

IDN-3 C-0 C-1

IDN-3 C-0 C
Nathanael Widjaja

ICHO
General instructions
Cover sheet

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



IDN-3 C-0 G-1

G0-1

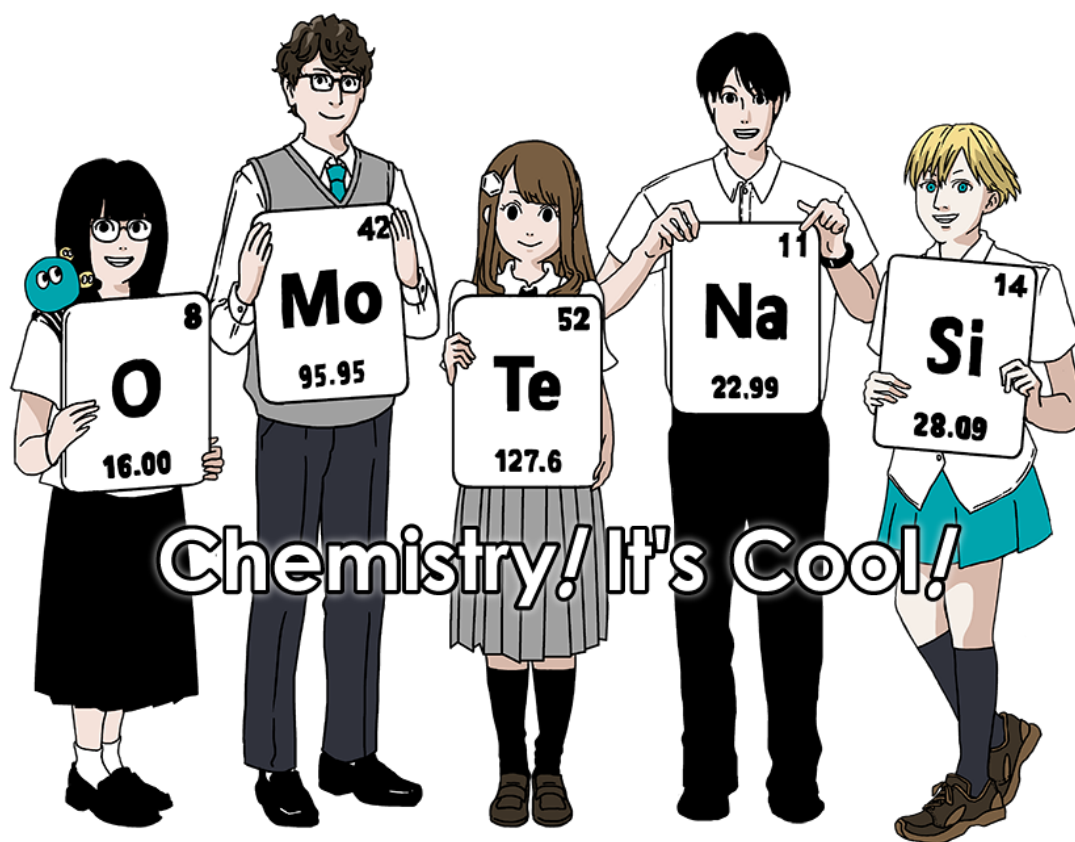
English (Official)

International Chemistry Olympiad 2021 Japan

53rd IChO2021 Japan

25th July - 2nd August, 2021

<https://www.icho2021.org>





IDN-3 C-0 G-2

G0-2

English (Official)

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

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

Physical Constants and Equations

Constants

| | |
|---|--|
| Speed of light in vacuum | $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ |
| Planck constant | $h = 6.62607015 \times 10^{-34} \text{ J s}$ |
| Elementary charge | $e = 1.602176634 \times 10^{-19} \text{ C}$ |
| Electron mass | $m_e = 9.10938370 \times 10^{-31} \text{ kg}$ |
| Electric constant (permittivity of vacuum) | $\epsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$ |
| Avogadro constant | $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$ |
| Boltzmann constant | $k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$ |
| Faraday constant | $F = N_A \times e = 9.64853321233100184 \times 10^4 \text{ C mol}^{-1}$ |
| Gas constant | $R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 8.2057366081 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ |
| Unified atomic mass unit | $u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$ |
| Standard pressure | $p = 1 \text{ bar} = 10^5 \text{ Pa}$ |
| Atmospheric pressure | $p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa}$ |
| Zero degree Celsius | $0^\circ \text{C} = 273.15 \text{ K}$ |
| Ångstrom | $1 \text{ Å} = 10^{-10} \text{ m}$ |
| Picometer | $1 \text{ pm} = 10^{-12} \text{ m}$ |
| Electronvolt | $1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}$ |
| Part-per-million | $1 \text{ ppm} = 10^{-6}$ |
| Part-per-billion | $1 \text{ ppb} = 10^{-9}$ |
| Part-per-trillion | $1 \text{ ppt} = 10^{-12}$ |
| pi | $\pi = 3.141592653589793$ |
| The base of the natural logarithm (Euler's number) | $e = 2.718281828459045$ |

Equations

| | |
|--|--|
| The ideal gas law | $PV = nRT$, where P is the pressure, V is the volume, n is the amount of substance, T is the absolute temperature of ideal gas. |
| Coulomb's law | $F = k_e \frac{q_1 q_2}{r^2}$, where F is the electrostatic force, $k_e (\approx 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2})$ is Coulomb's constant, q_1 and q_2 are the magnitudes of the charges, and r is the distance between the charges. |
| The first law of thermodynamics | $\Delta U = q + w$, where ΔU is the change in the internal energy, q is the heat supplied, w is the work done. |
| Enthalpy H | $H = U + PV$ |
| Entropy based on Boltzmann's principle S | $S = k_B \ln W$, where W is the number of microstates. |
| The change of entropy ΔS | $\Delta S = \frac{q_{\text{rev}}}{T}$, where q_{rev} is the heat for the reversible process. |
| Gibbs free energy G | $G = H - TS$ $\Delta_r G^\circ = -RT \ln K = -zFE^\circ$, where K is the equilibrium constant, z is the number of electrons, E° is the standard electrode potential. |
| Reaction quotient Q | $\Delta_r G = \Delta_r G^\circ + RT \ln Q$ For a reaction $aA + bB \rightleftharpoons cC + dD$ $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$, where $[A]$ is the concentration of A. |

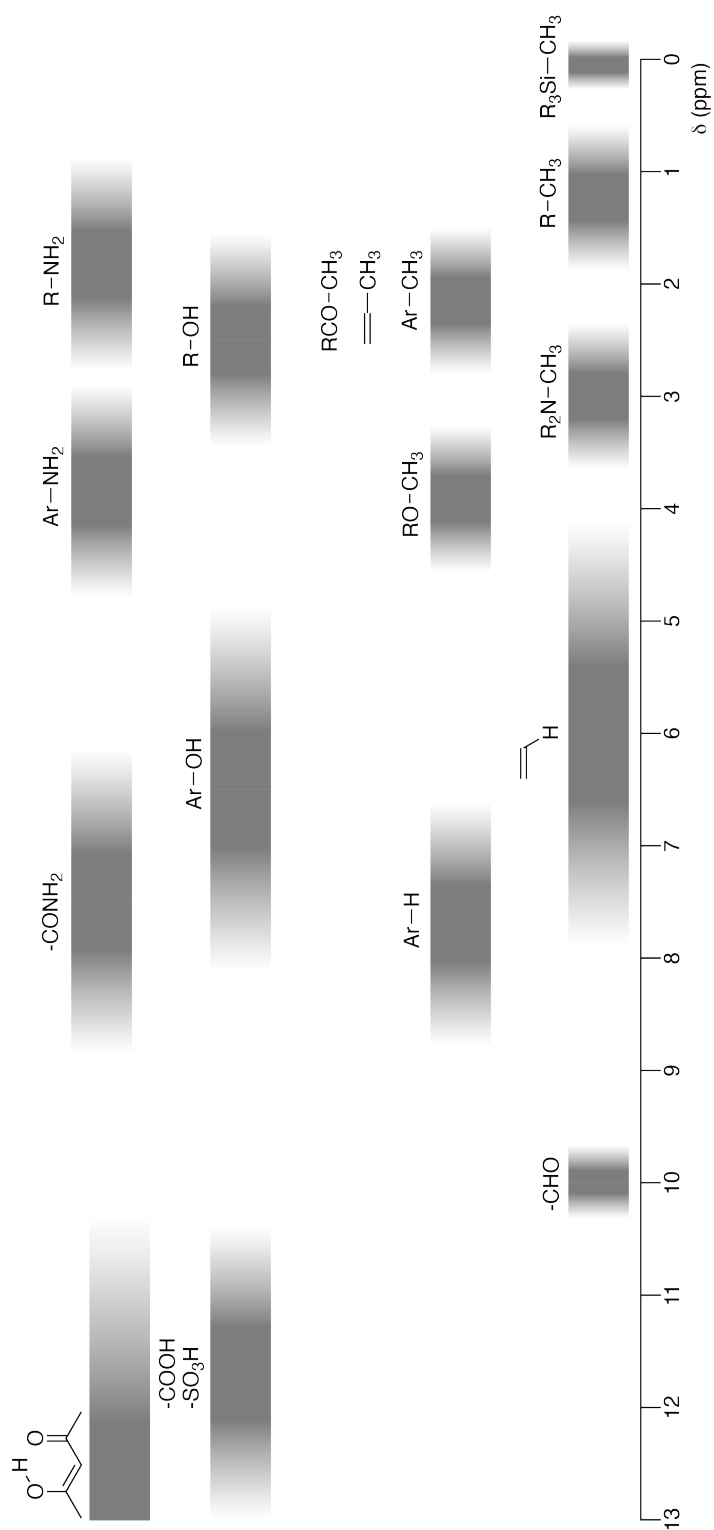
| | |
|---|--|
| Heat change Δq | $\Delta q = nc_m \Delta T$, where c_m is the temperature-independent molar heat capacity. |
| Nernst equation for re-dox reaction | $E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration of reduced substance. |
| Arrhenius equation | $k = A \exp\left(-\frac{E_a}{RT}\right)$, where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy. $\exp(x) = e^x$ |
| Lambert-Beer equation | $A = \varepsilon lc$, where A is the absorbance, ε is the molar absorption coefficient, l is the optical path length, c is the concentration of the solution. |
| Henderson-Hasselbalch equation | For an equilibrium $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, where equilibrium constant is K_a , $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ |
| Energy of a photon | $E = h\nu = h\frac{c}{\lambda}$, where ν is the frequency, λ is the wavelength of the light. |
| The sum of a geometric series | When $x \neq 1$, $1 + x + x^2 + \dots + x^n = \sum_{i=0}^n x^i = \frac{1 - x^{n+1}}{1 - x}$ |
| Approximation equation that can be used to solve problems | When $x \ll 1$, $\frac{1}{1 - x} \simeq 1 + x$ |

Periodic Table

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|--------------------------------|---------------------------------|----------------------------------|-------------------------------------|-------------------------------------|----------------------------------|---------------------------------|---------------------------------|----------------------------------|------------------------------------|-----------------------------------|-----------------------------------|----------------------------------|---------------------------------|-----------------------------------|-----------------------------------|----------------------------------|---------------------------------|
| 1 H Hydrogen 1.008 | | | | | | | | | | | | | | | | | 2 He Helium 4.003 |
| 3 Li Lithium 6.968 | 4 Be Beryllium 9.012 | | | | | | | | | | | | | | | 9 F Fluorine 18.998 | 10 Ne Neon 20.180 |
| 11 Na Sodium 22.990 | 12 Mg Magnesium 24.306 | | | | | | | | | | | | | | | 17 Cl Chlorine 35.452 | 18 Ar Argon 39.948 |
| 19 K Potassium 39.098 | 20 Ca Calcium 40.078 | 21 Sc Scandium 44.956 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 | 25 Mn Manganese 54.938 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933 | 28 Ni Nickel 58.693 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.630 | 33 As Arsenic 74.922 | 34 Se Selenium 78.971 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.798 |
| 37 Rb Rubidium 85.468 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.906 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.95 | 43 Tc Technetium [99] | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.906 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.868 | 48 Cd Cadmium 112.414 | 49 In Indium 114.818 | 50 Sn Tin 118.710 | 51 Sb Antimony 121.760 | 52 Te Tellurium 127.60 | 53 I Iodine 126.904 | 54 Xe Xenon 131.293 |
| 55 Cs Caesium 132.905 | 56 Ba Barium 137.327 | 57-71 La-Lu Lanthanoids | 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.948 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.207 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.217 | 78 Pt Platinum 195.084 | 79 Au Gold 196.967 | 80 Hg Mercury 200.592 | 81 Tl Thallium 204.384 | 82 Pb Lead 207.2 | 83 Bi Bismuth 208.98 | 84 Po Polonium [210] | 85 At Astatine [210] | 86 Rn Radon [222] |
| 87 Fr Francium [223] | 88 Ra Radium [226] | 89-103 Ac-Lr Actinoids | 104 Rf Rutherfordium [267] | 105 Db Dubnium [268] | 106 Sg Seaborgium [271] | 107 Bh Bohrium [272] | 108 Hs Hassium [277] | 109 Mt Meitnerium [276] | 110 Ds Darmstadtium [281] | 111 Rg Roentgenium [280] | 112 Cn Copernicium [285] | 113 Nh Nihonium [278] | 114 Fl Flerovium [289] | 115 Mc Moscovium [289] | 116 Lv Livermorium [293] | 117 Ts Tennessine [293] | 118 Og Oganesson [294] |
| 57-71 La-Lu Lanthanoids | | 57 La Lanthanum 138.905 | 58 Ce Cerium 140.116 | 59 Pr Praseodymium 140.908 | 60 Nd Neodymium 144.242 | 61 Pm Promethium [145] | 62 Sm Samarium 150.36 | 63 Eu Europium 151.964 | 64 Gd Gadolinium 157.25 | 65 Tb Terbium 158.925 | 66 Dy Dysprosium 162.500 | 67 Ho Holmium 164.930 | 68 Er Erbium 167.259 | 69 Tm Thulium 168.934 | 70 Yb Ytterbium 173.045 | 71 Lu Lutetium 174.967 | |
| 89-103 Ac-Lr Actinoids | | 89 Ac Actinium [227] | 90 Th Thorium 232.038 | 91 Pa Protactinium 231.036 | 92 U Uranium 238.029 | 93 Np Neptunium [237] | 94 Pu Plutonium [239] | 95 Am Americium [243] | 96 Cm Curium [247] | 97 Bk Berkelium [247] | 98 Cf Californium [252] | 99 Es Einsteinium [252] | 100 Fm Fermium [257] | 101 Md Mendelevium [258] | 102 No Nobelium [259] | 103 Lr Lawrencium [262] | |

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

¹H NMR Chemical Shifts



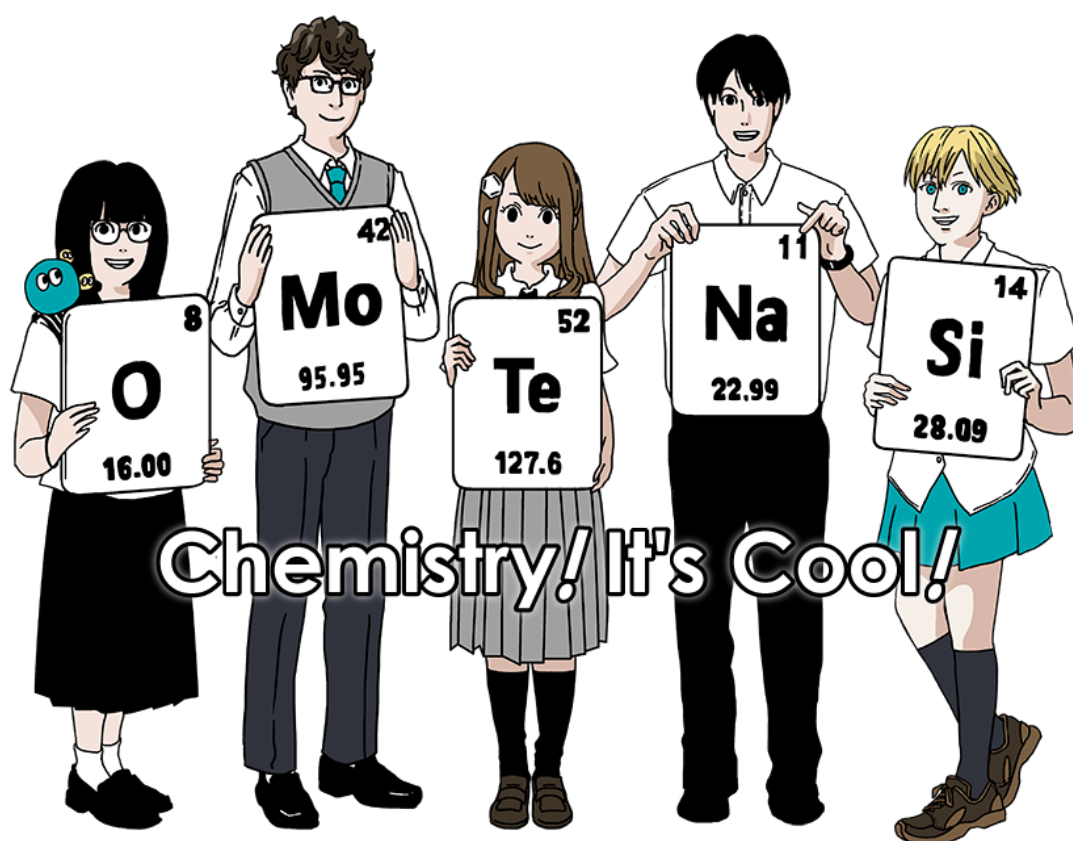
$\Delta\delta$ for one alkyl group-substitution: *ca.* +0.4 ppm

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Petunjuk Umum

- Gunakan hanya pena saja untuk menuliskan jawaban.
- Kalkulator yang digunakan harus yang *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.
- Semua jawaban harus dituliskan menggunakan pena di dalam kotak yang sesuai pada **lembar jawaban**. Gunakan bagian belakang lembar soal untuk corat-coret. Ingatlah bahwa jawaban yang dituliskan di luar kotak jawaban tidak akan dinilai.
- 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

| | Judul | Nilai Total | Persentase |
|---|---|-------------|------------|
| 1 | Hidrogen pada Permukaan Logam | 24 | 11 |
| 2 | Kapsul Waktu Isotop | 35 | 11 |
| 3 | Hukum Lambert-Beer? | 22 | 8 |
| 4 | Kimia Redoks Seng | 32 | 11 |
| 5 | Misteri Silikon | 60 | 12 |
| 6 | Kimia Padatan Logam Transisi | 45 | 13 |
| 7 | Bermain dengan Kearomatikan Non-benzenoid | 36 | 13 |
| 8 | Molekul Organik Dinamis dan Kiralitasnya | 26 | 11 |
| 9 | Kapsul Suka dan Benci | 23 | 10 |
| | Total | 100 | 100 |

Tetapan Fisik dan Persamaan

Tetapan

| | |
|---|--|
| Kecepatan cahaya dalam ruang hampa | $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ |
| Tetapan Planck | $h = 6.62607015 \times 10^{-34} \text{ J s}$ |
| Muatan Elementer | $e = 1.602176634 \times 10^{-19} \text{ C}$ |
| Massa Elektron | $m_e = 9.10938370 \times 10^{-31} \text{ kg}$ |
| Tetapan Listrik (permitivitas vakum) | $\epsilon_0 = 8.85418781 \times 10^{-12} \text{ F m}^{-1}$ |
| Tetapan Avogadro | $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$ |
| Tetapan Boltzmann | $k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$ |
| Tetapan Faraday | $F = N_A \times e = 9.64853321233100184 \times 10^4 \text{ C mol}^{-1}$ |
| Tetapan Gas | $R = N_A \times k_B = 8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 8.2057366081 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ |
| Satuan massa atom (<i>Unified atomic mass unit</i>) | $u = 1 \text{ Da} = 1.66053907 \times 10^{-27} \text{ kg}$ |
| Tekanan standar | $p = 1 \text{ bar} = 10^5 \text{ Pa}$ |
| Tekanan atmosfer | $p_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa}$ |
| Nol derajat Celsius | $0^\circ \text{C} = 273.15 \text{ K}$ |
| Ångstrom | $1 \text{ Å} = 10^{-10} \text{ m}$ |
| Picometer | $1 \text{ pm} = 10^{-12} \text{ m}$ |
| Electronvolt | $1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}$ |
| <i>Part-per-million</i> | $1 \text{ ppm} = 10^{-6}$ |
| <i>Part-per-billion</i> | $1 \text{ ppb} = 10^{-9}$ |
| <i>Part-per-trillion</i> | $1 \text{ ppt} = 10^{-12}$ |
| pi | $\pi = 3.141592653589793$ |
| basis logaritma netral (bilangan Euler) | $e = 2.718281828459045$ |

