General instructions

Cover sheet

Please return this cover sheet together with all the related question sheets.
International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July - 2nd August, 2021
https://www.icho2021.org
General Instruction

• You are allowed to use only pen to write the answer.
• Your calculator must be non-programmable.
• This examination has 9 problems.
• You can solve the problems in any order.
• You will have 5 hours to solve all problems.
• You can begin working only after the START command is given.
• All results must be written in the appropriate answer boxes with pen on the answer sheets. Use the back of the question sheets if you need scratch paper. Remember that answers written outside the answer boxes will not be graded.
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GOOD LUCK!

Problems and Grading Information

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## Physical Constants and Equations

### Constants

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<td>( F = N_A \times e = 9.64853321233100184 \times 10^4 \text{ C mol}^{-1} )</td>
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<td>Gas constant</td>
<td>( R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1} )</td>
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<td>The base of the natural logarithm (Euler’s number)</td>
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## Equations

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| **The ideal gas law** | \( PV = nRT \)  
  where \( P \) is the pressure, \( V \) is the volume, \( n \) is the amount of substance, \( T \) is the absolute temperature of ideal gas. |
| **Coulomb's law** | \( F = k_e \frac{q_1 q_2}{r^2} \)  
  where \( F \) is the electrostatic force, \( k_e \simeq 9.0 \times 10^9 \text{ N m}^{-2}\text{C}^{-2} \) is Coulomb's constant, \( q_1 \) and \( q_2 \) are the magnitudes of the charges, and \( r \) is the distance between the charges. |
| **The first law of thermodynamics** | \( \Delta U = q + w \)  
  where \( \Delta U \) is the change in the internal energy, \( q \) is the heat supplied, \( w \) is the work done. |
| **Enthalpy** | \( H = U + PV \) |
| **Entropy based on Boltzmann's principle** | \( S = k_B \ln W \)  
  where \( W \) is the number of microstates. |
| **The change of entropy** | \( \Delta S = \frac{\Delta q_{\text{rev}}}{T} \)  
  where \( \Delta q_{\text{rev}} \) is the heat for the reversible process. |
| **Gibbs free energy** | \( G = H - TS \)  
  \( \Delta_r G^\circ = -RT \ln K = -zFE^\circ \)  
  where \( K \) is the equilibrium constant, \( z \) is the number of electrons, \( E^\circ \) is the standard electrode potential. |
| **Reaction quotient** | \( \Delta_r G = \Delta_r G^\circ + RT \ln Q \)  
  For a reaction  
  \( aA + bB \rightleftharpoons cC + dD \)  
  \( Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \)  
  where \([A]\) is the concentration of \( A \). |
<table>
<thead>
<tr>
<th>Heat change $\Delta q$</th>
<th>$\Delta q = n c_m \Delta T$, where $c_m$ is the temperature-independent molar heat capacity.</th>
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<tr>
<td>Nernst equation for redox reaction</td>
<td>$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$, where $C_{\text{ox}}$ is the concentration of oxidized substance, $C_{\text{red}}$ is the concentration of reduced substance.</td>
</tr>
<tr>
<td>Arrhenius equation</td>
<td>$k = A \exp \left( -\frac{E_a}{RT} \right)$, where $k$ is the rate constant, $A$ is the pre-exponential factor, $E_a$ is the activation energy.</td>
</tr>
<tr>
<td>Lambert–Beer equation</td>
<td>$A = \varepsilon l c$, where $A$ is the absorbance, $\varepsilon$ is the molar absorption coefficient, $l$ is the optical path length, $c$ is the concentration of the solution.</td>
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<td>Henderson–Hasselbalch equation</td>
<td>For an equilibrium $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, where equilibrium constant is $K_a$, $\text{pH} = pK_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$</td>
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<td>Energy of a photon</td>
<td>$E = h \nu = \frac{h \lambda}{\nu}$, where $\nu$ is the frequency, $\lambda$ is the wavelength of the light.</td>
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<td>The sum of a geometric series</td>
<td>When $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$</td>
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<tr>
<td>Approximation equation that can be used to solve problems</td>
<td>When $x \ll 1$, $\frac{1}{1 - x} \approx 1 + x$</td>
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$\Delta \delta$ for one alkyl group-substitution: ca. +0.4 ppm
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<td>( \Delta_r G = \Delta_r G^\circ + RT \ln Q )</td>
<td>Reaction quotient ( Q )</td>
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For a reaction \( aA + bB \rightleftharpoons cC + dD \)

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</tr>
<tr>
<td>( [B]^b )</td>
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</tr>
<tr>
<td>( [C]^c )</td>
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<tr>
<td>( [D]^d )</td>
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, where \([A]\) is the concentration of A.
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<td>For an equilibrium ( HA \rightleftharpoons H^+ + A^- )</td>
<td>Henderson-Hasselbalch equation</td>
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<td>[ \text{pH} = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) ]</td>
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<td>[ E = h \nu = \frac{h}{\lambda} ]</td>
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<td>[ 1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1-x} ]</td>
<td>The sum of a geometric series when ( x \neq 1 )</td>
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</tr>
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<td>103</td>
<td>Lr</td>
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</tbody>
</table>

**Key:**
- **Symbol:** atomic number
- **Name:** atomic weight (in parenthesis for the radioactive element)
$\Delta \delta$ for one alkyl group-substitution: \textit{ca.} +0.4 ppm
Please return this cover sheet together with all the related question sheets.
Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

**Part A**

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, \( \text{H}_2(g) \rightarrow 2\text{H}(\text{ad}) \), where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (H\(_2\)) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of H\(_2\) is represented by two variables: the interatomic distance, \( d \), and the height relative to the surface metal atom, \( z \). It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the potential energy in units of kJ per mole of H\(_2\). The solid line spacing is 20 kJ mol\(^{-1}\), the dashed line spacing is 100 kJ mol\(^{-1}\), and the spacing between solid and dashed lines is 80 kJ mol\(^{-1}\). The zero-point vibration energy is ignored.
Fig.1 Definition of variables. Drawing is not in scale.

Fig.2
A.1 For each of the following items (i)–(iii), select the closest value from A–G. 6pt
(i) The interatomic distance for a gaseous H₂ 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)

<table>
<thead>
<tr>
<th></th>
<th>A. 0.03 nm</th>
<th>B. 0.07 nm</th>
<th>C. 0.11 nm</th>
<th>D. 0.15 nm</th>
<th>E. 0.19 nm</th>
<th>F. 0.23 nm</th>
<th>G. 0.27 nm</th>
</tr>
</thead>
</table>

A.2 For each of the following items (i)–(ii), select the closest value from A–H. 4pt
(i) the energy required for the dissociation of gaseous H₂ to gaseous H
[H₂(g) → 2H(g)]
(ii) the energy released during the adsorption of a gaseous H₂ [H₂(g) → 2H(ad)]

<table>
<thead>
<tr>
<th></th>
<th>A. 20 kJ mol⁻¹</th>
<th>B. 40 kJ mol⁻¹</th>
<th>C. 60 kJ mol⁻¹</th>
<th>D. 100 kJ mol⁻¹</th>
<th>E. 150 kJ mol⁻¹</th>
<th>F. 200 kJ mol⁻¹</th>
<th>G. 300 kJ mol⁻¹</th>
<th>H. 400 kJ mol⁻¹</th>
</tr>
</thead>
</table>
**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.

\[ \frac{k_1}{k_2} H_2(g) \xrightarrow{\text{H(ad)}} 2H(\text{ad}) \quad (1a) \]

\[ k_3 \xrightarrow{\text{H(ad)}} H(\text{ab}) \quad (1b) \]

The reaction rates per surface 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:

\[ r_1 = k_1 P_{H_2} (1 - \theta)^2 \quad (2) \]

\[ r_2 = k_2 \theta^2 \quad (3) \]

\[ r_3 = k_3 \theta \quad (4) \]

where \( k_1 [s^{-1} \text{Pa}^{-1}] \), \( k_2 [s^{-1}] \) and \( k_3 [s^{-1}] \) are the reaction rate constants and \( P_{H_2} \) is the pressure of \( H_2 \).

Among the sites available on the surface, \( \theta (0 \leq \theta \leq 1) \) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption (\( r_1, r_2 \gg r_3 \)) and that \( \theta \) remains constant.

**B.1** \( r_3 \) can be expressed as:

\[ r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{H_2} C}}} \quad (5) \]

Express \( C \) using \( k_1 \) and \( k_2 \).
A metal sample with a surface area of $S = 1.0 \times 10^{-3} \text{ m}^2$ was placed in a container ($1\text{ L} = 1.0 \times 10^{-3} \text{ m}^3$) with $\text{H}_2$ ($P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18} \text{ m}^{-2}$. The surface temperature was kept at $T = 400\text{ K}$. As the reaction (1) proceeded, $P_{\text{H}_2}$ decreased at a constant rate of $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$. Assume that $\text{H}_2$ is an ideal gas and that the volume of the metal sample is negligible.

