/\varepsilon_M$ عند λ_{B2}.

Lambert–Beer Law?

Part A

A.1 (10 pt)

(Continued on the next page)

A.1 (cont.)

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

Part B

B.1 (6 pt)

$\varepsilon_D/\varepsilon_M =$ ____________________

B.2 (6 pt)

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

IChO
Problem 4

Cover sheet

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

The Redox Chemistry of Zinc

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

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

Part A

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

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

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

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

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

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

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

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

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

Part B

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

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

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

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

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

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

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

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

كيمياء اكسدة-اختزال الزنك

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.

يستخدم الزنك منذ فترة طويلة كسبائك لمواد النحاس والفولاذ. يتم فصل الزنك الموجود في مياه الصرف الصناعي عن طريق الترسيب لانتزاع السموم من الماء، ويتم اختزال الراسب المتحصل عليه لاستردداه وإعادة استخدامه كزنك فلزي.

A Part

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

اتزان الذوبانية لهيدروكسيد الزنك $Zn(OH)_2(s)$ عند 25 °C وثوابت الاتزان الموافقة معطاة في المعادلات 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.

كما تعطى ذوبانية الزنك، S، (تركيز الزنك في محلول مائي مشبع) في المعادلة 5.

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

6pt **A.1**

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

عند الوصول الى حالة الاتزان في المعادلات 1-4 ، **احسب** المجال في قيم pH بحيث يكون تركيز $[Zn(OH)_2(aq)]$ هو الأعلى بين $[Zn^{2+}(aq)]$ و $[Zn(OH)_2(aq)]$ و $[Zn(OH)_4^{2-}(aq)]$.

5pt **A.2**

A saturated aqueous solution of $Zn(OH)_2(s)$ 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.

تم تحضير محلول مائي مشبع من $Zn(OH)_2(s)$ ذو قيمة pH=7.00 وتم ترشيحه. ثم أضيف NaOH إلى هذه الرشاحة لزيادة قيمة pH إلى 12.00. **احسب** النسبة المئوية المولارية للزنك المترسب عند ازدياد pH من 7.00 الى 12.00. تجاهل التغيرات الحاصلة في الحجم ودرجة الحرارة.

B Part

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

بعد ذلك، يتم تسخين هيدروكسيد الزنك الذي تم استرداده للحصول على أكسيد الزنك وفقًا للتفاعل أدناه:

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

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

يتم بعد ذلك اختزال أكسيد الزنك إلى الزنك الفلزي بالتفاعل مع الهيدروجين:

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

4pt **B.1**

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

حتى يستمر التفاعل (7) عند ضغط هيدروجين 1 bar، لذلك من الضروري خفض الضغط الجزئي لبخار الماء المتولد. **احسب** الحد الأعلى للضغط الجزئي لبخار الماء الذي يسمح باستمرار التفاعل (7) عند 300 °C . حيث تكون طاقات تكوين جيبس لأكسيد الزنك وبخار الماء عند 300 °C و 1 bar هما على التوالي، $\Delta G_{\mathrm{ZnO}}(300^\circ\mathrm{C}) = -2.90 \times 10^2$ kJ mol^{-1} و $\Delta G_{\mathrm{H_2O}}(300^\circ\mathrm{C}) = -2.20 \times 10^2$ kJ mol^{-1} .

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°.

يستخدم الزنك المعدني كمادة قطب سالب (انود) لبطاريات هواء–فلز. يتكون القطب من Zn و ZnO . يستخدم في تفاعل الاكسدة-الاختزال التالي لتوليد كهرباء بقوة دافعة كهربائية (e.m.f) عند 25 °C وضغط 1 bar، E°.

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

3pt **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.

تم تفريغ بطارية زنك-هواء عند 20 mA لمدة 24 ساعة. احسب التغير في كتلة القطب السالب (الانود) للبطارية.

Mt. Fuji

5pt **B.3**

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

بفرض ان التغير في e.m.f في بطارية زنك-هواء يعتمد على الوسط المحيط. **احسب** قيمة e.m.f عند قمة جبل فوجي، حيث درجة الحرارة والارتفاع $-38\,^\circ$C (فبراير) و 3776 m، على التوالي. ضغط الغلاف الجوي يمثل بالعلاقة

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

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

عند ارتفاع $h\,[\text{m}]$ ودرجة حرارة $T\,[^\circ\text{C}]$. تكون النسبة المولية للأكسجين في الغلاف الجوي 21% . والتغير في طاقة جيبس للتفاعل (8) هو $\Delta G_{\text{ZnO}}(-38^\circ\text{C}) = -3.26 \times 10^2$ kJ mol^{-1} عند $-38\,^\circ$C و 1 bar.

9pt **B.4**

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

احسب التغير في طاقة جيبس للتفاعل (6) عند $25\,^\circ$C . لاحظ أن قيم جهود الاختزال القياسية ، $E^\circ(\text{Zn}^{2+}/\text{Zn})$ و $E^\circ(\text{O}_2/\text{H}_2\text{O})$ عند $25\,^\circ$C و 1 bar معطاة في (10) و (11)، على التوالي.

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

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

The Redox Chemistry of Zinc

Part A

A.1 (6 pt)

______ $< \text{pH} <$ ______

A.2 (5 pt)

______________ %

Part B

B.1 (4 pt)

$p_{H_2O}=$ ______________ bar

B.2 (3 pt)

______________ g

B.3 (5 pt)

______________ V

B.4 (9 pt)

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

SAU-1 C-5 C-1

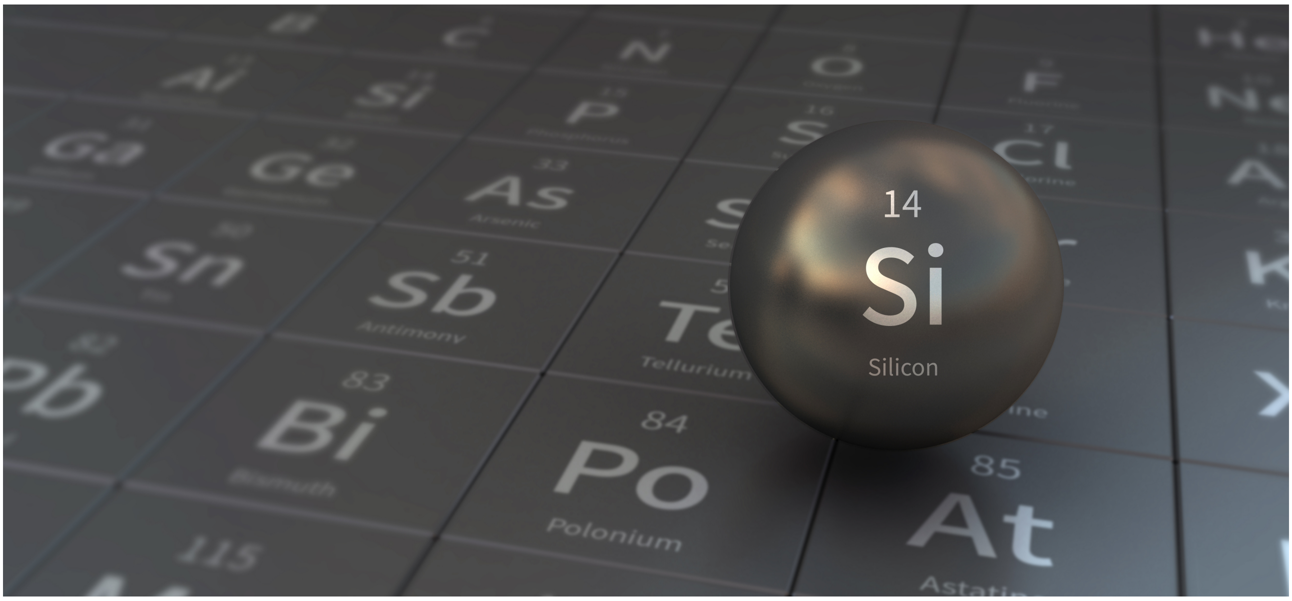
IChO
Problem 5

Cover sheet

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

Mysterious Silicon

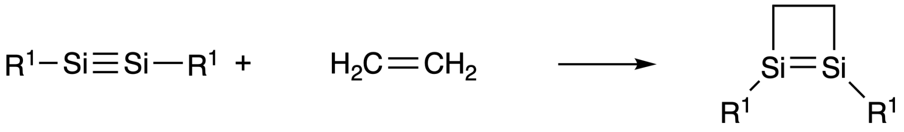
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



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

Part A

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



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

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

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

A.1	<u>**Draw**</u> 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	<u>**Calculate**</u> 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

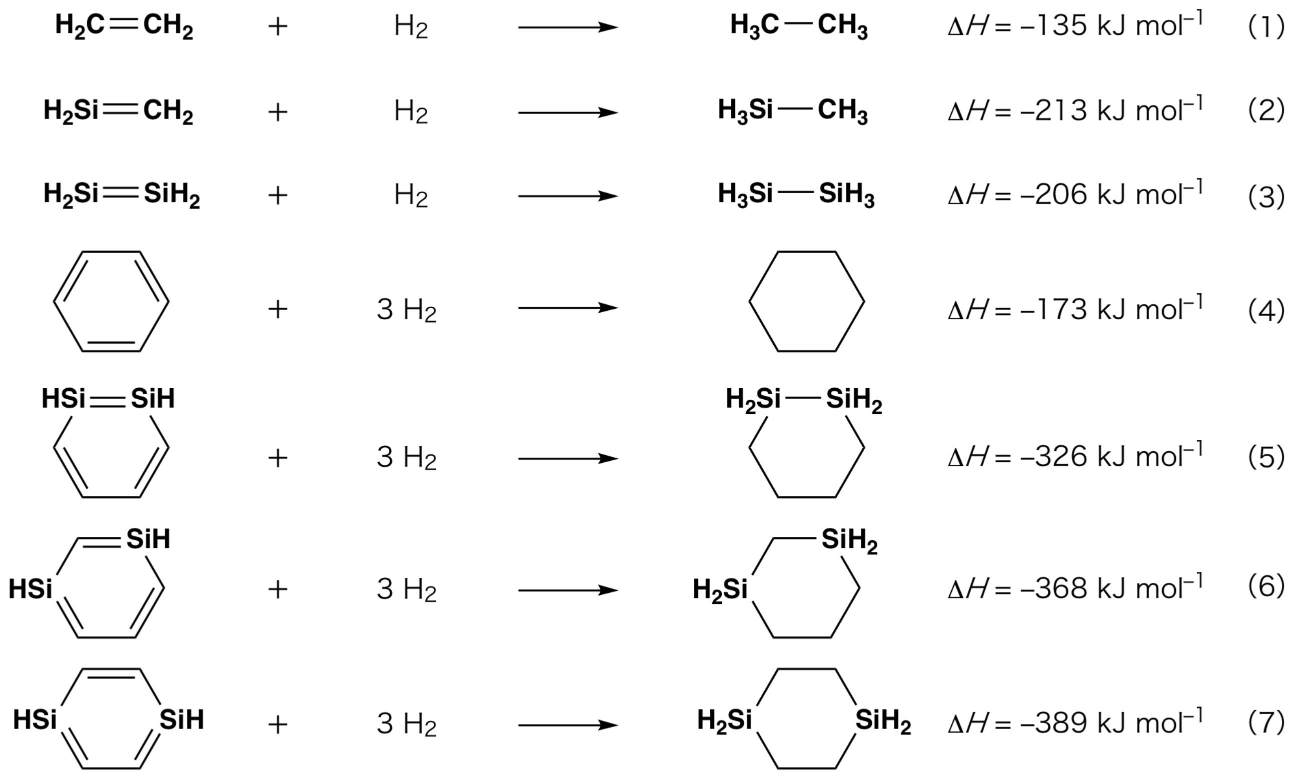


Fig. 1

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:

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

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

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

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

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

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

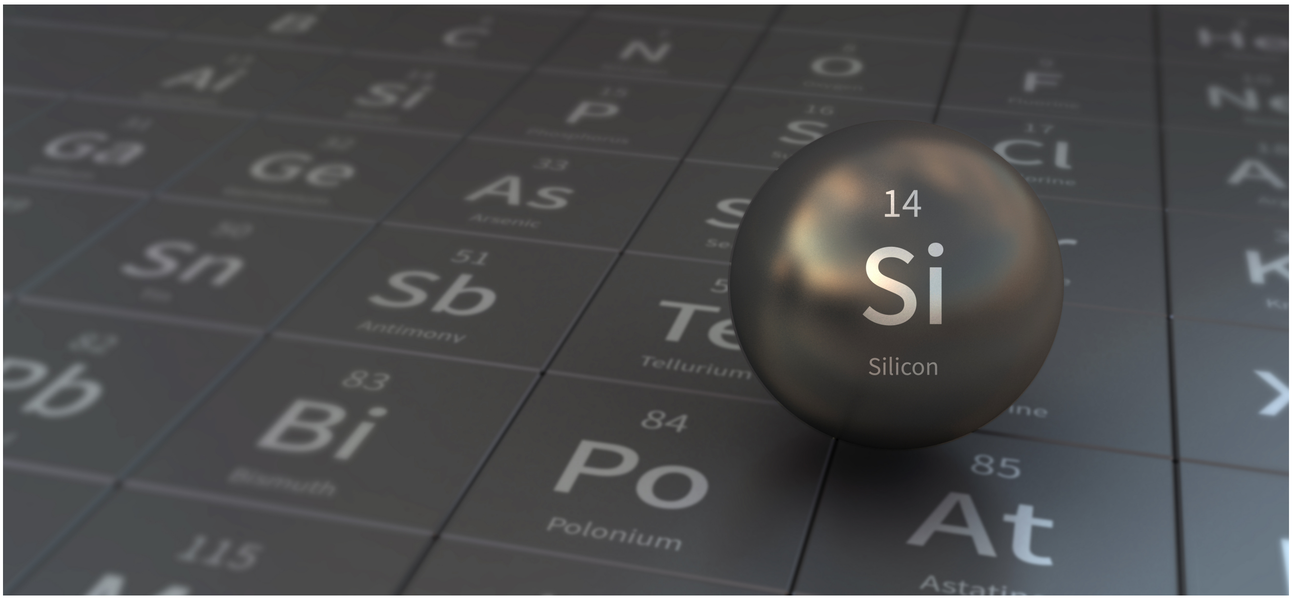
It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

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

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

السيلكون الغامض

total the of % 12								
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.

على الرغم من أن السيليكون هو أيضًا عنصر من المجموعة 14 مثل الكربون ، إلا أن خصائصه تختلف بشكل كبير.

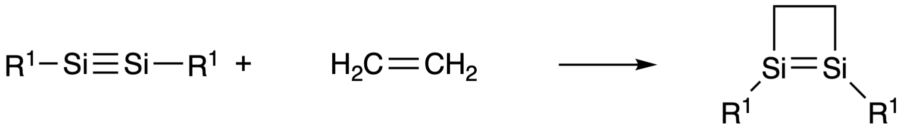
A Part

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

على عكس الرابطة الثلاثية بين الكربون والكربون ، فإن الرابطة الثلاثية للسيليكون والسيليكون في مركب تمت صياغته على أنه $R^1{-}Si \equiv Si{-}R^1$

ring بديل عضوي:R) شديد التفاعل. على سبيل المثال ، يتفاعل مع الإيثيلين لتشكيل منتج حلقي يحتوي على membered-four

.