Persamaan

| | |
|---|---|
| Hukum gas ideal | $PV = nRT$, dengan P adalah tekanan, V adalah volume, n adalah jumlah zat, T adalah temperatur absolut gas ideal. |
| Hukum Coulomb | $F = k_e \frac{q_1 q_2}{r^2}$, dengan F gaya elektrostatis, $k_e (\simeq 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2})$ adalah tetapan Coulomb, q_1 dan q_2 adalah besarnya muatan, dan r jarak antar muatan. |
| Hukum pertama termodinamika | $\Delta U = q + w$, dengan ΔU adalah perubahan energi dalam, q adalah kalor yang terlibat, w adalah kerja yang dilakukan. |
| Entalpi H | $H = U + PV$ |
| Entropi berdasarkan prinsip Boltzmann S | $S = k_B \ln W$, dengan W adalah jumlah keadaan-mikro (<i>microstates</i>). |
| Perubahan entropi ΔS | $\Delta S = \frac{q_{\text{rev}}}{T}$, dengan q_{rev} adalah kalor untuk proses reversibel. |
| Energi bebas Gibbs G | $G = H - TS$ $\Delta_r G^\circ = -RT \ln K = -zFE^\circ$, dengan K adalah tetapan kesetimbangan, z adalah jumlah elektron, E° adalah potensial elektroda standar. |
| Kuosisen reaksi Q | $\Delta_r G = \Delta_r G^\circ + RT \ln Q$ Untuk reaksi $aA + bB \rightleftharpoons cC + dD$ $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$, dengan $[A]$ adalah konsentrasi A. |

| | |
|--|---|
| Perubahan kalor Δq | $\Delta q = nc_m \Delta T$, dengan c_m adalah kapasitas kalor molar yang tidak bergantung temperatur |
| Persamaan Nernst untuk reaksi redoks | $E = E^\circ + \frac{RT}{zF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$, dengan C_{ox} adalah konsentrasi zat yang teroksidasi, C_{red} adalah konsentrasi zat yang tereduksi. |
| Persamaan Arrhenius | $k = A \exp\left(-\frac{E_a}{RT}\right)$, dengan k adalah tetapan laju, A adalah faktor pre-eksponensial, E_a adalah energi aktivasi. $\exp(x) = e^x$ |
| Persamaan Lambert-Beer | $A = \epsilon lc$, dengan A adalah absorptansi, ϵ adalah koefisien absorpsi molar, l adalah jarak tempuh cahaya, c adalah konsentrasi larutan. |
| Persamaan Henderson-Hasselbalch | Untuk suatu kesetimbangan , dengan tetapan kesetimbangan K_a , $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ |
| Energi foton | $E = h\nu = h\frac{c}{\lambda}$, dengan ν adalah frekuensi, λ adalah panjang gelombang cahaya. |
| Jumlah deret geometri | Ketika $x \neq 1$, $1 + x + x^2 + \dots + x^n = \sum_{i=0}^n x^i = \frac{1 - x^{n+1}}{1 - x}$ |
| Persamaan aproksimasi yang dapat digunakan untuk mengerjakan soal. | Ketika $x \ll 1$, $\frac{1}{1 - x} \simeq 1 + x$ |

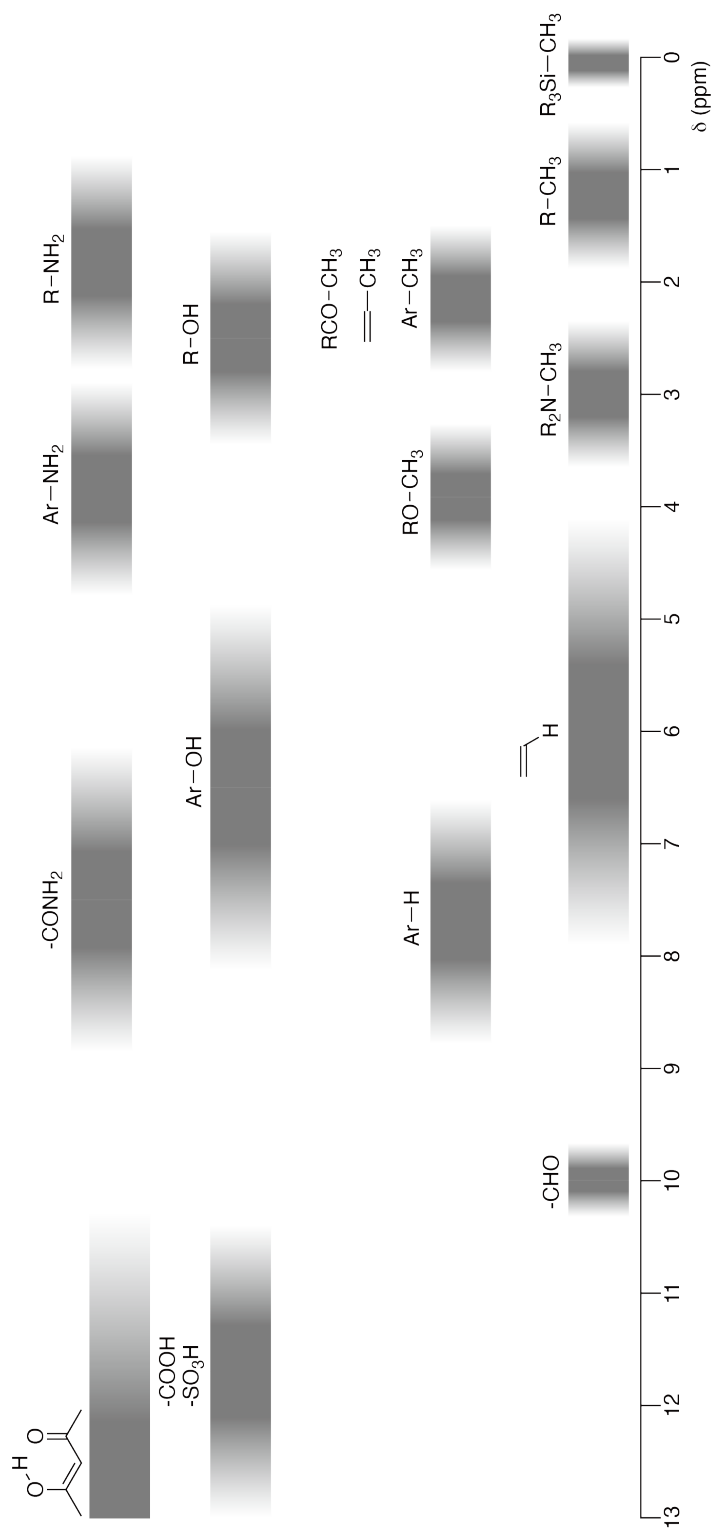
Tabel Periodik

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|--------------------------------|---------------------------------|----------------------------------|-------------------------------------|-------------------------------------|----------------------------------|---------------------------------|---------------------------------|----------------------------------|------------------------------------|-----------------------------------|-----------------------------------|----------------------------------|---------------------------------|-----------------------------------|-----------------------------------|----------------------------------|---------------------------------|
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Key:

| | |
|--------------------------------|--|
| 113 Nh Nihonium [278] | atomic number |
| | Symbol |
| | name |
| | atomic weight [in parenthesis for the radioactive element] |

Geseran Kimia ^1H NMR



$\Delta\delta$ untuk satu substitusi gugus-alkil: *ca.* +0.4 ppm

IDN-3 C-1 C-1

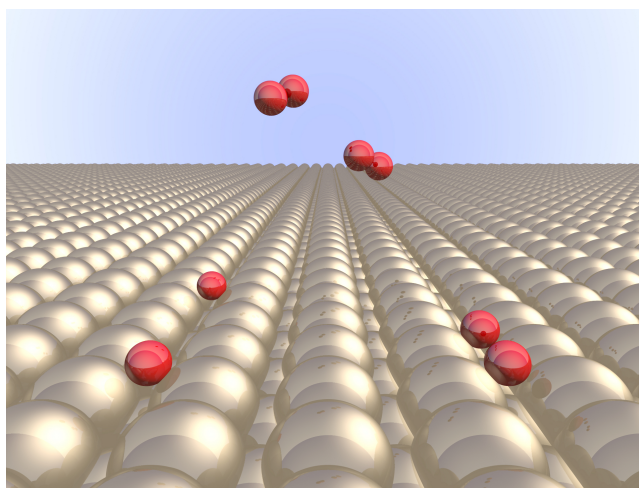
IDN-3 C-1 C
Nathanael Widjaja

ICHO
Problem 1
Cover sheet

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

Hydrogen at a Metal Surface

| 11 % of the total | | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----|-------|
| Question | A.1 | A.2 | B.1 | B.2 | B.3 | B.4 | Total |
| Points | 6 | 4 | 5 | 3 | 3 | 3 | 24 |
| Score | | | | | | | |



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

Part A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad})$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules (H_2) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of H_2 is represented by two variables: the interatomic distance, d , and the height relative to the surface metal atom, z . It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the potential energy in units of kJ per mole of H_2 . The solid line spacing is 20 kJ mol^{-1} , the dashed line spacing is 100 kJ mol^{-1} , and the spacing between solid and dashed lines is 80 kJ mol^{-1} . The zero-point vibration energy is ignored.

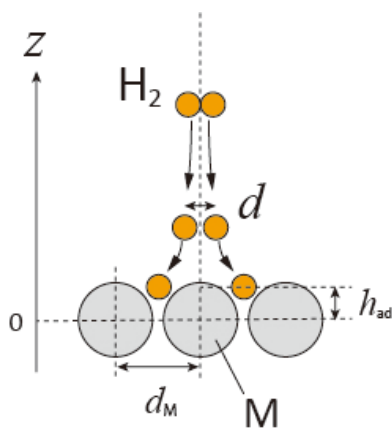


Fig.1 Definition of variables. Drawing is not in scale.

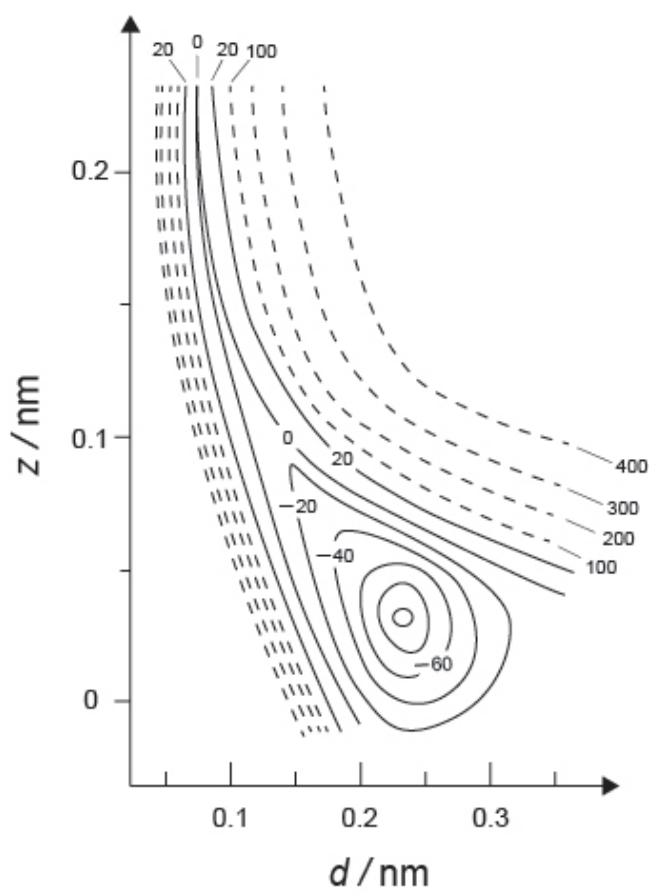


Fig.2

- A.1** For each of the following items (i)–(iii), **select** the closest value from A–G. 6pt
- (i) The interatomic distance for a gaseous H₂ molecule
 - (ii) The interatomic distance between metal atoms (d_M in Fig. 1)
 - (iii) The distance of adsorbed H atoms from the surface (h_{ad} in Fig. 1)

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

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.



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:

$$r_1 = k_1 P_{\text{H}_2} (1 - \theta)^2 \quad (2)$$

$$r_2 = k_2 \theta^2 \quad (3)$$

$$r_3 = k_3 \theta \quad (4)$$

where $k_1 [\text{s}^{-1} \text{Pa}^{-1}]$, $k_2 [\text{s}^{-1}]$ 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, θ ($0 \leq \theta \leq 1$) 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 θ remains constant.

B.1 r_3 can be expressed as:

5pt

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\text{H}_2} C}}} \quad (5)$$

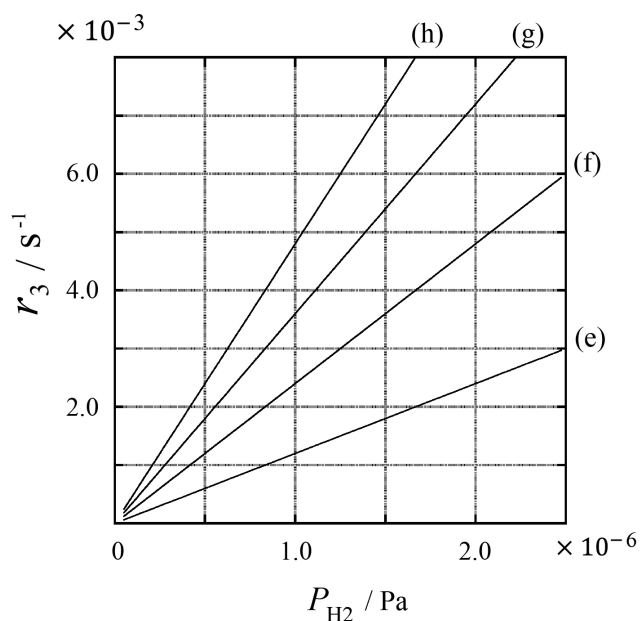
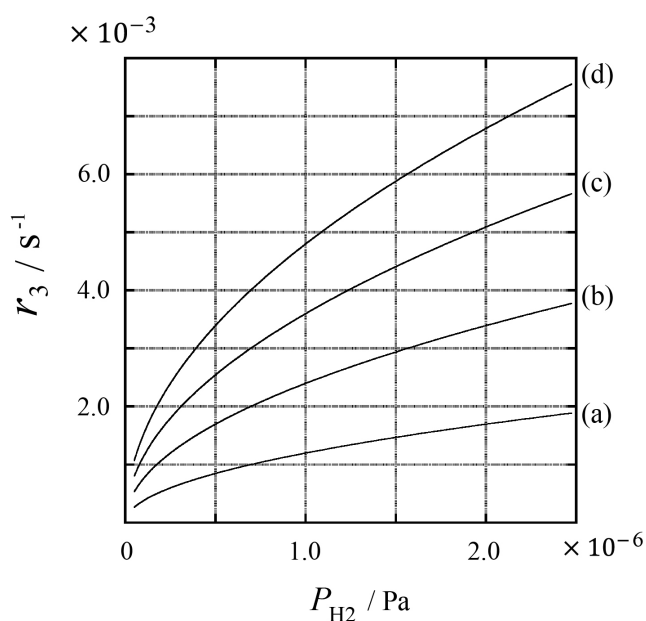
Express C using k_1 and k_2 .

A metal sample with a surface area of $S = 1.0 \times 10^{-3} \text{ m}^2$ was placed in a container ($V = 1.0 \times 10^{-3} \text{ m}^3$) with H_2 ($P_{\text{H}_2} = 1.0 \times 10^2 \text{ Pa}$). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18} \text{ m}^{-2}$. The surface temperature was kept at $T = 400 \text{ K}$. As the reaction (1) proceeded, P_{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 [$\text{mol s}^{-1} \text{ m}^{-2}$]. 3pt

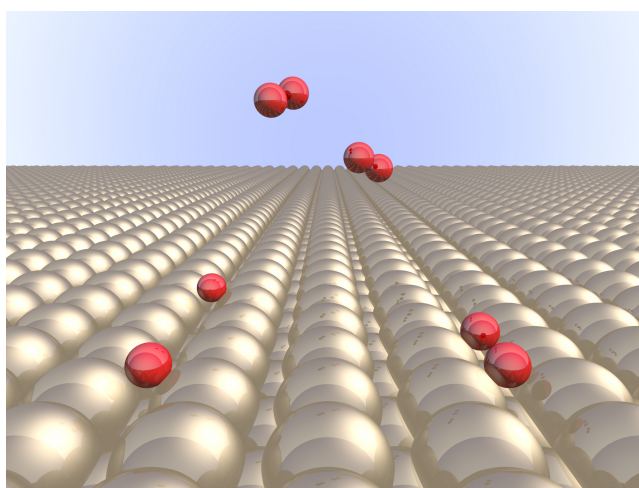
B.3 At $T = 400 \text{ K}$, C equals $1.0 \times 10^2 \text{ Pa}^{-1}$. Calculate the value of k_3 at 400 K. If you did not obtain the answer to **B.2**, use $A = 3.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2}$. 3pt

B.4 At a different T , $C = 2.5 \times 10^3 \text{ Pa}^{-1}$ and $k_3 = 4.8 \times 10^{-2} \text{ s}^{-1}$ are given. For r_3 as a function of P_{H_2} at this temperature, select the correct plot from (a)–(h). 3pt



Hidrogen pada Permukaan Logam

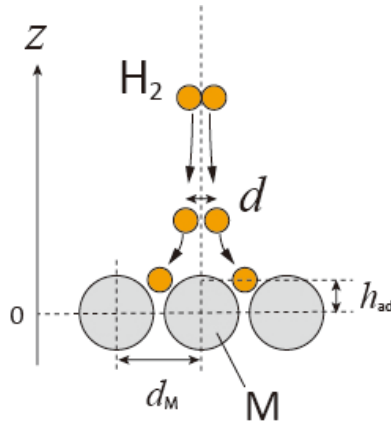
| 11 % dari total poin | | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----|-------|
| Pertanyaan | A.1 | A.2 | B.1 | B.2 | B.3 | B.4 | Total |
| Poin | 6 | 4 | 5 | 3 | 3 | 3 | 24 |
| Nilai | | | | | | | |



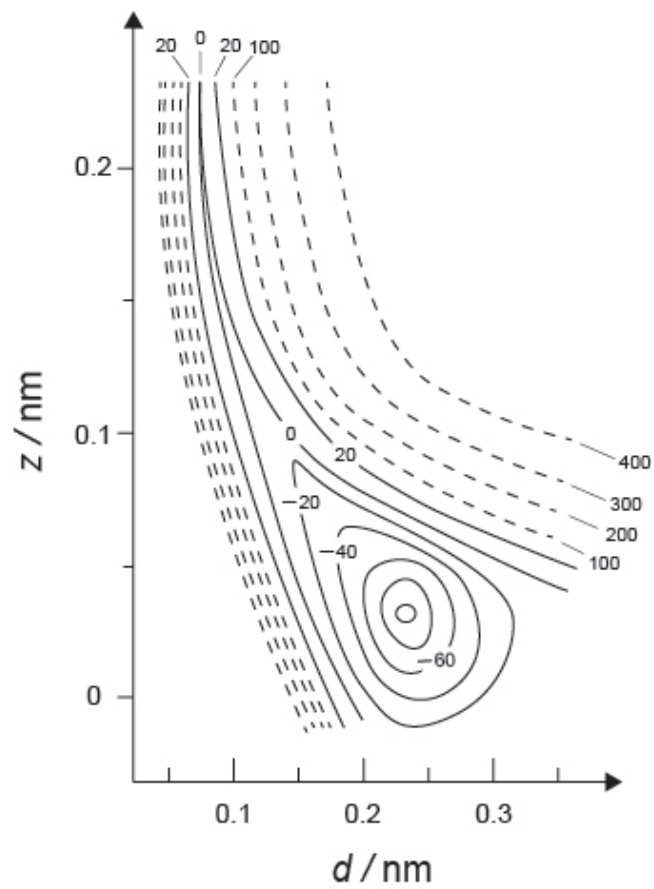
Hidrogen merupakan salah satu sumber energi di masa depan yang tidak bergantung pada energi fosil. Pada soal ini kita akan meninjau proses penyimpanan hidrogen dalam logam, yang mendasari teknologi penyimpanan dan transpor hidrogen.

Bagian A

Hidrogen diabsorpsi ke dalam fasa ruah (*bulk*) logam melalui permukaan logam. Pertama, mari kita tinjau proses adsorpsi hidrogen pada permukaan logam, $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{ad})$, dimana fasa gas and fasa teradsorpsi dari hidrogen ditunjukkan sebagai (g) dan (ad), secara berurutan. Molekul hidrogen (H_2) yang mencapai permukaan logam (M) mengalami disosiasi pada permukaan dan teradsorpsi sebagai atom H (Gambar 1). Energi potensial H_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_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. 6pt
- (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. 4pt
- (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(ad) menunjukkan atom hidrogen yang teradsorpsi dalam fasa ruah (*bulk*).