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

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

**B.4** At a different $T$, $C = 2.5 \times 10^3 \text{ Pa}^{-1}$ and $k_3 = 4.8 \times 10^{-2} \text{ s}^{-1}$ are given. For $r_3$ as a function of $P_{\text{H}_2}$ at this temperature, select the correct plot from (a)–(h). 3pt
Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

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, \( \text{H}_2(g) \rightarrow 2\text{H}(\text{ad}) \), where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (\( \text{H}_2 \)) that reach the metal surface (\( \text{M} \)) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of \( \text{H}_2 \) 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 \( \text{kJ} \) per mole of \( \text{H}_2 \). 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 Part

I would like to sum up what we have covered. Let us first consider the adsorption process of hydrogen at the metal surface, \( \text{H}_2(g) \rightarrow 2\text{H}(\text{ad}) \), where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (\( \text{H}_2 \)) that reach the metal surface (\( \text{M} \)) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of \( \text{H}_2 \) 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 \( \text{kJ} \) per mole of \( \text{H}_2 \). 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.
مكن (\(z\)) الارتفاع بالنسبة لسطح المعدن (2). يمكن افتراض أن المحور المار بذرتي الهيدروجين موازي للسطح، وأن مركز الثقل يقع دائماً على المحور العمودي المنقط (contour) الطاقة الكامنة لعملية التفكك على السطح، الأرقام الموضحة في الشكل 1. في شكل 2 يظهر مخطط المحور العمودي المنقط يظهر 20 كمول هيدروجين. تباعد الخطوط المنقطة يمثل 100 كمول-1. تم إزالات الطاقة الابرازية للنقطة نصفية (zero-point vibration energy).

شكل 1. تعريف المتغيرات. الرسم ليس للقياس.
For each of the following items (i)-(iii), select the closest value from A-G.

(i) The interatomic distance for a gaseous $\text{H}_2$ 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
For each of the following items (i)–(ii), select the closest value from A–H.

(i) the energy required for the dissociation of gaseous $\text{H}_2$ to gaseous $\text{H} (\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g}))$

(ii) the energy released during the adsorption of a gaseous $\text{H}_2 (\text{H}_2(\text{g}) \rightarrow 2\text{H(\text{ad})})$

<table>
<thead>
<tr>
<th></th>
<th>D. 100 kJ mol$^{-1}$</th>
<th>C. 60 kJ mol$^{-1}$</th>
<th>B. 40 kJ mol$^{-1}$</th>
<th>A. 20 kJ mol$^{-1}$</th>
<th>H. 400 kJ mol$^{-1}$</th>
<th>G. 300 kJ mol$^{-1}$</th>
<th>F. 200 kJ mol$^{-1}$</th>
<th>E. 150 kJ mol$^{-1}$</th>
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</table>
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.

\[ \text{H}_2(g) \rightleftharpoons \frac{k_1}{k_2} 2\text{H(ad)} \]  

(1a)

\[ \text{H(ad)} \rightarrow \text{H(ab)} \]  

(1b)

The reaction rates per surface 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:

\[ r_1 = k_1 P_{H_2} (1 - \theta)^2 \]  

(2)

\[ r_2 = k_2 \theta^2 \]  

(3)

\[ r_3 = k_3 \theta \]  

(4)

where \( k_1 \) \([s^{-1} Pa^{-1}]\), \( k_2 \) \([s^{-1}]\) and \( k_3 \) \([s^{-1}]\) are the reaction rate constants and \( P_{H_2} \) is the pressure of \( H_2 \).

Among the sites available on the surface, \( \theta \) (0 \( \leq \theta \leq 1 \)) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption \( (r_1, r_2 \gg r_3) \) and that \( \theta \) remains constant.

حيث [\( k_1 \) \([s^{-1} Pa^{-1}]\), \( k_2 \) \([s^{-1}]\) and \( k_3 \) \([s^{-1}]\)] عبارة عن ثوابت سرعة التفاعلات، و \( P_{H_2} \) عبارة عن ضغط الهيدروجين، ومن بين المواقع المتاحة على السطح، يمثل \( \theta \) (0 \( \leq \theta \leq 1 \)) نسبة المشغولة بذرات الهيدروجين. يُمكن افتراض أن سرعة احتمال التفاعل والانفصال الجسيمات من المعدن (desorption) يُمثل كثيرة بالنسبة لعملية الامتصاص إلى داخل المادة (adsorption) وان يبقى ثابتة. (\( r_1, r_2 \gg r_3 \))
$r_3$ can be expressed as:

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

Express $C$ using $k_1$ and $k_2$. 

$C = k_2 g k_1$ باستخدام $C$
A metal sample with a surface area of \( S = 1.0 \times 10^{-3} \, \text{m}^2 \) was placed in a container (1L = 1.0 \times 10^{-3} \, \text{m}^3) with \( \text{H}_2 \) \( (P_{\text{H}_2} = 1.0 \times 10^2 \, \text{Pa}) \). The density of hydrogen-atom adsorption sites on the surface was \( N = 1.3 \times 10^{18} \, \text{m}^{-2} \). The surface temperature was kept at \( T = 400 \, \text{K} \). As the reaction (1) proceeded, \( P_{\text{H}_2} \) decreased at a constant rate of \( v = 4.0 \times 10^{-4} \, \text{Pa} \, \text{s}^{-1} \). Assume that \( \text{H}_2 \) is an ideal gas and that the volume of the metal sample is negligible.

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

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

At a different \( T \), \( C = 2.5 \times 10^3 \, \text{Pa}^{-1} \) and \( k_3 = 4.8 \times 10^{-2} \, \text{s}^{-1} \) are given. For \( r_3 \) as a function of \( P_{\text{H}_2} \) at this temperature, select the correct plot from (a)-(h).
Hydrogen at a Metal Surface

Part A

A.1 (6 pt)

(i)  (ii)  (iii)

A.2 (4 pt)

(i)  (ii)
Part B

B.1 (5 pt)

\[ C = \]  

B.2 (3 pt)

\[ A = \text{mol s}^{-1} \text{m}^{-2} \]
<table>
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<td>$k_3 = \frac{\text{ }}{\text{s}^{-1}}$</td>
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<table>
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<th>B.4 (3 pt)</th>
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ICHo
Problem 2
Cover sheet

Please return this cover sheet together with all the related question sheets.
Molecular entities that differ only in isotopic composition, such as \( \text{CH}_4 \) and \( \text{CH}_3\text{D} \), are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

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

Let us consider the following equilibrium:

\[
\text{^{12}\text{C}^{16}\text{O}_2} + \text{^{12}\text{C}^{18}\text{O}_2} \rightleftharpoons 2\text{^{12}\text{C}^{16}\text{O}^{18}\text{O}} \quad K = \frac{[\text{^{12}\text{C}^{16}\text{O}^{18}\text{O}}]^2}{[\text{^{12}\text{C}^{16}\text{O}_2}[\text{^{12}\text{C}^{18}\text{O}_2]}]}
\] 

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

\[
S = k_B \ln W
\]

\( W = 1 \) for \( \text{^{12}\text{C}^{16}\text{O}_2} \) and \( \text{^{12}\text{C}^{18}\text{O}_2} \). In contrast, \( W = 2 \) for a \( \text{^{12}\text{C}^{16}\text{O}^{18}\text{O}} \) molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two \( \text{^{12}\text{C}^{16}\text{O}^{18}\text{O}} \) molecules, \( W = 2^2 = 4 \).
A.1 The enthalpy change, $\Delta H$, of eq. 3 is positive regardless of the temperature.

$$\text{H}_2 + \text{D} + \text{I} \rightleftharpoons \text{HD} + \text{HI} \quad (3)$$

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

The $\Delta H$ of the following process can be explained by molecular vibrations.

$$2\text{HD} \rightleftharpoons \text{H}_2 + \text{D}_2 \quad K = \frac{[\text{H}_2][\text{D}_2]}{[\text{HD}]^2} \quad (4)$$

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

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

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

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

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

A.2 The vibration of $\text{H}_2$ is at 4161.0 $\text{cm}^{-1}$ when reported as a wavenumber. **Calculate** the $\Delta H$ of the following equation at $T = 0\, \text{K}$ in units of $\text{J} \, \text{mol}^{-1}$.

$$2\text{HD} \rightarrow \text{H}_2 + \text{D}_2 \quad (8)$$

Assume that:
- only the vibrational energy contributes to the $\Delta H$.
- the $k$ values for $\text{H}_2$, HD, and $\text{D}_2$ are identical.
- the mass of H to be 1 Da and the mass of D to be 2 Da.
The molar ratio of $H_2$, $HD$, and $D_2$ depends on the temperature in a system in equilibrium. Here, $\Delta_{D_2}$ is defined as the change of the molar ratio of $D_2$.

$$\Delta_{D_2} = \frac{R_{D_2}}{R_{D_2}^*} - 1$$

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

### A.3 Calculate $\Delta_{D_2}$ with natural D abundance when the isotopic exchange is in equilibrium at the temperature where $K$ in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are $1.5576 \times 10^{-4}$ and $1 - 1.5576 \times 10^{-4}$, respectively.
In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO₂ molecules with molecular weights of 44 and 47, which are described as \( \text{CO}_2[44] \) and \( \text{CO}_2[47] \) below. The quantity \( \Delta_{47} \) is defined as:

\[
\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1
\]  

(10)

\( R_{47} \) refers to \( \frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]} \) in the sample and \( R_{47}^* \) to \( \frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]} \) at \( T \to +\infty \). The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

<table>
<thead>
<tr>
<th></th>
<th>( ^{12}\text{C} )</th>
<th>( ^{13}\text{C} )</th>
</tr>
</thead>
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<tr>
<td>natural abundance</td>
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<td>0.011112</td>
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<table>
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<tr>
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<th>( ^{17}\text{O} )</th>
<th>( ^{18}\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural abundance</td>
<td>0.997621</td>
<td>0.0003790</td>
<td>0.0020000</td>
</tr>
</tbody>
</table>

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

\[
\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4}
\]  

(11)

A.4 The \( R_{47} \) of fossil plankton obtained from the Antarctic seabed was \( 4.50865 \times 10^{-5} \). 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 \( \text{CO}_2[47] \) for the calculation.
Molecular entities that differ only in isotopic composition, such as CH₄ and CH₃D, are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

