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 Instructions

• You are only allowed to use pen to write the 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.
• 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 rough 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.
• You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to go to the toilet, 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>
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<tr>
<td>9 Likes and Dislikes of Capsules</td>
<td>23</td>
<td>10</td>
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<tr>
<td>Total</td>
<td>100</td>
<td></td>
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</tbody>
</table>
### Physical Constants and Equations

#### Constants

<table>
<thead>
<tr>
<th>Physical Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed of light in vacuum</td>
<td>$c = 2.99792458 \times 10^8$ m s$^{-1}$</td>
</tr>
<tr>
<td>Planck constant</td>
<td>$h = 6.62607015 \times 10^{-34}$ J s</td>
</tr>
<tr>
<td>Elementary charge</td>
<td>$e = 1.602176634 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Electron mass</td>
<td>$m_e = 9.10938370 \times 10^{-31}$ kg</td>
</tr>
<tr>
<td>Electric constant (permittivity of vacuum)</td>
<td>$\varepsilon_0 = 8.85418781 \times 10^{-12}$ F m$^{-1}$</td>
</tr>
<tr>
<td>Avogadro constant</td>
<td>$N_A = 6.02214076 \times 10^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>$k_B = 1.380649 \times 10^{-23}$ J K$^{-1}$</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>$F = N_A \times e = 9.64853321 \times 10^4$ C mol$^{-1}$</td>
</tr>
<tr>
<td>Gas constant</td>
<td></td>
</tr>
</tbody>
</table>
  - $R = N_A \times k_B = 8.3144626$ J K$^{-1}$ mol$^{-1}$
  - $= 8.2057366 \times 10^{-2}$ L atm K$^{-1}$ mol$^{-1}$
| Unified atomic mass unit | $u = 1$ Da $= 1.66053907 \times 10^{-27}$ kg |
| Standard pressure | $p = 1$ bar $= 10^5$ Pa |
| Atmospheric pressure | $p_{atm} = 1.01325 \times 10^5$ Pa |
| Zero degrees Celsius | $0$ °C $= 273.15$ K |
| Ångstrom | $1$ Å $= 10^{-10}$ m |
| Picometer | $1$ pm $= 10^{-12}$ m |
| Electronvolt | $1$ eV $= 1.602176634 \times 10^{-19}$ J |
| Part-per-million | $1$ ppm $= 10^{-6}$ |
| Part-per-billion | $1$ ppb $= 10^{-9}$ |
| Part-per-trillion | $1$ ppt $= 10^{-12}$ |
| Pi | $\pi = 3.141592653589793$ |
| The base of the natural logarithm (Euler’s number) | $e = 2.718281828459045$ |

---
### Equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PV = nRT$</td>
<td>The ideal gas law, 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>$F = k_e \frac{q_1 q_2}{r^2}$</td>
<td>Coulomb’s law, 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>$\Delta U = q + w$</td>
<td>The first law of thermodynamics, where $\Delta U$ is the change in the internal energy, $q$ is the heat supplied, $w$ is the work done.</td>
</tr>
<tr>
<td>$H = U + PV$</td>
<td>Enthalpy $H$,</td>
</tr>
<tr>
<td>$S = k_B \ln W$</td>
<td>Entropy based on Boltzmann’s principle $S$, where $W$ is the number of microstates.</td>
</tr>
<tr>
<td>$\Delta S = \frac{q_{\text{rev}}}{T}$</td>
<td>The change of entropy $\Delta S$, where $q_{\text{rev}}$ is the heat for the reversible process.</td>
</tr>
<tr>
<td>$G = H - TS$</td>
<td>Gibbs free energy $G$,</td>
</tr>
<tr>
<td>$\Delta_r G^\circ = -RT \ln K = -zFE^\circ$</td>
<td>$\Delta_r G^\circ$ is the change of the Gibbs free energy for a reaction, $K$ is the equilibrium constant, $z$ is the number of electrons, $E^\circ$ is the standard electrode potential.</td>
</tr>
<tr>
<td>$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$</td>
<td>Reaction quotient $Q$, 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>$\Delta q = n c_m \Delta T$, where $c_m$ is the temperature-independent molar heat capacity.</td>
</tr>
<tr>
<td>Nernst equation for a redox reaction</td>
<td>$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$, where $C_{\text{ox}}$ is the concentration of the oxidized substance, $C_{\text{red}}$ is the concentration of the 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, and $c$ 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>$E = h \nu = \frac{h \nu}{\lambda}$, 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 $x \neq 1$, $1 + x + x^2 + \ldots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$</td>
</tr>
<tr>
<td>Approximation equation that can be used to solve problems</td>
<td>When $x \ll 1$, $\frac{1}{1 - x} \approx 1 + x$</td>
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</table>
The Periodic Table

