Please return this cover sheet together with all the related question sheets.
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>Hydrogen at a Metal Surface</td>
<td>24</td>
<td>11</td>
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<tr>
<td>Isotope Time Capsule</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>Lambert–Beer Law?</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>The Redox Chemistry of Zinc</td>
<td>32</td>
<td>11</td>
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<tr>
<td>Mysterious Silicon</td>
<td>60</td>
<td>12</td>
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<tr>
<td>The Solid-State Chemistry of Transition Metals</td>
<td>45</td>
<td>13</td>
</tr>
<tr>
<td>Playing with Non-benzenoid Aromaticity</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>Dynamic Organic Molecules and Their Chirality</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>Likes and Dislikes of Capsules</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
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</table>
**Physical Constants and Equations**

**Constants**

<table>
<thead>
<tr>
<th>Physical Quantity</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>
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<td>Electronvolt</td>
<td>$1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}$</td>
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<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>( PV = nRT )</td>
<td>The ideal gas law, where ( P ) is the pressure, ( V ) is the volume, ( n ) is the amount of substance, and ( T ) is the absolute temperature of ideal gas.</td>
</tr>
<tr>
<td>( F = k_e \frac{q_1q_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, and ( w ) is the work done.</td>
</tr>
<tr>
<td>( H = U + PV )</td>
<td>Enthalpy, where ( H ) is the internal energy.</td>
</tr>
<tr>
<td>( S = k_B \ln W )</td>
<td>Entropy based on Boltzmann’s principle, where ( W ) is the number of microstates.</td>
</tr>
<tr>
<td>( \Delta S = \frac{q_{\text{rev}}}{T} )</td>
<td>The change of entropy, where ( q_{\text{rev}} ) is the heat for the reversible process.</td>
</tr>
<tr>
<td>( G = H - TS )</td>
<td>Gibbs free energy, where ( G ) is the free energy.</td>
</tr>
<tr>
<td>( \Delta_r G^\circ = -RT \ln K = -zFE^\circ )</td>
<td>Gibbs free energy, where ( K ) is the equilibrium constant, ( z ) is the number of electrons, and ( 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, where ([A]) is the concentration of A.</td>
</tr>
<tr>
<td>Equation Description</td>
<td>Equation</td>
</tr>
<tr>
<td>----------------------</td>
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</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>$A = \varepsilon l c$</td>
</tr>
<tr>
<td>Henderson–Hasselbalch equation</td>
<td>For an equilibrium $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$</td>
</tr>
<tr>
<td>Energy of a photon</td>
<td>$E = h\nu = \frac{h}{\lambda}$</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 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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<tr>
<td>Period</td>
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$^1$H NMR Chemical Shifts

$\Delta \delta$ for one alkyl group-substitution: *ca.* +0.4 ppm
International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July - 2nd August, 2021
https://www.icho2021.org
Petunjuk Umum

- Gunakan hanya pena saja untuk menuliskan jawaban.
- Kalkulator yang digunakan harus non-programmable.
- Ujian ini terdiri dari 9 soal.
- Anda boleh mengerjakan soal ujian tanpa berurutan.
- Waktu untuk mengerjakan semua soal ujian adalah 5 jam.
- Anda hanya boleh memulai mengerjakan soal setelah perintah MULAI diberikan.
- Tuliskan uraian perhitungan yang relevan di dalam kotak yang sesuai jika diperlukan. Nilai penuh akan diberikan hanya ketika uraian pekerjaan Anda dituliskan.
- Pengawas akan memberikan peringatan 30-menit sebelum perintah SELESAI diberikan.
- Anda harus berhenti mengerjakan soal ujian ketika perintah SELESAI diberikan. Jika Anda tidak berhenti menulis maka nilai ujian Anda akan di-nol-kan.
- Versi soal ujian berbahasa Inggris tersedia jika diminta hanya untuk klarifikasi saja.
- Anda tidak boleh meninggalkan ruang ujian tanpa izin. Jika memerlukan sesuatu (kalkulator rusak, perlu ke kamar kecil, dll.), angkat tangan Anda dan tunggu hingga pengawas Anda mendatangi Anda.

SEMOGA BERHASIL!

Soal dan Informasi Penilaian

<table>
<thead>
<tr>
<th>Judul</th>
<th>Nilai Total</th>
<th>Persentase</th>
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<tbody>
<tr>
<td>1 Hidrogen pada Permukaan Logam</td>
<td>24</td>
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<tr>
<td>2 Kapsul Waktu Isotop</td>
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<td>3 Hukum Lambert-Beer?</td>
<td>22</td>
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<td>4 Kimia Redoks Seng</td>
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<td>5 Misteri Silikon</td>
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<td>6 Kimia Padatan Logam Transisi</td>
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<tr>
<td>7 Bermain dengan Kearomatikan Non-benzenoid</td>
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<td>8 Molekul Organik Dinamis dan Kiralitasnya</td>
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<tr>
<td>9 Kapsul Suka dan Benci</td>
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<td><strong>Total</strong></td>
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</table>
## Tetapan Fisik dan Persamaan

### Tetapan

<table>
<thead>
<tr>
<th>Tetapan Fisik</th>
<th>Persamaan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kecepatan cahaya dalam ruang hampa</td>
<td>$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Tetapan Planck</td>
<td>$h = 6.62607015 \times 10^{-34} \text{ J s}$</td>
</tr>
<tr>
<td>Muatan Elementer</td>
<td>$e = 1.602176634 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>Massa Elektron</td>
<td>$m_e = 9.10938370 \times 10^{-31} \text{ kg}$</td>
</tr>
<tr>
<td>Tetapan Listrik (permittivitas vakum)</td>
<td>$\varepsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$</td>
</tr>
<tr>
<td>Tetapan Avogadro</td>
<td>$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$</td>
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<tr>
<td>Tetapan Boltzmann</td>
<td>$k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$</td>
</tr>
<tr>
<td>Tetapan Faraday</td>
<td>$F = N_A \times e = 9.6485321233100184 \times 10^4 \text{ C mol}^{-1}$</td>
</tr>
<tr>
<td>Tetapan Gas</td>
<td>$R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$= 8.2057366081 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Satuan massa atom (Unified atomic mass unit)</td>
<td>$u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$</td>
</tr>
<tr>
<td>Tekanan standar</td>
<td>$p = 1 \text{ bar} = 10^5 \text{ Pa}$</td>
</tr>
<tr>
<td>Tekanan atmosfer</td>
<td>$p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa}$</td>
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<tr>
<td>Nol derajat Celsius</td>
<td>$0^\circ \text{ C} = 273.15 \text{ K}$</td>
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<td>$1 \text{ ppt} = 10^{-12}$</td>
</tr>
<tr>
<td>Pi</td>
<td>$\pi = 3.141592653589793$</td>
</tr>
<tr>
<td>Basis logaritma netral (bilangan Euler)</td>
<td>$e = 2.718281828459045$</td>
</tr>
</tbody>
</table>
Persamaan

<table>
<thead>
<tr>
<th>Hukum gas ideal</th>
<th>$PV = nRT$, dengan $P$ adalah tekanan, $V$ adalah volume, $n$ adalah jumlah zat, $T$ adalah temperatur absolut gas ideal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hukum Coulomb</td>
<td>$F = k_e\frac{q_1q_2}{r^2}$, dengan $F$ gaya elektrostatik, $k_e (\approx 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2})$ adalah tetapan Coulomb, $q_1$ dan $q_2$ adalah besarnya muatan, dan $r$ jarak antar muatan.</td>
</tr>
<tr>
<td>Hukum pertama termodinamika</td>
<td>$\Delta U = q + w$, dengan $\Delta U$ adalah perubahan energi dalam, $q$ adalah kalor yang terlibat, $w$ adalah kerja yang dilakukan.</td>
</tr>
<tr>
<td>Entalpi $H$</td>
<td>$H = U + PV$</td>
</tr>
<tr>
<td>Entropi berdasarkan prinsip Boltzmann $S$</td>
<td>$S = k_B \ln W$, dengan $W$ adalah jumlah keadaan-mikro (microstates).</td>
</tr>
<tr>
<td>Perubahan entropi $\Delta S$</td>
<td>$\Delta S = \frac{q_{rev}}{T}$, dengan $q_{rev}$ adalah kalor untuk proses reversibel.</td>
</tr>
<tr>
<td>Energi bebas Gibbs $G$</td>
<td>$G = H - TS$, $\Delta_r G^\circ = -RT \ln K = -zFE^\circ$, $\Delta_r G^\circ = \Delta G + RT \ln Q$</td>
</tr>
<tr>
<td>Untuk reaksi $aA + bB \rightleftharpoons cC + dD$</td>
<td>$Q = \frac{</td>
</tr>
</tbody>
</table>