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

$$r_1 = k_1 P_{\text{H}_2} (1 - \theta)^2 \quad (2)$$

$$r_2 = k_2 \theta^2 \quad (3)$$

$$r_3 = k_3 \theta \quad (4)$$

dimana $k_1 [\text{s}^{-1} \text{Pa}^{-1}]$, $k_2 [\text{s}^{-1}]$ dan $k_3 [\text{s}^{-1}]$ adalah tetapan laju reaksi dan P_{H_2} adalah tekanan gas H_2 . Di antara sisi permukaan yang tersedia, θ ($0 \leq \theta \leq 1$) 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 θ selalu tetap.

B.1 r_3 dapat dituliskan sebagai:

5pt

$$r_3 = \frac{k_3}{1 + \sqrt{\frac{1}{P_{\text{H}_2} C}}} \quad (5)$$

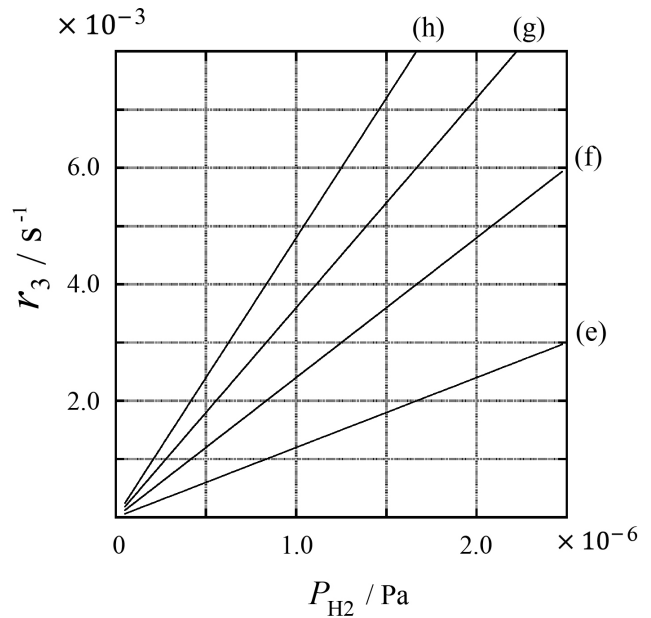
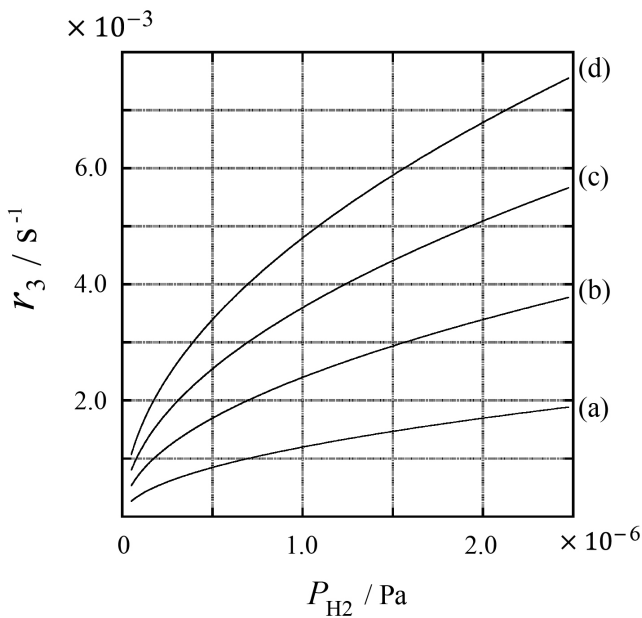
Tuliskan nilai C dalam k_1 dan k_2 .

Suatu sampel logam A dengan luas permukaan $S = 1.0 \times 10^{-3} \text{ m}^2$ dimasukkan ke dalam suatu wadah berukuran $1\text{L} = 1.0 \times 10^{-3} \text{ m}^3$ 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_{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 [$\text{mol s}^{-1} \text{ m}^{-2}$]. 3pt

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 $A = 3.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2}$. 3pt

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_{H_2} yang paling tepat dari pilihan (a)–(h). 3pt





IDN-3 C-1 A-1

A1-1
Indonesia (Indonesia)

Hidrogen pada Permukaan Logam

Bagian A

A.1 (6 pt)

| | | |
|-----|------|-------|
| (i) | (ii) | (iii) |
| | | |

A.2 (4 pt)

| | |
|-----|------|
| (i) | (ii) |
| | |



IDN-3 C-1 A-2

A1-2
Indonesia (Indonesia)

Bagian B

B.1 (5 pt)

$C =$ _____

B.2 (3 pt)

$A =$ _____ $\text{mol s}^{-1} \text{m}^{-2}$



IDN-3 C-1 A-3

A1-3
Indonesia (Indonesia)

B.3 (3 pt)

$k_3 =$ _____ s^{-1}

B.4 (3 pt)

IDN-3 C-2 C-1

IDN-3 C-2 C
Nathanael Widjaja

ICHO
Problem 2
Cover sheet

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

Isotope Time Capsule

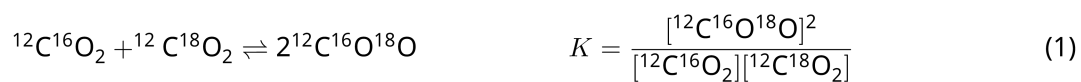
| 11 % of the total | | | | | |
|-------------------|-----|-----|-----|-----|-----------|
| Question | A.1 | A.2 | A.3 | A.4 | Total |
| Points | 8 | 8 | 10 | 9 | 35 |
| Score | | | | | |



Molecular entities that differ only in isotopic composition, such as CH_4 and CH_3D , are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

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

Let us consider the following equilibrium:



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

$$S = k_{\text{B}} \ln W \quad (2)$$

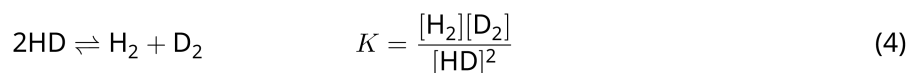
$W = 1$ for $^{12}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}_2$. In contrast, $W = 2$ for a $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}\text{C}^{16}\text{O}^{18}\text{O}$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

A.1 The enthalpy change, ΔH , of eq. 3 is positive regardless of the temperature. 8pt



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

The ΔH of the following process can be explained by molecular vibrations.



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

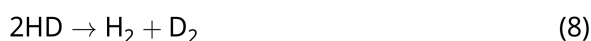
$$E = \frac{1}{2}h\nu \quad (5)$$

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

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

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

A.2 The vibration of H_2 is at 4161.0 cm^{-1} when reported as a wavenumber. 8pt
Calculate the ΔH of the following equation at $T = 0$ K in units of J mol^{-1} .



Assume that:

- only the vibrational energy contributes to the ΔH .
- 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_2 , HD , and D_2 depends on the temperature in a system in equilibrium. Here, Δ_{D_2} is defined as the change of the molar ratio of D_2 .

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

Here, R_{D_2} refers to $\frac{[\text{D}_2]}{[\text{H}_2]}$ in the sample and $R_{\text{D}_2}^*$ to $\frac{[\text{D}_2]}{[\text{H}_2]}$ at $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

A.3 Calculate Δ_{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 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, respectively. 10pt

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 Δ_{47} is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \quad (10)$$

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

| | ¹² C | ¹³ C |
|-------------------|-----------------|-----------------|
| natural abundance | 0.988888 | 0.011112 |

| | ¹⁶ O | ¹⁷ O | ¹⁸ O |
|-------------------|-----------------|-----------------|-----------------|
| natural abundance | 0.997621 | 0.0003790 | 0.0020000 |

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

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

A.4 The R_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-5} . **9pt**
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

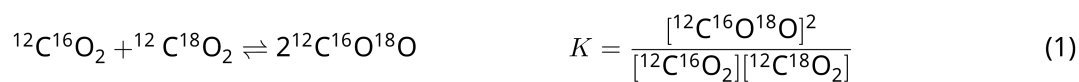
| 11 % dari total poin | | | | | |
|----------------------|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | A.3 | A.4 | Total |
| Poin | 8 | 8 | 10 | 9 | 35 |
| Nilai | | | | | |



Spesi molekular yang berbeda hanya pada komposisi isotop, seperti CH_4 dan CH_3D , 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 fasa gas.

Perhatikan kesetimbangan berikut:



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

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

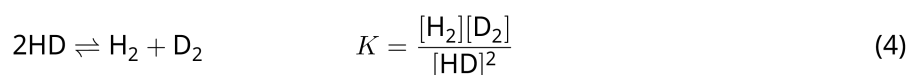
$W = 1$ untuk $^{12}\text{C}^{16}\text{O}_2$ dan $^{12}\text{C}^{18}\text{O}_2$. Sebaliknya, $W = 2$ untuk molekul $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ karena atom oksigen dapat dibedakan dalam molekul tersebut. Karena terdapat dua $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ molekul pada sisi kanan (produk) pada kesetimbangan reaksi 1, maka $W = 2^2 = 4$.

A.1 Perubahan entalpi, ΔH , reaksi 3 selalu bernilai positif pada semua rentang temperatur. 8pt



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

Nilai ΔH proses berikut dapat dijelaskan dengan vibrasi molekul.



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

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

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

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

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

A.2 Bilangan gelombang vibrasi H_2 adalah 4161.0 cm^{-1} . **Hitung** ΔH reaksi berikut pada $T = 0$ K dalam satuan J mol^{-1} . 8pt



Asumsikan bahwa:

- hanya energi vibrasi yang berkontribusi pada ΔH .
- nilai k bernilai sama untuk H_2 , HD , dan D_2 .
- massa H adalah 1 Da dan massa D adalah 2 Da.

Rasio molar H_2 , HD , dan D_2 bergantung pada temperatur sistem dalam kesetimbangan. Δ_{D_2} didefinisikan sebagai perubahan rasio molar D_2 .

$$\Delta_{D_2} = \frac{R_{D_2}}{R_{D_2}^*} - 1 \quad (9)$$

Pada persamaan di atas, R_{D_2} menunjukkan $\frac{[D_2]}{[H_2]}$ dalam sampel dan $R_{D_2}^*$ menunjukkan $\frac{[D_2]}{[H_2]}$ pada $T \rightarrow +\infty$. Perhatikan bahwa distribusi isotop menjadi acak/random pada $T \rightarrow +\infty$.

A.3 **Hitung** Δ_{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 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, secara berurutan. 10pt

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 $\text{CO}_2[44]$ dan $\text{CO}_2[47]$ di bawah ini. Besaran Δ_{47} didefinisikan sebagai:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \quad (10)$$

R_{47} menunjukkan rasio $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ dalam sampel dan R_{47}^* menunjukkan rasio $\frac{[\text{CO}_2[47]]}{[\text{CO}_2[44]]}$ pada $T \rightarrow +\infty$. Kelimpahan karbon dan oksigen di alam ditunjukkan di bawah ini; abaikan isotop yang tidak ditunjukkan.

| | ^{12}C | ^{13}C |
|--------------------|-----------------|-----------------|
| kelimpahan di alam | 0.988888 | 0.011112 |

| | ^{16}O | ^{17}O | ^{18}O |
|--------------------|-----------------|-----------------|-----------------|
| kelimpahan di alam | 0.997621 | 0.0003790 | 0.0020000 |

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

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

- A.4** Nilai R_{47} dari suatu fosil plankton yang diperoleh dari dasar Antartika adalah 4.50865×10^{-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 $\text{CO}_2[47]$ yang paling umum untuk perhitungan. 9pt



IDN-3 C-2 A-1

A2-1
Indonesia (Indonesia)

Kapsul Waktu Isotop

A.1 (8 pt)

$T \rightarrow 0 : K =$ _____ , $T \rightarrow +\infty : K =$ _____



IDN-3 C-2 A-2

A2-2
Indonesia (Indonesia)

A.2 (8 pt)

$\Delta H =$ _____ J mol^{-1}



IDN-3 C-2 A-3

A2-3
Indonesia (Indonesia)

A.3 (10 pt)

$\Delta_{D_2} =$ _____



IDN-3 C-2 A-4

A2-4
Indonesia (Indonesia)

A.4 (9 pt)

$T =$ _____ K

IDN-3 C-3 C-1

IDN-3 C-3 C
Nathanael Widjaja

ICHO
Problem 3
Cover sheet

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

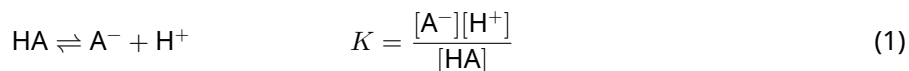
Lambert-Beer Law?

| 8 % of the total | | | | |
|------------------|-----|-----|-----|-----------|
| Question | A.1 | B.1 | B.2 | Total |
| Points | 10 | 6 | 6 | 22 |
| Score | | | | |

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

Part A

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



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.

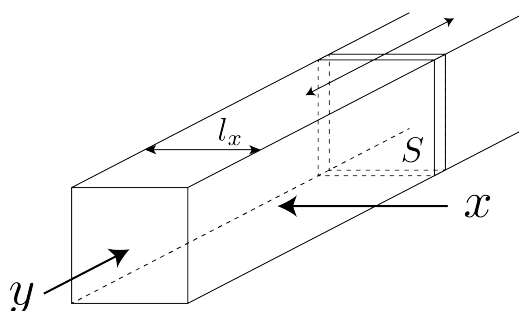
- | | | |
|------------|---|------|
| A.1 | The absorbance of X was A_1 at a wavelength of λ_1 . Then, solution X was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1 . Determine the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-} represent the absorption coefficients of HA and of A^- , respectively, at λ_1 . | 10pt |
|------------|---|------|

Part B

Let us consider the following equilibrium in the gas phase.



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 ε , 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.

| | Initial state | | After equilibrium | |
|------------------|---------------|---|-------------------|-------|
| | D | M | D | M |
| Partial pressure | P | 0 | p_D | p_M |
| Amount in moles | n_0 | 0 | n_D | n_M |
| Volume | V_0 | | V | |

B.1 The absorbance of the gas at λ_{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 λ_{B1} , where ε_D and ε_M represent the absorption coefficients of D and of M, respectively. 6pt

B.2 The absorbance of the gas at λ_{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 λ_{B2} . 6pt

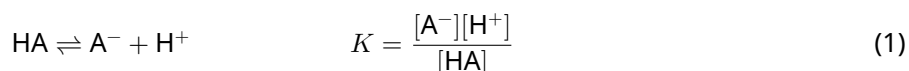
Hukum Lambert-Beer?

| 8 % dari total poin | | | | |
|---------------------|-----|-----|-----|-----------|
| Pertanyaan | A.1 | B.1 | B.2 | Total |
| Poin | 10 | 6 | 6 | 22 |
| Nilai | | | | |

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 $[A^-]$, $[HA]$, dan $[H^+]$ 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:



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

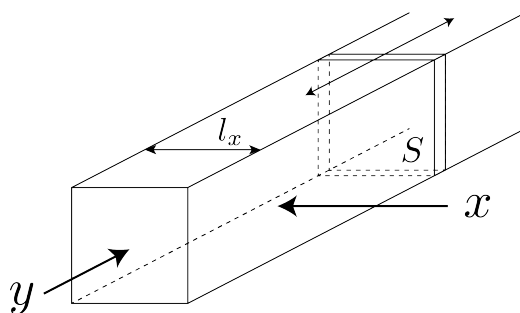
- | | |
|---|-------------|
| <p>A.1 Absorbansi X adalah A_1 pada panjang gelombang λ_1. Larutan X kemudian diencerkan sehingga volumenya menjadi dua kali volume awalnya menggunakan asam hidroklorida dengan pH = 2.500. Setelah pengenceran, absorbansi larutan masih tetap bernilai A_1 pada λ_1. Tentukan rasio $\epsilon_{HA}/\epsilon_{A^-}$, dimana ϵ_{HA} dan ϵ_{A^-} masing-masing adalah koefisien absorpsi HA dan A^- pada λ_1 secara berurutan.</p> | <p>10pt</p> |
|---|-------------|

Bagian B

Perhatikan kesetimbangan berikut.

$$D \rightleftharpoons 2M \quad (2)$$

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 . Absorbansi gas adalah $A = \epsilon(n/V)l$, dimana ϵ , 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

| | Kondisi awal | | Setelah tercapai kesetimbangan | |
|-----------------|--------------|---|--------------------------------|-------|
| | D | M | D | M |
| Tekanan parsial | P | 0 | p_D | p_M |
| Jumlah mol | n_0 | 0 | n_D | n_M |
| Volume | V_0 | | V | |

B.1 Absorbansi gas pada λ_{B1} diukur pada arah x ($l = l_x$) baik pada kondisi awal maupun setelah kesetimbangan tercapai adalah A_{B1} . **Tentukan** rasio ϵ_D/ϵ_M pada λ_{B1} , dimana ϵ_D dan ϵ_M masing-masing adalah koefisien absorpsi D dan M, secara berurutan. 6pt

B.2 Absorbansi gas pada λ_{B2} diukur pada arah y pada kondisi awal ($l = l_{y0}$) maupun setelah kesetimbangan tercapai ($l = l_y$) adalah A_{B2} . **Tentukan** rasio ϵ_D/ϵ_M pada λ_{B2} . 6pt



IDN-3 C-3 A-1

A3-1
Indonesia (Indonesia)

Hukum Lambert-Beer?

Bagian A

A.1 (10 pt)

(Berlanjut pada halaman berikutnya)



IDN-3 C-3 A-2

A3-2
Indonesia (Indonesia)

A.1 (cont.)

$\epsilon_{\text{HA}}/\epsilon_{\text{A}^-} =$



IDN-3 C-3 A-3

A3-3
Indonesia (Indonesia)

Bagian B

B.1 (6 pt)

$\epsilon_D/\epsilon_M =$ _____



IDN-3 C-3 A-4

A3-4
Indonesia (Indonesia)

B.2 (6 pt)

$\epsilon_D/\epsilon_M =$ _____

IDN-3 C-4 C-1

IDN-3 C-4 C
Nathanael Widjaja

ICHO
Problem 4
Cover sheet

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

The Redox Chemistry of Zinc

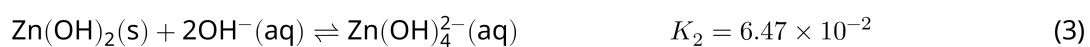
| 11 % of the total | | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----|-----------|
| Question | A.1 | A.2 | B.1 | B.2 | B.3 | B.4 | Total |
| Points | 6 | 5 | 4 | 3 | 5 | 9 | 32 |
| Score | | | | | | | |



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 $\text{Zn(OH)}_2(\text{s})$ at 25 °C and the relevant equilibrium constants are given in eq. 1-4.



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

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

A.1 When the equilibria in eq. 1–4 are established, **calculate** the pH range in which $[\text{Zn}(\text{OH})_2(\text{aq})]$ is the greatest among $[\text{Zn}^{2+}(\text{aq})]$, $[\text{Zn}(\text{OH})_2(\text{aq})]$ and $[\text{Zn}(\text{OH})_4^{2-}(\text{aq})]$. 6pt

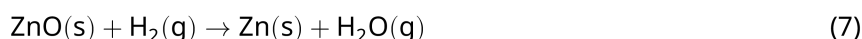
A.2 A saturated aqueous solution of $\text{Zn}(\text{OH})_2(\text{s})$ with $\text{pH} = 7.00$ was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. **Calculate** the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes. 5pt

Part B

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



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



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 $\Delta G_{\text{ZnO}}(300^\circ\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{H}_2\text{O}}(300^\circ\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$, respectively. 4pt

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



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. 3pt



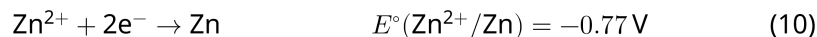
Mt. Fuji

- B.3** Consider the change of e.m.f. of a zinc-air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are -38°C (February) and 3776 m, respectively. The atmospheric pressure is represented by 5pt

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

at altitude h [m] and temperature T [$^\circ\text{C}$]. The molar ratio of oxygen in the atmosphere is 21%. The Gibbs energy change of reaction (8) is $\Delta G_{\text{ZnO}}(-38^\circ\text{C}) = -3.26 \times 10^2 \text{ kJ mol}^{-1}$ at -38°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. 9pt



Kimia Redoks Seng

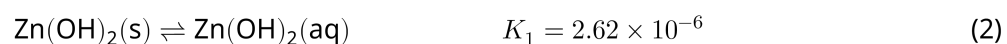
| 11 % dari total poin | | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | B.1 | B.2 | B.3 | B.4 | Total |
| Poin | 6 | 5 | 4 | 3 | 5 | 9 | 32 |
| Nilai | | | | | | | |



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 $\text{Zn(OH)}_2(\text{s})$ pada $25\text{ }^\circ\text{C}$ dan tetapan kesetimbangan masing-masing reaksi diberikan pada persamaan 1–4.



Kelarutan, S , seng (konsentrasi seng dalam suatu larutan jenuh) diberikan pada persamaan 5.

