G0-1

English (Official)

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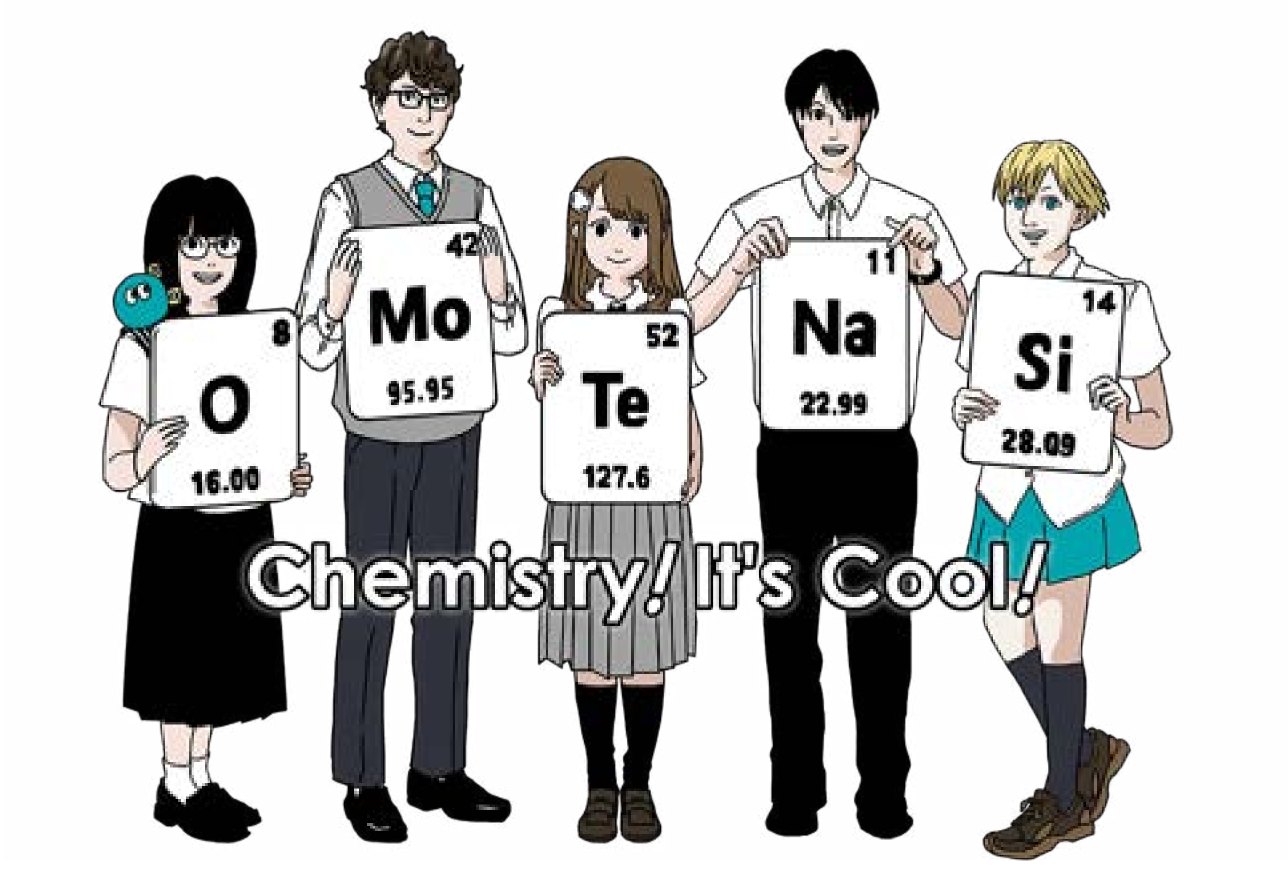


General Instruction

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

GOOD LUCK!

Problems and Grading Information

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

Physical Constants and Equations

Constants

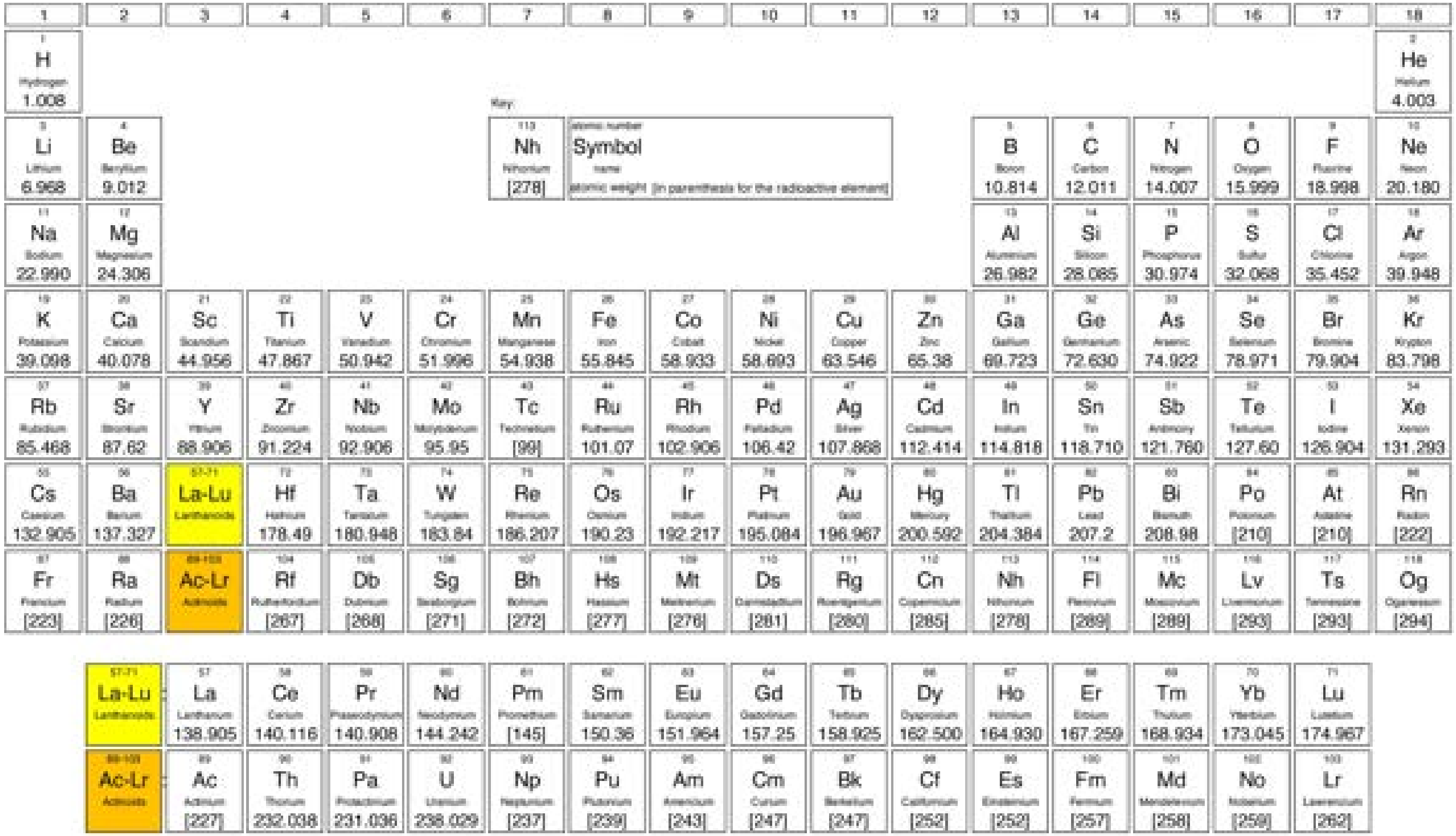
Speed of light in vacuum	$c = 2.99792458 \times 10^{8}$ m s^{-1}
Planck constant	$h = 6.62607015 \times 10^{-34}$ J s
Elementary charge	$e = 1.602176634 \times 10^{-19}$ C
Electron mass	$m_\mathrm{e} = 9.10938370 \times 10^{-31}$ kg
Electric constant (permittivity of vacuum)	$\varepsilon_0 = 8.85418781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

Equations

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

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

Periodic Table

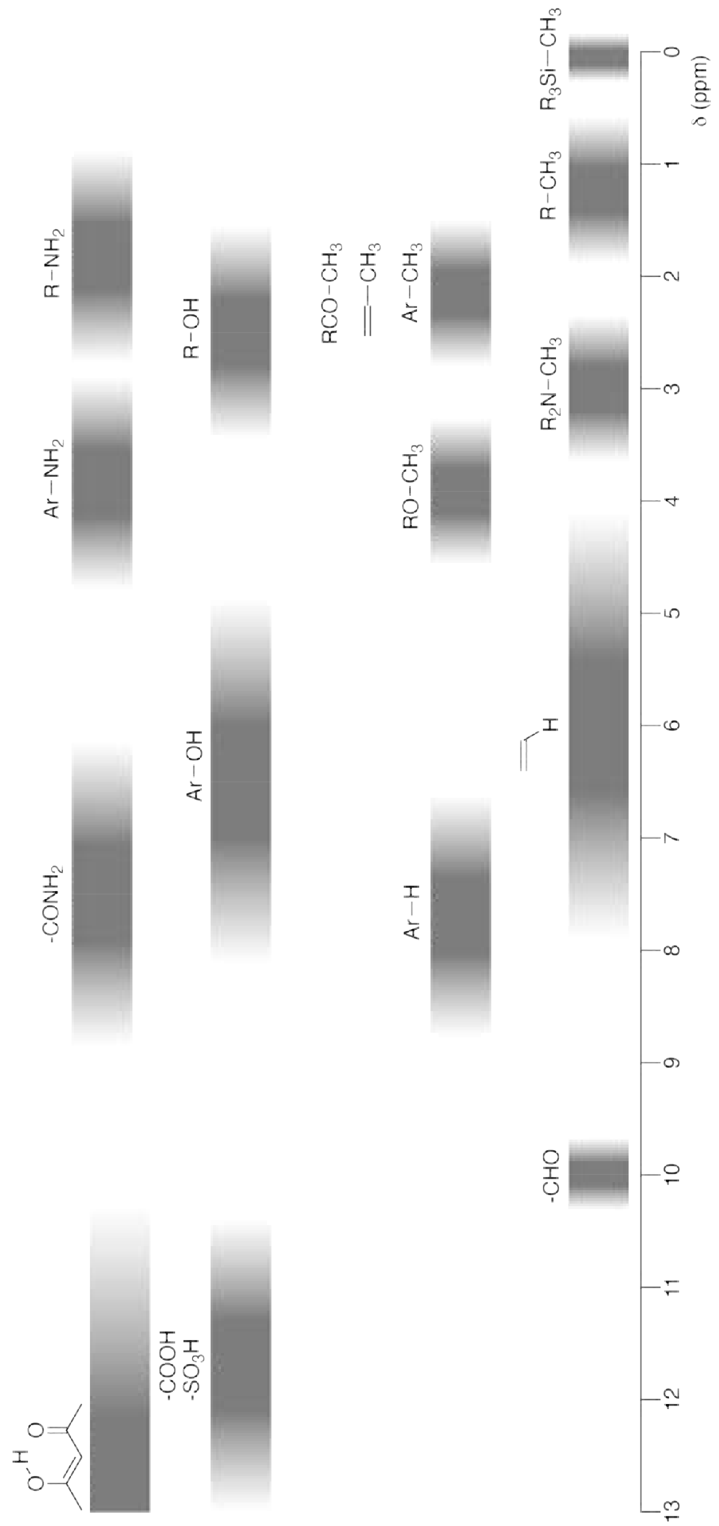


1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.968	4 Be Beryllium 9.012											5 B Boron 10.814	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.306											13 Al Aluminium 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.068	17 Cl Chlorine 35.452	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium [99]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.293
55 Cs Caesium 132.905	56 Ba Barium 137.327	57-71 La-Lu Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.384	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium [210]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Ac-Lr Actinoids	104 Rf Rutherfordium [267]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [272]	108 Hs Hassium [277]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [278]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [293]	118 Og Oganesson [294]
	57-71 La-Lu Lanthanoids	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.967	
	89-103 Ac-Lr Actinoids	89 Ac Actinium [227]	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [239]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [252]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]	

Key:

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

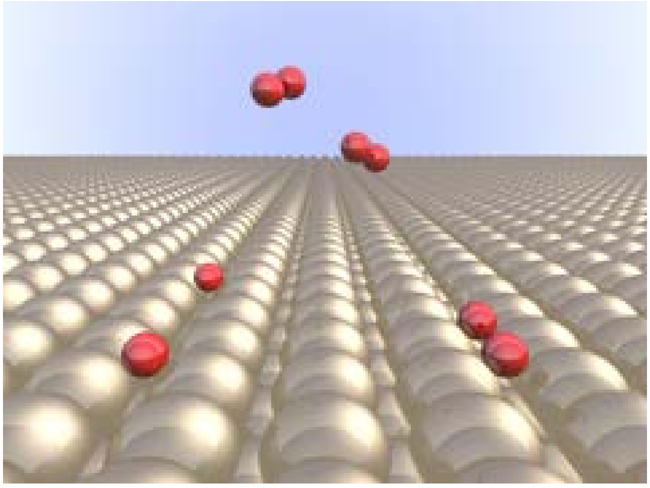
^{1}H NMR Chemical Shifts



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

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, $\mathrm{H_2(g)} \rightarrow \mathrm{2H(ad)}$, 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 $\mathrm{kJ\,mol^{-1}}$, the dashed line spacing is 100 $\mathrm{kJ\,mol^{-1}}$, and the spacing between solid and dashed lines is 80 $\mathrm{kJ\,mol^{-1}}$. The zero-point vibration energy is ignored.

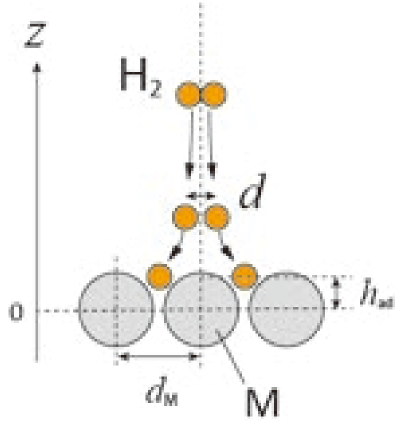


Fig.1 Definition of variables. Drawing is not in scale.

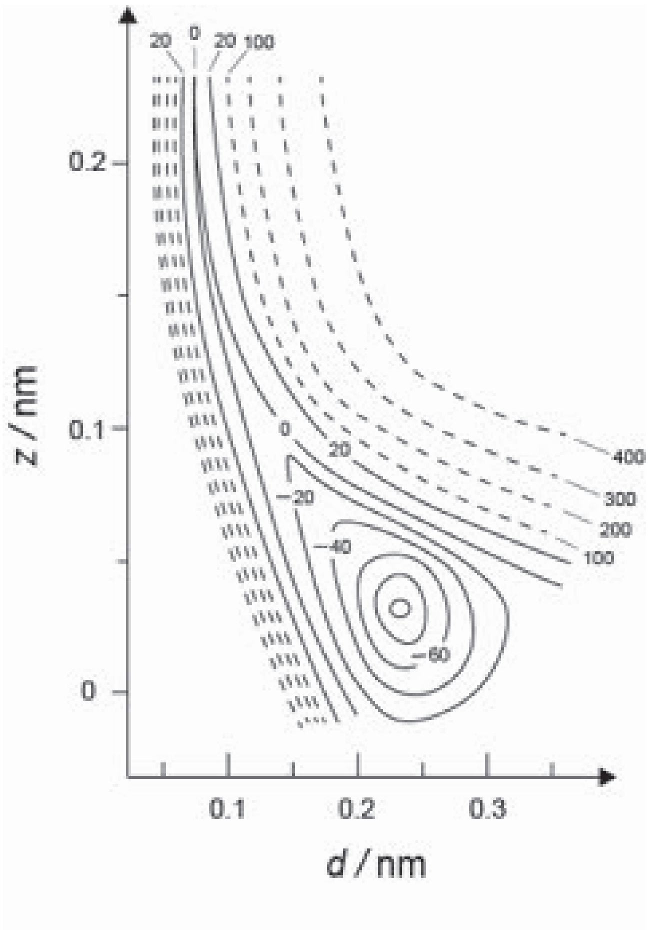


Fig.2

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	

(i) B (ii) F (iii) A

6 points in total:

2 point for (i), (ii) and (iii)

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}

(i) H (ii) D

4 points in total:

2 points for (i) and (ii)

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.