<table>
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<tr>
<th>1</th>
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<tr>
<td>H</td>
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<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
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<td>Mg</td>
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<td>Si</td>
<td>P</td>
<td>S</td>
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<td>Ar</td>
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<td>H</td>
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<td>V</td>
<td>Cr</td>
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<td>Cu</td>
<td>Zn</td>
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<td>Ge</td>
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<td>Br</td>
<td>Kr</td>
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<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
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<td>Sn</td>
<td>Sb</td>
<td>Te</td>
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<td>Xe</td>
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<td>114.818</td>
<td>118.710</td>
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<tr>
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<td>Ba</td>
<td>La</td>
<td>Lu</td>
<td>Hf</td>
<td>Ta</td>
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<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
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<td>123.905</td>
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<td>192.217</td>
<td>195.084</td>
<td>196.973</td>
<td>200.592</td>
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<td>207.2</td>
<td>208.98</td>
<td>210</td>
<td>223</td>
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</tbody>
</table>
| Fr | Ra | Ac-Lr | Actinoids | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn | Nh | Fl | Mc | Lr | Op 
| 223 | 226 | 244 | 259 | 261 | 269 | 277 | 286 | 293 | 302 | 306 | 308 | 310 | 313 | 318 | 320 | 325 | 326 |
${^1}$H NMR Chemical Shifts

Δδ for one alkyl group-substitution: *ca.* +0.4 ppm
Please return this cover sheet together with all the related question sheets.
Hydrogen is anticipated 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 transportation 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 \((\text{H}_2)\) that reach the metal surface \((M)\) dissociate at the surface and are adsorbed as \(\text{H}\) 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 \(\text{H}\) atoms is parallel to the surface and that the centre 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 \(\text{H}_2\). The solid line spacing is 20 kJ mol\(^{-1}\), the dashed line spacing is 100 kJ mol\(^{-1}\), and the spacing between solid and dashed lines is 80 kJ mol\(^{-1}\). The zero-point vibration energy is ignored.
Fig. 1 Definition of variables. Drawing is not to scale.

Fig. 2
A.1 For each of the following items (i)–(iii), select the closest value from A–G.

(i) The interatomic distance for a gaseous H\(_2\) molecule
(ii) The interatomic distance between metal atoms (\(d_M\) in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface (\(h_{ad}\) in Fig. 1)

<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>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E. 0.19 nm</td>
<td>F. 0.23 nm</td>
<td>G. 0.27 nm</td>
<td></td>
</tr>
</tbody>
</table>

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

(i) the energy required for the dissociation of gaseous H\(_2\) to gaseous H

\[H_2(g) \rightarrow 2H(g)\]

(ii) the energy released during the adsorption of gaseous H\(_2\)

\[H_2(g) \rightarrow 2H(ad)\]

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

\[
\begin{align*}
H_2(g) & \xrightarrow{k_1} 2H(ad) \quad (1a) \\
H(ad) & \xrightarrow{k_3} H(ab) \quad (1b)
\end{align*}
\]

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:

\[
\begin{align*}
r_1 &= k_1 P_{H_2} (1 - \theta)^2 \\
r_2 &= k_2 \theta^2 \\
r_3 &= k_3 \theta
\end{align*}
\]

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

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

\[ B.1 \quad r_3 \text{ can be expressed as:} \]

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

Express \( C \) using \( k_1 \) and \( k_2 \).
A metal sample with a surface area of \( S = 1.0 \times 10^{-3} \, \text{m}^2 \) was placed in a 1L container (1L = 1.0 \times 10^{-3} \, \text{m}^3) with \( \text{H}_2 \) at pressure \( P_{\text{H}_2} = 1.0 \times 10^2 \, \text{Pa} \). The density of hydrogen-atom adsorption sites on the surface was \( N = 1.3 \times 10^{18} \, \text{m}^{-2} \). The surface temperature was kept at \( T = 400 \, \text{K} \).