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

عندما يتم معالجة $R^1–Si \equiv Si–R^1$بألكين $R^2–C \equiv C–R^2$ يتشكل مركب four-membered-ring **A** كوسيط أولي. تفاعل إضافي لجزيء آخر من $R^2–C \equiv C–R^2$ مع A يوفر أيزومرين **B** و **C** ، وكلاهما يحتوي على هياكل مترافقة دورية تشبه البنزين ، وتسمى “ disilabenzenes ” التي تحتوي على six-membered-ring ويمكن صياغتها $(R^1–Si)_2(R^2–C)_4$

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

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

يُظهر تحليل ^{13}C NMR للهياكل العظمية six-membered-ring المتقابلة Si_2C_4 إشارتين لـ **B** وإشارة واحدة لـ **C**.

9pt **A.1**

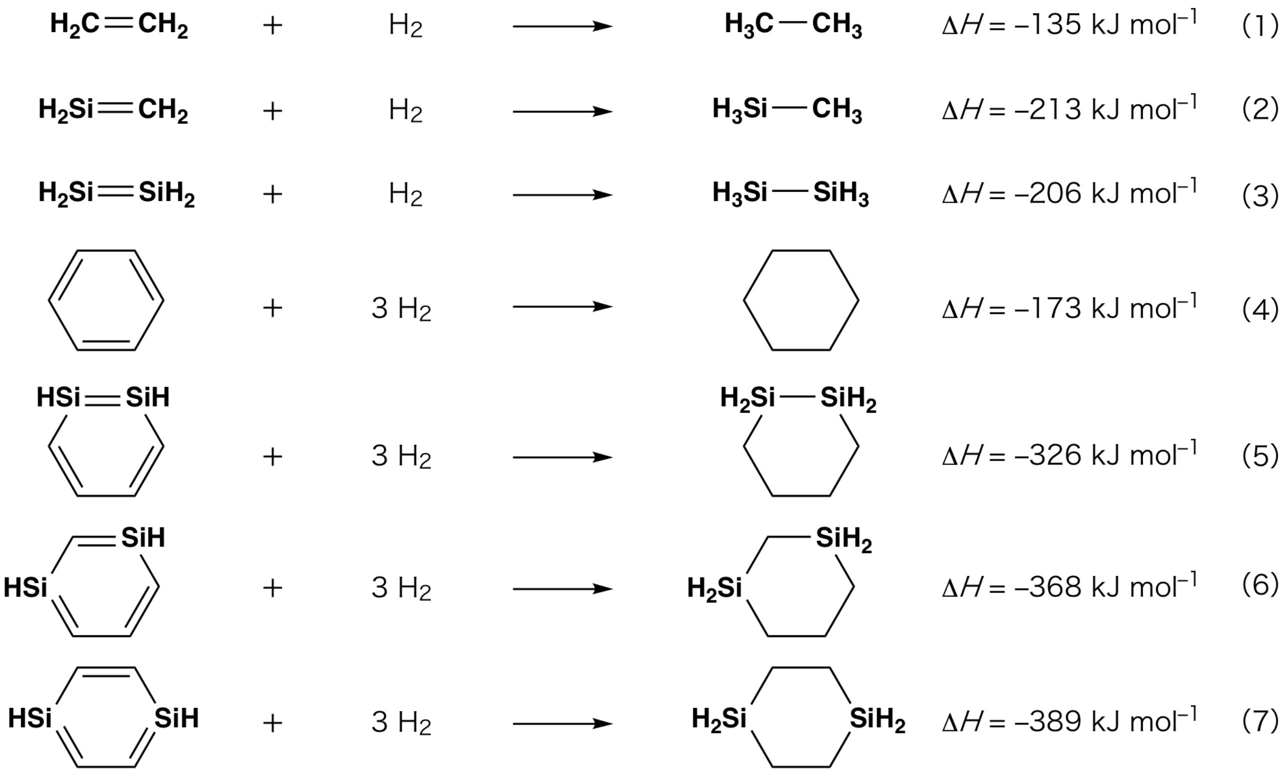
Draw the structural formulae of **A**, **B**, and **C** using R^1, R^2, Si, and C, with one of the possible resonance structures.

ارسم الصيغ البنائية لـ **A**, **B** و **C** باستخدام R^1, R^2, Si و C , مع أحد هياكل الرنين الممكنة

7pt **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).

احسب طاقة التثبيت العطري (ASE) للبنزين و **C** (في حالة $R^1 = R^2 = H$) كقيم موجبة ، مع الأخذ في الاعتبار تغير المحتوى الحراري في بعض تفاعلات الهدرجة للأنظمة غير المشبعة الموضحة أدناه (الشكل 1).


$H_2C{=}CH_2$ + H_2 → $H_3C{-}CH_3$ $\Delta H = -135$ kJ mol^{-1} (1)
$H_2Si{=}CH_2$ + H_2 → $H_3Si{-}CH_3$ $\Delta H = -213$ kJ mol^{-1} (2)
$H_2Si{=}SiH_2$ + H_2 → $H_3Si{-}SiH_3$ $\Delta H = -206$ kJ mol^{-1} (3)
+ 3 H_2 → $\Delta H = -173$ kJ mol^{-1} (4)
HSi SiH + 3 H_2 → H_2Si SiH_2 $\Delta H = -326$ kJ mol^{-1} (5)
HSi SiH + 3 H_2 → H_2Si SiH_2 $\Delta H = -368$ kJ mol^{-1} (6)
HSi SiH + 3 H_2 → H_2Si SiH_2 $\Delta H = -389$ kJ mol^{-1} (7)

1 Fig.

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.

عندما يتم تسخين محلول xylene من **C** ، فإنه يخضع لأزمرة لإعطاء خليط توازن من المركبات **D** و **E**. النسبة المولية هي

D : **E** = 1 : 40.0 at 50.0 ˚C and **D** : **E** = 1 : 20.0 at 120.0 ˚C.

6pt

A.3

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

احسب ΔH للتحويل من **D** إلى **E** . افترض أن ΔH لا تعتمد على درجة الحرارة

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.

تستمر الأزمرة من **C** إلى **D** و **E** عبر تحويلات من π-bonds إلى σ-bonds دون كسر أي σ-bonds . كشف تحليل NMR ^{13}C عن إشارة واحدة للهيكل العظمي Si_2C_4 لـ **D** و إشارتين لتلك الخاصة بـ **E**. الهيكل العظمي لـ **D** لا يحتوي على أي three-membered-ring , بينما يحتوي **E** على اثنين three-membered-rings تشترك في الحافة.

10pt

A.4

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

ارسم الصيغة البنائية لـ **D** و **E** باستخدام R^1, R^2, Si , و C

B Part

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.

السيليكون قادر على تكوين مركبات عالية التنسيق

(> four substituents)

مع عناصر كهربية مثل الفلور. نظرًا لأن الفلوريدات المعدنية غالبًا ما تستخدم كواشف للفلورة ، فإن فلوريدات السيليكون عالية التنسيق تعمل أيضًا ككواشف فلورة.

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

تفاعلات الفلورة لـ CCl_4 باستخدام Na_2SiF_6 تتم على النحو التالي

standardization **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).

التحضير:

محلول مائي **F** : 0.855 g من Na_2SiF_6 (188.053 g mol^{-1}) مذاب في الماء (الحجم الكلي: 200mL).

محلول مائي **G** : 6.86 g من $Ce_2(SO_4)_3$ (568.424 g mol^{-1}) مذاب في الماء (الحجم الكلي: 200mL)

· 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 $Si(OH)_4$.

الطريقة:

معايرة الترسيب لمحلول **F** 50.0 mL عن طريق إضافة محلول **G** بالتنقيط في وجود xylenol البرتقالي ، والذي ينسق إلى Ce^{3+} كدليل. بعد إضافة 18.8 mL من المحلول **G** ، يتغير لون المحلول من الأصفر إلى الأرجواني. الراسب المتكون هو مركب ثنائي يحتوي على Ce^{3+} ومركب السيليكون الناتج الوحيد هو $Si(OH)_4$

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

-
- **تفاعل ال CCl_4 مع ال Na_2SiF_6:**

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

(خسائر المادة على سبيل المثال ، التبخر لا يكاد يذكر أثناء العمليات التالية.)

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.

تمت إضافة (x [g]) Na_2SiF_6 إلى CCl_4 500.0 g وتم تسخينها إلى 300 درجة مئوية في وعاء التفاعل المحكم الغلق والمقاوم للضغط. تمت إزالة Na_2SiF_6 الغير متفاعل و NaCl المتولد عن طريق الفلترة . وتم تخفيف المادة المفلترة إلى حجم إجمالي قدره 1.00 L مع CCl_4 (محلول **H**) وأظهرت أطياف ^{29}Si و^{19}F NMR لمحلول **H** SiF_4 كمركب السيليكون الوحيد. في "طيف ^{19}F NMR ، بالإضافة إلى SiF_4 ، لوحظت الإشارات المقابلة لـ $CFCl_3$, CF_2Cl_2 , CF_3Cl و CF_4 (الجدول 1) نسب التكامل في طيف ^{19}F NMR متناسبة مع عدد مولات نوى الفلور.

1 Table

^{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:

SiF_4 يتم تحليله لتشكيل H_2SiF_6 وفقًا لما يلي:

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

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

محلول **H** 10 mL تمت إضافته لكمية زائدة من الماء , مما أدى إلى التحلل المائي الكامل لـSiF_4. بعد الفصل ، تم معادلة H_2SiF_6 ، المتولد من التحلل المائي في المحلول المائي وتحويله بالكامل إلى Na_2SiF_6 (محلول مائي **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).

تم إذابة الراسب Na_2SiF_6 الغير متفاعل و NaCl ، والذي تمت إزالته بالفلترة في الخطوة الأولية (تحته خط) ، تمامًا في الماء لإعطاء محلول مائي (محلول **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:

بعد ذلك, معايرة ترسيب إضافية باستخدام محلول **G** تم تنفيذها, ونقطة نهاية المعايرة مع **G** كانت كما يلي:

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

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

للمحلول **J** (الكمية الكاملة): 61.6 mL.

لكل 100 mL من محلول **K**: 44.4 mL .

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

وتجدر الإشارة هنا إلى أن تعايش NaCl أو SiO_2 ليس له أي تأثير على معايرة الترسيب.

15pt **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.

احسب كتلة NaCl المنتجة في وعاء التفاعل (المعلومات تحتها خط). **واحسب** الكتلة(x [g]) من Na_2SiF_6 المستخدمة كمواد أولية.

8pt **B.3**

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

77.8 % من CCl_4 ، المستخدمة كمواد أولية لم تتفاعل. **احسب** كتلة CF_3Cl المتولدة.

Mysterious Silicon

Part A

A.1 (9 pt)

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

A.2 (7 pt)

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

A.3 (6 pt)

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

A.4 (10 pt)

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

Part B

B.1 $(5\ \mathrm{pt})$

B.2 $(15\ \mathrm{pt})$

(Continued on the next page)

B.2 (cont.)

NaCl ： g, Na_2SiF_6 ： g

B.3 (8 pt)

CF_3Cl : ____________________ g

IChO
Problem 6
Cover sheet

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

The Solid-State Chemistry of Transition Metals

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

Volcano at Sakurajima island

Part A

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

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

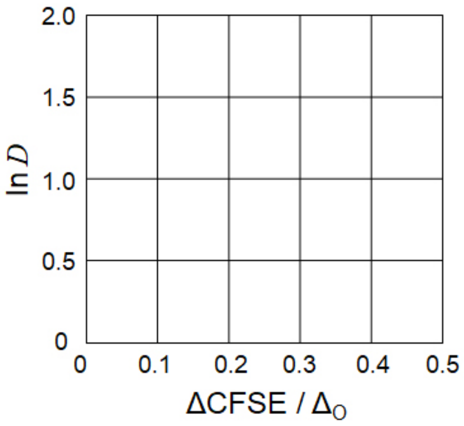
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of $Cr^{2+}$and Mn^{2+} as examples.

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

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

A.1 **Calculate** $|\text{CFSE}^O - \text{CFSE}^T|$ = ΔCFSE 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 ΔCFSE / Δ_O in the Cartesian coordinate system shown below.
Estimate D for Co^{2+}. 3pt



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

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

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

Part B

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

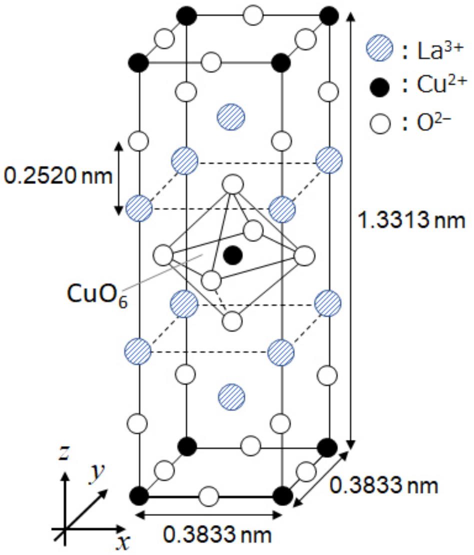


Fig. 1

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

B.1	**Write** the chemical formulae for **A** and **B**.	6pt

B.2	**Calculate** l_x and l_z using Fig. 1.	4pt

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

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

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

Part C

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

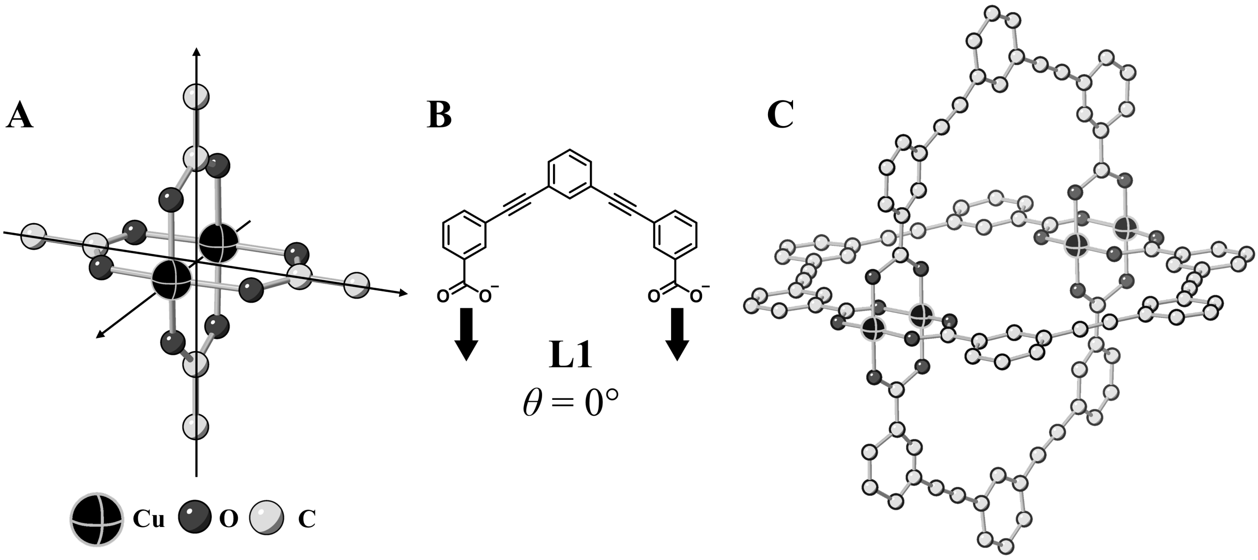
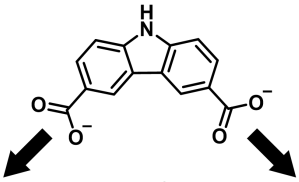