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

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

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 ($0 \le \theta \le 1$) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption ($r_1, r_2 \gg r_3$) and that θ remains constant.

B.1 r_3 can be expressed as: 5pt

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

Express C using k_1 and k_2.

From $r_1, r_2 \gg r_3$ and $r_1 = r_2 + r_3$,
$r_1 = r_2$.
Then $k_1 P_{\mathrm{H_2}}(1-\theta)^2 = k_2\theta^2$ (1')
Solve for θ:

$$\theta = \frac{1}{1+\sqrt{\dfrac{k_2}{P_{\mathrm{H_2}}k_1}}} \text{ (2')}$$

From $r_3 = k_3\theta$:

$$r_3 = \frac{k_3}{1+\sqrt{\dfrac{k_2}{P_{\mathrm{H_2}}k_1}}}$$

Thus, $\underline{C = \dfrac{k_1}{k_2}}$

5 points in total:
5 points for the final correct answer.
partial points:
(1') and (2'): 2 points each.

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 ($P_{\mathrm{H_2}} = 1.0 \times 10^2$ 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, $P_{\mathrm{H_2}}$ 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, $A\,[\text{mol s}^{-1}\text{ m}^{-2}]$. 3pt

The change in the amount of hydrogen atoms per unit time in the gas phase is $A \times S$. Thus,

$A \times S = \dfrac{2vV}{RT}$ (1')

$= 2 \times 4.0 \times 10^{-4} \times \dfrac{1.0 \times 10^{-3}}{8.31 \times 400} = 2.4 \times 10^{-10}$ mol s^{-1}

Therefore,

$\underline{A = 2.4 \times 10^{-7}\text{ mol s}^{-1}\text{ m}^{-2}}$

3 points in total:

2 points for (1'), and 1 point for the final answer.

-1 point if $A \times S = \dfrac{vV}{RT}$ (missing the factor 2).

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

The relationship between r_3 and A is:

$$A = r_3 \times \frac{N}{N_\mathrm{A}}$$

Thus,

$$r_3 = A \times \frac{N_\mathrm{A}}{N} = 1.1 \times 10^{-1}\ \mathrm{s}^{-1}\ (1')$$

Solution 1

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{k_2}{P_{\mathrm{H}_2} k_1}}} = \frac{k_3}{1 + \sqrt{\dfrac{1}{10000}}} = \frac{k_3}{1.01}\ (2')$$

Thus,

$$\underline{k_3 = 1.01 \times r_3 = 1.1 \times 10^{-1}\ \mathrm{s}^{-1}}$$

Solution 2

Under the condition $P_{\mathrm{H}_2} C \gg 1,$ it follows that:

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{k_2}{P_{\mathrm{H}_2} k_1}}} \approx \frac{k_3}{1} = k_3\ (3')$$

Thus,

$$\underline{k_3 = r_3 = 1.1 \times 10^{-1}\ \mathrm{s}^{-1}}$$

(1.7×10^{-1} s^{-1} with $A = 3.6 \times 10^{-7}$ mol s^{-1} m^{-2})

3 points in total:
2 points for the correct value (1').
(if correct formulation (1'), 1 point).
1 point for the final correct answer.
It does not affect the score whether the approximation of (3') is used or not.

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

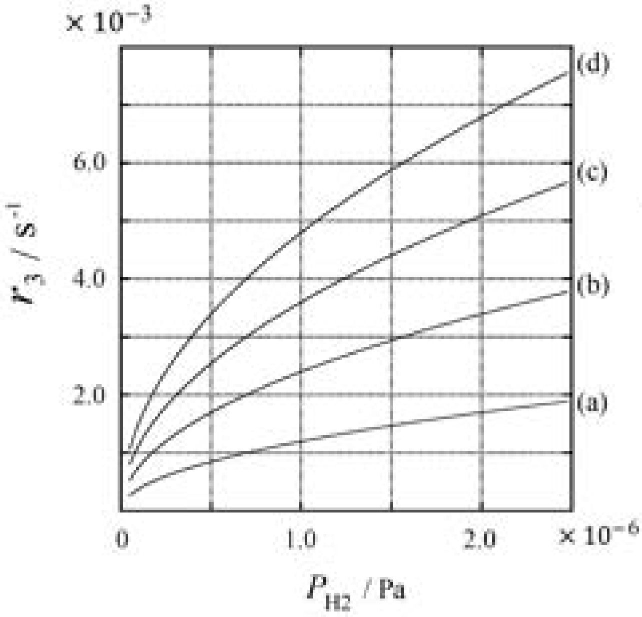
The figures show the region in which $P_{\mathrm{H_2}}C \ll 1$. Therefore,

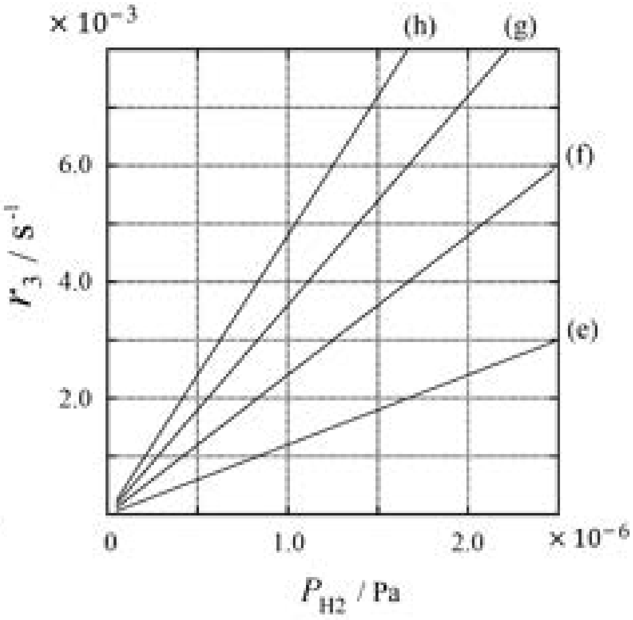
$$r_3 = \frac{k_3}{1+\sqrt{\dfrac{1}{P_{\mathrm{H_2}}C}}} \quad (1')$$

$$\approx \frac{k_3}{\sqrt{\dfrac{1}{P_{\mathrm{H_2}}C}}} = k_3\sqrt{P_{\mathrm{H_2}}C} = 2.4\sqrt{P_{\mathrm{H_2}}}$$

Thus, (b)

3 points in total:
3 points for selecting (b).





Isotope Time Capsule

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

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

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

Let us consider the following equilibrium:

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

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

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

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

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

$$\mathrm{H_2 + DI \rightleftharpoons HD + HI} \qquad (3)$$

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.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \to \ln K = -\dfrac{\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$

$\left(K = \exp\left[-\dfrac{\Delta H^\circ}{RT}\right] \exp\left[\dfrac{\Delta S^\circ}{R}\right]\right)$

$T \to 0$: As $\Delta H^\circ > 0$, $\ln K$ converges to $-\infty$ and therefore $K = 0$.

$T \to +\infty$: $\ln K \to \dfrac{\Delta S^\circ}{R}$

Given that ΔS° per 1 mole is $N_A k_B \ln W = R \ln 2$, $K = 2$.

8 points in total:

3 points for the correct answer for $T \to 0$,

5 points for the correct answer for $T \to +\infty$.

Partial points:

If neither the correct answer for $T \to 0$ nor that for $T \to +\infty$ is obtained: 2 points for showing that $\ln K = -\dfrac{\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$.

If the correct answer for $T \to +\infty$ is not obtained: 2 points for showing that $W = 2$.

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

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

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

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

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

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

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

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.

$\mu_{\text{H}_2} = 1/2\,\text{Da},\ \mu_{\text{HD}} = 2/3\,\text{Da},\ \mu_{\text{D}_2} = 1\,\text{Da}.$

Using $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, $\frac{\nu_{\text{HD}}}{\nu_{\text{H}_2}} = \sqrt{\frac{\mu_{\text{H}_2}}{\mu_{\text{HD}}}}$ and $\frac{\nu_{\text{D}_2}}{\nu_{\text{H}_2}} = \sqrt{\frac{\mu_{\text{H}_2}}{\mu_{\text{D}_2}}}$ are obtained.

The frequency of the H_2 vibration is 4161.0 cm^{-1} in units of wavenumbers.

Therefore, the frequencies of the molecular vibration for HD and D_2 are calculated to be 3603.5 cm^{-1} and 2942.3 cm^{-1}, respectively.

The difference of the zero-point energies of eq. 4 is calculated to be $(4161.0 + 2942.3)/2 - 3603.5 = -51.9\,\text{cm}^{-1}$.

$E = N_\text{A}h\nu = N_\text{A}hc\tilde{\nu}$ ($\tilde{\nu}$: frequency in wavenumbers), and therefore $E = \Delta H^\circ = -621\,\text{J}\,\text{mol}^{-1}$.

8 points in total:

2 points for the correct vibrational frequency of HD

(1 point for the correct μ value of HD,

1 point for the correct formulation $\left(\frac{\nu_{\text{HD}}}{\nu_{\text{H}_2}} = \sqrt{\frac{\mu_{\text{H}_2}}{\mu_{\text{HD}}}}\right)$ to calculate the vibrational frequency of HD),

2 points for the correct vibrational frequency of D_2

(1 point for the correct μ value of D_2,

1 point for the correct formulation $\left(\frac{\nu_{\text{D}_2}}{\nu_{\text{H}_2}} = \sqrt{\frac{\mu_{\text{H}_2}}{\mu_{\text{D}_2}}}\right)$ to calculate the vibrational frequency of D_2),

2 points for the correct conversion from cm^{-1} to $\text{J}\,\text{mol}^{-1}$

(partial points: 1 point for the correct conversion from cm^{-1} to J (N_A is missing)),

2 points for the correct energy difference

(partial points: -1 point when the value is not divided by 2, -1 point when the sign is wrong).

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

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

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

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

Let the sum of the concentrations of H_2, HD, and D_2 be C.

Solution 1:
$T \to +\infty\ (K = 1/4)$:
$[H_2]_0 = (1 - 1.5576 \times 10^{-4})^2 C = 9.9969 \times 10^{-1} C$
$[D_2]_0 = (1.5576 \times 10^{-4})^2 C = 2.4261 \times 10^{-8} C$

$K = 0.300$:
Let the amount of change in the molar ratio be x.

$$\frac{[H_2][D_2]}{[HD]^2} = \frac{\left(\frac{[H_2]_0}{C} + x\right)\left(\frac{[D_2]_0}{C} + x\right)}{\left(\frac{[HD]_0}{C} - 2x\right)^2} = K$$

Solve the equation for x when $K = 0.300$:

$$(1 - 4K)x^2 + \left(\frac{[H_2]_0}{C} + \frac{[D_2]_0}{C} + 4K\frac{[HD]_0}{C}\right)x + \left(\frac{[H_2]_0[D_2]_0}{C^2} - K\frac{[HD]_0^2}{C^2}\right) = 0,$$

$x = 4.8504 \times 10^{-9}$.
From this value, we obtain $[H_2] = 9.9969 \times 10^{-1} C$ and $[D_2] = 2.9112 \times 10^{-8} C$.

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 = \frac{\frac{2.9112 \times 10^{-8}}{9.9969 \times 10^{-1}}}{\frac{2.4261 \times 10^{-8}}{9.9969 \times 10^{-1}}} - 1 = 0.200$$

Solution 2:
By using an appropriate approximation, we can obtain the answer without calculating the concentration of each species.
Let the increase of $[D_2]$ be δ.

$$K = \frac{[H_2][D_2]}{[HD]^2} = \frac{([H_2]_0 + \delta)([D_2]_0 + \delta)}{([HD]_0 - 2\delta)^2} \simeq \frac{[H_2]_0([D_2]_0 + \delta)}{[HD]_0^2} = \frac{[H_2]_0[D_2]}{[HD]_0^2}$$

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 = \frac{\frac{[D_2]}{[H_2]}}{\frac{[D_2]_0}{[H_2]_0}} - 1 \simeq \frac{[D_2]}{[D_2]_0} - 1 = \frac{\frac{[H_2]_0[D_2]}{[HD]_0^2}}{\frac{[H_2]_0[D_2]_0}{[HD]_0^2}} - 1 \simeq \frac{0.300}{0.250} - 1 = 0.200$$

10 points in total:
1 point for the correct $[H_2]_0$,
1 point for the correct $[D_2]_0$,
2 points for the correct formulation for either $[H_2]$ or $[D_2]$,
2 points for the correct $[H_2]$,
2 points for the correct $[D_2]$,
and 2 points for the correct Δ_{D_2}.
Full marks when the correct Δ_{D_2} is shown using an appropriate approximation (without calculating each concentration).
Partial points: 5 points for showing that $[H_2]_0 \simeq [H_2]$.
No deficiency point when the sum of the concentration, C, is assumed to be 1.

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

The most common isotopologue of $CO_2[47]$ is $^{13}C^{16}O^{18}O$.
The molar ratio of $^{13}C^{16}O^{18}O$ in the case where all the isotopes are distributed randomly is:
$0.011112 \times 0.002000 \times 0.997621 \times 2$ [O is distinguishable] $= 4.43423 \times 10^{-5}$
The molar ratio of $^{12}C^{16}O_2$ ($CO_2[44]$) in the case where all the isotopes are distributed randomly is:
$0.988888 \times 0.997621^2 = 9.84188 \times 10^{-1}$
$$R^*_{47} = \frac{4.43423 \times 10^{-5}}{9.84188 \times 10^{-1}} = 4.50547 \times 10^{-5}$$
$\Delta_{47} = 7.06 \times 10^{-4}$
$T = 296$ K.

9 points in total:
2 points by indicating that the most common isotopologue of $CO_2[47]$ is $^{13}C^{16}O^{18}O$.
3 points for the correct molar ratio of $^{13}C^{16}O^{18}O$ (1 point when $\times 2$ is missing),
2 points for the correct molar ratio of $^{12}C^{16}O_2$,
2 points for the correct T.
(1 deficiency point when the calculated T is a negative value.)

Lambert–Beer Law?

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

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

Part A

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

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

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

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

$$K = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} = \frac{(1.00 \times 10^{-2})(1.00 \times 10^{-4})}{1.00 \times 10^{-3}} = 1.00 \times 10^{-3} \text{ mol L}^{-1}$$

Concentration before the dilution:
$[\text{HA}] = 1.00 \times 10^{-3}$ mol L^{-1}
$[\text{A}^-] = 1.00 \times 10^{-2}$ mol L^{-1}
$[\text{H}^+] = 1.00 \times 10^{-4}$ mol L^{-1}

Concentrations just after the dilution (nominal initial concentrations before the equilibrium):
$[\text{HA}] = 5.00 \times 10^{-4}$ mol L^{-1}
$[\text{A}^-] = 5.00 \times 10^{-3}$ mol L^{-1}

$$[\text{H}^+] = \frac{1.00 \times 10^{-4} + 3.16 \times 10^{-3}}{2} = 1.63 \times 10^{-3} \text{ mol L}^{-1}$$

(pH = 2.500 → $[\text{H}^+] = 3.16 \times 10^{-3}$ mol L^{-1})

Equilibrium after the dilution:

$$\frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} = \frac{(5.00 \times 10^{-3} - x)(1.63 \times 10^{-3} - x)}{5.00 \times 10^{-4} + x} = 1.00 \times 10^{-3} \text{ mol L}^{-1}$$

Solve the equation for x: $x = 1.19 \times 10^{-3}$ mol L^{-1}
→ $[\text{A}^-] = 3.81 \times 10^{-3}$ mol L^{-1}, $[\text{HA}] = 1.69 \times 10^{-3}$ mol L^{-1}.
Therefore,

$$1.00 \times 10^{-2}\varepsilon_{\text{A}^-} + 1.00 \times 10^{-3}\varepsilon_{\text{HA}} = 3.81 \times 10^{-3}\varepsilon_{\text{A}^-} + 1.69 \times 10^{-3}\varepsilon_{\text{HA}}$$

By solving this equation: $\underline{\varepsilon_{\text{HA}}/\varepsilon_{\text{A}^-} = 9.0}$

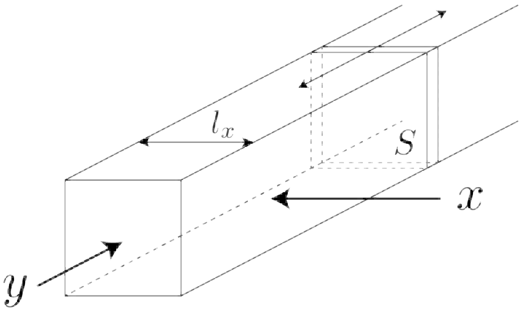
10 points in total:
2 points for the correct K value,
2 points for the formulation to give the correct [A$^-$] and [HA] values after dilution,
2 points for the correct [A$^-$] and [HA] values after dilution (1 point for each),
2 points for the formulation to give the correct relationship between ε_{A^-} and ε_{HA} using [A$^-$] and [HA], and 2 points for the correct relationship between ε_{A^-} and ε_{HA}.