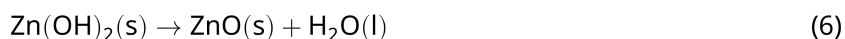
$$S = [\text{Zn}^{2+}(\text{aq})] + [\text{Zn}(\text{OH})_2(\text{aq})] + [\text{Zn}(\text{OH})_4^{2-}(\text{aq})] \quad (5)$$

A.1 Ketika kesetimbangan pada persamaan 1–4 tercapai, **hitung** rentang pH 6pt
dimana $[\text{Zn}(\text{OH})_2(\text{aq})]$ paling besar di antara $[\text{Zn}^{2+}(\text{aq})]$, $[\text{Zn}(\text{OH})_2(\text{aq})]$ dan
 $[\text{Zn}(\text{OH})_4^{2-}(\text{aq})]$.

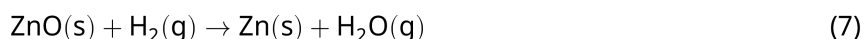
A.2 Larutan jenuh $\text{Zn}(\text{OH})_2(\text{s})$ dengan pH = 7.00 disiapkan dan disaring. Kemudian 5pt
kedalam filtrat ditambahkan NaOH untuk meningkatkan pH menjadi 12.00.
Hitung presentase molar Zn yang mengendap ketika pH bertambah dari 7.00
menjadi 12.00. Abaikan perubahan volume dan temperatur.

Bagian B

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

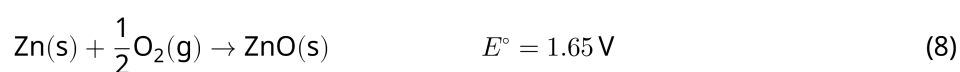


Seng oksida kemudian direduksi menjadi logam seng dengan reaksi menggunakan hidrogen:



B.1 Agar reaksi (7) dapat berlangsung pada kondisi tekanan hidrogen dijaga pada 4pt
1 bar, perlu untuk mengurangi tekanan parsial dari uap air yang dihasilkan.
Hitung batas atas tekanan uap air parsial agar reaksi (7) dapat berlangsung
pada 300 °C. Berikut nilai energi bebas Gibbs pembentukan untuk seng oksida
dan uap air pada 300 °C dan 1 bar untuk semua spesi gas yaitu masing-masing
 $\Delta G_{\text{ZnO}}(300^\circ\text{C}) = -2.90 \times 10^2 \text{ kJ mol}^{-1}$ dan $\Delta G_{\text{H}_2\text{O}}(300^\circ\text{C}) = -2.20 \times 10^2 \text{ kJ mol}^{-1}$

Logam seng digunakan sebagai elektroda negatif (anoda) pada baterai *metal-air*. Elektroda disusun dari Zn dan ZnO. Elektroda tersebut digunakan pada reaksi redoks berikut untuk menghasilkan listrik dengan *electromotive force* (e.m.f.) pada 25 °C dan tekanan 1 bar, E° .



B.2 Sebuah baterai *zinc-air* habis digunakan dengan arus 20 mA selama 24 jam. 3pt
Hitung perubahan massa elektroda negatif (anoda) dari baterai tersebut.



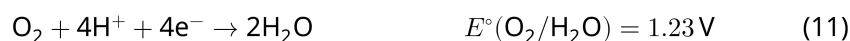
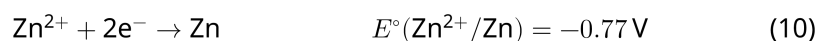
Gunung Fuji

- B.3** 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°C (Februari) and 3776 m. Tekanan atmosfer dinyatakan dengan persamaan: 5pt

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

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

- B.4** **Hitung** perubahan energi bebas Gibbs untuk reaksi (6) pada 25°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°C dan 1 bar masing-masing diberikan pada persamaan (10) dan (11). 9pt





IDN-3 C-4 A-1

A4-1
Indonesia (Indonesia)

Kimia Redoks Seng

Bagian A

A.1 (6 pt)

_____ < pH < _____



IDN-3 C-4 A-2

A4-2
Indonesia (Indonesia)

A.2 (5 pt)

_____ %



IDN-3 C-4 A-3

A4-3
Indonesia (Indonesia)

Bagian B

B.1 (4 pt)

$p_{\text{H}_2\text{O}} =$ _____ bar

B.2 (3 pt)

_____ g



IDN-3 C-4 A-4

A4-4
Indonesia (Indonesia)

B.3 (5 pt)

_____ v



IDN-3 C-4 A-5

A4-5
Indonesia (Indonesia)

B.4 (9 pt)

$\Delta G^\circ =$ _____ J mol^{-1}

IDN-3 C-5 C-1

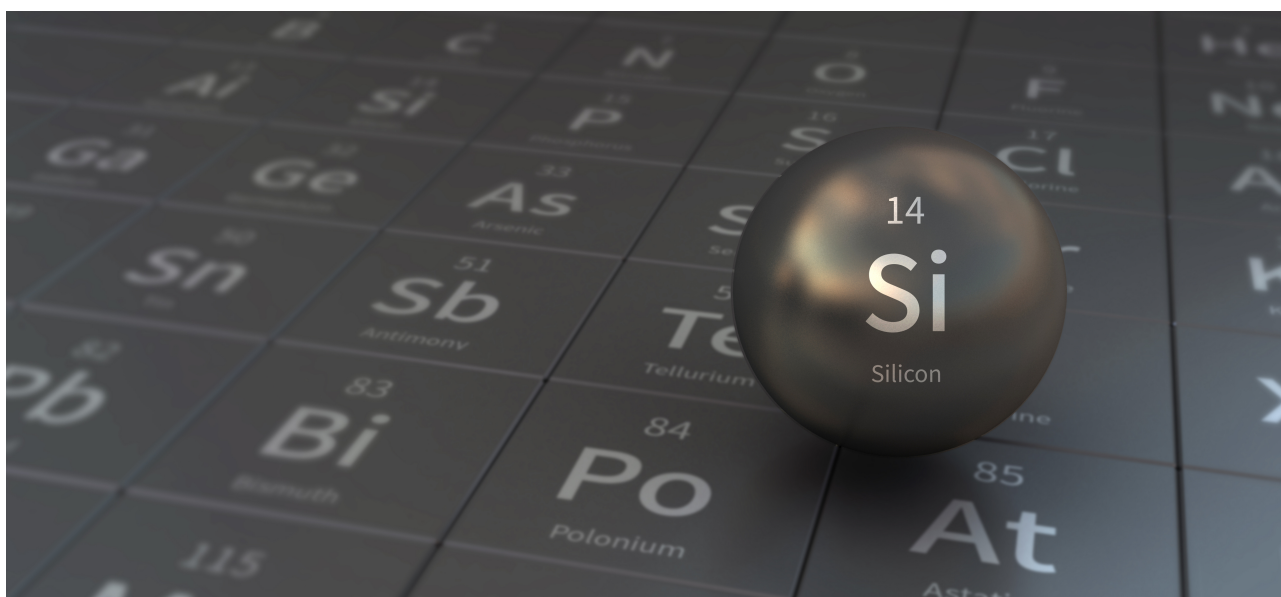
IDN-3 C-5 C
Nathanael Widjaja

ICHO
Problem 5
Cover sheet

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

Mysterious Silicon

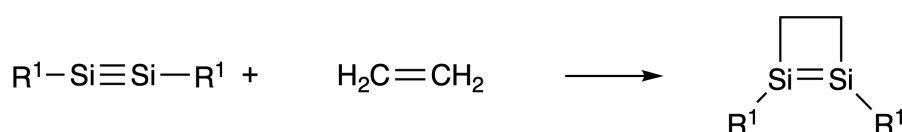
| 12 % of the total | | | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----------|
| Question | A.1 | A.2 | A.3 | A.4 | B.1 | B.2 | B.3 | Total |
| Points | 9 | 7 | 6 | 10 | 5 | 15 | 8 | 60 |
| Score | | | | | | | | |



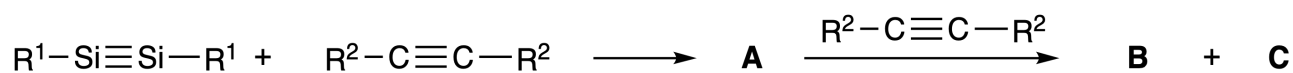
Although silicon is also a group 14 element like carbon, their properties differ significantly.

Part A

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



When $R^1-Si \equiv Si-R^1$ is treated with an alkyne ($R^2-C \equiv C-R^2$), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of $R^2-C \equiv C-R^2$ with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called 'disilabenzenes' that contain a six-membered ring and can be formulated as $(R^1-Si)_2(R^2-C)_4$.



The ^{13}C NMR analysis of the corresponding six-membered ring skeletons Si_2C_4 shows two signals for **B** and one signal for **C**.

A.1 **Draw** the structural formulae of **A**, **B**, and **C** using R^1 , R^2 , Si, and C, with one of the possible resonance structures. 9pt

A.2 **Calculate** the aromatic stabilization energy (ASE) for benzene and **C** (in the case of $R^1 = R^2 = H$) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1). 7pt

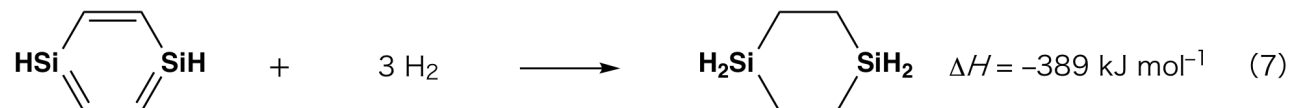
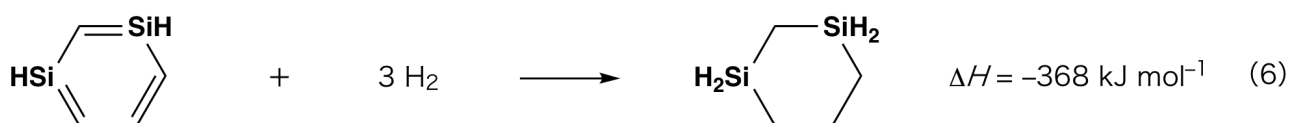


Fig. 1

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

A.3 Calculate ΔH for the transformation of **D** to **E**. Assume that ΔH does not depend on temperature. 6pt

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

A.4 Draw the structural formulae of **D** and **E** using R^1 , R^2 , Si, and C. 10pt

Part B

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

The fluorination reaction of CCl_4 using Na_2SiF_6 was carried out as follows.

- **Standardization of Na_2SiF_6 solution :**

- Preparation

Aqueous solution **F**: 0.855 g of Na_2SiF_6 ($188.053 \text{ g mol}^{-1}$) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $\text{Ce}_2(\text{SO}_4)_3$ ($568.424 \text{ g mol}^{-1}$) dissolved in water (total volume: 200 mL).

- Procedure

Precipitation titration of a solution **F** (50.0 mL) by dropwise adding solution **G** in the presence of xylenol orange, which coordinates to Ce^{3+} , as an indicator. After adding 18.8 mL of solution **G**, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce^{3+} , and the only resulting silicon compound is $\text{Si}(\text{OH})_4$.

B.1 Write the balanced equation for the reaction of Na_2SiF_6 with $\text{Ce}_2(\text{SO}_4)_3$. 5pt

- **Reaction of CCl_4 with Na_2SiF_6 :**

(Substance losses by *e.g.* evaporation are negligible during the following operations.)

Na_2SiF_6 (x [g]) was added to CCl_4 (500.0 g) and heated to 300 °C in a sealed pressure-resistant reaction vessel. The unreacted Na_2SiF_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_2Cl_2 , CF_3Cl , and CF_4 were observed (*cf.* Table 1). The integration ratios in the ^{19}F NMR spectrum are proportional to the number of fluorine nuclei.

Table 1

| ^{19}F NMR data | CFCl_3 | CF_2Cl_2 | CF_3Cl | CF_4 |
|--------------------------|-----------------|--------------------------|------------------------|---------------|
| Integration ratio | 45.0 | 65.0 | 18.0 | 2.0 |

SiF_4 is hydrolyzed to form H_2SiF_6 according to the following eq. 8:



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

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

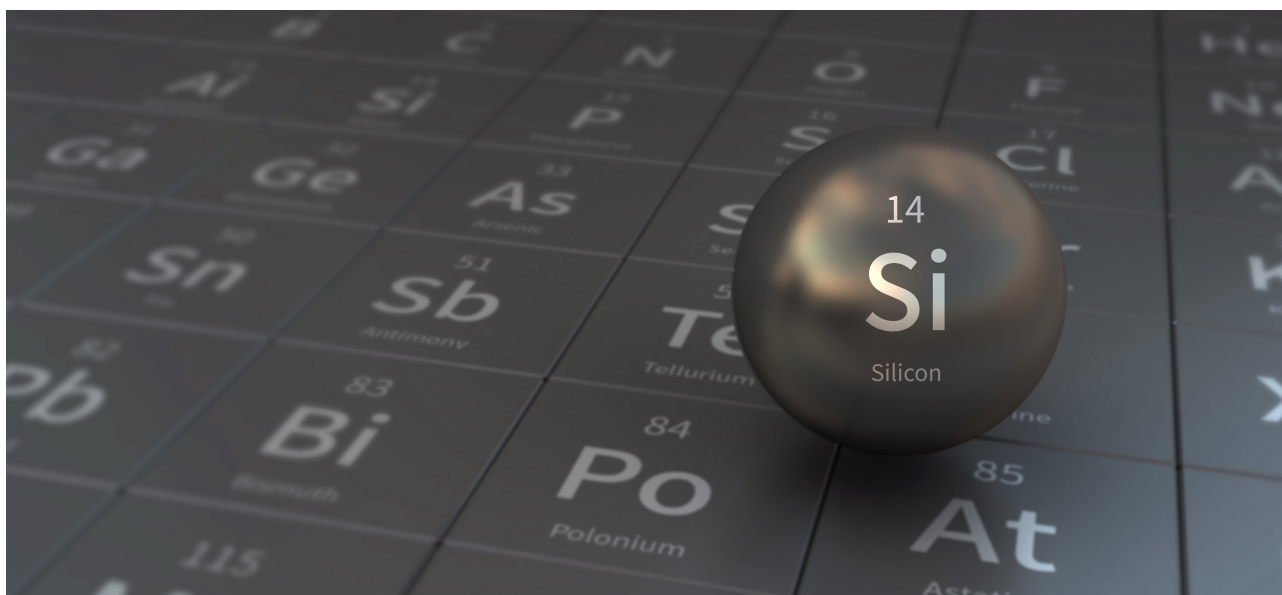
It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

B.2 Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and **calculate** the mass (x [g]) of the Na_2SiF_6 used as a starting material. 15pt

B.3 77.8% of the CCl_4 used as a starting material was unreacted. **Calculate** the mass of CF_3Cl generated. 8pt

Misteri Silikon

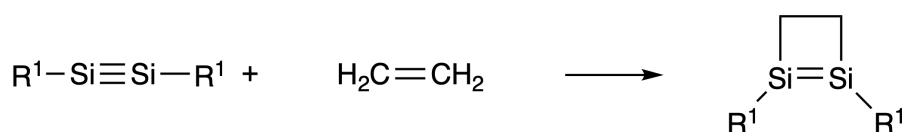
| 12 % dari total poin | | | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | A.3 | A.4 | B.1 | B.2 | B.3 | Total |
| Poin | 9 | 7 | 6 | 10 | 5 | 15 | 8 | 60 |
| Nilai | | | | | | | | |



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 $R^1-Si \equiv Si-R^1$ (R: substituen organik) yang sangat reaktif. Sebagai contoh, senyawa silikon tersebut bereaksi dengan etilena untuk menghasilkan sebuah produk yang mengandung senyawa cincin lingkaran empat.



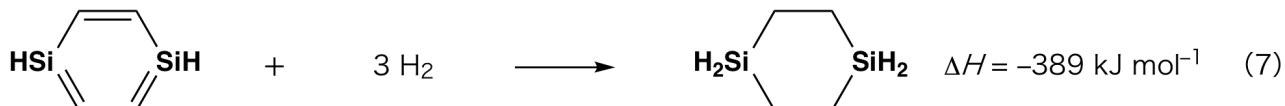
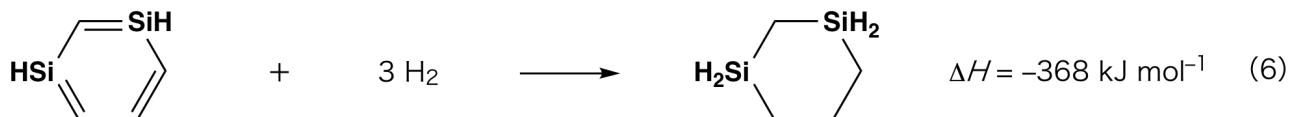
Ketika $R^1-Si \equiv Si-R^1$ direaksikan dengan senyawa alkuna ($R^2-C \equiv C-R^2$), senyawa cincin lingkaran empat **A** terbentuk sebagai produk awal. Selanjutnya reaksi senyawa $R^2-C \equiv C-R^2$ dengan **A** menghasilkan isomer **B** dan **C**, keduanya memiliki struktur konjugasi seperti benzena, sehingga disebut '*disilabenzenes*' yang memiliki cincin lingkaran enam dengan formula $(R^1-Si)_2(R^2-C)_4$.



Analisis ^{13}C NMR senyawa cincin lingkaran enam dengan kerangka Si_2C_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. 9pt

A.2 **Hitung** the aromatic stabilization energy (ASE) untuk benzena dan **C** (dengan $R^1 = R^2 = H$) sebagai nilai positif, dengan mempertimbangkan perubahan entalpi dalam beberapa reaksi hidrogenasi sistem tak jenuh ditunjukkan pada gambar di bawah ini (Gambar 1). 7pt



Gambar 1

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. 6pt

Isomerisasi **C** menjadi **D** dan menjadi **E** berlangsung melalui transformasi ikatan π menjadi ikatan σ tanpa pemutusan ikatan σ yang ada. Analisis ^{13}C NMR menunjukkan satu sinyal untuk kerangka Si_2C_4 pada **D** dan dua sinyal untuk **E**. Kerangka **D** tidak memiliki cincin lingkaran tiga, sementara **E** memiliki dua cincin lingkaran tiga yang berbagi di bagian tepinya (*edge sharing ring*).

A.4 **Gambarkan** struktur molekul **D** dan **E** dengan menggunakan simbol R^1 , R^2 , Si, dan C. 10pt

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 CCl_4 menggunakan Na_2SiF_6 dilakukan sebagai berikut.

- **Pembakuan larutan Na_2SiF_6 :**

- Preparasi

Larutan **F**: 0.855 g Na_2SiF_6 ($188.053 \text{ g mol}^{-1}$) dilarutkan dalam air (volume total : 200 mL).

Larutan **G**: 6.86 g $\text{Ce}_2(\text{SO}_4)_3$ ($568.424 \text{ g mol}^{-1}$) dilarutkan dalam air (volume total : 200 mL).

- Prosedur

Titrasi pengendapan larutan **F** (50.0 mL) dilakukan dengan penambahan larutan **G** tetes demi tetes menggunakan indikator *xenol orange*, yang berkoordinasi dengan Ce^{3+} . Setelah penambahan 18.8 mL larutan **G**, warna larutan berubah dari kuning menjadi magenta. Endapan yang terbentuk merupakan senyawa biner yang mengandung Ce^{3+} , dan satu-satunya senyawa silikon yang dihasilkan yaitu $\text{Si}(\text{OH})_4$.

B.1 **Tuliskan** persamaan reaksi yang setara untuk reaksi Na_2SiF_6 dengan $\text{Ce}_2(\text{SO}_4)_3$. 5pt

- **Reaksi CCl_4 dengan Na_2SiF_6 :**

(hilangnya senyawa selama tahap-tahap berikut berlangsung diabaikan, misalnya melalui proses pengapungan)

$\text{Na}_2\text{SiF}_6(x \text{ [g]})$ ditambahkan ke dalam CCl_4 (500.0 g) dan dipanaskan sampai 300 °C dalam wadah bertekanan tinggi (*pressure-resistant reaction vessel*). Na_2SiF_6 yang tidak bereaksi dan NaCl yang dihasilkan, dipisahkan dengan cara penyaringan. Filtrat yang diperoleh diencerkan dengan CCl_4 (larutan **H**) sampai volume total 1.00 L. Spektrum ^{29}Si dan ^{19}F NMR larutan **H** menunjukkan SiF_4 sebagai satu-satunya senyawa silikon. Selain SiF_4 , pada spektrum ^{19}F NMR, teramati sinyal-sinyal yang sesuai untuk CFCl_3 , CF_2Cl_2 , CF_3Cl , dan CF_4 (*cf.* Tabel 1). Rasio integrasi pada spektrum ^{19}F NMR sebanding dengan jumlah inti fluorin.