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

Let us consider the following equilibrium:

\[ ^{12}\text{C}^{16}\text{O}_2 + ^{12}\text{C}^{18}\text{O}_2 \rightleftharpoons 2^{12}\text{C}^{16}\text{O}^{18}\text{O} \]

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

\[ K = \frac{[^{12}\text{C}^{16}\text{O}^{18}\text{O}]^2}{[^{12}\text{C}^{16}\text{O}_2][^{12}\text{C}^{18}\text{O}_2]} \]

(1)
The enthalpy change, $\Delta H$, of eq. 3 is positive regardless of the temperature.

\[
\text{Calculate the equilibrium constants, } K, \text{ for eq. 3 at very low (think of } T \rightarrow 0) \text{ and very high (think of } T \rightarrow +\infty) \text{ temperatures. Assume that the reaction remains unchanged at these temperatures and that } \Delta H \text{ converges to a constant value for high temperatures.}
\]

The $\Delta H$ of the following process can be explained by molecular vibrations.

\[
2\text{HD} \rightleftharpoons H_2 + D_2 \quad K = \frac{|H_2||D_2|}{|HD|^2}
\]

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

\[
E = \frac{1}{2} h \nu
\]

Wherein $k$ is the force constant and $\mu$ 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:

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]
The vibration of $\text{H}_2$ is at 4161.0 cm$^{-1}$ when reported as a wavenumber. Calculate the $\Delta H$ of the following equation at $T = 0$ K in units of J mol$^{-1}$.

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

Assume that:

- only the vibrational energy contributes to the $\Delta H$
- the $k$ values for $\text{H}_2$, HD, and $\text{D}_2$ are identical
- the mass of H to be 1 Da and the mass of D to be 2 Da

A.2

$$\Delta H = \frac{m_1 m_2}{m_1 + m_2}$$

(7)
The molar ratio of H₂, HD, and D₂ depends on the temperature in a system in equilibrium. Here, ΔD₂ is defined as the change of the molar ratio of D₂.

\[ \Delta D_2 = \frac{R_{D_2}}{R_{D_2}^*} - 1 \]  

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

\[ \text{Calculate} \Delta D_2 \text{ with natural D abundance when the isotopic exchange is in equilibrium at the temperature where } K \text{ in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are } 1.5576 \times 10^{-4} \text{ and } 1 - 1.5576 \times 10^{-4}, \text{ respectively.} \]
In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO$_2$ molecules with molecular weights of 44 and 47, which are described as CO$_2^{[44]}$ and CO$_2^{[47]}$ below. The quantity $\Delta_{47}$ is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{44}} - 1$$

(10)

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

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C</td>
<td>0.011112</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>0.988888</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{18}$O</td>
<td>0.0020000</td>
</tr>
<tr>
<td>$^{17}$O</td>
<td>0.0003790</td>
</tr>
<tr>
<td>$^{16}$O</td>
<td>0.997621</td>
</tr>
</tbody>
</table>

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

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

(11)

The $R_{47}$ of fossil plankton obtained from the Antarctic seabed was $4.50865 \times 10^{-5}$. 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.

$\Delta_{47}$ قيمته للفاك أحفوري مأخوذ من قاع البيئ في القطب الجنوبي كانت $4.50865 \times 10^{-5}$. $R_{47}$ فذر درجة الحرارة باستخدام قيمة $R_{47}$. تفسير درجة الحرارة هذه بأنها درجة حرارة الهواء خلال العصر الذي عاش فيه العاقل. استخدم فقط النظر الأكثر شيوعاً لـ $[47]$ في CO$_2^{[47]}$ في حساباتك.
Isotope Time Capsule

A.1 (8 pt)

\[ T \to 0 : K = \ldots \ldots , \ T \to +\infty : K = \ldots \ldots \]
A.2 (8 pt)

\[ \Delta H = \text{ } \text{ } \text{J mol}^{-1} \]
Δ\textsubscript{D\textsubscript{2}} =
$T = \text{K}$
IChO
Problem 3
Cover sheet

Please return this cover sheet together with all the related question sheets.
Lambert–Beer Law?

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>B.1</th>
<th>B.2</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>22</td>
</tr>
</tbody>
</table>

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

**Part A**

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

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

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

A.1 The absorbance of X was $A_1$ at a wavelength of $\lambda_1$. Then, solution X was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still $A_1$ at $\lambda_1$. **Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where $\varepsilon_{HA}$ and $\varepsilon_{A^-}$ represent the absorption coefficients of HA and of A⁻, respectively, at $\lambda_1$. 

10pt
Part B
Let us consider the following equilibrium in the gas phase.

$$D \rightleftharpoons 2M$$

(Part 2)

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

Use the following definitions if necessary.

<table>
<thead>
<tr>
<th></th>
<th>Initial state</th>
<th>After equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td>$M$</td>
</tr>
<tr>
<td>Partial pressure</td>
<td>$P$</td>
<td>0</td>
</tr>
<tr>
<td>Amount in moles</td>
<td>$n_0$</td>
<td>0</td>
</tr>
<tr>
<td>Volume</td>
<td>$V_0$</td>
<td>$V$</td>
</tr>
</tbody>
</table>

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

**B.2** The absorbance of the gas at $\lambda_{B2}$ measured from direction $y$ was $A_{B2}$ both at the initial state ($l = l_y$) and after the equilibrium ($l = l_y$). **Determine** the ratio $\varepsilon_D/\varepsilon_M$ at $\lambda_{B2}$. 
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.

A Part

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

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

The absorbance of X was \(A_1\) at a wavelength of \(\lambda_1\). Then, solution X was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still \(A_1\) at \(\lambda_1\), Determine the ratio \(\varepsilon_{HA}/\varepsilon_{A^-}\), where \(\varepsilon_{HA}\) and \(\varepsilon_{A^-}\) represent the absorption coefficients of HA and of \(A^-\), respectively, at \(\lambda_1\).

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

10pt

The absorbance of X was \(A_1\) at a wavelength of \(\lambda_1\). Then, solution X was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still \(A_1\) at \(\lambda_1\), Determine the ratio \(\varepsilon_{HA}/\varepsilon_{A^-}\), where \(\varepsilon_{HA}\) and \(\varepsilon_{A^-}\) represent the absorption coefficients of HA and of \(A^-\), respectively, at \(\lambda_1\).

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

10pt

The absorbance of X was \(A_1\) at a wavelength of \(\lambda_1\). Then, solution X was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still \(A_1\) at \(\lambda_1\), Determine the ratio \(\varepsilon_{HA}/\varepsilon_{A^-}\), where \(\varepsilon_{HA}\) and \(\varepsilon_{A^-}\) represent the absorption coefficients of HA and of \(A^-\), respectively, at \(\lambda_1\).
Let us consider the following equilibrium in the gas phase.

\[
\text{D} \rightleftharpoons 2\text{M} \quad (2)
\]

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

Use the following definitions if necessary.

<table>
<thead>
<tr>
<th>After equilibrium</th>
<th>Initial state</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)</td>
<td>(D)</td>
</tr>
<tr>
<td>(P_M)</td>
<td>(P_D)</td>
</tr>
<tr>
<td>(n_M)</td>
<td>(n_D)</td>
</tr>
<tr>
<td>(V)</td>
<td>(V_0)</td>
</tr>
</tbody>
</table>

\(P\) is the partial pressure, \(n\) is the amount in moles, and \(V\) is the volume. Assume that all components of the gas mixture behave as ideal gases.

The absorbance of the gas at \(\lambda_{B1}\) measured from direction \(x\) \((l = l_x)\) was \(A_{B1}\) both at the initial state and after the equilibrium. **Determine** the ratio \(\varepsilon_D/\varepsilon_M\) at \(\lambda_{B1}\), where \(\varepsilon_D\) and \(\varepsilon_M\) represent the absorption coefficients of D and of M, respectively.
The absorbance of the gas at $\lambda_{B2}$ measured from direction $y$ was $A_{B2}$ both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). Determine the ratio $\varepsilon_D/\varepsilon_M$ at $\lambda_{B2}$.
Lambert–Beer Law?

Part A

A.1  (10 pt)
A.1 (cont.)

\[ \frac{\varepsilon_{HA}}{\varepsilon_{A^-}} = \]
\[ \frac{\varepsilon_D}{\varepsilon_M} = \]
\[ \frac{\varepsilon_D}{\varepsilon_M} = \]
Please return this cover sheet together with all the related question sheets.
The 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 $\text{Zn(OH)}_2(s)$ at $25^\circ \text{C}$ and the relevant equilibrium constants are given in eq. 1-4.

\[
\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \quad K_{sp} = 1.74 \times 10^{-17} \quad (1)
\]

\[
\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn(OH)}_2(aq) \quad K_1 = 2.62 \times 10^{-6} \quad (2)
\]

\[
\text{Zn(OH)}_2(s) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn(OH)}_4^{2-}(aq) \quad K_2 = 6.47 \times 10^{-2} \quad (3)
\]

\[
\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad K_w = 1.00 \times 10^{-14} \quad (4)
\]
The solubility, $S$, of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

$$S = [Zn^{2+}(aq)] + [Zn(OH)_2(aq)] + [Zn(OH)_{4}^{2-}(aq)]$$  \hspace{1cm} (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 $[Zn(OH)_{4}^{2-}(aq)]$. \hspace{1cm} 6pt

**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. \hspace{1cm} 5pt

**Part B**

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

$$Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(l)$$  \hspace{1cm} (6)

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

$$ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g)$$  \hspace{1cm} (7)

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

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

$$Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s) \hspace{1cm} E^\circ = 1.65$ V $$  \hspace{1cm} (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. \hspace{1cm} 3pt
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 $-38 \degree C$ (February) and 3776 m, respectively. The atmospheric pressure is represented by

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

(9)

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

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

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

(10)

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

(11)
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.