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 $\varepsilon_{\text{D}}/\varepsilon_{\text{M}}$ at λ_{B1}, where ε_{D} and ε_{M} represent the absorption coefficients of D and of M, respectively.	6pt

Solution 1:

The absorbance at the initial state is:

$$A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_x$$

The absorbance after equilibrium is:

$$A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_x$$

From the ideal gas law, the following relationship is obtained:

$$\frac{n_0}{V_0} = \frac{P}{RT} = \frac{n_{\text{D}} + n_{\text{M}}}{V} \text{ (*1)}$$

From these equations, the following relationship is obtained:

$$A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_x = \frac{\varepsilon_{\text{D}}(n_{\text{D}} + n_{\text{M}})}{V} l_x = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_x$$

$\rightarrow \varepsilon_{\text{D}} n_{\text{M}} = \varepsilon_{\text{M}} n_{\text{M}}$

$\rightarrow 0 = (\varepsilon_{\text{M}} - \varepsilon_{\text{D}}) n_{\text{M}}$

As $n_{\text{M}} > 0$ after the equilibrium, $\underline{\varepsilon_{\text{D}} = \varepsilon_{\text{M}}}$ holds at λ_{B1}.

Solution 2:

Using the ideal gas law, the absorbance at the initial state is expressed as:

$$A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_x = \varepsilon_{\text{D}} \frac{P}{RT} l_x \text{ (*2)}$$

The absorbance after equilibrium is:

$$A_{\text{B1}} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_x = \frac{\varepsilon_{\text{D}} p_{\text{D}} + \varepsilon_{\text{M}} p_{\text{M}}}{RT} l_x \text{ (*3)}$$

From these equations, the following relationship is obtained:

$$A_{\text{B1}} = \varepsilon_{\text{D}} \frac{P}{RT} l_x = \frac{\varepsilon_{\text{D}} p_{\text{D}} + \varepsilon_{\text{M}} p_{\text{M}}}{RT} l_x$$

Using the fact that $p_{\text{D}} = P - p_{\text{M}}$,

$\varepsilon_{\text{D}} P = \varepsilon_{\text{D}}(P - p_{\text{M}}) + \varepsilon_{\text{M}} p_{\text{M}} = \varepsilon_{\text{D}} P + (\varepsilon_{\text{M}} - \varepsilon_{\text{D}}) p_{\text{M}}$

$\rightarrow 0 = (\varepsilon_{\text{M}} - \varepsilon_{\text{D}}) p_{\text{M}}$

As $p_{\text{M}} > 0$ after the equilibrium, $\underline{\varepsilon_{\text{D}}/\varepsilon_{\text{M}} = 1}$ holds at λ_{B1}.

6 points in total:

3 points for showing conversion using ideal gas law (either eq. *1, *2, or *3).

Full marks when the correct relationship between ε_{D} and ε_{M} is shown even without any derivation written.

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 $\varepsilon_{\text{D}}/\varepsilon_{\text{M}}$ at λ_{B2}.	6pt

Solution 1:

The absorbance at the initial state is:

$$A_{\text{B2}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_{y0}$$

The absorbance after equilibrium is:

$$A_{\text{B2}} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_y$$

Using the fact that:

$$l_y = l_{y0} \frac{V}{V_0}$$

The absorbance after equilibrium is expressed as follows:

$$A_{\text{B2}} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_y = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V_0} l_{y0}$$

From these equations, the following relationship is obtained:

$$A_{\text{B2}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_{y0} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V_0} l_{y0}$$

Using the fact that:

$n_{\text{M}} = 2(n_0 - n_{\text{D}})$ (*4)

The following relationship is obtained:

$$\varepsilon_{\text{D}} n_0 = \varepsilon_{\text{D}} n_{\text{D}} + 2\varepsilon_{\text{M}}(n_0 - n_{\text{D}}) = 2\varepsilon_{\text{M}} n_0 + (\varepsilon_{\text{D}} - 2\varepsilon_{\text{M}}) n_{\text{D}}$$

$$\rightarrow (\varepsilon_{\text{D}} - 2\varepsilon_{\text{M}}) n_0 = (\varepsilon_{\text{D}} - 2\varepsilon_{\text{M}}) n_{\text{D}}$$

As $n_0 > n_{\text{D}}$ after the equilibrium, $\underline{\varepsilon_{\text{D}} = 2\varepsilon_{\text{M}}}$ holds at λ_{B2}.

Solution 2:

Using the fact that $V_0 = l_{y0} S$, the absorbance at the initial state is expressed as:

$$A_{\text{B2}} = \frac{\varepsilon_{\text{D}} n_0}{V_0} l_{y0} = \varepsilon_{\text{D}} \frac{n_0}{S}$$

Using the fact that $V = l_y S$, the absorbance after equilibrium is expressed as:

$$A_{\text{B2}} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{V} l_y = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{S}$$

From these equations, the following relationship is obtained:

$$A_{\text{B2}} = \varepsilon_{\text{D}} \frac{n_0}{S} = \frac{\varepsilon_{\text{D}} n_{\text{D}} + \varepsilon_{\text{M}} n_{\text{M}}}{S}$$

Using the fact that:

$n_{\text{M}} = 2(n_0 - n_{\text{D}})$ (*4)

The following relationship is obtained:

$$\varepsilon_{\text{D}} n_0 = \varepsilon_{\text{D}} n_{\text{D}} + 2\varepsilon_{\text{M}}(n_0 - n_{\text{D}}) = 2\varepsilon_{\text{M}} n_0 + (\varepsilon_{\text{D}} - 2\varepsilon_{\text{M}}) n_{\text{D}}$$

$$\rightarrow (\varepsilon_{\text{D}} - 2\varepsilon_{\text{M}}) n_0 = (\varepsilon_{\text{D}} - 2\varepsilon_{\text{M}}) n_{\text{D}}$$

As $n_0 > n_{\text{D}}$ after the equilibrium, $\underline{\varepsilon_{\text{D}}/\varepsilon_{\text{M}} = 2}$ holds at λ_{B2}.

6 points in total:

3 points for showing the relationship that n_{M} is twice of $n_0 - n_{\text{D}}$ as in eq.*4.

Full marks when the correct relationship between ε_{D} and ε_{M} is shown even without any derivation written.

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.

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

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 $[\mathrm{Zn}^{2+}(\mathrm{aq})]$, $[\mathrm{Zn(OH)_2(aq)}]$ and $[\mathrm{Zn(OH)_4^{2-}(aq)}]$.	6pt

Solution 1:
From $[\mathrm{Zn(OH)_2(aq)}] > [\mathrm{Zn}^{2+}]$:
$\dfrac{K_{\mathrm{sp}}}{[\mathrm{OH}^-]^2} < K_1$ (1')
Solve this for $[\mathrm{OH}^-]$:
$\mathrm{pH} > 8.4$
$[\mathrm{Zn(OH)_2(aq)}] > [\mathrm{Zn(OH)_4^{2-}}]$:
$K_1 > K_2[\mathrm{OH}^-]^2$ (2')
Solve this for $[\mathrm{OH}^-]$:
$\mathrm{pH} < 11.8$
Thus,
$\underline{8.4 < \mathrm{pH} < 11.8}$

Solution 2:
From (1):
$\log[\mathrm{Zn}^{2+}][\mathrm{OH}^-]^2 = \log\ \mathrm{K_{sp}}$
$\log[\mathrm{Zn}^{2+}] = \log \mathrm{K_{sp}} - 2\log[\mathrm{OH}^-]$
From (2'):
$\log[\mathrm{Zn(OH)_2(aq)}] = \log \mathrm{K_1}$
$[\mathrm{Zn(OH)_2(aq)}] > [\mathrm{Zn}^{2+}]$:
$\log \mathrm{K_{sp}} - 2\log[\mathrm{OH}^-] < \log \mathrm{K_1}$ (1')
$\log \mathrm{K_{sp}} - 2(\mathrm{pH} - 14) < \log \mathrm{K_1}$
From (3'):
$\log([\mathrm{Zn(OH)_4^{2-}}]/[\mathrm{OH}^-]^2) = \log\ \mathrm{K_2}$
$\log[\mathrm{Zn(OH)_4^{2-}}] = 2\log[\mathrm{OH}^-] + \log\ \mathrm{K_2}$
$[\mathrm{Zn(OH)_2(aq)}] > [\mathrm{Zn(OH)_4^{2-}}]$:
$\log \mathrm{K_1} > 2\log[\mathrm{OH}^-] + \log \mathrm{K_2}$ (2')
$\log \mathrm{K_1} > 2(\mathrm{pH} - 14) + \log \mathrm{K_2}$
Thus,
$\underline{8.4 < \mathrm{pH} < 11.8}$

6 points in total:
3 points for $8.4 < \mathrm{pH}$
3 points for $\mathrm{pH} < 11.8$.
Partial point:
If correct answers are not obtained;
(1') and (2'): 2 points each.

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

For pH=12.00:
$\log[\mathrm{Zn(OH)_4^{2-}}] = -29.19 + 2\,\mathrm{pH} = -5.19$
$\log[\mathrm{Zn(OH)_2(aq)}] = -5.58$
$\log[\mathrm{Zn^{2+}}] = 11.24 - 2\,\mathrm{pH} = -12.76$
Thus, $S = 9.0865 \times 10^{-6}\ \mathrm{mol\,L^{-1}}$ (1')
For pH=7.00:
$\log[\mathrm{Zn(OH)_4^{2-}}] = -29.19 + 2\,\mathrm{pH} = -15.19$
$\log[\mathrm{Zn(OH)_2(aq)}] = -5.58$
$\log[\mathrm{Zn^{2+}}] = 11.24 - 2\,\mathrm{pH} = -2.76$
Thus,
$S = 1.7404 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$ (2')
The percentage of zinc precipitated is:

$$\frac{1.7404 \times 10^{-3} - 9.0865 \times 10^{-6}}{1.7404 \times 10^{-3}} = 0.9948 = 99.5\%$$

5 points in total:
2 points for the correct value of (1').
2 points for the correct value of (2').
1 point for the final correct answer. The calculation for the negligible component is not required.

Part B

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

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

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

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

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

$Zn + \frac{1}{2}O_2 \rightarrow ZnO$, $\Delta G_{ZnO}(300°C) = -2.90 \times 10^2$ kJ mol^{-1}
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, $\Delta G_{H_2O}(300°C) = -2.20 \times 10^2$ kJ mol^{-1}
Thus,
$ZnO + H_2 \rightarrow Zn + H_2O$, $\Delta G = \Delta G_{H_2O}(300°C) - \Delta G_{ZnO}(300°C)$ (1')
$= 7.0 \times 10^1$ kJ mol^{-1}
$\ln K = \ln\frac{p_{H_2O}}{p_{H_2}} = -\frac{\Delta G}{RT}$ (2')
From $T = 573.15$ K,
$\underline{p_{H_2O} = 4.14 \times 10^{-7}\ \text{bar} = 4.1 \times 10^{-7}\ \text{bar}}$

4 points in total:
1 point for the correct formulation of (1').
2 point for the correct formulation of (2').
1 point for the correct final answer.

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, $E°$.

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

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

The reaction Zn → ZnO occurs at the negative electrode and consumes 2 mol electrons per mol Zn oxidized.
Thus, the weight change is:
$W = \frac{0.02 \times 24 \times 60 \times 60 \times 16}{2F}$ (1')
$\underline{= 0.14\ \text{g}}$

3 points in total;
2 points for the correct formulation (1').
1 point for the correct final answer.

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

Solution 1:
From (9), the air pressure at 3776 m and $T = -38\,^{\circ}\text{C}$ is
$P = 0.6011\,\text{bar}$ (1')
From the oxygen content of 21% , the partial pressure of oxygen is:
$P_{\text{O}_2} = 0.126\,\text{bar}$
From the Nernst equation ($T = -38\,^{\circ}\text{C}$) :

$$E(-38\,^{\circ}\text{C}) - E^{\circ}(-38\,^{\circ}\text{C}) = -\frac{RT}{2F}\ln\frac{1}{\sqrt{P_{\text{O}_2}}} = -0.01048\,\text{V} = -0.01\,\text{V}\ (2')$$

$$E^{\circ}(-38\,^{\circ}\text{C}) = -\frac{\Delta G^{\circ}(-38\,^{\circ}\text{C})}{2F} = \frac{326000}{2F} = 1.6894\,\text{V} = 1.69\,\text{V}\ (3')$$

From (2') and (3'):
$\underline{E(-38\,^{\circ}\text{C}) = 1.68\,\text{V}}$

Solution 2:
From (9), the air pressure at 3776 m and $T = -38\,^{\circ}\text{C}$ is
$P = 0.6011\,\text{bar}$ (1')
From the oxygen content of 21% , the partial pressure of oxygen is:
$P_{\text{O}_2} = 0.126\,\text{bar}$

$$\Delta G(-38\,^{\circ}\text{C}) = \Delta G^{\circ}(-38\,^{\circ}\text{C}) - \frac{1}{2}RT\ln P_{\text{O}_2}\ (2')$$

$$= -3.24 \times 10^{2}\,\text{kJ mol}^{-1}$$

$$E(-38\,^{\circ}\text{C}) = -\frac{\Delta G(-38\,^{\circ}\text{C})}{2F}\ (3')$$

$\underline{= 1.68\,\text{V}}$

($^{\circ}$ is used for 1 bar)

5 points in total:
1 point for the correct value of (1').
2 points for the correct formulation of (2').
1 point for the correct formulation of (3')
1 point for the correct final answer.

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

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

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

From (10):
$\mathrm{Zn^{2+} + 2e^- \rightarrow Zn}, E^\circ = -0.77\,\mathrm{V}$
$\Delta G^\circ = -2F \times -0.77$ (1')
$= 148.59\,\mathrm{kJ\,mol^{-1}}$
From (8):
$\mathrm{Zn + \frac{1}{2}O_2 \rightarrow ZnO}, E^\circ = 1.65\,\mathrm{V}$
$\Delta G^\circ = -2F \times 1.65$ (2')
$= -318.40\,\mathrm{kJ\,mol^{-1}}$
From (11):
$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}, E^\circ = 1.23\,\mathrm{V}$
$\Delta G^\circ = -4F \times 1.23$ (3')
$= -474.71\,\mathrm{kJ\,mol^{-1}}$
From (1):
$\mathrm{Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2(s)}, K_\mathrm{sp} = 1.74 \times 10^{-17}$
$\Delta G^\circ = -RT\,\mathrm{ln}K_\mathrm{sp}^{-1}$ (4')
$= -95.662\,\mathrm{kJ\,mol^{-1}}$
From (4):
$\mathrm{H^+ + OH^- \rightarrow H_2O}, K_\mathrm{w} = 1 \times 10^{-14}$
$\Delta G^\circ = -RT\,\mathrm{ln}K_\mathrm{w}^{-1}$ (5')
$= -79.912\,\mathrm{kJ\,mol^{-1}}$
From $\frac{(1')\times 2+(2')\times 2-(3')-(4')\times 2+(5')\times 4}{2}$
$\mathrm{Zn(OH)_2 \rightarrow ZnO + H_2O}, \Delta G^\circ = 3.0 \sim 3.4 \times 10^3\,\mathrm{J\,mol^{-1}}$
(distributed depending on the handling of figures)

9 points in total:
1 points for correct formulation (1').
1 points for correct formulation (2').
1 points for correct formulation (3').
2 points for correct formulation (4').
2 points for correct formulation (5').
2 point for the correct final answer.