Fig. 2

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



L2

$\theta = 90°$

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

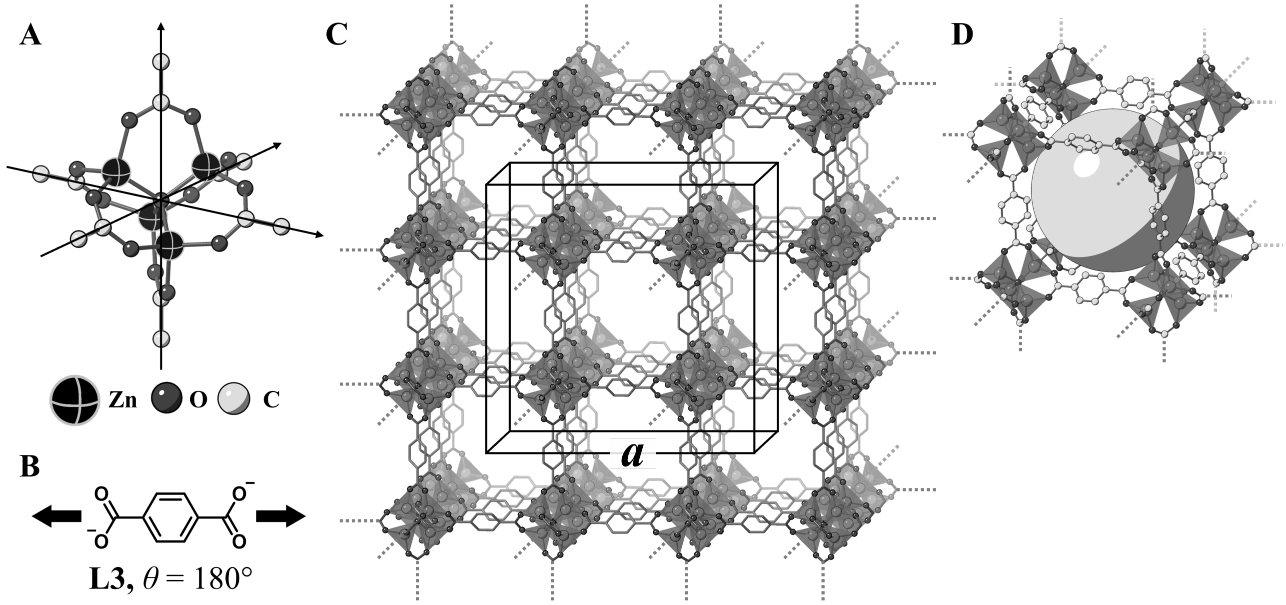


Fig. 3

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

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

كيمياء الحالة الصلبة للفلزات الانتقالية

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

A Part

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:

اليابان هي واحدة من الدول التي لديها أكبر عدد من البراكين في جميع أنحاء العالم. عندما تتبلور معادن السيليكات من الصهارة، يحصل اندماج جزء من أيونات المعادن الانتقالية (M^{n+}) في الصهارة في معادن السيليكات. تكون M^{n+} المدروسة في هذه المسألة مرتبطة تناسقيا مع أيونات الأكسيد (O^{2-}) وتشكل عدد تناسقي أربعة في شكل رباعي الأوجه (T_d) في الصهارة وتشكل عدد تناسقي ستة في شكل ثماني الوجوه (O_h) في معادن السيليكات، وكلاهما يظهر تكوين غزل الكتروني مرتفع. يمكن التعبير عن معامل التوزيع للايون M^{n+} بين معادن السيليكات والصهارة، D، بالعلاقة:

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

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

حيث $[M]_s$ و $[M]_l$ تمثل تراكيز M^{n+} في كل من معادن السيليكات والصهارة، على التوالي. يوضح الجدول أدناه قيم D لـ Cr^{2+} و Mn^{2+} كأمثلة.

	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.

بفرض Δ_O و $CFSE^O$ يمثلان طاقة الانقسام لمدارات- d للأيون M^{n+} وطاقة استقرار المجال البلوري في مجال O_h، على التوالي. وبفرض Δ_T و $CFSE^T$ يمثلانهما في مجال T_d .

6pt

A.1

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

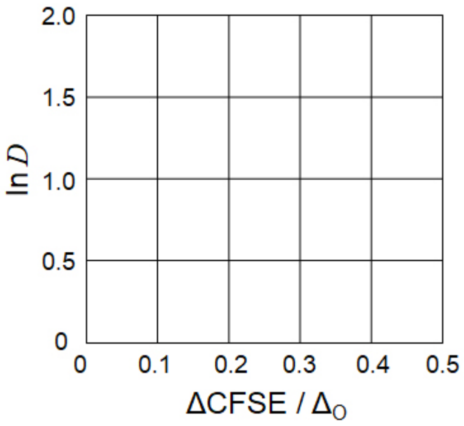
احسب $|CFSE^O - CFSE^T| = \Delta CFSE$ بدلالة المصطلحات Δ_O لكل من Cr^{2+} و Mn^{2+} و Co^{2+}؛
افترض $\Delta_T = 4/9\Delta_O$.

3pt

A.2

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

لوحظ وجود علاقة خطية من خلال رسم ln$D$ مقابل $\Delta CFSE/\Delta_O$ في نظام الإحداثيات الديكارتية الموضح أدناه.
عيِن D لأيون 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.

تتبلور أكاسيد المعادن MO (حيث المعدن يمثل أي من المعادن التالية Ca، Ti، V، Mn أو Co) على هيئة بلورة الملح الصخري حيث يتبنى M^{n+} الشكل الهندسي O_h مع تركيب إلكتروني مرتفع الغزل. ترتبط انثالبية الشبكة البلورية لهذه الأكاسيد بشكل أساسي بتأثيرات كولوم بين الشحنات التي تعتمد على أساس نصف قطر وشحنة الأيونات وبعض المساهمات من CFSE للأيون M^{n+} في مجال O_h.

3pt

A.3

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

اختر المجموعة المناسبة من انثالبيات الشبكة البلورية [kJ mol^{-1}] من أحد الخيارات (a) إلى (f).

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

B Part

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}).

مزيج أكسيد **A** ، يحتوي على La^{3+} و Cu^{2+}، يتبلور في خلية وحدة رباعية كما هو موضح في Fig.1. في الشكل الثماني $[CuO_6]$، يكون طول Cu–O على طول المحور z (l_z) ، أطول من تلك على المحور x (l_x) ، ويتشوه $[CuO_6]$ من الشكل المنتظم O_h. هذه التشوهات تؤدي الى ازالة التساوي الطاقي لمدارات e_g ($d_{x^2-y^2}$ و d_{z^2})

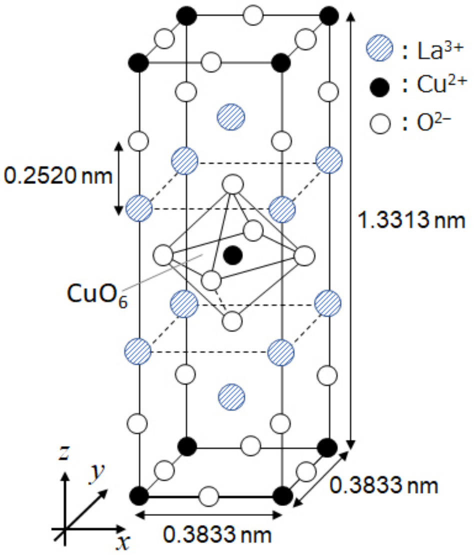


Fig. 1

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.

يمكن تشييد **A** عن طريق التحلل الحراري (الانحلال الحراري) للمعقد **B** ، والذي يتكون عن طريق خلط كلوريدات الفلزات في محلول أمونيا مائي مخفف يحتوي على حمض سكواريك (squaric acid) $C_4H_2O_4$، أي حمض ثنائي. يُظهر سلوك الانحلال الحراري لـ **B** في الهواء الجاف فقدًا في الوزن بنسبة 29.1% حتى 200 درجة مئوية بسبب فقد ماء التبلور ، متبوعًا بفقدان آخر للوزن حتى الوصول إلى 700 درجة مئوية بسبب إطلاق CO_2. إجمالي فقدان الوزن أثناء تكوين **A** من **B** هو 63.6% . وتجدر الإشارة إلى أنه يتم إطلاق الماء و CO_2 فقط في تفاعل الانحلال الحراري.

B.1 6pt

__**Write**__ the chemical formulae for **A** and **B**.

__**اكتب**__ الصيغة الكيميائية لكل من **A** و **B** .

4pt **B.2**

Calculate l_x and l_z using Fig. 1.

احسب l_x و l_z باستخدام 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.

من اجل Cu^{2+} في الشكل الثماني المشوه $[CuO_6]$ في **A** من Fig.1 ، **اكتب** أسماء المدارات المنقسمة e_g ($d_{x^2-y^2}$ و d_{z^2}) في (i) و (ii) ، **وارسم** التوزيع الالكتروني في المربع المنقط في ورقة إجابتك.

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.

يعتبر **A** مادة عازلة. ولدى استبدال أيون واحد من La^{3+} بأيون واحد من Sr^{2+} يظهر بالمقابل ثقب واحد في الشبكة البلورية التي يمكنها من توصيل الكهرباء. نتيجة لذلك، أظهر **A** الذي تم تطعيمه بأيون-Sr^{2+} موصلية فائقة تحت 38 K . عندما حدث تفاعل استبدال لـ **A** ، يتكون 2.05×10^{27} من الثقوب لكل متر مكعب.

4pt

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.

احسب النسبة المئوية لأيون Sr^{2+} المستبدل في مواقع أيون La^{3+} بنسبة مولية في تفاعل الاستبدال. لاحظ أن تكافؤات الأيونات المكونة والبنية البلورية لم تتغير أثناء تفاعل الاستبدال.

C Part

$Cu_2(CH_3CO_2)_4$ 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.

يتكون $Cu_2(CH_3CO_2)_4$ من أربع ليجاندات $CH_3CO_2^-$ مترابطة تناسقيا إلى اثنين من Cu^{2+} الشكل Fig.2A. يُظهر $Cu_2(CH_3CO_2)_4$ مستويات عالية من التناظر الهيكلي، مع محورين يمران عبر ذرات الكربون في الليجاندات الاربعة $CH_3CO_2^-$ ومحور يمر عبر أيونين من Cu^{2+}، وجميع المحاور موجهة بشكل متعامد بالنسبة لبعضها البعض. عند استخدام ليجاند ثنائي الكربوكسيل (dicarboxylate) بدلاً من $CH_3CO_2^-$، يتكون ”معقد ذو فجوات قفص“. يتكون معقد القفص $Cu_4(\mathbf{L1})_4$ من مستوي من ثنائي كربوكسيلات **L1** الشكل Fig.2B و Cu^{2+} الشكل Fig.2C. تحدد الزاوية θ بين اتجاهات التناسق لاثنين من الكربوكسيلات، المشار إليها بواسطة الأسهم في الشكل Fig.2B ، تركيب بنية معقد القفص. θ تساوي 0 درجة لـ **L1**. لاحظ أن ذرات الهيدروجين غير موضحة في الشكل Fig.2.

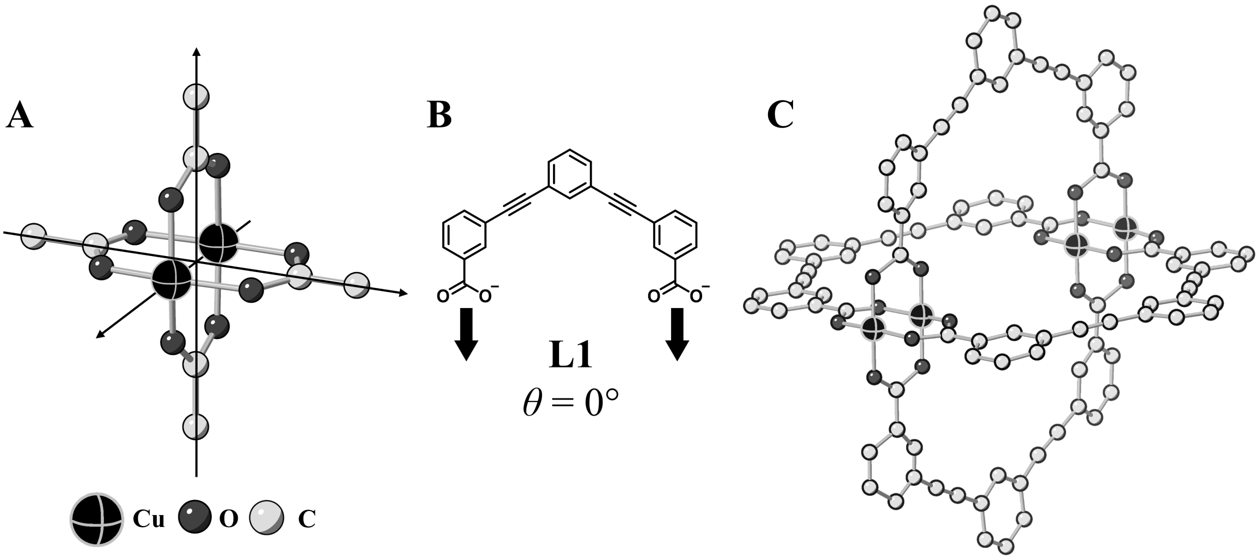


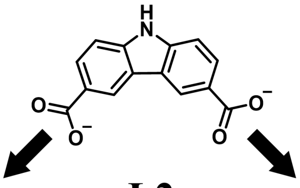
Fig. 2

5pt

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.

تم تثبيت الزاوية θ لثنائي كربوكسيلات المستوي **L2** الموضح أدناه عند زاوية 90 درجة.
إذا كان تركيب معقد القفص المتكون من **L2** وCu^{2+} هو $Cu_n(\mathbf{L2})_m$ ، **اذكر** أصغر مجموعة
من الاعداد الصحيحة لكل من n و m . افترض أن مجموعات CO_2^- لليجاند **L2** هي التي
ترتبط فقط برابطة تناسقية الى أيونات Cu^{2+}.



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 dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

يحتوي معقد الزنك $Zn_4O(CH_3CO_2)_6$، على أربع رباعيات السطوح من Zn^{2+} وستة من $CH_3CO_2^-$ وواحد من O^{2-} الشكل Fig.3A . في المعقد $Zn_4O(CH_3CO_2)_6$ يقع O^{2-} عند مركز نقطة الأصل، والمحاور الثلاثة التي تمر عبر ذرات الكربون في $CH_3CO_2^-$ متعامدة بالنسبة لبعضها البعض. عندما يتم استخدام p-benzenedicarboxylate (الشكل Fig.3B ، **L3** ، θ = 180) بدلاً من $CH_3CO_2^-$، ترتبط كلاسترات Zn^{2+} (المركبات العنقودية) ببعضها البعض لتشكيل مادة صلبة بلورية (**X**) والتي تسمى "بوليمر تناسقي مسامي" الشكل Fig3C . يكون تركيب **X** هو $[Zn_4O(\mathbf{L3})_3]_n$، وله هيكل بلوري مكعبي مع مسام بحجم النانو. يتم تمثيل أحد المسام على شكل كرة في الشكل Fig.3D ، ويتم تمثيل كل رباعي سطوح كلاستر Zn^{2+} على شكل متعدد السطوح رمادي غامق في الشكل Fig.3C و Fig.3D . لاحظ أن ذرات الهيدروجين غير موضحة في الشكل Fig.3.

