IChO
General instructions
Cover sheet

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

Chemistry! It's Cool!
General Instruction

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

GOOD LUCK!

Problems and Grading Information

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

**Constants**

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

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>The ideal gas law</td>
<td>$PV = nRT$ , where $P$ is the pressure, $V$ is the volume, $n$ is the amount of substance, $T$ is the absolute temperature of ideal gas.</td>
</tr>
<tr>
<td>Coulomb's law</td>
<td>$F = k_e \frac{q_1 q_2}{r^2}$ , where $F$ is the electrostatic force, $k_e(\approx 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2})$ is Coulomb's constant, $q_1$ and $q_2$ are the magnitudes of the charges, and $r$ is the distance between the charges.</td>
</tr>
<tr>
<td>The first law of thermodynamics</td>
<td>$\Delta U = q + w$ , where $\Delta U$ is the change in the internal energy, $q$ is the heat supplied, $w$ is the work done.</td>
</tr>
<tr>
<td>Enthalpy $H$</td>
<td>$H = U + PV$</td>
</tr>
<tr>
<td>Entropy based on Boltzmann's principle $S$</td>
<td>$S = k_B \ln W$ , where $W$ is the number of microstates.</td>
</tr>
<tr>
<td>The change of entropy $\Delta S$</td>
<td>$\Delta S = \frac{q_{\text{rev}}}{T}$ , where $q_{\text{rev}}$ is the heat for the reversible process.</td>
</tr>
<tr>
<td>Gibbs free energy $G$</td>
<td>$G = H - TS$ , $\Delta_r G^\circ = -RT \ln K = -zFE^\circ$ , where $K$ is the equilibrium constant, $z$ is the number of electrons, $E^\circ$ is the standard electrode potential.</td>
</tr>
<tr>
<td>Reaction quotient $Q$</td>
<td>$\Delta_r G = \Delta_r G^\circ + RT \ln Q$ For a reaction $aA + bB \rightleftharpoons cC + dD$ $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ , where $[A]$ is the concentration of $A$.</td>
</tr>
<tr>
<td>Topic</td>
<td>Equation</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Heat change $\Delta q$</td>
<td>$\Delta q = n c_m \Delta T$</td>
</tr>
<tr>
<td>Nernst equation for redox reaction</td>
<td>$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$</td>
</tr>
<tr>
<td>Arrhenius equation</td>
<td>$k = A \exp\left(-\frac{E_a}{RT}\right)$</td>
</tr>
<tr>
<td>Lambert–Beer equation</td>
<td>$A = \varepsilon lc$</td>
</tr>
<tr>
<td>Henderson–Hasselbalch equation</td>
<td>For an equilibrium</td>
</tr>
<tr>
<td>Energy of a photon</td>
<td>$E = h\nu = \frac{h\lambda}{\lambda}$</td>
</tr>
<tr>
<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>
</tr>
<tr>
<td>Approximation equation for problem solving</td>
<td>When $x \ll 1$, $\frac{1}{1-x} \simeq 1 + x$</td>
</tr>
</tbody>
</table>
\[ \Delta \delta \text{ for one alkyl group-substitution: } \text{ca. } +0.4 \text{ ppm} \]
International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July - 2nd August, 2021
https://www.icho2021.org

Chemistry! It's Cool!
General Instructions

- You are allowed to use pen only to write your answers.
- 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 by the invigilator.
- All results must be written in the appropriate answer boxes with pen on the answer sheets. If you need scratch paper, use the back of the question sheets. Remember that answers written outside the answer boxes will not be graded.
- Write relevant calculations in the appropriate boxes when necessary. Work must be shown to receive full credit for correct answers.
- The invigilator will announce a 30-minute warning before the STOP command.
- You must stop working when the STOP command is given. Failure to stop writing will lead to the nullification of your examination.
- The official English version of this examination is available by request for clarification only.
- You are not allowed to leave your seat without permission from the invigilator. If you need any assistance (broken calculator, need to use a restroom, etc.), raise your hand to get the attention of the invigilator.

GOOD LUCK!

Problems and Grading Information

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

### Constants

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

**TKM-3 C-0 G-3**

Turkmen (Turkmenistan)
### Equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
</table>
| **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, \( k_e (\approx 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2}) \) 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** | \( \Delta S = \frac{\Delta r G}{T} \)  
where \( \Delta r G \) is the change of Gibbs free energy. |
| **Gibbs free energy** | \( G = H - TS \)  
\( \Delta r G = -RT \ln K = -zFE^o \)  
where \( K \) is the equilibrium constant, \( z \) is the number of electrons, \( E^o \) is the standard electrode potential. |
| **Reaction quotient** | \( \Delta r G = \Delta r G^o + RT \ln Q \)  
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>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat change $\Delta q$</td>
<td>$\Delta q = n c_m \Delta T$, where $c_m$ is the temperature-independent molar heat capacity.</td>
</tr>
<tr>
<td>Nernst equation for redox reaction</td>
<td>$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{ox}}{C_{red}}$, where $C_{ox}$ is the concentration of oxidized substance, $C_{red}$ 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>
</tr>
<tr>
<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>
</tr>
<tr>
<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>
</tr>
<tr>
<td>The sum of a geometric series</td>
<td>When $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \frac{1-x^{n+1}}{1-x}$</td>
</tr>
<tr>
<td>Approximation equation that can be used to solve problems</td>
<td>When $x \ll 1$, $1 \approx 1 + x$</td>
</tr>
</tbody>
</table>
### Periodic Table

<table>
<thead>
<tr>
<th>Period 2</th>
<th>Period 3</th>
<th>Period 4</th>
<th>Period 5</th>
<th>Period 6</th>
<th>Period 7</th>
<th>Transition Metals</th>
<th>Actinides</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
</tr>
<tr>
<td>F</td>
<td>Ne</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>Ar</td>
<td>Cl</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
</tr>
<tr>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
</tr>
<tr>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>Kr</td>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
</tr>
<tr>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>I</td>
<td>Xe</td>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Ce</td>
<td>Pr</td>
<td>Nd</td>
</tr>
<tr>
<td>La-Lu</td>
<td>Ac-Lr</td>
<td>F</td>
<td>Ra</td>
<td>Fr</td>
<td>Ra</td>
<td>Ra</td>
<td></td>
</tr>
</tbody>
</table>