As the reaction (1) proceeded, \( P_{\text{H}_2} \) decreased at a constant rate of \( v = 4.0 \times 10^{-4} \, \text{Pa} \, \text{s}^{-1} \). Assume that \( \text{H}_2 \) is an ideal gas and that the volume of the metal sample is negligible.

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

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

**B.4** At a different \( T \), \( C = 2.5 \times 10^3 \, \text{Pa}^{-1} \) and \( k_3 = 4.8 \times 10^{-2} \, \text{s}^{-1} \). For \( r_3 \) as a function of \( P_{\text{H}_2} \) at this temperature, select the correct plot from (a)-(h).
# Hydrogen at a Metal Surface

## Part A

**A.1 (6 pt)**

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

**A.2 (4 pt)**

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

B.1 (5 pt)

\[ C = \]

B.2 (3 pt)

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

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

B.4 (3 pt)

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

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

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

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

Calculate the equilibrium constant, $K$, for eq. 3 at very low temperatures (as $T \to 0$) and at very high temperatures (as $T \to +\infty$). 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 considering molecular vibrations.

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

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

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

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

where $k$ 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:

$$
\mu = \frac{m_1m_2}{m_1 + m_2}
$$

A.2 The vibration of $H_2$ is at 4161.0 cm$^{-1}$.

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

$$
2HD \rightarrow H_2 + D_2
$$

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 is 1 Da and the mass of D is 2 Da.
In a system in equilibrium, the molar ratios among H\textsubscript{2}, HD, and D\textsubscript{2} depend on the temperature. We define \( \Delta_{D_2} \) 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 \( T \to +\infty \).

It should be noted here that the distribution of isotopes becomes random at \( T \to +\infty \).

A.3 Calculate \( \Delta_{D_2} \) when the isotopic exchange is equilibrated at the temperature where \( K \) in eq. 4 is 0.300. Assume that the natural abundance of D is \( 1.5576 \times 10^{-4} \) and the natural abundance of H is \( (1 - 1.5576 \times 10^{-4}) \).
A doubly substituted isotopologue contains two heavy isotope atoms in one molecule.
The molar ratio of the doubly substituted isotopologue increases with decreasing temperature.
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 $T \rightarrow +\infty$.

The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

<table>
<thead>
<tr>
<th></th>
<th>$^{12}$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 $4.50865 \times 10^{-5}$.  

**Estimate** the temperature using this $R_{47}$.

This temperature corresponds to the air temperature during the era in which the plankton lived.

Consider only the most common isotopologue of CO$_2$[47] for the calculation.
Isotope Time Capsule

A.1 (8 pt)

\[ T \to 0 : K = \quad , \quad T \to +\infty : K = \quad \]
\[ \Delta H = \text{J mol}^{-1} \]
\[ T = \text{K} \]
Please return this cover sheet together with all the related question sheets.
**Lambert–Beer Law?**

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>B.1</th>
<th>B.2</th>
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</thead>
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<td>6</td>
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</tr>
<tr>
<td>Score</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

**Part A**

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

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

In Part A, the optical path length is \( l \). 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 \( \lambda_1 \). Solution \( X \) was then diluted to twice its initial volume using hydrochloric acid with a pH = 2.500. After the dilution, the absorbance was still \( A_1 \) at \( \lambda_1 \).
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Determine</strong> the ratio ( \varepsilon_{HA}/\varepsilon_{A^-} ), where ( \varepsilon_{HA} ) and ( \varepsilon_{A^-} ) represent the absorption coefficients (at ( \lambda_1 )) of HA and A(^-), respectively.</td>
</tr>
</tbody>
</table>
Part B

Consider the following equilibrium in the gas phase.

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

A cuboidal container has a transparent movable wall with a cross-section of \( S \) (see the figure below). The container is filled with pure gas \( D \) at a pressure \( P \), and equilibrium is established while the total pressure is maintained at \( P \).

The absorbance of the gas is \( A = \varepsilon (n/V)l \), where \( \varepsilon \) is the absorption coefficient, \( n \) the amount of the gas in moles, \( V \) the volume of the gas, and \( l \) the optical path length. 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>
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</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 in direction \( x \) (i.e. \( l = l_x \)) 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 in direction \( y \) was \( A_{B2} \) both at the initial state (where \( l = l_y \)) and after the equilibrium (where \( l = l_y' \)).

Determine the ratio \( \varepsilon_D/\varepsilon_M \) at \( \lambda_{B2} \).
Lambert–Beer Law?