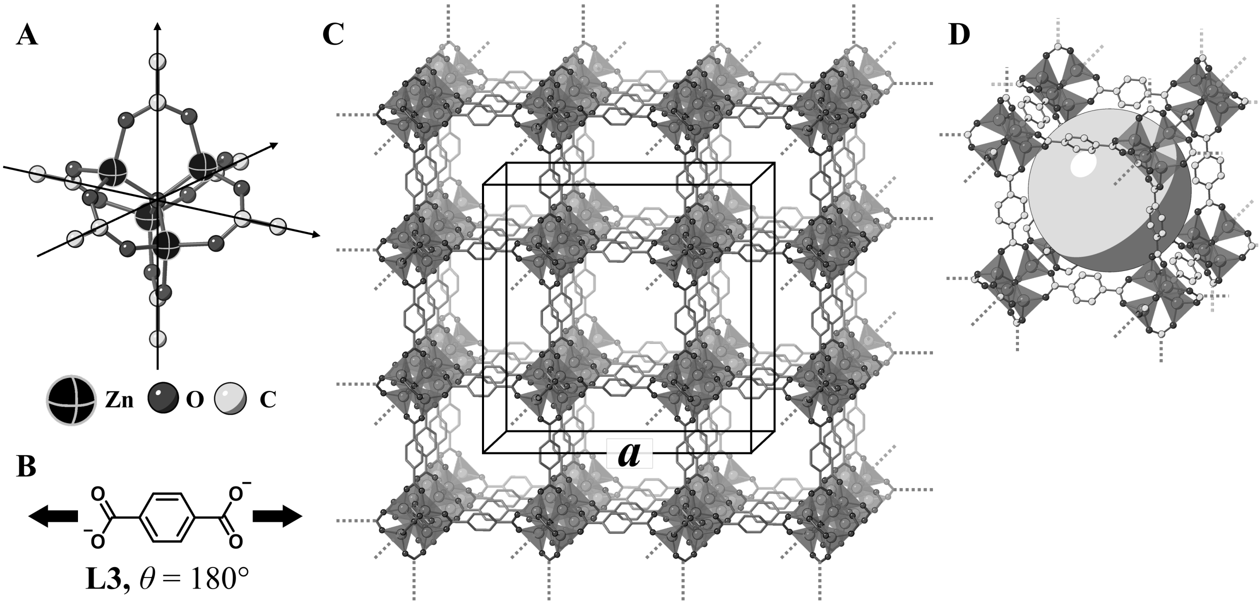


Fig. 3

5pt

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].

يحتوي **X** على خلية وحدة مكعبية طول ضلعها a الشكل Fig.3C وكثافة $0.592\ g\,cm^{-3}$.

احسب a بوحدة [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.

يحتوي **X** على عدد كبير من المسامات ، ويمكن لـ 1g من **X** استيعاب $3.0 \times 10^2\ mL$ من غاز CO_2 في المسام عند 1 bar و 25 درجة مئوية. **احسب** متوسط عدد الجزيئات من CO_2 لكل مسام واحد.

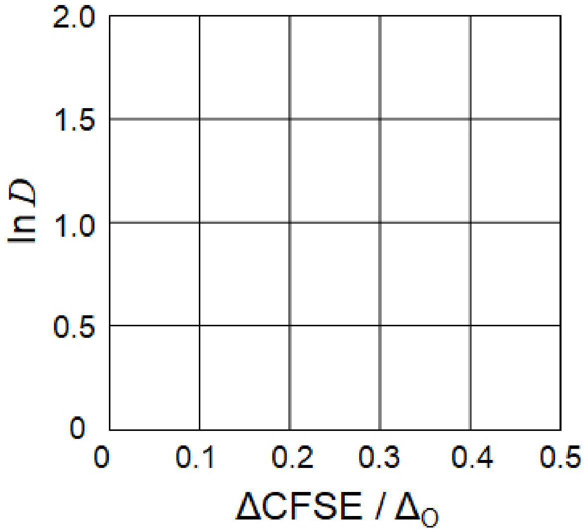
The Solid-State Chemistry of Transition Metals

Part A

A.1 (6 pt)

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

A.2 (3 pt)



D : ______________________

A.3 (3 pt)

____

Part B

B.1 (6 pt)

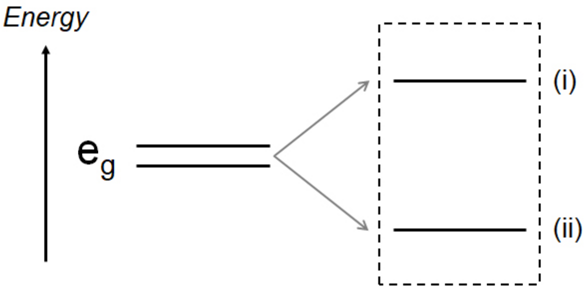
A : ____________________, B : ____________________

B.2 (4 pt)

$l_x =$ ____________________ nm, $l_z =$ ____________________ nm

B.3 (4 pt)

(i) : ______________________, (ii) : ______________________



B.4 (4 pt)

______________________ %

Part C

C.1 (5 pt)

$n =$ ____________________, $m =$ ____________________

C.2 (5 pt)

$a =$ ____________________ cm

C.3 (5 pt)

____

IChO
Problem 7
Cover sheet

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

Playing with Non-benzenoid Aromaticity

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

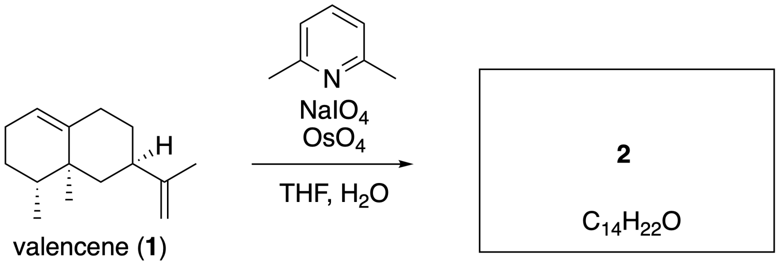
Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

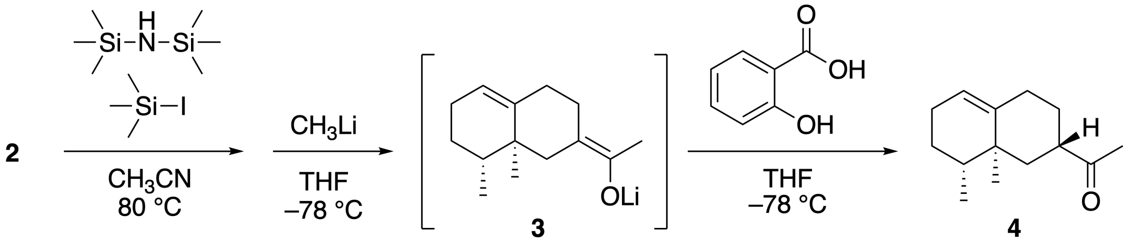
Photo courtesy: Tohoku Univ.

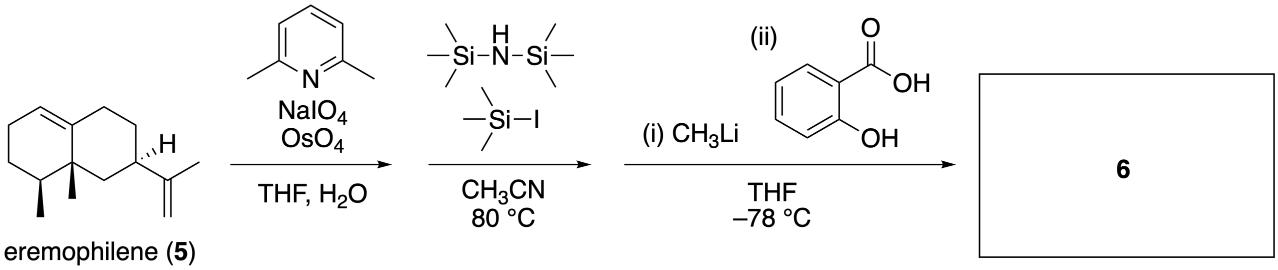
Part A

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

Inula linariifolia

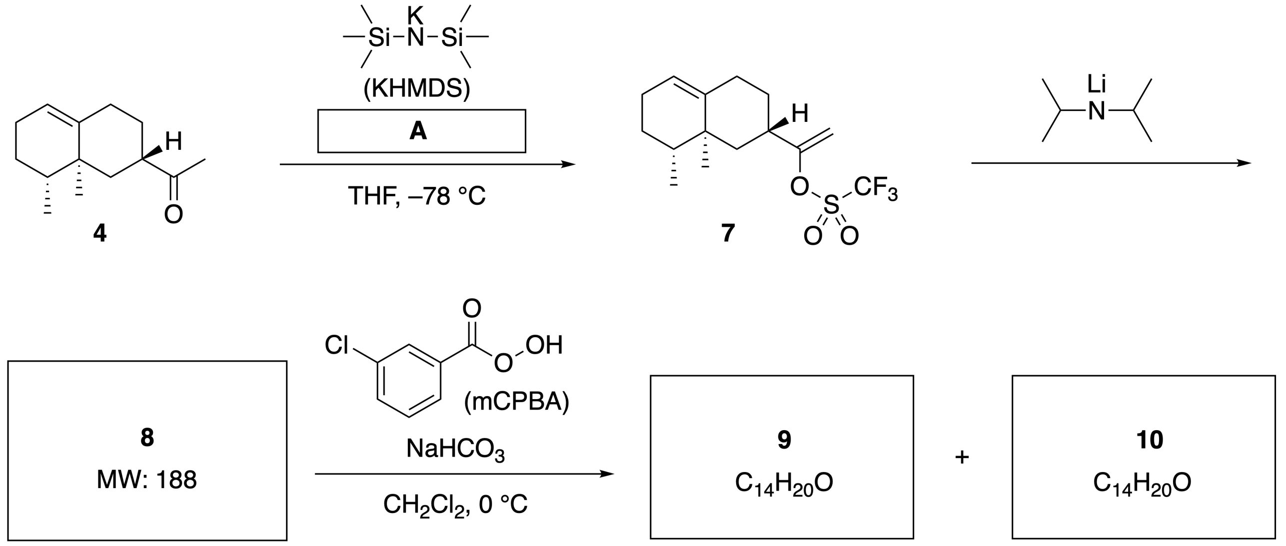


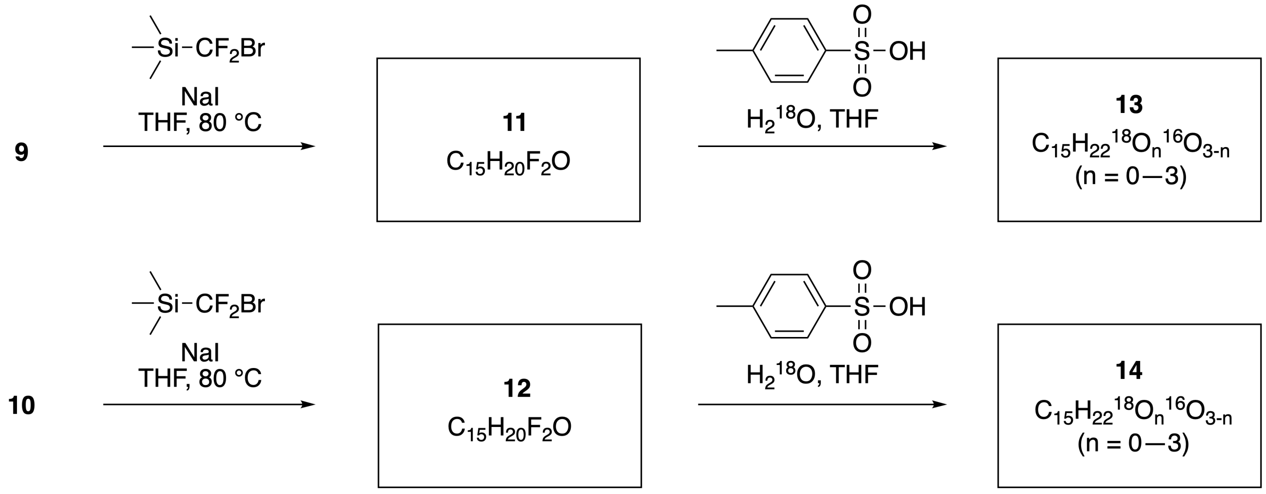


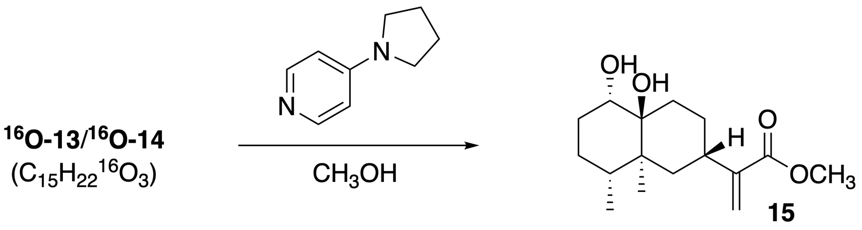


A.1	<u>**Draw**</u> the structures of **2** and **6** and clearly identify the stereochemistry where necessary.	5pt

Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-lineariifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.

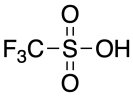






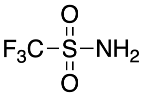
A.2 **Choose** the appropriate structure for **A**. 2pt

I



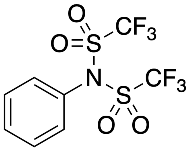
$F_3C-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

II

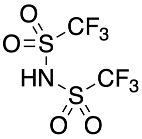


$F_3C-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-NH_2$

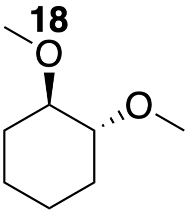
III



IV

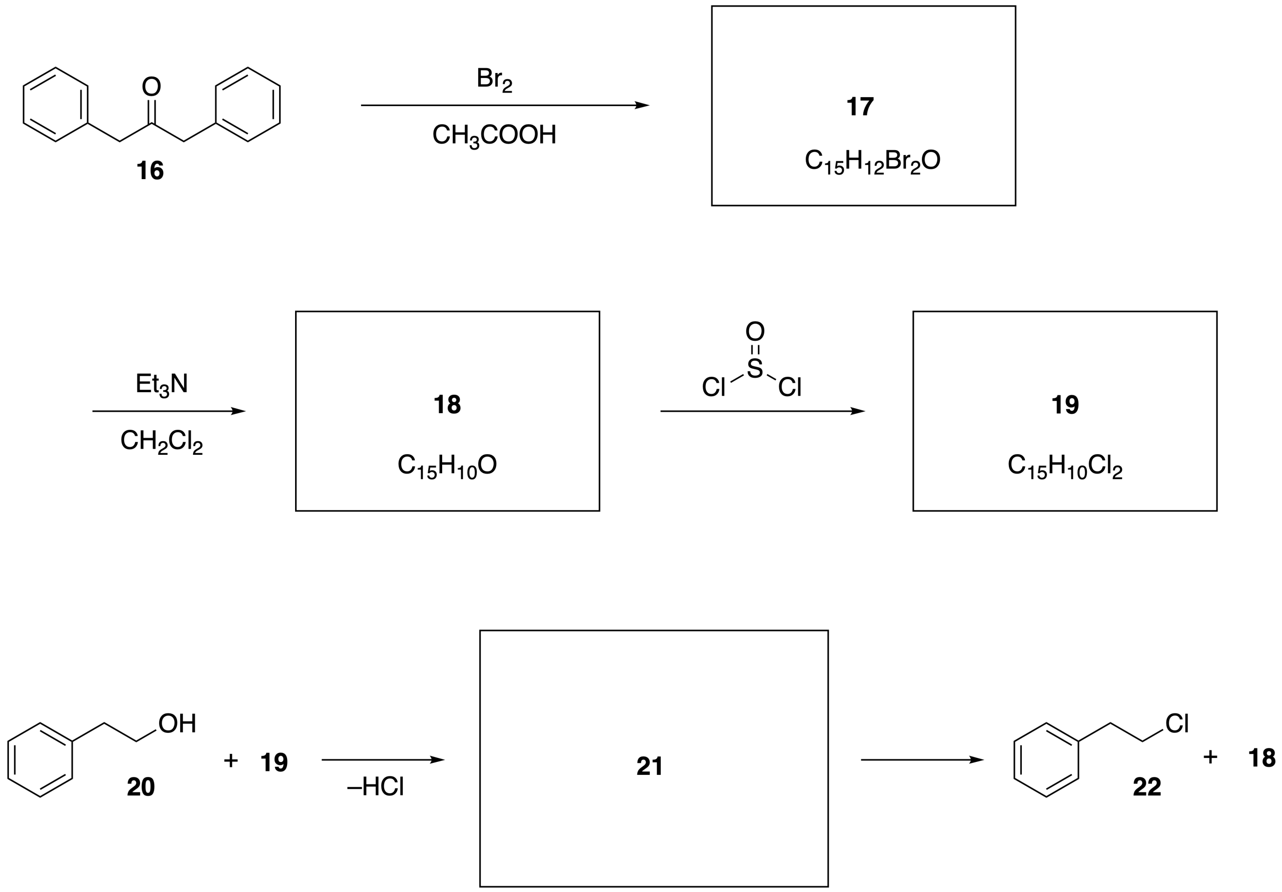


A.3 **Draw** the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, **indicate** the introduced ^{18}O atoms for **13** and **14** as shown in the example below. 19pt



Part B

Compound **19** is 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	<u>**Draw**</u> the structures of **17–19** and **21**. Identifying the stereochemistry is not necessary.	10pt

اللعب مع الأروماتية غير البنزينودية

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

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

افتتح البروفيسور Nozoe (1996-1902) مجال البحث عن المركبات non-benzenoid aromatic وهو الآن متوفر في كل مكان في الكيمياء العضوية.