**Key:**
- **IChO**
- **G0-6**
- **Turkmen (Turkmenistan)**

**Periodic Table Details:**
- **IChO**
- **G0-6**
- **Turkmen (Turkmenistan)**

**Notes:**
- The periodic table includes elements from hydrogen (H) to lawrencium (Lr).
- It is organized by atomic number, with elements listed in order from 1 to 118.
- Key elements include:
  - **IChO**
  - **G0-6**
  - **Turkmen (Turkmenistan)**

**Image Description:**
- The image contains a detailed periodic table with atomic numbers, symbols, and names of elements.
- The table is color-coded with different sections highlighted for easy identification.
- The table is oriented vertically, with elements arranged from left to right and top to bottom.

**Related Information:**
- **TKM-3 C-0 G-6**
- **Turkmenistan**

**Additional Notes:**
- The periodic table provides a comprehensive overview of the elements, their properties, and their positions within the periodic system.
$\Delta \delta$ for one alkyl group-substitution: $ca. +0.4$ ppm
Please return this cover sheet together with all the related question sheets.
Hydrogen at a Metal Surface

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>B.1</th>
<th>B.2</th>
<th>B.3</th>
<th>B.4</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>6</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>24</td>
</tr>
</tbody>
</table>

Score

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

**Part A**

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

Fig. 2
A.1 For each of the following items (i)–(iii), select the closest value from A–G. 6pt
(i) The interatomic distance for a gaseous H\(_2\) molecule
(ii) The interatomic distance between metal atoms (\(d_M\) in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface (\(h_{ad}\) in Fig. 1)

<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 H\(_2\) to gaseous H
[H\(_2\)(g) \(\rightarrow\) 2H(g)]
(ii) the energy released during the adsorption of a gaseous H\(_2\) [H\(_2\)(g) \(\rightarrow\) 2H(ad)]

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

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

\[
\begin{align*}
H_2(g) & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2H(ad) \\
H(ad) & \rightarrow H(ab)
\end{align*}
\]

(1a)

(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:

\[
\begin{align*}
R_1 &= k_1 P_{H_2} (1 - \theta)^2 \\
R_2 &= k_2 \theta^2 \\
R_3 &= k_3 \theta
\end{align*}
\]

(2)

(3)

(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 < \theta < 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:

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

(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 (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 \( v = 4.0 \times 10^{-4} \, \text{Pa s}^{-1} \). 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, \( A \, [\text{mol s}^{-1} \, \text{m}^{-2}] \).

**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 \( A = 3.6 \times 10^{-7} \, \text{mol s}^{-1} \, \text{m}^{-2} \).

**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).
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 hydrogen-storage technology.

**Part A**

As hydrogen is absorbed (*metalyň içine sorulmagy*) into the bulk of a metal surface, let us first consider the adsorption (*metalyň ýüzüne siňmegi*) process of hydrogen at the metal surface, \( \text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad}) \), 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 (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 (*dikligine*) dotted line in Figure 1. (*Figure1-da görkezilişi ýaly H atomlaryny birikdirýän oky, mydama metalyň ýüzüne parallel kabul ediň, agyrlyk merkezi hemişe görkezilen nokatly çyzgyň üstünde*)

Figure 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 \( \text{kJ} \text{ mol}^{-1} \), the dashed line spacing is 100 \( \text{kJ} \text{ mol}^{-1} \), and the spacing between solid and dashed lines is 80 \( \text{kJ} \text{ mol}^{-1} \). The zero-point vibration energy is ignored.
Figure 1. Definition of variables. Drawing is not to scale.

Figure 2.
A.1  For each of the following items (i)–(iii), SELECT the closest value from A–G. 6pt

(i) The interatomic distance for a gaseous H\(_2\) molecule

(ii) The interatomic distance between metal atoms (\(d_M\) in Figure 1)

(iii) The distance of adsorbed H atoms from the surface (\(h_{ad}\) in Figure 1)

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.03 nm</td>
<td>B</td>
<td>0.07 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>0.11 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>0.15 nm</td>
</tr>
<tr>
<td>E</td>
<td>0.19 nm</td>
<td>F</td>
<td>0.23 nm</td>
</tr>
<tr>
<td>G</td>
<td>0.27 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</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 H\(_2\) to gaseous H

\[ \text{[H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})] \]

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

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

\[
\begin{align*}
\text{H}_2(\text{g}) & \xrightarrow{k_1} 2\text{H(\text{ad})} & (1a) \\
\text{H(\text{ad})} & \xrightarrow{k_2} \text{H(ab)} & (1b)
\end{align*}
\]

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

\[
\begin{align*}
 r_1 &= k_1 P_{\text{H}_2} (1 - \theta)^2 \\
 r_2 &= k_2 \theta^2 \\
 r_3 &= k_3 \theta
\end{align*}
\]

where \( k_1 [\text{s}^{-1} \text{Pa}^{-1}] \), \( k_2 [\text{s}^{-1}] \) and \( k_3 [\text{s}^{-1}] \) are the reaction rate constants and \( P_{\text{H}_2} \) is the pressure of \( \text{H}_2 \). 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:  
\[
 r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\text{H}_2} C}}}
\]  
\[5\text{pt}\]

**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 (1a) and (1b) 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 temperature, $C = 2.5 \times 10^3 \text{ Pa}^{-1}$ and $k_3 = 4.8 \times 10^{-2} \text{ s}^{-1}$. For $r_3$ as a function of $P_{\text{H}_2}$ at this temperature, **SELECT** the correct curve from (a)–(h). 3pt
Hydrogen at a Metal Surface

Part A

A.1 (6 pt)

<table>
<thead>
<tr>
<th>(i)</th>
<th>(ii)</th>
<th>(iii)</th>
</tr>
</thead>
</table>

A.2 (4 pt)