Untuk reaksi $aA + bB \rightleftharpoons cC + dD$
<table>
<thead>
<tr>
<th>Persamaan</th>
<th>Deskripsi</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perubahan kalor</strong> $\Delta q$</td>
<td>$\Delta q = n c_m \Delta T$, dengan $c_m$ adalah kapasitas kalor molar yang tidak bergantung temperatur</td>
</tr>
<tr>
<td><strong>Persamaan Nernst untuk reaksi redoks</strong></td>
<td>$E = E^\circ + \frac{RT}{zF} \ln \frac{C_{ox}}{C_{red}}$, dengan $C_{ox}$ adalah konsentrasi zat yang teroksidasi, $C_{red}$ adalah konsentrasi zat yang tereduksi.</td>
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<tr>
<td><strong>Persamaan Arrhenius</strong></td>
<td>$k = A \exp\left(-\frac{E_a}{RT}\right)$, dengan $k$ adalah tetapan laju, $A$ adalah faktor pre-eksponensial, $E_a$ adalah energi aktivasi.</td>
</tr>
<tr>
<td><strong>Persamaan Lambert–Beer</strong></td>
<td>$A = \varepsilon l c$, dengan $A$ adalah absorbansi, $\varepsilon$ adalah koefisien absorpsi molar, $l$ adalah jarak tempuh cahaya, $c$ adalah konsentrasi larutan.</td>
</tr>
<tr>
<td><strong>Persamaan Henderson–Hasselbalch</strong></td>
<td>Untuk suatu kesetimbangan, dengan tetapan kesetimbangan $K_a$, $\text{pH} = pK_a + \log\left(\frac{[A]}{[HA]}\right)$</td>
</tr>
<tr>
<td><strong>Energi foton</strong></td>
<td>$E = h\nu = h\frac{\lambda}{c}$, dengan $\nu$ adalah frekuensi, $\lambda$ adalah panjang gelombang cahaya.</td>
</tr>
<tr>
<td><strong>Jumlah deret geometri</strong></td>
<td>Ketika $x \neq 1$, $1 + x + x^2 + \cdots + x^n = \sum_{i=0}^{n} x^i = \frac{1-x^{n+1}}{1-x}$</td>
</tr>
<tr>
<td><strong>Persamaan aproksimasi yang dapat digunakan untuk mengerjakan soal.</strong></td>
<td>Ketika $x \ll 1$, $\frac{1}{1-x} \approx 1 + x$</td>
</tr>
<tr>
<td>Period</td>
<td>1s</td>
</tr>
<tr>
<td>-------</td>
<td>----</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>Li</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
</tr>
<tr>
<td>4</td>
<td>K</td>
</tr>
<tr>
<td>5</td>
<td>Rb</td>
</tr>
<tr>
<td>6</td>
<td>Cs</td>
</tr>
<tr>
<td>7</td>
<td>Fr</td>
</tr>
</tbody>
</table>

Key: 1s = alkali metals, 2s = alkaline earth metals, 3s = transition metals, 4s = f-block elements, 5p = halogens, 6p = noble gases, 7s = actinides.
Δδ untuk satu substitusi gugus-alkil: ca. +0.4 ppm
Please return this cover sheet together with all the related question sheets.
Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

**Part A**

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $\text{H}_2(g) \rightarrow 2\text{H}($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 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 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 $\text{H}_2$ molecule
(ii) The interatomic distance between metal atoms ($d_m$ in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface ($h_{ad}$ in Fig. 1)

<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 $\text{H}_2$ to gaseous H

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

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

|   | 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.

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

(1a) (1b)

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

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

(2) (3) (4)

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 \( P_{H_2} \) is the pressure of \( H_2 \). Among the sites available on the surface, \( \theta \text{ (0} \leq \theta \leq 1) \) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption \( (r_1, r_2 \gg r_3) \) and that \( \theta \) remains constant.

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

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

(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 H$_2$ ($P_{H_2} = 1.0 \times 10^2 \text{ Pa}$). 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, $P_{H_2}$ decreased at a constant rate of $v = 4.0 \times 10^{-4} \text{ Pa s}^{-1}$. Assume that H$_2$ is an ideal gas and that the volume of the metal sample is negligible.

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

**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 $P_{H_2}$ at this temperature, select the correct plot from (a)–(h).
Hidrogen merupakan salah satu sumber energi di masa depan yang tidak bergantung pada energi fosil. Pada soal ini kita akan meninjau proses penyimpanan hidrogen dalam logam, yang mendasari teknologi penyimpanan dan transpor hidrogen.

Bagian A
Hidrogen diabsorpsi ke dalam fasa ruah (bulk) logam melalui permukaan logam. Pertama, mari kita tinjau proses adsorpsi hidrogen pada permukaan logam, H\textsubscript{2}(g) \rightarrow 2H(ad), dimana fasa gas and fasa ter-adsorpsi dari hidrogen ditunjukkan sebagai (g) dan (ad), secara berurutan. Molekul hidrogen (H\textsubscript{2}) yang mencapai permukaan logam (M) mengalami disosiasi pada permukaan dan teradsorpsi sebagai atom H (Gambar 1). Energi potensial H\textsubscript{2} bergantung pada dua variabel: jarak antar atom, \(d\), dan jarak relatif terhadap permukaan logam, \(z\). Asumsikan bahwa sumbu ikatan dua atom H sejajar dengan permukaan logam dan lokasi pusat massa (the center of gravity) selalu berada pada garis putus-putus vertikal yang ditunjukkan pada Gambar 1. Gambar 2 menunjukkan plot kontur dari energi potensial disosiasi pada permukaan. Angka yang ditunjukkan pada Gambar 2 merupakan energi potensial dalam kJ per mol H\textsubscript{2}. Jarak antara garis utuh (solid line spacing) adalah 20 kJ mol\(^{-1}\), jarak antara garis putus-putus (dashed line spacing) adalah 100 kJ mol\(^{-1}\), dan jarak antara garis utuh dan garis putus-putus adalah 80 kJ mol\(^{-1}\). Abaikan kontribusi dari zero-point vibration energy.
Gambar 1 Definisi variabel. Gambar tidak sesuai skala sebenarnya.

Gambar 2
A.1 Jawab pertanyaan berikut (i)–(iii) dengan memilih A-G yang mengandung jawaban dengan nilai terdekat.
(i) Jarak antaratom pada molekul gas H\(_2\)
(ii) Jarak antaratom logam (\(d_M\) pada Gambar 1)
(iii) Jarak atom H yang teradsorpsi dari permukaan logam (\(h_{ad}\) pada Gambar 1)

| A. 0.03 nm | B. 0.07 nm | C. 0.11 nm | D. 0.15 nm |
| E. 0.19 nm | F. 0.23 nm | G. 0.27 nm |

A.2 Jawab pertanyaan berikut (i)–(ii) dengan memilih A-H yang mengandung jawaban dengan nilai terdekat.
(i) Energi yang diperlukan untuk disosiasi gas H\(_2\) menjadi gas H 
[H\(_2\)(g) \(\rightarrow\) 2H(g)]
(ii) Energi yang dilepaskan pada adsorpsi gas 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\(^{-1}\) |
Bagian B

Atom hidrogen yang teradsorpsi selanjutnya dapat mengalami proses absorpsi ke fasa ruah (*bulk*), atau mengalami rekombinasi dan terdesorpsi kembali ke fasa gasnya, seperti ditunjukkan pada reaksi (1a) dan (1b). H(ab) menunjukkan atom hidrogen yang terabsorpsi dalam fasa ruah (*bulk*).

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

Laju reaksi tiap jumlah sisi permukaan adsorpsi, desorpsi, dan absorpsi masing-masing adalah \(r_1\)\([s^{-1}]\), \(r_2\)\([s^{-1}]\) dan \(r_3\)\([s^{-1}]\), secara berurutan. Masing-masing hukum laju reaksi tersebut dapat dituliskan sebagai berikut:

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

dimana \(k_1\)\([s^{-1} Pa^{-1}]\), \(k_2\)\([s^{-1}]\) dan \(k_3\)\([s^{-1}]\) adalah tetapan laju reaksi dan \(P_{H_2}\) adalah tekanan gas \(H_2\). Di antara sisi permukaan yang tersedia, \(\theta\) \((0 \leq \theta \leq 1)\) adalah fraksi sisi permukaan yang diisi oleh atom H. Asumsikan bahwa adsorpsi dan desorpsi berlangsung lebih cepat daripada absorpsi \((r_1, r_2 \gg r_3)\) dan asumsikan juga bahwa \(\theta\) selalu tetap.

**B.1** \(r_3\) dapat dituliskan sebagai:

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

**Tuliskan** nilai \(C\) dalam \(k_1\) dan \(k_2\).
Suatu sampel logam A dengan luas permukaan \( S = 1.0 \times 10^{-3} \text{ m}^2 \) dimasukkan ke dalam suatu wadah berukuran 1L = 1.0 \times 10^{-3} \text{ m}^3 bersama dengan gas H\(_2\) (\( P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa} \)). Kerapatan sisi adsorpsi atom hidrogen pada permukaan \( N = 1.3 \times 10^{18} \text{ m}^{-2} \). Temperatur pada permukaan \( T = 400 \text{ K} \). Seiring dengan berjalannya reaksi (1), \( P_{\text{H}_2} \) berkurang dengan laju tetap sebesar \( v = 4.0 \times 10^{-4} \text{ Pa s}^{-1} \). Asumsikan bahwa H\(_2\) adalah gas ideal dan volume sampel logam dapat diabaikan.

**B.2** Hitung jumlah atom H (dalam mol) yang terabsorpsi tiap satuan luas permukaan tiap satuan waktu, \( A \) [mol s\(^{-1}\) m\(^{-2}\)].

**B.3** Pada \( T = 400 \text{ K} \), \( C \) bernilai 1.0 \times 10^2 \text{ Pa}^{-1}. Hitung nilai \( k_3 \) pada 400 K. Jika Anda tidak mendapatkan jawaban pertanyaan **B.2**, gunakan \( A = 3.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \).

**B.4** Pada \( T \) yang berbeda, \( C = 2.5 \times 10^3 \text{ Pa}^{-1} \) dan \( k_3 = 4.8 \times 10^{-2} \text{ s}^{-1} \). Pada temperatur tersebut, pilih plot \( r_3 \) sebagai fungsi dari \( P_{\text{H}_2} \) yang paling tepat dari pilihan (a)–(h).

