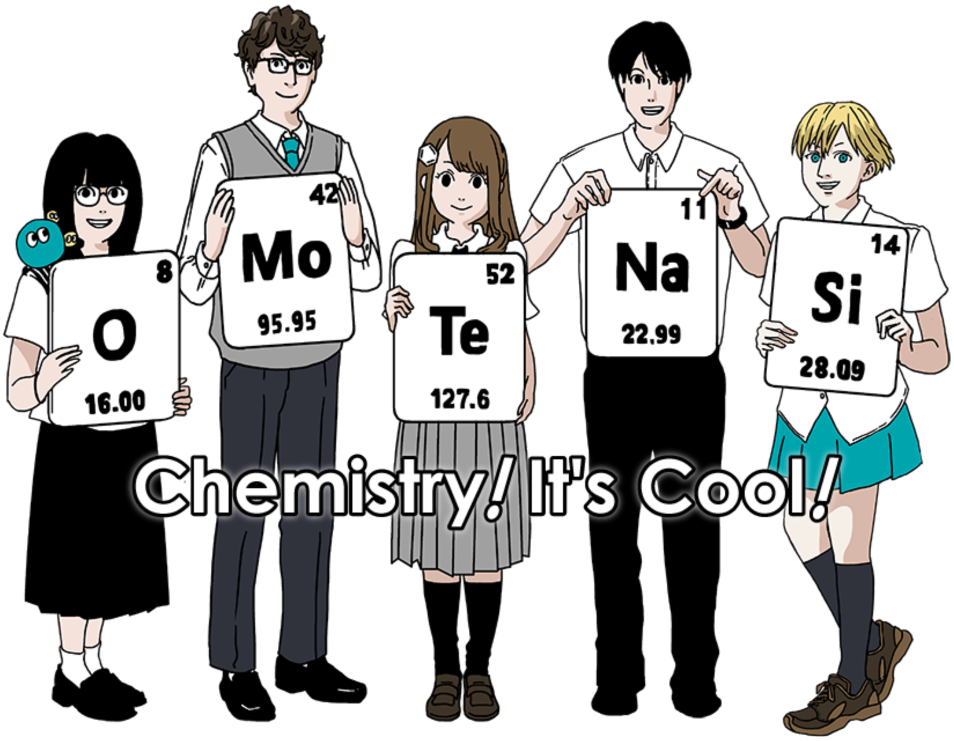
International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July – 2nd August, 2021
https://www.icho2021.org



Educational Version

Published in April, 2022

The preparation of the problems for the 53rd International Chemistry Olympiad (ChO2021) started with the first meeting of the Science Committee on April 24th (Sunday), 2018. Since then, the Science Committee had actively worked for over three years, and the fruits of the activity were summarized as the IChO2021 Official English version, which is available on the IChO2021 website.

The problems of IChO must satisfy the following criteria:
- The problems must be of high standard and quality, for which highly talented students from all over the world should use the best of their creative ability.
- The knowledge required to solve the problems must be open to all students. Only the secondary education-level (as international baccalaureate) of knowledge is allowed to use for the problems.
- If any knowledge beyond the secondary education-level is necessary to solve the problems, it must be announced preliminarily, and at least two problems regarding this knowledge must be included in the preparatory problems.
- The number of advanced fields of knowledge must not exceed six, and each of them must be in the range that all students can master in a two- or three-hour lecture.
- The total length of the problems must not exceed 25,000 characters, so that the students have enough time to read all the problems during the examination time.
- The problems never ask any knowledge itself.
- The solutions must be logically derived from the problems and must be represented only by equations and chemical formulae.

The problems prepared under these criteria should be creative, intellectually stimulative, and educationally valuable. Since the members of the Science Committee are the professors who actively engage in research and education in various fields of chemistry, they worked hard to prepare high-quality problems with their sincere professionalism. The Science Committee "finalized" the problems (February version) along with the preparatory problems on February 1st, 2021.

International Jury is, however, the only body that can finalize the problems for the competition. In defense of the problems from comments at the International Jury, the Science Committee had to further shorten the length of the problems, and had to simplify the problems to avoid ambiguity in grading. For example, questions based on similar ideas and questions on physical chemistry in the problems of organic chemistry were deleted to shorten the total length of the problems. In addition, a question that is very sensitive to significant figures and a question that is based on the linearity of data were deleted or simplified to avoid ambiguity in grading. After these intensive trimmings, the problems became slim to be suitable for the competition. However, at the same time, some narratives and tastes that fascinated us in the February version had been lost.

In IChO2021, the Official English version was greatly admired in the International Jury. The Science Committee is proud of this praise. However, it should be noted that some essences in the February version, which is another most fruitful works achieved by the Science Committee, are missing in the Official English version. Thus, we decided to prepare this Educational version, where the highly polished Official English version is made up with the missing contents of February version.

The Educational version reflects the entire works made by the Science Committee. We sincerely hope that the Educational version is widely utilized in chemical education as well as the Official English version.

Vice-Chair of IChO2021 Science Committee
Nobuhiro Kihara
April, 2022

I am very pleased to publish the Educational Version of the 53rd IChO Problems 2021. This Educational Version has been edited by imparting the following information to the official IChO Problems/Solutions (https://www.icho2021.org/problems/icho2021/).

1) Questions that were unfortunately deleted before the publication of the official IChO Problems because of the IChO exam length regulation. (after yellow highlight)
2) Questions that were unfortunately deleted before the publication of the official IChO Problems because of potential difficulty in marking by following the IChO marking regulation. (after yellow highlight)
3) Tutorial comments and useful literature for further study (Written in pale green)

I sincerely hope that you can touch the passion of the Science Committee members through this Educational Version and that this Version is valuable for young people who participated in IChO, high school students who are eager to participate in IChO, and their mentors.

I would like to express my deepest gratitude to all the Theoretical Problem Subcommittee members for their great efforts in creating both preparatory and IChO2021 problems. I would also like to thank the reviewers for their valuable comments and suggestions.

All the best for all those who have been involved in IChO,

Hideki Yorimitsu
On behalf of 53rd IChO 2021 Theoretical Problem Subcommittee, Science Committee

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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, $m_e = 9.10938370 \times 10^{-31}$ kg

Electric constant (permittivity of vacuum), $\varepsilon_0 = 8.85418781 \times 10^{-12}$ F m^{-1}

Avogadro constant, $N_A = 6.02214076 \times 10^{23}$ mol^{-1}

Boltzmann constant, $k_B = 1.380649 \times 10^{-23}$ J K^{-1}

Faraday constant, $F = N_A \times e = 9.64853321233100184 \times 10^{4}$ C mol^{-1}

Gas constant, $R = N_A \times k_B = 8.31446261815324$ 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, $p_{atm} = 1.01325 \times 10^{5}$ Pa

Zero degree Celsius, 0 °C = 273.15 K

Ångström, 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.

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: $S = k_B \ln W$

, where W is the number of microstates.

The change of entropy ΔS:

$$\Delta S = \frac{q_{rev}}{T}$$

, where q_{rev} is the heat for the reversible process.

Gibbs free energy G: $G = H - TS$

$\Delta_r G^0 = -RT \ln K = -zFE^0$

, where K is the equilibrium constant, z is the number of electrons, E^0 is the standard electrode potential.

Reaction quotient Q: $\Delta_r G = \Delta_r G^0 + RT \ln Q$

For a reaction

$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

, where [A] is the concentration of A.

Heat change Δq: $\Delta q = nc_m \Delta T$

, where c_m is the temperature-independent molar heat capacity.

Nernst equation for redox reaction:

$$E = E^0 + \frac{RT}{zF} \ln\left(\frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}\right)$$

, 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

$HA \rightleftharpoons H^+ + A^-$

, where equilibrium constant is K_a,

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

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 $x \neq 1$,

$$1 + x + x^2 + \ldots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$$

Approximation equation that can be used to solve problems:

When $x \ll 1$,

$$\frac{1}{1 - x} \sim 1 + x$$

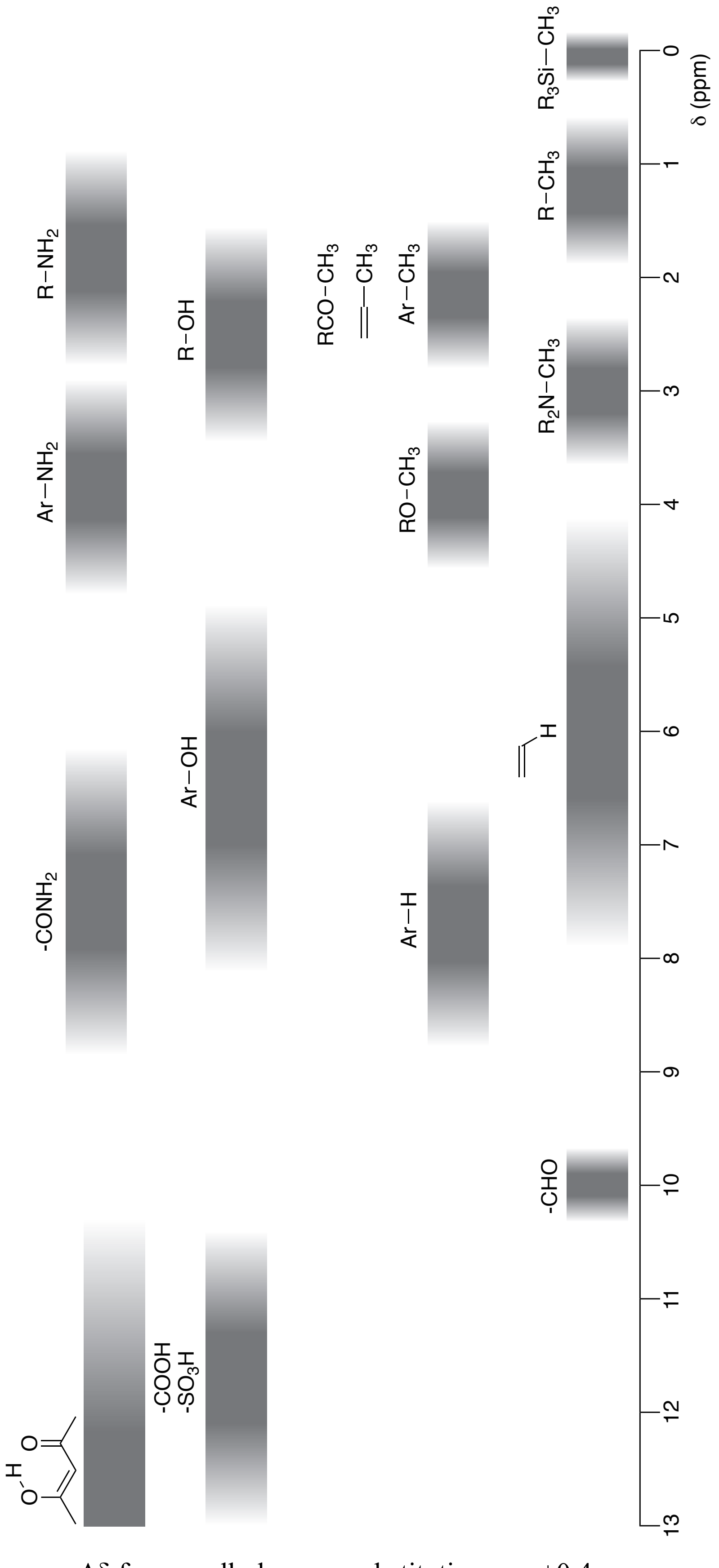
Periodic table

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

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.00798																	2 He Helium 4.002602
3 Li Lithium 6.968	4 Be Beryllium 9.012183											5 B Boron 10.814	6 C Carbon 12.0106	7 N Nitrogen 14.00686	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989769	12 Mg Magnesium 24.306											13 Al Aluminium 26.981539	14 Si Silicon 28.085	15 P Phosphorus 30.973762	16 S Sulfur 32.068	17 Cl Chlorine 35.452	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium [99]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	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 126.90447	54 Xe Xenon 131.293
55 Cs Caesium 132.905452	56 Ba Barium 137.327	57-71 La-Lu Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	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 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.384	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	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]

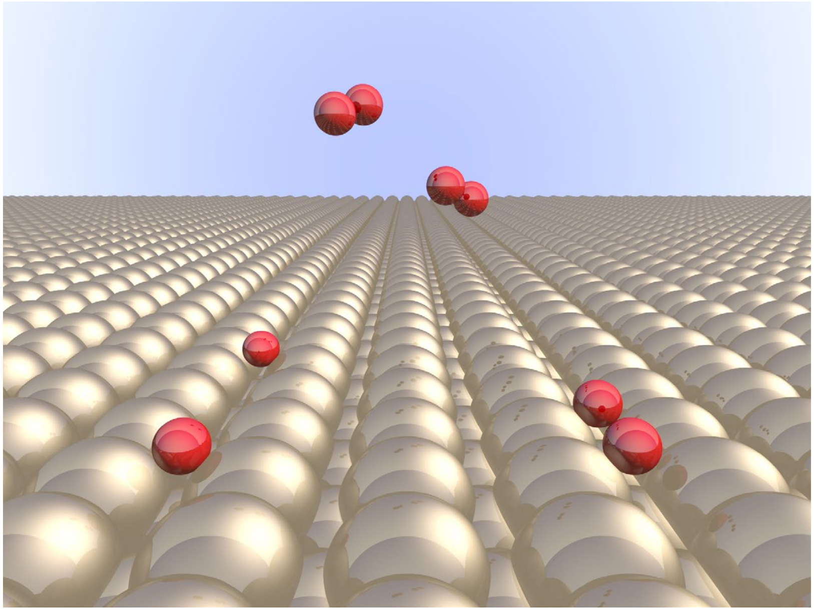
57-71 La-Lu Lanthanoids :	57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90766	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
89-103 Ac-Lr Actinoids :	89 Ac Actinium [227]	90 Th Thorium 232.0377	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium [237]	94 Pu Plutonium [239]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [252]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]

^{1}H NMR Chemical Shifts



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

Question 1: Hydrogen at a Metal Surface



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 metal, which is related to hydrogen-transport and -storage technology.

Part A

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

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

(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

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

(i) The energy required for the dissociation of gaseous H_2 molecule to gaseous H [H_2 (g) → 2H (g)].

(ii) The energy released during the adsorption of a gaseous H_2 [H_2 (g) → 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

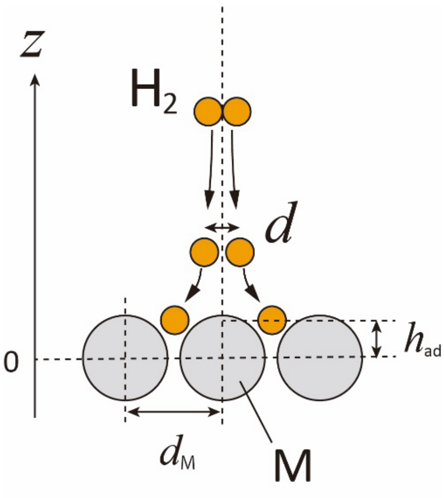


Fig. 1 Definition of variables. Drawing is not in scale.

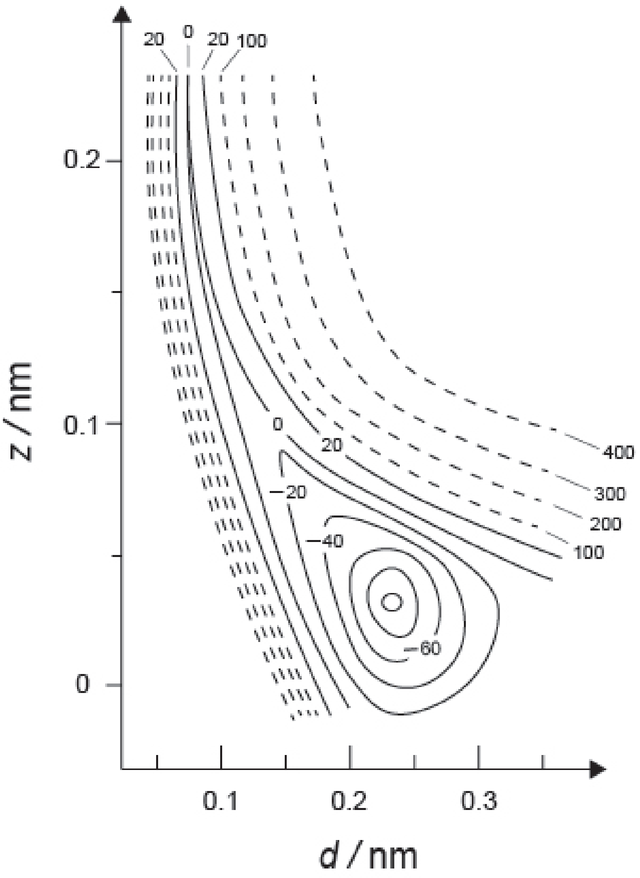


Fig. 2 Potential energy for the adsorption process of hydrogen at the metal surface as a function of *d* and *z*.

In **Part A**, dissociative adsorption process of hydrogen molecules on a metal surface is considered using two-dimensional potential by taking the intramolecular distance as a variable in addition to the distance between the molecule and the surface. In general, there are as many variables as the number of degrees of freedom (six) of the reactant (in this case, hydrogen molecule), and the six-dimensional potential can be considered by considering all of them.

Part B

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

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

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

The reaction rates per site for adsorption, desorption, and absorption are r_1 [s^{-1}], r_2 [s^{-1}], and r_3 [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 $P_{\mathrm{H_2}}$ [Pa] 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:

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

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,

$$k_1 P_{\mathrm{H_2}} (1 - \theta)^2 = k_2 \theta^2$$

Solve for θ:

$$\theta = \frac{1}{1 + \sqrt{\frac{k_2}{P_{\mathrm{H_2}} k_1}}}$$

From $r_3 = k_3 \theta$:

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

Thus,

$$C = \frac{k_1}{k_2}$$

This is a question regarding the equilibrium steady state between the second-order adsorption process (2) and the second-order desorption process (3). The expression of θ is different from that of the well-known first-order Langmuir equation.

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

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

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

$$A \times S = \frac{2vV}{RT}$$

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

Therefore,

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

The reduction rate of hydrogen molecules in the container is obtained from the pressure change, which is associated with the rate of absorption into the metal. Note that 1 mol of hydrogen molecule corresponds to 2 mol of hydrogen atom.

B.3 At T = 400 K, C equals 1.0×10^2 Pa^{-1}. **Calculate** the value of k_3 at 400 K.

The relationship between r_3 and A is:

$$A = r_3 \times \frac{N}{N_A}$$

Thus,

$$r_3 = A \times \frac{N_A}{N} = 1.1 \times 10^{-1}\ \mathrm{s}^{-1}$$

Solution 1:

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\mathrm{H_2}} C}}} = \frac{k_3}{1 + \sqrt{\frac{1}{10000}}} = \frac{k_3}{1.01}$$

Thus,

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

Solution 2:

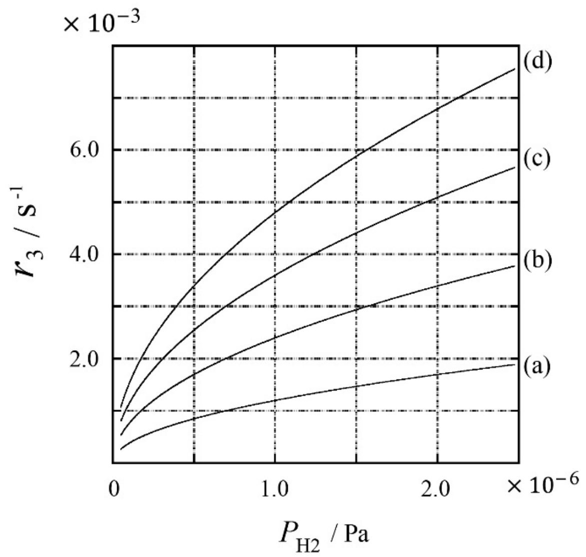
Under the conditions ($P_{\mathrm{H_2}} C \gg 1$), it follows that:

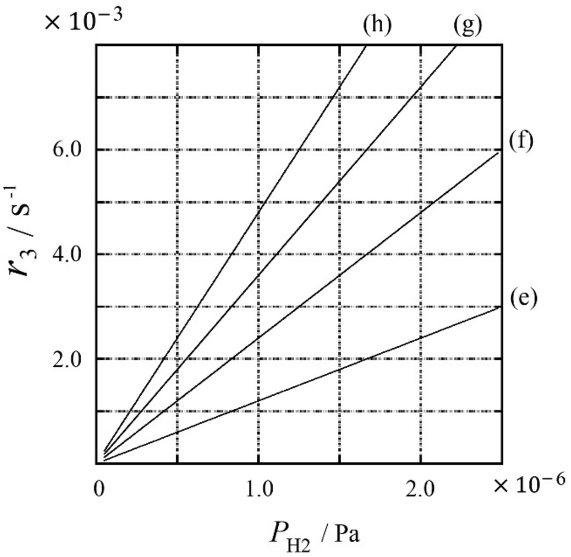
$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\mathrm{H_2}} C}}} \cong \frac{k_3}{1} = k_3$$

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

Because r_3 and A are directly related, one can find the value of r_3. k_3 and r_3 are related in the equation of **B.1**. In the present case, one can find k_3 from $r_3 \cong k_3$ ($P_{\mathrm{H_2}} C \gg 1$). In this situation, the adsorption sites on the surface are almost saturated ($\theta \cong 1$). In general, the reaction rate (r_3, etc.) depends on the pressure and θ, but the reaction rate constant (k_3, etc.) depends only on the temperature.