Part A

A.1 (10 pt)

(Continued on the next page)
A.1 (cont.)

\[ \frac{\varepsilon_{HA}}{\varepsilon_{A^-}} = \]
Part B

B.1 (6 pt)

$$\frac{\varepsilon_D}{\varepsilon_M} = \text{______________}$$
B.2 (6 pt)

\[ \frac{\varepsilon_D}{\varepsilon_M} = \]
IChO
Problem 4
Cover sheet

Please return this cover sheet together with all the related question sheets.
The Redox Chemistry of Zinc

<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>
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<td>5</td>
<td>4</td>
<td>3</td>
<td>5</td>
<td>9</td>
<td>32</td>
</tr>
</tbody>
</table>

Zinc has long been used in alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to purify the water. The precipitate is reduced to recover 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 eq. 1–4.

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

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

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

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

$$S = [\text{Zn}^{2+}(\text{aq})] + [\text{Zn(OH)}_2(\text{aq})] + [\text{Zn(OH)}_4^{2-}(\text{aq})]$$  \hspace{1cm} (5)

**A.1** 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 $[\text{Zn(OH)}_4^{2-}(\text{aq})]$ once the equilibria in eq. 1–4 are established.

**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 the pH is increased 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:

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

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

$$\text{ZnO}(s) + \text{H}_2(g) \rightarrow \text{Zn}(s) + \text{H}_2\text{O}(g)$$  \hspace{1cm} (7)

**B.1** It is necessary to reduce the partial pressure of the water vapour formed, so reaction (7) can proceed at a constant hydrogen pressure of 1 bar.

**Calculate** the upper limit for the partial pressure of water vapour to allow reaction (7) to proceed at 300 °C.

Gibbs free energies of formation at 300 °C and 1 bar for all gaseous species are:

$\Delta G_{\text{ZnO}}(300{^\circ}\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$

$\Delta G_{\text{H}_2\text{O}}(300{^\circ}\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$
Metallic zinc is used as a negative electrode (anode) material for metal-air batteries. The electrode consists of Zn and ZnO.

At 25 °C and pressure of 1 bar, the following redox reaction generates electricity with the electromotive force (e.m.f.), $E^\circ$.

$$\text{Zn}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{ZnO}(s) \quad E^\circ = 1.65 \text{ V}$$ (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) of the battery.

**Mt. Fuji**

**B.3** Consider the change in e.m.f. of a zinc–air battery due to the environment.

**Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are −38 °C (February) and 3776 m, respectively.

The atmospheric pressure is represented by

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

at altitude $h \ [\text{m}]$ and temperature $T \ [\text{°C}]$.

The molar proportion of oxygen in the atmosphere is 21%.

The Gibbs free energy change of reaction (8) at −38 °C and 1 bar is

$$\Delta G_{\text{ZnO}}(−38 \text{°C}) = −3.26 \times 10^2 \text{ kJ mol}^{-1}.$$
B.4 **Calculate** the Gibbs free energy change for reaction (6) at 25°C.

The standard reduction potentials at 25°C and 1 bar, \( E^\circ(\text{Zn}^{2+}/\text{Zn}) \) and \( E^\circ(\text{O}_2/\text{H}_2\text{O}) \) are given as (10) and (11).

\[
\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.77 \text{V} \quad (10)
\]

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

Part A

A.1 (6 pt)

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

**B.1 (4 pt)**

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

**B.2 (3 pt)**

\[ \_\_\_\_\_\_ g \]
B.3 (5 pt)
\[ \Delta G^\circ = \text{J mol}^{-1} \]
Please return this cover sheet together with all the related question sheets.
The group 14 elements carbon and silicon differ significantly in their properties.

**Part A**

Unlike the carbon–carbon triple bond, the silicon–silicon triple bond, \( \text{R}^1\equiv\text{Si} \equiv \text{Si} \equiv \text{R}^1 \) (R: organic substituent), is extremely reactive. For example, it reacts with ethene to form a four-membered ring.

\[
\text{R}^1\equiv\text{Si} \equiv \text{Si} \equiv \text{R}^1 + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \begin{array}{c}
\text{Si} \\ \equiv \\
\text{Si} \\
\equiv \\
\text{R}^1 \\
\end{array}
\]

When \( \text{R}^1\equiv\text{Si} \equiv \text{Si} \equiv \text{R}^1 \) is treated with an alkyne \( \text{R}^2\equiv\text{C} \equiv \text{C} \equiv \text{R}^2 \), the four-membered-ring compound A is formed as an initial intermediate. Further reaction of A with another molecule of \( \text{R}^2\equiv\text{C} \equiv \text{C} \equiv \text{R}^2 \) gives isomers B and C, both of which have benzene-like cyclic conjugated structures.