<table>
<thead>
<tr>
<th>(i)</th>
<th>(ii)</th>
</tr>
</thead>
</table>
Part B

B.1 (5 pt)

\[ C = \]

B.2 (3 pt)

\[ A = \text{mol s}^{-1} \text{ m}^{-2} \]
**B.3** (3 pt)

\[ k_3 = \text{______________} \text{ s}^{-1} \]

**B.4** (3 pt)

________________________
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 CH$_4$ and CH$_3$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:

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

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

$$S = k_B \ln W$$

$W = 1$ for $^{12}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}_2$. In contrast, $W = 2$ for a $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecules, $W = 2^2 = 4$. 

$$K = \frac{[^{12}\text{C}^{16}\text{O}^{18}\text{O}]^2}{[^{12}\text{C}^{16}\text{O}_2][^{12}\text{C}^{18}\text{O}_2]}$$
A.1  The enthalpy change, $\Delta H$, of eq. 3 is positive regardless of the temperature. 8pt

$$H_2 + DI \rightleftharpoons HD + HI$$  (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.

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

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

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

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$  (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:

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$  (7)

A.2  The vibration of $H_2$ is at 4161.0 cm$^{-1}$ when reported as a wavenumber. 8pt

**Calculate** the $\Delta H$ of the following equation at $T = 0$ K in units of J mol$^{-1}$.

$$2HD \rightarrow H_2 + D_2$$  (8)

Assume that:

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

$$\Delta_{\text{D}_2} = \frac{R_{\text{D}_2}}{R_{\text{D}_2}^*} - 1$$ (9)

Here, $R_{\text{D}_2}$ refers to $\frac{[\text{D}_2]}{[\text{H}_2]}$ in the sample and $R_{\text{D}_2}^*$ to $\frac{[\text{D}_2]}{[\text{H}_2]}$ at $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

A.3 **Calculate** $\Delta_{\text{D}_2}$ 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 CO₂[44] and CO₂[47] below. The quantity $\Delta_{47}$ is defined as:

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

$R_{47}$ 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 $T \rightarrow +\infty$. 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>
<tbody>
<tr>
<td>natural abundance</td>
<td>0.988888</td>
<td>0.011112</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$^{16}\text{O}$</th>
<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:

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

**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 CO₂[47] for the calculation.
Molecular entities (bölejikler) that differ only in isotopic composition, such as CH$_4$ and CH$_3$D, are called isotopologues.

Isotopologues are considered to have the same chemical characteristics. In nature, however, there are slight differences between isotopologues.

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

Let us consider the following equilibrium:

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

$$K = \frac{\left[^{12}\text{C}^{16}\text{O}^{18}\text{O}\right]^2}{\left[^{12}\text{C}^{16}\text{O}_2\right]\left[^{12}\text{C}^{18}\text{O}_2\right]}$$  \hspace{1cm} (1)

The entropy, $S$, increases as the number of possible microscopic states of a system, $W$, increases:

$$S = k_B \ln W$$  \hspace{1cm} (2)

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

$$H_2 + DI \rightleftharpoons HD + HI$$  \hspace{1cm} (3)

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

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

$$2HD \rightleftharpoons H_2 + D_2 \hspace{1cm} K = \frac{[H_2][D_2]}{[HD]^2}$$  \hspace{1cm} (4)

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

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

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

In equation 6, $k$ is the force constant and $\mu$ is the reduced mass.

Reduced mass is expressed in terms of the mass of the two atoms in the diatomic molecule, $m_1$ and $m_2$, according to:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$  \hspace{1cm} (7)

The wavenumber corresponding to the vibration of H$_2$ is 4161.0 cm$^{-1}$. **CALCULATE** $\Delta H$ of the following equation at $T = 0$ K in units of J mol$^{-1}$.

$$2HD \rightarrow H_2 + D_2$$  \hspace{1cm} (8)

Assume that:

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

\[ \Delta_{D_2} = \frac{R_{D_2}}{R'_{D_2}} - 1 \]  

(9)

Here, \( R_{D_2} \) refers to \( \frac{[D_2]}{[H_2]} \) in the sample and \( R'_{D_2} \) to \( \frac{[D_2]}{[H_2]} \) at \( T \to +\infty \). Note 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 equation 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 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:

$$\Delta_{47} = \frac{R_{47}}{R^*_47} - 1$$  \hspace{1cm} (10)

$R_{47}$ refers to $[CO_2[47]]$ in the sample and $R^*_47$ to $[CO_2[47]]$ 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>$^{12}$C</th>
<th>$^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural abundance</td>
<td>0.988888</td>
<td>0.011112</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$^{16}$O</th>
<th>$^{17}$O</th>
<th>$^{18}$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:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4}$$  \hspace{1cm} (11)

A.4 The $R_{47}$ of fossil plankton obtained from the Antarctic seabed was $4.50865 \times 10^{-5}$. Calculate the approximate 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. (Hasaplamalar üçin CO2[47]-niň diñe iň köp duş gelyän izotopologyny hasaba alyň)
Isotope Time Capsule

A.1 (8 pt)

\[ T \to 0 : K = \] \[ T \to +\infty : K = \]
ΔΗ = ________ J mol⁻¹
Δ Δ₂ =
IChO
Problem 3
Cover sheet

Please return this cover sheet together with all the related question sheets.
In this problem, ignore the absorption of the cell and the solvent. The temperatures of all solutions and gases are kept constant at 25 °C.

**Part A**

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

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

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

**A.1** The absorbance of X was \(A_1\) at a wavelength of \(\lambda_1\). 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 \(\varepsilon_{\text{HA}}/\varepsilon_{\text{A}^-}\), where \(\varepsilon_{\text{HA}}\) and \(\varepsilon_{\text{A}^-}\) represent the absorption coefficients of HA and of A\(^-\), respectively, at \(\lambda_1\).
Part B

Let us consider the following equilibrium in the gas phase.

\[ D \rightleftharpoons 2M \quad (2) \]

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.

![Diagram of a cuboid container with a transparent movable wall]

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></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 (\( l = l_y0 \)) 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.

**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:

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

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.