B.4 At different T, C = 2.5×10³ Pa⁻¹ and k_3 = 4.8×10⁻² s⁻¹ are given. For r_3 as a function of P_{H_2} at this temperature, **select** the correct plot from (a)–(h).





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

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{H_2}C}}}$$

$$\cong \frac{k_3}{\sqrt{\frac{1}{P_{H_2}C}}} = k_3\sqrt{P_{H_2}C} = 2.4\sqrt{P_{H_2}}$$

Thus, (b)

Because the temperature is different, k_3 and C are also different from the previous question. The horizontal axis of the graph represents the region of $P_{H_2}C \ll 1$. This corresponds to the region where θ is small, and it can be seen from the equation of **B.1** that r_3 depends on the square root of P_{H_2}. In this situation, the adsorption sites on the surface are almost vacant ($\theta \ll 1$), but the predetermined conditions $r_1, r_2 \gg r_3$ are maintained. However, when the pressure decreases to about $P_{H_2} = 1 \times 10^{-8}$ Pa (the line is excluded in the graph), this condition does not hold and the equation of **B.1** is no longer valid.

Question 2: Isotope Time Capsule

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.

Let us consider the following equilibrium:

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

The entropy, S, increases with increasing the number of possible combinations, W:

$$S = k_B \ln W \qquad (2)$$

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. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}C^{16}O^{18}O$ molecules, $W = 2^2 = 4$.

The following question **A.1** is not included in the official IChO Problems 2021 because of the IChO exam length regulation.

A.1 The equilibrium of the oxygen isotope is accomplished between CO_2 and H_2O over a long period. A separation factor, α, of the oxygen atom for this equilibrium is defined as follows.

$$\alpha = \frac{^{18}O/^{16}O \text{ in } CO_2}{^{18}O/^{16}O \text{ in } H_2O} = \frac{(2[C^{18}O_2]+[C^{16}O^{18}O])/(2[C^{16}O_2]+[C^{16}O^{18}O])}{[H_2{}^{18}O]\,/\,[H_2{}^{16}O]} \qquad (3)$$

When $T \to +\infty$, α is expressed without using $[C^{16}O^{18}O]$ as follows.

$$\alpha = \frac{[C^{18}O_2]^a\,/\,[C^{16}O_2]^b}{[H_2{}^{18}O]^c\,/\,[H_2{}^{16}O]^d} \qquad (4)$$

Using eq. 1, **calculate** the values of a−d.

$$\frac{[C^{16}O^{18}O]^2}{[C^{16}O_2][C^{18}O_2]} = 4 \rightarrow [C^{16}O^{18}O] = 2[C^{16}O_2]^{1/2}[C^{18}O_2]^{1/2}$$

Therefore,

$$\frac{2[C^{18}O_2] + [C^{16}O^{18}O]}{2[C^{16}O_2] + [C^{16}O^{18}O]} = \frac{2[C^{18}O_2] + 2[C^{16}O_2]^{\frac{1}{2}}[C^{18}O_2]^{\frac{1}{2}}}{2[C^{16}O_2] + 2[C^{16}O_2]^{\frac{1}{2}}[C^{18}O_2]^{\frac{1}{2}}}$$

$$= \frac{[C^{18}O_2]^{\frac{1}{2}}\left([C^{16}O_2]^{\frac{1}{2}} + [C^{18}O_2]^{\frac{1}{2}}\right)}{[C^{16}O_2]^{\frac{1}{2}}\left([C^{16}O_2]^{\frac{1}{2}} + [C^{18}O_2]^{\frac{1}{2}}\right)} = \frac{[C^{18}O_2]^{\frac{1}{2}}}{[C^{16}O_2]^{\frac{1}{2}}}$$

Substitute this relationship into eq. 3:

$$\alpha = \frac{(2[C^{18}O_2] + [C^{16}O^{18}O])/(2[C^{16}O_2] + [C^{16}O^{18}O])}{[H_2{}^{18}O] \,/\, [H_2{}^{16}O]} = \frac{[C^{18}O_2]^{\frac{1}{2}} \,/\, [C^{16}O_2]^{\frac{1}{2}}}{[H_2{}^{18}O] \,/\, [H_2{}^{16}O]}$$

Therefore, $a = b = 1/2$, $c = d = 1$.

A.2 The enthalpy change, ΔH, of eq. 5 is positive regardless of the temperature.

$$H_2 + DI \rightleftarrows HD + HI \qquad (5)$$

Calculate the equilibrium constant, K, for eq. 5 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 low / high temperatures.

$\Delta G = \Delta H - T\Delta S = -RT \ln K \rightarrow \ln K = -\Delta H / RT + \Delta S / R$

$(K = \exp(-\Delta H / RT) \exp(\Delta S / R))$

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

$T \to +\infty$: $\ln K = \Delta S / R$

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

The followings are the other examples of K for $T \to +\infty$.

$H_2O + HDS \rightleftarrows HDO + H_2S$	$K \to 1$
$NH_3 + HD \rightleftarrows NH_2D + H_2$	$K \to 3/2$
$^{14}N^{15}NO + {}^{14}NO \rightleftarrows {}^{14}N_2O + {}^{15}NO$	$K \to 1$

The molecules whose W is not 1 are; HDS: $W = 2$, HDO: $W = 2$, HD: $W = 2$, NH_2D: $W = 3$.

Note that two nitrogen atoms in $^{14}N^{15}NO$ are not equivalent, and therefore $K = 1$ for $T \to +\infty$.

The following question **A.3** is not included in the official IChO Problems 2021 because of potential difficulty in marking by following the IChO marking regulation.

By using the temperature dependence of the equilibrium constant between isotopologues in substances, we can estimate the temperature at which the substances existed. The temperature dependence of the equilibrium constant can be determined experimentally. As an example, let us estimate the temperature at which the $CaCO_3$ was produced in water using the isotope ratio of oxygen, ^{18}O / ^{16}O. A separation factor of the oxygen atom for the equilibrium between $CaCO_3$ and H_2O is defined as follows. [*Geochim. Cosmochim. Acta* **61**, 3461 (1997)]

$$\alpha = \frac{^{18}\mathrm{O}/^{16}\mathrm{O}\ \text{ in } \mathrm{CaCO_3}}{^{18}\mathrm{O}/^{16}\mathrm{O}\ \text{ in } \mathrm{H_2O}} \tag{6}$$

The temperature dependence of α in 10 − 40 °C is determined as follows where T is given as absolute temperature (unit: K).

$$\ln \alpha = \frac{18.03}{T} - 3.242\times10^{-2} \tag{7}$$

A.3 ^{18}O / ^{16}O of $CaCO_3$ produced at a certain temperature was 2.051741×10^{-3}. By assuming that ^{18}O / ^{16}O of H_2O is 1.988557×10^{-3} regardless of the temperature, **estimate** the temperature at which the $CaCO_3$ was produced.

$\alpha = 2.051741\times10^{-3} / 1.988557\times10^{-3} = 1.031774$

$T = 18.03 / (\ln \alpha + 3.242\times10^{-2}) = \underline{283.0\ \mathrm{K}}$

For the estimation of the temperature using ^{18}O / ^{16}O, we have to assume ^{18}O / ^{16}O of H_2O. However, ^{18}O / ^{16}O of H_2O varies with time and place. To solve this problem, the molecule which contains two rare isotopes, called doubly-substituted isotopologue, can be used.

The ΔH of eq. 8 originates from molecular vibration.

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

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

$$E = \frac{1}{2}h\nu \tag{9}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{10}$$

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:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{11}$$

A.4 The vibrational frequency of H_2 is 4161.0 cm^{-1} in units of wavenumbers. **Calculate** the ΔH of the following equation at $T = 0$ K in units of J mol^{-1}.

$$2HD \rightarrow H_2 + D_2 \tag{12}$$

Assume that:

- only the vibrational energy contributes to the ΔH.
- the k values for H_2, HD, and D_2 are identical.
- the masses of H and D are 1.0078 Da and 2.0141 Da, respectively.

$\mu_{H_2} = 0.5039$ Da, $\mu_{HD} = 0.6717$ Da, $\mu_{H_2} = 1.0071$ Da

Using $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, $\frac{\nu_{HD}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}}$ and $\frac{\nu_{D_2}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}}$ 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 3604.0 cm^{-1} and 2943.4 cm^{-1}, respectively.

The difference of the zero-point energies of eq. 12 is calculated to be

$\tilde{\nu}$ = (4161.0 + 2943.4) / 2 − 3604.0 = −51.8 cm^{-1}.

$E = N_A h\nu = N_A hc\tilde{\nu}$ ($\tilde{\nu}$: frequency in wavenumbers), and therefore $E = \Delta H$ = −620 J mol^{-1}.

As the temperature increases, the equilibrium constant K of eq. 8 converges to 1/4 because the contribution of entropy to K overwhelms the contribution of enthalpy. Therefore, the abundance ratio among H_2, HD, and D_2 depends on the temperature. Although the amount of this change is quite small, the ratio of change is observable for D_2, the amount of which is inherently very small. Let us use this dependence on the temperature in a system in equilibrium. Δ_{D2} is defined as the ratio of change of the molar ratio of D_2.

$$\Delta_D = \frac{R_{D2}}{R_{D2}^*} - 1 \tag{13}$$

Here, R_{D2} refers to [D_2] / [H_2] in the sample and R_{D2}^* to [D_2] / [H_2] at $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

A.5 **Calculate** Δ_{D2} with natural D abundance when the isotopic exchange is in equilibrium at the temperature where K in eq. 8 is 0.300. Assume that the natural abundance ratios of D and H are 1.5576×10^{-4} and $1 - 1.5576\times10^{-4}$, respectively.

Solution 1:

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

・$T \rightarrow +\infty$ (K = 1/4)

$[H_2]_0 = (1 - 1.5576 \times 10^{-4})^2 C$ = 9.9969×10^{-1} C

$[D_2]_0 = (1.5576 \times 10^{-4})^2 C$ = 2.4261×10^{-8} C

• K = 0.300

Let the amount of change in the molar ratio be x.

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

Solve the equation for x when K = 0.300:

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

$x = 4.8504 \times 10^{-9}$.

From this value, we obtain $[\mathrm{H_2}] = 9.9969\times10^{-1}\,C$ and $[\mathrm{D_2}] = 2.9112\times10^{-8}\,C$.

$$\Delta_{\mathrm{D2}} = \frac{R_{\mathrm{D2}}}{R_{\mathrm{D2}}^*} - 1 = \frac{2.9112\times10^{-8}/9.9969\times10^{-1}}{2.4261\times10^{-8}/9.9969\times10^{-1}} - 1 = 0.200$$

Solution 2:

By using an appropriate approximation, we can obtain the answer without calculating the concentration of each species. The use of this approximation is rationalized considering that the values of $[\mathrm{H_2}]$, $[\mathrm{HD}]$, and $[\mathrm{D_2}]$ differ by 4 orders of magnitudes while the required significant digits for K are 3.

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

$$\Delta_{\mathrm{D2}} = \frac{R_{\mathrm{D2}}}{R_{\mathrm{D2}}^*} - 1 = \frac{[\mathrm{D_2}]/[\mathrm{H_2}]}{[\mathrm{D_2}]_0/[\mathrm{H_2}]_0} - 1 \simeq \frac{[\mathrm{D_2}]}{[\mathrm{D_2}]_0} - 1 = \frac{[\mathrm{H_2}]_0[\mathrm{D_2}]/[\mathrm{HD}]_0^2}{[\mathrm{H_2}]_0[\mathrm{D_2}]_0/[\mathrm{HD}]_0^2} - 1 \simeq \frac{0.300}{0.250} - 1 \simeq 0.200$$

The problem raised in **A.3** is that ^{18}O / ^{16}O of H_2O varies with time and place despite the absolute value of the abundance ratio is required for the estimation of temperature. In contrast, Solution 2 above shows that the abundance ratio of D does not affect the numerical value of Δ_{D2} (if the abundance ratio of D is significantly small). This is the reason why we use the ratio of change of the molar ratio such as Δ_{D2} and Δ_{47} (next question).

In general, as described in the example above, the molar ratio of the doubly-substituted isotopologue that contains two heavy isotope atoms in one molecule increases as the temperature decreases. 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:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \qquad (14)$$

R_{47} refers to [CO_2[47]] / [CO_2[44]] in the sample and R_{47}^* to [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	0.000379	0.002000

A.6 **List all** possible isotopologues of CO_2[47], indicating the isotopes of carbon and oxygen explicitly (for example: $^{12}C^{16}O_2$). **Indicate** which is the most common isotopologue among these.

$^{13}C^{16}O^{18}O$, $^{12}C^{17}O^{18}O$, $^{13}C^{17}O_2$
Most common isotopologue: $^{13}C^{16}O^{18}O$

The temperature dependence of Δ_{47} is determined as follows, where T is given as the absolute temperature in units of K: [*Geochim. Cosmochim. Acta* **61**, 3461 (1997)]

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920\times10^{-4} \qquad (15)$$

A.7 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. [*Paleoceanography* **30**, 1305 (2015)]

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 indistinguishable] = 4.43423×10^{-5}.
The molar ratio of $^{12}C^{16}O_2$ in the case where all the isotopes are distributed randomly is $0.988888 \times 0.997621^2 = 9.84188\times10^{-1}$.

$R_{47}^* = 4.43423\times10^{-5} / 9.84188\times10^{-1} = 4.50547\times10^{-5}$
$\Delta_{47} = 7.06\times10^{-4}$
$T = 296$ K

One of the technical problems for this method is the requirement of high-accuracy measurement of R_{47}. This is the reason why the use of doubly-substituted isotopologue has not been popular yet.

Question 3: Lambert–Beer Law?

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.

The following **Part A** is not included in the official IChO Problems 2021 because of the IChO exam length regulation.

Part A

A.1 The absorption value of an aqueous solution of substances A and B, which do not interact with each other, was 1.00 at the wavelength of λ_1. This solution was diluted twice using pure water. **Choose one** of the correct absorption values of this diluted solution at λ_1.

□ Less than 0.50	■0.50	□ More than 0.50

A.2 The absorbance values of hydrochloric acid with pH = 3 containing a small amount of methyl orange (pK_a = 3.5), which is used as a pH indicator, at wavelengths of 400 nm, 465 nm, and 500 nm were A_{400}, A_{465}, and A_{500}, respectively. This solution was diluted 10 times using pure water. **Choose one** of the correct absorption values of this diluted solution at wavelengths of 400 nm, 465 nm, and 500 nm. Refer to the absorption spectrum of methyl orange (Fig. 1) if necessary. The Isosbestic points of methyl orange exist at wavelengths of 352 nm and 465 nm.

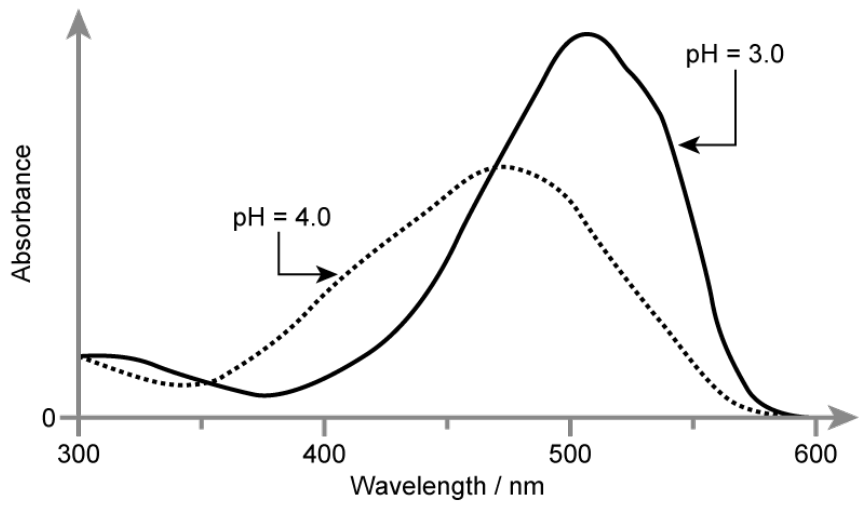


Fig. 1 Absorption spectra of methyl orange solution with pH = 3.0 and 4.0. The concentration of methyl orange for both solutions is the same. [*RSC Adv.*, **10**, 11311 (2020)]

At 400 nm: □ Less than A_{400}/10 (< A_{400}/10) □ A_{400}/10 ■ More than A_{400}/10 (> A_{400}/10) At 465 nm: □ Less than A_{465}/10 (< A_{465}/10) ■ A_{465}/10 □ More than A_{465}/10 (> A_{465}/10) At 500 nm: ■ Less than A_{500}/10 (< A_{500}/10) □ A_{500}/10 □ More than A_{500}/10 (> A_{500}/10)

Note that the pH after dilution is 4 and therefore the composition of protonated and deprotonated species changes by the dilution.

The message of **Part A** is that Lambert−Beer law holds only when the chemicals do not show any chemical change (such as acid−base equilibrium). Through the use of this fact, we made a seemingly mysterious situation in **Part B**; absorbance does not change even if the solution was diluted.

Part B

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

$$\mathrm{AH} \rightleftarrows \mathrm{A^-} + \mathrm{H^+} \qquad K = \frac{[\mathrm{A^-}][\mathrm{H^+}]}{[\mathrm{AH}]} \qquad (1)$$

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

B.1 The absorbance of **X** was A_2 at a wavelength of λ_2. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. The absorbance of the diluted solution was also A_2 at λ_2. **Calculate** the ratio of $\varepsilon_{AH} : \varepsilon_A$, where ε_{AH} and ε_A represent the absorption coefficients of AH and of A⁻, respectively, at λ_2.

$$K = \frac{[\mathrm{A^-}][\mathrm{H^+}]}{[\mathrm{AH}]} = \frac{(1.00\times10^{-2})(1.00\times10^{-4})}{1.00\times10^{-3}} = 1.00\times10^{-3}\ \mathrm{mol\ L^{-1}}$$

Concentrations before the dilution:

[AH] = 1.00×10^{-3} mol L^{-1}

[A⁻] = 1.00×10^{-2} mol L^{-1}

[H⁺] = 1.00×10^{-4} mol L^{-1}

Concentrations just after the dilution (nominal initial concentrations before the equilibrium):

[AH] = 5.00×10^{-4} mol L^{-1}

[A⁻] = 5.00×10^{-3} mol L^{-1}

[H⁺] = (1.00×10^{-4} + 3.16×10^{-3}) / 2 = 1.63×10^{-3} mol L^{-1}

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

Equilibrium after the dilution:

$$\frac{[\mathrm{A^-}][\mathrm{H^+}]}{[\mathrm{AH}]} = \frac{(5.00\times10^{-3}-x)(1.63\times10^{-3}-x)}{(5.00\times10^{-4}+x)} = 1.00\times10^{-3}\ \mathrm{mol\ L^{-1}}$$

Solve the equation for x: x = 1.19×10^{-3} mol L^{-1}

→ [A⁻] = 3.81×10^{-3} mol L^{-1}, [AH] = 1.69×10^{-3} mol L^{-1}

Therefore,

$$1.00\times10^{-2}\varepsilon_{\mathrm{A}} + 1.00\times10^{-3}\varepsilon_{\mathrm{AH}} = 3.81\times10^{-3}\varepsilon_{\mathrm{A}} + 1.69\times10^{-3}\varepsilon_{\mathrm{AH}}$$

By solving this equation: **$\varepsilon_{AH} = 9.0\ \varepsilon_A$**

In the case where $\varepsilon_{AH} > 9.0\ \varepsilon_A$, absorbance at λ_2 increases by dilution! We would like to emphasize that the concentration of chemicals fulfills conservation law even under such a seemingly mysterious situation.

The following question **B.2** is not included in the official IChO Problems 2021 because of the IChO exam length regulation.

B.2 **X** was diluted to four times its initial volume using hydrochloric acid with a certain pH value. The absorbance of this diluted solution was also A_2 at λ_2. **Calculate** the pH value of the hydrochloric acid used for the dilution.