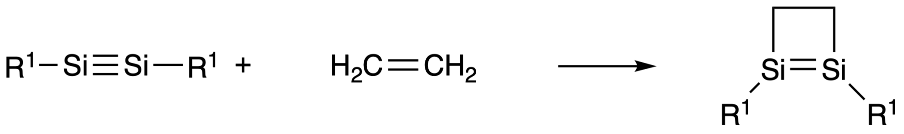
Mysterious Silicon

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

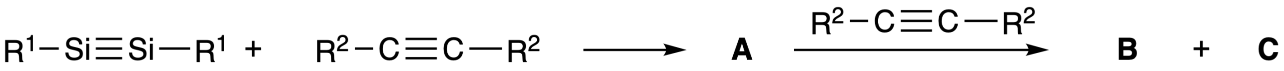
Although silicon is also a group 14 element like carbon, their properties differ significantly.

Part A

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



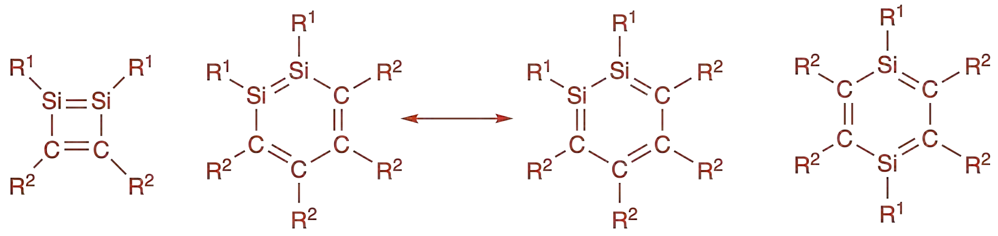
When $R^1{-}Si \equiv Si{-}R^1$ is treated with an alkyne ($R^2{-}C \equiv C{-}R^2$), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of $R^2{-}C \equiv C{-}R^2$ with **A** affords isomers **B** and **C**, both of which have benzene-like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



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

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

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



A **B** **C**

Any resonance structure is acceptable.

9 points in total: 3 points for each correct answer.**A**: 3 points (2 points when the Si=Si–C=C four-membered ring skeleton is drawn correctly.)**B**: 3 points: (2 points when the Si–Si–C–C–C–C six-membered ring skeleton is drawn correctly. 1 point when 1,4- or 1,3-disilabenzene is depicted. 0 points when only the 1,4- or 1,3-disilabenzene is shown and R^1 and R^2 are drawn incorrectly.)**C**: 3 points: (2 points when the Si–C–C–Si–C–C six-membered ring skeleton is drawn correctly. 1 point when 1,2- or 1,3-disilabenzene is depicted. 0 points when only the 1,2- or 1,3-disilabenzene is shown and R^1 and R^2 are drawn incorrectly.)

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

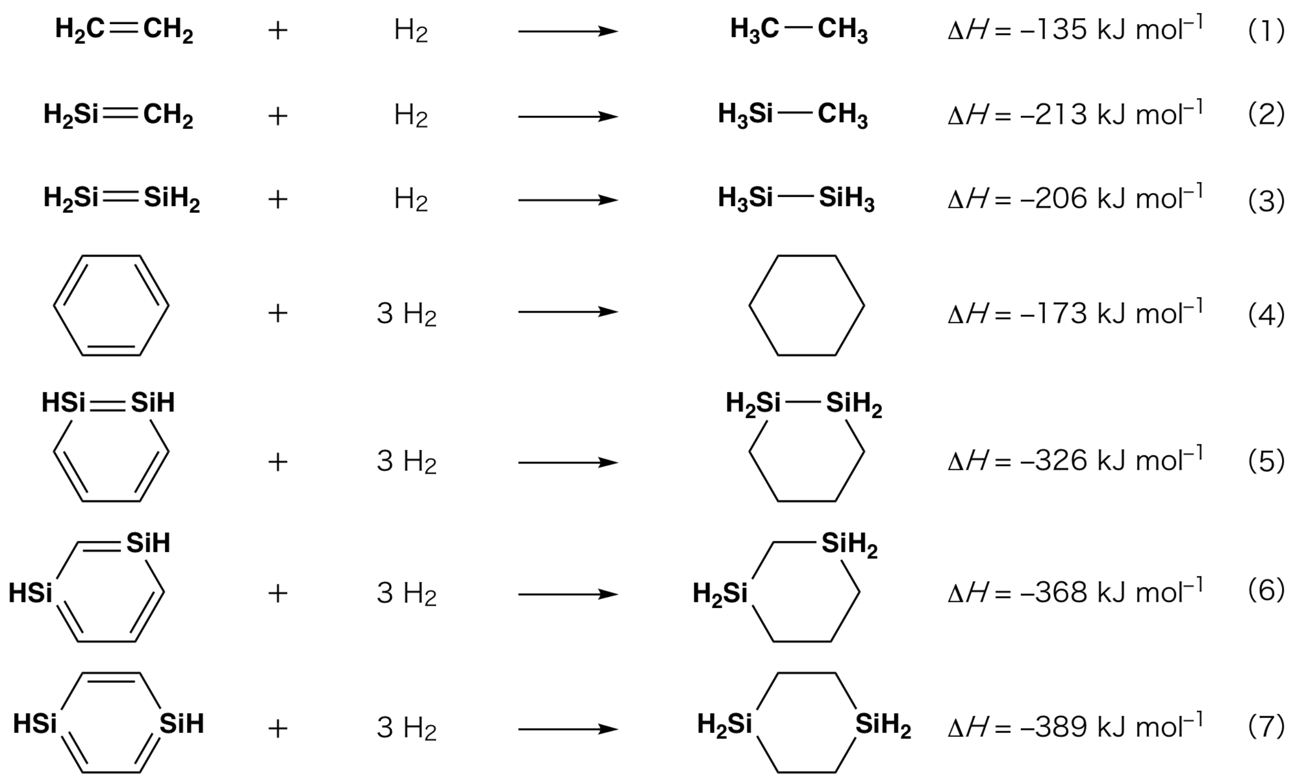


Fig. 1

The aromatic stabilization energy (ASE) can be calculated as the difference of the sum of the heat of hydrogenation of each double bond and the heat of hydrogenation of the aromatic compound.
ASE for benzene: $\underline{135 \times 3 - 173 \ = \ 232\ \mathrm{kJ\,mol^{-1}}}$
ASE for 1,4-disilabenzene (C=C + 2 Si=C): $\underline{(135 + 213 \times 2) - 389 = 172\ \mathrm{kJ\,mol^{-1}}}$

7 points in total: 3 points for ASE for benzene and 4 points for compound **C**.
3 points for the correct ASE value for benzene (2 points when the values have the correct magnitude but are negative.).
4 points for the correct ASE value for compound **C**, 1,4-disilabenzene. (3 points when the values have the correct magnitude but are negative.) (4 points for the ASE value for 1,2-disilabenzene $(206 + 135 \times 2) - 326 = 150\ \mathrm{kJ\,mol^{-1}}$ or $(213 \times 2 + 135) - 326 = 235\ \mathrm{kJ\,mol^{-1}}$ when the 1,2-disilabenzene is written as a structure of **C**. 4 points for the ASE value for 1,3-disilabenzene$(135 + 213 \times 2) - 368 = 193\ \mathrm{kJ\,mol^{-1}}$ when the 1,3-disilabenzene is written as a structure of **C**.)

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

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

T = 50 °C = 323.15 K $\left(\frac{1}{RT}=0.3722\right)$: $K_{\mathrm{DE}}=40$

T = 120 °C = 393.15 K $\left(\frac{1}{RT}=0.3095\right)$: $K_{\mathrm{DE}}=20$

According to $\ln K_{\mathrm{DE}}=-\frac{\Delta H}{RT}+\frac{\Delta S}{R}$

$$\Delta H=-\frac{\ln(K_{\mathrm{DE50}})-\ln(K_{\mathrm{DE120}})}{\frac{1}{RT_{50}}-\frac{1}{RT_{120}}}=-\frac{\ln 40-\ln 20}{0.3722-0.3059}=-10.5\ \mathrm{kJ\ mol^{-1}}$$

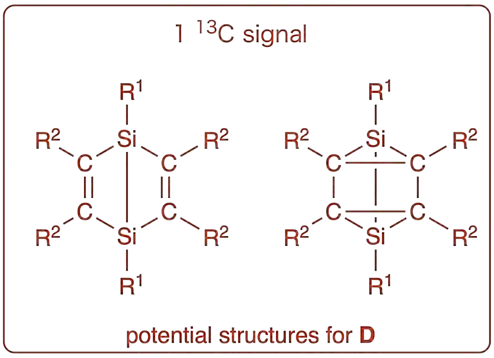
---

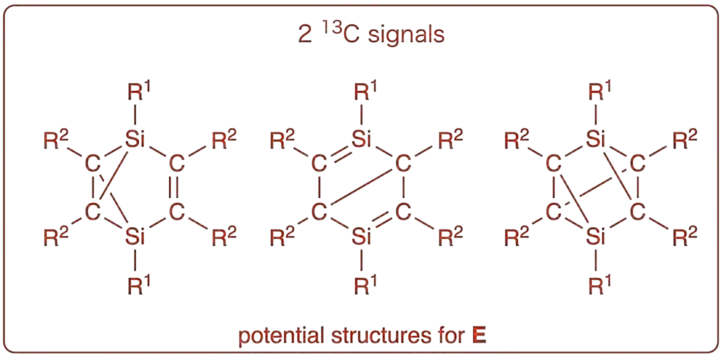
6 points: (+4 points for the correct equation. -2 points for the positive value.)

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.

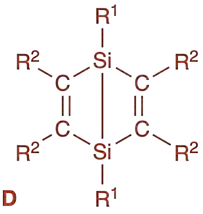
A.4 **Draw** the structural formulae of **D** and **E** using R^1, R^2, Si, and C. 10pt

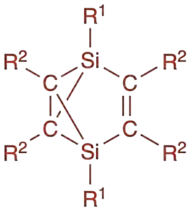
Based on the signals observed in the ^{13}C NMR spectra, the following structures could be suggested for **D** and **E**:





In addition, considering that **D** has no three-membered ring in its skeleton while **E** has two three-membered rings that share an edge, the structures of **D** and **E** can be determined to be those shown below:


D


E

10 points in total: 5 points for each correct structure.
(4 points for incorrect substituents R^1 or R^2. 3 points for other candidates based on the information from the ^{13}C NMR spectra; 2 points for Si-regioisomers that would satisfy the ^{13}C NMR spectral information; 1 point for Si-regioisomers that would not satisfy the ^{13}C NMR spectral information.)
For **D**: 2 points for other Dewer-benzene structure (because "not contain any three-membered rings"). For **E**: 2 points for other benzvalene structure (because "two three-membered rings that share an edge.").

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

Na_2SiF_6 = 188.053 g mol^{-1}. The concentration of Na_2SiF_6 in solution **F** is

$$\frac{0.855\ \text{g}}{200\ \text{mL}} = \frac{4.548 \times 10^{-3}\ \text{mol}}{0.2\ \text{L}} = 2.274 \times 10^{-2}\ \text{mol L}^{-1}\ (\mathbf{F})$$

$Ce_2(SO_4)_3$ = 568.424 g mol^{-1}. The concentration of $Ce_2(SO_4)_3$ in solution **G** is

$$\frac{6.860\ \text{g}}{200\ \text{mL}} = \frac{1.207 \times 10^{-2}\ \text{mol}}{0.2\ \text{L}} = 6.034 \times 10^{-2}\ \text{mol L}^{-1}\ (\mathbf{G})$$

The concentration of Ce^{3+} ions in **G** is $6.034 \times 10^{-2} \times 2 = 1.207 \times 10^{-2}$ mol L^{-1}.

In 50.0 mL of solution **F**: $2.274 \times 10^{-2} \times \frac{50.0}{1000} = 1.137 \times 10^{-3}$ mol of Na_2SiF_6 was included.

In 18.8 mL of solution **G**: $6.034 \times 10^{-2} \times \frac{18.8}{1000} = 1.134 \times 10^{-3}$ mol of $Ce_2(SO_4)_3$ was included. Accordingly, Na_2SiF_6 should react with $Ce_2(SO_4)_3$ in a 1:1 ratio.

Ans. $Na_2SiF_6 + Ce_2(SO_4)_3 + 4\,H_2O \longrightarrow 2\,CeF_3 + Si(OH)_4 + Na_2SO_4 + 2\,H_2SO_4$

5 points: (+1 points when "$Na_2SiF_6 + Ce_2(SO_4)_3$" is written on the left side, and +2 points when "CeF_3" is written on the right side of the equation; +1 points when "$Si(OH)_4$" is written on the right side of the equation.) Full mark for showing ionic compounds, which soluble in water as ions/ion pairs such as $NaHSO_4$, Na^+, H^+, and etc. (The calculation procedure is not necessary.)

- **Reaction of $CCl_4$with Na_2SiF_6:**

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

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

Table 1

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

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

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

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

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

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

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

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

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

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

$3\,SiF_4 + 2\,H_2O \longrightarrow SiO_2 + 2\,H_2SiF_6$
The ratio of the consumed SiF_4 and the generated H_2SiF_6 should be 3:2.
As Na_2SiF_6 reacts with $Ce_2(SO_4)_3$ in a 1:1 ratio, the amount of SiF_6^{2-} in the aqueous solution **J** is $(6.034 \times 10^{-2}\ \text{mol L}^{-1}) \times (61.6 \times 10^{-3}\ \text{L}) = 3.717 \times 10^{-3}$ mol. Considering the equation shown above, 10 mL of the diluted solution **H** contains $3.717 \times 10^{-3}\ \text{mol} \times \frac{3}{2} = 5.576 \times 10^{-3}$ mol of SiF_4. Thus, 1.00 L of diluted solution **H** contains $5.576 \times 10^{-3}\ \text{mol} \times \frac{1000}{10} = 5.576 \times 10^{-1}$ mol of SiF_4.
The amount of fluorine atoms that replace the chlorine atoms of CCl_4 should be twice the amount of SiF_4 formed during the reaction. Thus, $2 \times 0.5576 = 1.115$ mol of F^- should replace Cl^- to result in the formation of NaCl. $1.115\ \text{mol} \times 58.44\ \text{g mol}^{-1} = 65.17$ g of NaCl was formed.
Ans.: 65.2 g (NaCl)
As Na_2SiF_6 reacts with $Ce_2(SO_4)_3$ in a 1:1 ratio, the amount of SiF_6^{2-} in 100 mL of aqueous solution K is $44.4 \times 10^{-3}\ \text{L} \times (6.034 \times 10^{-2}\ \text{mol L}^{-1}) = 2.679 \times 10^{-3}$ mol. Accordingly, the residual amount of Na_2SiF_6 in 10.0 L of aqueous solution **K** is $2.679 \times 10^{-3}\ \text{mol} \times \frac{10.0\ \text{L}}{100\ \text{mL}} = 0.2679$ mol. In total, the amount of Na_2SiF_6 used as a starting material is $(0.2679\ \text{mol} + 0.5576\ \text{mol}) \times 188.0\ \text{g mol}^{-1} = 155.2$ g
Ans.: 155 g (Na_2SiF_6)

15 points in total:
·10 points for the correct amount of NaCl:
+3 points for the amount of SiF_6^{2-} in solution **J** (3.717×10^{-3}mol)
+2 point for the amount of SiF_4 in 10 mL of the diluted solution **H** (5.576×10^{-3} mol)
+2 point for the amount of SiF_4 in 1.00 L of the solution **H** (5.576×10^{-1} mol)
+2 points for the amount of NaCl in mol (1.115mol)
+1 point when the amount of NaCl is shown in gram.
·5 points for the correct amount of Na_2SiF_6:
+2 points for the amount of SiF_6^{2-} in solution **K** (2.68×10^{-3}mol)
+1 point for the amount of SiF_6^{2-} before dilution to prepare solution **K** (2.68×10^{-1}mol)
+1 point for the addition of the amount of SiF_4 in solution H (8.26×10^{-1}mol)
+1 for answering the initial amount of Na_2SiF_6 in [g].