These so-called ‘disilabenzenes’ contain a six-membered ring and can be formulated as \( (\text{R}^1\equiv\text{Si})_2(\text{R}^2\equiv\text{C})_4 \).
C NMR analysis of the corresponding Si₂C₆ six-membered ring skeletons shows two signals for B and one signal for C.

### A.1 Draw the structural formulae of A, B, and C using R¹, R², Si, and C, as one of the possible resonance structures.

### A.2 Calculate the aromatic stabilisation energy (ASE) for benzene and C (in the case of R¹ = R² = H) as positive values, given the enthalpy change of some hydrogenation reactions of unsaturated systems shown below (Fig. 1).

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

### A.3 Calculate \( \Delta H \) for the transformation of D to E.

Assume that \( \Delta H \) does not depend on temperature.

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

### A.4 Draw the structural formulae of D and E using \( R^1 \), \( R^2 \), Si, and C.

---

### Part B

Silicon is able to form highly coordinated compounds (more than four substituents) with electronegative elements such as fluorine. Like metal fluorides, highly coordinated silicon fluorides can also act as fluorination reagents.

The fluorination reaction of \( \text{CCl}_4 \) using \( \text{Na}_2\text{SiF}_6 \) was carried out as follows.

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

- **Reaction of \( \text{CCl}_4 \) with \( \text{Na}_2\text{SiF}_6 \):**
  (Substance losses, e.g. by evaporation, are negligible during the following steps.)
  \( \text{Na}_2\text{SiF}_6 (x \text{ g}) \) was added to \( \text{CCl}_4 \) (500.0 g) and heated to 300 °C in a sealed vessel.
  The unreacted \( \text{Na}_2\text{SiF}_6 \) and \( \text{NaCl} \) produced were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with \( \text{CCl}_4 \) (solution H).

  The \(^{29}\text{Si}\) and \(^{19}\text{F}\) NMR spectra of solution H showed \( \text{SiF}_4 \) as the only silicon compound. In the \(^{19}\text{F}\) NMR spectrum, in addition to \( \text{SiF}_4 \), signals corresponding to \( \text{CFCl}_3 \), \( \text{CF}_2\text{Cl}_2 \), \( \text{CF}_3\text{Cl} \), and \( \text{CF}_4 \) were observed (cf. Table 1). The integrals in the \(^{19}\text{F}\) NMR spectrum are proportional to the number of fluorine nuclei.
SiF₄ is hydrolysed to form H₂SiF₆ according to the following eq. 8:

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

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

The precipitate of unreacted Na₂SiF₆ and NaCl, which was removed by filtration in the initial step (previously 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 the entire amount of solution J: 61.6 mL.
- For 100 mL of solution K: 44.4 mL.

The presence of NaCl or SiO₂ has no effect on the precipitation titration.

---

### Table 1

<table>
<thead>
<tr>
<th>¹⁹F NMR data</th>
<th>CFCl₃</th>
<th>CF₂Cl₂</th>
<th>CF₃Cl</th>
<th>CF₄</th>
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</thead>
<tbody>
<tr>
<td>Integral</td>
<td>45.0</td>
<td>65.0</td>
<td>18.0</td>
<td>2.0</td>
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</tbody>
</table>

---

B.2 **Calculate** the mass of NaCl produced in the reaction vessel (information previously underlined), and **calculate** the mass (\(x\) [g]) of the Na₂SiF₆ used as starting material.

B.3 77.8% of the CCl₄ used as a starting material did not react. **Calculate** the mass of CF₃Cl generated.
## Mysterious Silicon

### Part A

<table>
<thead>
<tr>
<th>A.1 (9 pt)</th>
<th>A (3 pt)</th>
<th>B (3 pt)</th>
<th>C (3 pt)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>A.2 (7 pt)</th>
</tr>
</thead>
</table>

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

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

A.4 (10 pt)

D (5 pt)  

E (5 pt)
Part B

B.1 (5 pt)

B.2 (15 pt)

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

NaCl : g, Na₂SiF₆ : g
B.3 (8 pt)

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

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

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

Volcano at Sakurajima island

Part A
Japan has many volcanoes. When silicate minerals crystallize from magma, some 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$^{2-}$). They adopt a four-coordinate tetrahedral ($T_d$) geometry in the magma and a 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>

In an $O_h$ field, $\Delta \sigma$ is the energy separation of the d-orbitals of $M^{n+}$ and CFSE$^O$ is the crystal-field stabilization energy. $\Delta T$ and CFSE$^T$ are the equivalents in a $T_d$ field.