Concentrations before the dilution:

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

Concentrations after the dilution:

$$\frac{[A^-][H^+]}{[AH]} = \frac{(2.50 \times 10^{-3} - x)[H^+]}{(2.50 \times 10^{-4} + x)} = 1.00 \times 10^{-3}\ \text{mol L}^{-1}$$

As the absorbance is not changed by the dilution, the following relationship holds:

$$1.00 \times 10^{-2}\varepsilon_A + 1.00 \times 10^{-3}\varepsilon_{AH} = (2.50 \times 10^{-3} - x)\varepsilon_A + (2.50 \times 10^{-4} + x)\varepsilon_{AH}$$

Solve the equation for x using $\varepsilon_{AH} = 9.0\ \varepsilon_A$: $x = 1.8\times10^{-3}$ mol L^{-1}

→ $[A^-] = 7.2\times10^{-4}$ mol L^{-1}, $[AH] = 2.0\times10^{-3}$ mol L^{-1}

Using these values provides the concentration of protons after the dilution: $[H^+] = 2.8\times10^{-3}$ mol L^{-1}

Let the concentration of the hydrochloric acid used for the dilution be C:

$[(3C + 1.00\times10^{-4}) / 4] - x = 2.8\times10^{-3}$ mol L^{-1}

Solve the equation for C: $C = 6.1\times10^{-3}$ mol L^{-1} → **pH = 2.21**

Part C

Let us consider the following equilibrium in the gas phase.

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

This gas is filled with a cuboid container that has a transparent movable wall with a cross−section of S as shown in Fig. 2. The partial pressures of D and M are p_{D} and p_{M}, respectively. Lambert–Beer law also holds for the absorption value of gas: the absorption value A of the gas is the product of the absorption coefficient ε, the number density of the gas n/V (n is the mole number of the gas and V is the volume of the gas), and the optical path length of l: $A = \varepsilon\,(n/V)\,l$. Assume that the temperature of the gas was kept at a constant value and the gas is an ideal gas.

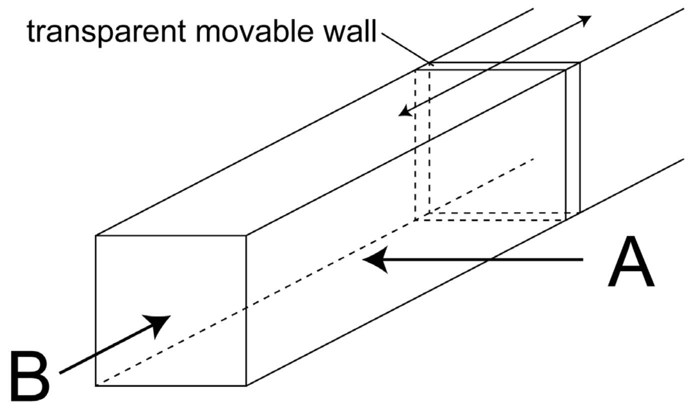


Fig. 2 A container with a transparent movable wall and the direction of absorption measurements.

C.1 The container is filled with pure gas D at the pressure P_0 and the volume V_0, and the equilibrium is achieved under constant pressure. The absorption values of the gas at the wavelength of λ_{3a} **measured from the direction of A** are A_{3a} both just after the filling (only gas D exists) and after the equilibrium is achieved. After this, the pressure was set to be P_1 and the equilibrium is achieved. **Calculate** the absorption values of the gas at the wavelength of λ_{3a} **measured from the direction of A.**

Hint: First, determine the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at λ_{3a}, where ε_{D} and ε_{M} represent the absorption coefficients of D and of M, respectively.

Using the Lambert–Beer law, the absorbance of D and M at an arbitrary volume V are expressed as follows. Here, let the optical path length be l_{A}. The ideal gas law is used.

$$A_{\mathrm{D}} = \varepsilon_{\mathrm{D}}\left(\frac{n_{\mathrm{D}}}{V}\right) l_{\mathrm{A}} = \varepsilon_{\mathrm{D}}\frac{p_{\mathrm{D}}}{RT} l_{\mathrm{A}}$$

$$A_{\mathrm{M}} = \varepsilon_{\mathrm{M}}\left(\frac{n_{\mathrm{M}}}{V}\right) l_{\mathrm{A}} = \varepsilon_{\mathrm{M}}\frac{p_{\mathrm{M}}}{RT} l_{\mathrm{A}}$$

First, determine the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at λ_{3a}. There are two ways of solutions.

Solution 1:

Let the initial number of moles of D be n_0. The absorbance at the initial state is:

$$A_{3a} = A_{\mathrm{D}} = \frac{\varepsilon_{\mathrm{D}} n_0}{V_0} l_{\mathrm{A}}$$

The absorbance after equilibrium is:

$$A_{3a} = A_{\mathrm{D}} + A_{\mathrm{M}} = \frac{\varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}}}{V} l_{\mathrm{A}}$$

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

$$\frac{n_0}{V_0} = \frac{P_0}{RT} = \frac{n_{\mathrm{D}} + n_{\mathrm{M}}}{V}$$

From these equations, the following relationship is obtained:

$$A_{3a} = \frac{\varepsilon_{\mathrm{D}} n_0}{V_0} l_{\mathrm{A}} = \frac{\varepsilon_{\mathrm{D}}(n_{\mathrm{D}} + n_{\mathrm{M}})}{V} l_{\mathrm{A}} = \frac{\varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}}}{V} l_{\mathrm{A}}$$

$$\varepsilon_{\mathrm{D}} n_{\mathrm{M}} = \varepsilon_{\mathrm{M}} n_{\mathrm{M}}$$

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

As $n_{\mathrm{M}} > 0$ after the equilibrium, $\boldsymbol{\varepsilon_{\mathrm{D}}(\lambda_{3a}) = \varepsilon_{\mathrm{M}}(\lambda_{3a})}$ holds.

Solution 2:

The absorbance at the initial state is:

$$A_{3a} = A_{\mathrm{D}} = \varepsilon_{\mathrm{D}}\frac{P_0}{RT} l_{\mathrm{A}}$$

The absorbance after equilibrium is:

$$A_{3a} = A_{\mathrm{D}} + A_{\mathrm{M}} = \frac{\varepsilon_{\mathrm{D}} p_{\mathrm{D}} + \varepsilon_{\mathrm{M}} p_{\mathrm{M}}}{RT} l_{\mathrm{A}}$$

From these equations, the following relationship is obtained:

$$A_{3a} = \varepsilon_{\mathrm{D}} \frac{P_0}{RT} l_{\mathrm{A}} = \frac{\varepsilon_{\mathrm{D}} p_{\mathrm{D}} + \varepsilon_{\mathrm{M}} p_{\mathrm{M}}}{RT} l_{\mathrm{A}}$$

Using the fact that $p_{\mathrm{D}} = P_0 - p_{\mathrm{M}}$,

$$\varepsilon_{\mathrm{D}} P_0 = \varepsilon_{\mathrm{D}}(P_0 - p_{\mathrm{M}}) + \varepsilon_{\mathrm{M}} p_{\mathrm{M}} = \varepsilon_{\mathrm{D}} P_0 + (\varepsilon_{\mathrm{M}} - \varepsilon_{\mathrm{D}}) p_{\mathrm{M}}$$

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

As $p_{\mathrm{M}} > 0$ after the equilibrium, $\boldsymbol{\varepsilon_{\mathrm{D}}(\lambda_{3a}) = \varepsilon_{\mathrm{M}}(\lambda_{3a})}$ holds.

Lambert–Beer law at the pressure at P_1 is as follows.

$$A(p = P_1) = \left(\varepsilon_{\mathrm{D}} \frac{p_{\mathrm{D}}}{RT} + \varepsilon_{\mathrm{M}} \frac{p_{\mathrm{M}}}{RT}\right) l_{\mathrm{A}} = \varepsilon_{\mathrm{D}} \left(\frac{p_{\mathrm{D}}}{RT} + \frac{p_{\mathrm{M}}}{RT}\right) l_{\mathrm{A}} = \varepsilon_{\mathrm{D}} \frac{P_1}{RT} l_{\mathrm{A}} = \varepsilon_{\mathrm{D}} \frac{P_0}{RT} l_{\mathrm{A}} \cdot \frac{P_1}{P_0} = \boldsymbol{A_{3a} \frac{P_1}{P_0}}$$

C.2 The container is filled with the gas D at the pressure P_0 and the volume V_0, and the equilibrium is achieved under constant pressure. The absorption values of the gas at the wavelength of λ_{3b} **measured from the direction of B** are A_{3b} both just after the filling and after the equilibrium is achieved. After this, the pressure was set to be P_2 and the equilibrium is achieved. **Calculate** the absorption values of the gas at the wavelength of λ_{3b} **measured from the direction of B**.

Hint: First, determine the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at λ_{3b}.

Using the Lambert–Beer law, the absorbance of D and M at an arbitrary volume V are expressed as follows. Here, let the optical path length be l_{B}. Note that $V = l_{\mathrm{B}} S$.

$$A_{\mathrm{D}} = \varepsilon_{\mathrm{D}} \left(\frac{n_{\mathrm{D}}}{V}\right) l_{\mathrm{B}} = \varepsilon_{\mathrm{D}} \frac{n_{\mathrm{D}}}{S}$$

$$A_{\mathrm{M}} = \varepsilon_{\mathrm{M}} \left(\frac{n_{\mathrm{M}}}{V}\right) l_{\mathrm{B}} = \varepsilon_{\mathrm{M}} \frac{n_{\mathrm{M}}}{S}$$

First, determine the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at λ_{3b}. There are two ways of solutions.

Solution 1:

Let the initial number of moles of D be n_0. The absorbance at the initial state (optical path length: l_{B0}) is:

$$A_{3b} = A_{\mathrm{D}} = \frac{\varepsilon_{\mathrm{D}} n_0}{V_0} l_{\mathrm{B0}}$$

The absorbance after equilibrium (optical path length: l_{Bf}) is:

$$A_{3b} = A_D + A_M = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V} l_{Bf} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V} l_{B0} \frac{V}{V_0} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V_0} l_{B0}$$

From these equations, the following relationship is obtained:

$$A_{3b} = \frac{\varepsilon_D n_0}{V_0} l_{B0} = \frac{\varepsilon_D n_D + \varepsilon_M n_M}{V_0} l_{B0}$$

Using the fact that $n_M = 2(n_0 - n_D)$,

$$\varepsilon_D n_0 = \varepsilon_D n_D + 2\varepsilon_M (n_0 - n_D) = 2\varepsilon_M n_0 + (\varepsilon_D - 2\varepsilon_M) n_D$$

$$(\varepsilon_D - 2\varepsilon_M) n_0 = (\varepsilon_D - 2\varepsilon_M) n_D$$

As $n_0 > n_D$ after the equilibrium, the equality $\boldsymbol{\varepsilon_D(\lambda_{3b}) = 2\varepsilon_M(\lambda_{3b})}$ holds.

Solution 2:

Let the initial number of moles of D be n_0. The absorbance at the initial state is:

$$A_{3b} = A_D = \varepsilon_D \frac{n_0}{S}$$

The absorbance after equilibrium is:

$$A_{3b} = A_D + A_M = \varepsilon_D \frac{n_D}{S} + \varepsilon_M \frac{n_M}{S}$$

From these equations, the following relationship is obtained:

$$A_{3b} = \varepsilon_D \frac{n_0}{S} = \varepsilon_D \frac{n_D}{S} + \varepsilon_M \frac{n_M}{S}$$

Using the fact that $n_M = 2(n_0 - n_D)$,

$$\varepsilon_D n_0 = \varepsilon_D n_D + 2\varepsilon_M (n_0 - n_D) = 2\varepsilon_M n_0 + (\varepsilon_D - 2\varepsilon_M) n_D$$

$$(\varepsilon_D - 2\varepsilon_M) n_0 = (\varepsilon_D - 2\varepsilon_M) n_D$$

As $n_0 > n_D$ after the equilibrium, the equality $\boldsymbol{\varepsilon_D(\lambda_{3b}) = 2\varepsilon_M(\lambda_{3b})}$ holds.

Lambert–Beer law at the pressure at P_2 is as follows.

$$A(p = P_2) = \varepsilon_D \frac{n_D}{S} + \varepsilon_M \frac{n_M}{S} = \varepsilon_D \frac{n_D + n_M/2}{S} = \varepsilon_D \frac{n_0}{S} = \boldsymbol{A_{3b}}$$

These questions in **Part C** can be solved without calculating anything by considering what happens inside the container.

The result of **C.1** shows that the absorption value of the gas at the wavelength of λ_{3a} measured from the direction of A is proportional to the pressure of the container. This is because the number density of particles in the optical path is proportional to the pressure (in the case of an ideal gas), and the absorbance measured from the direction of A is determined only by the **number density** of particles in the optical path regardless of D or M since $\varepsilon_D(\lambda_{3a}) = \varepsilon_M(\lambda_{3a})$ holds. $\varepsilon_D(\lambda_{3a}) = \varepsilon_M(\lambda_{3a})$ is obtained from the fact that the absorption value remains constant by the observation of the absorption value under the condition of the constant pressure and optical path length after filling the gas D, which means that the absorption values do not change whether the particle in the optical path is D or M.

The result of **C.2** shows that the absorption value of the gas at the wavelength of λ_{3b} measured from the direction of B is independent of the pressure of the container. The absorption value measured from the direction of B is proportional to the number density of particles in the optical path multiplied by the length in the direction of B, which is proportional to the **number** of particles in the optical path. Because $\varepsilon_{\mathrm{D}}(\lambda_{3\mathrm{b}}) = 2\varepsilon_{\mathrm{M}}(\lambda_{3\mathrm{b}})$, the absorbance measured from the direction of B is determined by the number of "monomers" M in the optical path if we count "dimer" D as "2 monomers". In this interpretation, the number of "monomers" does not depend on the pressure and therefore the absorbance becomes constant. $\varepsilon_{\mathrm{D}}(\lambda_{3\mathrm{b}}) = 2\varepsilon_{\mathrm{M}}(\lambda_{3\mathrm{b}})$ is obtained from the fact that the absorption value remains constant by the observation of the absorption value under the condition of the constant number of monomers (count "dimer" D as "2 monomers") after filling the gas D, which means that the absorption values do not change when the particle in the optical path changes from D to M. This result is based on only the conservation law of particles and therefore the assumption of an ideal gas is not required.

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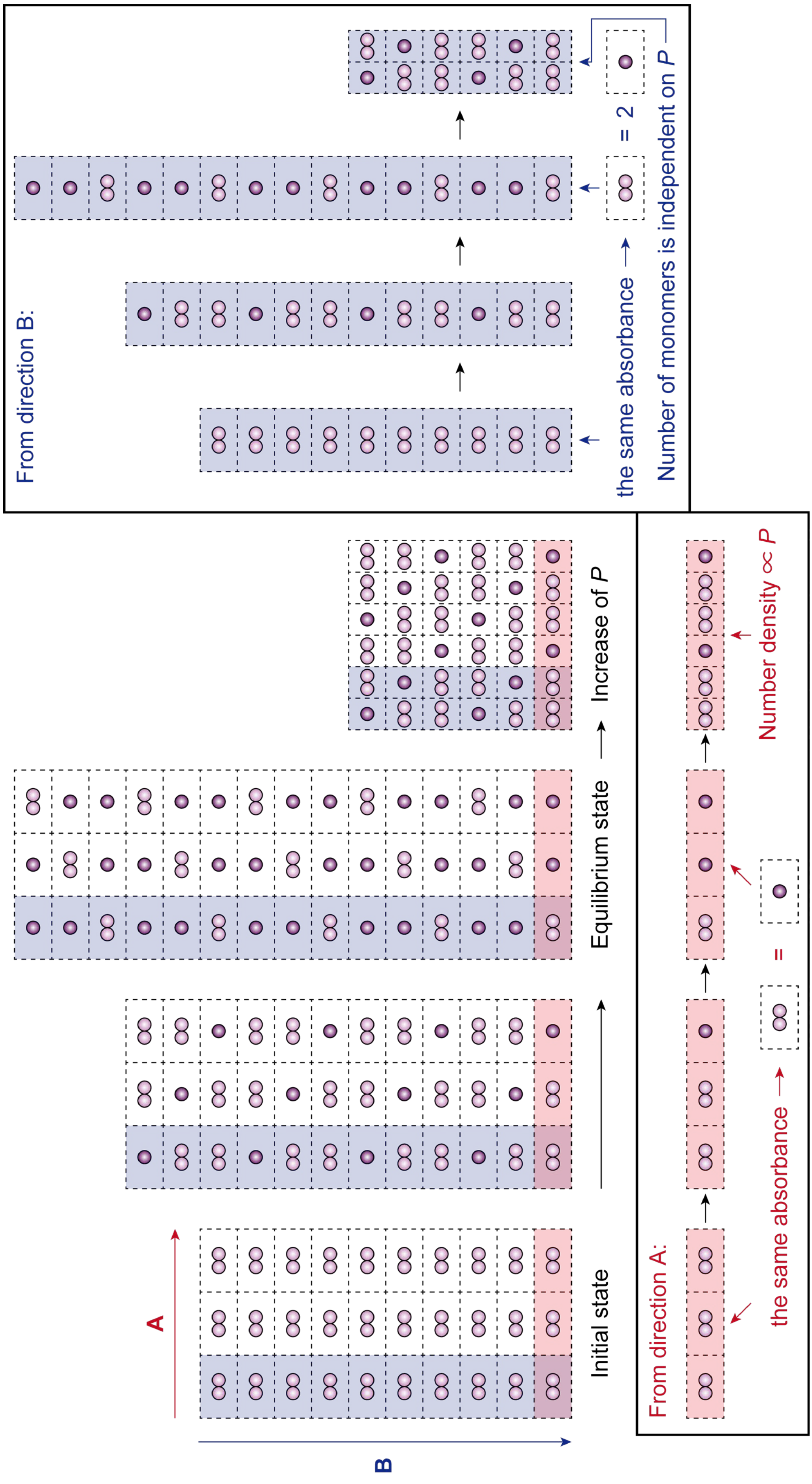


A
B
Initial state
Equilibrium state
Increase of P
From direction A:
the same absorbance
=
Number density ∝ P
From direction B:
the same absorbance
= 2
Number of monomers is independent on P

Problem 4: Redox Chemistry of Zinc

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

Part A

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

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

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

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

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

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

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

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

Solution 1:

From $[\mathrm{Zn(OH)_2\ (aq)}] > [\mathrm{Zn^{2+}(aq)}]$: $\frac{K_{sp}}{[\mathrm{OH^-}]^2} < K_1$

Solve this for $[\mathrm{OH^-}]$: $8.4 < \mathrm{pH}$

From $[\mathrm{Zn(OH)_2\ (aq)}] > [\mathrm{Zn(OH)_4^{2-}}]$: $K_1 > K_2[\mathrm{OH^-}]^2$

Solve this for $[\mathrm{OH^-}]$: $\mathrm{pH} < 11.8$

Thus,

$$\underline{8.4 < \mathrm{pH} < 11.8}$$

Solution 2:

From (1):

$\log[Zn^{2+}][OH^-]^2 = \log K_{sp}$

$\log[Zn^{2+}] = \log K_{sp} - 2\log[OH^-]$

From (2):

$\log[Zn(OH)_2\ (aq)] = \log K_1$

$[Zn(OH)_2\ (aq)] > [Zn^{2+}(aq)]$:

$\log K_{sp} - 2\log[OH^-] < \log K_1$

$\log K_{sp} - 2(-14 + pH) < \log K_1$

From (3):

$\log[Zn(OH)_4^{2-}]/[OH^-]^2 = \log K_2$

$\log[Zn(OH)_4^{2-}] = 2\log[OH^-] + \log K_2$

$[Zn(OH)_2\ (aq)] > [Zn(OH)_4^{2-}]$:

$\log K_1 > 2\log[OH^-] + \log K_2$

$\log K_1 > 2(-14 + pH) + \log K_2$

Thus,

$$\underline{8.4 < pH < 11.8}$$

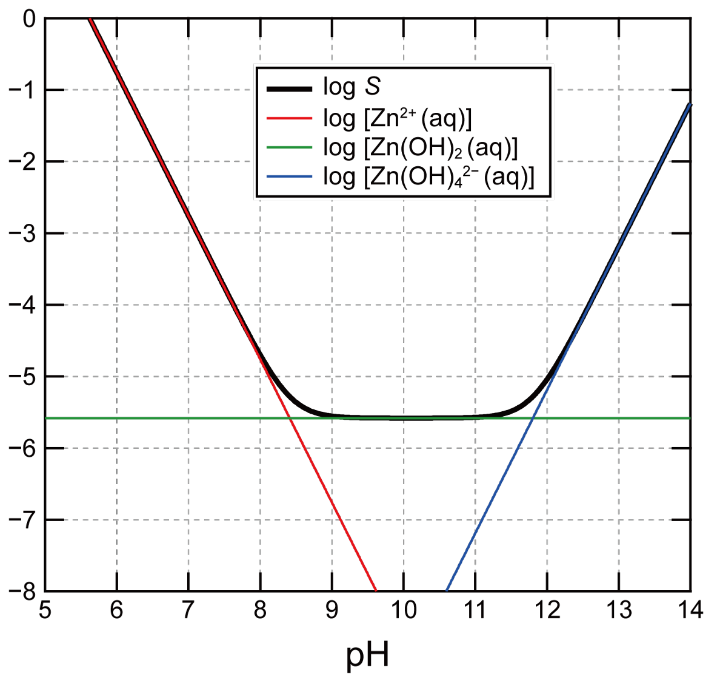


Fig. pH dependences of each species

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

For $\mathrm{pH} = 12.00$:

$\log[\mathrm{Zn(OH)_4^{2-}}] = -29.19 + 2\ \mathrm{pH} = -5.19$

$\log[\mathrm{Zn(OH)_2\ (aq)}] = -5.58$

$\log[\mathrm{Zn^{2+}}] = 11.24 - 2\ \mathrm{pH} = -12.76\ \text{(negligible)}$

Thus,

$$S = 9.0865 \times 10^{-6}\ \mathrm{mol\ L^{-1}}$$

For $\mathrm{pH} = 7.00$:

$\log[\mathrm{Zn^{2+}}] = 11.24 - 2\ \mathrm{pH} = -2.76$

$\log[\mathrm{Zn(OH)_2\ (aq)}] = -5.58$

$\log[\mathrm{Zn(OH)_4^{2-}}] = -29.19 + 2\ \mathrm{pH} = -15.19\ \text{(negligible)}$

Thus,

$$S = 1.7404 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$$

The percentage of zinc precipitated is:

$$\frac{1.7404 - 0.0090865}{1.7404} = 0.9948$$

$$\underline{= 99.5\%}$$

In **Part A**, we consider from the viewpoint of the equilibrium constant that the saturated solubility of zinc hydroxide, which is a poorly soluble salt, increases as the acidity or basicity increases. This is because the salt dissolves as a zinc ion when it is acidic and as a complex ion when it is basic. Since the saturated solubility changes according to the exponential function with respect to pH, it was shown that most of the zinc present in the aqueous solution can be recovered as a precipitate by appropriately changing the pH.