![Graph](image-url)
Hidrogen pada Permukaan Logam

Bagian A

**A.1 (6 pt)**

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

**A.2 (4 pt)**

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

B.1 (5 pt)

\[ C = \quad \]

B.2 (3 pt)

\[ A = \quad \text{mol s}^{-1}\text{m}^{-2} \]
$$k_3 = \text{_________} \text{ s}^{-1}$$
IChO
Problem 2
Cover sheet

Please return this cover sheet together with all the related question sheets.
Isotope Time Capsule

<table>
<thead>
<tr>
<th>Question</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
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<td>8</td>
<td>8</td>
<td>10</td>
<td>9</td>
<td>35</td>
</tr>
</tbody>
</table>

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:

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

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

(1)

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

\[ S = k_B \ln W \]  

(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 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, \( W = 2^2 = 4 \).
A.1 The enthalpy change, $\Delta H$, of eq. 3 is positive regardless of the temperature.

\[ H_2 + DI \rightleftharpoons HD + HI \]  
(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:

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

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]  
(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$^{-1}$.

\[ 2HD \to H_2 + D_2 \]  
(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 H\textsubscript{2}, HD, and D\textsubscript{2} depends on the temperature in a system in equilibrium. Here, $\Delta_{D_2}$ is defined as the change of the molar ratio of D\textsubscript{2}.

$$\Delta_{D_2} = \frac{R_{D_2}}{R'_{D_2}} - 1$$  \hspace{1cm} (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 $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

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

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

$R_{47}$ refers to $[\text{CO}_2[47]]$ in the sample and $R^*_{47}$ to $[\text{CO}_2[47]]$ 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>$^{12}\text{C}$</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:

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

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

Spesi molekular yang berbeda hanya pada komposisi isotop, seperti CH₄ dan CH₃D, disebut isotopolog. Isotopolog memiliki karakter/sifat kimia yang sama. Pada kenyataannya, di alam terdapat sedikit perbedaan pada sifat kimia isotopolog.

Asumsikan bahwa semua senyawa pada pertanyaan ini berada dalam fase gas.

Perhatikan kesetimbangan berikut:

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

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

Entropi, \( S \), meningkat seiring dengan meningkatnya jumlah *microscopic states* yang mungkin dalam suatu sistem, \( W \):

\[ S = k_B \ln W \]  \( \text{(2)} \)

\( W = 1 \) untuk \(^{12}\text{C}^{16}\text{O}_2\) dan \(^{12}\text{C}^{18}\text{O}_2\). Sebaliknya, \( W = 2 \) untuk molekul \(^{12}\text{C}^{16}\text{O}^{18}\text{O}\) karena atom oksigen dapat dibedakan dalam molekul tersebut. Karena terdapat dua \(^{12}\text{C}^{16}\text{O}^{18}\text{O}\) molekul pada sisi kanan (produk) pada kesetimbangan reaksi 1, maka \( W = 2^2 = 4 \).
A.1 Perubahan entalpi, $\Delta H$, reaksi 3 selalu bernilai positif pada semua rentang temperatur.

\[ \text{H}_2 + \text{DI} \rightleftharpoons \text{HD} + \text{HI} \]  

*(3)*

**Hitung** tetapan kesetimbangan, $K$, untuk reaksi 3 pada temperatur yang sangat rendah ($T \to 0$) dan pada temperatur yang sangat tinggi ($T \to +\infty$). Asumsikan bahwa reaksi tersebut tidak berubah pada rentang temperatur tersebut dan nilai $\Delta H$ menuju ke suatu nilai tetap temperatur tinggi.

Nilai $\Delta H$ proses berikut dapat dijelaskan dengan vibrasi molekul.

\[ 2\text{HD} \rightleftharpoons \text{H}_2 + \text{D}_2 \]

\[ K = \frac{[\text{H}_2][\text{D}_2]}{[\text{HD}]^2} \]  

*(4)*

Pada $T = 0$ K, energi vibrasi suatu molekul diatomik dengan frekuensi vibrasi $\nu$ [s$^{-1}$] adalah:

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

*(5)*

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

*(6)*

Dimana $k$ adalah tetapan pegas *(force constant)* dan $\mu$ adalah massa tereduksi *(reduced mass)*, yang bergantung pada massa masing-masing atom, $m_1$ dan $m_2$ dalam molekul diatomik menurut persamaan:

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]  

*(7)*

A.2 Bilangan gelombang vibrasi $\text{H}_2$ adalah 4161.0 cm$^{-1}$. **Hitung** $\Delta H$ reaksi berikut pada $T = 0$ K dalam satuan J mol$^{-1}$.

\[ 2\text{HD} \to \text{H}_2 + \text{D}_2 \]  

*(8)*

Asumsikan bahwa:
- hanya energi vibrasi yang berkontribusi pada $\Delta H$.
- nilai $k$ bernilai sama untuk $\text{H}_2$, HD, dan $\text{D}_2$.
- massa H adalah 1 Da dan massa D adalah 2 Da.
Rasio molar $\text{H}_2$, HD, dan D$_2$ bergantung pada temperatur sistem dalam kesetimbangan. $\Delta_{\text{D}_2}$ didefinisikan sebagai perubahan rasio molar D$_2$.

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

Pada persamaan di atas, $R_{\text{D}_2}$ menunjukkan $[\text{D}_2]$ dalam sampel dan $R_{\text{D}_2}^*$ menunjukkan $[\text{D}_2]$ pada $T \to +\infty$. Perhatikan bahwa distribusi isotop menjadi acak/random pada $T \to +\infty$.

**A.3 Hitung** $\Delta_{\text{D}_2}$ dengan kelimpahan D di alam ketika pertukaran isotop berada pada kesetimbangan pada suatu temperatur dimana nilai $K$ reaksi 4 adalah 0.300. Asumsikan bahwa rasio kelimpahan D dan H di alam adalah $1.5576 \times 10^{-4}$ and $1 - 1.5576 \times 10^{-4}$, secara berurutan.
Pada umumnya, rasio molar isotopolog tersubstitusi ganda, yang mengandung dua isotop berat dalam satu molekul, meningkat seiring dengan menurunnya temperatur. Tinjau rasio molar molekul CO$_2$ dengan massa molekul 44 dan 47, yang dapat dituliskan sebagai CO$_2$[44] dan CO$_2$[47] di bawah ini. Besaran $\Delta_{47}$ didefinisikan sebagai:

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

(10)

$R_{47}$ menunjukkan rasio $[\text{CO}_2[47]]$ dalam sampel dan $R^*_{47}$ menunjukkan rasio $[\text{CO}_2[47]]$ pada $T \to +\infty$. Kelimpahan karbon dan oksigen di alam ditunjukkan di bawah ini; abaikan isotop yang tidak ditunjukkan.

<table>
<thead>
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<th>$^{13}\text{C}$</th>
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<tr>
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<td>0.011112</td>
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<th>$^{17}\text{O}$</th>
<th>$^{18}\text{O}$</th>
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<tbody>
<tr>
<td>kelimpahan di alam</td>
<td>0.997621</td>
<td>0.0003790</td>
<td>0.0020000</td>
</tr>
</tbody>
</table>

Kebergantungan $\Delta_{47}$ pada temperatur ditunjukkan pada persamaan berikut, dimana $T$ adalah temperatur absolut dalam satuan K:

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

(11)

A.4 Nilai $R_{47}$ dari suatu fosil plankton yang diperoleh dari dasar Antartika adalah $4.50865 \times 10^{-5}$. **Perkirakan** temperatur dengan menggunakan nilai $R_{47}$ tersebut. Temperatur ini dapat diinterpretasikan sebagai temperatur udara pada saat plankton tersebut masih hidup. Gunakan hanya isotopolog CO$_2$[47] yang paling umum untuk perhitungan.
Kapsul Waktu Isotop

A.1 (8 pt)

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

$\Delta H = \underline{\hphantom{0} \quad J \text{ mol}^{-1}}$
Δ $D_2 = \underline{\underline{\underline{}}}$
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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</tr>
</tbody>
</table>

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

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

$$HA \rightleftharpoons A^- + H^+ \quad \quad K = \frac{[A^-][H^+]}{[HA]}$$ (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 $\varepsilon_{HA}/\varepsilon_{A^-}$, where $\varepsilon_{HA}$ and $\varepsilon_{A^-}$ represent the absorption coefficients of HA and of $A^-$, respectively, at $\lambda_1$. 10pt
Part B

Let us consider the following equilibrium in the gas phase.

\[ \text{D} \rightleftharpoons 2\text{M} \]  \hspace{1cm} (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.

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<tr>
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<th>After equilibrium</th>
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<tr>
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<td>M</td>
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<tr>
<td>Partial pressure</td>
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</tr>
<tr>
<td>Amount in moles</td>
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<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 (\( l = l_y0 \)) and after the equilibrium (\( l = l_y \)). **Determine** the ratio \( \varepsilon_D/\varepsilon_M \) at \( \lambda_{B2} \).
Pada soal ini, abaikan absorpsi oleh wadah dan pelarut. Suhu semua larutan dan gas selalu tetap 25 °C.

**Bagian A**

Larutan X dalam air disiapkan dengan menggunakan HA dan NaA. Konsentrasi $[\text{A}^-]$, $[\text{HA}]$, dan $[\text{H}^+]$ dalam larutan X masing-masing adalah $1.00 \times 10^{-2} \text{ mol L}^{-1}$, $1.00 \times 10^{-3} \text{ mol L}^{-1}$, and $1.00 \times 10^{-4} \text{ mol L}^{-1}$, secara berurutan, dan berhubungan dengan kesetimbangan asam-basa berikut:

$$\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+$$

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

Jarak yang ditempuh cahaya adalah $l$ pada Bagian A. Akaikan perubahan massa jenis saat pengenceran. Asumsikan bahwa tidak ada reaksi kimia yang terjadi selain reaksi 1.

| A.1 Absorbsi X adalah $\lambda_1$ pada panjang gelombang $\lambda_1$. Larutan X kemudian dicairkan sehingga volumenya menjadi dua kali volume awalnya menggunakan asam hidroklorida dengan $pH = 2.500$. Setelah pengenceran, absorbsi larutan masih tetap bernilai $\lambda_1$ pada $\lambda_1$. **Tentukan** rasio $\varepsilon_{HA}/\varepsilon_{A^-}$, dimana $\varepsilon_{HA}$ dan $\varepsilon_{A^-}$ masing-masing adalah koefisien absorbsi HA dan A$^-$ pada $\lambda_1$ secara berurutan. | 10pt |
Bagian B
Perhatikan kesetimbangan berikut.

\[ \mathrm{D} \rightleftharpoons 2\mathrm{M} \]  \hspace{1cm} (2)

Suatu gas murni D diisikan ke dalam wadah berbentuk kotak hingga tekanan mencapai \( P \). Kotak tersebut memiliki dinding transparan yang dapat bergerak dengan luas \( S \) (lihat gambar di bawah ini), dan kesetimbangan tercapai saat tekanan total bernilai tetap sebesar \( P \). Absorbsi gas adalah \( A = \varepsilon(n/V)l \), dimana \( \varepsilon, n, V \), dan \( l \) adalah koefisien absorpsi, jumlah mol gas, volume gas, dan jarak tempuh cahaya, secara berurutan. Asumsikan bahwa semua gas dalam campuran berperilaku sebagai gas ideal.