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

500.0 g = 3.250 mol of CCl_4 was initially used as a starting material. Thus, the amount of the products that contain at least one F atom is 3.250 mol $\times$ 0.222 $=$ 0.721 mol.
The ratio of integrals in the ^{19}F NMR spectrum is $CFCl_3 : CF_2Cl_2 : CF_3Cl : CF_4$ = 45.0 : 65.0 : 18.0 : 2.0. Thus, the mole ratio of these compounds should be $CFCl_3 : CF_2Cl_2 : CF_3Cl : CF_4$ = 45.0 : 32.5 : 6.0 : 0.5 = 90 : 65 : 12 : 1. Accordingly, the amount of CF_3Cl (104.46 g mol^{-1}) is

$$0.721\ \text{mol} \times \frac{12}{90+65+12+1} = 0.0515\ \text{mol} = 0.0515 \times 104.46\ \text{g} = 5.38\ \text{g}$$

Ans.: 5.38 g

8 points: (6 points for the answer in [mol]; 4 points for the correct molar ratio of substances $CFCl_3 : CF_2Cl_2 : CF_3Cl : CF_4$ = 90 : 65 : 12 : 1).

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

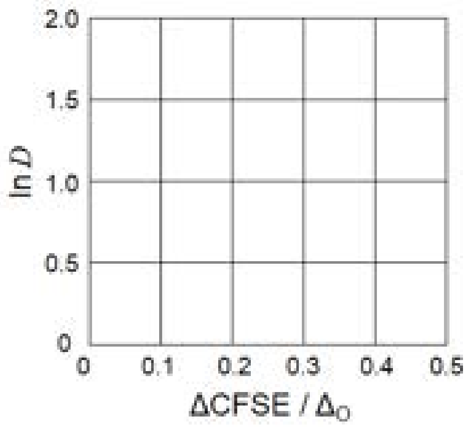
Let Δ_O and CFSE^O be the energy separation of the d-orbitals of M^{n+} and the crystal-field stabilization energy in a O_h field, respectively. Let Δ_T and CFSE^T be those in a T_d field.

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

The d-orbitals of a six-coordinate octahedral complex split into two groups e_g ($d_{x^2-y^2}$, d_{z^2}), and t_{2g} (d_{xy}, d_{yz}, d_{zx}) with an energy separation of Δ_O. The energies of the e_g and t_{2g} orbitals relative to the barycenter are +0.60Δ_O and –0.40Δ_O, respectively. Likewise, the d-orbitals of a four-coordinate tetrahedral complex split into two groups t_2 (d_{xy}, d_{yz}, d_{zx}) and e ($d_{x^2-y^2}$, d_{z^2}) with an energy separation of Δ_T. The energies of the t_2 and e orbitals relative to the barycenter are +0.40Δ_T and –0.60Δ_T, respectively. Therefore, in the case of a high-spin electron configuration, CFSE^O and CFSE^T for Cr^{2+} ($3d^4$: $t_{2g}{}^3e_g{}^1$ or $e^2t_2{}^2$) are –0.60Δ_O and –0.40Δ_T (= –0.18Δ_O), respectively. CFSE^O and CFSE^T for Mn^{2+} ($3d^5$: $t_{2g}{}^3e_g{}^2$ or $e^2t_2{}^3$) are both zero. CFSE^O and CFSE^T for Co^{2+} ($3d^7$: $t_{2g}{}^4e_g{}^3$ or $e^4t_2{}^3$) are –0.80Δ_O and –1.2Δ_T (= –0.53Δ_O), respectively. Accordingly, $|\text{CFSE}^O - \text{CFSE}^T|$ = ΔCFSE values for each metal ion are,
Cr^{2+}: |–0.60Δ_O – (–0.18Δ_O)| = $\underline{0.42\Delta_O}$, Mn^{2+}: $\underline{0}$, Co^{2+}: |–0.80Δ_O – (–0.53Δ_O)| = $\underline{0.27\Delta_O}$

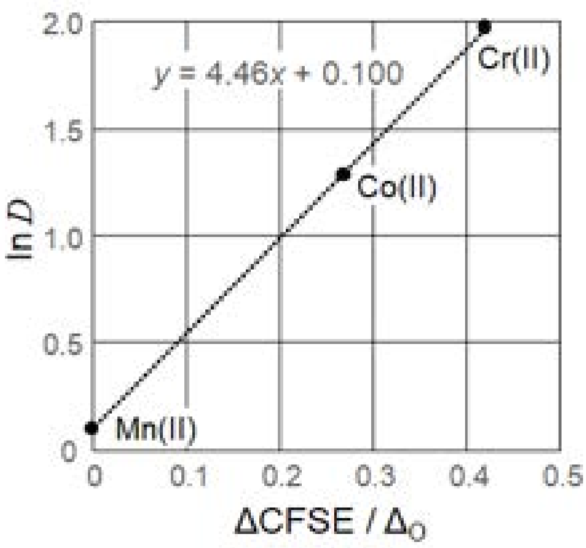
6 points in total: 2 points each for ΔCFSE of the three divalent metal ions.

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



The coordinates of Mn^{2+} and Cr^{2+} are (0, 0.095) and (0.42, 1.97), respectively. The linear regression line calculated from these coordinates would be
$y = 4.46x + 0.100$
ΔCFSE of Co^{2+} is $0.27\Delta_O$
Therefore, $D = \exp(4.46 \times 0.27 + 0.100) = \underline{3.68\ (= 3.7)}$

Whether the graph is drawn does not affect grading.
If the coordinates of Mn^{2+} and Cr^{2+} are correctly plotted and the D is estimated with guide of the graph, full mark is given.



3 points for the calculation of D.
Partial credit of 2 points if the ln$D$ is correctly estimated from the linear regression line or the graph.
If the intercept of the linear regression line is assumed as zero (i.e., Mn^{2+} is at the origin of the coordinate), full mark is given.
In order to avoid double punishment with A.1: If the answers of A.1 were wrong but the coordinates of Mn^{2+} and Cr^{2+} are correctly plotted in the graph (or simultaneous equations are given) according to the answers of A.1, and D of Co^{2+} is correctly estimated from ln$D$ assuming a linear relationship, full mark is given.

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

The lattice enthalpy is determined by the Coulomb interactions, which are proportional to the product of the valences of the constituent ions and inversely proportional to the sum of the ionic radii. As the target compounds are oxides of divalent metal ions, we should consider the ionic radii of the metal ions. The radii of divalent metal ions within the same period decrease with increasing atomic number. Let us compare the lattice enthalpies of CaO and MnO with no contribution from the CFSE: The ionic radius of Mn^{2+} is smaller than that of Ca^{2+}, and therefore, the lattice enthalpy is higher for MnO. So, the participants should choose (a), (b), or (c). Then, let us compare the lattice enthalpies of TiO (d^2) and VO (d^3): The ionic radius of V^{2+} is smaller than that of Ti^{2+}, and the CFSE is higher for VO than for TiO. Accordingly, the lattice enthalpy is also higher for VO. Based on these observations, the answer should be (a) or (c). Finally, let us compare the lattice enthalpies of TiO (d^2) and CoO (d^7): The ionic radius of Co^{2+} is smaller than that of Ti^{2+}, while their CFSEs are equal. Thus, the lattice enthalpy is higher for CoO. Thus, the correct answer is (a). Partial credit is given for (b) and (c).

3 points for the correct answer (a). Partial credit of 2 points for (c) and 1 point for (b).

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}).

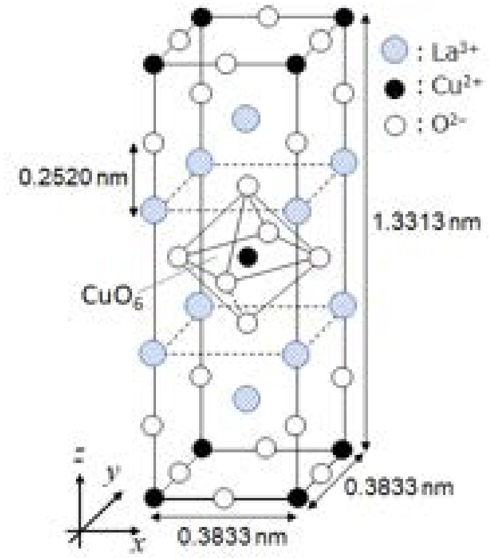


Fig. 1

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

The unit cell shown in Fig. 1 contains four La^{3+}, two Cu^{2+}, and eight O^{2-} ions. Therefore, **A**: La_2CuO_4. As the formula weight of La_2CuO_4 is 405.3, that of **B** should be 1113.5 considering the following equation: 405.3 ÷ (1 – 0.636). Given that the weight loss due to crystallization water is 29.1%, the number of molecules of crystallization water is 18.00 considering the following equation: (1113.5 × 0.291) ÷ 18 ($18H_2O$; M = 324). Complex **B** is a trinuclear complex that consists of two La^{3+} and one Cu^{2+} ions. Considering that the synthetic solution is basic, the squaric acid is deprotonated and coordinates to the metal ion as $C_4O_4{}^{2-}$. The number of squaric acid molecules is 4.00 based on the following equation: (1113.5 – 138.9 × 2 – 63.5 – 324) ÷ 112 ($C_4O_4{}^{2-}$; M = 112). B: $La_2Cu(C_4O_4)_4(H_2O)_{18}$ ($La_2CuC_{16}O_{34}H_{36}$)

6 points in total (2 and 4 points for **A** and **B**, respectively). Partial credit of 2 points for the correct number of crystallization water ($La_2Cu(H_2O)_{18}$) for **B**. (full marks are also given for **A**: $La_4Cu_2O_8$ and **B**: $La_4Cu_2(C_4O_4)_8(H_2O)_{36}$ ($La_4Cu_2C_{32}O_{68}H_{72}$), which correspond to the numbers of elements in the unit cell)

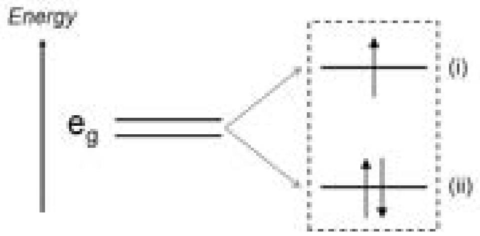
B.2 Calculate l_x and l_z using Fig. 1. 4pt

l_x: 0.3833 ÷ 2 = 0.1917 (= 0.192 nm).
l_z: (1.3313 – 0.2520 × 2) ÷ 4 = 0.2068 (= 0.207 nm)

4 points in total (2 points for each correct answer).

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

(i) $d_{x^2-y^2}$, (ii) d_{z^2}



4 points in total: 2 points for the correct names of the orbitals in (i) and (ii), and 2 points for the correct electron configuration in the dotted box. Full mark is given even spin up and down directions of the electrons are not shown (the electrons can be shown in arrows, lines, circles etc.).

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

The corresponding reaction equation, where the amount of Sr^{2+} is x%, is:
$La_2CuO_4 + (2x/100)Sr^{2+} \rightarrow [La_{2(1-x/100)}Sr_{(2x/100)}CuO_4]^{(2x/100)-} + (2x/100)La^{3+}$
The charge of $[La_{2(1-x/100)}Sr_{(2x/100)}CuO_4]$ is negative, and the amount of doped holes is $(2x/100)h^+$ per mole. The volume of the unit cell is $0.3833^2 \times 1.3313 = 0.1956$ nm^3. The unit cell contains four La^{3+}, two Cu^{2+}, and eight O^{2-} ions, i.e., the unit contains two La_2CuO_4. Accordingly, the number of holes per unit cell is (4x/100).
Since the concentration of holes is the number of holes divided by the unit cell volume, the following equation is satisfied: $(4x/100)/(0.1956 \times 10^{-27}) = 2.05 \times 10^{-27}$, x = 10%
Alternative answer without giving the substitution reaction; density of La^{3+} in the unit cell $4/(0.3833^2 \times 1.3313) = 20.45$ nm^{-3}
Density of holes in the unit cell is 2.05 nm^{-3}
Therefore, the percentage of substitution is $2.05/20.45 \times 100$ = 10%

4 points for the correct answer; whether the substitution reaction is given does not affect grading; partial credit of 1 point for 20% (forgetting that the unit cell contains two La_2CuO_4).

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.

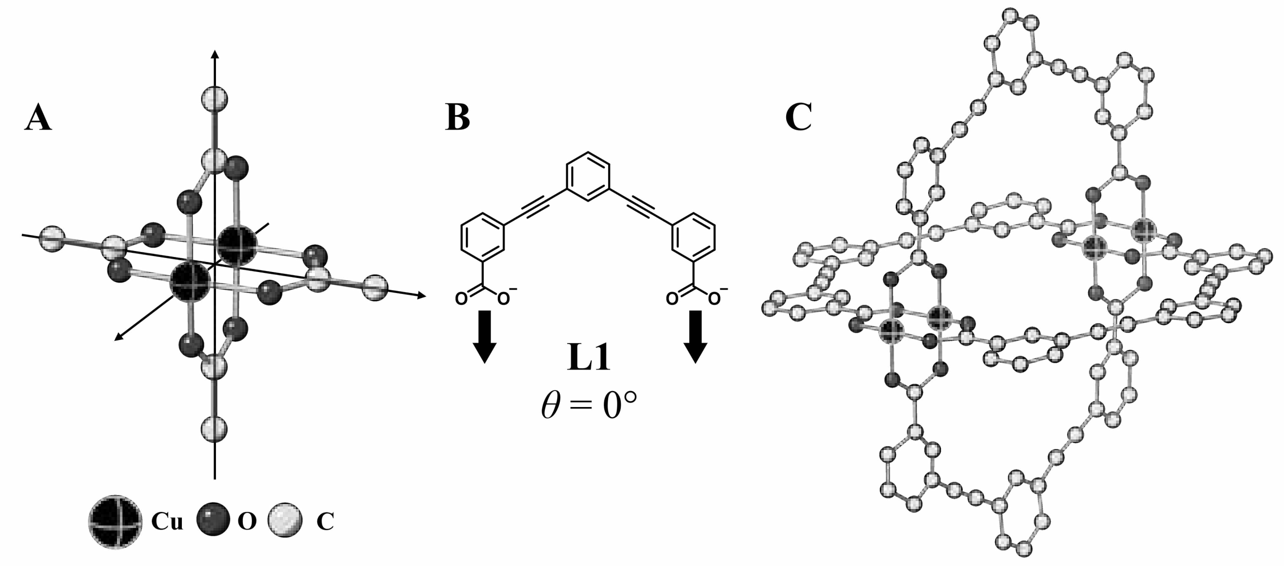
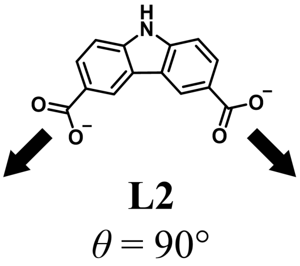
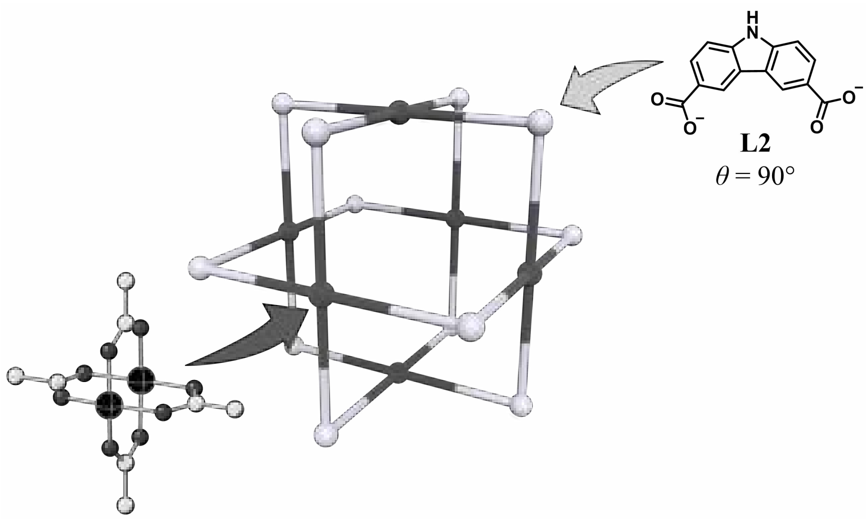


Fig. 2

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



$n = m = 12$



5 points in total. Partial credit of 2 points for all answers with $n : m = 1 : 1$ (charge neutrality is satisfied but Cu^{2+} would not be 4-coordinate) or $n = 6$, $m = 12$ (Cu^{2+} is 4-coordinate but the complex would be an anion).