Photo courtesy: Tohoku Univ.

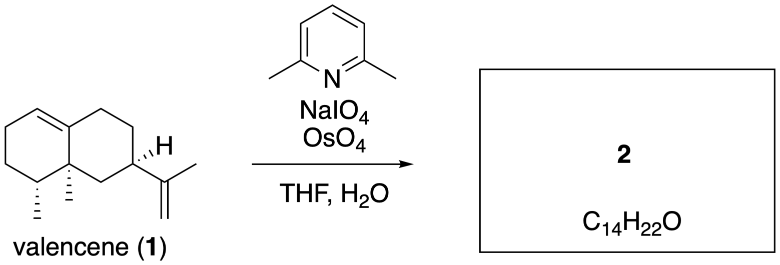
A Part

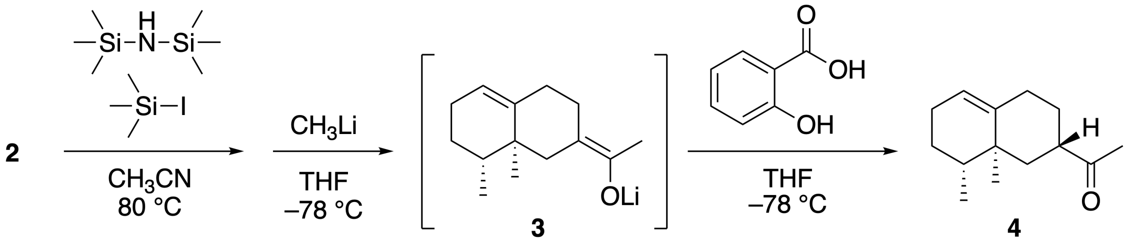
Leariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (**1**), a one-step conversion yields **2**, before a three-step conversion via **3** yields ketone **4**. Eremophilene (**5**) is converted into **6** by performing the same four-step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

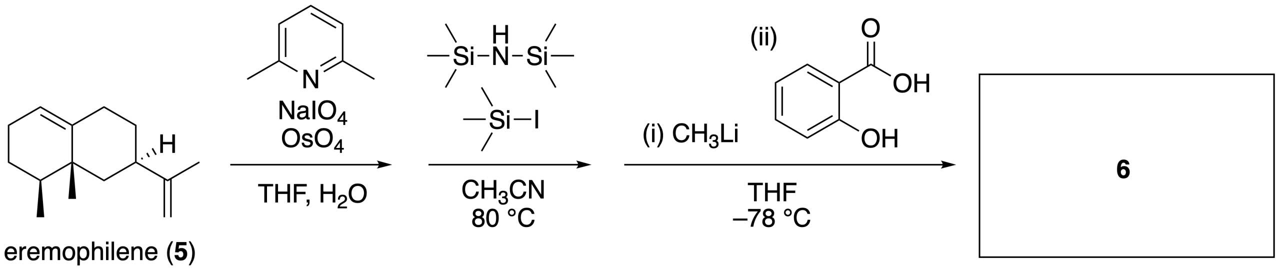
Leariifolianone هو منتج طبيعي له هيكل فريد ، تم عزله من

Inula linariifolia . ينتج من valencene **(1)** بالتحول عن طريق خطوة واحدة المركب **2** ، قبل التحول عن طريق ثلاث خطوات للمركب **3** الذي ينتج عنه الكيتون **4**. يتم تحويل Eremophilene (**5**) إلى **6** عن طريق إجراء نفس التحول المكون من أربع خطوات.

Inula linariifolia







5pt **A.1**

Draw the structures of **2** and **6** and clearly identify the stereochemistry where necessary.

ارسم تراكيب **2** و **6** وحدد الكيمياء الفراغية بوضوح عند الضرورة.

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-leariifolianones **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.

بعد ذلك ، يتم تحويل الكيتون **4** إلى استر **15**. يحتفظ المركب **8** (الوزن الجزيئي: 188) بجميع المراكز الفراغية الموجودة في **7**. تحتوي المركبات **9** و **10** على خمسة مراكز فراغية ولا توجد روابط ثنائية بين الكربون والكربون. أفترض أن $H_2{}^{18}O$ يستخدم بدلًا من $H_2{}^{16}O$ لتشييد

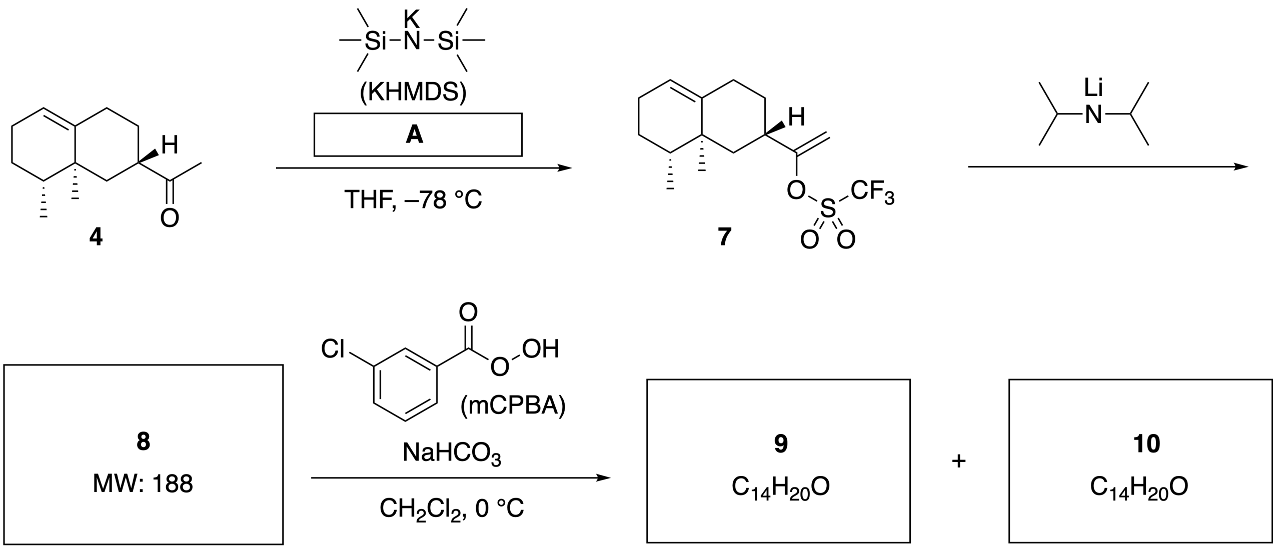
^{18}O labelled-leariifolianones-

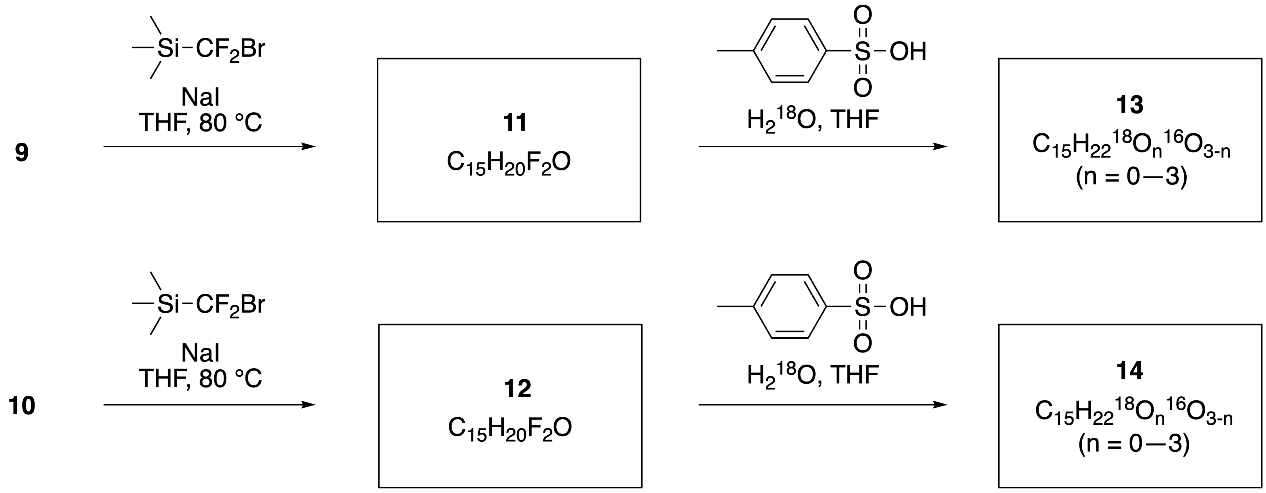
13 و **14** من **11** و **12**, على التوالي.

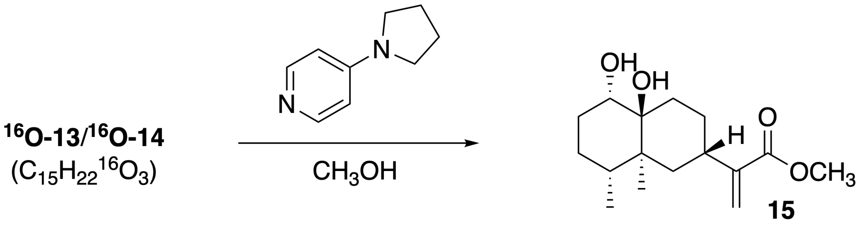
المركبات **13** و **14** هي labelled isotopomers - ^{18}O

تجاهل isotopic labelling

المركبات **13** و **14** تعطي نفس الناتج **15** مع كيمياء فراغية متطابقة.


4
(KHMDS)
A
THF, –78 °C
7
8
MW: 188
(mCPBA)
NaHCO3
CH2Cl2, 0 °C
9
C14H20O
+
10
C14H20O


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

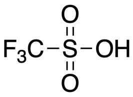

16O-13/16O-14
(C15H22 16O3)
CH3OH
15

2pt **A.2**

Choose the appropriate structure for **A**.

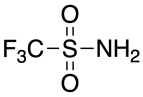
اختر التركيب الهيكلي المناسب لـ **A** .

I



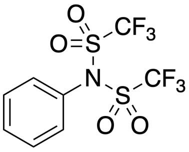
$F_3C-\overset{O}{\underset{O}{S}}-OH$

II

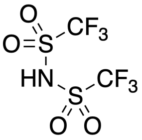


$F_3C-\overset{O}{\underset{O}{S}}-NH_2$

III



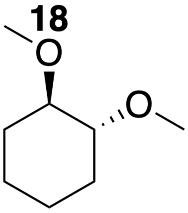
IV



19pt **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.

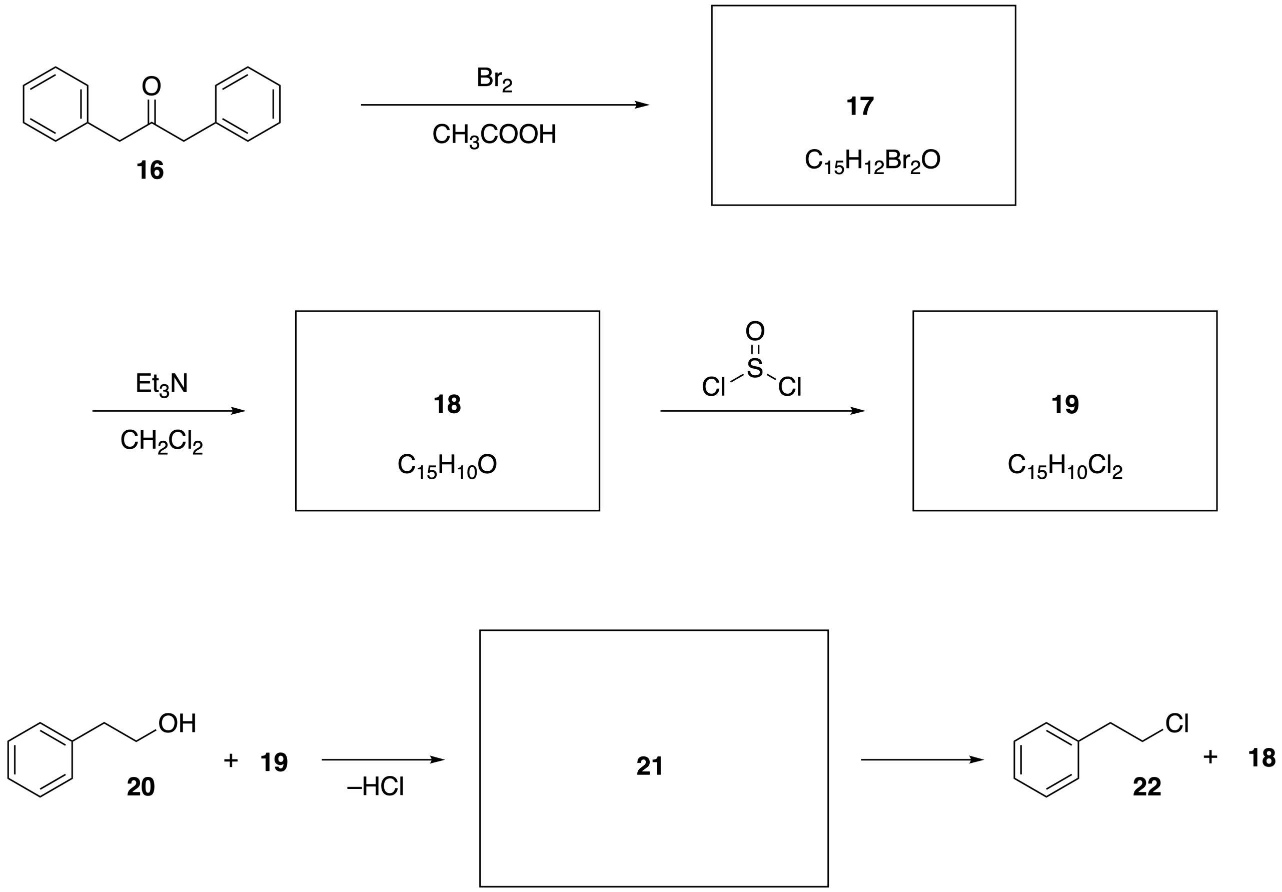
ارسم تراكيب هيكلية **8-14** وحدد الكيمياء الفراغية بوضوح عند الضرورة. **أشر** أيضًا إلى ذرات ^{18}O في **13** و **14** كما هو موضح في المثال أدناه.



B Part

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**.