Gunakan definisi di bawah ini jika diperlukan

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<tr>
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</tr>
<tr>
<td>Jumlah mol</td>
<td>( n_0 ) \hspace{1cm} n_D \hspace{1cm} n_M</td>
</tr>
<tr>
<td>Volume</td>
<td>( V_0 ) \hspace{1cm} V</td>
</tr>
</tbody>
</table>

\[ \begin{align*}
\text{B.1} & \quad \text{Absorbsi gas pada } \lambda_{B1} \text{ diukur pada arah } x \text{ (} l = l_x \text{) baik pada kondisi awal maupun setelah kesetimbangan tercapai adalah } A_{B1}. \text{ \textbf{Tentukan} rasio } \varepsilon_D/\varepsilon_M \text{ pada } \lambda_{B1}, \text{ dimana } \varepsilon_D \text{ dan } \varepsilon_M \text{ masing-masing adalah koefisien absorpsi D dan M, secara berurutan.} \\
\text{B.2} & \quad \text{Absorbsi gas pada } \lambda_{B2} \text{ diukur pada arah } y \text{ pada kondisi awal (} l = l_y \text{) maupun setelah kesetimbangan tercapai (} l = l_y' \text{) adalah } A_{B2}. \text{ \textbf{Tentukan} rasio } \varepsilon_D/\varepsilon_M \text{ pada } \lambda_{B2}. 
\end{align*} \]
Hukum Lambert–Beer?

Bagian A

A.1 (10 pt)

(Berlanjut pada halaman berikutnya)
\[ \varepsilon_{HA} / \varepsilon_{A^-} = \]
\[ \varepsilon_D / \varepsilon_M = \]
$\frac{\varepsilon_D}{\varepsilon_M} =$
IChO
Problem 4
Cover sheet

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

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

Part A

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

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

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

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

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

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

**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 \( \text{Zn(OH)}_2(s) \) with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. Calculate the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.

**Part B**

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

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

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

\[
\text{ZnO(s)} + \text{H}_2(g) \rightarrow \text{Zn(s)} + \text{H}_2\text{O(g)}
\]  

**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 \( \Delta G_{\text{ZnO(300°C)}} = -2.90 \times 10^2 \text{ kJ mol}^{-1} \) and \( \Delta G_{\text{H}_2\text{O(300°C)}} = -2.20 \times 10^2 \text{ kJ mol}^{-1} \), 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, \( E^\circ \).

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

**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

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

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

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

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

<table>
<thead>
<tr>
<th>Pertanyaan</th>
<th>A.1</th>
<th>A.2</th>
<th>B.1</th>
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<td>32</td>
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</table>

Seng sudah lama digunakan sebagai paduan logam material perunggu dan baja. Seng yang terdapat pada limbah industri dipisahkan dengan pengendapan untuk detoksifikasi air, dan endapan yang diperoleh direduksi untuk didaur ulang dan digunakan kembali sebagai logam seng.

Bagian A

Kesetimbangan larutan seng hidroksida Zn(OH)$_2$(s) pada 25 °C dan tetapan kesetimbangan masing-masing reaksi diberikan pada persamaan 1–4.

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

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

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

\[
\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad K_w = 1.00 \times 10^{-14} \quad (4)
\]
Kelarutan, \( S \), seng (konsentrasi seng dalam suatu larutan jenuh) diberikan pada persamaan 5.

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

(5)

A.1 Ketika kesetimbangan pada persamaan 1–4 tercapai, hitung rentang pH dimana \([\text{Zn(OH)}_2(\text{aq})]\) paling besar di antara \([\text{Zn}^{2+}(\text{aq})]\), \([\text{Zn(OH)}_2(\text{aq})]\) dan \([\text{Zn(OH)}_4^{2-}(\text{aq})]\).

A.2 Larutan jenuh \(\text{Zn(OH)}_2(s)\) dengan \(\text{pH} = 7.00\) disiapkan dan disaring. Kemudian kedalam filtrat ditambahkan \(\text{NaOH}\) untuk meningkatkan \(\text{pH}\) menjadi 12.00. Hitung presentase molar Zn yang mengendap ketika \(\text{pH}\) bertambah dari 7.00 menjadi 12.00. Abaikan perubahan volume dan temperatur.

Bagian B

Selanjutnya, seng hidroksida yang diperoleh dipanaskan untuk memperoleh seng oksida sesuai dengan persamaan reaksi berikut:

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

(6)

Seng oksida kemudian direduksi menjadi logam seng dengan reaksi menggunakan hidrogen:

\[
\text{ZnO}(s) + \text{H}_2(g) \rightarrow \text{Zn}(s) + \text{H}_2\text{O}(g)
\]  

(7)

B.1 Agar reaksi (7) dapat berlangsung pada kondisi tekanan hidrogen dijaga pada 1 bar, perlu untuk mengurangi tekanan parcial dari uap air yang dihasilkan. Hitung batas atas tekanan uap air parcial agar reaksi (7) dapat berlangsung pada 300 \(^\circ\)C. Berikut nilai energi bebas Gibbs pembentukan untuk seng oksida dan uap air pada 300 \(^\circ\)C dan 1 bar untuk semua spesi gas yaitu masing-masing \(\Delta G_{\text{ZnO}}(300 \text{ }^\circ\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1}\) dan \(\Delta G_{\text{H}_2\text{O}}(300 \text{ }^\circ\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1}\).

Logam seng digunakan sebagai elektroda negatif (anoda) pada baterai \textit{metal-air}. Elektroda disusun dari Zn dan ZnO. Elektroda tersebut digunakan pada reaksi redoks berikut untuk menghasilkan listrik dengan \textit{electromotive force} (e.m.f.) pada 25 \(^\circ\)C dan tekanan 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 Sebuah baterai \textit{zinc-air} habis digunakan dengan arus 20 mA selama 24 jam. Hitung perubahan massa elektroda negatif (anoda) dari baterai tersebut.
Diketahui perubahan nilai e.m.f. dari baterai zinc-air tergantung pada lingkungan. **Hitung** nilai e.m.f. pada puncak gunung Fuji, yang memiliki temperatur dan ketinggian masing-masing \(-38\, ^\circ C \) (Februari) dan 3776 m. Tekanan atmosfer dinyatakan dengan persamaan:

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

dengan ketinggian \(h \text{[m]}\) dan temperatur \(T \text{[\degree C]}\). Perbandingan molar oksigen di udara sebesar 21\%. Perubahan energi bebas Gibbs untuk reaksi (8) adalah \(\Delta G^{\circ}_{ZnO}(\text{-38 \degree C}) = -3.26 \times 10^2 \text{ kJ mol}^{-1}\) pada \(-38 \degree C\) dan 1 bar.

**B.4** **Hitung** perubahan energi bebas Gibbs untuk reaksi (6) pada 25 \degree C. Perhatikan bahwa nilai potensial reduksi standar \(E^{\circ}(\text{Zn}^{2+}/\text{Zn})\) dan \(E^{\circ}(\text{O}_2/\text{H}_2\text{O})\) pada 25 \degree C dan 1 bar masing-masing diberikan pada persamaan (10) dan (11).

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

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^{\circ}(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V} \tag{11}
\]
Kimia Redoks Seng

Bagian A

A.1 (6 pt)

< pH <
A.2 (5 pt)
Bagian B

B.1 (4 pt)

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

B.2 (3 pt)

___ g
B.3 (5 pt)
\[ \Delta G^* = \text{J mol}^{-1} \]
Please return this cover sheet together with all the related question sheets.
Mysterious Silicon

<table>
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<th>Question</th>
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<th>A.2</th>
<th>A.3</th>
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</table>

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

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

When \( R^1 \equiv Si \equiv R^1 \) 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 C (in the case of $R^1 = R^2 = \text{H}$) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1).

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH}_2 + \text{H}_2 \quad \rightarrow \quad \text{H}_3\text{C} &= \text{CH}_3 \quad \Delta H = -135 \text{ kJ mol}^{-1} \quad (1) \\
\text{H}_2\text{Si} &= \text{CH}_2 + \text{H}_2 \quad \rightarrow \quad \text{H}_3\text{Si} &= \text{CH}_3 \quad \Delta H = -213 \text{ kJ mol}^{-1} \quad (2) \\
\text{H}_2\text{Si} &= \text{SiH}_2 + \text{H}_2 \quad \rightarrow \quad \text{H}_3\text{Si} &= \text{SiH}_3 \quad \Delta H = -206 \text{ kJ mol}^{-1} \quad (3) \\
\text{H}_2\text{Si} &= \text{SiH} + 3 \text{H}_2 \quad \rightarrow \quad \text{H}_3\text{Si} &= \text{SiH}_2 \quad \Delta H = -173 \text{ kJ mol}^{-1} \quad (4) \\
\text{HSi} &= \text{SiH} + 3 \text{H}_2 \quad \rightarrow \quad \text{H}_2\text{Si} &= \text{SiH}_2 \quad \Delta H = -326 \text{ kJ mol}^{-1} \quad (5) \\
\text{HSi} &= \text{SiH} + 3 \text{H}_2 \quad \rightarrow \quad \text{H}_2\text{Si} &= \text{SiH}_2 \quad \Delta H = -368 \text{ kJ mol}^{-1} \quad (6) \\
\text{HSi} &= \text{SiH} + 3 \text{H}_2 \quad \rightarrow \quad \text{H}_2\text{Si} &= \text{SiH}_2 \quad \Delta H = -389 \text{ kJ mol}^{-1} \quad (7)
\end{align*}
\]
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 $50.0 \, ^\circ C$ and $D : E = 1 : 20.0$ at $120.0 \, ^\circ C$.