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.

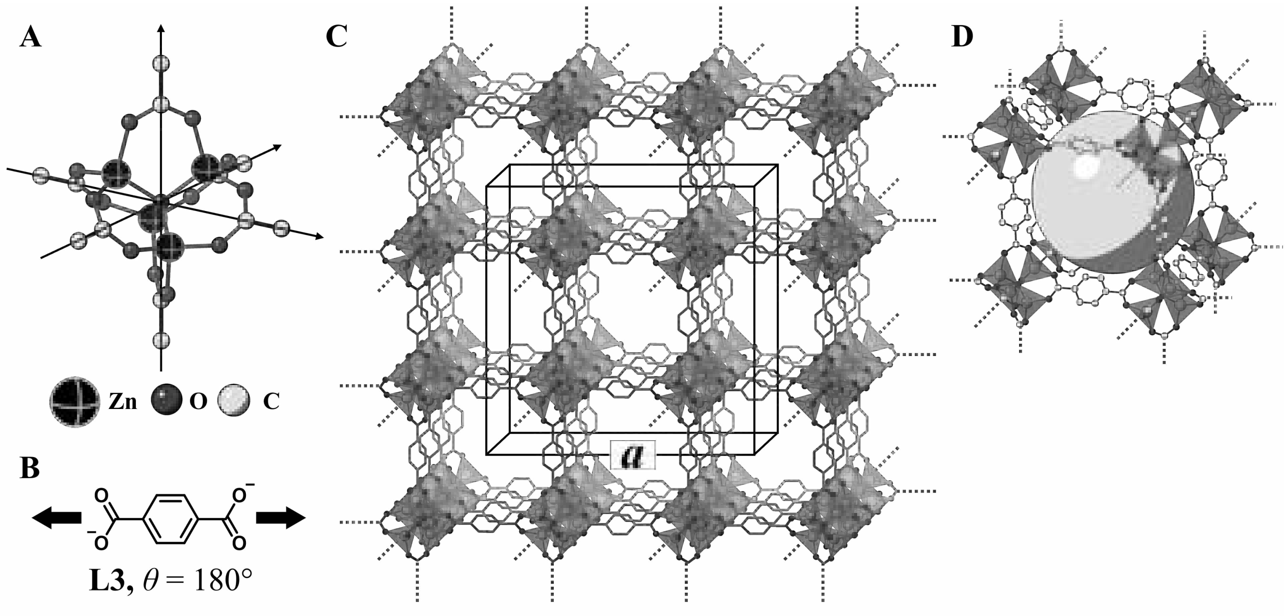


Fig. 3

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

The molecular weight of Zn$_4$O$(\mathbf{L3})_3$ is 770.
According to Figure 3C, there are eight Zn$_4$O$(\mathbf{L3})_3$ units in the unit cell. Therefore, the molecular weight per unit cell can be calculated as 770 × 8 = 6160.
The weight of the unit cell is $6160 \div N_\text{A} = 1.02 \times 10^{-20}$ g
Let the length of the side of the unit cell be a [cm], then, (1.02×10^{-20}) g / a^3 [cm^3] = 0.592 g cm^{-3}.
a = 2.6×10^{-7} cm

5 points in total.
Partial credit of 3 points for the correct formulation to derive the molecular weight of the unit cell; 2 points for the correct value of a.

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

There is one pore per $Zn_4O(\mathbf{L3})_3$ unit.
Number of pores [mol] per 1 [g] of **X**: 1 [g] / 770 = 0.00130.
Based on the ideal gas equation, 3.0×10^2 [mL] of adsorbed CO_2 corresponds to:
(1×10^5 [Pa] × 3.0×10^{-4} [m^3]) / (8.31 × 298 [K]) = 0.0121 [mol] of CO_2.
Therefore, 0.0121 ÷ 0.00130 = 9.3 molecules of CO_2 per pore.

5 points in total.
Partial credit of 3 points for the correct formulation to calculate the number of pores in 1 g; 2 points for the correct calculation of the number of molecules of CO_2 per pore.

Playing with Non-benzenoid Aromaticity

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

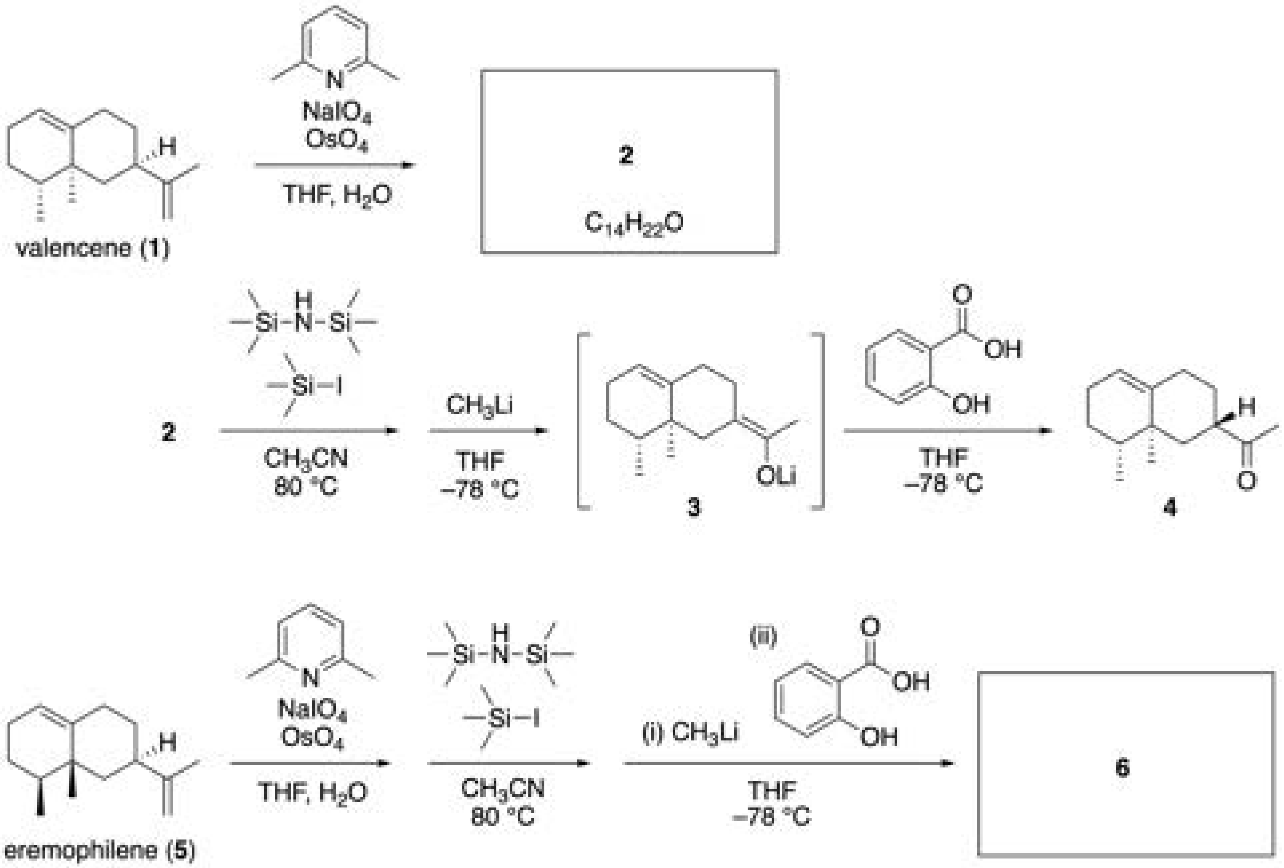
Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

Photo courtesy: Tohoku Univ.

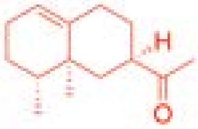
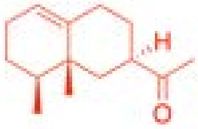
Part A

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

Inula linariifolia



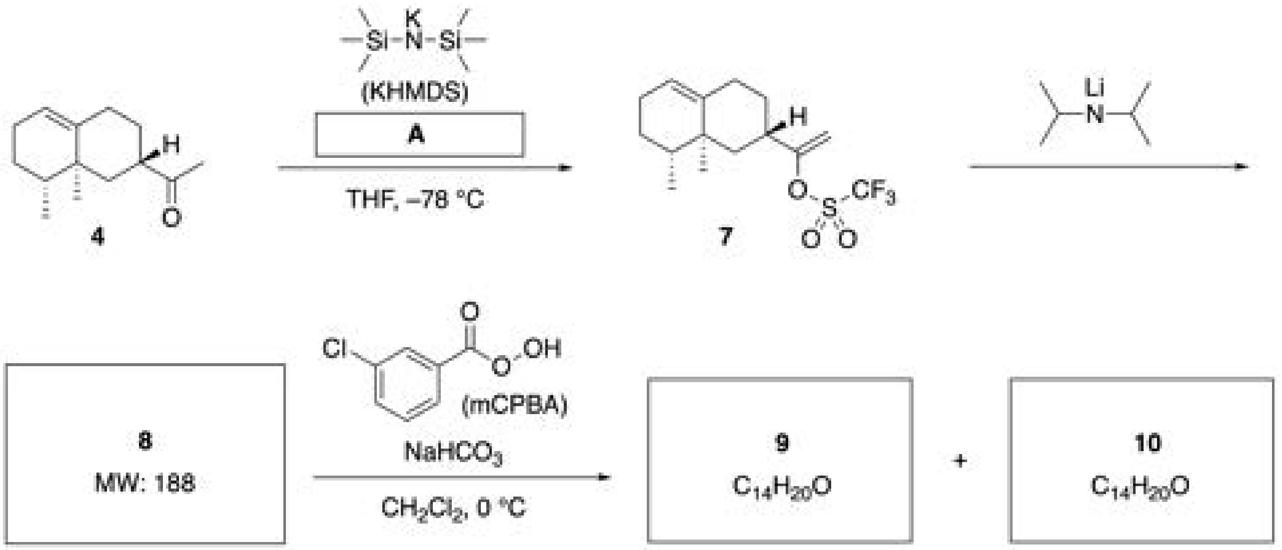
A.1 **Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary. 5pt

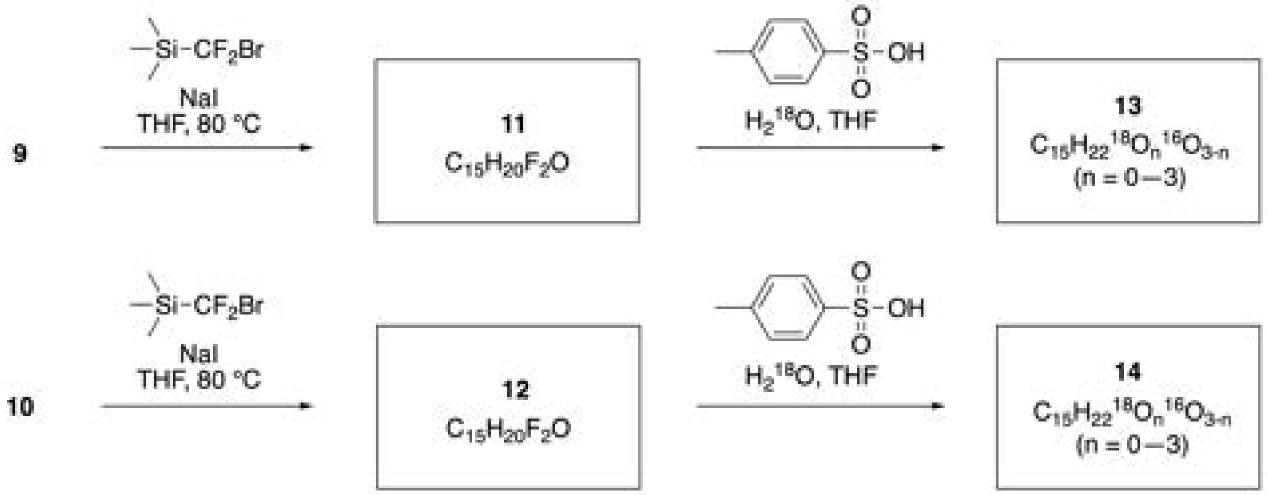
2 (2 pt) 	**6** (3 pt) 

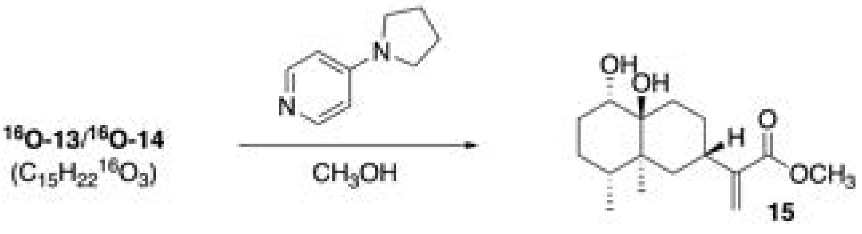
2 (2 pt in total):
–1 pt for missing double bond,
–1 pt for stereochemistry error.

6 (3 pt in total):
–1 pt for missing double bond,
–2 pt for stereochemistry error.

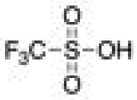
Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-lineariifolianones **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.


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

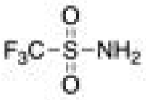

9
NaI
THF, 80 °C
11
C$_{15}$H$_{20}$F$_2$O
H$_2$^{18}O, THF
13
C$_{15}$H$_{22}$^{18}O$_n$^{16}O$_{3-n}$
(n = 0−3)
10
NaI
THF, 80 °C
12
C$_{15}$H$_{20}$F$_2$O
H$_2$^{18}O, THF
14
C$_{15}$H$_{22}$^{18}O$_n$^{16}O$_{3-n}$
(n = 0−3)


^{16}O-13/^{16}O-14
(C$_{15}$H$_{22}$^{16}O$_3$)
CH$_3$OH
15

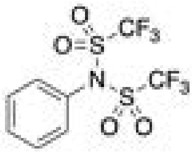
A.2 **Choose** the appropriate structure for **A**. 2pt

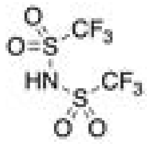
I 

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

II 

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

III 

IV 

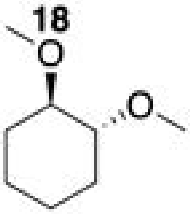
III

A is reacted with the potassium enolate of **4**, thus **I**, **II**, **IV** are inappropriate because these reagents have acidic protons.