Part B

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

$$Zn(OH)_2\ (s) \rightarrow ZnO\ (s) + H_2O\ (l) \qquad (6)$$

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

$$ZnO\ (s) + H_2\ (g) \rightarrow Zn\ (s) + H_2O\ (g) \qquad (7)$$

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 the zinc oxide and water vapor at 300 °C and 1 bar are ΔG_{ZnO} (300 °C) = −2.90×10^2 kJ mol^{-1} and ΔG_{H2O} (300 °C) = −2.20×10^2 kJ mol^{-1}, respectively.

$$\mathrm{Zn} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{ZnO},\ \Delta G_{\mathrm{ZnO}}(300\ ^\circ\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O}, \Delta G_{\mathrm{H_2O}}(300\ ^\circ\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\ mol^{-1}}$$

Thus,

$$\mathrm{ZnO} + \mathrm{H_2} \rightarrow \mathrm{Zn} + \mathrm{H_2O}, \Delta G = \Delta G_{\mathrm{H_2O}}(300\ ^\circ\mathrm{C}) - \Delta G_{\mathrm{ZnO}}(300\ ^\circ\mathrm{C})$$

$$\Delta G = -\Delta G_1 + \Delta G_2 = 7.0\ \times 10^1\ \mathrm{kJ\ mol^{-1}}$$

$$\ln K = \ln \frac{p_{\mathrm{H2O}}}{p_{\mathrm{H2}}} = -\frac{\Delta G}{RT}$$

From $T = 573.15$ K,

$$\underline{p_{\mathrm{H2O}} = 4.14 \times 10^{-7}\ \mathrm{bar} = 4.1 \times 10^{-7}\ \mathrm{bar}}$$

The reduction reaction of zinc oxide with hydrogen does not proceed in the standard state because the standard Gibbs energy change is positive. However, the Gibbs energy change becomes negative by lowering the partial pressure of the product (water vapor), and thus, the reaction proceeds. Thus, the Gibbs energy change can be increased or decreased by controlling the partial pressure in most cases (when the product or reactant contains a gas).

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

$$\mathrm{Zn\ (s)} + \tfrac{1}{2}\mathrm{O_2\ (g)} \rightarrow \mathrm{ZnO\ (s)}, \qquad E° = 1.65\ \mathrm{V} \qquad (8)$$

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.

The reaction $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ occurs at the negative electrode and consumes 2 mol electrons per mol Zn oxidized.

Thus, the weight change is:

$$W = \frac{0.02\ \mathrm{A}\ \times 24 \times 60 \times 60}{2\ F} \times 16$$

$$\underline{= 0.14\ \mathrm{g}}$$

We consider the reaction that occurs at the electrode of zinc-air battery when it is discharged, and calculate the amount of zinc oxide deposited from Faraday's law.

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 °C (February) and 3776 m, respectively. The atmospheric pressure is represented by

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

at altitude h [m] and temperature T [°C]. The molar ratio of oxygen in the atmosphere is 21 %. The Gibbs energy change of reaction (8) is ΔG_{ZnO} (−38 °C) = -3.26×10^2 kJ mol^{-1} (1 bar).

Mt. Fuji

Solution 1:

From (9), the air pressure at $3776\ \mathrm{m}$ and $T = -38\ ℃$ is

$$P = 0.6011\ \mathrm{bar}$$

From the oxygen content of 21%, the partial pressure of oxygen is:

$$P_{O_2} = 0.126\ \mathrm{bar}$$

From the Nernst equation ($T = -38\ ℃$):

$$E(-38\ ℃) - E^{\circ}(-38\ ℃) = -\frac{RT}{2F}\ln\frac{1}{\sqrt{P_{O_2}}} = -0.01048\ \mathrm{V} = -0.01\ \mathrm{V}$$

$$E^{\circ}(-38\ ℃) = -\frac{\Delta G^{\circ}(-38\ ℃)}{2\ F} = \frac{326000}{2\ F} = 1.6894\ \mathrm{V} = 1.69\ \mathrm{V}$$

Thus,

$$\underline{\boldsymbol{E(-38\ ℃) = 1.68\ \mathrm{V}}}$$

Solution 2:

From (9), the air pressure at $3776\ \mathrm{m}$ and $T = -38\ ℃$ is

$$P = 0.6011\ \mathrm{bar}$$

From the oxygen content of 21%, the partial pressure of oxygen is:

$$P_{O_2} = 0.126\ \mathrm{bar}$$

$$\Delta G(-38\ ℃) = \Delta G^{\circ}(-38\ ℃) - \frac{1}{2}RT\ln P_{O_2} = -3.24\times10^{2}\ \mathrm{kJ\ mol^{-1}}$$

Thus,

$$E(-38\ ℃) = -\frac{\Delta G(-38\ ℃)}{2\ F}$$

$$\underline{= 1.68\ \mathrm{V}}$$

(° is used for 1 bar)

We consider how the electromotive force of a zinc-air battery depends on temperature and pressure. The Nernst equation is used in order to study the dependence of the electromotive force on the pressure and temperature (Solution 1). It can also be obtained from Gibbs energy (Solution 2). The Nernst equation is the same with the pressure dependence of Gibbs energy, both of which are ascribed to the pressure dependence of entropy.

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

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

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, \qquad E° (O_2/H_2O) = 1.23\ V \qquad (11)$$

From (10):

$Zn^{2+} + 2\ e^- \rightarrow Zn,\ E^\circ = -0.77\ V$

$\Delta G^\circ = -2F \times -0.77 = 148.61\ kJ\ mol^{-1} \quad (1')$

From (8):

$Zn + \frac{1}{2}O_2 \rightarrow ZnO, E^\circ = 1.65\ V$

$\Delta G^\circ = -2F \times 1.65 = -318.45\ kJ\ mol^{-1} \quad (2')$

From (11) :

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O,\ E^\circ = 1.23\ V$

$\Delta G^\circ = -4 \times F \times 1.23 = -474.71\ kJ\ mol^{-1} \quad (3')$

From (1):

$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2(s),\ K_{sp} = 1.74 \times 10^{-17}$

$\Delta G^\circ = -RT\ \ln K_{sp}^{-1} = -95.612\ kJ\ mol^{-1} \quad (4')$

From (4):

$H^+ + OH^- \rightarrow H_2O,\ K_w = 1 \times 10^{-14}$

$\Delta G^\circ = -RT \ln K_w^{-1} = -79.912\ kJ\ mol^{-1} \quad (5')$

From $\frac{(1')\times2+(2')\times2-(3')-(4')\times2+(5')\times4}{2}$:

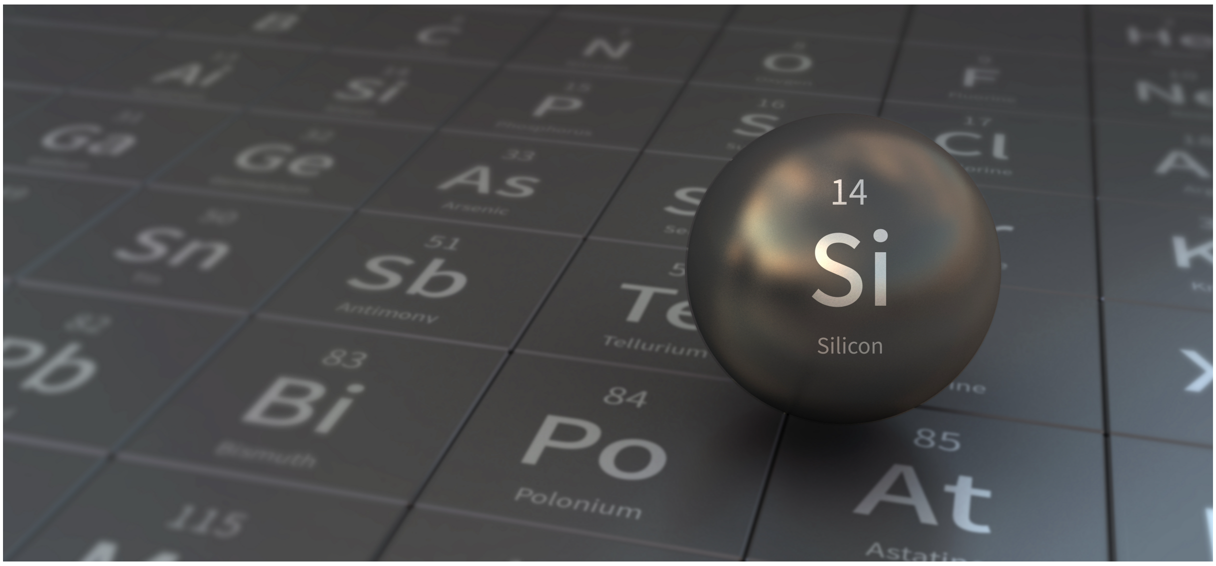
$$Zn(OH)_2\ (s) \rightarrow ZnO + H_2O,$$

$$\underline{\Delta G^\circ = 3.0 \sim 3.4\ kJ\ mol^{-1}}$$

(distributed depending on the handling of figures)

The Gibbs energy change of the decomposition reaction of zinc hydroxide is calculated by combining those of the four elementary reactions. The electromotive force, solubility product, equilibrium constant, etc. are given for each elementary reaction, but it should be understood that all of these can be associated with the Gibbs energy change of each elementary reaction.

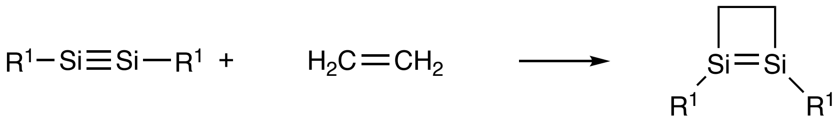
Question 5: Mysterious Silicon



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

Part A

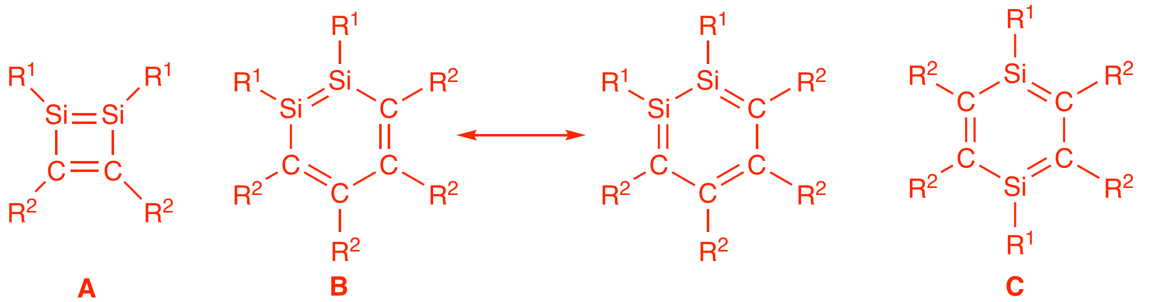
Unlike the carbon–carbon triple bond, the silicon–silicon triple bond in a compound formulated as R^1–Si≡Si–R^1 (R: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.



When R^1–Si≡Si–R^1 is treated with an alkyne (R^2–C≡C–R^2), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of R^2–C≡C–R^2 with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called 'disilabenzenes' that contain a six-membered ring and can be formulated as $(R^1–Si)_2(R^2–C)_4$. The ^{13}C NMR analysis of the corresponding six-membered ring skeletons Si_2C_4 shows two signals for **B** and one signal for **C**.

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

A.1 **<u>Draw</u>** the structural formulae of **A**, **B**, and **C** using R^1, R^2, Si, and C.



Intermediate **A** is a four-membered ring compound, which is formed by the addition of an alkyne $R^2C{\equiv}CR^2$ to $R^1Si{\equiv}SiR^1$. In consideration of the [2+2] cycloaddition reaction of $R^1Si{\equiv}SiR^1$ with ethylene giving the corresponding Si=Si-C-C- four-membered ring, compound **A** is assumed to be a 1,2-disilacyclobutadiene derivative with -Si=Si-C=C- skeleton. When another molecule of acetylene is inserted into the Si-C moiety of intermediate **A**, the corresponding 1,2-disilabenzene is formed. On the other hand, when acetylene is inserted into the Si-Si moiety of **A**, the corresponding 1,4-disilabenzene is formed. It should be helpful information that the product is noted as "disilabenzene Si_2C_4," and the structural formulas of H-substituted disilabenzenes are shown in Figure 1. Based on the information that ^{13}C NMR spectra of compounds **B** and **C** show that two signals and one signal, respectively, compound **B** is the 1,2-disilabenzene and compound **C** is the 1,4-disilabenzene.

A.2 **Calculate** the aromatic stabilization energy [kJ mol^{-1}] for benzene and **C** (in the case of R^1 = R^2 = H) as positive values, using Fig. 1.

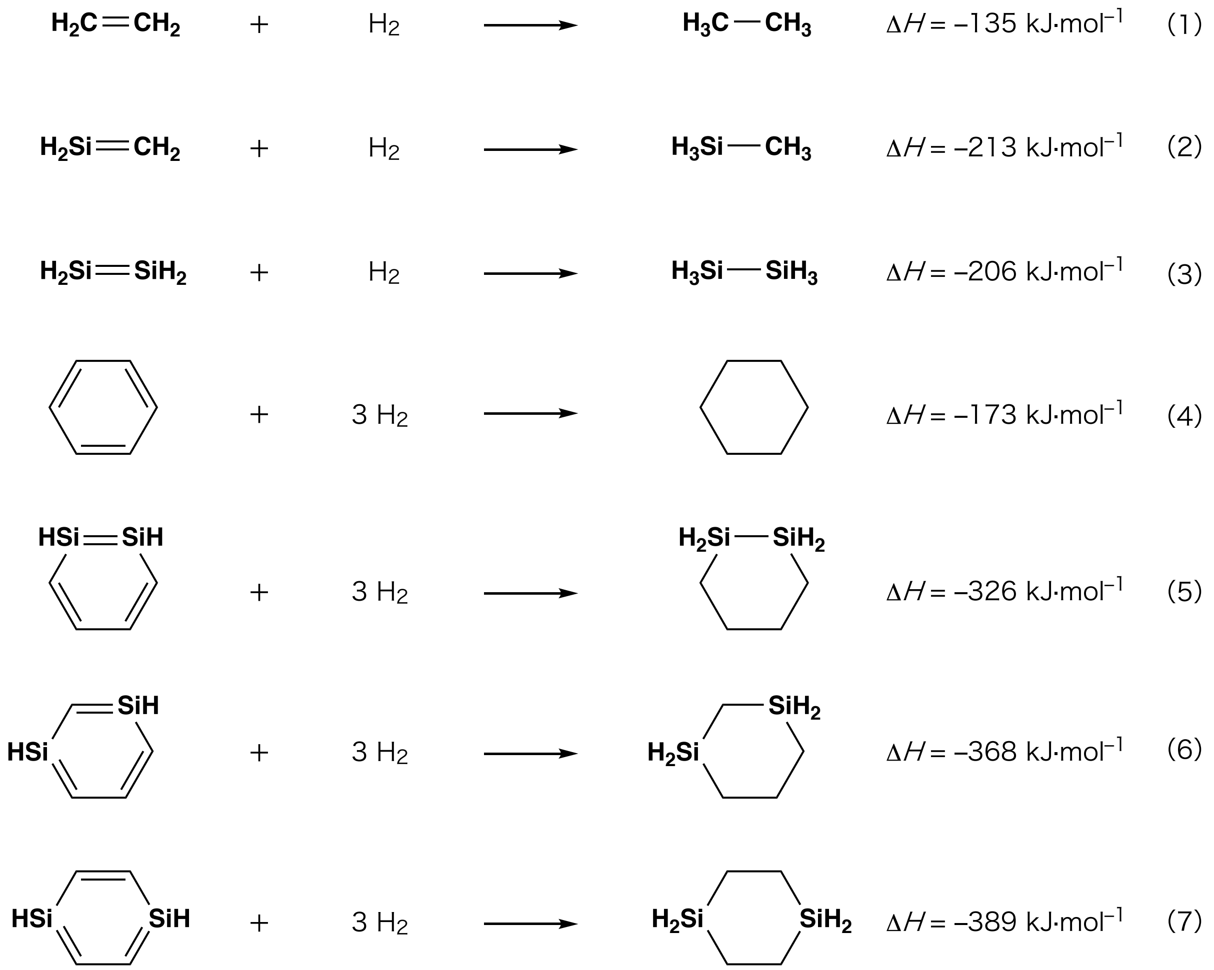


Fig. 1 Enthalpy change in some hydrogenation reactions of unsaturated systems.

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: 135 × 3 – 173 = <u>232 kJ mol^{-1}</u>

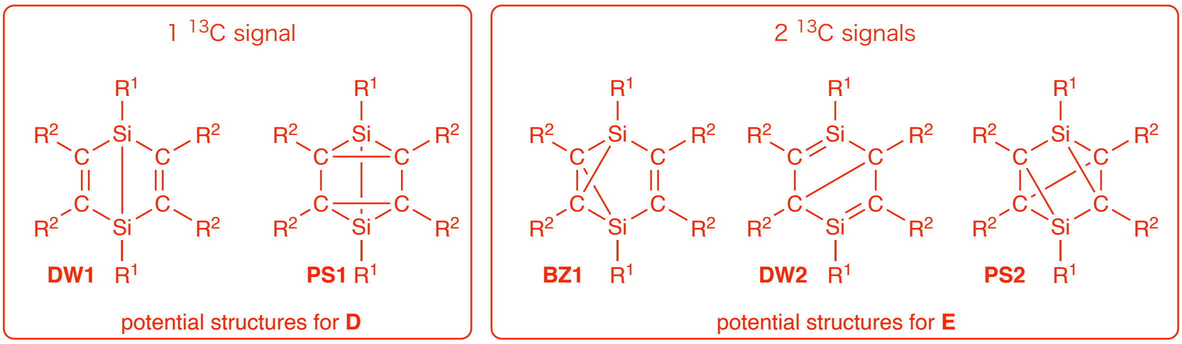
ASE for 1,4-disilabenzene (C=C + 2 Si=C): (135 + 213 × 2) – 389 = <u>172 kJ mol^{-1}</u>

A.3 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. **Calculate** ΔH [kJ mol^{-1}] for the transformation of **D** to **E**. Assume that ΔH does not depend on temperature.

T = 50 °C = 323.15 K ($1/RT$ = 0.3722): K_{DE} = 40
T = 120 °C = 393.15 K ($1/RT$ = 0.3059): K_{DE} = 20
According to $\ln K_{DE} = -(\Delta H°/RT) + \Delta S°/R$:
$\Delta H° = -(\ln 40 - \ln 20) / (0.3722 - 0.3059) = \underline{-10.5\ \text{kJ mol}^{-1}}$

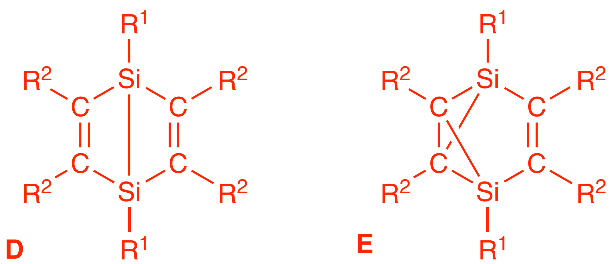
A.4 The isomerization from **C** to **D** and to **E** proceeds via transformations of π-bonds into σ-bonds without breaking any σ-bonds. A ^{13}C NMR analysis revealed one signal for the Si_2C_4 skeleton of **D** and two signals for that of **E**. The skeleton of **D** does not contain any three-membered rings, while **E** has two three-membered rings that share an edge. **Draw** the structural formulae of **D** and **E** using R^1, R^2, Si, and C.

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



(**DW**: Dewar benzene type, **PS**: Prismane type, **BZ**: Benzvalene type)

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:



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.