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

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

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

Part B

Silicon is able to form highly coordinated compounds (> four substituents) with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

The fluorination reaction of CCl$_4$ using Na$_2$SiF$_6$ was carried out as follows.

- **Standardization of Na$_2$SiF$_6$ solution**: 6pt
  - 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 xylene 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$_6$**: 10pt
  (Substance losses by e.g. evaporation are negligible during the following operations.)
  Na$_2$SiF$_6$(x [g]) was added to CCl$_4$ (500.0 g) and heated to $300 \, ^\circ C$ 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.

<table>
<thead>
<tr>
<th>$^{19}$F NMR data</th>
<th>CFCl$_3$</th>
<th>CF$_2$Cl$_2$</th>
<th>CF$_3$Cl</th>
<th>CF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integration ratio</td>
<td>45.0</td>
<td>65.0</td>
<td>18.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
SiF$_4$ is hydrolyzed to form H$_2$SiF$_6$ according to the following eq. 8:

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

**B.2** Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and **calculate** the mass (x [g]) of the Na$_2$SiF$_6$ used as a starting material.

**B.3** 77.8% of the CCl$_4$ used as a starting material was unreacted. **Calculate** the mass of CF$_3$Cl generated.
Misteri Silikon

<table>
<thead>
<tr>
<th>Pertanyaan</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
<th>A.4</th>
<th>B.1</th>
<th>B.2</th>
<th>B.3</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poin</td>
<td>9</td>
<td>7</td>
<td>6</td>
<td>10</td>
<td>5</td>
<td>15</td>
<td>8</td>
<td>60</td>
</tr>
</tbody>
</table>

Meskipun silikon merupakan unsur golongan 14 seperti karbon, sifat kedua unsur tersebut berbeda.

Bagian A

Berbeda dengan ikatan rangkap tiga pada karbon-karbon, ikatan rangkap tiga pada silikon-silikon dalam sebuah senyawa diformulasikan sebagai R₁–Si≡Si–R₁ (R: substituen organik) yang sangat reaktif. Sebagai contoh, senyawa silikon tersebut bereaksi dengan etilena untuk menghasilkan sebuah produk yang mengandung senyawa cincin lingkar empat.

\[
R₁–Si≡Si–R₁ + H₂C≡CH₂ \rightarrow \begin{array}{c}
\text{R₁} \\
\text{Si} \\
\text{Si} \\
\text{R₁}
\end{array}
\]

Ketika R₁–Si≡Si–R₁ direaksikan dengan senyawa alkuna (R²–C≡C–R²), senyawa cincin lingkar empat A terbentuk sebagai produk awal. Selanjutnya reaksi senyawa R²–C≡C–R² dengan A menghasilkan isomer B dan C, keduanya memiliki struktur konjugasi seperti benzena, sehingga disebut ‘disilabenzes’ yang memiliki cincin lingkar enam dengan formula (R₁–Si)₂(R²–C)₄.
Analisis $^{13}$C NMR senyawa cincin lingkar enam dengan kerangka $\text{Si}_2\text{C}_4$ menunjukkan adanya dua sinyal untuk B dan satu sinyal untuk C.

### A.1 Gambarkan struktur molekul A, B, dan C dengan menuliskan simbol $R^1$, $R^2$, Si, dan C, dengan menggambarkan salah satu struktur resonansi yang mungkin.

### A.2 Hitung the aromatic stabilization energy (ASE) untuk benzena dan C (dengan $R^1 = R^2 = \text{H}$) sebagai nilai positif, dengan mempertimbangkan perubahan entalpi dalam beberapa reaksi hidrogenasi sistem tak jenuh ditunjukkan pada gambar di bawah ini (Gambar 1).

\[
\begin{align*}
H_2\text{C} &= \text{CH}_2 & + & H_2 & \longrightarrow & H_3\text{C} &= \text{CH}_3 & \Delta H = -135 \text{ kJ mol}^{-1} & (1) \\
H_2\text{Si} &= \text{CH}_2 & + & H_2 & \longrightarrow & H_3\text{Si} &= \text{CH}_3 & \Delta H = -213 \text{ kJ mol}^{-1} & (2) \\
H_2\text{Si} &= \text{SiH}_2 & + & H_2 & \longrightarrow & H_3\text{Si} &= \text{SiH}_3 & \Delta H = -206 \text{ kJ mol}^{-1} & (3) \\
\end{align*}
\]

\[
\begin{align*}
\text{Cyclic} & + 3 \text{ H}_2 & \longrightarrow & \text{Cyclic} & \Delta H = -173 \text{ kJ mol}^{-1} & (4) \\
\text{HSi} &= \text{SiH} & + & 3 \text{ H}_2 & \longrightarrow & \text{H}_2\text{Si} &= \text{SiH}_2 & \Delta H = -326 \text{ kJ mol}^{-1} & (5) \\
\text{HSi} & + 3 \text{ H}_2 & \longrightarrow & \text{H}_2\text{Si} & \Delta H = -368 \text{ kJ mol}^{-1} & (6) \\
\text{HSi} & + 3 \text{ H}_2 & \longrightarrow & \text{H}_2\text{Si} & \Delta H = -389 \text{ kJ mol}^{-1} & (7) \\
\end{align*}
\]

Gambar 1
IChO

Q5-3

Indonesia (Indonesia)

Ketika larutan xylene C dipanaskan, senyawa tersebut mengalami isomerisasi untuk menghasilkan campuran senyawa D dan E dalam kesetimbangan. Perbandingan molar yaitu D : E = 1 : 40.0 pada 50.0 °C dan D : E = 1 : 20.0 pada 120.0 °C.

A.3 Hitung ΔH untuk transformasi D menjadi E. Asumsikan ΔH tidak tergantung temperatur.

Isomerisasi C menjadi D dan menjadi E berlangsung melalui transformasi ikatan π menjadi ikatan σ tanpa pemutusan ikatan σ yang ada. Analisis 13C NMR menunjukkan satu sinyal untuk kerangka Si2C4 pada D dan dua sinyal untuk E. Kerangka D tidak memiliki cincin lingkar tiga, sementara E memiliki dua cincin lingkar tiga yang berbagi di bagian tepinya (edge sharing ring).

A.4 Gambarkan struktur molekul D dan E dengan menggunakan simbol R1, R2, Si, dan C.

Bagian B

Silikon dapat membentuk senyawa dengan bilangan koordinasi tinggi (> empat substituen) dengan unsur-unsur yang elektronegatif seperti fluorin. Karena logam fluorida sering digunakan sebagai reagen fluorinasi, silikon fluorida dengan koordinasi tinggi juga digunakan sebagai bahan fluorinasi.

Reaksi fluorinasi CCl4 menggunakan Na2SiF6 dilakukan sebagai berikut.

- Pembuakan larutan Na2SiF6:
  - Preparasi
    Larutan F: 0.855 g Na2SiF6 (188.053 g mol⁻¹) dilarutkan dalam air (volume total : 200 mL).
    Larutan G: 6.86 g Ce2(SO4)3 (568.424 g mol⁻¹) dilarutkan dalam air (volume total : 200 mL).
  - Prosedur
    Titrisi pengendapan larutan F (50.0 mL) dilakukan dengan penambahan larutan G tetes demi tetes menggunakan indikator xylene orange, yang berkoordinasi dengan Ce³⁺. Setelah penambahan 18.8 mL larutan G, warna larutan berubah dari kuning menjadi magenta. Endapan yang terbentuk merupakan senyawa biner yang mengandung Ce³⁺, dan satu-satunya senyawa silikon yang dihasilkan yaitu Si(OH)4.

B.1 Tuliskan persamaan reaksi yang setara untuk reaksi Na2SiF6 dengan Ce2(SO4)3.

- Reaksi CCl4 dengan Na2SiF6:
  (hilangnya senyawa selama tahap-tahap berlangsung diabaikan, misalnya melalui proses penguang)
  Na2SiF6(x [g]) ditambahkan ke dalam CCl4 (500.0 g) dan dipanaskan sampai 300°C dalam wadah bertekanan tinggi (pressure-resistant reaction vessel). Na2SiF6 yang tidak bereaksi dan NaCl yang dihasilkan, dipisahkan dengan cara penyaringan. Filtrat yang diperoleh diencerkan dengan CCl4 (larutan H) sampai volume total 1.00 L. Spektrum 29Si dan 19F NMR larutan H menunjukkan SiF4 sebagai satu-satunya senyawa silikon. Selain SiF4, pada spektrum 19F NMR, teramati sinyal-sinyal yang sesuai untuk CFCI3, CF2Cl2, CF3Cl, dan CF4 (cf. Tabel 1). Rasio integrasi pada spektrum 19F NMR sebanding dengan jumlah inti fluorin.
SiF₄ terhidrolisis membentuk H₂SiF₆ menurut persamaan reaksi 8:

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

Larutan H (10 mL) ditambahkan ke dalam air yang berlebih, yang menyebabkan SiF₄ terhidrolisis sempurna. Setelah pemisahan, H₂SiF₆ yang terbentuk dari hidrolisis dalam larutan dinetralkan dan dikonversi sempurna menjadi Na₂SiF₆ (larutan J).

Endapan Na₂SiF₆ yang tidak bereaksi dan NaCl, yang dipisahkan dengan penyaringan pada tahap awal (lihat yang digarisbawahi), larut sempurna dalam air untuk menghasilkan larutan K (10.0 L).

Kemudian, titrasi pengendapan tambahan dengan menggunakan larutan G dilakukan dan titik akhir titrasi dengan larutan G sebagai berikut:
- Untuk larutan J (seluruh larutan): 61.6 mL.
- Untuk 100 mL larutan K: 44.4 mL.

Perhatikan bahwa adanya NaCl atau SiO₂ tidak mempengaruhi titrasi pengendapan.