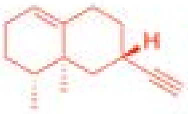
2 pt in total

others: 0 pt

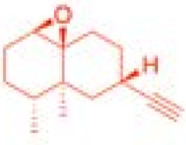
A.3 **Draw** the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, **indicate** the introduced ^{18}O atoms for **13** and **14** as shown in the example below. 19pt



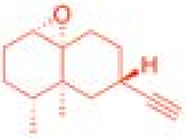
8 (3 pt)



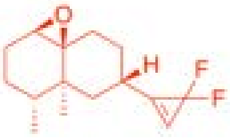
9 (2 pt)



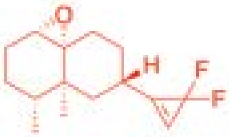
10 (2 pt)



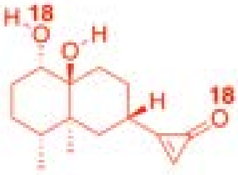
11 (2 pt)



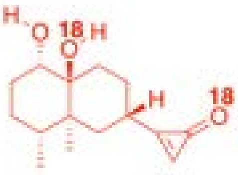
12 (2 pt)



13 (4 pt)



14 (4 pt)



8 (3 pt in total):
–1 pt each for missing one double bond or drawing an allene instead of an alkyne,
0 pt for incorrect planar structure,
-2 pt for an opposite stereochemistry next to the alkyne,
-2 pt for other stereochemistry errors.

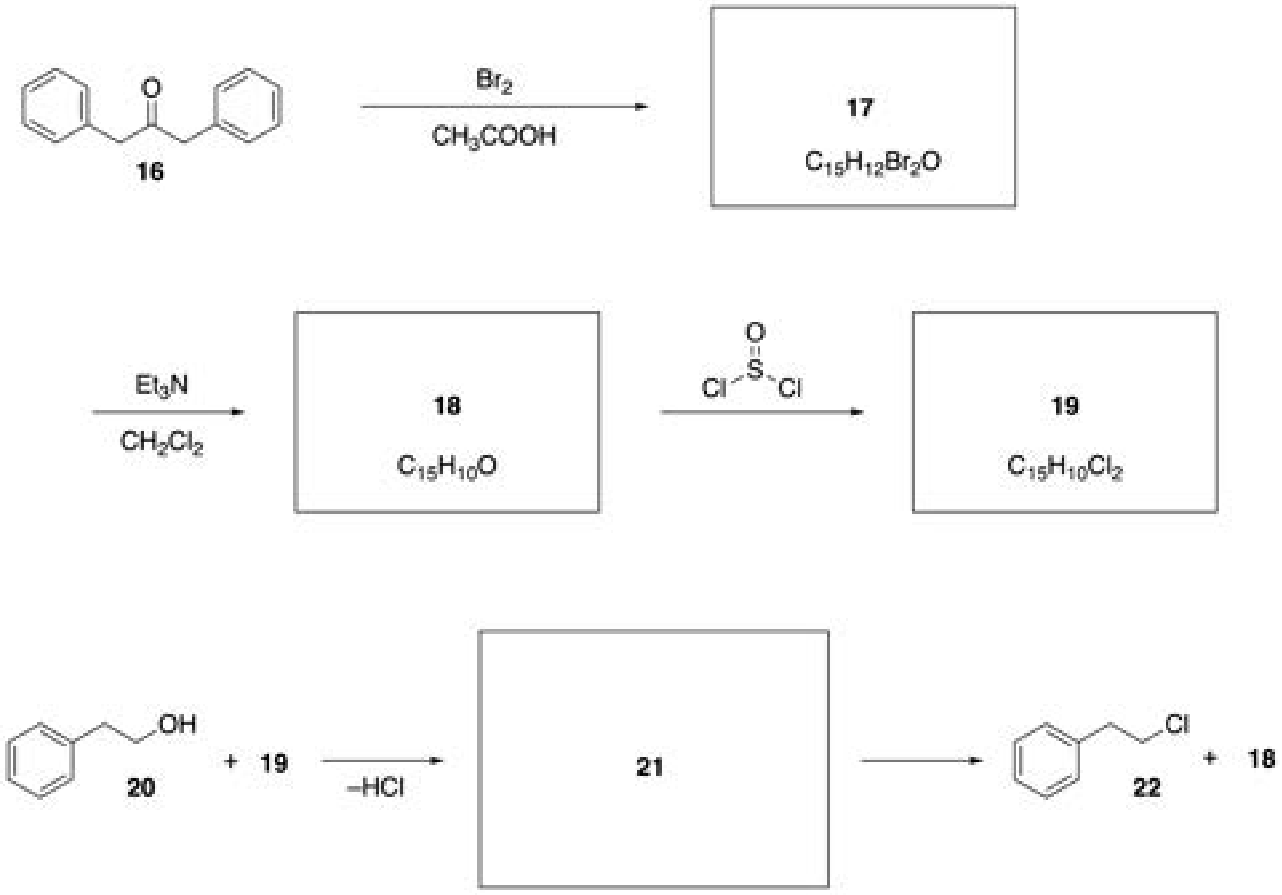
9–12 (2 pt each, 8 pt in total):
–1 pt each for missing atoms (e.g., fluorine atom, oxygen of epoxide),
-1 pt for stereochemistry error,
Two sets of compounds **9**, **11**, **13** and **10**, **12, 14** are interconvertible,

Structures of 13 and 14/^{18}O **labelling on hydroxy groups of 13 and 14 (3 pt each, 6 pt in total):**
-1 pt each for incorrect or unclear ^{18}O labelling on the diol moiety,
-1 pt each for incomplete transformation (diol only, ketone only),
0 pt for incorrect planar structure other than the above,
-2 pt for stereochemistry error.

^{18}O **labelling on carbonyl group of 13 and 14 (1 pt each, 2 pt in total):**
0 pt when ^{18}O is incorporated in the carbonyl group of neither **13** nor **14**.

Part B

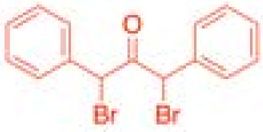
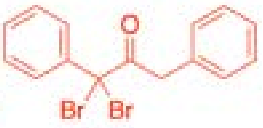
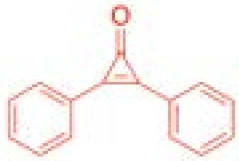
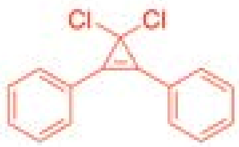
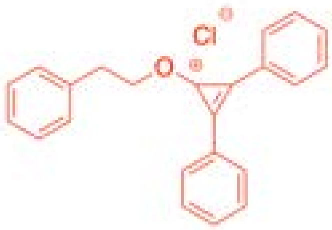
Compound **19** is synthesized as shown below. In relation to non-benzenoid aromaticity, **19** can be used as an activator for alcohols, and **20** was converted to **22** via ion-pair intermediate **21**. Although the formation of **21** was observed by NMR, **21** gradually decomposes to give **18**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

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

17 (2 pt in total):
stereochemistry is ignored,
0 pt for bromination on aryl ring.

18 (2 pt in total):

19 (3 pt in total):
Full mark for ionic structure.

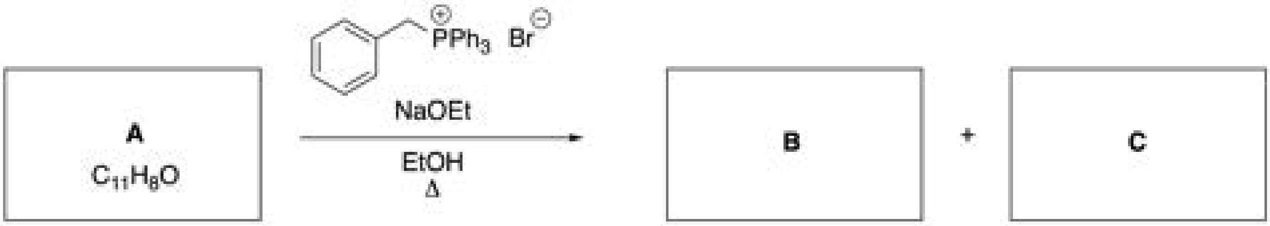
21 (3 pt in total):
–1 pt when Cl^- is omitted,
–1 pt when C–Cl is covalent,
–1 pt each for other errors on connectivity,
–1 pt when the alkoxide and chlorocyclopropenium are given.

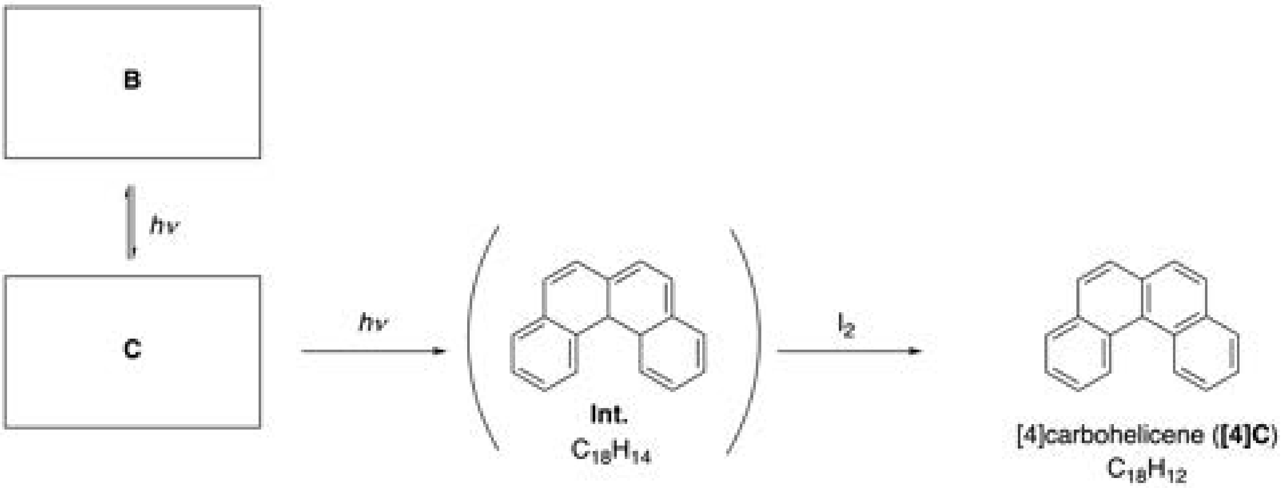
Dynamic Organic Molecules and Their Chirality

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

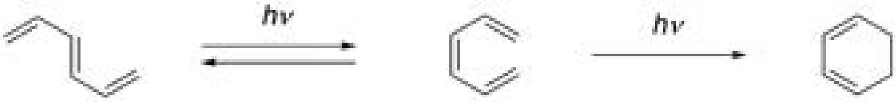
Part A

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.





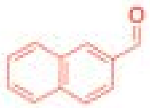
The photoreaction proceeds in a manner similar to the following example.



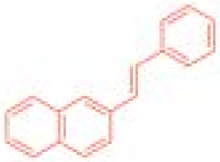
Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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

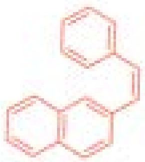
A (3 pt)



B (3 pt)

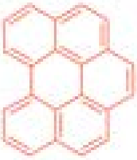


C (3 pt)

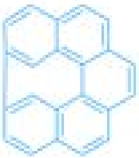


3 points each. When **B** and **C** are reversed, give 1 point each. When missing double bonds in **B** and **C**, -1 point each.
If **B** is blank and **C** is the trans-isomer (i.e. **B**), give 2 points for **C**.
-1 point for each "circled" answer (**this is applied for all the following questions in Q8**)

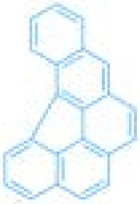
A.2 Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product **D** whose molecular weight was 2 Da lower than that of [5]carbohelicene. The ^{1}H NMR chemical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



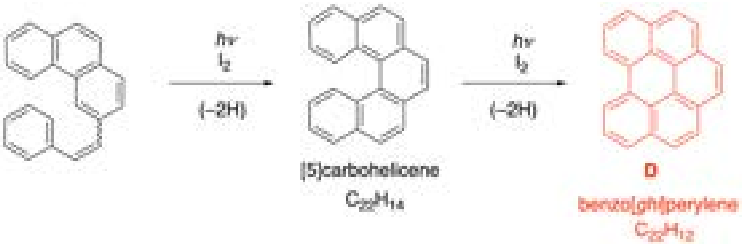
D



D'

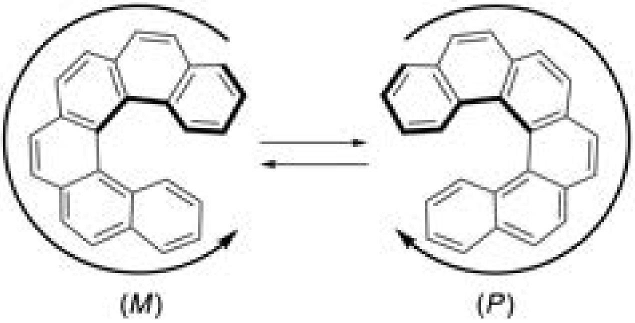


D''



Structural isomer **D'**: 1 point
Structural isomer **D''**: 1 point
Any careless mistakes such as contamination with sp^3 carbons: -1 point each.

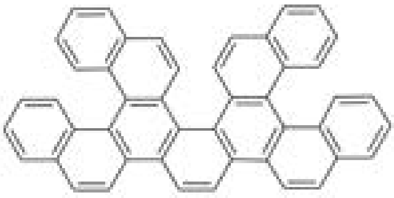
[5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (*M*) or (*P*) as shown below.



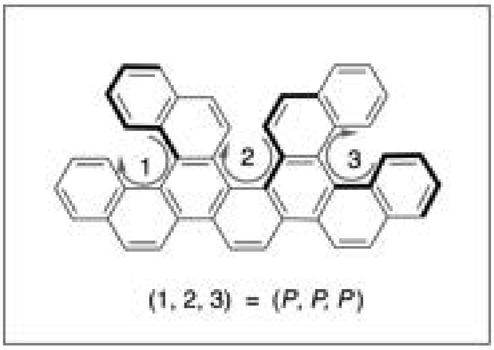
[n]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.

Photo courtesy: The Japan Prize Foundation

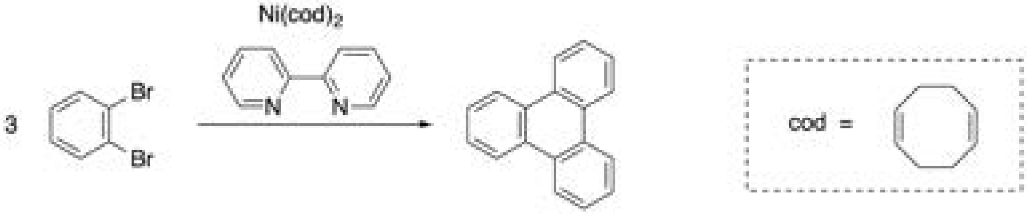
Multiple helicenes are molecules that contain two or more helicene-like structures. If its helical chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound **E** contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described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

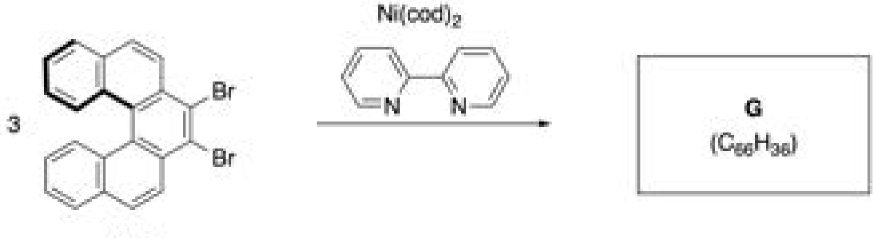


E

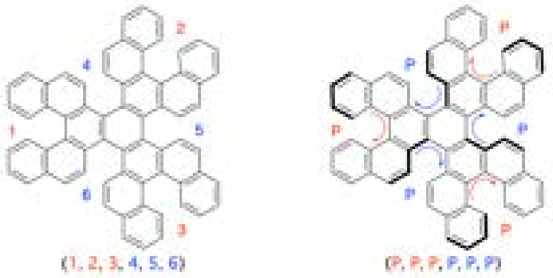


A.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify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

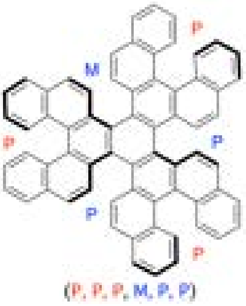


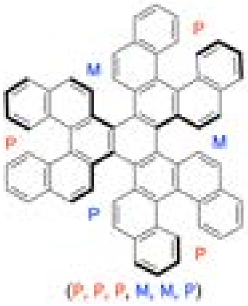


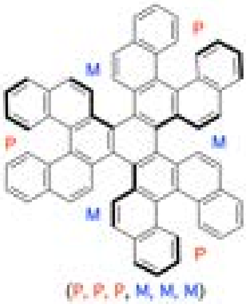
(*P*)-**F**



A representative example



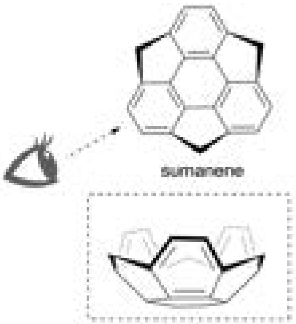




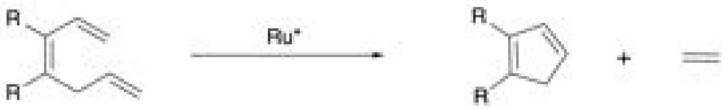
One structure should be drawn fully; chemical structure (2 points) and its stereochemistry (1 point for the original chirality (outside), 1 point for the new chirality (inside))
For the other three isomers (1 point each).
Overcount (answering the same stereochemistry multiple times for an isomer) (-1 point each; this reduction is applied repeatedly up to 4 times).
0 points if no representative structure is drawn.