يتم تشييد المركب **19** كما هو موضح أدناه. فيما يتعلق بالأروماتية غير البينزينودية ، يمكن استخدام **19** كمنشط للكحولات ، وتم تحويل **20** إلى **22** عبر مركب وسطي زوج أيوني **21**. على الرغم من أن تكوين **21** قد لوحظ بواسطة NMR فإن **21** يتحلل تدريجيًا لإعطاء **18** و **22** .



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

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

10pt

B.1

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

ارسم تراكيب لـ **19-17** و **21**. تحديد الكيمياء الفراغية ليس ضروريًا.

Playing with Non-benzenoid Aromaticity

Part A

A.1 (5 pt)

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

A.2 (2 pt)

A.3 (19 pt)

8 (3 pt)

9 (2 pt)

10 (2 pt)

11 (2 pt)

12 (2 pt)

13 (4 pt)

14 (4 pt)

Part B

B.1 (10 pt)

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

IChO
Problem 8

Cover sheet

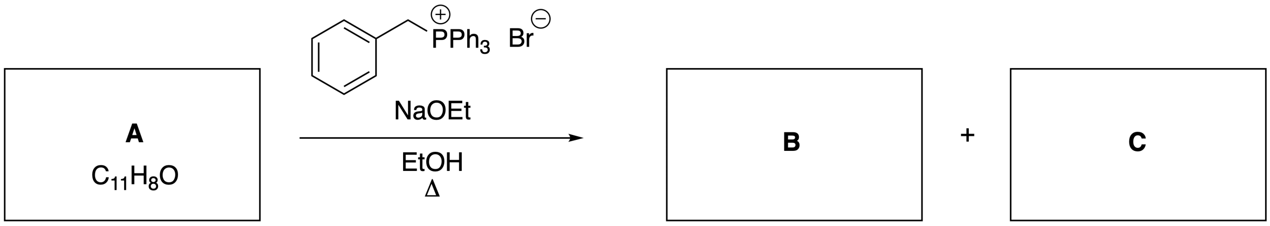
Please return this cover sheet together with all the related question sheets.

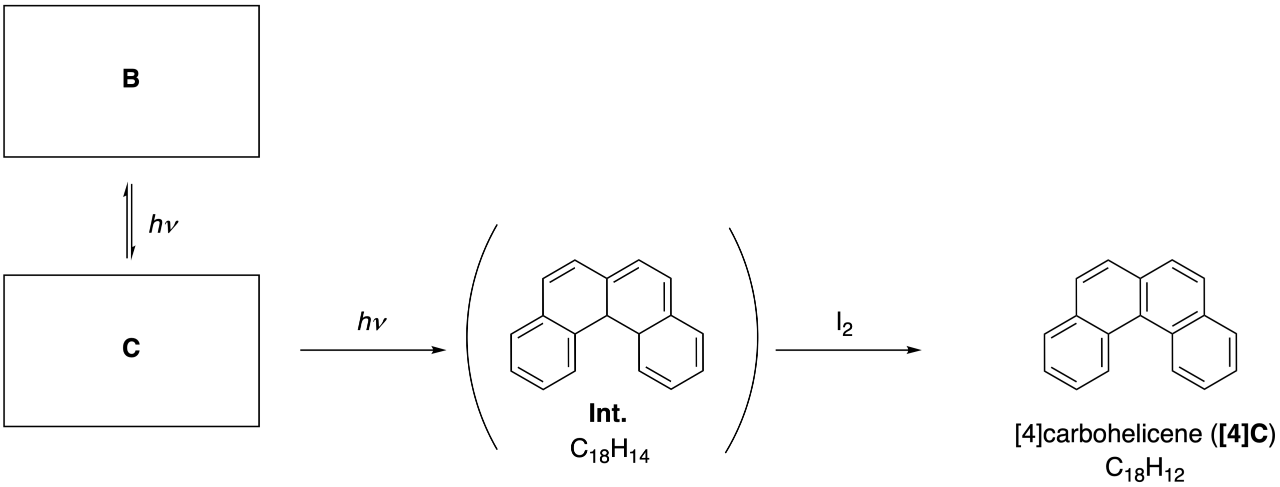
Dynamic Organic Molecules and Their Chirality

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

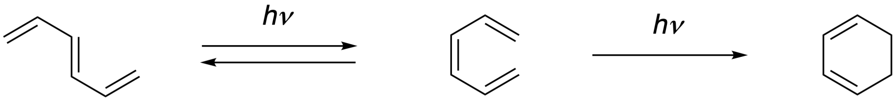
Part A

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





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

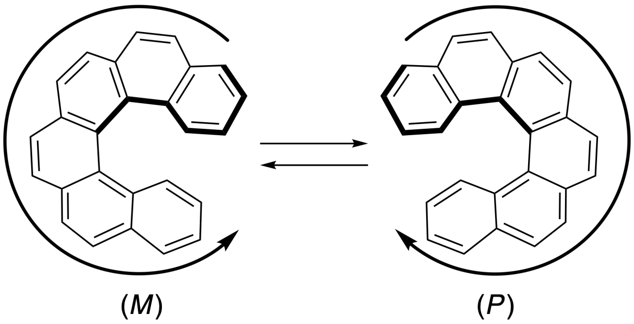


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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

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

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



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

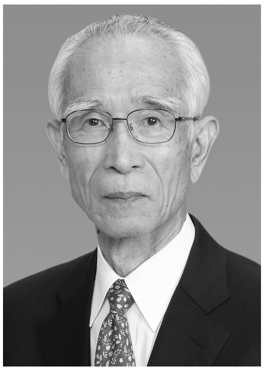
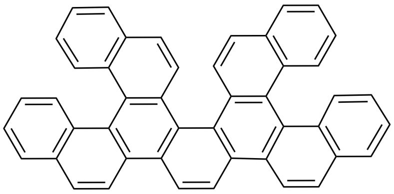
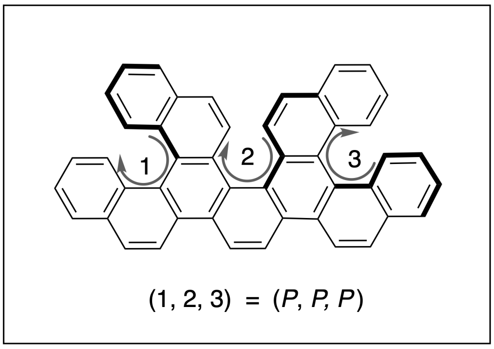


Photo courtesy: The Japan Prize Foundation

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

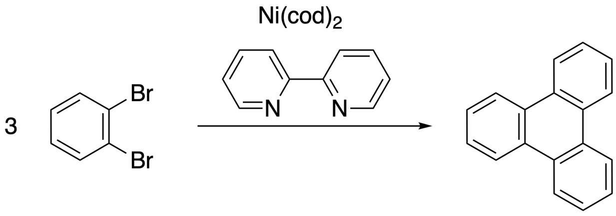


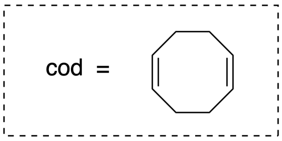
E

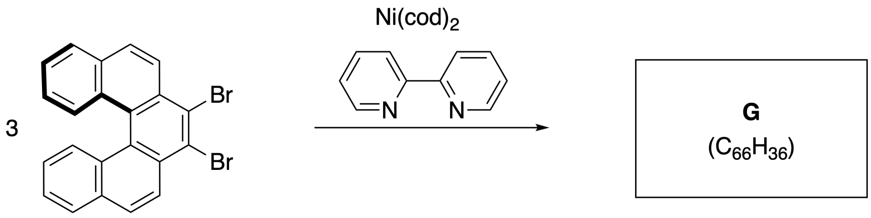


(1, 2, 3) = (*P*, *P*, *P*)

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



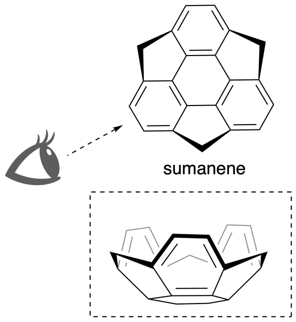




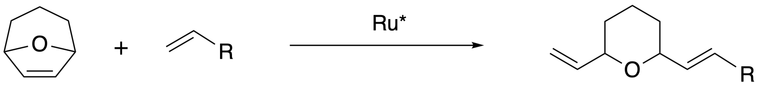
(*P*)-**F**

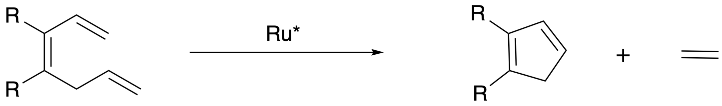
Part B

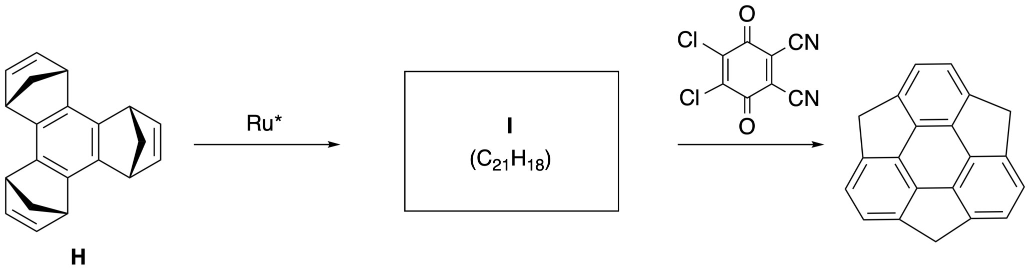
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



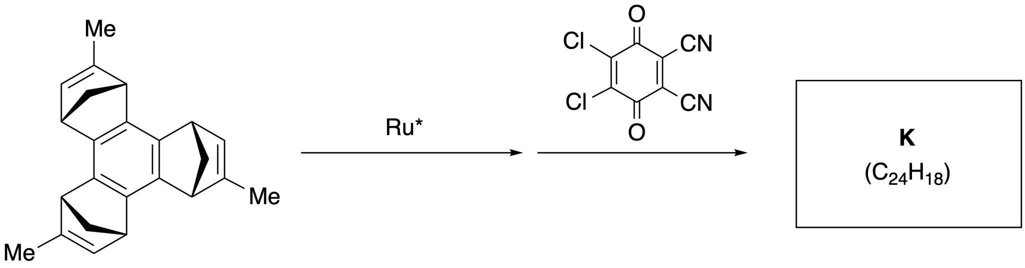
Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.







B.1 **<u>Draw</u>** 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. <u>**Draw**</u> the structure of **K** with the appropriate stereochemistry.	4pt

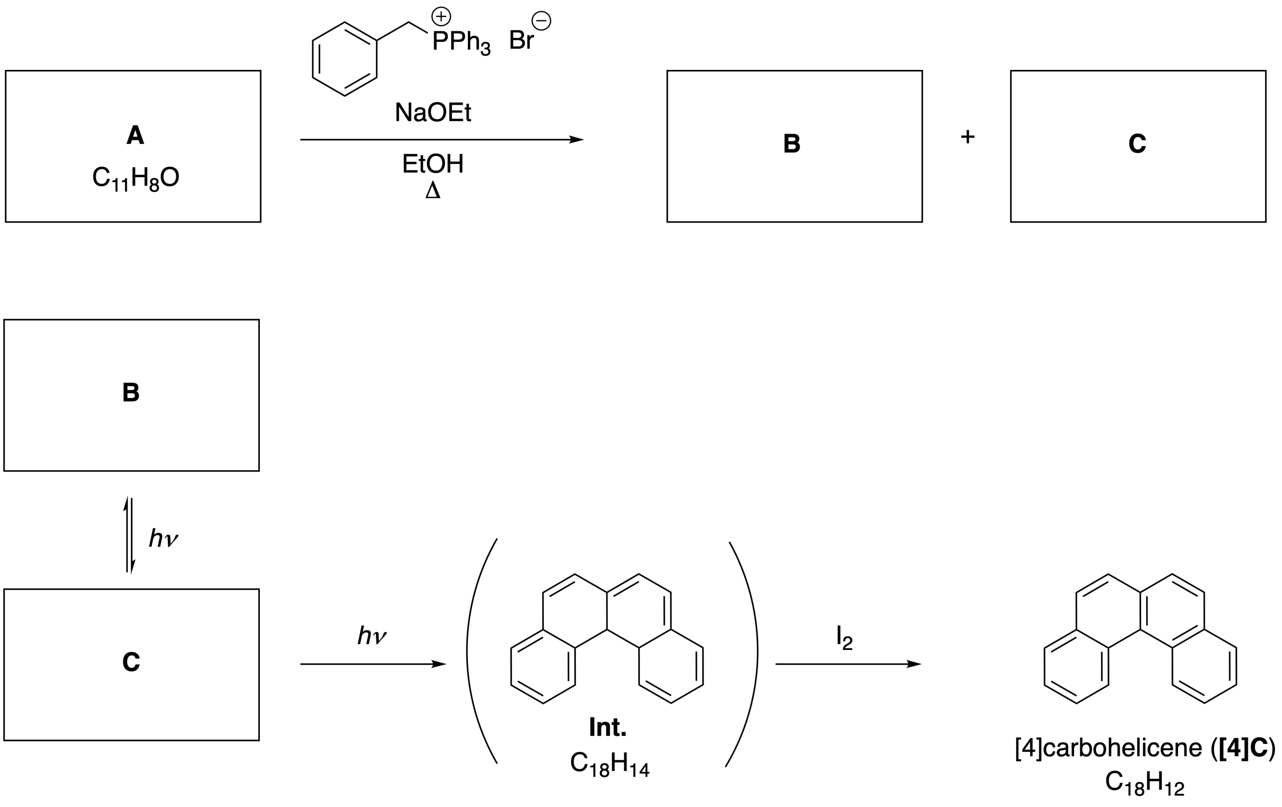
الجزيئات العضوية الديناميكية و كيراليتها

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

A Part

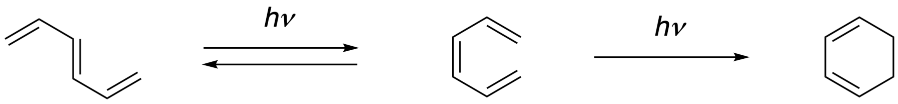
Polycyclic aromatic hydrocarbons with successive ortho-connections are called [n]carbohelicenes (here, n represents the number of six-membered rings) (see below). [4]Carbohelicene (**[4]C**) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (**Int.**) that is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

الهيدروكربونات الاروماتية متعددة الحلقات (Polycyclic aromatic hydrocarbons) التي ترتبط بشكل متعاقب بموقع الاورثو تسمى ([n]carbohelicenes) وهنا الحرف (n) يرمز الى عدد الحلقات السداسية في المركب (انظر بالاسفل), [4]carbohelicene او (**[4]C**) تم تحضيره بفعالية عن طريق التفاعلات المتعاقبة باستخدام التفاعلات الضوئية كما هو موضح بالاسفل عن طريق مركب وسطي (intermediate (**Int**)) الذي يتأكسد بسهولة باليود (iodine) .



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

التفاعلات الضوئية تتم بنفس الطريقة كما هو موضح بالمثال التالي.



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.

ملاحظة: في كل فقرات السؤال 8, من فضلك ارسم روابط احادية و ثنائية بشكل متناوب في اجاباتك على السؤال كما هو موضح في مثال الكربوهيليسينات (carbohelicene), لا تضع دوائر لأنظمة مدارات π المترافقة.

A.1 9pt

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

ارسم تراكيب من **A** الى **C**, يجب تمييز المتماكبات الفراغية .