Tabel 1

| Data ¹⁹ F NMR | CFCl ₃ | CF ₂ Cl ₂ | CF ₃ Cl | CF ₄ |
|--------------------------|-------------------|---------------------------------|--------------------|-----------------|
| Rasio integrasi | 45.0 | 65.0 | 18.0 | 2.0 |

SiF₄ terhidrolisis membentuk H₂SiF₆ menurut persamaan reaksi 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*). 15pt

B.3 Sebanyak 77.8% CCl₄, yang digunakan sebagai material awal, tidak bereaksi. **Hitung** massa CF₃Cl yang dihasilkan. 8pt



IDN-3 C-5 A-1

A5-1
Indonesia (Indonesia)

Misteri Silikon

Bagian A

A.1 (9 pt)

A (3 pt)

B (3 pt)

C (3 pt)

A.2 (7 pt)

C_6H_6 : _____ kJ mol^{-1} , **C** : _____ kJ mol^{-1}



IDN-3 C-5 A-2

A5-2
Indonesia (Indonesia)

A.3 (6 pt)

$\Delta H =$ _____ kJ mol^{-1}

A.4 (10 pt)

D (5 pt)

E (5 pt)



IDN-3 C-5 A-3

A5-3
Indonesia (Indonesia)

Bagian B

B.1 (5 pt)

B.2 (15 pt)

(Continued on the next page)



IDN-3 C-5 A-4

A5-4
Indonesia (Indonesia)

B.2 (cont.)

NaCl : _____ g, Na₂SiF₆ : _____ g



IDN-3 C-5 A-5

A5-5
Indonesia (Indonesia)

B.3 (8 pt)

CF_3Cl : _____ g

IDN-3 C-6 C-1

IDN-3 C-6 C
Nathanael Widjaja

ICHO
Problem 6
Cover sheet

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

The Solid-State Chemistry of Transition Metals

| 13 % of the total | | | | | | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------|
| Question | A.1 | A.2 | A.3 | B.1 | B.2 | B.3 | B.4 | C.1 | C.2 | C.3 | Total |
| Points | 6 | 3 | 3 | 6 | 4 | 4 | 4 | 5 | 5 | 5 | 45 |
| Score | | | | | | | | | | | |



Volcano at Sakurajima island

Part A

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

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

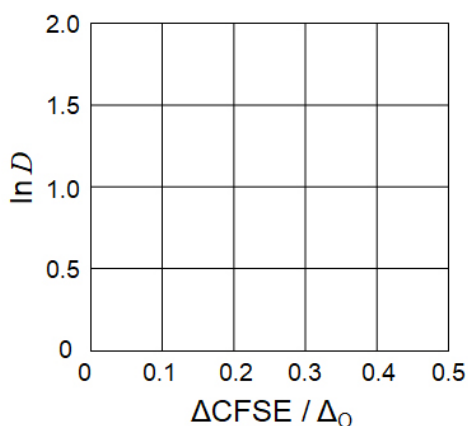
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

| | Cr^{2+} | Mn^{2+} |
|-----|-----------|-----------|
| D | 7.2 | 1.1 |

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

A.1 Calculate $|CFSE^O - CFSE^T| = \Delta CFSE$ in terms of Δ_o for Cr^{2+} , Mn^{2+} , and Co^{2+} ; assume $\Delta_T = 4/9\Delta_o$. 6pt

A.2 A linear relationship is observed by plotting $\ln D$ against $\Delta CFSE / \Delta_o$ in the Cartesian coordinate system shown below. 3pt
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). 3pt

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

Part B

A mixed oxide **A**, which contains La^{3+} and Cu^{2+} , crystallizes in a tetragonal unit cell shown in Fig.1. In the $[\text{CuO}_6]$ 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}).

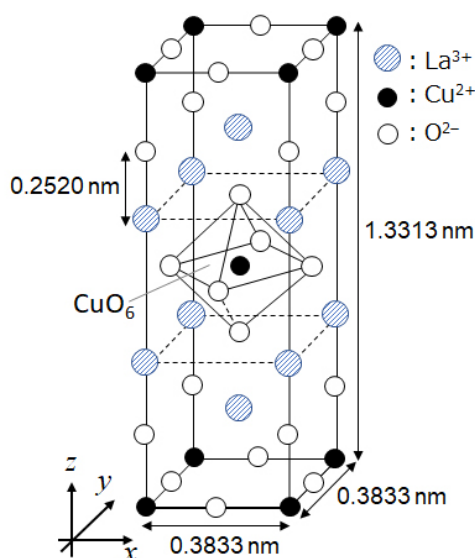


Fig. 1

A can be synthesized by thermal decomposition (pyrolysis) of complex **B**, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid $\text{C}_4\text{H}_2\text{O}_4$, i.e., a diacid. The pyrolysis behavior of **B** in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of 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 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**, 2.05×10^{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. 4pt

Part C

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ is composed of four CH_3CO_2^- coordinated to two Cu^{2+} (Fig. 2A). $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four CH_3CO_2^- and an axis passing through the two Cu^{2+} , all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of CH_3CO_2^- , a "cage complex" is formed. The cage complex $\text{Cu}_4(\text{L1})_4$ is composed of planar dicarboxylate **L1** (Fig. 2B) and Cu^{2+} (Fig. 2C). The angle θ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The θ is 0° for **L1**. Note that hydrogen atoms are not shown in Fig. 2.

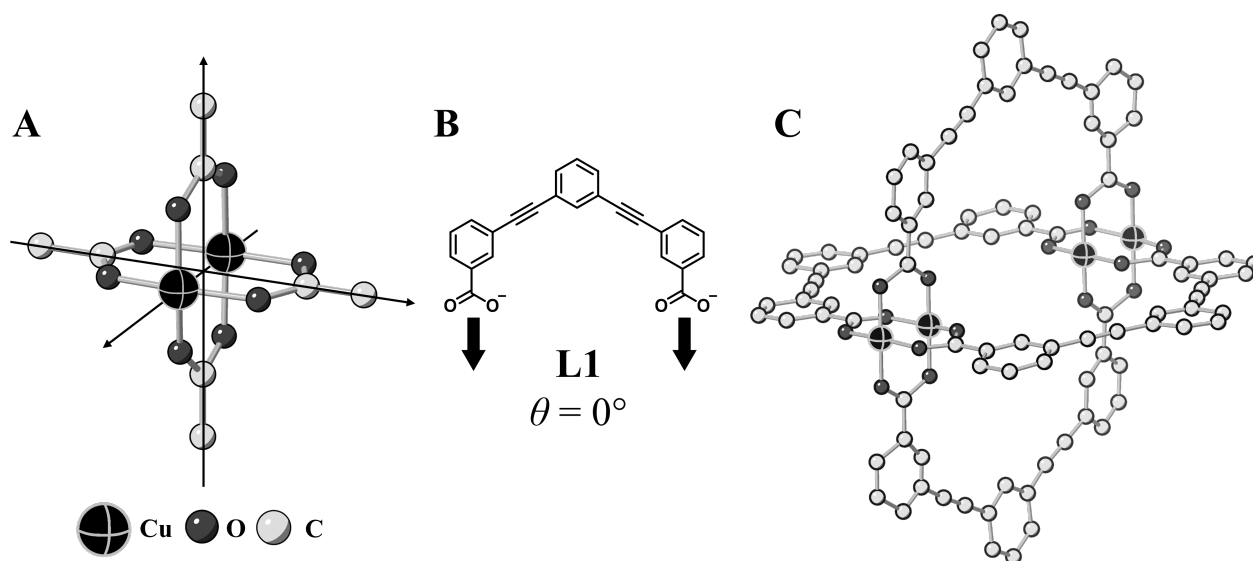
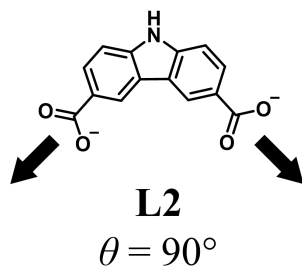


Fig. 2

- C.1** The θ of the planar dicarboxylate **L2** below is fixed to 90° . If the composition of the cage complex formed from **L2** and Cu^{2+} is $\text{Cu}_n(\text{L2})_m$, **give** the smallest integer combination of n and m . Assume that only the CO_2^- groups of **L2** form a coordination bond to Cu^{2+} ions. 5pt



A zinc complex, $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$, contains four tetrahedral Zn^{2+} , six CH_3CO_2^- , and one O^{2-} (Fig. 3A). In $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$, the O^{2-} is located at the origin, and the three axes passing through the carbon atoms of CH_3CO_2^- are oriented orthogonal relative to each other. When *p*-benzenedicarboxylate (Fig. 3B, **L3**, $\theta = 180^\circ$) is used instead of CH_3CO_2^- , the Zn^{2+} clusters are linked to each other to form a crystalline solid (**X**) that is called a “porous coordination polymer” (Fig. 3C). The composition of **X** is $[\text{Zn}_4\text{O}(\text{L3})_3]_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral Zn^{2+} cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

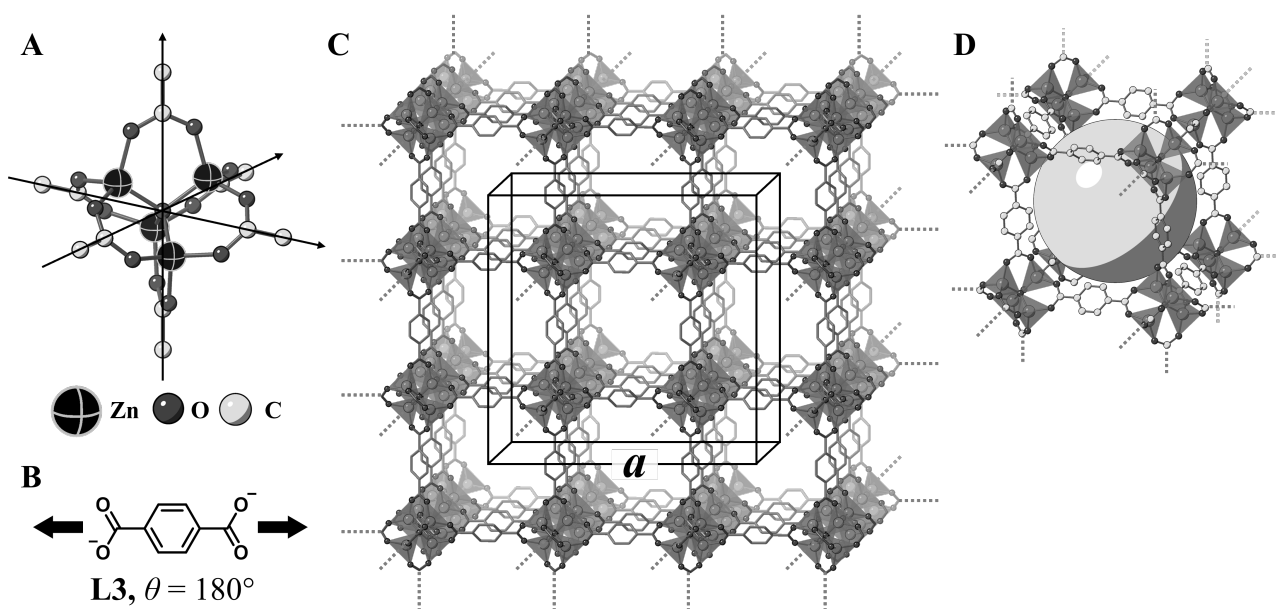


Fig. 3

C.2 **X** has a cubic unit cell with a side length of a (Fig. 3C) and a density of 0.592 g cm^{-3} . **Calculate** a in [cm]. 5pt

C.3 **X** contains a considerable number of pores, and 1 g of **X** can accommodate $3.0 \times 10^2 \text{ mL}$ of CO_2 gas in the pores at 1 bar and 25°C . **Calculate** the average number of CO_2 molecules per pore. 5pt

Kimia Padatan Logam Transisi

| 13 % dari total poin | | | | | | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | A.3 | B.1 | B.2 | B.3 | B.4 | C.1 | C.2 | C.3 | Total |
| Poin | 6 | 3 | 3 | 6 | 4 | 4 | 4 | 5 | 5 | 5 | 45 |
| Nilai | | | | | | | | | | | |



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 oktahedral (O_h) dalam mineral silikat, keduanya menunjukkan sifat konfigurasi elektron dalam keadaan spin tinggi. Koefisien distribusi ion M^{n+} antara mineral silikat dan magma, D , dapat diungkapkan dengan:

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

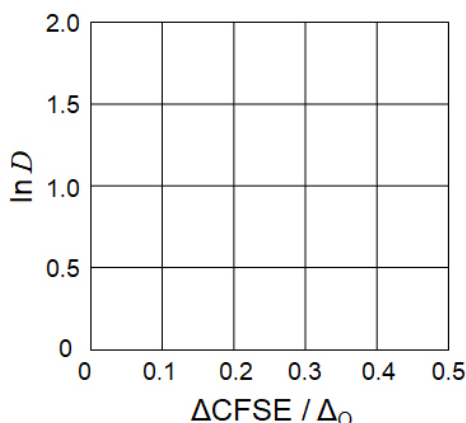
dengan $[M]_s$ dan $[M]_l$ masing-masing merupakan konsentrasi ion M^{n+} dalam mineral silikat dan magma. Tabel di bawah ini menunjukkan nilai D untuk ion Cr^{2+} dan Mn^{2+} sebagai contoh.

| | Cr^{2+} | Mn^{2+} |
|-----|-----------|-----------|
| D | 7.2 | 1.1 |

Δ_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 Δ_T dan $CFSE^T$ merupakan dalam medan T_d .

A.1 **Hitung** $|CFSE^O - CFSE^T| = \Delta CFSE$ dalam ungkapan Δ_O untuk Cr^{2+} , Mn^{2+} , dan Co^{2+} ; asumsi $\Delta_T = 4/9\Delta_O$. 6pt

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+} . 3pt



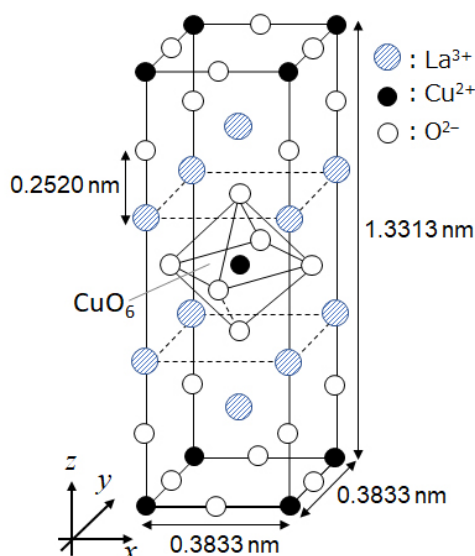
Oksida logam MO, (M: Ca, Ti, V, Mn, or Co) mengkristal dengan struktur *rock-salt* dimana ion M^{n+} memiliki geometri O_h dengan konfigurasi elektron dalam keadaan spin tinggi. Energi kisi oksida logam tersebut berkaitan dengan interaksi gaya Coulomb yang tergantung pada jari-jari dan muatan ion serta 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 $[kJ\ mol^{-1}]$ oksida logam berikut. 3pt

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

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 $[\text{CuO}_6]$, panjang ikatan Cu-O pada sumbu z (l_z) lebih panjang dibandingkan pada sumbu x (l_x), dan $[\text{CuO}_6]$ 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* $\text{C}_4\text{H}_2\text{O}_4$, 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.

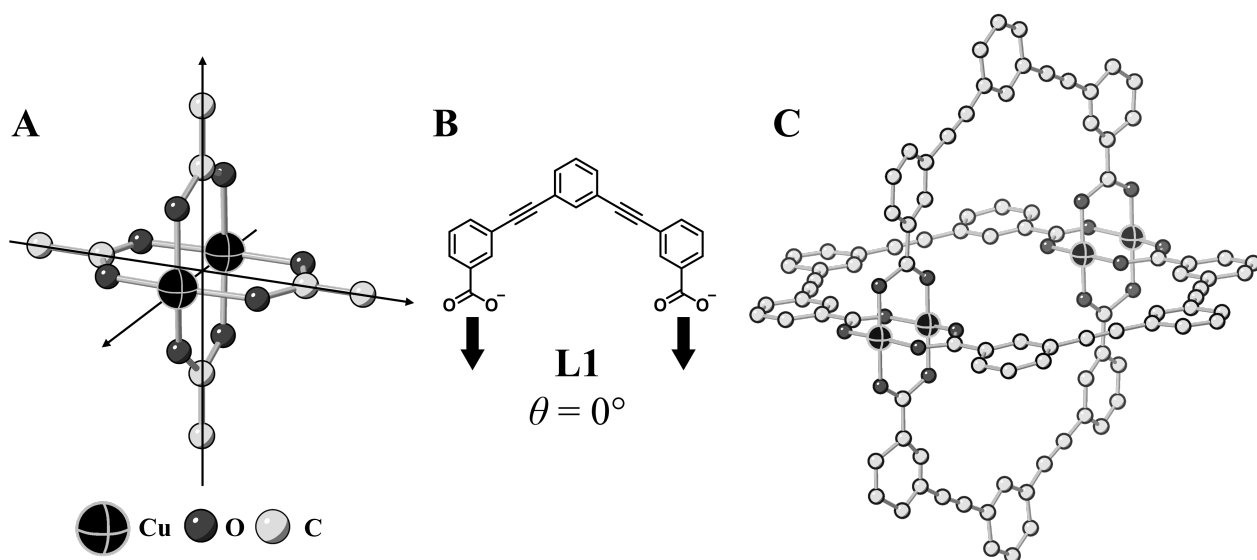
| | | |
|------------|---|-----|
| B.1 | Tuliskan rumus molekul A dan B . | 6pt |
| B.2 | Hitung l_x dan l_z menggunakan Gambar 1. | 4pt |
| B.3 | Untuk Cu^{2+} dalam kerangka oktahedron $[\text{CuO}_6]$ yang terdistorsi dalam A pada Gambar 1, tuliskan nama orbital e_g ($d_{x^2-y^2}$ dan d_{z^2}) yang mengalami pembelahan menjadi (i) dan (ii), dan gambar konfigurasi elektron dalam <i>dotted box</i> pada lembar jawaban. | 4pt |

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+} (Sr^{2+} -doped **A**) menunjukkan sifat superkonduktivitas di bawah 38 K. Ketika reaksi subsitusi berlangsung pada **A**, 2.05×10^{27} *hole* m^{-3} terbentuk.

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

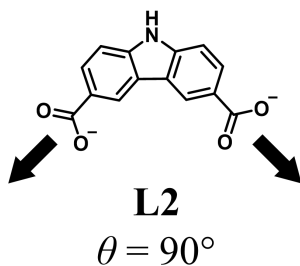
Bagian C

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ terdiri dari empat ion CH_3CO_2^- yang terkoordinasi pada dua ion Cu^{2+} (Gambar 2A). $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ menunjukkan level simetri struktur yang tinggi, dengan dua sumbu koordinat melewati atom karbon dari empat ion CH_3CO_2^- dan sebuah sumbu melewati dua ion Cu^{2+} . Semua sumbu berorientasi ortogonal relatif satu sama lain. Ketika ligan dikarboksilat digunakan sebagai pengganti CH_3CO_2^- , sebuah "cage complex" dapat terbentuk. "The cage complex" $\text{Cu}_4(\text{L1})_4$ terdiri dari dikarboksilat planar **L1** (Gambar 2B) dan kompleks Cu^{2+} (Gambar 2C). Sudut θ merupakan sudut antara arah dua gugus karboksilat, yang ditunjukkan dengan tanda panah pada Gambar 2B. Sudut θ menentukan struktur "cage complex". Nilai θ adalah 0° untuk **L1**. Perhatikan bahwa atom-atom hidrogen tidak ditunjukkan pada Gambar 2.