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

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

\[
\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn(OH)}_2(aq) \quad K_1 = 2.62 \times 10^{-6} \tag{2}
\]

\[
\text{Zn(OH)}_2(s) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn(OH)}^2_4(aq) \quad K_2 = 6.47 \times 10^{-2} \tag{3}
\]
IChO

SAU-4 C-4 Q-2

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

\begin{equation}
S = [\text{Zn}^{2+}(\text{aq})] + [\text{Zn(OH)}_2(\text{aq})] + [\text{Zn(OH)}_4^{2-}(\text{aq})]
\end{equation}

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

A.1

A saturated aqueous solution of $\text{Zn(OH)}_2(s)$ 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.

A.2

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

\begin{equation}
\text{Zn(OH)}_2(s) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)}
\end{equation}

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

\begin{equation}
\text{ZnO(s)} + \text{H}_2(g) \rightarrow \text{Zn(s)} + \text{H}_2\text{O(g)}
\end{equation}
In order for reaction (7) to proceed at a hydrogen pressure kept at 1 bar, it is necessary to reduce the partial pressure of the generated water vapor. **Calculate** the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 °C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are \( \Delta G_{\text{ZnO}}(300 \, ^\circ \text{C}) = -2.90 \times 10^2 \text{kJ mol}^{-1} \) and \( \Delta G_{\text{H}_2\text{O}}(300 \, ^\circ \text{C}) = -2.20 \times 10^2 \text{kJ mol}^{-1} \), respectively.

لتحقيق التفاعل (7) عند ضغط هيدروجين 1 bar، انخفاض ضغط الغاز الماء المولد لتفادي التفاعل (7) عند 300 °C. حيث تكون الطاقة التي تشكل بين الأكسيد الزئبق والبخار للماء عند 1 bar و 300 °C وهما على التوالي: \( \Delta G_{\text{ZnO}}(300 \, ^\circ \text{C}) = -2.90 \times 10^2 \text{kJ mol}^{-1} \) و \( \Delta G_{\text{H}_2\text{O}}(300 \, ^\circ \text{C}) = -2.20 \times 10^2 \text{kJ mol}^{-1} \).

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

يستخدم الزئبق المعادني كمادة قطب سالب (انود) لبطاريات الهواء-فلز. يتكون القطب من ZnO و Zn. يستخدم في تفاعل الأكسدة-الاختزال التالي لتوليد كهرباء بقوة دافعة كهربائية (e.m.f) عند 25 °C و 1 bar 1 bar.

\[
\text{Zn(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{ZnO(s)} \quad E^\circ = 1.65 \text{V} \tag{8}
\]

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

تم تفعيل بطارية زئبق-هواء عند 20 mA لمدة 24 ساعة. حسب التغيير في كتلة القطب السالب (الانود) للبطارية.
Consider the change of e.m.f. of a zinc-air battery depending on the environment. Calculate the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are $-38^\circ\text{C}$ (February) and 3776 m, respectively. The atmospheric pressure is represented by

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

(9)

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

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

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

(10)

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

(11)
The Redox Chemistry of Zinc

Part A

A.1 (6 pt)

\[ < \text{pH} < \]
A.2 (5 pt)
Part B

B.1 (4 pt)

\[ p_{H_2O} = \] bar

B.2 (3 pt)

\[ \text{g} \]
B.3 (5 pt)

V
ΔG° = J mol$^{-1}$
Please return this cover sheet together with all the related question sheets.
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 \( R^1 - \text{Si} \equiv \text{Si} - R^1 \) (\( R^1 \): organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.

\[
R^1 - \text{Si} \equiv \text{Si} - R^1 + \quad H_2C = CH_2 \quad \rightarrow \quad \boxed{\begin{array}{c}
\text{Si} \\ - \text{Si} \\ - \text{Si} \\ - \text{Si} \\
\text{R}^1 \\
\text{R}^1
\end{array}}
\]

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

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

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

\[
\begin{align*}
\text{H}_2\text{C} &\equiv \text{CH}_2 + \text{H}_2 & \rightarrow & \text{H}_3\text{C} &\equiv \text{CH}_3 & \Delta H = -135 \text{ kJ mol}^{-1} & \quad (1) \\
\text{H}_2\text{Si} &\equiv \text{CH}_2 + \text{H}_2 & \rightarrow & \text{H}_3\text{Si} &\equiv \text{CH}_3 & \Delta H = -213 \text{ kJ mol}^{-1} & \quad (2) \\
\text{H}_2\text{Si} &\equiv \text{SiH}_2 + \text{H}_2 & \rightarrow & \text{H}_3\text{Si} &\equiv \text{SiH}_3 & \Delta H = -206 \text{ kJ mol}^{-1} & \quad (3) \\
& + 3 \text{H}_2 & \rightarrow & & & \Delta H = -173 \text{ kJ mol}^{-1} & \quad (4) \\
\text{HSi} &\equiv \text{SiH} + 3 \text{H}_2 & \rightarrow & & & \Delta H = -326 \text{ kJ mol}^{-1} & \quad (5) \\
\text{HSi} &\equiv \text{SiH} + 3 \text{H}_2 & \rightarrow & & & \Delta H = -368 \text{ kJ mol}^{-1} & \quad (6) \\
\text{HSi} &\equiv \text{SiH} + 3 \text{H}_2 & \rightarrow & & & \Delta H = -389 \text{ kJ mol}^{-1} & \quad (7)
\end{align*}
\]

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

### A.3 Calculate \( \Delta H \) for the transformation of D to E. Assume that \( \Delta H \) does not depend on temperature.

The isomerization from C to D and to E proceeds via transformations of \( \pi \)-bonds into \( \sigma \)-bonds without breaking any \( \sigma \)-bonds. A \(^{13}\)C NMR analysis revealed one signal for the Si\(_2\)C\(_4\) skeleton of D and two signals for that of E. The skeleton of D does not contain any three-membered rings, while E has two three-membered rings that share an edge.

### A.4 Draw the structural formulae of D and E using \( R_1, R_2, Si, \) and C.

### 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\(_2\)SiF\(_6\) was carried out as follows.

- **Standardization of Na\(_2\)SiF\(_6\) solution**
  - Preparation
  Aqueous solution F: 0.855 g of Na\(_2\)SiF\(_6\) (188.053 g mol\(^{-1}\)) dissolved in water (total volume: 200 mL).
  Aqueous solution G: 6.86 g of Ce\(_2\)(SO\(_4\))\(_3\) (568.424 g mol\(^{-1}\)) dissolved in water (total volume: 200 mL).
  - Procedure
  Precipitation titration of a solution F (50.0 mL) by dropwise adding solution G in the presence of xylenol orange, which coordinates to Ce\(^{3+}\), as an indicator. After adding 18.8 mL of solution G, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce\(^{3+}\), and the only resulting silicon compound is Si(OH)\(_4\).

- **Write the balanced equation for the reaction of Na\(_2\)SiF\(_6\) with Ce\(_2\)(SO\(_4\))\(_3\).**

- **Reaction of CCl\(_4\) with Na\(_2\)SiF\(_6\):**
  (Substance losses by e.g. evaporation are negligible during the following operations.)

Na\(_2\)SiF\(_6\) (\( x \) g) was added to CCl\(_4\) (500.0 g) and heated to 300 °C in a sealed pressure-resistant reaction vessel. The unreacted Na\(_2\)SiF\(_6\) and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with CCl\(_4\) (solution H). The \(^{29}\)Si and \(^{19}\)F NMR spectra of solution H showed SiF\(_4\) as the only silicon compound. In the \(^{19}\)F NMR spectrum, in addition to SiF\(_4\), signals corresponding to CF\(_3\)Cl, CF\(_2\)Cl\(_2\), CF\(_3\)Cl, and CF\(_4\) were observed (cf. Table 1). The integration ratios in the \(^{19}\)F NMR spectrum are proportional to the number of fluorine nuclei.

<table>
<thead>
<tr>
<th>(^{19})F NMR data</th>
<th>CF(_3)Cl</th>
<th>CF(_2)Cl(_2)</th>
<th>CF(_3)Cl</th>
<th>CF(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integration ratio</td>
<td>45.0</td>
<td>65.0</td>
<td>18.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
SiF₄ is hydrolyzed to form H₂SiF₆ according to the following eq. 8:

$$3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6$$  \hspace{1cm} (8)

Solution H (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF₄. After separation, the H₂SiF₆ generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na₂SiF₆ (aqueous solution J).

The precipitate of unreacted Na₂SiF₆ and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution K; 10.0 L).

Then, additional precipitation titrations using solution G were carried out, and the endpoints of the titrations with G were as follows:
- For solution J (entire amount): 61.6 mL.
- For 100 mL of solution K: 44.4 mL.

It should be noted here that the coexistence of NaCl or SiO₂ has no effect on the precipitation titration.

| B.2 | Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and calculate the mass (x [g]) of the Na₂SiF₆ used as a starting material. | 15pt |
| B.3 | 77.8% of the CCl₄ used as a starting material was unreacted. Calculate the mass of CF₃Cl generated. | 8pt |
Although silicon is also a group 14 element like carbon, their properties differ significantly.

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

A Part

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

على عكس الرابطة الثلاثية بين الكربون والكربون، فإن الرابطة الثلاثية للسيليكون والسيليكون في مركب تمت $R^1\equiv Si\equiv R^1$ صياغته على أنه شدید التفاعل. على سبيل المثال، يتفاعل مع الإثيلين لتشكيل منتج حلقي يحتوي على ring membered-four.
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 $C$.