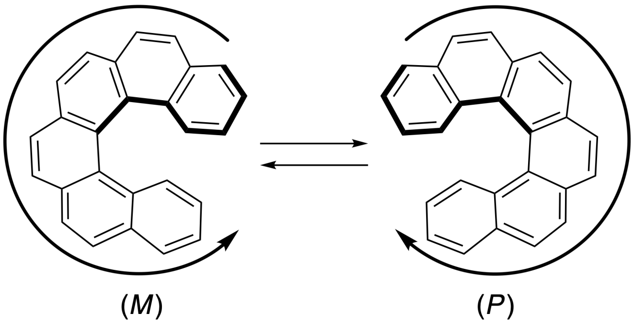
A.2 3pt

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)**]**

محاولات لتشييد ([5]carbohelicene) من ملح فوسفونيوم مشابه (phosphonium salt) و نتج اثار من مركب مناسب في البداية بكمية قليلة جدا من [5]carbohelicene ، ولكن التشييد نتج عنه الناتج **D** الذي له وزن جزيئي تعتبر اقل بمقدار 2Da من تلك لـ [5]carbohelicene ، الانزياحات الكيميائية (chemical shifts) للرنين النووي المغناطيسي البروتوني (^{1}H NMR) لـ **D** مدرجة بالاسفل, أرسم التركيب الكيميائي لـ **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)**]**

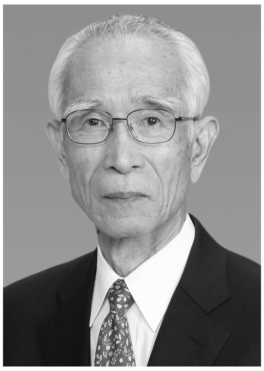
The [5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (*M*) or (*P*) as shown below.

تحتوي [5]- و [n]carbohelicenes الاكبر على helical chirality كيرالية ملتفة بشكل حلزوني و التحول البيني (interconversion) بين الاينانتوميرين لهذة الكيراليتات (helicenes) بطيء بشكل كبير في درجة حرارة الغرفة. الكيرالية لـ [n]carbohelicenes مشار اليها بالرموز (M) او (P) كما هو موضح بالاسفل.



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

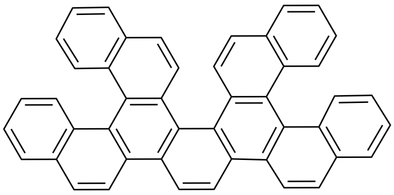
ال [n]Carbohelicenes ذو n اكبر من 4 يمكن فصلها اينانتوميريا عن طريق كروماتوقرافيا العمود الكيرالي (chiral column chromatography), الذي تم تطويره بواسطة البروفيسور يوشي اوكاموتو



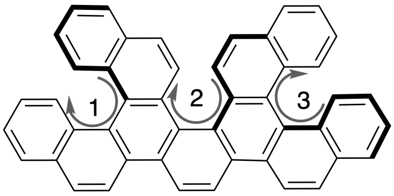
Foundation Prize Japan The courtesy: Photo

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.

الهيليسينات المتعددة هي مركبات تحتوي على اثنين او اكثر من تراكيب اشباه الهيليسين, اذا اخذنا بعين الاعتبار الكيرالية الملتفة فان ذلك يعني وجود ايزوميرات فراغية (stereoisomers) متعددة في الهيليسينات المتعددة, على سبيل المثال: المركب **E** يحتوي على ثلاثة مثيلات لتركيب ال [5]carbohelicene في جزيء واحد. واحدة من المتماكبات الفراغية توصف كالاتي (P , P , P) كما هو موضح بالاسفل.



E

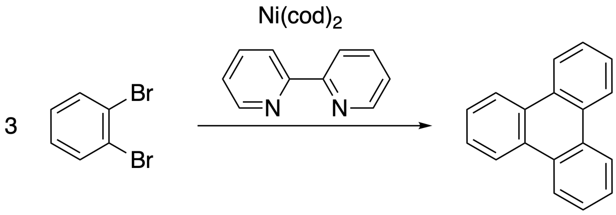


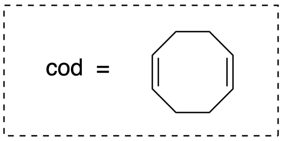
(1, 2, 3) = (*P*, *P*, *P*)

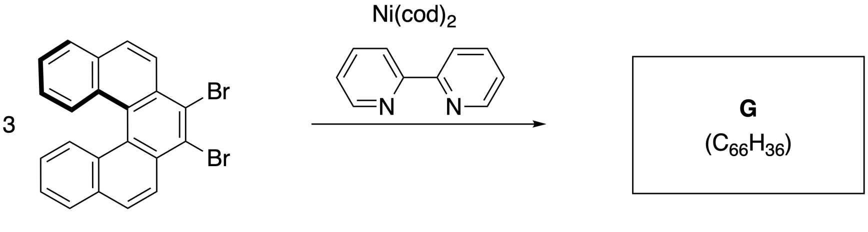
7pt **A.3**

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*).

الترايمرة باستخدام النيكل لـ (1,2-dibromobenzene) ينتج عنه triphenylene , عندما يتعرض الاينانتومير **F** Fg -(P) لنفس التفاعل ينتج عنة الهيليسين المتعدد **G** ($C_{66}H_{36}$), علما بان التحويل البيني بين المتماكبات الفراغية (interconversion لا يحدث اثناء التفاعل، **حدد جميع** الايزوميرات الفراغية (stereoisomers) الممكنة للمركب **G** الناتجة عن هذة العملية بدون تكرار. كمرجع, يجب ان يرسم ايزومير واحد بالكامل كما هو موضح بالاعلى مع كيرالية محددة كما في المثال اعلاه مع استخدام الارقام, كذلك يجب ادراج الايزوميرات الفراغية الاخرى عن طريق التعريف بالارقام حسب مواقع الارقام بـالرموز M و P في اماكن الارقام. على سبيل المثال: للمركب **E** يجب ادراجها كالتالي:
(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*).







(*P*)-**F**

B Part

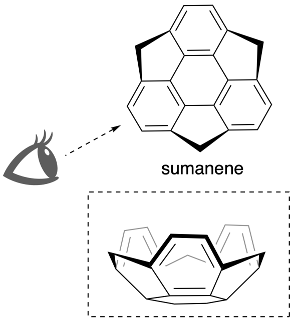
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower.

The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.

السومانين (Sumanene) مركب هيدروكاربوني يشبه الوعاء والذي اعلن عنه بالبداية في اليابان في عام 2003, الاسم ” sumanene ” مشتق من الكلمة السنسكريتية الهندية ”suman” والتي تعني وردة دوار الشمس.

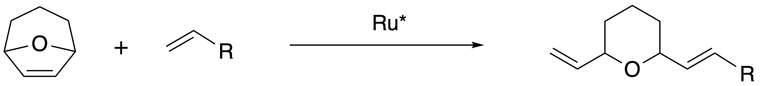
امكن تشييد Sumanene عن طريق تفاعلات متعاقبة تتكون من فتح الحلقة و اغلاق الحلقة وتغيير المواضع تعرف metathesis:

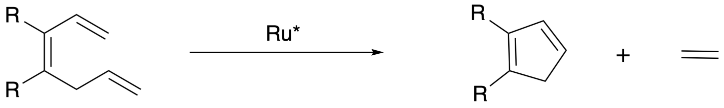
(ring-opening and a ring-closing metathesis)

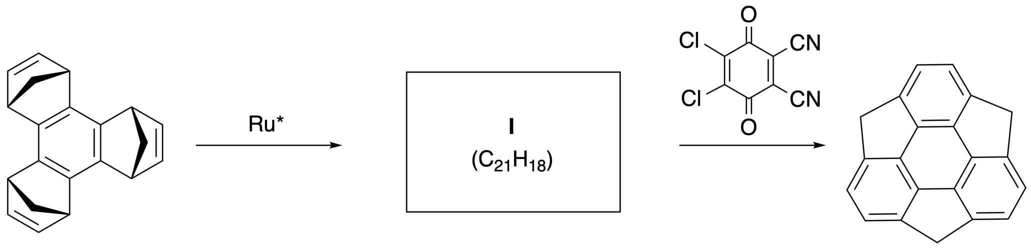


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.

يتم تحفيز تفاعلات metathesis باستخدام (Representative metathesis) حافز الروثينيوم (Ru*) كما هو موضح بالاسفل.







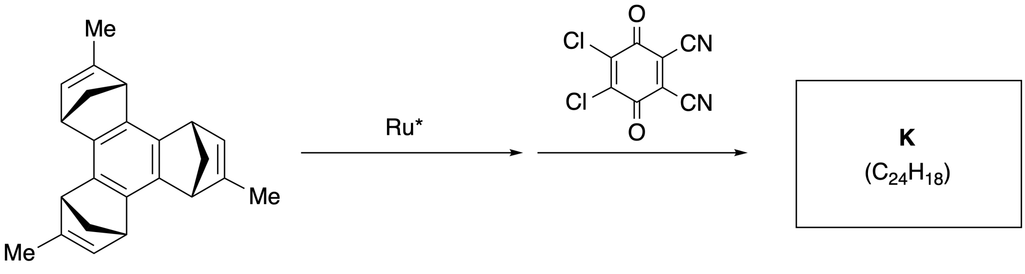
H

3pt

B.1

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

ارسم تركيب الناتج الوسطي **I** (الكيمياء الفراغية لهذا المركب غير مطلوب)



J

4pt

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.

بدءا من المركب الابتدائي **J** الفعال ضوئيا يتكون بنفس ترتيب التفاعل المركب الفعال
ضوئيا مشتق sumanene derivative **K** . المراكز الفراغية (stereocenters) في **J** لا
تعاني من انعكاس (inversion) خلال تفاعل (metathesis reaction).
ارسم التركيب الكيميائي للمركب **K** مع مراعاة الكيمياء الفراغية للمركب.

Dynamic Organic Molecules and Their Chirality

Part A

A.1 (9 pt)

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

A.2 (3 pt)

A.3 (7 pt)

Part B

B.1 (3 pt)

B.2 (4 pt)

SAU-1 C-9 C
Mohammad AlHudaithi

IChO
Problem 9
Cover sheet

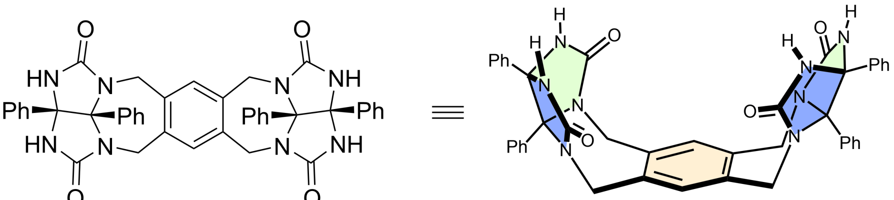
Please return this cover sheet together with all the related question sheets.

Likes and Dislikes of Capsule

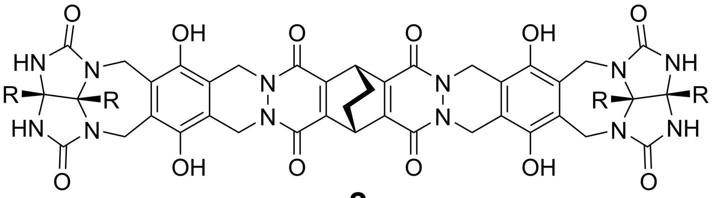
10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	**Total**
Points	13	2	2	3	3	**23**
Score						

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

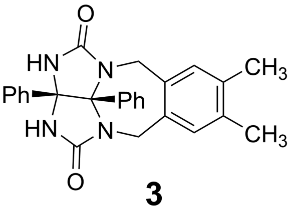
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

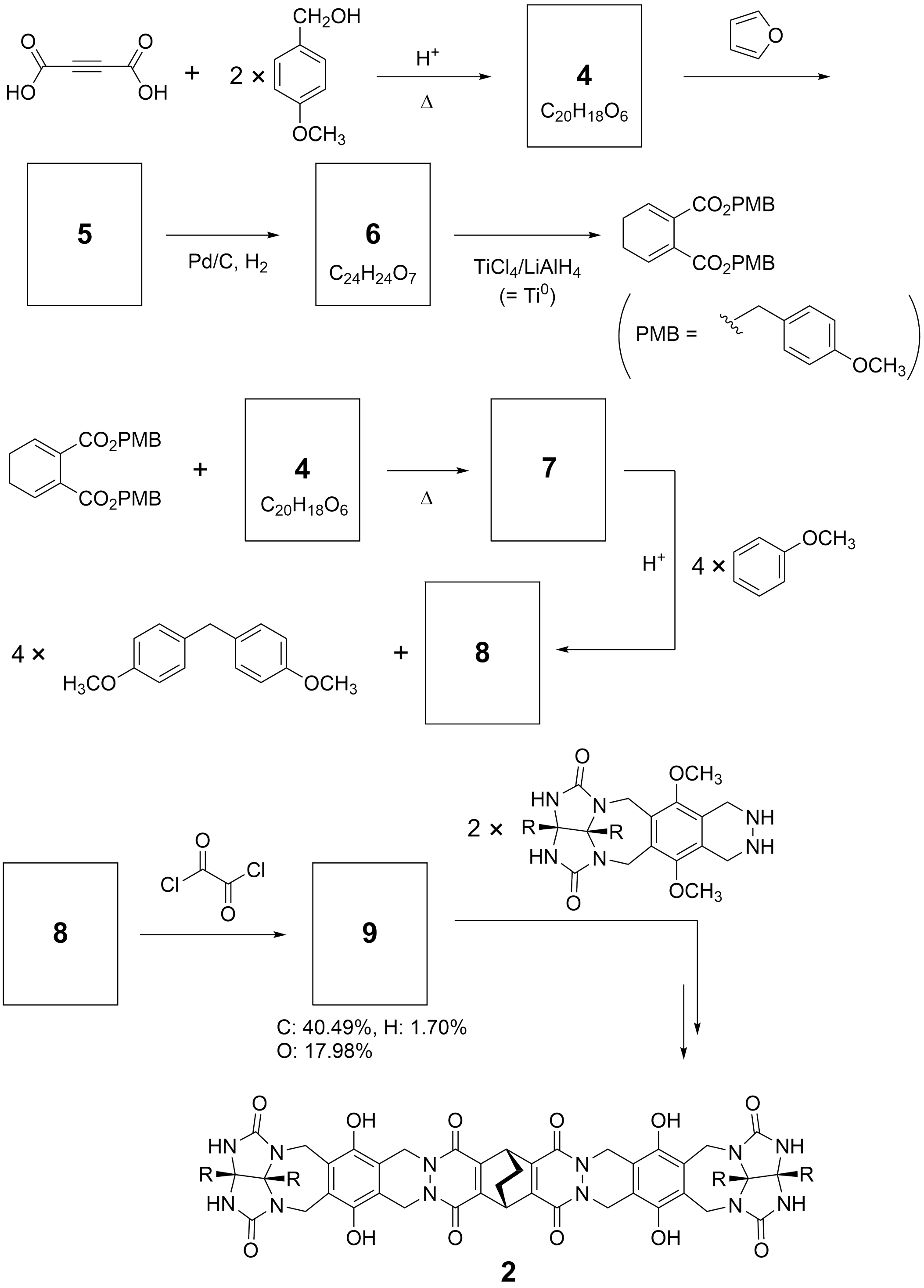


2



3

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



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

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

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

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

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

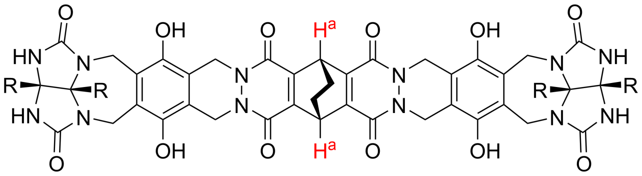
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