**B.2** Hitung massa NaCl yang dihasilkan dalam wadah reaksi (informasi yang digarisbawahi), dan hitung massa (x [g]) Na₂SiF₆ yang digunakan sebagai material awal (starting material).

**B.3** Sebanyak 77.8% CCl₄, yang digunakan sebagai material awal, tidak bereaksi. Hitung massa CF₂Cl yang dihasilkan.
Misteri Silikon

Bagian A

A.1 (9 pt)

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

A.2 (7 pt)

\[ \text{C}_6\text{H}_6 : \quad \text{kJ mol}^{-1}, \quad \text{C} : \quad \text{kJ mol}^{-1} \]
A.3 (6 pt)

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

A.4 (10 pt)

D (5 pt)  

E (5 pt)
Bagian B

B.1 (5 pt)

B.2 (15 pt)

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

NaCl : \[ \text{g} \]

\[ \text{g} \]

Na\(_2\)SiF\(_6\) : \[ \text{g} \]
B.3 (8 pt)

CF₃Cl: ___________ g
IChO
Problem 6
Cover sheet

Please return this cover sheet together with all the related question sheets.
Part A

Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions (M\textsuperscript{n+}) in the magma is incorporated into the silicate minerals. The M\textsuperscript{n+} studied in the problem are coordinated by oxide ions (O\textsuperscript{2-}) and adopt a four-coordinate tetrahedral (T_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\textsuperscript{n+} between the silicate minerals and magma, \( D \), can be expressed by:

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

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

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

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

A.2 A linear relationship is observed by plotting $\ln D$ against $\Delta\text{CFSE} / \Delta_O$ in the Cartesian coordinate system shown below. Estimate $D$ for 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>
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<td>3810</td>
<td>3916</td>
</tr>
<tr>
<td>(b)</td>
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<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>
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<td>3916</td>
</tr>
<tr>
<td>(e)</td>
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<td>3916</td>
<td>3878</td>
<td>3460</td>
<td>3913</td>
</tr>
<tr>
<td>(f)</td>
<td>3810</td>
<td>3913</td>
<td>3916</td>
<td>3460</td>
<td>3878</td>
</tr>
</tbody>
</table>
Part B

A mixed oxide $A$, which contains $\text{La}^{3+}$ and $\text{Cu}^{2+}$, crystallizes in a tetragonal unit cell shown in Fig. 1. In the $[\text{CuO}_6]$ octahedron, the Cu-O length along the $z$-axis ($l_z$) is longer than that of the $x$-axis ($l_x$), and $[\text{CuO}_6]$ is distorted from the regular $O_h$ geometry. This distortion removes the degeneracy of the $e_g$ orbitals ($d_{x^2-y^2}$ 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 $C_4H_2O_4$, i.e., a diacid. The pyrolysis behavior of $B$ in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of $CO_2$. The total weight loss during the formation of $A$ from $B$ is 63.6%. It should be noted that only water and $CO_2$ are released in the pyrolysis reaction.

| B.1 | Write the chemical formulae for $A$ and $B$. | 6pt |
| B.2 | Calculate $l_x$ and $l_z$ using Fig. 1. | 4pt |
| B.3 | For $\text{Cu}^{2+}$ in the distorted $[\text{CuO}_6]$ octahedron in $A$ of Fig. 1, write the names of the split $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet. | 4pt |
**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\(_4\)(L\(_1\)L\(_1\)L\(_1\)L\(_1\))\(_4\) is composed of planar dicarboxylate L\(_1\) (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 L\(_1\). Note that hydrogen atoms are not shown in Fig. 2.

**Fig. 2**
C.1 The $\theta$ of the planar dicarboxylate $L_2$ below is fixed to $90^\circ$. If the composition of the cage complex formed from $L_2$ and $\text{Cu}^{2+}$ is $\text{Cu}_n(L_2)_m$, give the smallest integer combination of $n$ and $m$. Assume that only the CO$_2^-$ groups of $L_2$ form a coordination bond to Cu$^{2+}$ ions.

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

---

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

**C.3** X contains a considerable number of pores, and 1 g of X can accommodate $3.0 \times 10^2$ mL of CO$_2$ gas in the pores at 1 bar and 25 °C. **Calculate** the average number of CO$_2$ molecules per pore.
Kimia Padatan Logam Transisi

<table>
<thead>
<tr>
<th>Pertanyaan</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>
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<tbody>
<tr>
<td>Poin</td>
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<td>4</td>
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<td>5</td>
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</tbody>
</table>

Gunung berapi di pulau Sakurajima

Bagian A

Jepang merupakan salah satu negara yang memiliki jumlah gunung berapi cukup banyak. Ketika mineral silikat mengkristal dari magma, sebagian ion-ion logam transisi \( (M^{n+}) \) yang terdapat pada magma bergabung dengan mineral silikat. Ion \( M^{n+} \) yang dipelajari dalam soal ini berkoordinasi dengan ion oksida \( (O^{2-}) \) dan memiliki geometri tetrahedral \( (T_d) \) dalam magma dan memiliki geometri oktaheral \( (O_h) \) dalam mineral silikat, keduanya menunjukkan sifat konfigurasi elektron dalam keadaan spin tinggi. Koeffisien distribusi ion \( M^{n+} \) antara mineral silikat dan magma, \( D \), dapat diungkapkan dengan:

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

dengan \([M]_s\) dan \([M]_l\) masing-masing merupakan konsentrasi ion \( M^{n+} \) dalam mineral silikat dan magma. Tabel di bawah ini menunjukkan nilai \( D \) untuk ion \( Cr^{2+} \) dan \( Mn^{2+} \) sebagai contoh.

<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>
$\Delta_O$ dan CFSE$^O$ masing-masing merupakan energi pembelahan orbital d untuk ion M$^{n+}$ dan energi penstabilan medan kristal dalam medan $O_h$. Untuk $\Delta_T$ dan CFSE$^T$ merupakan dalam medan $T_d$.

**A.1** Hitung $|CFSE^O-CFSE^T| = \Delta CFSE$ dalam ungkapan $\Delta_O$ untuk Cr$^{2+}$, Mn$^{2+}$, dan Co$^{2+}$; asumsi $\Delta_T = 4/9\Delta_O$.

**A.2** Hubungan linier diamati dengan mengalurkan ln$D$ terhadap $\Delta CFSE / \Delta_O$ dalam sistem koordinat Cartesian seperti yang ditunjukkan di bawah ini. 

Hitung $D$ untuk Co$^{2+}$.

Oksida logam MO, (M: Ca, Ti, V, Mn, or Co) mengkristal dengan struktur rock-salt dimana ion M$^{n+}$ memiliki geometri $O_h$ dengan konfigurasi elektron dalam keadaan spin tinggi. Energi kisi oksida logam tersebut berkaitan dengan interaksi gaya Coulomb yang tergantung pada jari-jari dan muatan ion serta beberapa kontribusi CFSE ion M$^{n+}$ dalam medan ligan $O_h$.

**A.3** Pilih di antara pilihan (a) sampai (f) yang paling sesuai untuk entalpi kisi $[kJ \text{ mol}^{-1}]$ oksida logam berikut.

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

Suatu campuran oksida A, yang mengandung ion La\(^{3+}\) dan Cu\(^{2+}\), mengkristal dalam sel satuan tetragonal yang ditunjukkan pada Gambar 1. Dalam kerangka oktahedron [CuO\(_6\)], panjang ikatan Cu–O pada sumbu z (l\(_z\)) lebih panjang dibandingkan pada sumbu x (l\(_x\)), dan [CuO\(_6\)] mengalami distorsi dari geometri regular O\(_h\). Distorsi tersebut menghilangkan keadaan degenerasi orbital e\(_g\) (d\(_{x^2−y^2}\) dan d\(_{z^2}\)).

Gambar 1

A dapat disintesis melalui dekomposisi termal (pirolisis) senyawa kompleks B. Senyawa B dibentuk dari campuran logam klorida yang dilarutkan dalam larutan amonia yang mengandung squaric acid C\(_4\)H\(_2\)O\(_4\), yaitu merupakan diacid. Reaksi pirolisis B di udara kering menunjukkan adanya pengurangan berat sebanyak 29.1\% pada temperatur sampai 200 °C. Hal ini disebabkan oleh pelepasan air kristal. Selanjutnya, pengurangan massa lainnya terjadi pada temperatur sampai 700 °C yang disebabkan oleh lepasnya CO\(_2\). Total pengurangan massa selama pembentukan A dari B adalah 63.6\%. Perlu diperhatikan bahwa hanya air dan CO\(_2\) yang hilang dalam reaksi pirolisis tersebut.

B.1 Tuliskan rumus molekul A dan B.

B.2 Hitung l\(_x\) dan l\(_z\) menggunakan Gambar 1.

B.3 Untuk Cu\(^{2+}\) dalam kerangka oktahedron [CuO\(_6\)] yang terdistorsi dalam A pada Gambar 1, tuliskan nama orbital e\(_g\) (d\(_{x^2−y^2}\) dan d\(_{z^2}\)) yang mengalami pembelahan menjadi (i) dan (ii), dan gambarkan konfigurasi elektron dalam dotted box pada lembar jawaban.
A merupakan sebuah insulator. Ketika satu La$^{3+}$ disubsitusi oleh satu Sr$^{2+}$, satu hole terbentuk dalam kisi kristal yang dapat menghantarkan listrik. A yang terdoping Sr$^{2+}$-doped A menunjukkan sifat superkonduktivitas di bawah 38 K. Ketika reaksi subsitusi berlangsung pada A, $2.05 \times 10^{27}$ hole m$^{-3}$ terbentuk.

**B.4 Hitung** presentase Sr$^{2+}$ yang mensubsitusi La$^{3+}$ berdasarkan perbandingan 4pt mol dalam reaksi subsitusi. Perhatikan bahwa valensi ion penyusun dan struktur kristal tidak berubah oleh reaksi subsitusi.