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

**Calculate** the aromatic stabilization energy (ASE) for benzene and $C$ (in the case of $R^1$ = $R^2$ = H) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1).
\[
\begin{align*}
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\text{HSi} &= \text{SiH} + 3 \text{H}_2 \rightarrow \text{H}_2\text{Si} = \text{SiH}_2 & \Delta H &= -368 \text{ kJ mol}^{-1} \\
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\[ D : E = 1 : 40.0 \text{ at } 50.0 \degree C \text{ and } D : E = 1 : 20.0 \text{ at } 120.0 \degree C. \]

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\[ \text{Preparation:} \]

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Precipitation titration of a solution \( F \) (50.0 mL) by dropwise adding solution \( G \) in the presence of xylenol orange, which coordinates to \( \text{Ce}^{3+} \), 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 \( \text{Ce}^{3+} \), and the only resulting silicon compound is \( \text{Si(OH)}_4 \).  

\[
\begin{align*}
\text{Ce}_2(\text{SO}_4)_3 & \text{ with } \text{Na}_2\text{SiF}_6 \\
\text{B.1} & \\
\text{Write} \text{ the balanced equation for the reaction of } \text{Na}_2\text{SiF}_6 \text{ with } \text{Ce}_2(\text{SO}_4)_3.
\end{align*}
\]

Solution \( H \) (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of \( \text{SiF}_4 \). After separation, the \( \text{H}_2\text{SiF}_6 \) generated from the hydrolysis in the aqueous solution was neutralized and completely converted to \( \text{Na}_2\text{SiF}_6 \) (aqueous solution \( J \)).
The precipitate of unreacted Na$_2$SiF$_6$ and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution K; 10.0 L).

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

- For solution J (entire amount): 61.6 mL.
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It should be noted here that the coexistence of NaCl or SiO$_2$ has no effect on the precipitation titration.

**B.2**

Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and calculate the mass \((x\ [g]) \) of the Na$_2$SiF$_6$ used as a starting material.

**B.3**

77.8% of the CCl$_4$ used as a starting material was unreacted. **Calculate** the mass of CF$_3$Cl generated.

<table>
<thead>
<tr>
<th>15pt</th>
<th><strong>Calculate</strong> the mass of the NaCl produced in the reaction vessel (information underlined), and <strong>calculate</strong> the mass ((x\ [g]) ) of the Na$_2$SiF$_6$ used as a starting material.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8pt</td>
<td>77.8% of the CCl$_4$ used as a starting material was unreacted. <strong>Calculate</strong> the mass of CF$_3$Cl generated.</td>
</tr>
</tbody>
</table>
# Mysterious Silicon

## Part A

**A.1** (9 pt)

<table>
<thead>
<tr>
<th>A (3 pt)</th>
<th>B (3 pt)</th>
<th>C (3 pt)</th>
</tr>
</thead>
</table>

**A.2** (7 pt)

\[
C_6H_6 : \quad \text{kJ mol}^{-1} \quad \text{C} : \quad \text{kJ mol}^{-1}
\]
A.3 (6 pt)

\[ \Delta H = \text{kJ mol}^{-1} \]

A.4 (10 pt)

D (5 pt)  

E (5 pt)
Part B

B.1 (5 pt)

....................................................................................................................................

B.2 (15 pt)

(Continued on the next page)
NaCl : ______ g, Na$_2$SiF$_6$ : ______ g
B.3 (8 pt)

CF$_3$Cl: ________ g
IChO
Problem 6
Cover sheet

Please return this cover sheet together with all the related question sheets.
The Solid-State Chemistry of Transition Metals

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>B.1</th>
<th>B.2</th>
<th>B.3</th>
<th>B.4</th>
<th>C.1</th>
<th>C.2</th>
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<td></td>
</tr>
</tbody>
</table>

Volcano at Sakurajima island

Part A

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

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

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

<table>
<thead>
<tr>
<th>Cr\textsuperscript{2+}</th>
<th>Mn\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D )</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
</tr>
</tbody>
</table>
Let $\Delta_O$ and $\text{CFSE}^O$ be the energy separation of the d-orbitals of $M^{n^+}$ and the crystal-field stabilization energy in a $O_h$ field, respectively. Let $\Delta_T$ and $\text{CFSE}^T$ be those in a $T_d$ field.

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

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

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

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

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>TiO</th>
<th>VO</th>
<th>MnO</th>
<th>CoO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3460</td>
<td>3878</td>
<td>3913</td>
<td>3810</td>
<td>3916</td>
</tr>
<tr>
<td>(b)</td>
<td>3460</td>
<td>3916</td>
<td>3878</td>
<td>3810</td>
<td>3913</td>
</tr>
<tr>
<td>(c)</td>
<td>3460</td>
<td>3913</td>
<td>3916</td>
<td>3810</td>
<td>3878</td>
</tr>
<tr>
<td>(d)</td>
<td>3810</td>
<td>3878</td>
<td>3913</td>
<td>3460</td>
<td>3916</td>
</tr>
<tr>
<td>(e)</td>
<td>3810</td>
<td>3916</td>
<td>3878</td>
<td>3460</td>
<td>3913</td>
</tr>
<tr>
<td>(f)</td>
<td>3810</td>
<td>3913</td>
<td>3916</td>
<td>3460</td>
<td>3878</td>
</tr>
</tbody>
</table>
Part B

A mixed oxide \( A \), which contains \( \text{La}^{3+} \) and \( \text{Cu}^{2+} \), crystallizes in a tetragonal unit cell shown in Fig. 1. In the \([\text{CuO}_6]\) octahedron, the Cu–O length along the \( z \)-axis \( (l_z) \) is longer than that of the \( x \)-axis \( (l_x) \), and \([\text{CuO}_6]\) is distorted from the regular \( O_h \) geometry. This distortion removes the degeneracy of the \( e_g \) orbitals (\( d_{xz} - d_{yz} \) and \( d_{z^2} \)).

**Fig. 1**

\( A \) can be synthesized by thermal decomposition (pyrolysis) of complex \( B \), which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid \( C_4H_2O_4 \), i.e., a diacid. The pyrolysis behavior of \( B \) in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of \( \text{CO}_2 \). The total weight loss during the formation of \( A \) from \( B \) is 63.6%. It should be noted that only water and \( \text{CO}_2 \) are released in the pyrolysis reaction.

### B.1 Write the chemical formulae for \( A \) and \( B \).

6pt

### B.2 Calculate \( l_x \) and \( l_z \) using Fig. 1.

4pt

### B.3 For \( \text{Cu}^{2+} \) in the distorted \([\text{CuO}_6]\) octahedron in \( A \) of Fig. 1, write the names of the split \( e_g \) orbitals (\( d_{xz} - d_{yz} \) and \( d_{z^2} \)) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet.

4pt
A is an insulator. When one La³⁺ is substituted with one Sr²⁺, one hole is generated in the crystal lattice that can conduct electricity. As a result, the Sr²⁺-doped A shows superconductivity below 38 K. When a substitution reaction took place for A, \(2.05 \times 10^{27}\) holes m\(^{-3}\) were generated.

B.4 **Calculate** the percentage of Sr²⁺ substituted for La³⁺ 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.

**Part C**

\(\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\) is composed of four \(\text{CH}_3\text{CO}_2^-\) coordinated to two Cu²⁺ (Fig. 2A). \(\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\) exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four \(\text{CH}_3\text{CO}_2^-\) and an axis passing through the two Cu²⁺, all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of \(\text{CH}_3\text{CO}_2^-\), a “cage complex” is formed. The cage complex \(\text{Cu}_4(\text{L}_1\text{L}_1\text{L}_1)_4\) is composed of planar dicarboxylate \(\text{L}_1\) (Fig. 2B) and Cu²⁺ (Fig. 2C). The angle \(\theta\) between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The \(\theta\) is 0° for \(\text{L}_1\). Note that hydrogen atoms are not shown in Fig. 2.
C.1 The $\theta$ of the planar dicarboxylate $L_2$ below is fixed to 90°. If the composition of the cage complex formed from $L_2$ and $Cu^{2+}$ is $Cu_n(L_2)_m$, give the smallest integer combination of $n$ and $m$. Assume that only the $CO_2^-$ groups of $L_2$ form a coordination bond to $Cu^{2+}$ ions.

\[ L_2 \]
\[ \theta = 90° \]
A zinc complex, Zn$_4$O(CH$_3$CO$_2$)$_6$, contains four tetrahedral Zn$^{2+}$, six CH$_3$CO$_2^-$, and one O$^{2-}$ (Fig. 3A). In Zn$_4$O(CH$_3$CO$_2$)$_6$, the O$^{2-}$ is located at the origin, and the three axes passing through the carbon atoms of CH$_3$CO$_2^-$ are oriented orthogonal relative to each other. When p-benzenedicarboxylate (Fig. 3B, L3, $\theta = 180^\circ$) is used instead of CH$_3$CO$_2^-$, 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$_4$O(L3)$_3$]$_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral Zn$^{2+}$ cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

**Fig. 3**

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

C.3 X contains a considerable number of pores, and 1 g of X can accommodate $3.0 \times 10^2$ mL of CO$_2$ gas in the pores at 1 bar and 25 °C. **Calculate** the average number of CO$_2$ molecules per pore.
Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions ($M^{n+}$) in the magma is incorporated into the silicate minerals. The $M^{n+}$ studied in the problem are coordinated by oxide ions ($O^{2-}$) and adopt a four-coordinate tetrahedral ($T_d$) geometry in the magma and six-coordinate octahedral ($O_h$) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration. The distribution coefficient of $M^{n+}$ between the silicate minerals and magma, $D$, can be expressed by:

\[
D = \frac{[M]^i}{[M]^s}
\]
where $|M_s|$ and $|M_l|$ are the concentrations of $M^{n+}$ in the silicate minerals and the magma, respectively. The table below shows the $D$ values of $Cr^{2+}$ and $Mn^{2+}$ as examples.