**A.1** $\Delta$CFSE is defined as:

$$\Delta\text{CFSE} = |\text{CFSE}^O - \text{CFSE}^T|$$

**Calculate** $\Delta$CFSE in terms of $\Delta \sigma$ for Cr$^{2+}$, Mn$^{2+}$, and Co$^{2+}$.

Assume $\Delta T = 4/9 \Delta \sigma$.

**A.2** A linear relationship is observed by plotting $\ln D$ against $\Delta$CFSE / $\Delta \sigma$ as shown below.

**Estimate** $D$ for Co$^{2+}$.
Metal oxides, MO (where M is Ca, Ti, V, Mn, or Co), crystallise 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>
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<td>(c)</td>
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<tr>
<td>(d)</td>
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<tr>
<td>(e)</td>
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<tr>
<td>(f)</td>
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<td>3913</td>
<td>3916</td>
<td>3460</td>
<td>3878</td>
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</table>
Part B

A mixed oxide \( \text{A} \), which contains \( \text{La}^{3+} \) and \( \text{Cu}^{2+} \), crystallises in a tetragonal unit cell shown in Fig. 1. The \([\text{CuO}_6]\) octahedron is distorted from the regular \( O_h \) geometry: the Cu–O length along the \( z \)-axis \( (l_z) \) is longer than that of the \( x \)-axis \( (l_x) \).

This distortion removes the degeneracy of the \( e_g \) orbitals \( (d_{x^2-y^2} \) and \( d_{z^2}) \).

\( \text{A} \) can be synthesised by thermal decomposition of complex \( \text{B} \). \( \text{B} \) is formed by mixing metal chlorides in dilute aqueous ammonia solution containing the diacid, squaric acid \( \text{C}_4\text{H}_2\text{O}_4 \).

The thermal decomposition of \( \text{B} \) in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallisation water, followed by another weight loss up to 700 °C due to the release of \( \text{CO}_2 \).

The total weight loss during the formation of \( \text{A} \) from \( \text{B} \) is 63.6%. Only water and \( \text{CO}_2 \) are released in the thermal decomposition reaction.

| B.1 | Write the chemical formulae for \( \text{A} \) and \( \text{B} \). | 6pt |
| B.2 | Calculate \( l_x \) and \( l_z \) using Fig. 1. | 4pt |
| B.3 | Complete the diagram in your answer sheet for \( \text{Cu}^{2+} \) in the distorted \([\text{CuO}_6]\) octahedron in \( \text{A} \) 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).  
  • Draw the electron configuration in the dotted box. | 4pt |
\textbf{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 \textbf{A} shows superconductivity below 38 K.

When a substitution reaction took place for \textbf{A}, $2.05 \times 10^{27}$ holes m$^{-3}$ were generated.

\textbf{B.4} \textit{Calculate} the percentage of La$^{3+}$ substituted by Sr$^{2+}$ based on the mole ratio in the substitution reaction.

Note that the valence of the constituent ions and the crystal structure are not altered by the substitution reaction.

\textbf{Part C}

Cu$_2$(CH$_3$CO$_2$)$_4$ is composed of four CH$_3$CO$_2^-$ ions coordinated to two Cu$^{2+}$ ions (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.

A “cage complex” is formed if a dicarboxylate ligand is used instead of CH$_3$CO$_2^-$. 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.

For L1 $\theta = 0^\circ$.

\textit{Note that hydrogen atoms are not shown in Fig. 2.}
C.1 The θ of the planar dicarboxylate \( \text{L2} \) below is fixed to 90°. 
The cage complex formed from \( \text{L2} \) and Cu\(^{2+} \) is \( \text{Cu}_n(\text{L2})_m \). 