<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>
<tr>
<td>Score</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 $\frac{\varepsilon_{HA}}{\varepsilon_{A^-}}$, where $\varepsilon_{HA}$ and $\varepsilon_{A^-}$ represent the absorption coefficients of HA and of $A^-$, respectively, at $\lambda_1$. 

10 pt
Part B

Let us consider the following equilibrium in the gas phase.

\[ D \rightleftharpoons 2M \quad (2) \]

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></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 \( \lambda_{B2} \).
Lambert–Beer Law?

Part A

A.1 (10 pt)

(Continued on the next page)
$\frac{\varepsilon_{HA}}{\varepsilon_{A^-}} =$
Part B

B.1 (6 pt)

\( \epsilon_D / \epsilon_M = \)
B.2 (6 pt)

\[ \varepsilon_D / \varepsilon_M = \]
IChO
Problem 4
Cover sheet

Please return this cover sheet together with all the related question sheets.
Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

**Part A**

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

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

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

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

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

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

**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.

**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.

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, $E^\circ$.

$$Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s) \hspace{1cm} E^\circ = 1.65 \text{ V}$$  \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.
B.3 Consider the change of e.m.f. of a zinc–air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are $-38^\circ$C (February) and 3776 m, respectively. The atmospheric pressure is represented by

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

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

B.4 **Calculate** the Gibbs energy change for reaction (6) at 25°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°C and 1 bar are given as (10) and (11), respectively.

$$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \hspace{2cm} E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.77 \text{ V}$$  \hspace{1cm} (10)

$$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \hspace{2cm} E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$$  \hspace{1cm} (11)
The Redox Chemistry of Zinc

Zinc has long been used in alloys for brass and steel materials. The zinc contained in industrial wastewater is removed by precipitation to detoxify the water, and the precipitate obtained 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°C and the relevant equilibrium constants are given in equations 1–4.

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

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

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

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

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

**A.1** When the equilibria in equations 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.2** 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 mole percent of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.

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

$$\text{Zn(OH)}_2 (s) \rightarrow \text{ZnO} (s) + \text{H}_2 \text{O} (l)$$ (6)

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

$$\text{ZnO} (s) + \text{H}_2 (g) \rightarrow \text{Zn} (s) + \text{H}_2 \text{O} (g)$$ (7)

**B.1** In order for reaction (7) to proceed at a constant hydrogen pressure of 1 bar, **CALCULATE** the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 °C. 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.

Metallurgical 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, $E^\circ$:

$$\text{Zn}(s) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{ZnO}(s) \quad E^\circ = 1.65 \text{ V}$$ (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) in the battery.
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 (deppe) of Mt. Fuji, where the temperature and altitude are −38°C (February) and 3776 m, respectively. The atmospheric pressure is represented by equation 9 below at altitude $h$ [m] and temperature $T$ [°C].

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

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

B.4  **CALCULATE** the Gibbs energy change for reaction (6) at 25°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°C and 1 bar are given as (10) and (11), respectively.

$$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn} \hspace{1cm} E^\circ(\text{Zn}^{2+/\text{Zn}}) = -0.77 \text{ V} \hspace{1cm} (10)$$

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \hspace{1cm} E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V} \hspace{1cm} (11)$$
The Redox Chemistry of Zinc

Part A

A.1 (6 pt)

< pH <
A.2 (5 pt)

%
Part B

B.1 (4 pt)

\[ P_{H_2O} = \text{bar} \]

B.2 (3 pt)

\[ \text{g} \]
B.3 (5 pt)
ΔG° = J mol⁻¹
IChO
Problem 5
Cover sheet

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 $R^1\equiv Si\equiv Si\equiv R^1$ (R: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.

$$R^1\equiv Si\equiv Si\equiv R^1 + H_2C\equiv CH_2 \rightarrow \begin{array}{c} \equiv \text{Si} \equiv \\ Si \equiv \text{Si} \end{array} R^1\equiv R^1$$

When $R^1\equiv Si\equiv Si\equiv R^1$ is treated with an alkyne ($R^2\equiv C\equiv C\equiv R^2$), the four-membered-ring compound A is formed as an initial intermediate. Further reaction of another molecule of $R^2\equiv C\equiv C\equiv R^2$ 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 $(R^1\equiv Si)_2(R^2\equiv C)_4$. 
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 $R^1$, $R^2$, Si, and 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).

Fig. 1

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 & \rightarrow \text{H}_3\text{C}=\text{CH}_3 \quad \Delta H = -135 \text{ kJ mol}^{-1} \\
\text{H}_2\text{Si}=\text{CH}_2 + \text{H}_2 & \rightarrow \text{H}_3\text{Si}=\text{CH}_3 \quad \Delta H = -213 \text{ kJ mol}^{-1} \\
\text{H}_2\text{Si}=\text{SiH}_2 + \text{H}_2 & \rightarrow \text{H}_3\text{Si}=\text{SiH}_3 \quad \Delta H = -206 \text{ kJ mol}^{-1} \\
\text{H}_2\text{Si}=\text{SiH} + 3 \text{ H}_2 & \rightarrow \text{H}_3\text{Si}=\text{SiH}_2 \quad \Delta H = -173 \text{ kJ mol}^{-1} \\
\text{H}_2\text{Si}=\text{SiH} + 3 \text{ H}_2 & \rightarrow \text{H}_2\text{Si} = \text{SiH}_2 \quad \Delta H = -326 \text{ kJ mol}^{-1} \\
\text{H}_2\text{Si}=\text{SiH} + 3 \text{ H}_2 & \rightarrow \text{H}_2\text{Si} = \text{SiH}_2 \quad \Delta H = -368 \text{ kJ mol}^{-1} \\
\text{H}_2\text{Si}=\text{SiH} + 3 \text{ H}_2 & \rightarrow \text{H}_2\text{Si} = \text{SiH}_2 \quad \Delta H = -389 \text{ kJ mol}^{-1}
\end{align*}
\]
When a xylene solution of C is heated, it undergoes isomerization to give an equilibrium mixture of compounds D and E. The molar ratio is D : E = 1 : 40.0 at 50.0 °C and D : E = 1 : 20.0 at 120.0 °C.