**Bagian C**

Cu$_2$(CH$_3$CO$_2$)$_4$ terdiri dari empat ion CH$_3$CO$_2^-$ yang terkoordinasi pada dua ion Cu$^{2+}$ (Gambar 2A). Cu$_2$(CH$_3$CO$_2$)$_4$ menunjukkan level simetri struktur yang tinggi, dengan dua sumbu koordinat melewati atom karbon dari empat ion CH$_3$CO$_2^-$ dan sebuah sumbu melewati dua ion Cu$^{2+}$. Semua sumbu berorientasi ortogonal relatif satu sama lain. Ketika ligan dikarboksilat digunakan sebagai pengganti CH$_3$CO$_2^-$, sebuah "cage complex" dapat terbentuk. "The cage complex" Cu$_4$(L$_1$)$_4$ terdiri dari dikarboksilat planar L$_1$ (Gambar 2B) dan kompleks Cu$^{2+}$ (Gambar 2C). Sudut $\theta$ merupakan sudut antara arah dua gugus karboksilat, yang ditunjukkan dengan tanda panah pada Gambar. 2B. Sudut $\theta$ menentukan struktur "cage complex". Nilai $\theta$ adalah $0^\circ$ untuk L$_1$. Perhatikan bahwa atom-atom hidrogen tidak ditunjukkan pada Gambar 2.
C.1 Nilai \( \theta \) untuk dikarboksilat planar \( \text{L2} \) adalah 90°. Jika komposisi cage complex yang dibentuk dari \( \text{L2} \) dan \( \text{Cu}^{2+} \) adalah \( \text{Cu}_n(\text{L2})_m \), berikan kombinasi bilangan bulat terkecil untuk \( n \) dan \( m \). Asumsikan hanya gugus \( \text{CO}_2^- \) dari \( \text{L2} \) yang membentuk ikatan koordinasi dengan ion \( \text{Cu}^{2+} \).
Kompleks seng, Zn₄O(CH₃CO₂)₆, terdiri dari empat tetrahedral Zn²⁺, enam CH₃CO₂⁻, dan satu O²⁻ (Gambar 3A). Pada Zn₄O(CH₃CO₂)₆, ion O²⁻ terletak pada pusat koordinat, dan tiga sumbu melewati atom C dari CH₃CO₂⁻ berorientasi ortogonal relatif satu sama lain. Ketika p-benzenedicarboxylate (Gambar 3B, L3, θ = 180°) digunakan sebagai pengganti CH₃CO₂⁻, cluster Zn²⁺ dihubungkan satu sama lain untuk membentuk padatan kristal (X) yang disebut sebagai “porous coordination polymer” (Gambar 3C). Komposisi X yaitu [Zn₄O(L3)₃]ₙ, yang memiliki struktur kristal kubus dengan pori-pori berukuran nano. Satu pori digambarkan sebagai bola pada Gambar 3D, dan tiap cluster tetrahedron Zn²⁺ digambarkan sebagai polihedron abu-abu gelap pada Gambar 3C dan 3D. Perhatikan bahwa atom-atom hidrogen tidak ditunjukkan pada Gambar 3.

Gambar 3

<table>
<thead>
<tr>
<th>IDN-4 C-6 Q-6</th>
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<th>Indonesia (Indonesia)</th>
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</table>

<table>
<thead>
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<th>C.2</th>
<th>X memiliki unit sel tipe kubus dengan panjang rusuk $a$ (Gambar 3C) dan memilik densitas sebesar 0.592 g cm⁻³. <strong>Tentukan</strong> $a$ dalam [cm].</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>C.3</th>
<th>X mengandung banyak pori, dimana setiap 1 g X dapat diisi oleh $3.0 \times 10^2$ mL CO₂ pada 1 bar dan 25 °C. <strong>Hitung</strong> jumlah rata-rata molekul CO₂ per pori.</th>
</tr>
</thead>
</table>
Kimia Padatan Logam Transisi

Bagian A

A.1 (6 pt)

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

\[ \ln D \]

\[ \Delta CFSE / \Delta O \]

\( D : \) __________

A.3 (3 pt)

_________
Bagian 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) :

\[ \text{Energy} \]

\[ e_g \]

\[ \text{(i)} \]

\[ \text{(ii)} \]

B.4 (4 pt)

\%
**Bagian C**

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<thead>
<tr>
<th>C.1 (5 pt)</th>
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</tr>
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<td>( n = )</td>
<td>( m = )</td>
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</table>

<table>
<thead>
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<th>C.2 (5 pt)</th>
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<tr>
<td>( a = ) cm</td>
<td></td>
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</table>
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

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

I  F$_3$C–S–OH  
II  F$_3$C–S–NH$_2$  
III  O=S$_2$CF$_3$ \( \text{N} \)  
IV  O=S$_2$CF$_3$  

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

1H NMR (CD$_3$CN, ppm)  
20: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)  
21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

B.1 Draw the structures of 17–19 and 21. Identifying the stereochemistry is not necessary.
Bermain dengan Kearomatikan Non-benzenoid

<table>
<thead>
<tr>
<th>Pertanyaan</th>
<th>A.1</th>
<th>A.2</th>
<th>A.3</th>
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<td>5</td>
<td>2</td>
<td>19</td>
<td>10</td>
<td>36</td>
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</tbody>
</table>

Prof Nozoe (1902-1996) membuka bidang penelitian senyawa aromatik non-benzenoid, yang sekarang ada di mana-mana dalam kimia organik.

Bagian A

Selanjutnya, keton 4 dikonversi menjadi ester 15. Senyawa 8 (berat molekul: 188) mempertahankan semua stereocenter di 7. Senyawa 9 dan 10 memiliki lima stereocenter dan tidak ada ikatan rangkap karbon-
IChO

Q7-3

Indonesia (Indonesia)


\[ \text{H}_2^{15}\text{O} \text{ untuk sintesis linearifolianone berlabel-}^{18}\text{O} \text{ dari 11 dan 12. Senyawa 13 dan 14 adalah isotopomer berlabel-}^{18}\text{O. Dengan mengabaikan pelabelan isotop, baik 13 dan 14 keduanya menghasilkan produk 15 yang sama dengan stereokimia yang identik.} \]
A.2 **Pilih** struktur A yang paling tepat.  

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

A.3 **Gambarkan** struktur 8–14 dan identifikasi dengan jelas stereokimianya di posisi yang tepat. Selain itu, **tuliskan** atom-atom \( ^{18}\text{O} \) yang terdapat pada 13 dan 14 seperti contoh berikut.
Bagian B


\[ \text{16} \xrightarrow{\text{Br}_2, \text{CH}_3\text{COOH}} \text{17} \quad \text{C}_{15}\text{H}_{12}\text{Br}_2\text{O} \]

\[ \text{16} \xrightarrow{\text{Et}_3\text{N}, \text{CH}_2\text{Cl}_2} \text{18} \quad \text{C}_{15}\text{H}_{10}\text{O} \]

\[ \text{18} \xrightarrow{\text{Cl}_2\text{S}_2\text{Cl}_2} \text{19} \quad \text{C}_{15}\text{H}_{10}\text{Cl}_2 \]

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

\[ \text{21} \xrightarrow{} \text{22} + \text{18} \]

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

\( 21: \delta 8.5-7.3 \text{ (15H), 5.5 (2H), 3.4 (2H)}\)

B.1 **Gambarkan** struktur 17–19 dan 21. Identifikasi stereokimia tidak diperlukan. 10pt
Bermain dengan Kearomatikan Non-benzenoid

Bagian A

A.1 (5 pt)

2 (2 pt) 6 (3 pt)

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)
Bagian B

<p>| | |</p>
<table>
<thead>
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<th></th>
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<tr>
<td>B.1 (10 pt)</td>
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<tr>
<td>17 (2 pt)</td>
<td>18 (2 pt)</td>
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<tr>
<td>19 (3 pt)</td>
<td>21 (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

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<th>A.2</th>
<th>A.3</th>
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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.

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

| A.1 | **Draw** the structures of A–C. Stereoisomers should be distinguished. | 9pt |
| A.2 | Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product D whose molecular weight was 2 Da lower than that of [5]carbohelicene. The \(^1\)H NMR chemical shifts of D are listed below. **Draw** the structure of D. | 3pt |

\[ [D \ (\delta, \ ppm \ in \ CS_2, \ r.t.), \ 8.85 \ (2H), \ 8.23 \ (2H), \ 8.07 \ (2H), \ 8.01 \ (2H), \ 7.97 \ (2H), \ 7.91 \ (2H)] \]

[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.

\[
\begin{align*}
&M \quad \text{(M)} \\
&P \quad \text{(P)}
\end{align*}
\]

[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 \( \text{J} \), the same reaction sequence gives the optically active sumanene derivative \( \text{K} \). The stereocenters in \( \text{J} \) suffer no inversion during the metathesis reaction. Draw the structure of \( \text{K} \) with the appropriate stereochemistry.
Molekul Organik Dinamis dan Kiralitasnya

<table>
<thead>
<tr>
<th>Pertanyaan</th>
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<th>A.2</th>
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</tbody>
</table>

Bagian A

Hidrokarbon aromatik polisiklik dengan hubungan-orto berurutan disebut \([n]\)carbohelicene (di sini, \(n\) mewakili banyaknya cincin lingkar-enam) (lihat di bawah). \([4]\)Carbohelicene \((4[C])\) dibuat secara efisien dengan rute yang menggunakan fotoreaksi seperti ditunjukkan di bawah ini, melalui suatu intermediet \((\text{Int.})\) yang dapat langsung dioksidasi oleh iod.