Give the smallest integer combination of \( n \) and \( m \).
Assume that only the CO\(_2^-\) groups of \( \text{L2} \) form a coordination bond to Cu\(^{2+} \) ions.
A zinc complex, Zn₄O(CH₃CO₂)₆, contains four tetrahedral Zn²⁺, 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 Zn²⁺ 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 Zn²⁺ cluster is represented as a dark grey polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

---

### C.2 X has a cubic unit cell with a side length of a (see Fig. 3C) and a density of 0.592 g cm⁻³.

**Calculate** a in [cm].

---

### C.3 X contains a considerable number of pores.

1 g of X can accommodate $3.0 \times 10^4$ 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

A.1 (6 pt)

\[ \text{Cr}^{2+} : \Delta_{\text{O}}, \text{Mn}^{2+} : \Delta_{\text{O}}, \text{Co}^{2+} : \Delta_{\text{O}} \]
\[ D : \] 

\[ \ln D \]

\[ \frac{\Delta CFSE}{\Delta_O} \]
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) : ........................................

\[ \text{Energy} \]

\[ e_g \]

\[ (i) \quad (ii) \]

B.4 (4 pt)
<table>
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</thead>
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<td><strong>C.1 (5 pt)</strong></td>
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<tr>
<td>( n = ) ( m = )</td>
</tr>
<tr>
<td><strong>C.2 (5 pt)</strong></td>
</tr>
<tr>
<td>( a = ) cm</td>
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Please return this cover sheet together with all the related question sheets.
Playing with Non-benzenoid Aromaticity

<table>
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Prof. Nozoe (1902–1996) founded the research field of non-benzenoid aromatic compounds.

Photo credit: Tohoku Univ.

Part A

Linearifolianone is a natural product 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 stereo-centres in 7. Compounds 9 and 10 have five stereocentres and no carbon-carbon double bonds.

Assume that H$_2^{18}$O is used instead of H$_2^{16}$O for the synthesis of $^{18}$O-labelled-lineariifolianones 13 and 14 from 11 and 12, respectively.

Compounds 13 and 14 are $^{18}$O-labelled isotopomers. Both 13 and 14 provide the same product 15 with identical stereochemistry ignoring isotopic labelling.
\[ \text{4} \xrightarrow{\text{K, Si-N-Si (KHMDSS)}} \text{A} \xrightarrow{\text{THF, -78 °C}} \text{7} \xrightarrow{\text{Li, N}} \]

\[ \text{8} \xrightarrow{\text{Cl, O, O-H, mCPBA, NaHCO}_3, \text{CH}_2\text{Cl}_2, 0 °C} \text{9} + \text{10} \]

\[ \text{9} \xrightarrow{\text{Nal, THF, 80 °C}} \text{11} \]
\[ \text{10} \xrightarrow{\text{Nal, THF, 80 °C}} \text{12} \]

\[ \text{13} \xrightarrow{\text{H}_2\text{O}, \text{THF}} \]
\[ \text{14} \xrightarrow{\text{H}_2\text{O}, \text{THF}} \]

\[ \text{15} \xrightarrow{\text{CH}_3\text{OH}} \]

\[ \text{16O-13/16O-14 (C}_{15}\text{H}_{22}{ }^{16}\text{O}_3) \]
A.2 **Choose** the appropriate structure for A.  

I. $\text{F}_3\text{C-S-OH}$  

II. $\text{F}_3\text{C-S-NH}_2$  

III. $\text{N-S=O}$

IV. $\text{O=S-CF}_3$  

---

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

![Example Structure]
Part B

Compound 19 is synthesised as shown below. Linking 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.

\[ \text{16} \xrightarrow{\text{Br}_2, \text{CH}_3\text{COOH}} \text{17} \]

\[ \text{Et}_3\text{N}, \text{CH}_2\text{Cl}_2 \quad \text{18} \]

\[ \text{O} \quad \text{19} \quad \text{Cl}_2\text{S}_2\text{Cl} \]

\[ \text{20} + 19 \xrightarrow{-\text{HCl}} \text{21} \quad \xrightarrow{} \quad \text{22} + 18 \]

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

B.1 Draw the structures of 17–19 and 21. Stereochemistry is not required. 10pt
### Playing with Non-benzenoid Aromaticity

#### Part A

<table>
<thead>
<tr>
<th>A.1 (5 pt)</th>
</tr>
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<tbody>
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#### A.2 (2 pt)
### Part B

**B.1 (10 pt)**

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<td><strong>19</strong> (3 pt)</td>
<td><strong>21</strong> (3 pt)</td>
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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>
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<td>3</td>
<td>7</td>
<td>3</td>
<td>4</td>
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</tbody>
</table>

**Part A**

Polycyclic aromatic hydrocarbons with successive ortho-connections are called [n]carbohelicenes (here, \( n \) represents the number of six-membered rings) (see below).