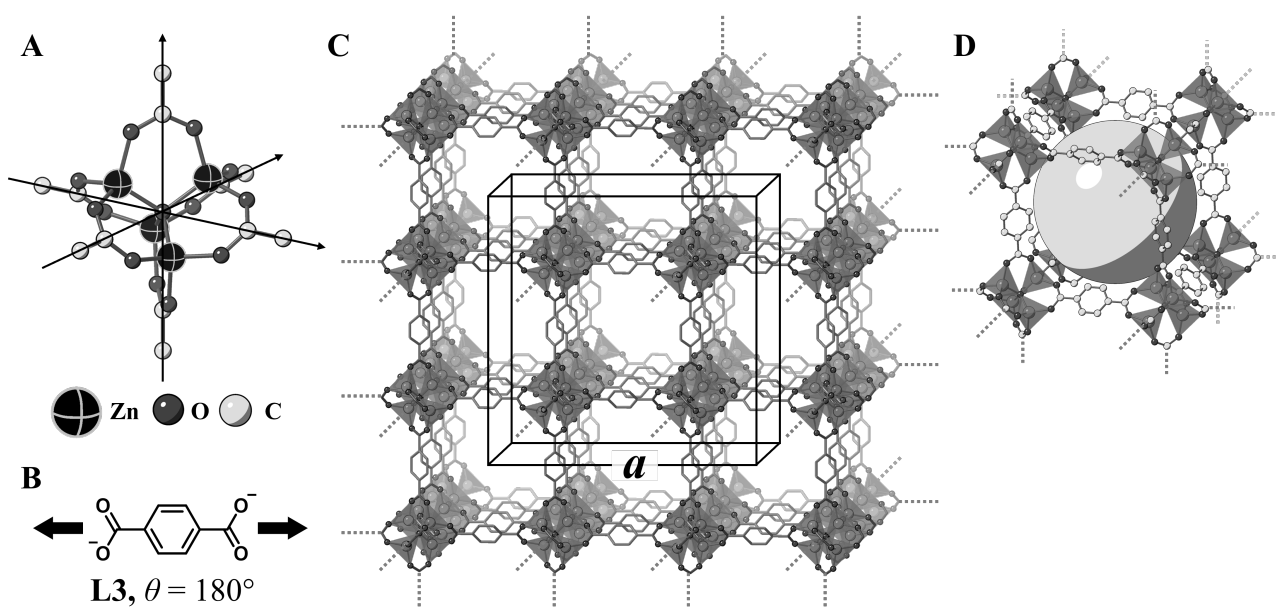


Gambar 2

- C.1 Nilai θ untuk dikarboksilat planar **L2** adalah 90° . Jika komposisi *cage complex* yang dibentuk dari **L2** dan Cu^{2+} adalah $\text{Cu}_n(\text{L2})_m$, **berikan** kombinasi bilangan bulat terkecil untuk n dan m . Asumsikan hanya gugus CO_2^- dari **L2** yang membentuk ikatan koordinasi dengan ion Cu^{2+} . 5pt



Kompleks seng, $Zn_4O(CH_3CO_2)_6$, terdiri dari empat tetrahedral Zn^{2+} , enam $CH_3CO_2^-$, dan satu O^{2-} (Gambar 3A). Pada $Zn_4O(CH_3CO_2)_6$, ion O^{2-} terletak pada pusat koordinat, dan tiga sumbu melewati atom C dari $CH_3CO_2^-$ berorientasi ortogonal relatif satu sama lain. Ketika *p*-benzenedicarboxylate (Gambar 3B, **L3**, $\theta = 180^\circ$) digunakan sebagai pengganti $CH_3CO_2^-$, *cluster* Zn^{2+} dihubungkan satu sama lain untuk membentuk padatan kristalin (**X**) yang disebut sebagai "*porous coordination polymer*" (Gambar 3C). Komposisi **X** yaitu $[Zn_4O(L3)_3]_n$, yang memiliki struktur kristal kubus dengan pori-pori berukuran nano. Satu pori digambarkan sebagai bola pada Gambar 3D, dan tiap *cluster* tetrahedron Zn^{2+} digambarkan sebagai polihedron abu-abu gelap pada Gambar 3C dan 3D. Perhatikan bahwa atom-atom hidrogen tidak ditunjukkan pada Gambar 3.



Gambar 3

C.2 **X** memiliki unit sel tipe kubus dengan panjang rusuk a (Gambar 3C) dan memiliki densitas sebesar 0.592 g cm^{-3} . **Tentukan** a dalam [cm]. 5pt

C.3 **X** mengandung banyak pori, dimana setiap 1 g **X** dapat diisi oleh $3.0 \times 10^2 \text{ mL}$ CO_2 pada 1 bar dan $25^\circ C$. **Hitung** jumlah rata-rata molekul CO_2 per pori. 5pt



IDN-3 C-6 A-1

A6-1
Indonesia (Indonesia)

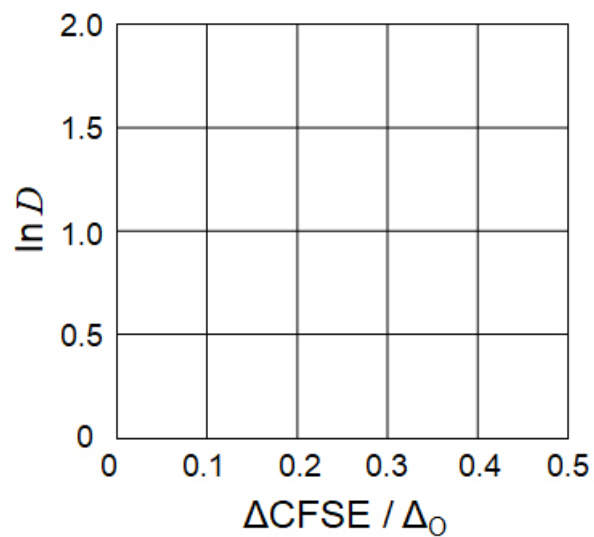
Kimia Padatan Logam Transisi

Bagian A

A.1 (6 pt)

Cr^{2+} : _____ Δ_o , Mn^{2+} : _____ Δ_o , Co^{2+} : _____ Δ_o

A.2 (3 pt)



D : _____

A.3 (3 pt)



IDN-3 C-6 A-3

A6-3
Indonesia (Indonesia)

Bagian B

B.1 (6 pt)

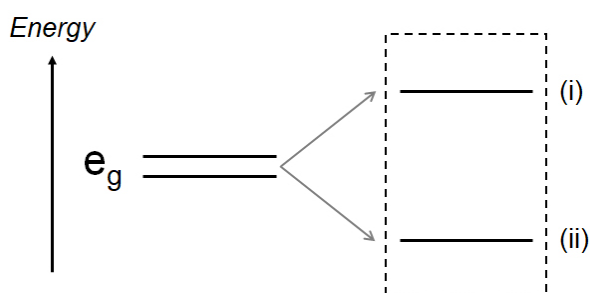
A : _____, B : _____

B.2 (4 pt)

$l_x =$ _____ nm, $l_z =$ _____ nm

B.3 (4 pt)

(i) : _____ , (ii) : _____



B.4 (4 pt)

_____ %



IDN-3 C-6 A-5

A6-5
Indonesia (Indonesia)

Bagian C

C.1 (5 pt)

$n =$ _____, $m =$ _____

C.2 (5 pt)

$a =$ _____ cm



IDN-3 C-6 A-6

A6-6
Indonesia (Indonesia)

C.3 (5 pt)

IDN-3 C-7 C-1

IDN-3 C-7 C
Nathanael Widjaja

ICHO
Problem 7
Cover sheet

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

Playing with Non-benzenoid Aromaticity

| 13 % of the total | | | | | |
|-------------------|-----|-----|-----|-----|-----------|
| Question | A.1 | A.2 | A.3 | B.1 | Total |
| Points | 5 | 2 | 19 | 10 | 36 |
| Score | | | | | |

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



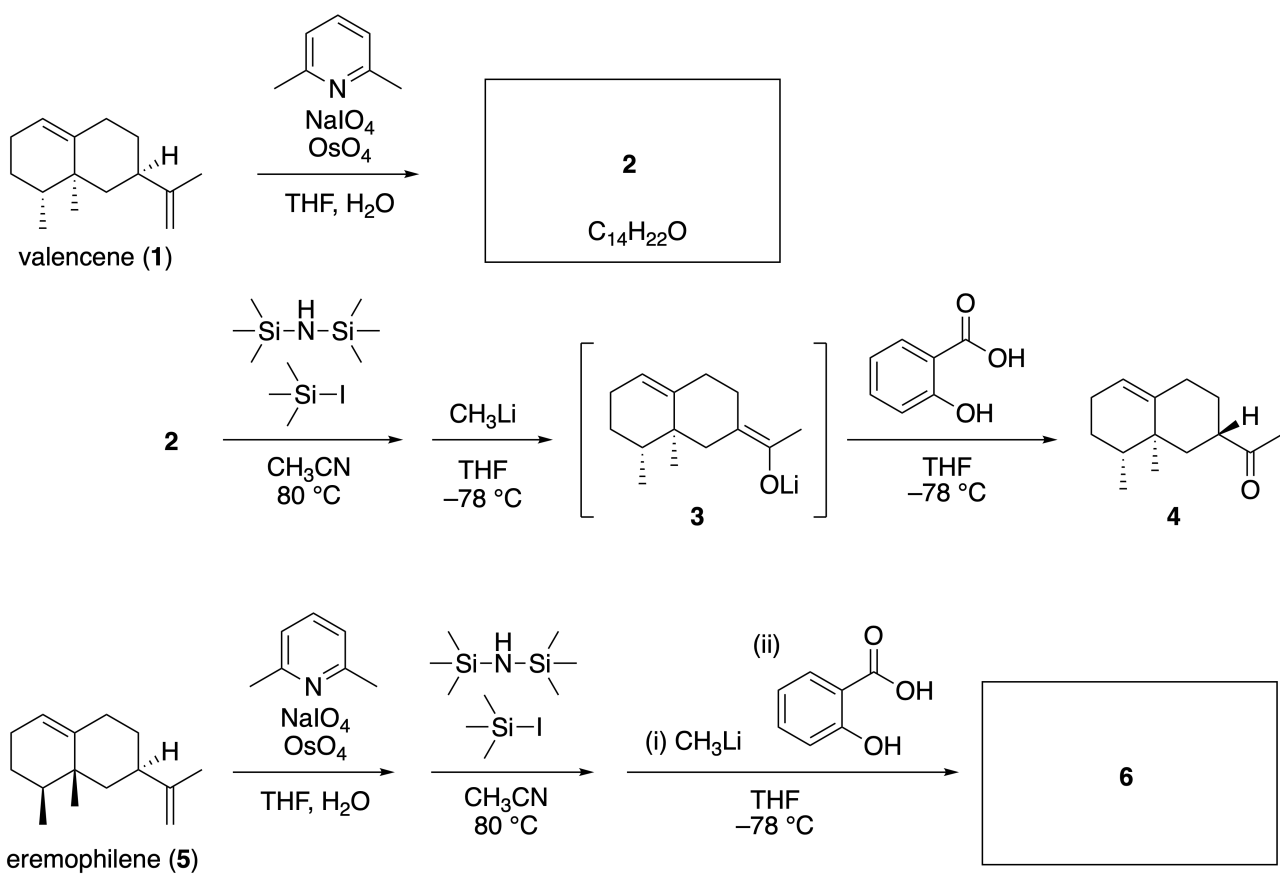
Photo courtesy: Tohoku Univ.

Part A

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



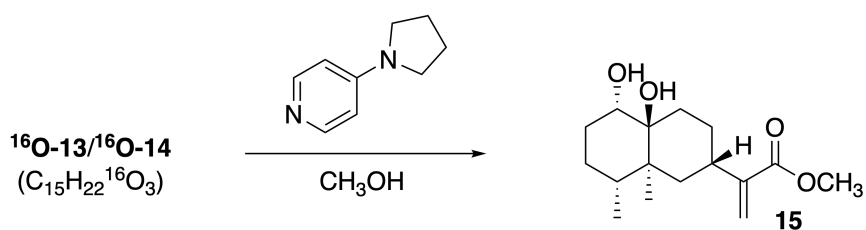
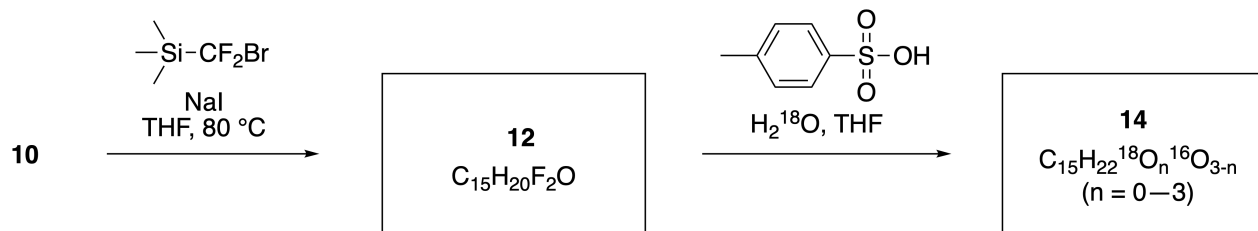
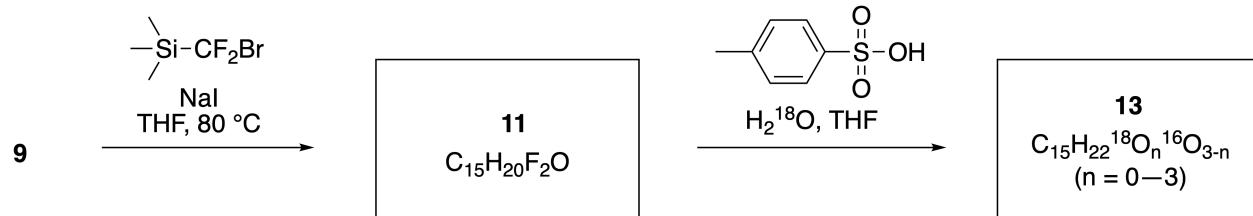
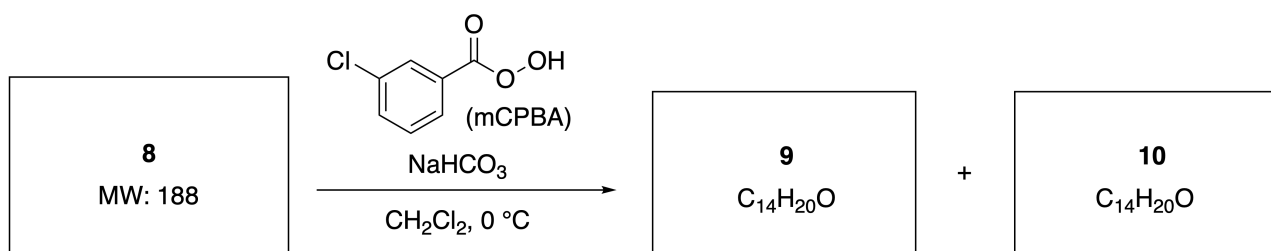
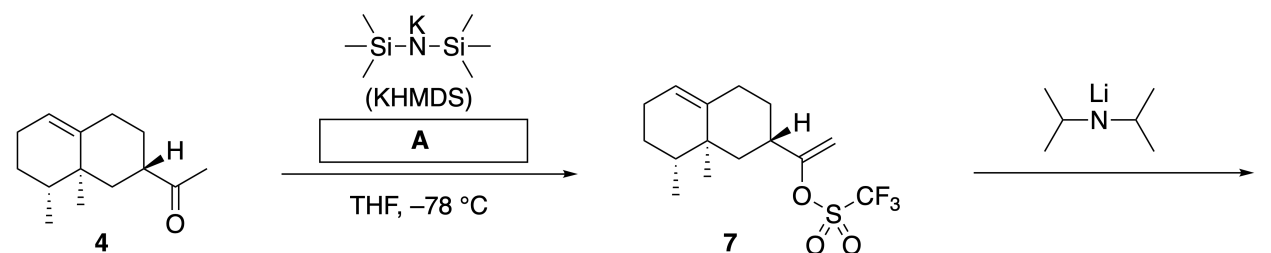
Inula linariifolia



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

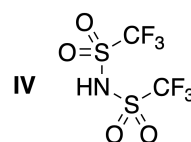
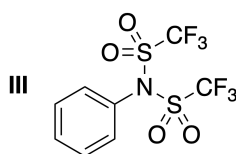
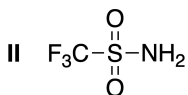
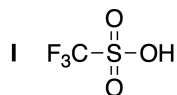
Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume

that H_2^{18}O is used instead of H_2^{16}O for the synthesis of ^{18}O -labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O -labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.



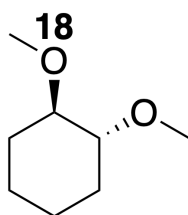
A.2 Choose the appropriate structure for **A**.

2pt



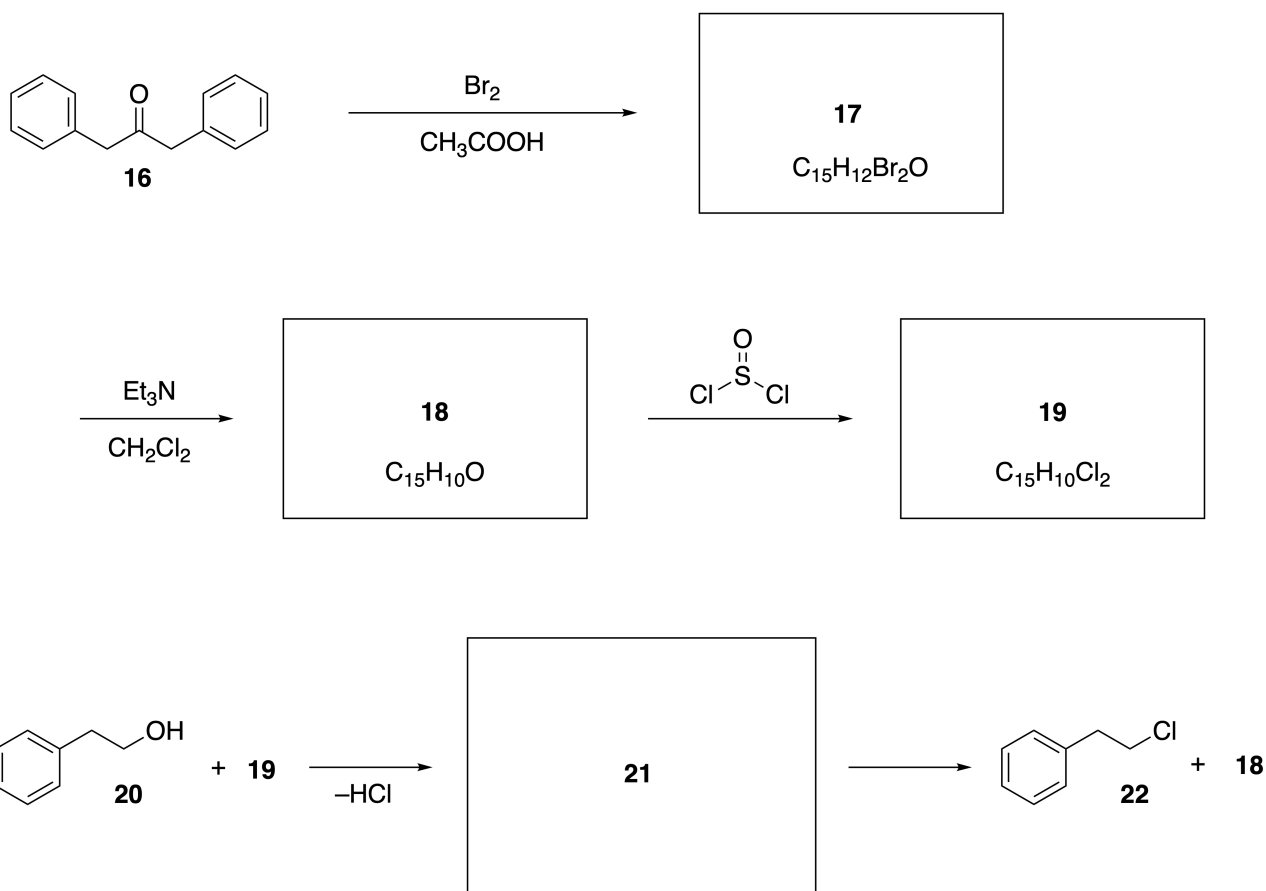
A.3 Draw the structures of **8-14** and clearly identify the stereochemistry where necessary. Also, indicate the introduced ^{18}O atoms for **13** and **14** as shown in the example below.

19pt



Part B

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



^1H NMR (CD_3CN , ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)

21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

B.1 **Draw** the structures of **17–19** and **21**. Identifying the stereochemistry is not necessary. 10pt

Bermain dengan Kearomatikan Non-benzenoid

| 13 % dari total poin | | | | | |
|----------------------|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | A.3 | B.1 | Total |
| Poin | 5 | 2 | 19 | 10 | 36 |
| Nilai | | | | | |

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



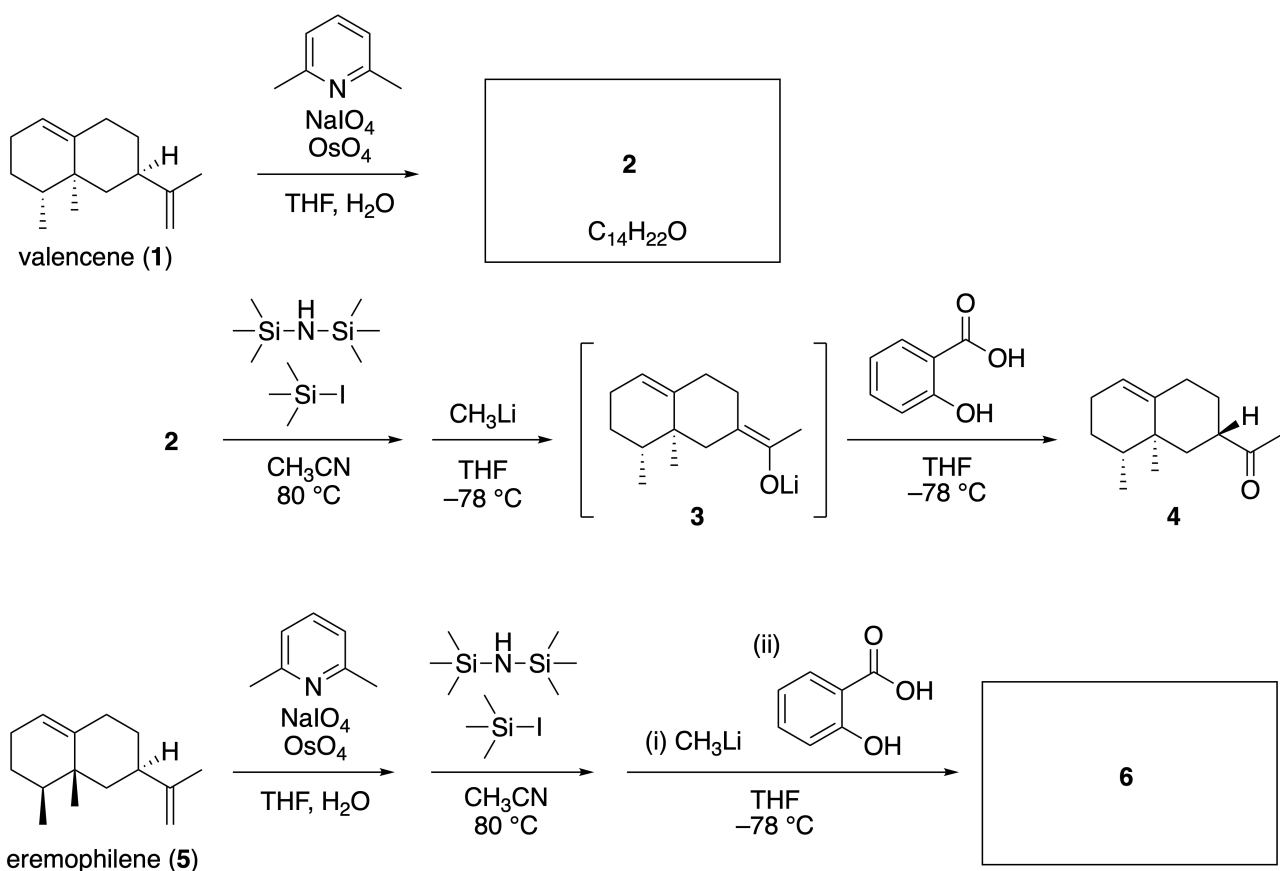
Photo courtesy: Tohoku Univ.