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

The isomerization from C to D and to E proceeds via transformations of π-bonds into σ-bonds without breaking any σ-bonds. A 13C NMR analysis revealed one signal for the Si2C4 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 R1, R2, 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 CCl4 using Na2SiF6 was carried out as follows.

• Standardization of Na2SiF6 solution:
  · Preparation
    Aqueous solution F: 0.855 g of Na2SiF6 (188.053 g mol⁻¹) dissolved in water (total volume: 200 mL).
    Aqueous solution G: 6.86 g of Ce2(SO4)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 Ce3⁺, 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 Ce3⁺, and the only resulting silicon compound is Si(OH)4.

B.1 Write the balanced equation for the reaction of Na2SiF6 with Ce2(SO4)3.

• Reaction of CCl4 with Na2SiF6:
  (Substance losses by e.g. evaporation are negligible during the following operations.)
  Na2SiF6(x [g]) was added to CCl4 (500.0 g) and heated to 300 °C in a sealed pressure-resistant reaction vessel. The unreacted Na2SiF6 and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with CCl4 (solution H). The 29Si and 19F NMR spectra of solution H showed SiF4 as the only silicon compound. In the 19F NMR spectrum, in addition to SiF4, signals corresponding to CFCl3, CF2Cl2, CF3Cl, and CF4 were observed (cf. Table 1). The integration ratios in the 19F NMR spectrum are proportional to the number of fluorine nuclei.

<table>
<thead>
<tr>
<th>19F NMR data</th>
<th>CFCl3</th>
<th>CF2Cl2</th>
<th>CF3Cl</th>
<th>CF4</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>
SiF$_4$ is hydrolyzed to form H$_2$SiF$_6$ according to the following eq. 8:

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

Solution H (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of SiF$_4$. After separation, the H$_2$SiF$_6$ generated from the hydrolysis in the aqueous solution was neutralized and completely converted to Na$_2$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.
- For 100 mL of solution K: 44.4 mL.

It should be noted here that the coexistence of NaCl or SiO$_2$ has no effect on the precipitation titration.

<table>
<thead>
<tr>
<th>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.</th>
<th>15pt</th>
</tr>
</thead>
</table>

| B.3 77.8% of the CCl$_4$ used as a starting material was unreacted. Calculate the mass of CF$_3$Cl generated. | 8pt |
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 written as $R^1\text{Si} \equiv \text{Si} \equiv R^1$ (R: organic substituent), is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.

\[
R^1\text{Si} \equiv \text{Si} \equiv R^1 + H_2C=\text{CH}_2 \rightarrow \text{Si} \equiv \text{Si}
\]

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

A.1 DRAW the structures of A, B, and C using $R_1$, $R_2$, Si, and C. (Only one resonance structure is needed, if applicable.)

A.2 CALCULATE the aromatic stabilization energy (ASE) for benzene and compound C (where $R_1 = R_2 = \text{H}$) as positive values. The enthalpy change of some hydrogenation reactions of unsaturated systems is shown below (Figure 1).

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

Figure 1.
When a xylene solution of C is heated, it undergoes isomerization to give an equilibrium mixture of compounds D and E. The mole 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 D 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. (E maddada, 2 sany 3 agzaly halkalar, 1 sany tarapy paylasjar)

A.4 **DRAW** the structures 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. Metal fluorides are often used as fluorination reagents and 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)$_4$.

B.1 **WRITE** the balanced equation for the reaction of Na$_2$SiF$_6$ with Ce$_2$(SO$_4$)$_3$. 5pt

**Reaction of CCl$_4$ with Na$_2$SiF$_6$**:
( Substance losses, *e.g.* by evaporation, are negligible during the following steps.)
- 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 CFCl$_3$, 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.
SiF₄ is hydrolyzed to form H₂SiF₆ according to the following equation:

\[
3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6
\]

- 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 above), 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. The entire amount of solution J required 61.6 mL of titrant to reach the endpoint. Separately, 100 mL of solution K used 44.4 mL of titrant to reach the endpoint. It should be noted here that the coexistence of NaCl or SiO₂ has no effect on the precipitation titration.

- For solution J (entire(āhli) 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.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>F NMR data</strong></td>
</tr>
<tr>
<td>Integration ratio</td>
</tr>
</tbody>
</table>

**B.2** CALCULATE the mass of the NaCl produced in the reaction vessel (underlined above), and **CALCULATE** the mass (\(x\) [g]) of the Na₂SiF₆ used as a starting material.

**B.3** 77.8% of the CCl₄ used as a starting material was unreacted. **CALCULATE** the mass of CF₃Cl generated.
Mysterious Silicon

Part A

A.1 (9 pt)

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

A.2 (7 pt)

\( C_6H_6 : \quad \text{kJ mol}^{-1}, \quad C : \quad \text{kJ mol}^{-1} \)
Δ\(H\) = \(\text{kJ mol}^{-1}\)

\[A.\,\text{(6 pt)}\]

\[A.\,\text{(10 pt)}\]

D (5 pt)  E (5 pt)
Part B

B.1 (5 pt)

---

B.2 (15 pt)

(Continued on the next page)
B.2 (cont.)

NaCl : __________ g, Na₂SiF₆ : __________ g
B.3 (8 pt)

CF₂Cl: __________ g
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>
<th>C.3</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>45</td>
</tr>
<tr>
<td>Score</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<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^{n+}) in the magma is incorporated into the silicate minerals. The M^{n+} studied in the problem are coordinated by oxide ions (O^{2-}) and adopt a four-coordinate tetrahedral (T_d) geometry in the magma and six-coordinate octahedral (O_h) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration. The distribution coefficient of M^{n+} between the silicate minerals and magma, D, can be expressed by:

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

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

<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.

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

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

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

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$_4$H$_2$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 CO$_2$. The total weight loss during the formation of A from B is 63.6%. It should be noted that only water and CO$_2$ are released in the pyrolysis reaction.

B.1 Write the chemical formulae for A and B.  