Quantification of Na_2SiF_6:

·Preparation

Aqueous solution **F**: 0.855 g of Na_2SiF_6 dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ 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 $Si(OH)_4$.

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

SiF_4 is hydrolyzed to form H_2SiF_6 according to equation 8:

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

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

The precipitate of unreacted Na_2SiF_6 and NaCl, which was removed by filtration in the initial step (underline (a)), 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.

Table 1

^{19}F NMR data	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4
Chemical shift (δ)	0.0	−8.0	−28.6	−62.3
Integration ratio	45.0	65.0	18.0	2.0

B.1 **Write** the reaction formulae for the reaction of Na_2SiF_6 with $Ce_2(SO_4)_3$.

Na_2SiF_6 = 188.0 [g·mol^{-1}]. The concentration of Na_2SiF_6 in solution **F** is 0.855 g / 200 mL = 4.548 × 10^{-3} mol / 0.2 L = 2.274 × 10^{-2} mol·L^{-1} (**F**)

$Ce_2(SO_4)_3$ = 568.4 [g·mol^{-1}]. The concentration of $Ce_2(SO_4)_3$ in solution **G** is 6.860 g / 200 mL = 1.207 × 10^{-2} mol / 0.2 L = 6.034 × 10^{-2} [mol·L^{-1}] (**G**)

The concentration of Ce^{3+} ions in **G** is 6.034 × 10^{-2} [mol·L^{-1}] × 2 = 1.207 × 10^{-1} [mol·L^{-1}]

In 50.0 mL of solution **F**: 2.274 × 10^{-2} × (50.0/1000) [mol] = 1.137 × 10^{-3} [mol] of Na_2SiF_6 was included.

In 18.8 mL of solution **G**: 6.034 × 10^{-2} × (18.8/1000) [mol] = 1.134 × 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 (SiF_6^{2-} reacts with Ce^{3+} in a 1:2 ratio)

$Na_2SiF_6 + Ce_2(SO_4)_3 + 4\ H_2O \rightarrow 2\ CeF_3 + Si(OH)_4 + Na_2SO_4 + 2\ H_2SO_4$

B.2 **Calculate** the weights [g] of NaCl produced and of Na_2SiF_6 used (x [g]) as a starting material.

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 × 10^{-2} [mol·L^{-1}] × (61.6 × 10^{-3} [L]) = 3.717 × 10^{-3} [mol]. Considering the equation

$$3\ SiF_4 + 2\ H_2O \rightarrow SiO_2 + 2\ H_2SiF_6,$$

the ratio of the consumed SiF_4 and the generated H_2SiF_6 should be 3:2, and therefore 10 mL of the diluted solution **H** contains 3.717 × 10^{-3} [mol] × (3/2) = 5.576 × 10^{-3} [mol] of SiF_4. Thus, 1.00 L of diluted solution **H** contains 5.576 × 10^{-3} [mol] × (1000/10) = 0.5576 [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 × 0.5576 = 1.115 [mol] of F^- should replace Cl^- to result in the formation of NaCl.

1.115 [mol] × 58.4 [g·mol^{-1}]= 65.12 [g] of NaCl was formed.

Answer: 65.1 [g]

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 44.4×10^{-3} [L]× (6.034×10^{-2} [mol·L^{-1}]) = 2.679×10^{-3} [mol]. Accordingly, the residual amount of Na_2SiF_6 in 10.0 L of aqueous solution **K** is 2.679×10^{-3} [mol] × 100 = 0.2679 [mol].
In total, the amount of Na_2SiF_6 used as a starting material is (0.2679 [mol] + 0.5576 [mol]) × 188.0 [g·mol^{-1}] = 155.2 [g]
Answer: 155 [g]

B.3 77.8% of the CCl_4 used as a starting material was unreacted. **Calculate** the weight [g] of CF_3Cl generated.

500.0 [g] = 3.25 [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 3.25 [mol] × 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 : 65 : 18 : 2.0. Thus, the
mole ratio of these compounds should be $CFCl_3$: CF_2Cl_2 : CF_3Cl : CF_4 = 45 : 32.5 : 6 : 0.5 = 90 : 65 : 12 : 1.
Accordingly, the amount of CF_3Cl (104.46 [g·mol^{-1}]) is 0.721 [mol] × (12 / (90 + 65 + 12 + 1)) = 0.0515 [mol] = 0.0515 [mol] × 104.46 [g·mol^{-1}] = 5.38 [g]
Answer: 5.38 [g]

Subject Intention:
1. To learn the process of the structural identification of the unknown products based on the spectral features and the reaction patterns. To realize that an unfamiliar benzene derivative where its carbon atoms are replaced by silicon atoms, exhibits the considerable aromatic stabilization.
2. To realize that silicon compounds are one of unique main group elements that can have up to six bondings, and learn the process of quantitative understanding the phenomenon of such an unfamiliar fluorination reaction using highly coordinated silicon fluoride in a step-by-step manner based on the precipitation titration.

Problem 6. The Solid-State Chemistry of Transition Metals

Volcano at Sakurajima island

Part A

Japan is one of the countries with the highest numbers of volcanos. 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, K_p, can be expressed by:

$$K_p = \frac{[M]_s}{[M]_l} \qquad (1)$$

where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. Table 1 shows the K_p values of Cr^{2+}, Mn^{2+}, and Fe^{2+}.

Fe^{2+} in Table 1 is not included in the official IChO Problems 2021 because of potential difficulty in marking by following the IChO marking regulation.

Table 1

	Cr^{2+}	Mn^{2+}	Fe^{2+}
K_p	7.2	1.1	2.0

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

A.1 **Calculate** $|\Delta_O^M - \Delta_T^M| = \Delta_A$ with units of Δ_O for Cr^{2+}, Mn^{2+}, and Fe^{2+}; assume $\Delta_T = 4/9\Delta_O$.

As explained above, the d-orbitals of a six-coordinate octahedral complex split into two groups e_g (dx^2-y^2, dz^2) and t_{2g} (d_{xy}, d_{yz}, d_{zx}) with energy separation of Δ_O. The energies of the e_g and t_{2g} orbitals relative to the barycenter are $+0.60\Delta_O$ and $-0.40\Delta_O$, 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 (dx^2-y^2, dz^2) with energy separation of Δ_T. The energies of the t_2 and e orbitals relative to the barycenter are $+0.40\Delta_T$ and $-0.60\Delta_T$, respectively. Therefore, in the case of high-spin electron configuration,

Δ_O^M and Δ_T^M for Cr^{2+} ($3d^4$: $t_{2g}^3e_g^1$ or $e^2t_2^2$) are $-0.60\Delta_O$ and $-0.40\Delta_T$ (= $-0.18\Delta_O$), respectively.

Δ_O^M and Δ_T^M for Mn^{2+} ($3d^5$: $t_{2g}^3e_g^2$ or $e^2t_2^3$) are both zero.

Δ_O^M and Δ_T^M for Fe^{2+} ($3d^6$: $t_{2g}^4e_g^2$ or $e^3t_2^3$) are $-0.40\Delta_O$ and $-0.60\Delta_T$ (= $-0.27\Delta_O$), respectively.

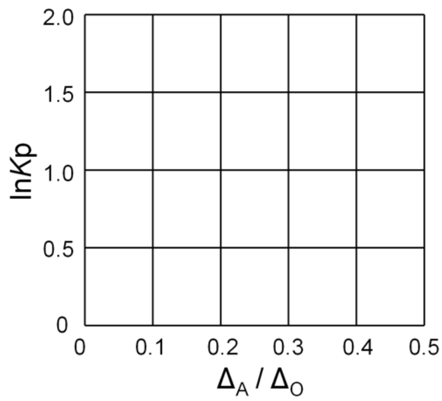
According to these values, $|\Delta_O^M - \Delta_T^M|$ (= Δ_A) for each metal ions are,

Cr^{2+}: $|-0.60\Delta_O - (-0.18\Delta_O)| = \underline{0.42\ \Delta_O}$

Mn^{2+}: $\underline{0}$

Fe^{2+}: $|-0.40\Delta_O - (-0.27\Delta_O)| = \underline{0.13\ \Delta_O}$

A.2 A linear relationship can be obtained by plotting $\ln K_p$ against Δ_A / Δ_O on the graph at right. **Estimate** K_p for Co^{2+} by using this graph.



Co^{2+} ($3d^7$): $|-0.80\Delta_O - (-0.53\Delta_O)| = 0.27\ \Delta_O$

1. By using the graph and least squares method; $y \simeq 4.45x + 0.100$

Therefore, $K_p = \exp(4.45 \times 0.27 + 0.100) = 3.67 \simeq \underline{3.7}$

2. By calculation; 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,

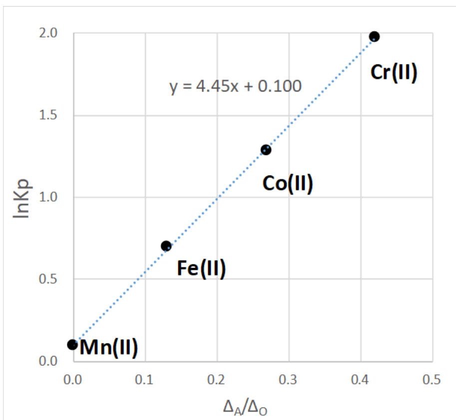
$y \simeq 4.46x + 0.100$

Therefore, $K_p = \exp(4.46 \times 0.27 + 0.100) = 3.68 \simeq \underline{3.7}$

3. If the participants use Fe^{2+} (0.13, 0.69) instead of Mn^{2+}, the regression line would be,

$y \simeq 4.57x + 0.100$

Then, $K_p = \exp(4.57 \times 0.27 + 0.100) = 3.79 \simeq \underline{3.8}$



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

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

One way to reach the correct answer: 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 comparable. Thus, the lattice enthalpy is higher for CoO. Thus, the correct answer is (a).

In **Part A**, we wish to introduce the structural diversity of d-metal complexes. We also show that the states of d-metal ions in crystals can be understood using the crystal field theory usually applied to d-metal complexes, which are molecules.

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 (dx^2-y^2 and dz^2).

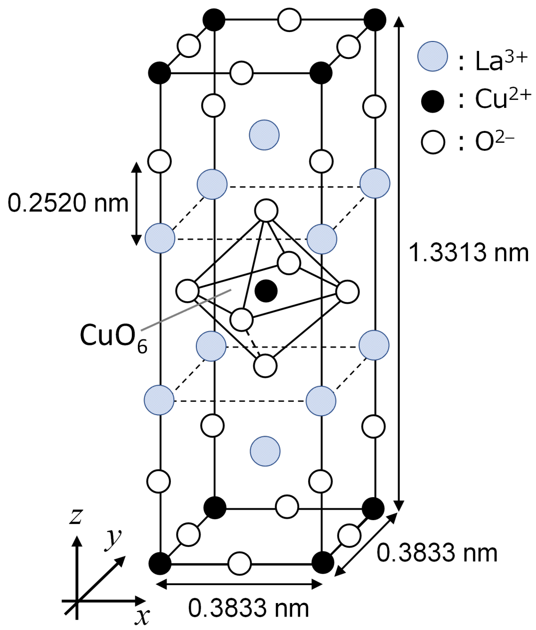


Fig. 1

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 loss of crystallization water, followed by another weight loss up to 700 °C due to the release of CO_2. The total weight loss prior to the formation of **A** 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 of **A** and **B**.

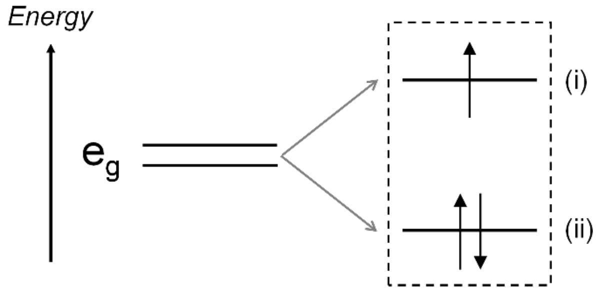
The unit cell shown in Fig. 1 contains four La^{3+}, two Cu^{2+}, and eight O^{2-} ions. Therefore, **A:** La_2CuO_4. As the formula weight of La_2CuO_4 is 405.3, that of **B** should be 1113.5 considering the following equation: 405.3 ÷ (1 – 0.636). Given that the weight loss due to crystallization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

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

l_x: 0.3833 ÷ 2 = 0.1917 ≈ 0.192 nm

l_z: (1.3313 – 0.2520 × 2) ÷ 4 = 0.2068 ≈ 0.207 nm

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 ($dx^2\!-\!y^2$ and dz^2) in (i) and (ii), and **draw** the electron configuration in the dotted box in your answer sheet.



(i) $dx^2\!-\!y^2$, (ii) dz^2

B.4 **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. **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.

The corresponding reaction equation, where the amount of Sr is x%, is:

$La_2CuO_4 + (2x/100)Sr^{2+} \rightarrow [La_{\{2\times(1-x/100)\}}Sr_{(2x/100)}CuO_4]^{(2x/100)-} + (2x/100)La^{3+}$

The charge of $[La_{\{2\times(1-x/100)\}}Sr_{(2x/100)}CuO_4]$ is negative, and the amount of doped holes is $(2x/100)$ h^+. 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: $(4x/100) / (0.1956 \times 10^{-27}) = 2.05 \times 10^{27}$. $\underline{x = 10\%}$

In **Part B**, we wish to introduce the structures, related reactions, and functions of mixed transition-metal oxides with La_2CuO_4 as an example. We also present the structural diversity based on Jahn-Teller distortion of Cu^{2+} (d^9 configuration), and the functions related with elemental substitution.

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 $[Cu_4(L1)_4]$ 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.

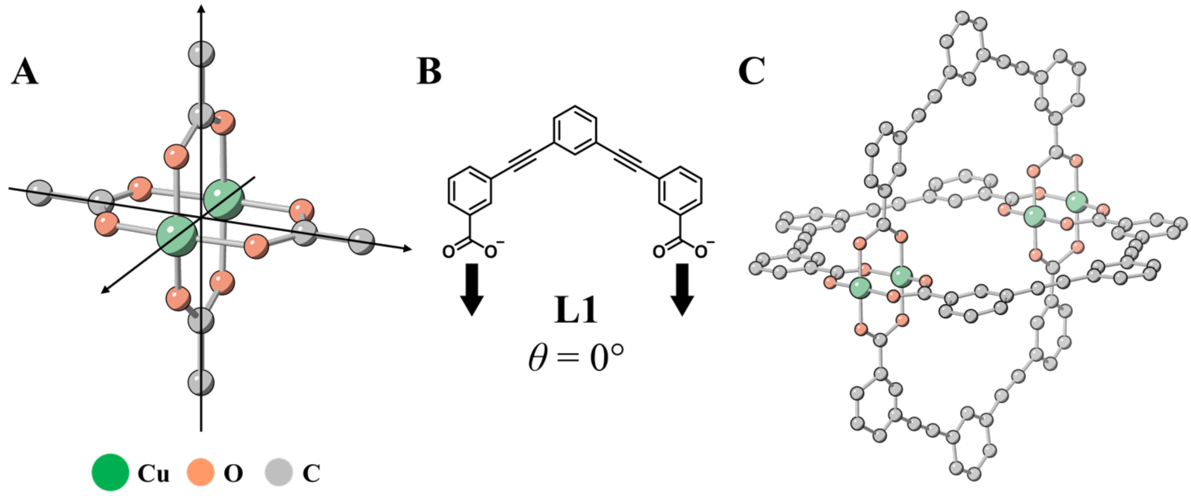
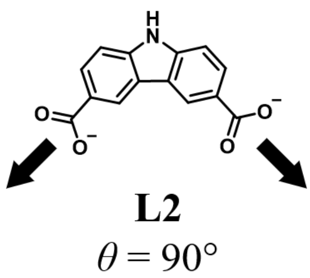
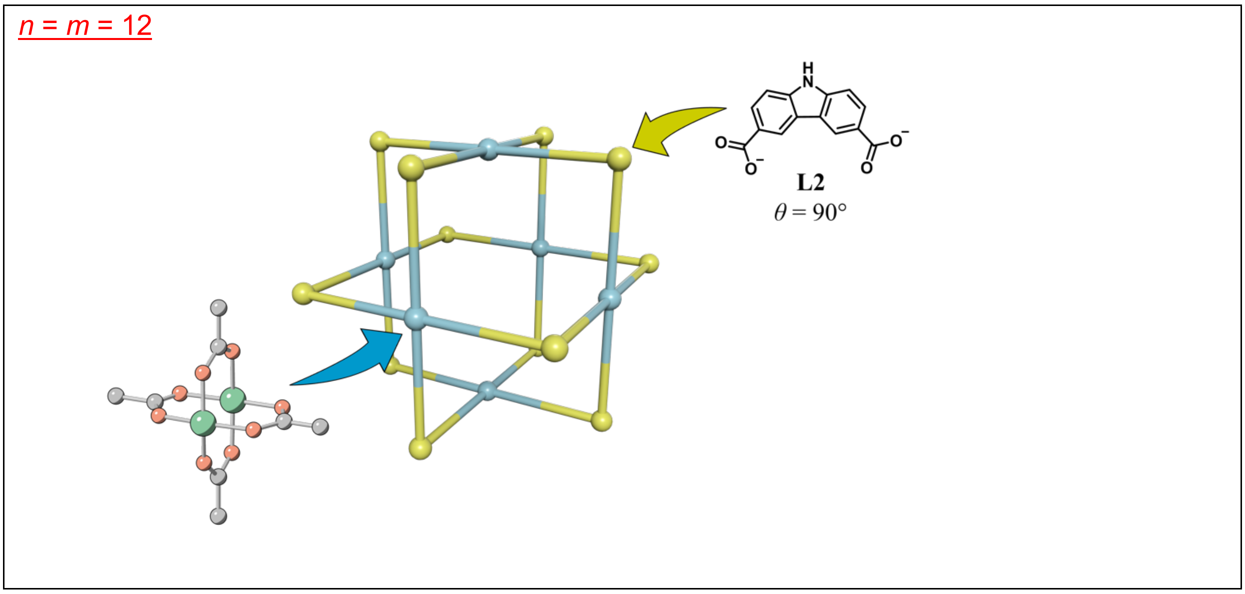


Fig. 2

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 $[Cu_n(L2)_m]$, **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.





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 [$Zn_4O(L3)_3]_n$, 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.

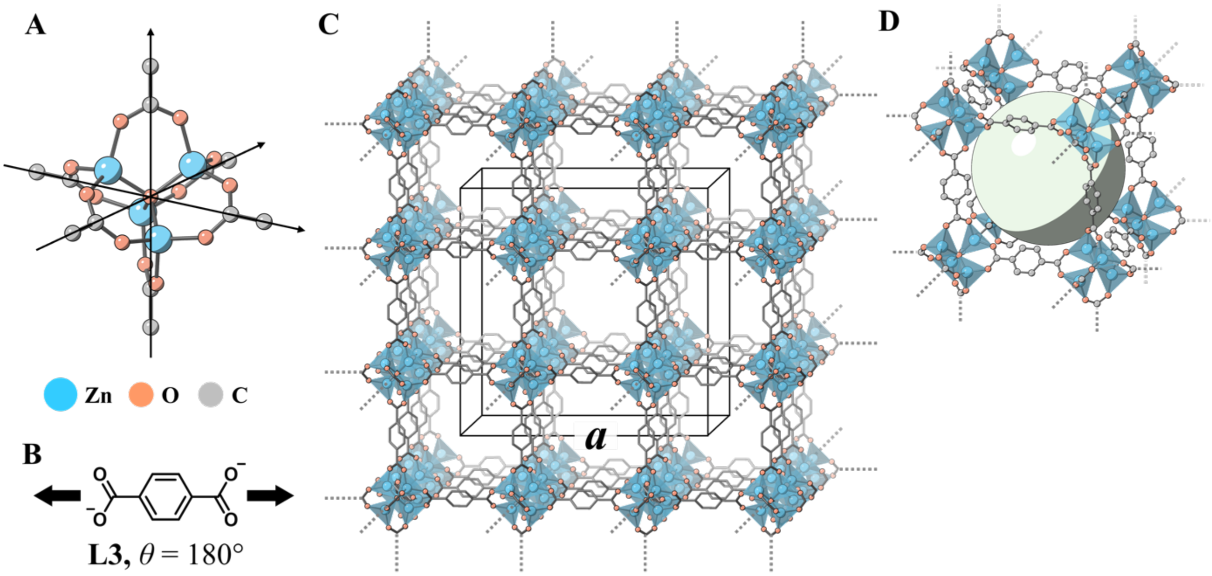


Fig. 3

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}. **<u>Calculate</u>** a in [cm].

The molecular weight of $Zn_4O(L3)_3$ is 770.

According to Fig. 3C, there are eight $Zn_4O(L3)_3$ units in the unit cell. Therefore, the molecular weight per unit cell can be calculated as $770 \times 8 = 6160$.

The weight of the unit cell is $6160 \div N_A = 1.02 \times 10^{-20}$ 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}.

<u>$a = 2.6 \times 10^{-7}$ cm</u>

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. **<u>Calculate</u>** the average number of CO_2 molecules per pore.