Bagian A

Lineariifolianone merupakan senyawa alam dengan struktur unik, yang diisolasi dari *Inula linariifolia*. Dari *valencene* (**1**), konversi satu-tahap menghasilkan **2**, sebelum konversi tiga-tahap melalui **3** menghasilkan keton **4**. *Eremophilene* (**5**) dikonversi menjadi **6** dengan melakukan konversi empat-tahap yang sama.



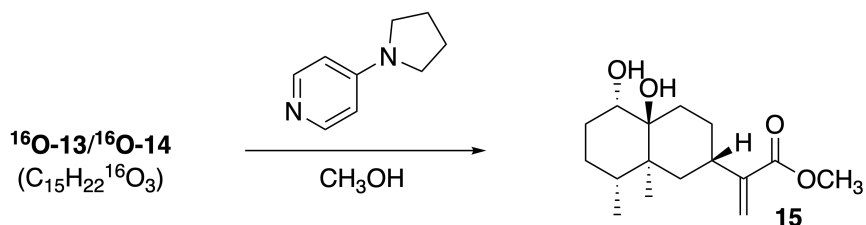
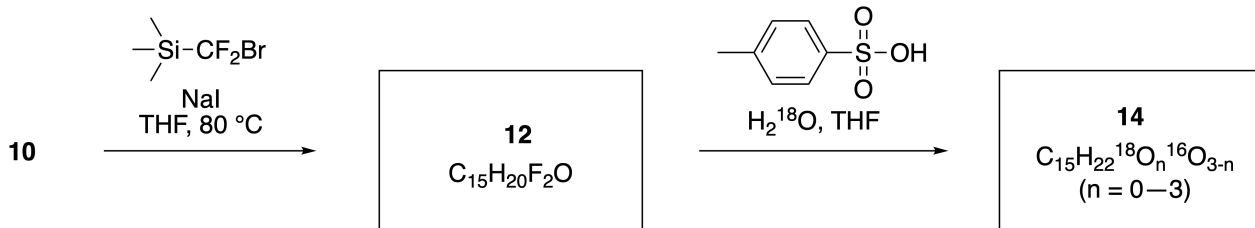
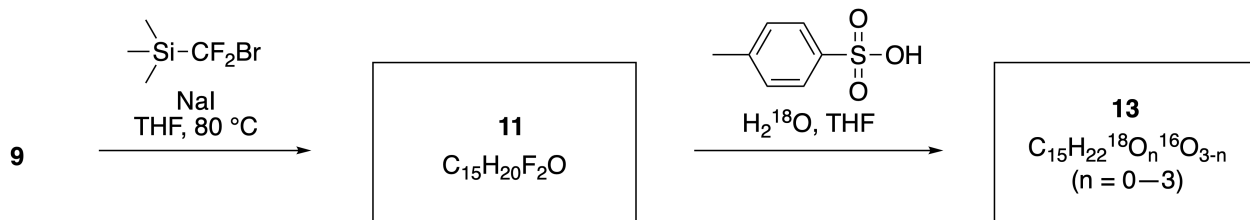
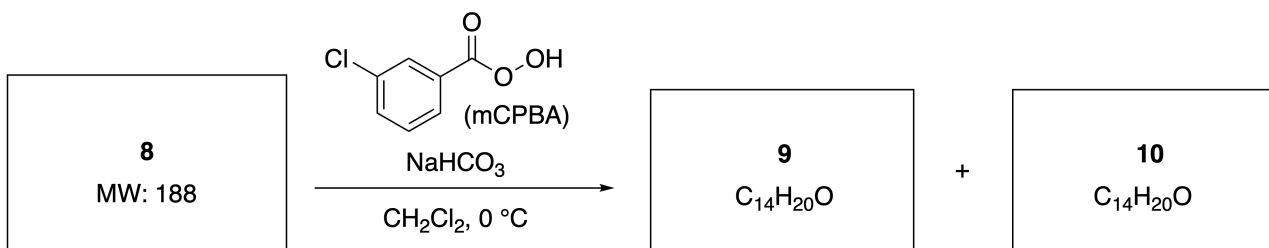
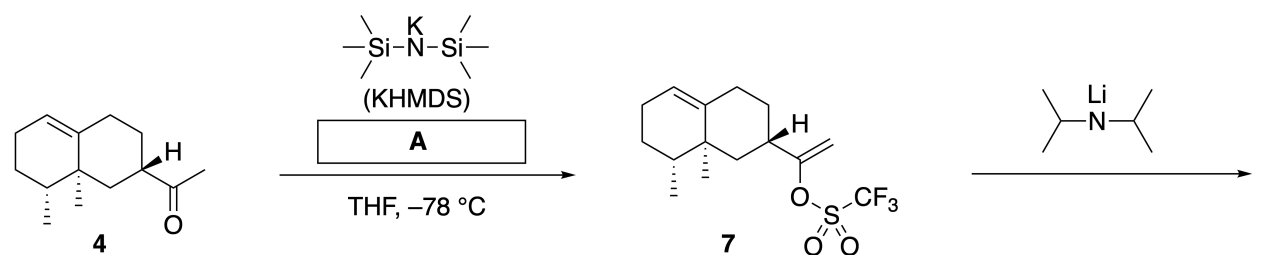
Inula linariifolia



A.1 Gambarkan struktur 2 dan 6 serta identifikasi dengan jelas stereokimianya di 5pt posisi yang tepat.

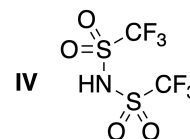
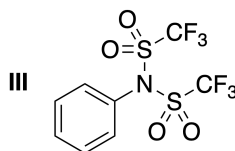
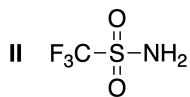
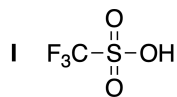
Selanjutnya, keton 4 dikonversi menjadi ester 15. Senyawa 8 (berat molekul: 188) mempertahankan semua stereocenter di 7. Senyawa 9 dan 10 memiliki lima stereocenter dan tidak ada ikatan rangkap karbon-

karbon. Asumsikan bahwa H_2^{18}O digunakan sebagai pengganti H_2^{16}O untuk sintesis *lineariifoliane* berlabel- ^{18}O **13** dan **14** secara berturut-turut dari **11** dan **12**. Senyawa **13** dan **14** adalah isotopomer berlabel- ^{18}O . Dengan mengabaikan pelabelan isotop, baik **13** dan **14** keduanya menghasilkan produk **15** yang sama dengan stereokimia yang identik.



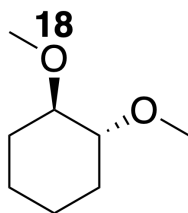
A.2 Pilih struktur **A** yang paling tepat.

2pt



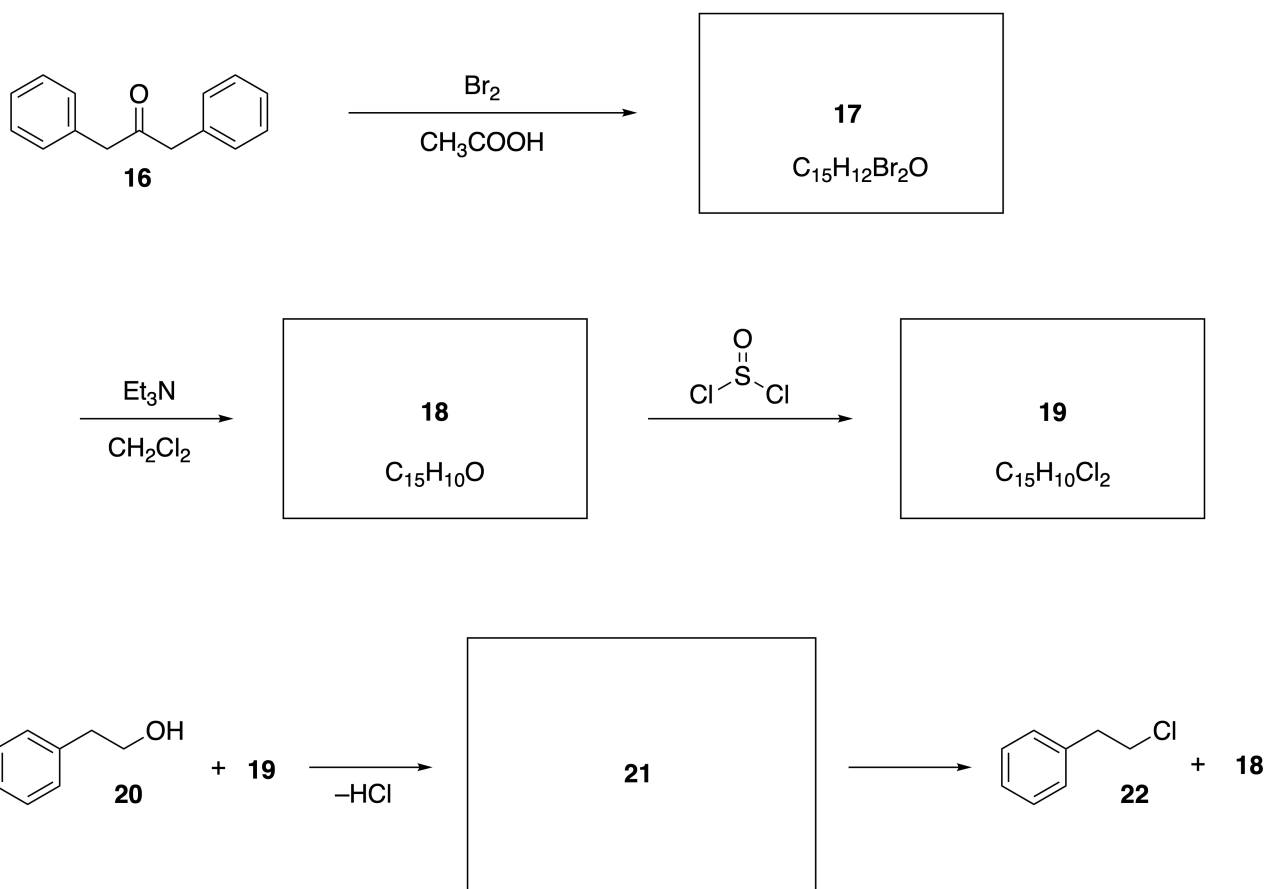
A.3 Gambarkan struktur **8-14** dan identifikasi dengan jelas stereokimianya di posisi yang tepat. Selain itu, tuliskan atom-atom ^{18}O yang terdapat pada **13** dan **14** seperti contoh berikut.

19pt



Bagian B

Senyawa **19** disintesis seperti ditunjukkan di bawah ini. Sehubungan dengan kearomatikan non-benzenoid, **19** dapat digunakan sebagai aktivator alkohol, dan **20** dikonversi menjadi **22** melalui intermediet pasangan-ion **21**. Walaupun pembentukan **21** teramati oleh NMR, namun **21** secara bertahap terurai menjadi **18** dan **22**.



^1H NMR (CD_3CN , ppm) **20**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)

21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

B.1 **Gambarkan** struktur **17–19** dan **21**. Identifikasi stereokimia tidak diperlukan. 10pt



IDN-3 C-7 A-1

A7-1
Indonesia (Indonesia)

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)



IDN-3 C-7 A-3

A7-3
Indonesia (Indonesia)

Bagian B

B.1 (10 pt)

17 (2 pt)

18 (2 pt)

19 (3 pt)

21 (3 pt)

IDN-3 C-8 C-1

IDN-3 C-8 C
Nathanael Widjaja

ICHO
Problem 8
Cover sheet

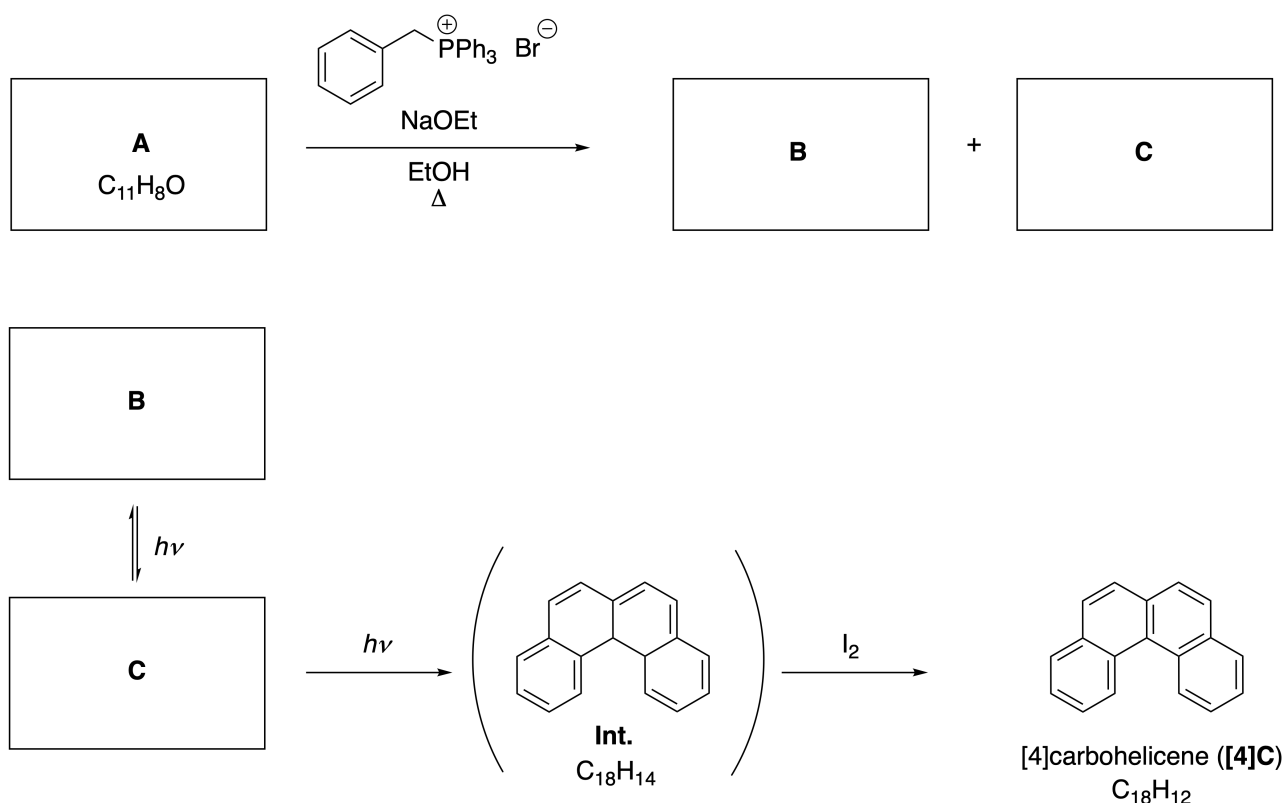
Please return this cover sheet together with all the related question sheets.

Dynamic Organic Molecules and Their Chirality

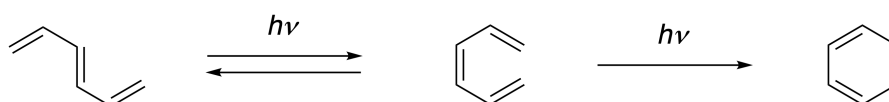
| 11 % of the total | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----------|
| Question | A.1 | A.2 | A.3 | B.1 | B.2 | Total |
| Points | 9 | 3 | 7 | 3 | 4 | 26 |
| Score | | | | | | |

Part A

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



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

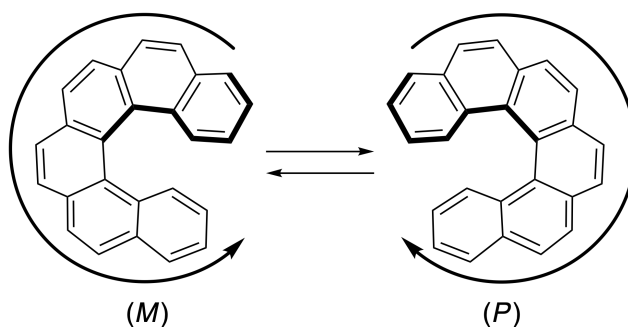


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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 ^1H NMR chemical shifts of **D** are listed below. **Draw** the structure of **D**.
[D (δ , ppm in CS_2 , r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]

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



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

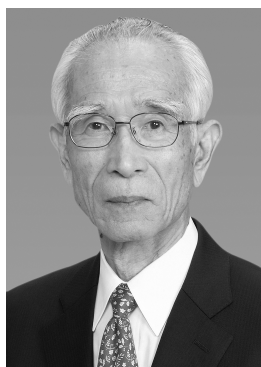
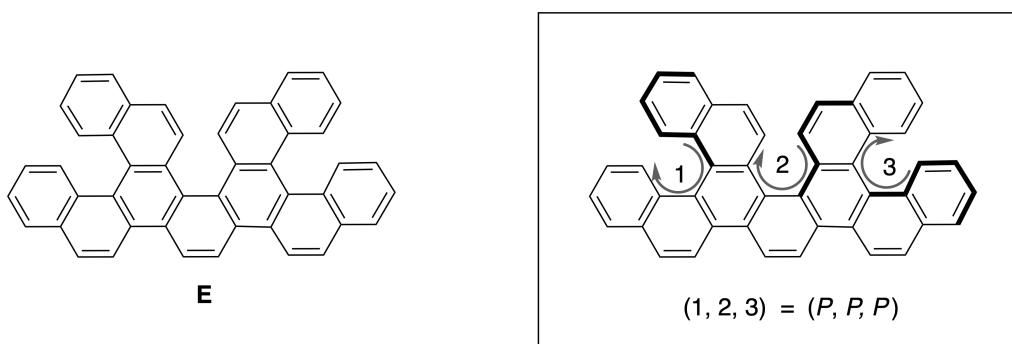
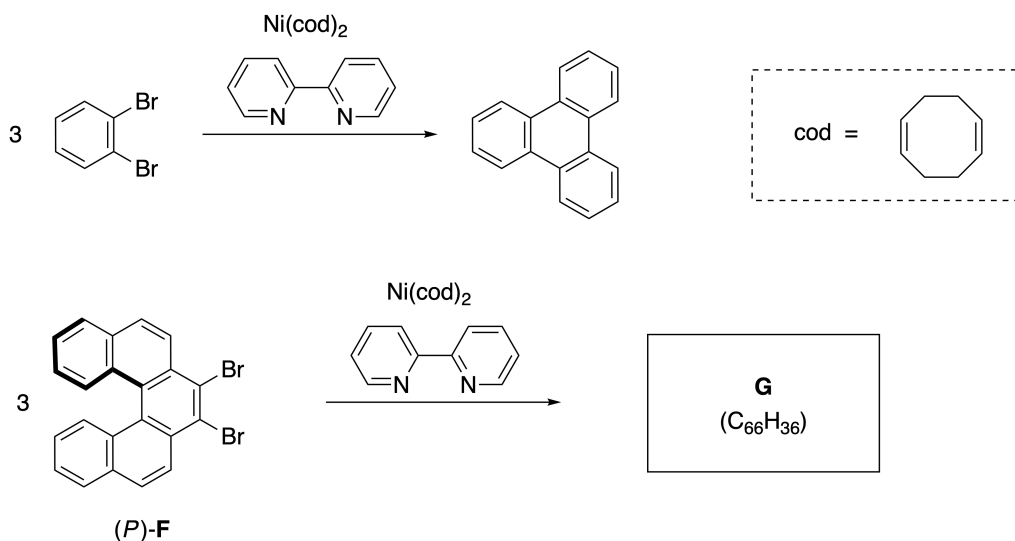