<table>
<thead>
<tr>
<th></th>
<th>$Cr^{2+}$</th>
<th>$Mn^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>7.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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

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

Estimate $D$ for $Co^{2+}$.

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

\[ \text{Calculate: } |CFSE^O - CFSE^T| = \Delta CFSE \text{ in terms of } \Delta_O \text{ for } Cr^{2+}, Mn^{2+}, \text{ and } Co^{2+}; \]
\[ \text{Assume } \Delta_T = 4/9\Delta_O. \]

Estimate $D$ for $Co^{2+}$.

A linear relationship is observed by plotting $\ln D$ against $\Delta CFSE / \Delta_O$ in the Cartesian coordinate system shown below.

Estimate $D$ for $Co^{2+}$.
Choose the appropriate set of lattice enthalpies [kJ mol\(^{-1}\)] from one of the options (a) to (f).

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>TiO</th>
<th>VO</th>
<th>MnO</th>
<th>CoO</th>
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<tr>
<td>(a)</td>
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<td>3878</td>
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<td>3916</td>
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<tr>
<td>(d)</td>
<td>3810</td>
<td>3878</td>
<td>3913</td>
<td>3460</td>
<td>3916</td>
</tr>
<tr>
<td>(e)</td>
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<td>3916</td>
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<td>3913</td>
</tr>
<tr>
<td>(f)</td>
<td>3810</td>
<td>3913</td>
<td>3916</td>
<td>3460</td>
<td>3878</td>
</tr>
</tbody>
</table>

The CFSE of \(M^{n+}\) in the \(O_h\) field.

The metal elements (Co or Mn, V, Ti, Ca) have the following compounds in the \(O_h\) field.

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

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>TiO</th>
<th>VO</th>
<th>MnO</th>
<th>CoO</th>
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<td>(a)</td>
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<td>(c)</td>
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<tr>
<td>(e)</td>
<td>3810</td>
<td>3916</td>
<td>3878</td>
<td>3460</td>
<td>3913</td>
</tr>
<tr>
<td>(f)</td>
<td>3810</td>
<td>3913</td>
<td>3916</td>
<td>3460</td>
<td>3878</td>
</tr>
</tbody>
</table>
A mixed oxide $A$, which contains $\text{La}^{3+}$ and $\text{Cu}^{2+}$, crystallizes in a tetragonal unit cell shown in Fig.1. In the $[\text{CuO}_6]$ octahedron, the Cu–O length along the z-axis ($l_z$) is longer than that of the x-axis ($l_x$), and $[\text{CuO}_6]$ is distorted from the regular $O_h$ geometry. This distortion removes the degeneracy of the $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$).

In the figure (Fig.1), a tetragonal unit cell is shown containing $\text{La}^{3+}$ and $\text{Cu}^{2+}$, where $[\text{CuO}_6]$ octahedra form a mixed oxide structure. The Cu–O bond lengths along the z-axis ($l_z$) are longer than along the x-axis ($l_x$), indicating a distortion from the regular $O_h$ geometry.

$A$ 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 $\text{C}_4\text{H}_2\text{O}_4$, i.e., a diacid. The pyrolysis behavior of $B$ in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of $\text{CO}_2$. The total weight loss during the formation of $A$ from $B$ is 63.6%. It should be noted that only water and $\text{CO}_2$ are released in the pyrolysis reaction.

### Write
The chemical formulae for $A$ and $B$.

B.1

اكتب الصيغة الكيميائية لكل من $A$ و $B$.
4pt Calculate $l_x$ and $l_z$ using Fig. 1.

Fig. 1.

**B.2**

For Cu$^{2+}$ in the distorted [CuO$_6$] octahedron in A of Fig. 1, write the names of the split e$_g$ orbitals (d$_{x^2-y^2}$ and d$_{z^2}$) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet.

**B.3**

From Fig. 1, Cu$^{2+}$ in the distorted [CuO$_6$] octahedron in A of Fig. 1, write the names of the split e$_g$ orbitals (d$_{x^2-y^2}$ and d$_{z^2}$) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet.
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, $2.05 \times 10^{27}$ holes m$^{-3}$ were generated.

<table>
<thead>
<tr>
<th>B.4</th>
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</table>

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.

C Part

Cu$_2$(CH$_3$CO$_2$)$_4$ is composed of four CH$_3$CO$_2^-$ coordinated to two Cu$^{2+}$ (Fig. 2A). Cu$_2$(CH$_3$CO$_2$)$_4$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four CH$_3$CO$_2^-$ 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$_3$CO$_2^-$, a “cage complex” is formed. The cage complex Cu$_4$(L$_1$L$_1$L$_1$)$_4$ is composed of planar dicarboxylate L$_1$ (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 L$_1$. Note that hydrogen atoms are not shown in Fig. 2.

Fig.2A and Fig.2B show the structure of Cu$_4$(L$_1$L$_1$L$_1$)$_4$ with one Cu$^{2+}$ located at each corner of the box. The Cu$^{2+}$ ions are coordinated to four CH$_3$CO$_2^-$ ligands, forming a square in the plane of the paper. The L$_1$L$_1$L$_1$ ligands are positioned at the corners of the cube, with each L$_1$L$_1$L$_1$ ligand bonding to two Cu$^{2+}$ ions. The structure is highly symmetrical, with four mirror planes passing through the center of the cube and the center of each face.

Fig.2C shows the structure of Cu$_4$(L$_1$L$_1$L$_1$)$_4$ with the cage complex highlighted in orange. The cage complex is composed of two parts: the four Cu$^{2+}$ ions and the four L$_1$L$_1$L$_1$ ligands. The Cu$^{2+}$ ions are located at the corners of the cube, and the L$_1$L$_1$L$_1$ ligands are positioned at the centers of the faces of the cube. The structure is highly symmetrical, with four mirror planes passing through the center of the cube and the center of each face.

Fig.2D shows the structure of Cu$_4$(L$_1$L$_1$L$_1$)$_4$ with the cage complex highlighted in orange. The cage complex is composed of two parts: the four Cu$^{2+}$ ions and the four L$_1$L$_1$L$_1$ ligands. The Cu$^{2+}$ ions are located at the corners of the cube, and the L$_1$L$_1$L$_1$ ligands are positioned at the centers of the faces of the cube. The structure is highly symmetrical, with four mirror planes passing through the center of the cube and the center of each face.

Fig.2E shows the structure of Cu$_4$(L$_1$L$_1$L$_1$)$_4$ with the cage complex highlighted in orange. The cage complex is composed of two parts: the four Cu$^{2+}$ ions and the four L$_1$L$_1$L$_1$ ligands. The Cu$^{2+}$ ions are located at the corners of the cube, and the L$_1$L$_1$L$_1$ ligands are positioned at the centers of the faces of the cube. The structure is highly symmetrical, with four mirror planes passing through the center of the cube and the center of each face.

Fig.2F shows the structure of Cu$_4$(L$_1$L$_1$L$_1$)$_4$ with the cage complex highlighted in orange. The cage complex is composed of two parts: the four Cu$^{2+}$ ions and the four L$_1$L$_1$L$_1$ ligands. The Cu$^{2+}$ ions are located at the corners of the cube, and the L$_1$L$_1$L$_1$ ligands are positioned at the centers of the faces of the cube. The structure is highly symmetrical, with four mirror planes passing through the center of the cube and the center of each face.

Fig.2G shows the structure of Cu$_4$(L$_1$L$_1$L$_1$)$_4$ with the cage complex highlighted in orange. The cage complex is composed of two parts: the four Cu$^{2+}$ ions and the four L$_1$L$_1$L$_1$ ligands. The Cu$^{2+}$ ions are located at the corners of the cube, and the L$_1$L$_1$L$_1$ ligands are positioned at the centers of the faces of the cube. The structure is highly symmetrical, with four mirror planes passing through the center of the cube and the center of each face.
The θ of the planar dicarboxylate $\text{L}_2$ below is fixed to 90°. If the composition of the cage complex formed from $\text{L}_2$ and $\text{Cu}^{2+}$ is $\text{Cu}_n(\text{L}_2)_m$, give the smallest integer combination of $n$ and $m$. Assume that only the CO$_2$ groups of $\text{L}_2$ form a coordination bond to $\text{Cu}^{2+}$ ions.

تم تثبيت الزاوية θ للثنائي كربوكسيلات المستوى $\text{L}_2$ الموضح أدناه عند زاوية 90 درجة. إذا كان تركيب معقد القفص المتكون من $\text{L}_2$ هو $\text{Cu}_n(\text{L}_2)_m$، أذكر أصغر مجموعة من الأعداد الصحيحة لكل من $n$ و $m$ . افترض أن مجموعات CO$_2$ هم التي ترتبط فقط برابطة تناسقية إلى أيونات $\text{Cu}^{2+}$.
A zinc complex, \( \text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)^6 \), contains four tetrahedral \( \text{Zn}^{2+} \), six \( \text{CH}_3\text{CO}_2^- \), and one \( \text{O}^{2-} \) (Fig. 3A). In \( \text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)^6 \), the \( \text{O}^{2-} \) is located at the origin, and the three axes passing through the carbon atoms of \( \text{CH}_3\text{CO}_2^- \) are oriented orthogonal relative to each other. When \( \text{p-benzenedicarboxylate} \) (Fig. 3B, \( \text{L}_3, \theta = 180\degree \)) is used instead of \( \text{CH}_3\text{CO}_2^- \), the \( \text{Zn}^{2+} \) clusters are linked to each other to form a crystalline solid \( \text{X} \) that is called a “porous coordination polymer” (Fig. 3C). The composition of \( \text{X} \) is \( [\text{Zn}_4\text{O}(\text{L}_3)_3]^n \), and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral \( \text{Zn}^{2+} \) cluster is represented as dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

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

\( 5\text{pt} \)

\( \text{C.2} \)
X contains a considerable number of pores, and 1 g of X can accommodate \(3.0 \times 10^2\) mL of CO\(_2\) gas in the pores at 1 bar and 25 °C. Calculate the average number of CO\(_2\) molecules per pore.