There is one pore per $Zn_4O(L3)_3$ 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:

$(1 \times 10^5$ [Pa] $\times$ 3.0×10^{-4} [m^3]) / $(8.31 \times 298$ [K]) = 0.0121 [mol] of CO_2.

Therefore, $0.0121 \div 0.00130$ = <u>9.3 molecules</u> of CO_2 per pore.

The following question **C.4** is not included in the official IChO Problems 2021 because of the IChO exam length regulation.

Let's try to describe the structure of the complex geometrically here, as shown in Fig. 4. As shown in Figs. 4a and 4b, $[Cu_2(CO_2)_4]$ is represented by a square panel with four carbons connected. The structure of $[Cu_2(CO_2)_4]$ is then described by connecting the square panels using straight lines connecting the carbons of the two CO_2^- groups of the dicarboxylate (Fig. 4C).

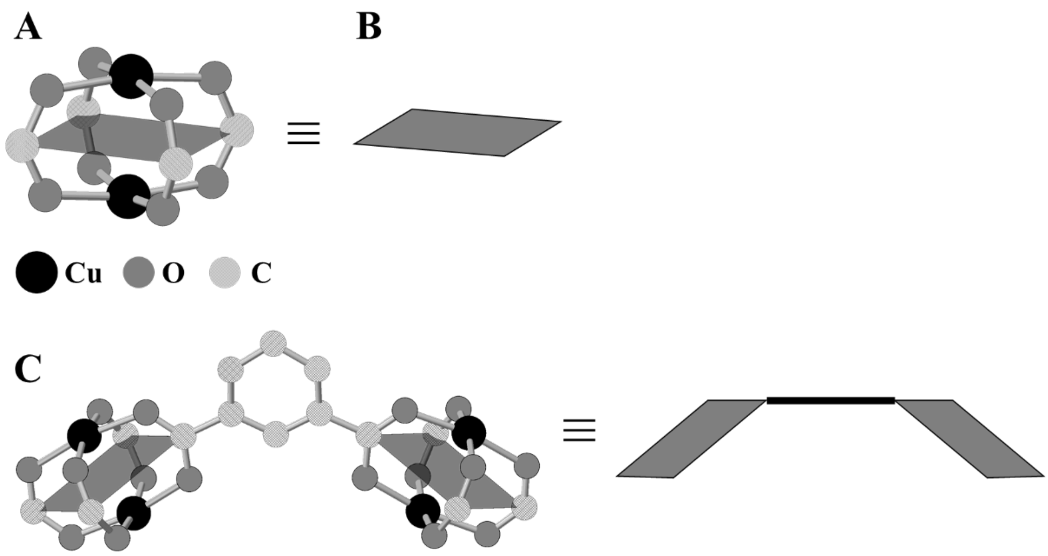


Fig. 4

C.4 Following the notation in Fig. 4, the structures of the various coordination polymers consisting of $[Cu_2(CO_2)_4]$ can be represented by connecting the vertices of the square panels with straight lines. For the structures of the four coordination polymers described in this way (Fig. 5, right), **select** the most suitable dicarboxylate (Fig. 5, left) to form each of them, and connect the lines to be 1:1. Note that only the CO_2^- group is assumed to coordinate with the Cu^{2+} ion, and all dicarboxylates are represented by a straight line connecting the carbons of the two CO_2^- group. The dotted line on the right side of Fig. 5 indicates that the same structure continues.

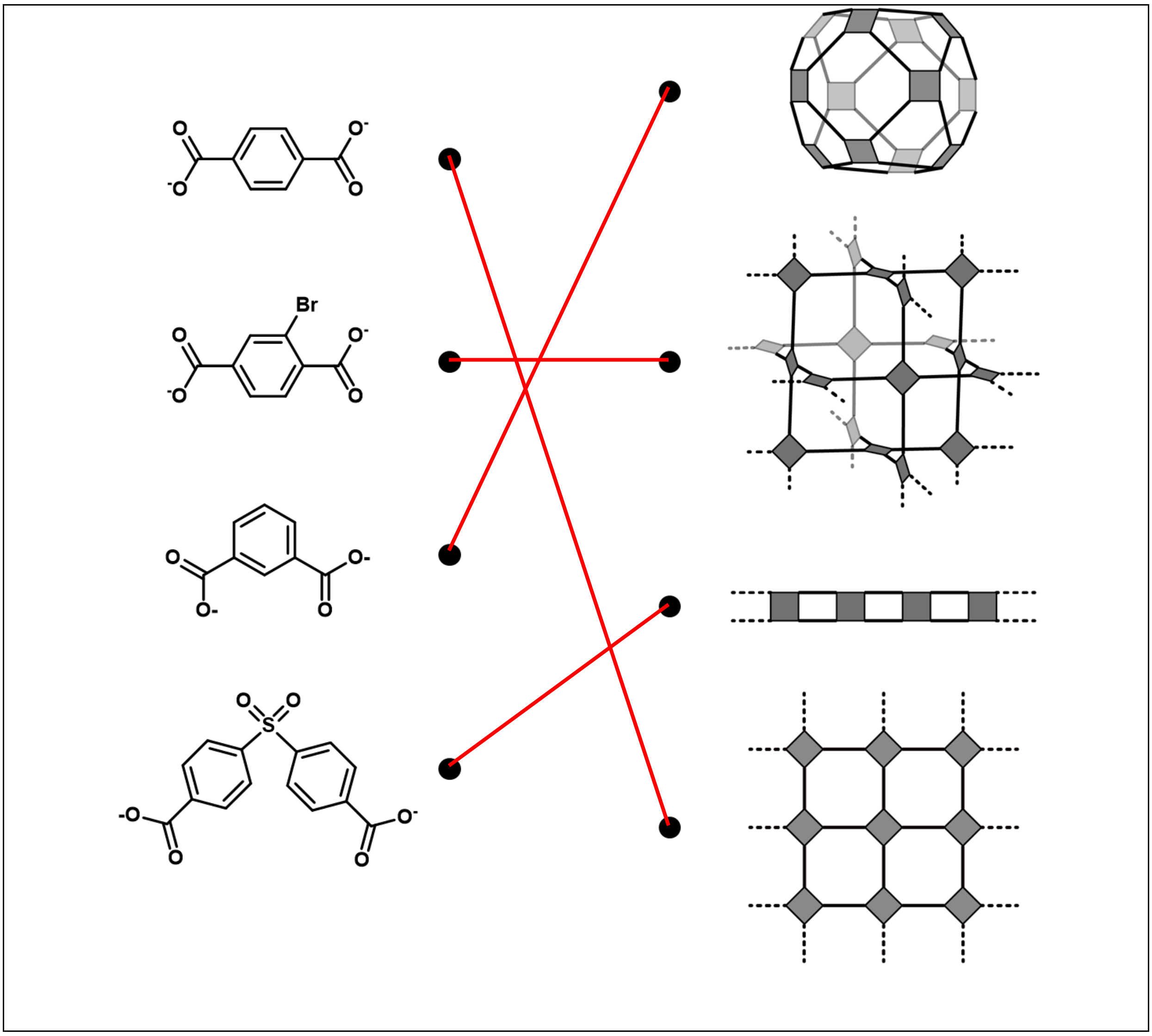


Fig. 5

In **Part C**, we would like the examinee to imagine and understand to construct more diverse structures of coordination complexes architectures by changing the organic ligands.

Question 7：Playing with Non-benzenoid Aromaticity

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

Photo courtesy: Department of Chemistry, Graduate School of Science, Tohoku University.

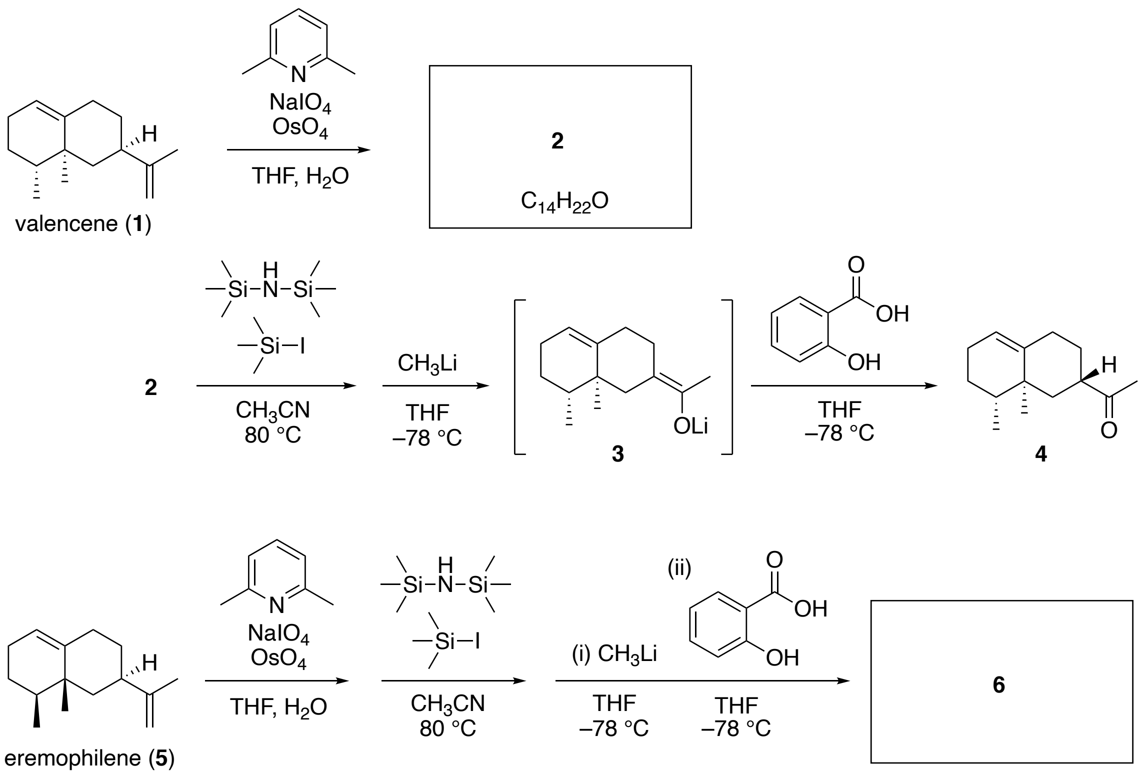
Part A

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.

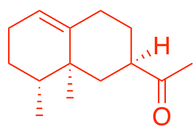
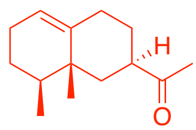
Inula linariifolia

Further reading:

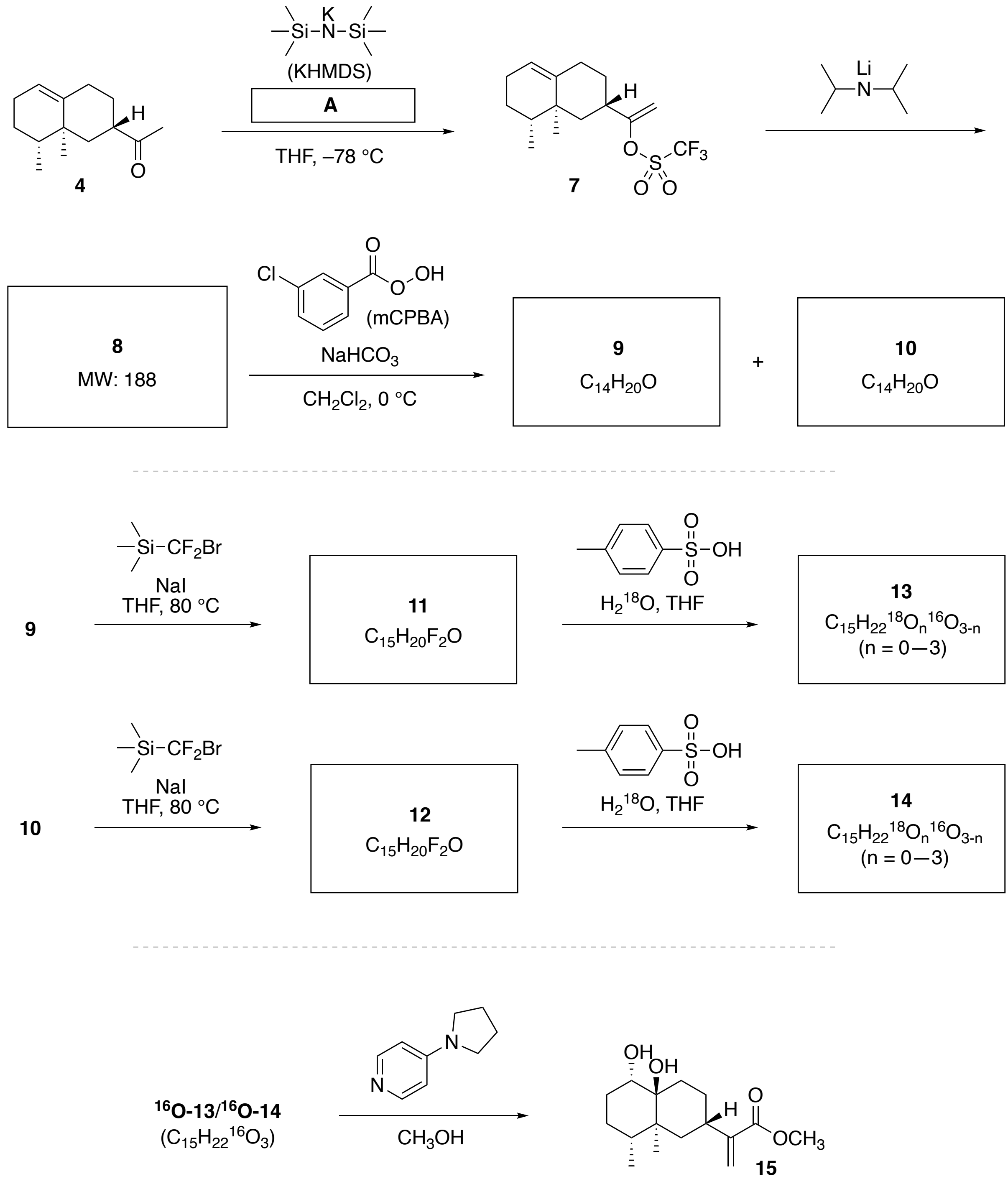
Erik J. Sorensen, *et al.*, "Synthesis of (+)-Lineariifolianone and Related Cyclopropenone-Containing Sesquiterpenoids" *The Journal of Organic Chemistry* **2019**, Vol. 84, Iss. 9, 5524–5534.



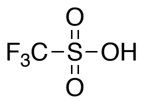
A.1 **Draw** the structure of **2** and **6** and clearly identify the stereochemistry where necessary.

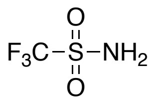
2	**6**
	

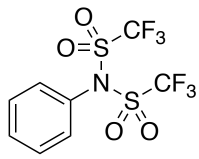
Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled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

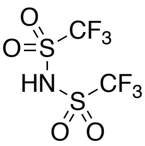


A.2 **Choose** the appropriate structure for **A**.

I 

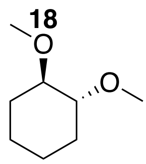
II 

III 

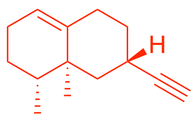
IV 

III

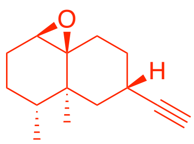
A.3 **Draw** the structures of **8**–**14** and clearly identify the stereochemistry where necessary. Also, **indicate** the introduced ^{18}O atoms for **13** and **14** as shown in the example on the right.



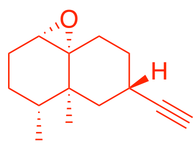
8



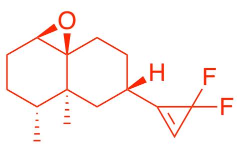
9



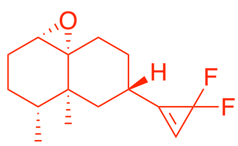
10



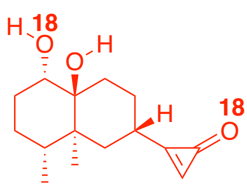
11



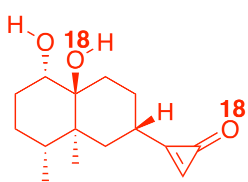
12



13

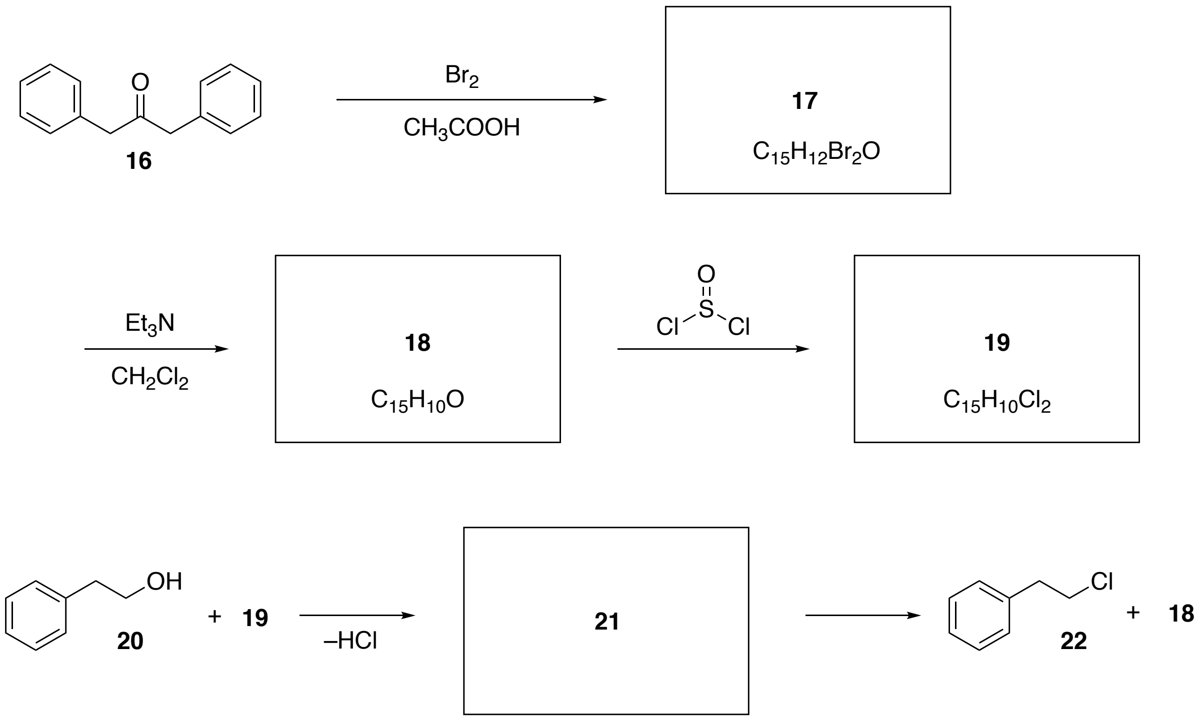


14



Part B

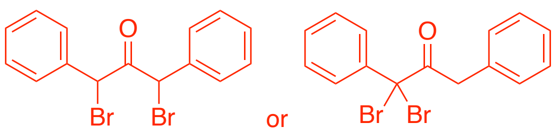
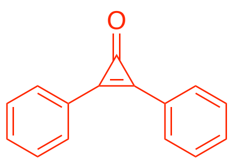
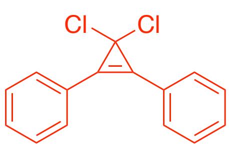
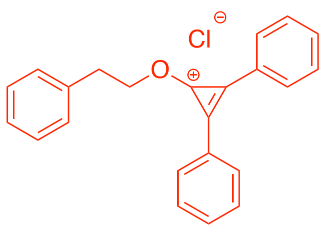
Compound **19** is synthesized as shown below. In relation to non-benzenoid aromaticity, **19** can be used as an activator for alcohols, and **20** was converted to **22** via ion-pair intermediate **21**. Although the formation of **21** was observed by NMR, **21** gradually decomposes to give **18**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

17 	**18** 
19 	**21** 

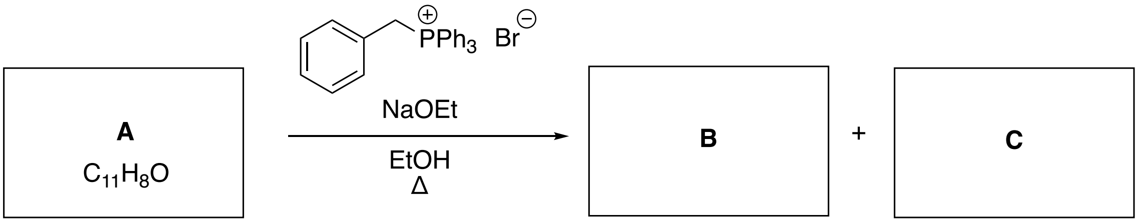
Further reading:

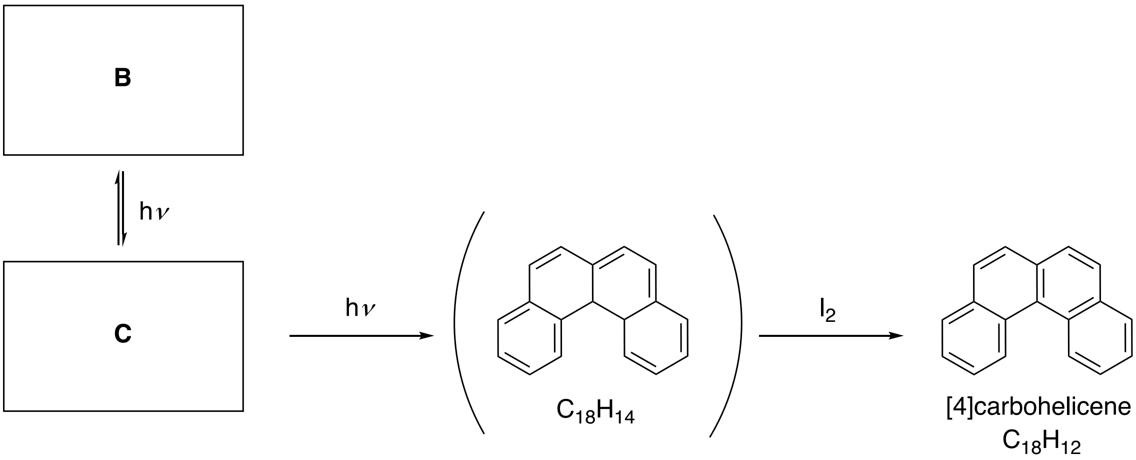
Tristan H. Lambert, *et al.*, "Aromatic Cation Activation of Alcohols: Conversion to Alkyl Chlorides Using Dichlorodiphenylcyclopropene" *Journal of the American Chemical Society* **2009**, Vol. 131, Iss. 39, 13930–13931.