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

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

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

**Part C**

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$_4$(L1L1L1)$_4$ is composed of planar dicarboxylate L1 (Fig. 2B) and Cu$^{2+}$ (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 L1. Note that hydrogen atoms are not shown in Fig. 2.
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.
A zinc complex, Zn₄O(CH₃CO₂)₆, contains four tetrahedral Zn³⁺, six CH₃CO₂⁻, and one O²⁻ (Fig. 3A). In Zn₄O(CH₃CO₂)₆, the O²⁻ is located at the origin, and the three axes passing through the carbon atoms of CH₃CO₂⁻ are oriented orthogonal relative to each other. When p-benzenedicarboxylate (Fig. 3B, L₃, θ = 180°) is used instead of CH₃CO₂⁻, the Zn³⁺ 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 [Zn₄O(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 Zn³⁺ 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 × 10² mL of CO₂ gas in the pores at 1 bar and 25 °C. Calculate the average number of CO₂ molecules per pore.
The Solid-State Chemistry of Transition Metals

Part A

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

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

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

<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>

Volcano at Sakurajima island
Δ₀ is the energy separation of the d-orbitals of Mⁿ⁺, and CFSE₀ is the crystal-field stabilization energy in a Oₘ field. Let Δₜ and CFSEₜ be those in a Tₜₖ field.

A.1 CALCULATE ΔCFSE, defined as |CFSE₀ − CFSEₜ| in terms of Δ₀ for Cr²⁺, Mn²⁺, and Co²⁺; assume Δₜ = 4/9Δ₀.

A.2 A linear relationship is observed by plotting lnD against ΔCFSE / Δ₀ in the Cartesian coordinate system shown below. CALCULATE the approximate value of D for Co²⁺.

Metal oxides MO (M: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure wherein the Mⁿ⁺ adopts an Oₘ geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is primarily determined by the Coulombic interactions (due to the radius and charge of the ions) with some contribution from the CFSE of Mⁿ⁺ in the Oₘ 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 $A$, containing $\text{La}^{3+}$ and $\text{Cu}^{2+}$, crystallizes in a tetragonal unit cell shown in Figure 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 $d_{z^2}$).

$A$ 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 ($C_4H_2O_4$), a diacid. Upon pyrolysis in dry air to 200 °C, $B$ loses 29.1% of its mass due to the loss of crystallization water. Another weight loss is observed when heating is continued 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.

<table>
<thead>
<tr>
<th>B.1</th>
<th>WRITE the chemical formula for $A$ and $B$.</th>
<th>6pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.2</td>
<td>CALCULATE $l_x$ and $l_z$ using Figure 1.</td>
<td>4pt</td>
</tr>
<tr>
<td>B.3</td>
<td>For $\text{Cu}^{2+}$ in the distorted $[\text{CuO}<em>6]$ octahedron in $A$ of Figure 1, WRITE the names of the split $e_g$ orbitals ($d</em>{x^2-y^2}$ and $d_{z^2}$) on lines (i) and (ii), and PLACE electrons on the energy diagram in the dotted box on your answer sheet.</td>
<td>4pt</td>
</tr>
</tbody>
</table>
**A** is an insulator. One hole is generated in the crystal lattice of **A** when one La\(^{3+}\) is substituted with one Sr\(^{2+}\). As a result, the Sr\(^{2+}\)-doped **A** conducts electricity and shows superconductivity below 38 K. When the substitution described takes place in **A**, \(2.05 \times 10^{27}\) holes m\(^{-3}\) were generated.

### B.4 CALCULATE

the percentage of Sr\(^{2+}\) substituted for La\(^{3+}\) based on the mole ratio in the substitution. Note that the valencies of the constituent ions and the crystal structure are not altered by the substitution.

---

**Part C**

Cu\(_2\)(CH\(_3\)CO\(_2\))\(_4\) is composed of four CH\(_3\)CO\(_2\)\(^-\) coordinated to two Cu\(^{2+}\) (Figure 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\(_4\)(L1)\(_4\) is composed of planar dicarboxylate L1 (Figure 2B) and Cu\(^{2+}\) (Figure 2C). The structure of the cage complex is determined by the angle \(\theta\) between the coordination directions of the two carboxylates, indicated by the arrows in Figure 2B. \(\theta\) is 0° for L1. Hydrogen atoms are not shown in Figure 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 $L_2$ coordinate to Cu$^{2+}$ ions.
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 \( \text{O}^{2-} \) (Figure 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 \( p \)-benzenedicarboxylate (Figure 3B, \( \text{L}_3, \theta = 180^\circ \)) 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 (X) that is called a “porous coordination polymer” (Figure 3C). The composition of X is \([\text{Zn}_4\text{O} (\text{L}_3\text{L}_3\text{L}_3)]^m\), and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Figure 3D, and each tetrahedral \( \text{Zn}^{2+} \) cluster is represented as a dark gray polyhedron in Figures 3C and 3D. Hydrogen atoms are not shown in Figure 3.

**Figure 3.**

| C.2 | X has a cubic unit cell with a side length of \( a \) (Figure 3C) and a density of 0.592 g cm\(^{-3}\). **CALCULATE** \( a \) in [cm]. | 5pt |
| C.3 | X contains a considerable number of pores, and 1 g of X can accommodate \( 3.0 \times 10^2 \) mL of \( \text{CO}_2 \) gas in the pores at 1 bar and 25 °C. **CALCULATE** the average number of \( \text{CO}_2 \) molecules per pore. | 5pt |
The Solid-State Chemistry of Transition Metals

Part A

A.1 (6 pt)

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

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

A.3 (3 pt)

\[
\ln D \quad \text{vs.} \quad \frac{\Delta CFSE}{\Delta O}
\]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \]

\[ 0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \]
Part B

B.1 (6 pt)

A: ___________________ , B: ___________________

B.2 (4 pt)

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

(i) : , (ii) :

\[ e_g \]

\[ \text{Energy} \]

\[ (i) \]

\[ (ii) \]

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)
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.

Part A

Lineariifolanone 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.  