English:

Calculate the average number of CO\(_2\) molecules per pore.

Arabic:

يحتوي X على عدد كبير من المسامات، ويمكن لـ 1 g من X استيعاب 3.0 \(\times\) 10\(^2\) mL غاز CO\(_2\) في المسام عند 1 bar و 25 درجة مئوية. حسب متوسط عدد الجزيئات من CO\(_2\) لكل مسام واحد.
The Solid-State Chemistry of Transition Metals

Part A

A.1 (6 pt)

\[ \text{Cr}^{2+} : \Delta_0, \text{Mn}^{2+} : \Delta_0, \text{Co}^{2+} : \Delta_0 \]
A.2 (3 pt)

\[ D : \ \text{____________________} \]

A.3 (3 pt)

\[ \text{______________} \]
Part B

B.1 (6 pt)

A: _______________, B: _______________

B.2 (4 pt)

\[ l_x = \text{_________ nm, } l_z = \text{_________ nm} \]
B.3 (4 pt)

(i) : ___________________________, (ii) : ___________________________

B.4 (4 pt)
Part C

C.1 (5 pt)

\[ n = \quad , \quad m = \quad \]

C.2 (5 pt)

\[ a = \quad \text{cm} \]
C.3 (5 pt)
IChO
Problem 7
Cover sheet

Please return this cover sheet together with all the related question sheets.
Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

Photo courtesy: Tohoku Univ.

Part A

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

Then, ketone 4 is converted into ester 15. Compound 8 (molecular weight: 188) retains all the stereocenters in 7. Compounds 9 and 10 have five stereocenters and no carbon-carbon double bonds. Assume...
that H$_2^{18}$O is used instead of H$_2^{16}$O for the synthesis of $^{18}$O-labelled-linearifilianones 13 and 14 from 11 and 12, respectively. Compounds 13 and 14 are $^{18}$O-labelled isotopomers. Ignoring isotopic labelling, both 13 and 14 provide the same product 15 with identical stereochemistry.
A.2 Choose the appropriate structure for A. 2pt

I $\text{F}_3\text{C-S-OH}$ II $\text{F}_3\text{C-S-NH}_2$ III $\text{O=S-CF}_3$ IV $\text{O=S-CF}_3$

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

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

\[
\begin{align*}
\text{Br}_2 & \quad \text{CH}_3\text{COOH} \\
\text{Et}_3\text{N} & \quad \text{CH}_2\text{Cl}_2 \\
\text{HCl} & \quad \text{+} \\
\text{OH} & \quad + \\
\end{align*}
\]

\[
\begin{align*}
\text{17} & : \text{C}_{15}\text{H}_{12}\text{Br}_2\text{O} \\
\text{18} & : \text{C}_{15}\text{H}_{10}\text{O} \\
\text{19} & : \text{C}_{15}\text{H}_{10}\text{Cl}_2 \\
\text{20} & : \delta 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H) \\
\text{21} & : \delta 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)
\end{align*}
\]

B.1 Draw the structures of 17–19 and 21. Identifying the stereochemistry is not necessary.
A Part

Lineariiifolianone 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.

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

هو منتج طبيعي له هيكل فريد، تم عزله من *Inula linariifolia*. ينتج من *Inula linariifolia* bullvalencene (1) بالتحويل عن طريق خطوة واحدة المركب 2، قبل التحول عن طريق ثلاث خطوات للمركب 3 الذي ينتج عنه الكيتون 4. يتم تحويل *Eremophilene* (5) إلى 6 عن طريق إجراء نفس التحول المكون من أربع خطوات.
Inula linariifolia

valencene (1) + NaIO₄, OsO₄ → 2

2 + CH₂CN 80 °C → CH₃Li, THF, -78 °C → 3

3 + benzilic acid, THF, -78 °C → 4

eremophilenec (5) + NaIO₄, OsO₄ → 2

2 + CH₂CN 80 °C → CH₃Li, THF, -78 °C → 3

3 (ii) + benzilic acid, THF, -78 °C → 6
5pt **Draw** the structures of 2 and 6 and clearly identify the stereochemistry where necessary.

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

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

\(^{18}O\)-labelled isotopomers.

المركبات 13 و 14 هي 14

تجاهل isotopic labelling تفعلي نفس الناتج 15 مع كيمياء فراغية متطابقة.
Choose the appropriate structure for A.

A.2

I. \( \text{F}_3\text{C-S-OH} \)
II. \( \text{F}_3\text{C-S-NH}_2 \)
III. \( \text{O-S-CF}_3 \)
IV. \( \text{O-S-CF}_3 \)

Draw the structures of 8–14 and clearly identify the stereochemistry where necessary. Also, indicate the introduced \(^{18}\text{O}\) atoms for 13 and 14 as shown in the example below.

A.3

8–14

\( \text{O} \)

\( \text{O} \)

\( \text{O} \)

\( \text{O} \)

\( \text{O} \)

\( \text{O} \)
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.

B Part

Identifying the stereochemistry is not necessary.

Draw the structures of 17–19 and 21. 

{$^{1}$H NMR (CD$_3$CN, ppm): 20: $\delta$ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H) 

21: $\delta$ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)
# Playing with Non-benzenoid Aromaticity

## Part A

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<table>
<thead>
<tr>
<th>A.2 (2 pt)</th>
</tr>
</thead>
</table>
A.3 (19 pt)

8 (3 pt)

9 (2 pt)  10 (2 pt)

11 (2 pt)  12 (2 pt)

13 (4 pt)  14 (4 pt)
## Part B

**B.1** (10 pt)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>19</td>
<td>21</td>
</tr>
</tbody>
</table>

17 (2 pt)  
18 (2 pt)  
19 (3 pt)  
21 (3 pt)
Please return this cover sheet together with all the related question sheets.
Polycyclic aromatic hydrocarbons with successive ortho-connections are called \([n]\)carbohelicenes (here, \(n\) represents the number of six-membered rings) (see below). \([4]\)Carbohelicene (\([4]C\)) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (\textbf{Int.}) that is readily oxidized by iodine.

The photoreaction proceeds in a manner similar to the following example.
Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated \( \pi \) systems.

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

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

\[ \text{[D (\( \delta \), ppm in CS}_2, \text{ r.t.}, 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]} \]

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

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

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

\[
\text{E}
\]

\[
(1, 2, 3) = (P, P, P)
\]

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

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

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

B.1 **Draw** the structure of intermediate I (its stereochemistry is not required). 3pt
B.2 Starting from the optically active precursor J, the same reaction sequence gives the optically active sumanene derivative K. The stereocenters in J suffer no inversion during the metathesis reaction. **Draw** the structure of K with the appropriate stereochemistry.
A Part

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

الكي الزيادات الديناميكية وكيراليتها

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
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<th>B.1</th>
<th>A.3</th>
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<td>3</td>
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<td></td>
</tr>
</tbody>
</table>

Score

![Chemical structure diagram](image)
The photoreaction proceeds in a manner similar to the following example.

ائف اذن الفاعلية تتم بنفس الطريقة كما هو موضح بالمثال التالي.

\[ \text{CH}_2 = \text{CH}_2 \xrightarrow{hv} \text{CH}_2 = \text{CH}_2 \]

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

مراجعة: في كل فقرات السؤال 8، من فضلك ارسم روابط احادية و ثنائية بشكل متناوب في اجابتك (carbohelicene) على السؤال كما هو موضح في مثال الكربوهيليسينات. لا تضع دوائر لأنظمة مدارات \( \pi \) المتزامنة.

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

ارسم تركيب من A إلى C، يجب تمييز المتماكنات الفراغية.

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


[D (δ, ppm in CS\(_2\), r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]

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

تحتوي [5]- والكبيري [n]carbohelicenes على كيرالية ملتقة بشكل حلزوني وتحول بين الاثنين ينتمون للكيراليات (helicenes) بطيء بشكل كبير في درجة حرارة الغرفة. (interconversion) الكيرالية لـ [n]carbohelicenes مشابه إليها بالرموز (M) أو (P) كما هو موضح بالأسفل.
The [n]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.

الإلم ذو n أكبر من 4 يمكن فصلها انتانوميريا عن طريق كروماتوغرافيا العمود الكيرالي (chiral column chromatography)

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

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

\(\text{When using the binomial } 1,2\text{-dibromobenzene) (C}_{66}H_{36} \text{ G) G.}\) This reaction does not form a mirror image of \(F\). If \(F\) is an enantiomer, then \(G\) is also an enantiomer. Interconversion is not possible by rotation around the single bond in the molecule. The stereoisomers of \(G\) can be identified by listing the location numbers and \(M\) and \(P\) labels according to the same numbering. For instance, the other stereoisomers of \(E\) should be listed as \((1, 2, 3) = (P, M, P), (P, P, M), (P, P, P), (M, M, M), (M, M, P), (M, P, P), (M, P, M),\) and \((M, P, M).\)
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower.