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

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

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

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



2

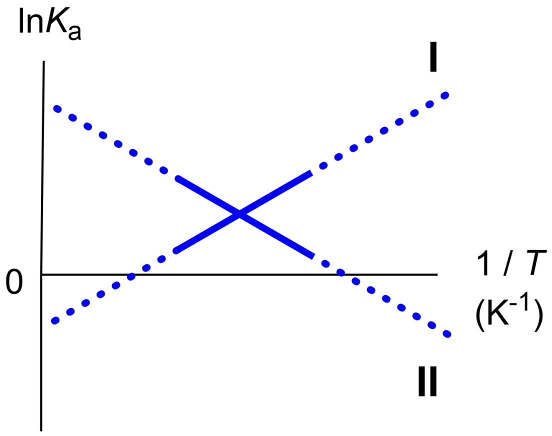
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

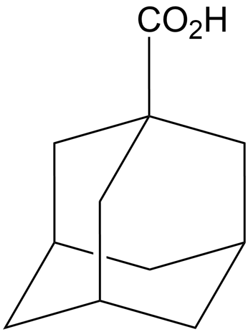
A.4 **Determine** the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2}_2$ giving each H^a signal. 3pt

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

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

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





AdA

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

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

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

يحب ويكره الكبسولة

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

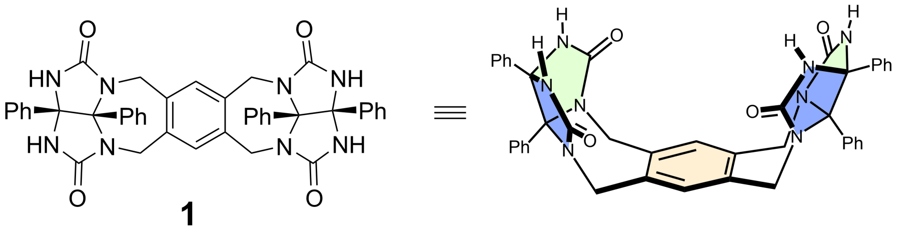
جزء

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

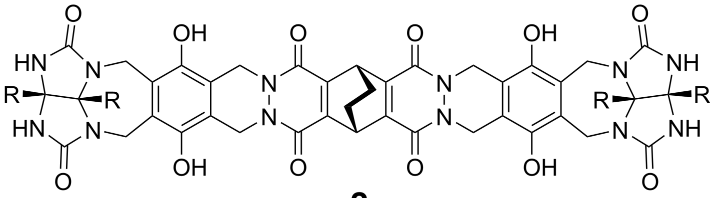
الأولاد الجيدون لا يفعلون ذلك, لكن اذا قمت بقص كرة التنس يمكنك فصل قطعتين على شكل حرف ال (U) بالانجليزية.

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.

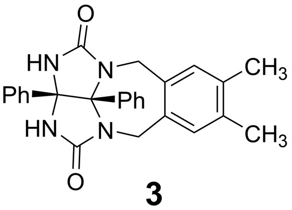
طبقا لهذة الفكرة: تم تحضير مركب **1** و مركب **2** على شكل حرف ”U“ جزيئات بأحجام مختلفة, تم تحضير مركب **3** للمقارنة مع مركب **1** وتمت دراسة مدى قدرة المركبات على الكبسلة ” encapsulation ”



1



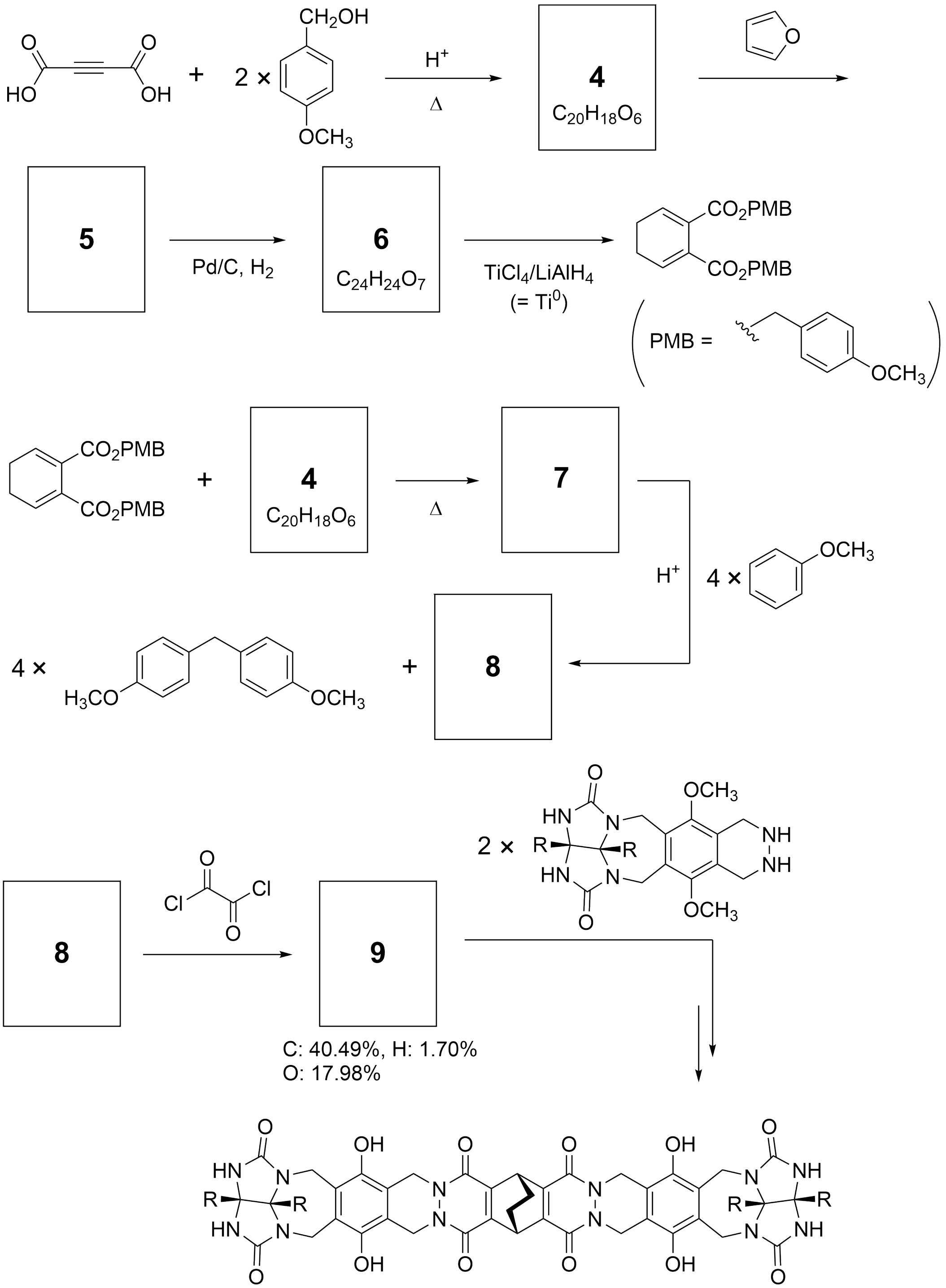
2



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.

التشييد الكلي للمركب **2** موضح بالاسفل, التركيب العنصري للمركب **9** هو كالتالي: الكاربون بنسبة % 40.49 و الهايدروجين بنسة % 1.70 و الأكسجين بنسبة % 17.98


HO
OH
O
O
+
2 ×
CH2OH
OCH3
H+
Δ
4
C20H18O6
O
5
Pd/C, H2
6
C24H24O7
TiCl4/LiAlH4
(= Ti0)
CO2PMB
CO2PMB
PMB =
OCH3
CO2PMB
CO2PMB
+
4
C20H18O6
Δ
7
H+
4 ×
OCH3
4 ×
H3CO
OCH3
+
8
8
Cl
Cl
O
O
9
C: 40.49%, H: 1.70%
O: 17.98%
2 ×
HN
N
R
R
HN
N
O
O
OCH3
OCH3
NH
NH
OH
OH
N
N
NH
NH

2

13pt **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.

أرسم المركبات من **4 - 9** , ليس من الضروري توضيح المتماكبات (الكيمياء الفراغية),
استخدم الرمز "PMB" كإختصار بدلا من رسم تركيبة المركب كاملة ل p-methoxybenzyl
الموضح في المخطط بالأعلى

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.

في الطيف الكتلي للمركب **1**, قمة الايون المتوافق مع ثنائي المركب (1_2) كان واضحا, بينما لم تتم ملاحظة القمة لأي أيون للثنائي ل(3_2) في الطيف الكتلي للمركب **3**. في الرنين النووي المغناطيسي البروتوني $^1H\ NMR$ لمحلول من 1_2 , جميع البروتونات من (NH) من المركب **1** متطابقة مغناطيسيا و الانزياح الكيميائي chemical shift كان مختلف كثيرا عن الانزياح الكيميائي لبروتونات ال(NH) في المركب **3**. هذه المعطيات تدل على وجود روابط هيدروجينية بين ال (NH) للمركب **1** و الذرة اكس لجزيء اخر من المركب **1** لانتاج ما يعرف بالكبسولة الثنائية

dimeric capsule

2pt **A.2**

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

ضع دائرة على جميع ذرة(ات) **X** الممكنة في **1**

2pt **A.3**

Give the number of the hydrogen bonds in the dimeric capsule ($\mathbf{1}_2$).

أعطي عدد الروابط الهيدروجينية في الكبسولة الثنائية (1_2)

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:

الكبسولة الثنائية للمركب **1** ($\mathbf{1}_2$) تحتوي على فراغ داخلي يمكن لمركب Z صغير كفاية التكبسل بداخله, هذة الظاهرة يمكن تفسيرها بالمعادلة التالية:

$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z@}\mathbf{1}_2 \qquad (1)$$

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

ثابت التوازن للتكبسل ل Z بداخل $\mathbf{1}_2$ معطى بالمعادلة التالية:

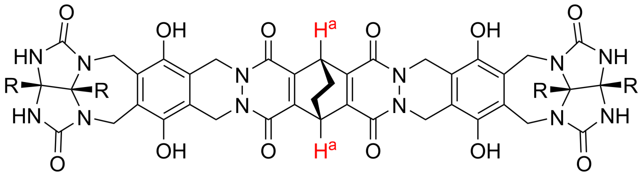
$$K_\mathrm{a} = \frac{[\mathrm{Z@}\mathbf{1}_2]}{[\mathrm{Z}][\mathbf{1}_2]} \qquad (2)$$

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.

التكبسل للمركب بداخل الكبسولة يمكن متابعتها عن طريق الرنين النوي المغناطيسي (NMR), على سبيل المثال $\mathbf{1}_2$ في C_6D_6 يعطي إشارات مختلفة في طيف الرنين المغناطيسي النووي البروتوني (^{1}H NMR) قبل وبعد اضافة 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.

المركب **2** ايضا يمكن من خلاله تكوين كبسولة ثنائية أكبر وأكثر صلابة ($\mathbf{2}_2$),تم قياس أطياف الرنين النووي المغناطيسي البروتوني ^{1}H NMR ل $\mathbf{2}_2$ في المذيبات C_6D_6 و C_6D_5F و أيضا في الخليط من المذيبات C_6D_6/C_6D_5F مع مراعاة إبقاء كافة المعطيات الأخرى ثابتة, الانزياحات الكيميائية chemical shifts للبروتون H^a في المركب **2** في المذيبات المذكورة بالأعلى تم تلخيصها في الأسفل و لا يوجد أي إشارة طيفية اخرى للبروتون H^a في **2**, غير المذكورة بالأسفل. افترض أن الفراغ بداخل الكبسولة يتم ملئه دائما بأكبر عدد ممكن من جزيئات المذيب وأن كل إشارة تتوافق مع نوع واحد من الكبسولة المملؤة.



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

3pt

A.4

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

حدد عدد جزيئات C_6D_6 و C_6D_5F المتكبسلة في $\mathbf{2}_2$ تعطي كل واحد
اشارة H^a

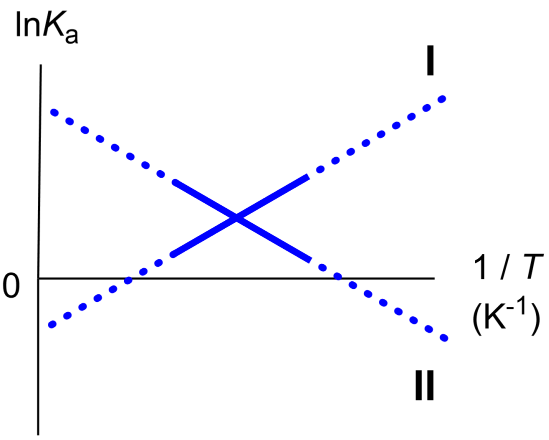
^{1}H NMR measurements in C_6D_6 revealed that $\mathbf{2}_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants (K_a) which are expressed below were determined for various temperatures. [solvent@$\mathbf{2}_2$] denotes a species containing one or more solvent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

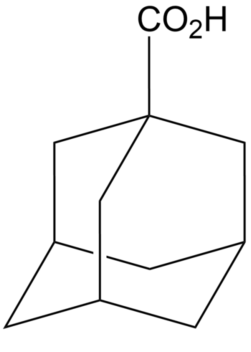
اضهرت قياسات الرنين النووي المغناطيسي البروتوني (^{1}H NMR) ل C_6D_6 ان $\mathbf{2}_2$ يمكنها ان تحوي جزيء واحد من
1-adamantanecarboxylic acid
او (AdA)
و ثابت التكبسل (K_a) يمكن وصفه بالمعادلة الموضحة بالأسفل وتم حسابه في درجات حرارة مختلفة. الرمز
[solvent@ $\mathbf{2}_2$]
يصف جسيم يحتوي على واحد أو أكثر من جزيئات المذيب.

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

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.

بالمثل, قيم K_a ل(CH_4) و $\mathbf{1}_2$ المعطاة من المعادلة (2) في درجات حرارة مختلفة في C_6D_6 تم استنتاجها عن طريق قياسات اطياف ال ^{1}H NMR, المنحنى لثابتي التكبسل المعطاة كالتالي
as ln K_a vs 1/T
موضحة بالأسفل.





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).

لا وجود لمركب C_6D_6 متكبسل في $\mathbf{1}_2$. في الخط **II** التغير الانتروبي (ΔS) هو (1) و التغير الانثالبي (ΔH) هو (2), وذلك دلالة على أن القوة التي تقود الى الكبسلة في الخط **II** هي (3), وبالتالي فان الخط **I** يتوافق مع (4) و الخط **II** يتوافق مع (5).

3pt **A.5**

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

اختار الخيار الصحيح في الفجوات (1)-(5) في الفقرة التالية من A و B

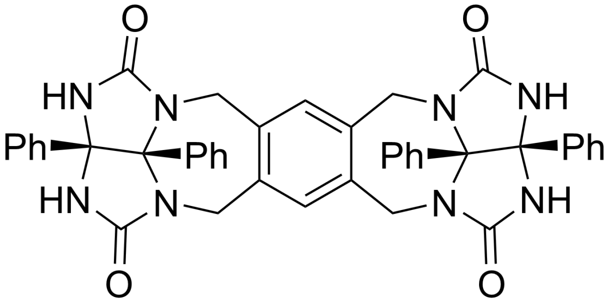
	A	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and AdA
(5)	$\mathbf{1}_2$ and CH_4	$\mathbf{2}_2$ and ADA

Likes and Dislikes of Capsule

A.1 (13 pt)

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

A.2 (2 pt)



A.3 (2 pt)

A.4 (3 pt)

δ (ppm) of H^a	numbers of C_6D_6	numbers of C_6D_5F
4.60 ppm		
4.71 ppm		
4.82 ppm		

A.5 (3 pt)

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

(4) :
(5) :