Fotoreaksi berlangsung dengan cara yang serupa dengan contoh berikut.
Catatan: Untuk semua Pertanyaan 8, gambarkan ikatan tunggal dan ikatan rangkap berselang-seling dalam jawaban Anda seperti yang dicontohkan pada carbohelicene. Jangan gunakan lingkaran untuk sistem $\pi$ terkonjugasi.

| A.1 | Gambarkan struktur A–C. Stereosomer harus jelas dibedakan. | 9pt |


Photo courtesy: The Japan Prize Foundation

![Diagram multiple helicene E](image)

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

A.3 Trimerisasi 1,2-dibromobenzena yang dimediasi-nikel menghasilkan triphenylene. Ketika reaksi yang sama diterapkan pada suatu enantiomer F, yaitu \((P)\)-F, diperoleh multiple helicene G \((C_{66}H_{36})\). Mengingat bahwa interkonversi antara stereoisomer tidak terjadi selama reaksi, **identifikasi semua** kemungkinan stereoisomer G yang terbentuk dalam proses ini, tanpa duplikasi. Sebagai referensi, satu isomer harus digambarkan secara lengkap dengan kiralitas yang didefinisikan seperti pada contoh di atas, dengan label numerik; stereoisomer lainnya harus dituliskan dengan nomor lokasi serta label M dan P sesuai dengan penomoran yang sama. Misalnya, stereoisomer E lainnya harus dituliskan sebagai \((1, 2, 3) = (P, M, P), (P, M, M), (P, P, M), (M, M, M), (M, M, P), (M, P, M), (M, P, P),\) dan \((M, P, M)\).

![Diagram trimerisasi 1,2-dibromobenzena](image)

\(\text{Ni}(\text{cod})_2\)
Bagian B

Sumanene adalah hidrokarbon berbentuk mangkuk yang pertama kali dilaporkan di Jepang pada tahun 2003. Nama "sumanene" berasal dari kata Sanskerta-Hindi "suman" yang berarti bunga matahari. Sin-
tesis sumanene dicapai melalui serangkaian reaksi yang terdiri dari metatesis pembukaan-cincin dan penutupan-cincin.

Reaksi metatesis representatif yang dikatalisis oleh katalis rutenium (Ru*) ditunjukkan di bawah ini.

B.1 **Gambarkan** struktur intermediet I (stereokimianya tidak diperlukan). 3pt

---

**IChO**

IDN-4 C-8 Q-4

Indonesia (Indonesia)
B.2 Dimulai dari prekursor optis aktif J, serangkaian reaksi yang sama menghasilkan turunan *sumanene* K yang optis aktif. *Stereocenters* dalam J tidak mengalami inversi selama reaksi metatesis. **Gambarkan** struktur K dengan stereokimianya yang sesuai.
# Molekul Organik Dinamis dan Kiralitasnya

## Bagian A

### A.1 (9 pt)

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 pt</td>
<td>3 pt</td>
<td>3 pt</td>
</tr>
</tbody>
</table>

### A.2 (3 pt)

<p>| |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>
A.3 (7 pt)
Bagian B

B.1 (3 pt)

B.2 (4 pt)
ICHo
Problem 9
Cover sheet

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>
</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 (**1**₂) 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 **1**₂, all the NH protons derived from 1 were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of 3. These data indicate that hydrogen bonds are formed between the NH moieties of 1 and atoms **X** of another molecule of 1 to form the dimeric capsule.

A.2 *Circle* all the appropriate atom(s) **X** in 1.

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

\[ Z + 1₂ \rightarrow Z@1₂ \]  

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

\[ K_a = \frac{[Z@1₂]}{[Z][1₂]} \]  

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

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 each Hₐ signal.
$^1$H NMR measurements in C$_6$D$_6$ revealed that 2$_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants ($K_a$) which are expressed below were determined for various temperatures. [solvent@2$_2$] denotes a species containing one or more solvent molecules.

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

Similarly, the $K_a$ values of CH$_4$ and 1$_2$ given as eq (2) at various temperatures in C$_6$D$_6$ were also determined by $^1$H NMR measurements. The plots of the two association constants (as ln $K_a$ vs 1/T) are shown below.

No C$_6$D$_6$ molecule is encapsulated in 1$_2$. 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 CH$_4$</td>
<td>2$_2$ and AdA</td>
</tr>
<tr>
<td>(5)</td>
<td>1$_2$ and CH$_4$</td>
<td>2$_2$ and AdA</td>
</tr>
</tbody>
</table>
Kapsul Suka dan Benci

<table>
<thead>
<tr>
<th>Pertanyaan</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>Poin</td>
<td>13</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>23</td>
</tr>
<tr>
<td>Nilai</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Anak yang baik tidak melakukan ini, tetapi jika Anda membuka jahitan bola tenis, Anda dapat membongkarnya menjadi dua bagian berbentuk-U.

Berdasarkan ide ini, senyawa 1 dan 2 disintesis sebagai molekul berbentuk-U dengan ukuran berbeda. Senyawa 3 dibuat sebagai pembanding senyawa 1 dan perilaku enkapsulasi senyawa-senyawa tersebut dipelajari.
Rute sintesis menuju 2 ditunjukkan di bawah ini. Komposisi unsur senyawa 9: C; 40.49%, H; 1.70%, dan O; 17.98% (% massa).
A.1 Gambarkan struktur 4-9; stereokimianya dapat diabaikan. Gunakan "PMB" sebagai substituen alih-alih menggambarkan seluruh molekul gugus \( p\)-methoxybenzyl yang ditunjukkan pada skema di atas.
Pada spektrum massa 1, puncak ion yang mewakili dimernya (12) jelas teramati, sedangkan puncak ion untuk 32 tidak teramati pada spektrum 3. Pada spektrum 1H NMR larutan 12, semua proton NH yang bersal dari 1 teramati memiliki lingkungan kimia yang ekivalen, dan geseran kimianya signifikan berbeda dengan proton NH pada 3. Data ini menunjukkan bahwa ikatan hidrogen terbentuk antara gugus NH pada 1 dengan atom X pada molekul 1 lainnya untuk membentuk kapsul dimer.

| A.2 | Lingkari semua atom X yang sesuai dalam 1. | 2pt |
| A.3 | Tuliskan jumlah ikatan hidrogen dalam kapsul dimer (12). | 2pt |
Kapsul dimer 1 ($1_2$) memiliki ruang internal tempat suatu molekul kecil Z dapat dienkapsulasi. Fenomena ini dinyatakan dengan persamaan berikut:

$$Z + 1_2 \rightarrow Z@1_2$$  (1)

Tetapan kesetimbangan enkapsulasi Z ke dalam $1_2$ dinyatakan sebagai berikut:

$$K_a = \frac{\text{Z@1}_2}{\text{Z}\cdot1_2}$$  (2)

Enkapsulasi suatu molekul ke dalam suatu kapsul dapat dimonitor dengan spektroskopi NMR. Misalnya, $1_2$ dalam $C_6D_6$ sebelum dan sesudah penambahan CH$_4$ memberikan sinyal berbeda pada spektrum $^1$H NMR.

Senyawa 2 juga membentuk kapsul dimer ($2_2$) yang kaku dan lebih besar. Spektrum $^1$H NMR 2 diukur dalam $C_6D_6$, $C_6D_5F$, dan campuran pelarut $C_6D_6/C_6D_5F$, dengan kondisi lainnya dibuat tetap. Geseran kimia proton H$^a$ pada 2 dalam pelarut-pelarut tersebut dirangkum di bawah ini, dan tidak ada sinyal H$^a$ lainnya pada 2 yang teramati, kecuali yang sudah tercantum. Asumsikan bahwa interior kapsul selalu terisi oleh jumlah molekul pelarut terbanyak yang mungkin masuk dan bahwa setiap sinyal mewakili satu spesi kapsul yang terisi.

<table>
<thead>
<tr>
<th>pelarut</th>
<th>$\delta$ (ppm) H$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6D_6$</td>
<td>4.60</td>
</tr>
<tr>
<td>$C_6D_5F$</td>
<td>4.71</td>
</tr>
<tr>
<td>$C_6D_6 / C_6D_5F$</td>
<td>4.60, 4.71, 4.82</td>
</tr>
</tbody>
</table>

**A.4 Tentukan** jumlah molekul $C_6D_6$ dan $C_6D_5F$ yang terenkapsulasi di dalam $2_2$. 3pt berdasarkan sinyal H$^a$ pada tabel.
Pengukuran $^1$H NMR dalam C$_6$D$_6$ menunjukkan bahwa 2 dapat memuat satu molekul 1-adamantanecarboxylic acid (AdA), dan tetapan kesetimbangan asosiasi ($K_a$) yang dinyatakan berikut ditentukan pada berbagai temperatur. [solvent@2] adalah spesi yang mengandung satu atau lebih molekul pelarut.

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

Demikian pula, nilai $K_a$ CH$_4$ dan 1, yang dinyatakan dengan persamaan (2) pada berbagai temperatur dalam C$_6$D$_6$ juga ditentukan melalui pengukuran $^1$H NMR. Aluran dua tetapan asosiasi (sebagai ln $K_a$ vs 1/T) ditunjukkan di bawah ini.

Tidak ada molekul C$_6$D$_6$ yang terenkapsulasi di dalam 1. Pada garis II, perubahan entropi ($\Delta S$) adalah (1) dan perubahan entalpi ($\Delta H$) adalah (2), yang menunjukkan bahwa gaya pendorong enkapsulasi pada garis II adalah (3). Dengan demikian, garis I mewakili (4), dan garis II mewakili (5).

### A.5 Isilah pertanyaan (1)-(5) dengan huruf A atau B yang bersesuaian dengan uraian paragraf di atas.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>positif</td>
<td>negatif</td>
</tr>
<tr>
<td>(2)</td>
<td>positif</td>
<td>negatif</td>
</tr>
<tr>
<td>(3)</td>
<td>$\Delta S$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td>(4)</td>
<td>1 dan CH$_4$</td>
<td>2 dan AdA</td>
</tr>
<tr>
<td>(5)</td>
<td>1 dan CH$_4$</td>
<td>2 dan AdA</td>
</tr>
</tbody>
</table>
# Kapsul Suka dan Benci

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

A.3 (2 pt)

A.4 (3 pt)

<table>
<thead>
<tr>
<th>$\delta$ (ppm) H</th>
<th>jumlah C$_6$D$_5$</th>
<th>jumlah C$_6$D$_5$F</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>
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</tr>
</tbody>
</table>

A.5 (3 pt)

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