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

Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.
**B.1**

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

![Structure of Intermediate I](image)

**B.2**

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

![Reaction Scheme](image)
Dynamic Organic Molecules and Their Chirality

Part A

<table>
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<td>B (3 pt)</td>
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<td>C (3 pt)</td>
</tr>
</tbody>
</table>

| A.2 (3 pt) |
Part B

B.1 (3 pt)

B.2 (4 pt)
Please return this cover sheet together with all the related question sheets.
Likes and Dislikes of Capsule

<table>
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<th>A.3</th>
<th>A.4</th>
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<td></td>
</tr>
</tbody>
</table>

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

Based on this idea, compounds 1 and 2 were synthesized as U-shaped molecules with different sizes. Compound 3 was prepared as a comparison of 1 and the encapsulation behavior of these compounds was investigated.
The synthetic route to 2 is shown below. The elemental composition of compound 9: C; 40.49%, H; 1.70%, and O; 17.98% by mass.
A.1 **Draw** the structures of 4-9; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of p-methoxybenzyl group shown in the scheme above.

In the mass spectrum of 1, the ion peak corresponding to its dimer (12) was clearly observed, whereas an ion peak for 32 was not observed in the spectrum of 3. In the 1H NMR spectra of a solution of 12, all the NH protons derived from 1 were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of 3. These data indicate that hydrogen bonds are formed between the NH moieties of 1 and atoms X of another molecule of 1 to form the dimeric capsule.

| A.2 | **Circle** all the appropriate atom(s) X in 1. | 2pt |
| A.3 | **Give** the number of the hydrogen bonds in the dimeric capsule (12). | 2pt |
The dimeric capsule of 1 (1,2) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

\[ Z + 1_2 \rightarrow Z@1_2 \]  (1)

The equilibrium constant of the encapsulation of Z into 12 is given as below:

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

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, 12 in C\(_6\)D\(_6\) gave different signals in the \(^1\)H NMR spectra before and after addition of CH\(_4\).

Compound 2 also forms a rigid and larger dimeric capsule (2,2). The \(^1\)H NMR spectrum of 2,2 was measured in C\(_6\)D\(_6\), C\(_6\)D\(_5\)F, and a C\(_6\)D\(_6\)/C\(_6\)D\(_5\)F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H\(^a\) proton of 2 in the above solvents are summarized below, and no other signals from the H\(^a\) in 2, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.

<table>
<thead>
<tr>
<th>solvent</th>
<th>(\delta) (ppm) of H(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)D(_6)</td>
<td>4.60</td>
</tr>
<tr>
<td>C(_6)D(_5)F</td>
<td>4.71</td>
</tr>
<tr>
<td>C(_6)D(_6)/C(_6)D(_5)F</td>
<td>4.60, 4.71, 4.82</td>
</tr>
</tbody>
</table>

A.4 Determine the number of C\(_6\)D\(_6\) and C\(_6\)D\(_5\)F molecules encapsulated in 2,2 giving each H\(^a\) signal.
\( ^1\text{H} \) NMR measurements in C\(_6\)D\(_6\) revealed that 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. \([\text{solvent}@2]\) denotes a species containing one or more solvent molecules.

\[
K_a = \frac{[\text{Z}@2_2]}{[\text{Z}][\text{solvent}@2_2]}
\]  

Similarly, the \( K_a \) values of CH\(_4\) and 1, given as eq (2) at various temperatures in C\(_6\)D\(_6\) were also determined by \( ^1\text{H} \) NMR measurements. The plots of the two association constants (as \( \ln K_a \) vs \( 1/T \)) are shown below.

No C\(_6\)D\(_6\) molecule is encapsulated in 1. In line II, the entropy change \( (\Delta S) \) is (1) and enthalpy change \( (\Delta H) \) is (2), indicating that the driving force for the encapsulation in line II is (3). Therefore, line I corresponds to (4), and line II corresponds to (5).

---

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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
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<td>negative</td>
</tr>
<tr>
<td>2</td>
<td>positive</td>
<td>negative</td>
</tr>
<tr>
<td>3</td>
<td>( \Delta S )</td>
<td>( \Delta H )</td>
</tr>
<tr>
<td>4</td>
<td>1 and CH(_4)</td>
<td>2 and AdA</td>
</tr>
<tr>
<td>5</td>
<td>1 and CH(_4)</td>
<td>2 and AdA</td>
</tr>
</tbody>
</table>
A good kid doesn't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.

Based on this idea, compounds 1 and 2 were synthesized as U-shaped molecules with different sizes. Compound 3 was prepared as a comparison of 1 and the encapsulation behavior of these compounds was investigated.
The synthetic route to 2 is shown below. The elemental composition of compound 9: C; 40.49%, H; 1.70%, and O; 17.98% by mass.

التشديد الكلي للمركب 2 موضح بالأسفل, التركيب العنصري للمركب 9 هو كالتالي: الكأربون بنسبة % 40.49 و الهيدروجين بنسبة % 1.70 و الأكسجين بنسبة % 17.98
13pt **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.

**A.1**

Aräsmarärkaätaaänämtä renewable wärraenämtä (läkämäaä eëmäälätä). p-methoxybenzyl ämäkkäänaanämtä "PMB" käaxäetä bâdaanänämtä rimäeäämkäänaanämtä p-methoxybenzyl, äemäkkäänaanämtä ämäÄmäämkäänaanämtä summaränämtä wäeëmäälañtä, ämäÄmäämkäänaanämtä summaränämtä

In the mass spectrum of 1, the ion peak corresponding to its dimer (1₂) was clearly observed, whereas an ion peak for 3₂ was not observed in the spectrum of 3. In the ¹H NMR spectra of a solution of 1₂, 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 (₁₁₁₂).

**A.4**

**Circle** all the appropriate atom(s) X in 1.
The dimeric capsule of 1 (1₂) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

\[ Z + 1₂ \rightarrow Z@1₂ \]  

The equilibrium constant of the encapsulation of Z into 1₂ is given as below:

\[ K_a = \frac{[Z@1₂]}{[Z][1₂]} \]  

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, 1₂ in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

The tautomer of the tautomer Z inside the capsule could be observed by NMR spectroscopy. For example, 1₂ in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

Compound 2 also forms a rigid and larger dimeric capsule (2₂). The ¹H NMR spectrum of 2₂ was measured in C₆D₆, C₆D₅F, and a C₆D₆/C₆D₅F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H₃ proton of 2 in the above solvents are summarized below, and no other signals from the H₃ in 2, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.

The dimeric capsule of 1 (1₂) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

\[ Z + 1₂ \rightarrow Z@1₂ \]

The equilibrium constant of the encapsulation of Z into 1₂ is given as below:

\[ K_a = \frac{[Z@1₂]}{[Z][1₂]} \]

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, 1₂ in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

The tautomer of the tautomer Z inside the capsule could be observed by NMR spectroscopy. For example, 1₂ in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

Compound 2 also forms a rigid and larger dimeric capsule (2₂). The ¹H NMR spectrum of 2₂ was measured in C₆D₆, C₆D₅F, and a C₆D₆/C₆D₅F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H₃ proton of 2 in the above solvents are summarized below, and no other signals from the H₃ in 2, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.
<table>
<thead>
<tr>
<th>δ (ppm) of H&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td>4.60</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>4.71</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;5&lt;/sub&gt;F</td>
</tr>
<tr>
<td>4.60, 4.71, 4.82</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt; / C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;5&lt;/sub&gt;F</td>
</tr>
</tbody>
</table>

3pt **Determine** the number of C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>D<sub>5</sub>F molecules encapsulated in 2, giving each H<sup>a</sup> signal.

A.4 حدد عدد جزيئات C<sub>6</sub>D<sub>6</sub> و C<sub>6</sub>D<sub>5</sub>F المتكتسة في 2 تعطي كل واحد H<sup>a</sup> إشارة
$^1$H NMR measurements in C$_6$D$_6$ revealed that 2 can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants ($K_a$) which are expressed below were determined for various temperatures. [solvent@2] denotes a species containing one or more solvent molecules.

Similarly, the $K_a$ values of CH$_4$ and 1, given as eq (2) at various temperatures in C$_6$D$_6$ 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.

No C$_6$D$_6$ molecule is encapsulated in 1. In line II, the entropy change ($\Delta S$) is (1) and enthalpy change ($\Delta H$) 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).
Choose the correct options in gaps (1)–(5) in the following paragraph from A and B.

<table>
<thead>
<tr>
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<th>B</th>
<th>A</th>
</tr>
</thead>
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<td>(2)</td>
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<td>ΔS</td>
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<tr>
<td>(4)</td>
<td>2 and AdA</td>
<td>1 and CH₄</td>
</tr>
<tr>
<td>(5)</td>
<td>2 and ADA</td>
<td>1 and CH₄</td>
</tr>
</tbody>
</table>
Likes and Dislikes of Capsule

A.1 (13 pt)

4 (2 pt) 5 (3 pt)

6 (2 pt) 7 (2 pt)

8 (2 pt) 9 (2 pt)
A.2 (2 pt)

![Chemical structure image]

A.3 (2 pt)

A.4 (3 pt)

<table>
<thead>
<tr>
<th>$\delta$ (ppm) of $H^a$</th>
<th>numbers of $C_6D_6$</th>
<th>numbers of $C_6D_5F$</th>
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<tbody>
<tr>
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<td>4.82 ppm</td>
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</table>

A.5 (3 pt)

(1) :  

(2) :  

(3) :  

(4) :  

(5) :  