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 $\text{H}_2^{18}\text{O}$ is used instead of $\text{H}_2^{16}\text{O}$ for the synthesis of $^{18}\text{O}$-labelled-linearifolianones 13 and 14 from 11 and 12, respectively. Compounds 13 and 14 are $^{18}\text{O}$-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.

\[
\begin{align*}
\text{I} & \quad \text{F}_3\text{C-S-} \text{OH} \\
\text{II} & \quad \text{F}_3\text{C-S-} \text{NH}_2 \\
\text{III} & \quad \text{O=S-CF}_3 \\
\text{IV} & \quad \text{O=S-CF}_3 \\
\end{align*}
\]

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.
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.

\[ 16 \xrightarrow{\text{Br}_2, \text{CH}_3\text{COOH}} 17 \]
\[ 16 \xrightarrow{\text{Et}_3\text{N}, \text{CH}_2\text{Cl}_2} 18 \xrightarrow{\text{Cl}_2\text{S}_2\text{Cl}_2} 19 \]
\[ 20 + 19 \xrightarrow{\text{HCl}} 21 \xrightarrow{} 22 + 18 \]

$^1$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)

**B.1** *Draw* the structures of 17–19 and 21. Identifying the stereochemistry is not necessary. 10pt
Prof. Nozoe (1902–1996) started the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.

![Photo courtesy: Tohoku Univ.](image)

### Part A

Lineariifolianone is a natural product with a unique structure that was first isolated from *Inula linariifolia*. From valencene (1), a one-step conversion gives compound 2. A three-step conversion of 2, 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.
Ketone 4 is ultimately 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 $\text{H}_2^{18}\text{O}$ is used instead of $\text{H}_2^{16}\text{O}$ for the synthesis of $^{18}\text{O}$-labelled linearifolianones 13 and 14 from 11 and 12, respectively. Compounds 13 and 14 are $^{18}\text{O}$-labelled isotopomers. Ignoring isotopic labelling, both 13 and 14 provide the same product 15 with identical stereochemistry.
A.2 **CHOOSE** the appropriate structure for reagent A.  

1. \( \text{O} \text{S}^\text{CF}_3 \text{O} \)  
2. \( \text{O} \text{S}^\text{CF}_3 \text{NH}_2 \)  
3. \( \begin{array}{c} \text{N} \\ \text{S}^\text{CF}_3 \\ \text{O} \text{S}^\text{CF}_3 \end{array} \)  
4. \( \text{O} \text{S}^\text{CF}_3 \text{HN} \text{S}^\text{CF}_3 \)

---

A.3 **DRAW** the structures of 8-14 and clearly identify the stereochemistry where necessary. Also, **LABEL** the \( ^{18} \text{O} \) atoms in compounds 13 and 14 using the notation shown below:

![18O Atom Diagram]
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 the ion-pair intermediate 21. Although the formation of 21 was observed by NMR, 21 gradually decomposes to give 18 and 22.

\[
\begin{align*}
\text{16} & \quad \text{Br}_2 \quad \text{CH}_3\text{COOH} \\
& \quad \text{17} \\
& \quad \text{C}_{15}\text{H}_{12}\text{Br}_2\text{O} \\
\text{Et}_3\text{N} \quad \text{CH}_2\text{Cl}_2 & \quad \text{18} \\
& \quad \text{C}_{15}\text{H}_{10}\text{O} \\
\text{Cl}_2\text{S} & \quad \text{19} \\
& \quad \text{C}_{15}\text{H}_{10}\text{Cl}_2 \\
\text{20} + 19 & \quad \text{21} \\
& \quad \text{22} \quad \text{18} \\
\end{align*}
\]

\(^1\text{H} \text{NMR (CD}_3\text{CN, ppm)} \quad 20: \delta 7.4-7.2 \ (5\text{H}), \ 3.7 \ (2\text{H}), \ 2.8 \ (2\text{H}), \ 2.2 \ (1\text{H}) \\
21: \delta 8.5-7.3 \ (15\text{H}), \ 5.5 \ (2\text{H}), \ 3.4 \ (2\text{H})

B.1 DRAW the structures of 17–19 and 21. Ignore stereochemistry. 10pt
# Playing with Non-benzenoid Aromaticity

## Part A

<table>
<thead>
<tr>
<th>A.1 (5 pt)</th>
<th>2 (2 pt)</th>
<th>6 (3 pt)</th>
</tr>
</thead>
</table>

| A.2 (2 pt) |
A.3 (19 pt)

8 (3 pt)

9 (2 pt)

10 (2 pt)

11 (2 pt)

12 (2 pt)

13 (4 pt)

14 (4 pt)
Part B

B.1 (10 pt)

<table>
<thead>
<tr>
<th>17 (2 pt)</th>
<th>18 (2 pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>19 (3 pt)</th>
<th>21 (3 pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Please return this cover sheet together with all the related question sheets.
**Dynamic Organic Molecules and Their Chirality**

<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>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>9</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>26</td>
</tr>
</tbody>
</table>

Score

**Part A**

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

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

\[ \text{alkene} \xrightarrow{\text{hv}} \text{alkene} \xrightarrow{\text{hv}} \text{cyclohexane} \]
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.

<table>
<thead>
<tr>
<th>A.1</th>
<th>Draw the structures of A–C. Stereoisomers should be distinguished.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.2</td>
<td>Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product D whose molecular weight was 2 Da lower than that of [5]carbohelicene. The ( ^1 )H NMR chemical shifts of D are listed below. Draw the structure of D. [D (( \delta ), ppm in CS(_2), r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]</td>
</tr>
</tbody>
</table>

[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.

![diagram of carbohelicene with (M) and (P) enantiomers](image-url)

\([n]\)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.

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.
Dynamic Organic Molecules and Their Chirality

<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>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>9</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>4</td>
<td>26</td>
</tr>
</tbody>
</table>

Score

Part A

Polycyclic aromatic hydrocarbons with successive ortho-connections are called \([n]\)carbohelicenes (\(n\) represents the number of six-membered rings; see below). \([4]\)Carbohelicene (\([4]\)C) is efficiently prepared according to the synthesis shown below. The key photochemical reaction proceeds via the intermediate (Int.) that is then easily oxidized by iodine.