Question 8：Dynamic Organic Molecules and Their Chirality

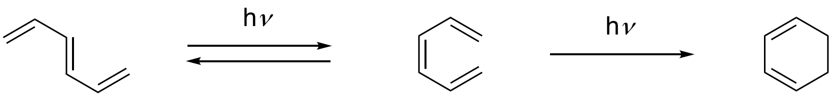
Part A

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

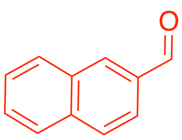
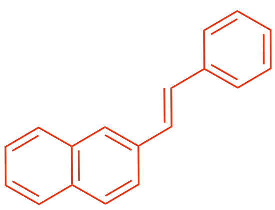
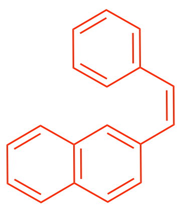




The photoreaction proceeds in a manner similar to the following example.

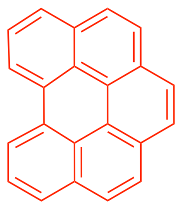


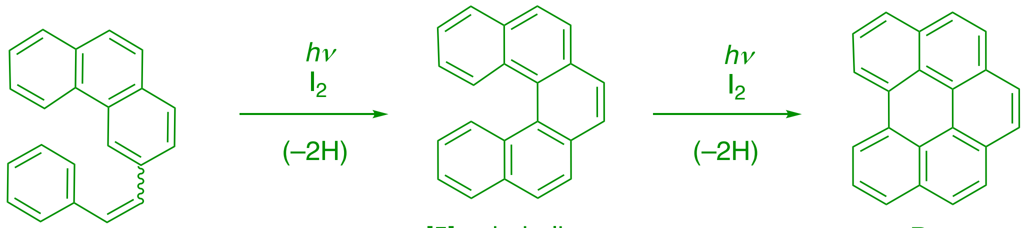
A.1 <u>**Draw**</u> the structures of **A**–**C**. Stereoisomers should be distinguished.

A	**B**	**C**
		

A.2 Attempts to synthesize [5]carbohelicene in the same way resulted in the formation of only a trace amount of [5]carbohelicene, instead affording an unexpected 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. **<u>Draw</u>** the structure of **D**.

D (δ, ppm in CS_2, 20 ℃): 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)



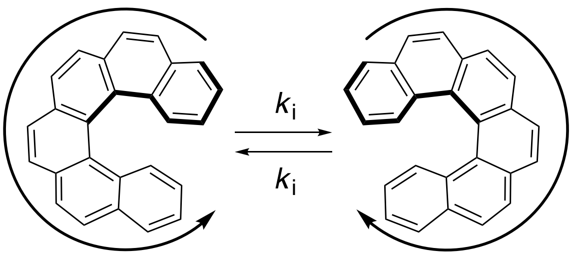


[5]carbohelicene
$C_{22}H_{14}$

D
benzo[*ghi*]perylene
$C_{22}H_{12}$

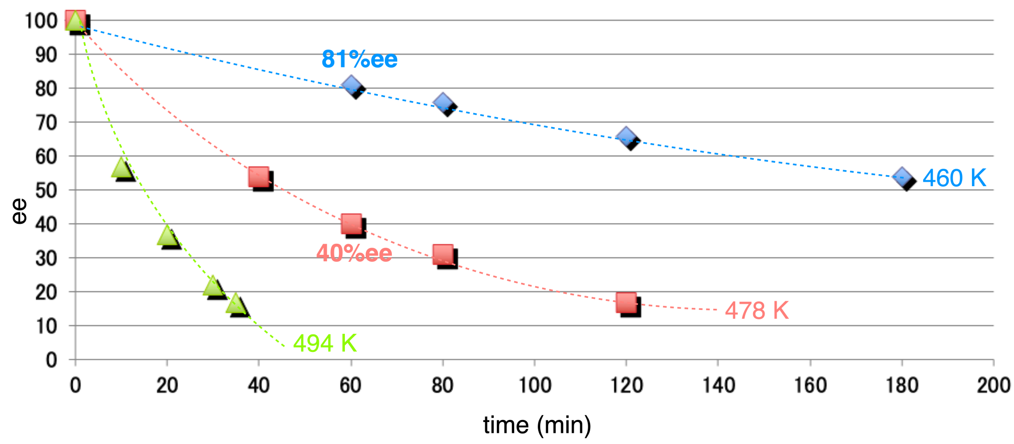
The following questions **A.3** and **A.4** are not included in the official IChO Problems 2021 because of potential difficulty in marking by following the IChO marking regulation.

[6]Carbohelicene, which is prepared by the same photoreaction, can be enantiomerically separated on a chiral column, a process developed by Prof. Yoshio Okamoto. Here, the chirality of [n]carbohelicenes are defined as (*M*) or (*P*) as shown below.



(*M*) (*P*)

A.3 Enantiomerically pure [6]carbohelicene gradually racemizes upon heating with an helical inversion rate constant k_i. The activation barrier in this case can be determined by plotting the enantiomeric excess as a function of time as shown in the figure below. **<u>Calculate</u>** the racemization rate constant, k_r, and the activation barrier, E_a, using the enantiomeric excess at 60 min. Consider the relationship $k_r = 2k_i$. The rate of the racemization process is independent of the concentration.

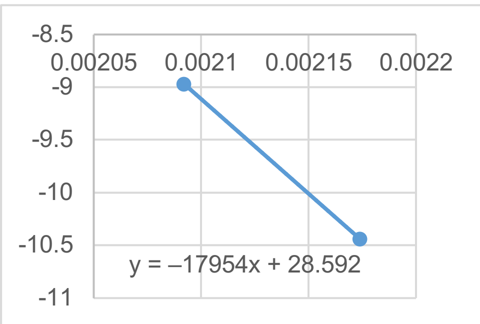


First, k_r is calculated according to Figure 1. Given that the racemization is a unimolecular first-order reaction,

$\ln(ee) = -k_r t + y$

, wherein y is a constant. By recalling $k_r = 2k_i$ and using the ee values at t = 0 s and 3600 s, at T = 460 K and 478 K, k_i are calculated to be $2.927 \times 10^{-5}\ s^{-1}$ and $1.273 \times 10^{-4}\ s^{-1}$, respectively.

Second, according to the Arrhenius equation, $\ln k_i = -E_a/(RT) + \ln A$, a plot of $\ln k_i$ versus $1/T$ gives a straight line shown on the right, whose gradient can be used to determine $-E_a/R$ as -17954. Given $R = 8.31\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, E_a is calculated to be $149.27\ kJ\ mol^{-1}$ = <u>$1.5\times10^{2}\ kJ\ mol^{-1}$</u>



A.4 The racemization kinetics of [5]carbohelicene was estimated to be E_a = 98.5 kJ mol^{-1} with a frequency factor in the Arrhenius equation (preexponential factor) of A = 2.43$\times$10^{12} s^{-1}. Based on these parameters, **estimate** the half life of the enantiomeric excess (i.e., the time at which 50%ee is observed) of [5]carbohelicene at 300 K.

k_i is calculated to be 1.748 x 10^{-5} s^{-1} by using the Arrhenius equation ln k_i = –E_a/(RT) + ln A with E_a = 98.5 kJ mol^{-1}, A = 2.43 x 10^{12} s^{-1}, R = 8.31 J·K^{-1}·mol^{-1}, and T = 300 K.

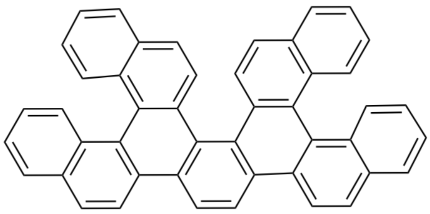
k_r = 2k_i = 3.496 x 10^{-5} s^{-1} = 2.098 x 10^{-3} min^{-1}

With ln (ee) = –k_rt + y, the half life = – (ln 0.5)/k_r = 330 min

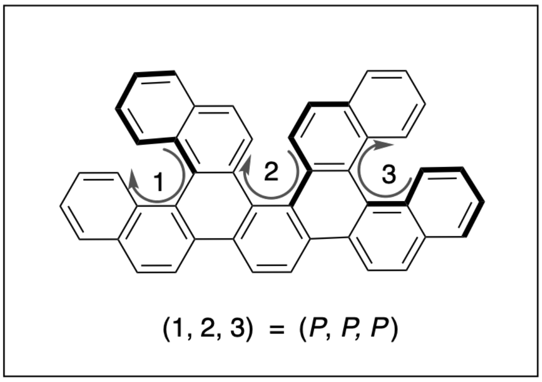
A message from **A.3** and **A.4** is that the dynamic behavior of [n]carbohelicenes can be quantitatively analyzed. The racemization activation energy is reasonably higher for [6]carbohelicene than that for [5]carbohelicene. Because the chiral separation experiment is routinely conducted around room temperature, [6]carbohelicene can be fully separated while [5]carbohelicene cannot due to the rate of racemization.

The following question **A.5** was modified and is different from the corresponding question in the official IChO Problems 2021 because of potential difficulty in marking by following the IChO marking regulation.

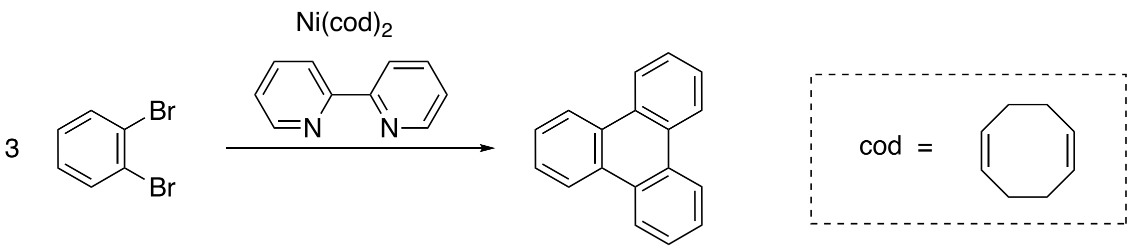
Multiple helicenes are molecules that contain two or more helicene-like structures. If its planar chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound **E** ($C_{46}H_{26}$) contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as (*P*, *P*, *P*) as shown below.

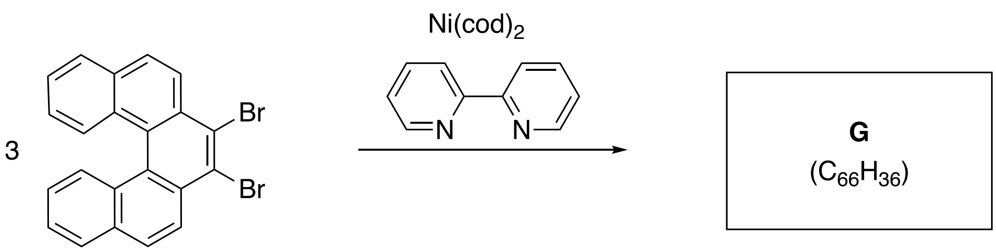


E



A.5 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to a racemic mixture of **F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. **<u>Draw</u>** all the possible stereoisomers of **G**. As a reference, one isomer should be drawn completely with the chirality defined as in the example above; The other isomers should be listed using *M* and *P*. For instance, the other stereoisomers of **E** can 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*).

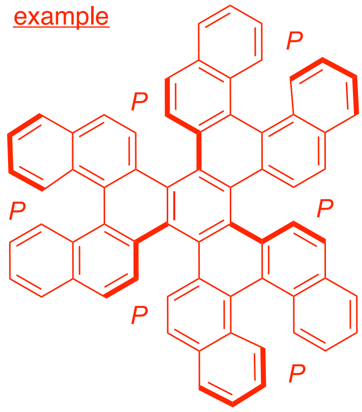




F

(①, ②, ③, ④, ⑤, ⑥)

example



(*P*, *P*, *P*, *P*, *P*, *P*)

First, consider all the possible isomers with respect to ①∼③.
Second, for each case, consider all the possible isomers with respect to ④∼⑥.
You then can list up all the possible cases.

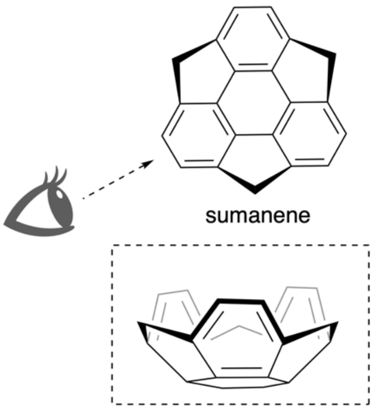
Carefully check the same compounds.
ent- means the enantiomer of each compound.

Finally, you find 10 diastereomers and 20 stereoisomers including enantiomers.

(①, ②, ③)	(①, ②, ③, ④, ⑤, ⑥)	compound
(*P*, *P*, *P*)	(*P*, *P*, *P*, *P*, *P*, *P*)	1
	(*P*, *P*, *P*, *M*, *P*, *P*)	2
	(*P*, *P*, *P*, *M*, *M*, *P*)	3
	(*P*, *P*, *P*, *M*, *M*, *M*)	4
(*M*, *P*, *P*)	(*M*, *P*, *P*, *P*, *P*, *P*)	5
	(*M*, *P*, *P*, *M*, *P*, *P*)	6
	(*M*, *P*, *P*, *P*, *M*, *P*)	6
	(*M*, *P*, *P*, *P*, *P*, *M*)	7
	(*M*, *P*, *P*, *M*, *M*, *P*)	8
	(*M*, *P*, *P*, *P*, *M*, *M*)	9
	(*M*, *P*, *P*, *M*, *P*, *M*)	9
	(*M*, *P*, *P*, *M*, *M*, *M*)	10
(*M*, *M*, *P*)	(*M*, *M*, *P*, *P*, *P*, *P*)	*ent*-10
	(*M*, *M*, *P*, *M*, *P*, *P*)	*ent*-9
	(*M*, *M*, *P*, *P*, *M*, *P*)	*ent*-8
	(*M*, *M*, *P*, *P*, *P*, *M*)	*ent*-9
	(*M*, *M*, *P*, *M*, *M*, *P*)	*ent*-6
	(*M*, *M*, *P*, *P*, *M*, *M*)	*ent*-6
	(*M*, *M*, *P*, *M*, *P*, *M*)	*ent*-7
	(*M*, *M*, *P*, *M*, *M*, *M*)	*ent*-5
(*M*, *M*, *M*)	(*M*, *M*, *M*, *P*, *P*, *P*)	*ent*-4
	(*M*, *M*, *M*, *M*, *P*, *P*)	*ent*-3
	(*M*, *M*, *M*, *M*, *M*, *P*)	*ent*-2
	(*M*, *M*, *M*, *M*, *M*, *M*)	*ent*-1

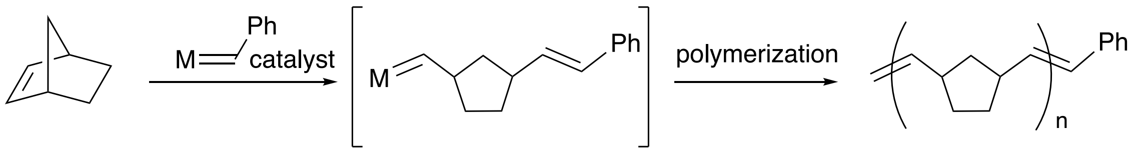
Part B

Sumanene is a hydrocarbon that was first reported in Japan in 2003. It was named after *Suman* that means sunflower in both Hindi and Sanskrit and has a bowl-shaped structure as shown below.



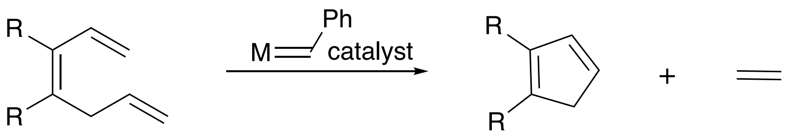
The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis. Representative metathesis reactions catalyzed by a ruthenium catalyst are shown below.

Ring-opening metathesis

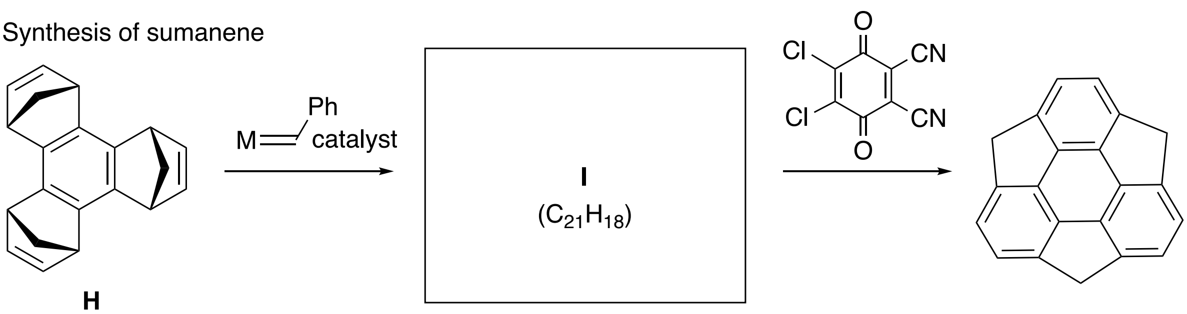


$M = RuCl_2[P(C_6H_{11})_3]_2$

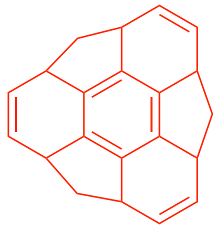
Ring-closing metathesis



Synthesis of sumanene

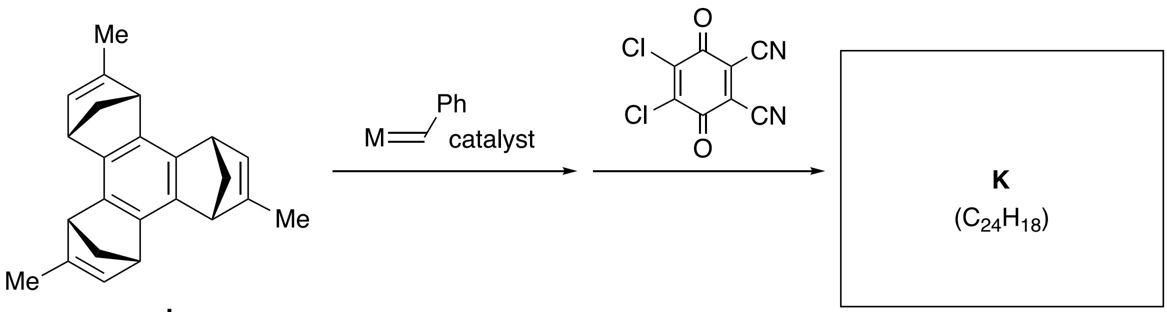


B.1 **Draw** the structure of intermediate **I** (its stereochemistry is not required).

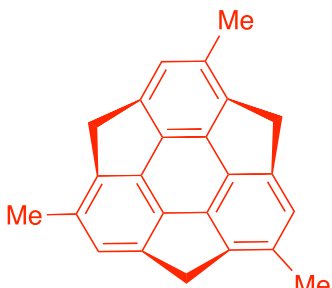


I

B.2 Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K** with retention of the stereochemistry. **Draw** the structure of **K** with the appropriate stereochemistry.