[4]Carbohelicene ([4]C) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (Int.) that is readily oxidized by iodine.

![Chemical Structure](image1.png)

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

![Chemical Structure](image2.png)
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.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A.1</strong></td>
<td><strong>Draw</strong> the structures of A–C. Stereoisomers should be distinguished.</td>
</tr>
<tr>
<td><strong>A.2</strong></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.</td>
</tr>
<tr>
<td></td>
<td><strong>Draw</strong> the structure of D.</td>
</tr>
<tr>
<td></td>
<td>The $^1$H NMR chemical shifts of D are listed below.</td>
</tr>
<tr>
<td></td>
<td>[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 very slow at room temperature. The chirality of [n]carbohelicenes is defined as \( (M) \) or \( (P) \) as shown below.

\[ (M) \leftrightarrow (P) \]

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

Photo credit: The Japan Prize Foundation
A molecule that contains two or more helicene-like structures is called a multiple-helicene. If helical chirality is considered there can be several stereoisomers of a multiple-helicene.

For example, compound E contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as (P, P, P) as shown below.
The nickel-mediated trimerisation 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 duplicating stereoisomers.

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 catalysed by a ruthenium catalyst (Ru*) are shown below.

B.1 **Draw** the structure of intermediate I (its stereochemistry is not required). 3pt
Starting from the optically active precursor J, the same reaction sequence gives the optically active sumanene derivative K. The stereocentres in J suffer no inversion during the metathesis reaction. **Draw** the structure of K with the appropriate stereochemistry.
# Dynamic Organic Molecules and Their Chirality

## Part A

<table>
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<td>B (3 pt)</td>
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<table>
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Part B

B.1 (3 pt)

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

<table>
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<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
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If you cut a tennis ball along the seam, you can disassemble it into two U-shaped pieces.

Compounds 1 and 2 are U-shaped molecules with different sizes, inspired by this idea. Compound 3 was prepared for comparison with 1 and the encapsulation behaviour of these compounds was investigated.
The synthetic route to 2 is shown below. 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; stereochemistry can be neglected. Use the "PMB" abbreviation 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 spectrum 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:

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

(1)

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

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

(2)

Encapsulation of a molecule into a capsule can be monitored by NMR spectroscopy. For example, I₂ in C₆D₆ gave different signals in the ¹H NMR spectra before and after addition of CH₄.

Compound 2 also forms a larger, rigid 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 Hₐ in 2, except for those 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 filled capsule.

<table>
<thead>
<tr>
<th>solvent</th>
<th>δ (ppm) of Hₐ</th>
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<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 each Hₐ signal.  

3pt
1H NMR measurements in C₆D₆ revealed that 2 can incorporate one molecule of 1-adamantanecarboxylic acid (AdA).

The association constants (Kₐ) which are expressed below were determined for various temperatures. [solvent@2] denotes a species containing one or more solvent molecules.

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

(3)

Similarly, the Kₐ values of CH₄ and 1 shown in eq (2) were also determined by ¹H NMR measurements at various temperatures in C₆D₆. The plots of the two association constants (as ln Kₐ vs 1/T) are shown below.

No C₆D₆ is encapsulated in 1.

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

In line II, the entropy change (ΔS) is (1) and enthalpy change (ΔH) is (2), indicating that the driving force for the encapsulation in line II is (3). Therefore, line I corresponds to (4), and line II corresponds to (5).

<table>
<thead>
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<th></th>
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<th>B</th>
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<td>negative</td>
</tr>
<tr>
<td>(2)</td>
<td>positive</td>
<td>negative</td>
</tr>
<tr>
<td>(3)</td>
<td>ΔS</td>
<td>ΔH</td>
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<tr>
<td>(4)</td>
<td>1 and CH₄</td>
<td>2 and AdA</td>
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<td>(5)</td>
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**Likelihood and Dislikes of Capsule**

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<tr>
<td>8 (2 pt)</td>
<td>9 (2 pt)</td>
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</table>
A.2 (2 pt)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{HN} & \quad \text{HN} \\
\text{N} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

A.3 (2 pt)

A.4 (3 pt)

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

A.5 (3 pt)

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

(4) : (5) :