The photochemical reaction 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.

<table>
<thead>
<tr>
<th>A.1</th>
<th>DRAW the structures of A–C. Stereoisomers should be distinguished.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.2</td>
<td>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, product D whose molecular weight was 2 Da lower than that of [5]carbohelicene was isolated. The $^1$H NMR chemical shifts of D are listed below. DRAW the structure of D.</td>
</tr>
</tbody>
</table>

[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)]

[5]- and larger [n]carbohelicenes have helical(spiral) chirality and interconversion between enantiomers of these helicenes is very 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 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. Considering helical chirality, 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) and shown below.

\[
\text{E} \quad (1, 2, 3) = (P, P, P)
\]

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. Interconversion between stereoisomers does not occur during the reaction. **DRAW** one possible stereoisomer of G with the chirality defined as in the example above, including numerical labels. **LIST ALL** remaining stereoisomers with location numbers and M and P labels according to the same numbering. For instance, the other stereoisomers of E would be listed as \((1, 2, 3) = (P, M, P), (P, M, M), (P, P, M), (M, M, M), (M, M, P), (M, P, P), (M, P, M), \) and \((M, P, M)\).
Part B

Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name “sumanene” comes from a Sanskrit-Hindi word “suman” that means sunflower. The synthesis of sumanene was originally completed by a reaction sequence consisting 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 (ignore stereochemistry). 3pt
Starting with the optically active precursor $J$, the same reaction sequence gives the optically active sumanene derivative $K$. The stereocenters in $J$ are unchanged during the metathesis reaction. **DRAW** the structure of $K$ with appropriate stereochemistry.
# Dynamic Organic Molecules and Their Chirality

## 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 (3 pt)

---
A.3 (7 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>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
<th>A.5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>13</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>23</td>
</tr>
<tr>
<td>Score</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<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.

A.3 **Give** the number of the hydrogen bonds in the dimeric capsule (1₂).
The dimeric capsule of 1 (I₂) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

\[ Z + 1₂ \rightarrow Z@1₂ \]  

(1)

The equilibrium constant of the encapsulation of Z into I₂ is given as below:

\[ K_a = \frac{[Z@1₂]}{[Z][1₂]} \]  

(2)

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.

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 Hₐ proton of 2 in the above solvents are summarized below, and no other signals from the Hₐ 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>δ (ppm) of Hₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆D₆</td>
<td>4.60</td>
</tr>
<tr>
<td>C₆D₅F</td>
<td>4.71</td>
</tr>
<tr>
<td>C₆D₆/C₆D₅F</td>
<td>4.60, 4.71, 4.82</td>
</tr>
</tbody>
</table>

A.4 **Determine** the number of C₆D₆ and C₆D₅F molecules encapsulated in 2₂ giving three points each Hₐ signal.
$^1$H NMR measurements in C₆D₆ revealed that $2_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants ($K_a$) which are expressed below were determined for various temperatures. [solvent@$2_2$] denotes a species containing one or more solvent molecules.

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

Similarly, the $K_a$ values of CH₄ and $1_2$ given as eq (2) at various temperatures in C₆D₆ 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 C₆D₆ molecule is encapsulated in $1_2$. 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>
<tbody>
<tr>
<td>1</td>
<td>positive</td>
<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>$1_2$ and CH₄</td>
<td>$2_2$ and AdA</td>
</tr>
<tr>
<td>5</td>
<td>$1_2$ and CH₄</td>
<td>$2_2$ and AdA</td>
</tr>
</tbody>
</table>
Likes and Dislikes of Capsule

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
<th>A.5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Points</td>
<td>13</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>23</td>
</tr>
</tbody>
</table>

Score

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

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

1

2

3
The synthetic route to 2 is shown below. The composition of compound 9 by mass is C: 40.49%, H: 1.70%, and O: 17.98%.
A.1 **DRAW** the structures of 4-9; ignore stereochemistry. Use "PMB" as a substituent instead of drawing the whole structure of the 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 were observed to be chemically equivalent. The chemical shift was significantly different from that of the NH protons of 3. These data indicate that hydrogen bonds are formed between the NH groups 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 compound 1.

A.3 **WRITE** the number of hydrogen bonds in the dimeric capsule (1₂).
The dimeric capsule of $1$ ($1_2$) has an internal space where an appropriate small molecule $Z$ can be encapsulated. This phenomenon is expressed by the following equation:

$$Z + 1_2 \rightarrow Z@1_2$$  \hspace{1cm} (1)

The equilibrium constant of the encapsulation of $Z$ into $1_2$ is given below:

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

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, $1_2$ 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 large 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 kept constant. The chemical shifts for the $H^a$ protons of $2$ in the solvents given above are summarized below. No other signals due to the $H^a$ protons in $2$ were observed (except for those listed). 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. 3pt
$^1$H NMR measurements in C$_6$D$_6$ revealed that 2 can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants ($K_a$), expressed below, were determined at various temperatures. [solvent@2] denotes a species containing one or more solvent molecules.

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

(3)

Similarly, $K_a$ values of CH$_4$ and 1 (equation 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).

A.5 WRITE the correct letter, A or B, to fill in (1)–(5) in the following paragraph.  

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>positive</td>
<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>
# Likes and Dislikes of Capsule

**A.1** (13 pt)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4</strong> (2 pt)</td>
<td><strong>5</strong> (3 pt)</td>
</tr>
<tr>
<td><strong>6</strong> (2 pt)</td>
<td><strong>7</strong> (2 pt)</td>
</tr>
<tr>
<td><strong>8</strong> (2 pt)</td>
<td><strong>9</strong> (2 pt)</td>
</tr>
</tbody>
</table>
A.2 (2 pt)

![Chemical Structure]

A.3 (2 pt)

A.4 (3 pt)

<table>
<thead>
<tr>
<th>δ (ppm) of H</th>
<th>numbers of C₆D₆</th>
<th>numbers of C₆D₅F</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.60 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.71 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.82 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A.5 (3 pt)

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

(4) :  (5) :