J



K

Further reading:

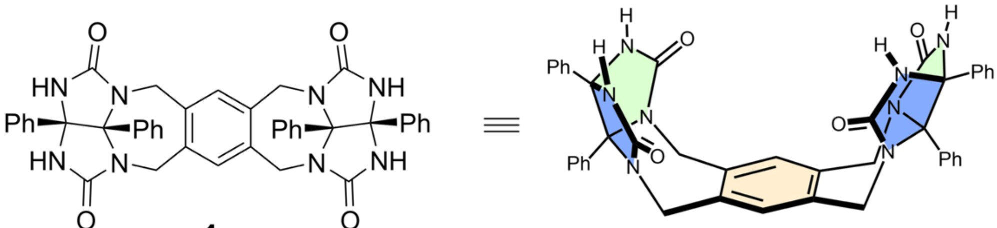
Hidehiro Sakurai, Taro, Daiko, Toshikazu Hirao, "A Synthesis of Sumanene, a Fullerene Fragment" *Science* **2003**, Vol. 301, Iss. 5641, 1878.

Question 9：Likes and Dislikes of Capsule

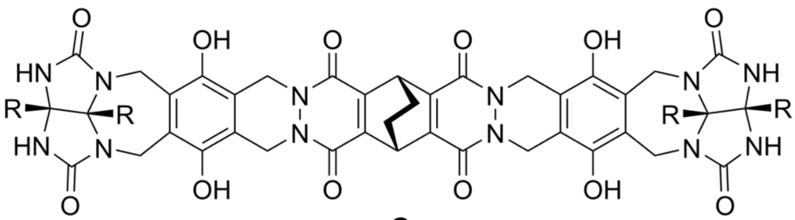
Part A

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

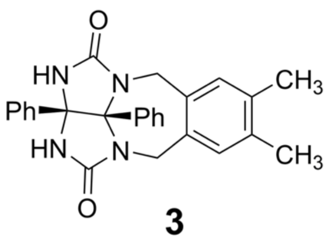
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

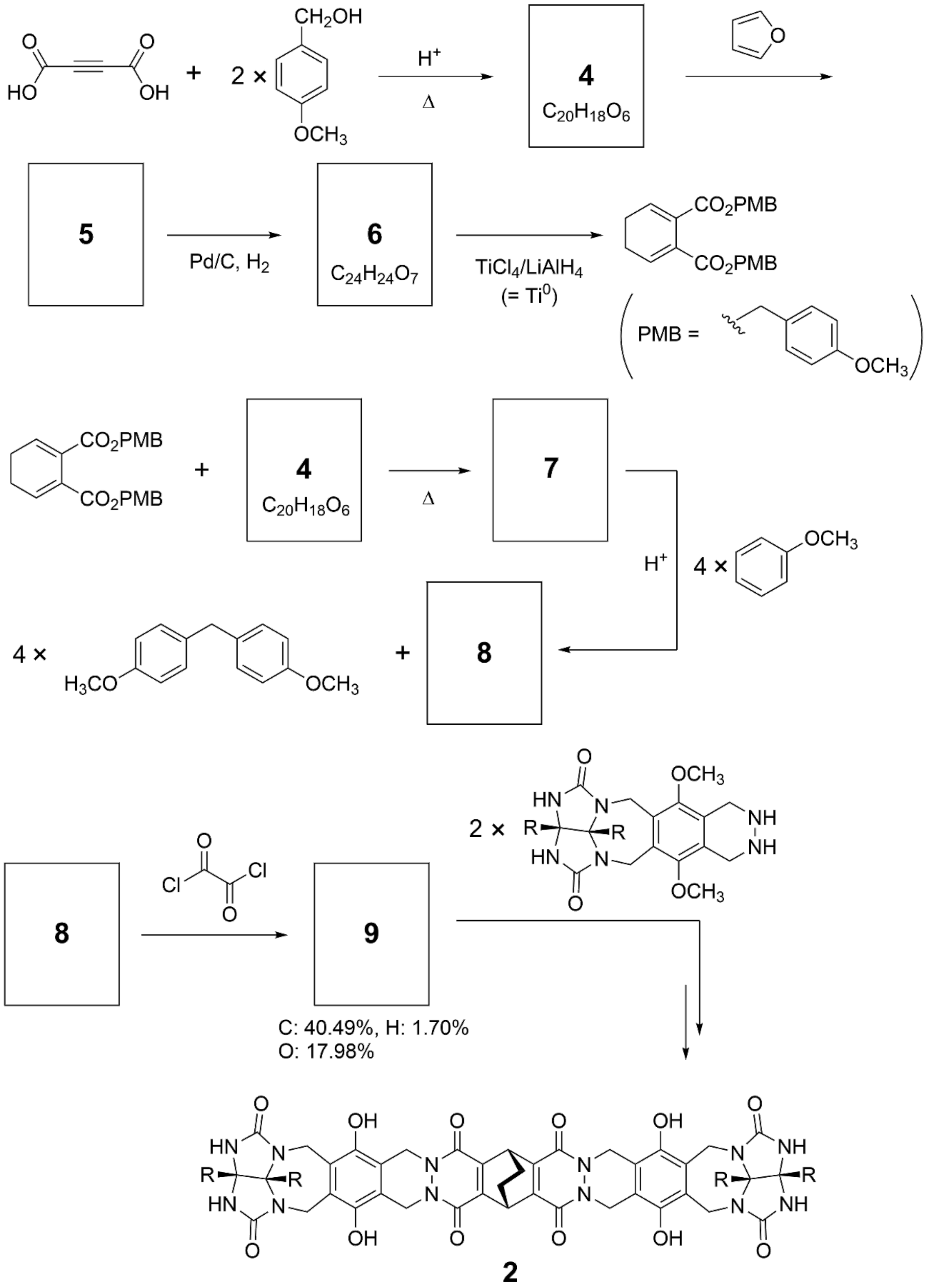


2

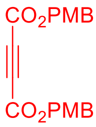
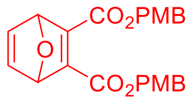
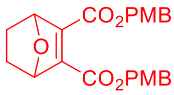
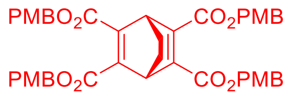
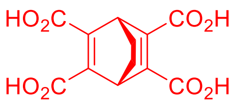
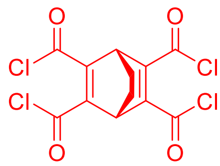


3

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

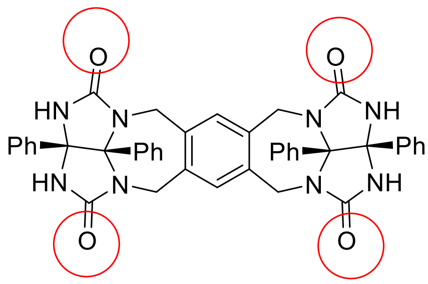


A.1 **Draw** the structures of **4**–**9**; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above.

4 	**5** 
6 	**7** 
8 	**9** 

In the mass spectrum of **1**, the ion peak corresponding to its dimer (**1**$_2$) was clearly observed, whereas an ion peak for **3**$_2$ was not observed in the spectrum of **3**. In the ^{1}H NMR spectra of a solution of **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**.



A.3 **Give** the number of the hydrogen bonds in the dimeric capsule (**1**$_2$).

8

The eight NH protons in **1**$_2$ are observed equally, thus the number of hydrogen bonds in **1**$_2$ are obviously 8.

The following questions **A.4** and **A.5** are not included in the official IChO Problems 2021 because of the IChO exam length regulation.

The dimeric capsule of compound **1** has an internal space and can encapsulate the appropriate small molecules. The ^{1}H NMR spectrum of methane and compound **1** (2.00×10^{-2} mmol) in C_6D_6 (1.00 mL) was measured. The assignment of characteristic signals and chemical shifts and integral values are shown below. Here, methane inside and outside the capsule was observed separately in the ^{1}H NMR analysis.

Attribution of protons	Chemical shifts (ppm)	integrals
(a) NH protons of the methane-encapsulated capsule	9.25	2.50
(b) NH protons of the empty capsule	9.20	1.76
(c) Protons of methane outside the capsule	0.23	3.20
(d) Protons of methane inside the capsule	–0.91	1.25

Under the above conditions, all compounds **1** form the dimeric capsule, and the volume of the solution does not change by adding **1** and methane.

A.4 **Determine** the concentrations of the methane inclusion capsule and the empty capsule, respectively.

The concentration of compound **1** is 2.00×10^{-2} mmol/1.00 mL, therefore, the sum of concentration of the empty and inclusion capsules is 1.00×10^{-2} mmol/1.00 mL. In the NMR analysis, the integration ratio of the empty capsule to the inclusion capsule is 1.76 to 2.50. Thus,

[inclusion capsule] = $1.00 \times 10^{-2} \times (2.50/(1.76 + 2.50)) = 0.587 \times 10^{-2}$ mol/L

[empty capsule] = $1.00 \times 10^{-2} \times (1.76/(1.76 + 2.50)) = 0.413 \times 10^{-2}$ mol/L

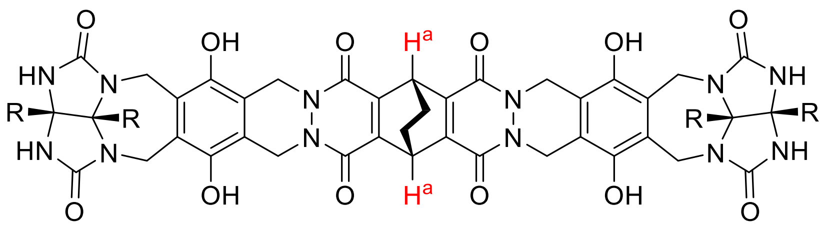
A.5 **Determine** the association constant (K_a) for methane and the dimeric capsule. Note that the association constant (K_a) for incorporated molecule Z and capsule $\mathbf{1}_2$ is given by equations 1 and 2.

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

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

In the NMR spectrum, the integral ratio of NH (8H) and internal methane (equivalent to 4H) is 2.5:1.25, indicating that methane incorporated into the capsule is a single molecule, i.e., a 1:1 complex is formed. Therefore, the concentration of the inclusion capsule and the concentration of methane inside the capsule are equal (0.587×10^{-2} mol/L), and the concentration of methane outside the capsule is $(3.20/1.25) \times 0.587 \times 10^{-2}$ mol/L = 1.50×10^{-2} mol/L from the corresponding integral ratio.
Therefore, the association constant K_a is calculated as follows:
$K_a = [0.587 \times 10^{-2}]/([0.413 \times 10^{-2}] \times [1.50 \times 10^{-2}]) = 94.8\ M^{-1}$

Compound **2** also forms a rigid and larger dimeric capsule (**2**$_2$). The ^{1}H NMR spectrum of **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. 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.



2

solvent	Chemical shifts (ppm)	integrals
(a) C_6D_6	4.60	2.10
(b) C_6D_5F	4.71	5.21
(c) mixed solvents of C_6D_6 and C_6D_5F	4.60, 4.71, 4.82	2.48

A.6 __**Determine**__ the number of C_6D_6 and C_6D_5F molecules encapsulated in **2**$_2$ giving each H^a signal.

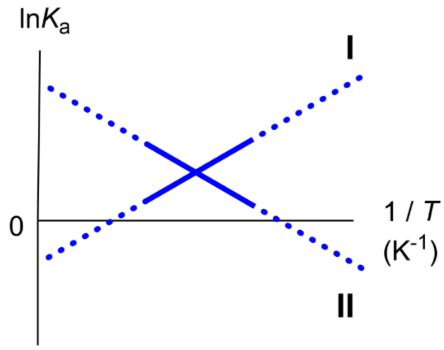
H^a	C_6D_6	C_6D_5F
4.60	(2) molecule(s)	(0) molecule(s)
4.71	(0) molecule(s)	(2) molecule(s)
4.82	(1) molecule(s)	(1) molecule(s)

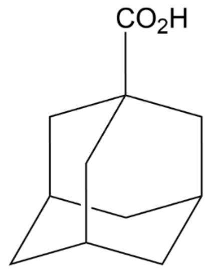
The observation of the third signal in the mixed solvent indicates that two solvent molecules are initially encapsulated in the capsule. Thus, the signal at 4.82 ppm is ascribed to a capsule containing one molecule of C_6D_6 and one molecule of C_6D_5F.

[1]H NMR measurements in C_6D_6 revealed that **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.

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

Similarly, the K_a values of CH_4 and **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

A.7 <u>**Choose**</u> the correct options in gaps (1)–(5) in the following paragraph from A and B.

No C_6D_6 molecule is encapsulated in **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	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	**1**$_2$ and CH_4	**2**$_2$ and AdA
(5)	**1**$_2$ and CH_4	**2**$_2$ and AdA

(1): A
(2): A
(3): A
(4): A
(5): B

Transforming $\Delta G = -RT\ln K_a = \Delta H - T\Delta S$ gives $\ln K_a = -\Delta H/R \times (1/T) + \Delta S/R$

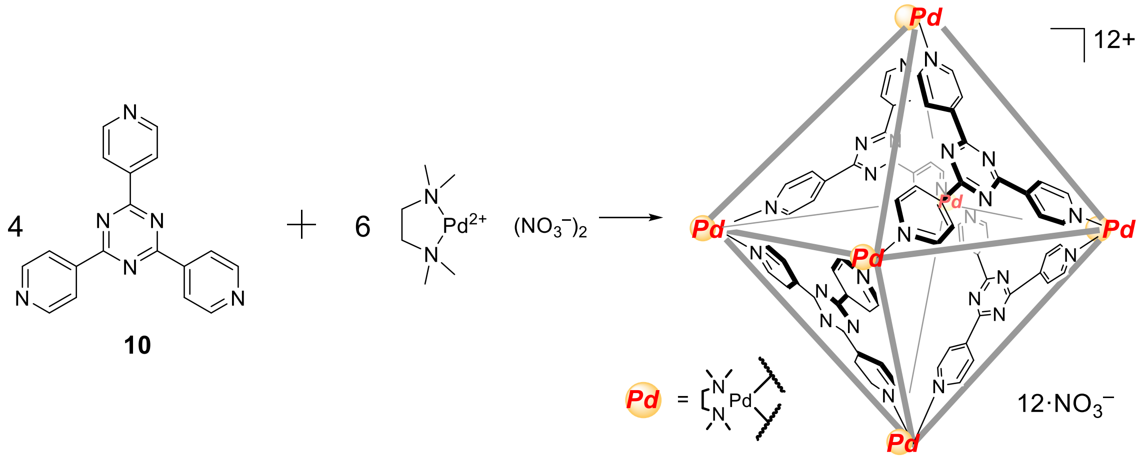
(If ΔH is negative, the slope is positive; if the y-intercept is negative, ΔS is negative.)

The relationship between **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 **1**$_2$ and CH_4. Therefore, the plot with a negative slope ($\Delta H > 0$) and positive y-intercept ($\Delta S > 0$) is **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.

The following **Part B** is not included in the official IChO Problems 2021 because of the IChO exam length regulation.

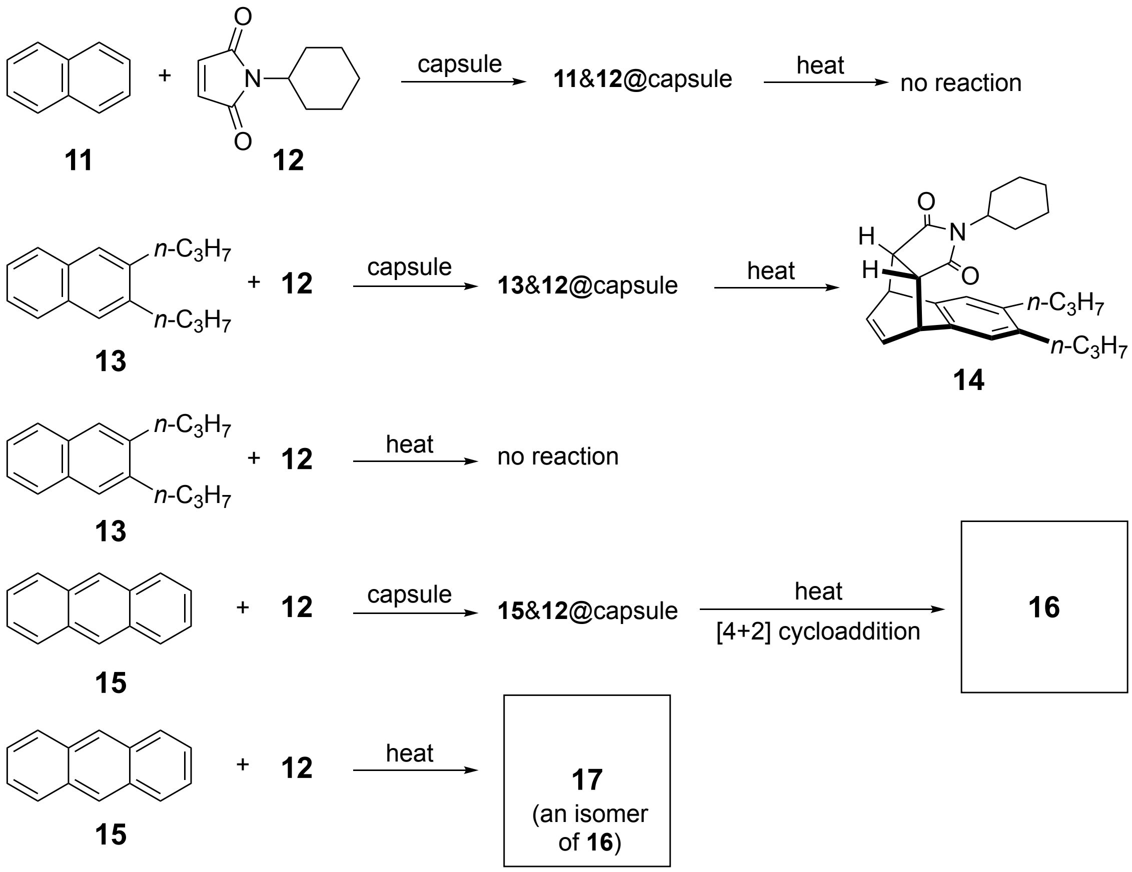
Part B

Four plate-shape molecules **10** quantitatively form an octahedral capsule with large internal space by coordination bonds with six palladium clips. This capsule can be used as a "small flask" for organic reactions.

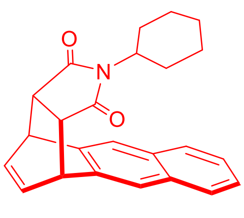
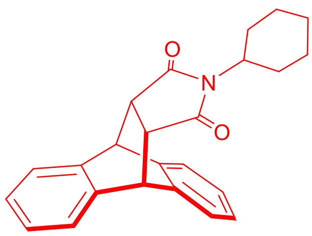


When compounds **11** and **12** were added to an aqueous solution of the octahedral capsule and the resulting mixture was stirred, one molecule of **11** and one molecule of **12** were incorporated into the octahedral capsule. However, no new compounds were observed when the solution was heated. Compounds **13** and **12** were also encapsulated into the capsule, and compound **14** was obtained upon heating of the solution. In the absence of the capsule, no reaction occurred even after heating. Compounds **15** and **12** were also encapsulated and were quantitatively converted, upon heating, to compound **16**, a product of the [4+2] cycloaddition reaction. Heating a solution of **15** and **12** in the absence of the capsule gave compound **17**, a structural isomer of **16**.

Note that the notation “**11**&**12**@capusule” indicates that compounds **11** and **12** are encapsulated in the capsule.



B.1 Compound **16** has stereoisomers, but the reaction in the capsule provided only **16**. Contrarily, there are no stereoisomers in compound **17**. Draw the structures of **16** and **17** with their stereochemistry clearly shown.

16	**17**
	

The results of the reactions of **12** with **11** and with **13** tell that the [4+2] cycloaddition reaction (a Diels-Alder reaction) does not proceed when the total volume of the encapsulated molecules is small enough to allow them to move within the capsule and that the reaction occurs when the encapsulation is so tight to fix the two molecules in close proximity then to induce this intrinsically slow dearomatizing bimolecular reaction. Notably, the cycloaddition reaction between **13** and **12** took place on the sterically more accessible benzene ring. The propyl side chains of **13** and the cyclohexyl group of **12** are oriented in the same direction, which would originate from the tightest packing of the two molecules **13** and **12** in the capsule and led to the selective formation of **14**.
The reaction between **15** and **12** in the capsule should follow the rules above and proceeded from tight encapsulation to form **16**. The formation of compound **17** is a well-known reaction, which occurs at the 9 and 10 positions of anthracene to allow two benzene rings to remain. Products **16** and **17** are identifiable by considering the information about stereoisomerism of each product.

Further reading:

Makoto Fujita, *et al.,* "Naphthalene Diels–Alder in a Self-Assembled Molecular Flask" *Journal of the American Chemical Society* **2010**, Vol. 132, Iss. 9, 2866–2867.

Makoto Fujita, *et al.,* "Functional Molecular Flasks: New Properties and Reactions within Discrete, Self-Assembled Hosts" *Angewandte Chemie International Edition* **2009**, Vol. 48, Iss. 19, 3418–3438.