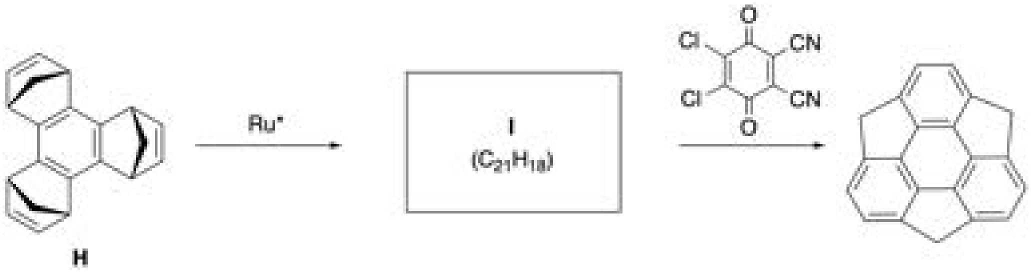
Part B

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

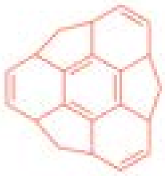


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.

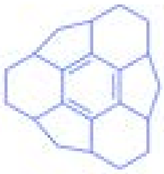




B.1	**Draw** the structure of intermediate **I** (its stereochemistry is not required).	3pt

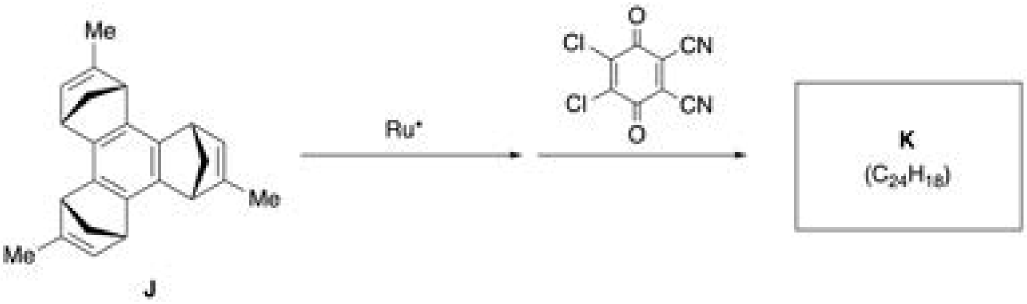


I

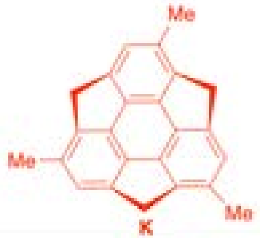


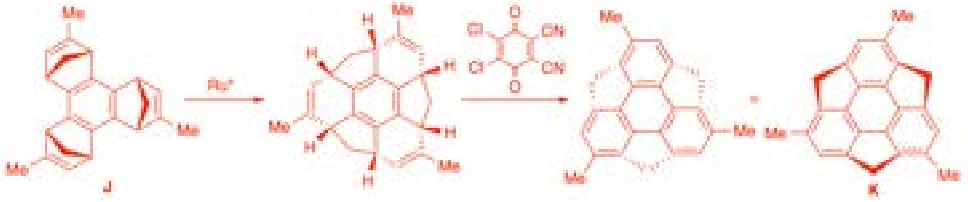
I'

Double bond saturation (such as **I'**): 0 points.
Any careless mistakes such as contamination with wrong sp^2 carbon atoms: -1 point each.
Any different carbon frameworks: 0 points.



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





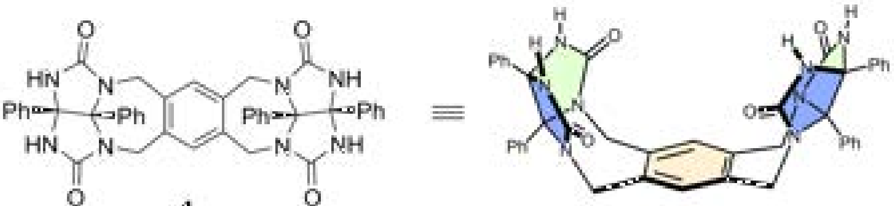
No stereochemistry: 1 point.
The other enantiomer: 2 points.
Lower-symmetry structure (Me at a different position): 0 points.

Likes and Dislikes of Capsule

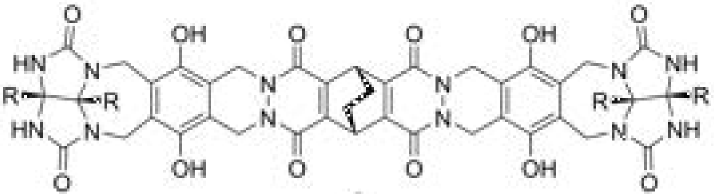
10 % of the total						
Question	A.1	A.2	A.3	A.4	A.5	**Total**
Points	13	2	2	3	3	**23**
Score						

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

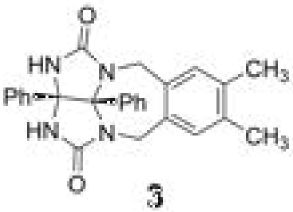
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

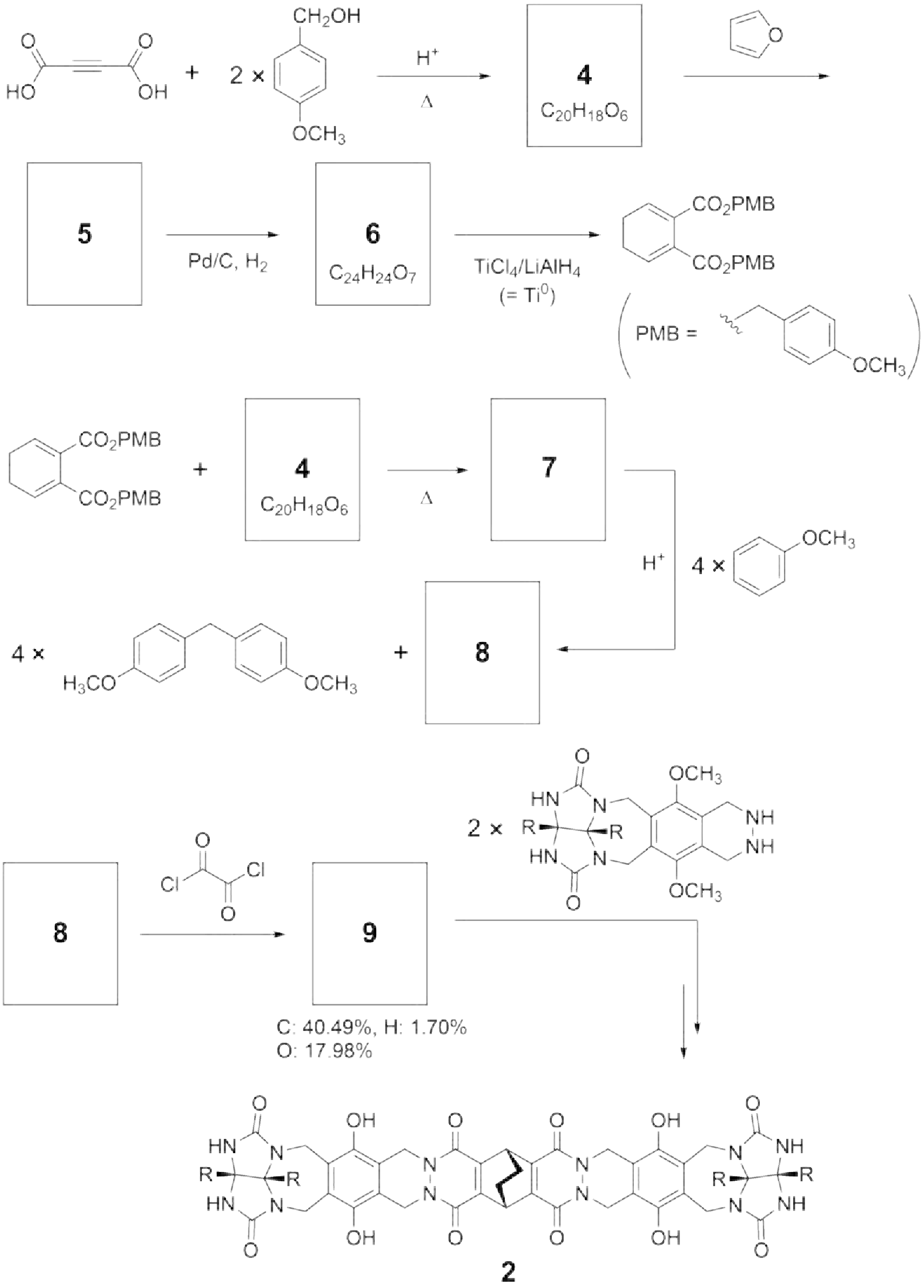


2

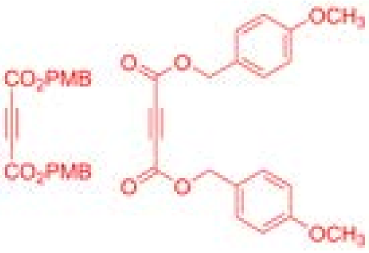
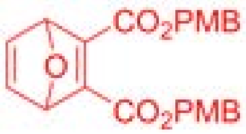
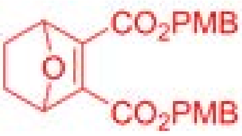
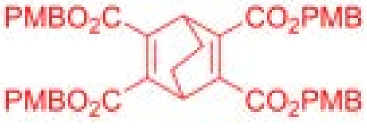
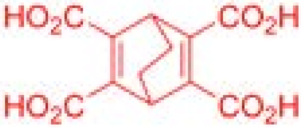
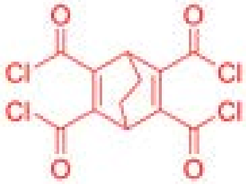


3

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.



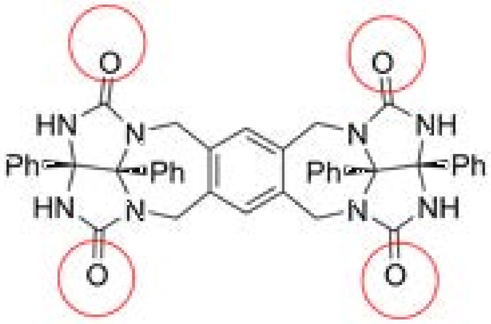
A.1	**Draw** the structures of **4–9**; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above.	13pt

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

·2 points for the correct structures of compounds **4** and **6-9**.
·3 points for the correct structure of compound **5.**
·For compounds **4-9**, any careless mistakes such as the wrong number of carbons or forgetting to write double or triple bonds: -1 point each.
·For compound **6**, 1 point for structures that show the reduced double bond in a different position.
·Full mark will be given if a structure of *p*-methoxybenzyl group is drawn instead of using PMB.
· minimum score: 0 points.

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



2 points for the correct answer

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

8 (because 8 NH protons were observed equally in the ^{1}H NMR spectrum of the dimer.)
2 points for the correct answer.

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:

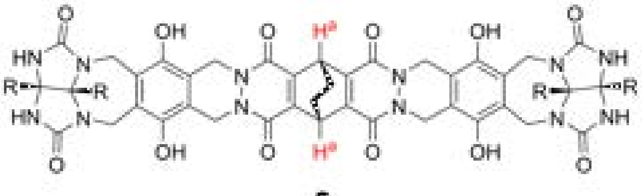
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z@}\mathbf{1}_2 \qquad (1)$$

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

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

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.

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 point for the correct number of encapsulated C_6D_6 and C_6D_5F molecules for each NMR signal.

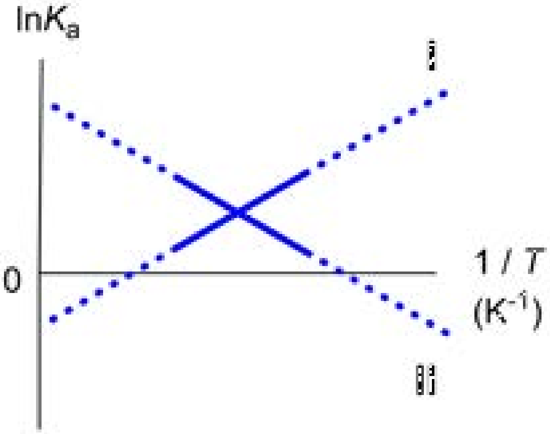
δ (ppm) of H^a	numbers of C_6D_6	numbers of C_6D_5F
4.60 ppm	2	0
4.71 ppm	0	2
4.82 ppm	1	1

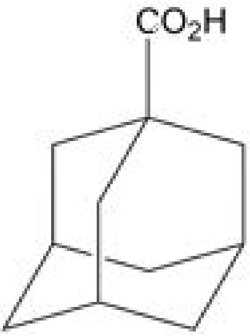
The observation of the third signal in the mixed solvent indicates that two solvent molecules are initially encapsulated in the capsule. Thus, the signal at 4.82 ppm is ascribed to a capsule containing one molecule of C_6D_6 and one molecule of C_6D_5F.

^{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.

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

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

(1): A (2): A (3): A
(4): A (5): B
3 points in total
2 points for correct answers for (1)-(3).
1 point for correct answers for (4) and (5).
No points when the former part ((1)-(3)) is incorrect even if the latter part ((4) and (5)) is correct.

Transforming $\Delta G = -RT \ln K_a = \Delta H - T\Delta S$ gives

$$\ln K_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

(If ΔH is negative, the slope is positive; if the y-intercept is negative, ΔS is negative.)
The relationship between $\mathbf{1}_2$ and CH_4 is that the entropy change is unfavorable ($\Delta S < 0$) given that the two components become one component. Nevertheless, the encapsulation of CH_4 occurs ($\Delta G < 0$), indicating that the enthalpy change is exothermic and favorable ($\Delta H < 0$). This result indicates a plot with a positive slope and a negative y-intercept for $\mathbf{1}_2$ and CH_4.
Therefore, the plot with a negative slope ($\Delta H > 0$) and positive y-intercept ($\Delta S > 0$) is $\mathbf{2}_2$ and AdA. This is due to the release of the two molecules of C_6D_6 that were initially encapsulated and the encapsulation of one molecule of AdA.