Photo courtesy: The Japan Prize Foundation

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

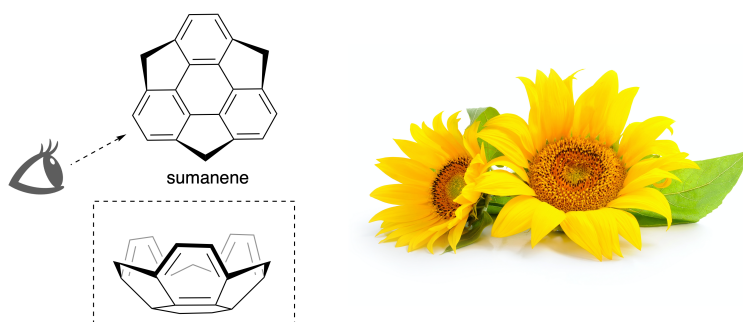


- A.3** The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (P) -**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify 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) . 7pt

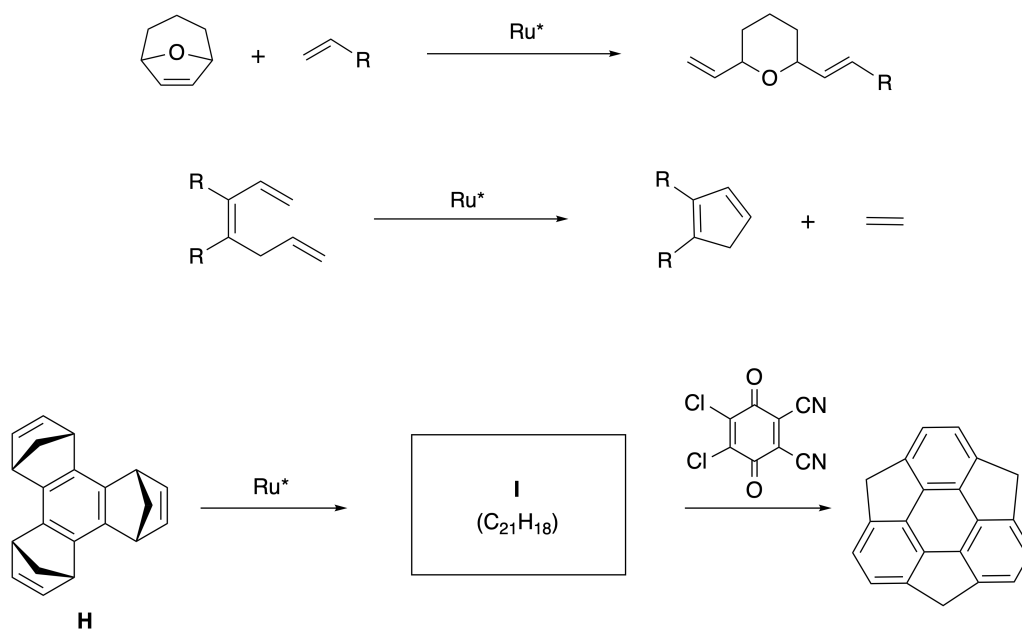


Part B

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

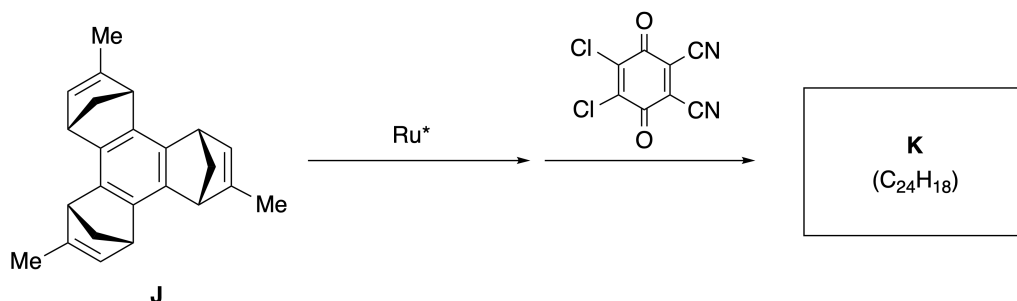


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru^*) are shown below.



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

3pt



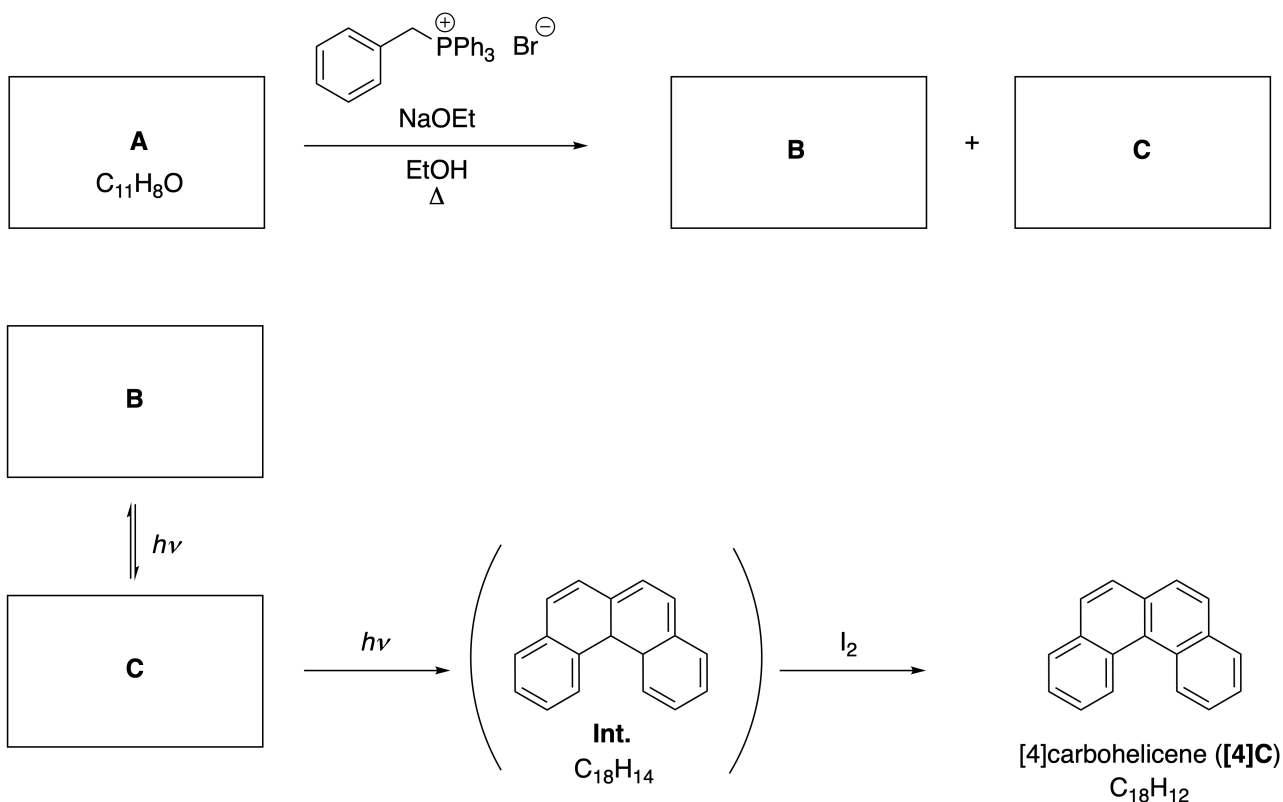
- B.2** Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. **Draw** the structure of **K** with the appropriate stereochemistry. 4pt

Molekul Organik Dinamis dan Kiralitasnya

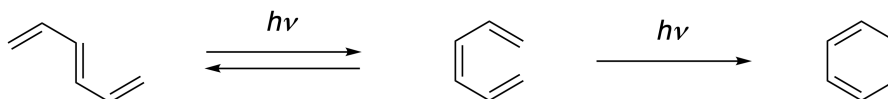
| 11 % dari total poin | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | A.3 | B.1 | B.2 | Total |
| Poin | 9 | 3 | 7 | 3 | 4 | 26 |
| Nilai | | | | | | |

Bagian A

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



Fotoreaksi berlangsung dengan cara yang serupa dengan contoh berikut.

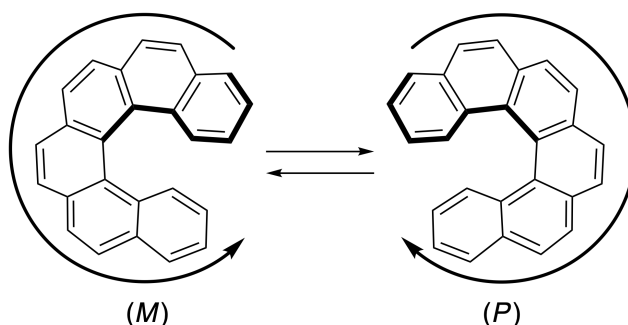


Catatan: Untuk semua Pertanyaan 8, gambarkan ikatan tunggal dan ikatan rangkap berselang-seling dalam jawaban Anda seperti yang dicontohkan pada *carbohelicene*. Jangan gunakan lingkaran untuk sistem π terkonjugasi.

A.1 **Gambarkan** struktur **A-C**. Stereoisomer harus jelas dibedakan. 9pt

A.2 Upaya untuk sintesis [5]*carbohelicene* dari garam fosfonium yang sama dan senyawa awal yang sesuai hanya sedikit menghasilkan [5]*carbohelicene*, sebagai gantinya justru menghasilkan produk **D** yang berat molekulnya 2 Da lebih kecil daripada [5]*carbohelicene*. Geseran kimia $^1\text{H NMR}$ **D** tercantum di bawah ini. **Gambarkan** struktur **D**.
[D (δ , ppm dalam CS_2 , r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]

[5]- dan [n]*carbohelicene* yang lebih besar memiliki kiralitas heliks dan interkonversi antara enantiomer *helicene* ini berlangsung sangat lambat pada suhu kamar. Kiralitas [n]*carbohelicene* didefinisikan sebagai (*M*) atau (*P*) seperti ditunjukkan di bawah ini.



[n]*Carbohelicene* dengan n lebih besar daripada 4 dapat dipisahkan secara enantiomer menggunakan kromatografi kolom kiral, yang dikembangkan oleh Prof. Yoshio Okamoto.

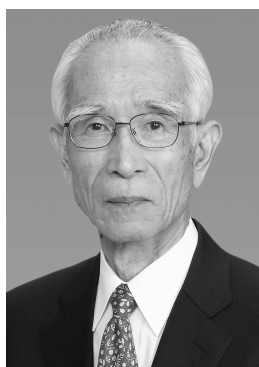
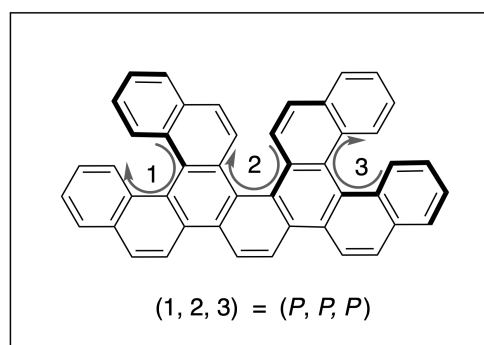
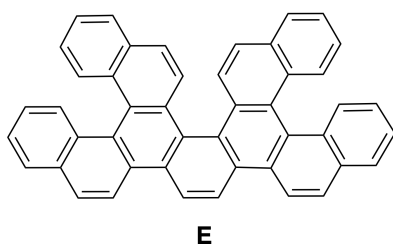
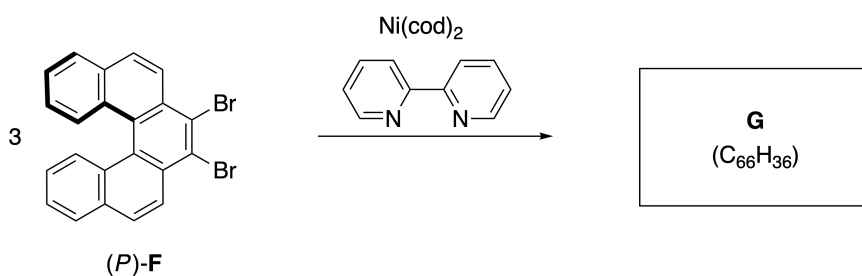
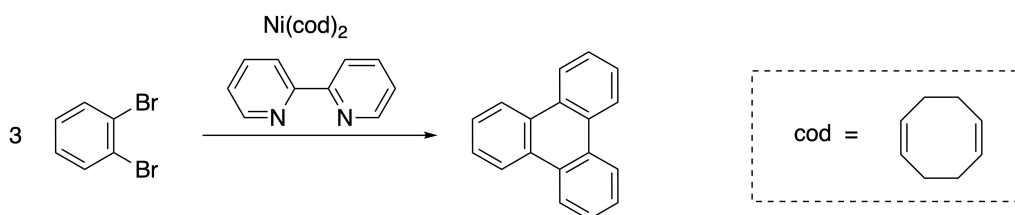


Photo courtesy: The Japan Prize Foundation

Multiple helicene adalah molekul yang mengandung dua atau lebih struktur mirip-*helicene*. Jika kiralitas heliksnya dipertimbangkan, beberapa stereoisomer berada dalam bentuk *multiple helicene*. Contohnya, senyawa **E** mengandung tiga bagian mirip-[5]*carbohelicene* dalam satu molekul. Salah satu stereoisomernya digambarkan sebagai (*P, P, P*) seperti ditunjukkan di bawah ini.

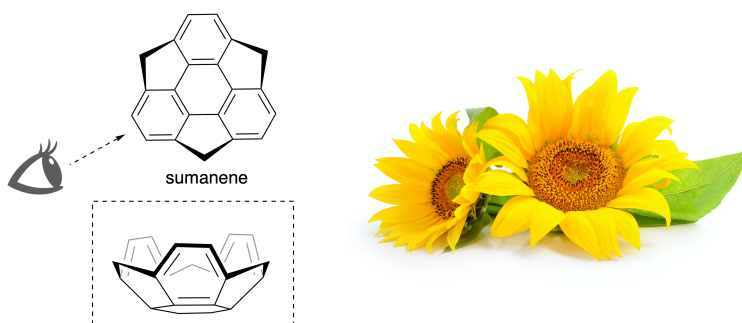


- A.3** Trimerisasi 1,2-dibromobenzena yang dimediasi-nikel menghasilkan *triphenylene*. 7pt
Ketika reaksi yang sama diterapkan pada suatu enantiomer **F**, yaitu (*P*)-**F**, diperoleh *multiple helicene* **G** ($C_{66}H_{36}$). Mengingat bahwa interkonversi antara stereoisomer tidak terjadi selama 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, P*), dan (*M, P, M*).

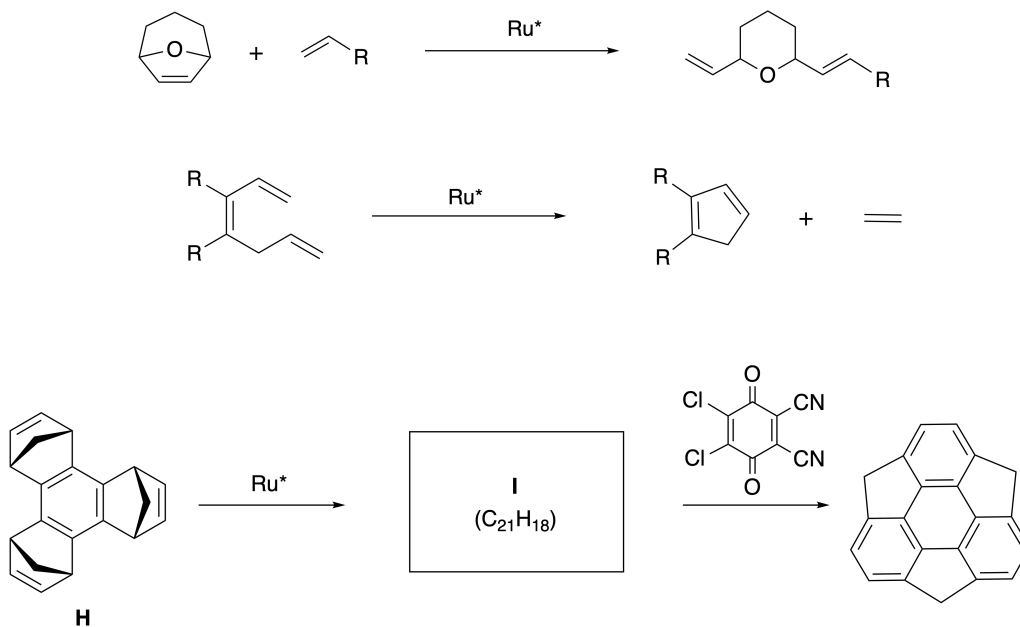


Bagian B

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. Sintesis *sumanene* dicapai melalui serangkaian reaksi yang terdiri dari metatesis pembukaan-cincin dan penutupan-cincin.

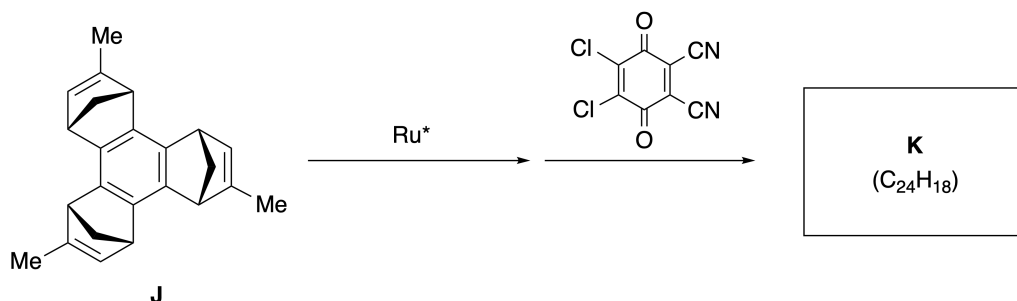


Reaksi metatesis representatif yang dikatalisis oleh katalis rutenium (Ru^*) ditunjukkan di bawah ini.



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

3pt



- 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. 4pt



IDN-3 C-8 A-1

A8-1
Indonesia (Indonesia)

Molekul Organik Dinamis dan Kiralitasnya

Bagian A

A.1 (9 pt)

A (3 pt)

B (3 pt)

C (3 pt)

A.2 (3 pt)



IDN-3 C-8 A-2

A8-2
Indonesia (Indonesia)

A.3 (7 pt)



IDN-3 C-8 A-3

A8-3
Indonesia (Indonesia)

Bagian B

B.1 (3 pt)

B.2 (4 pt)

IDN-3 C-9 C-1

IDN-3 C-9 C
Nathanael Widjaja

ICHO
Problem 9
Cover sheet

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

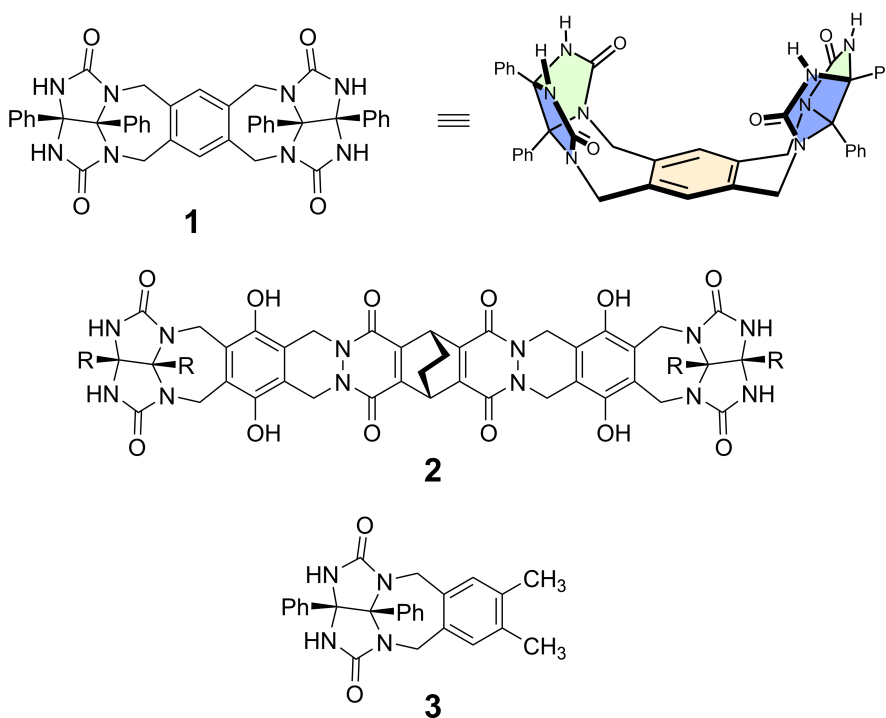
Likes and Dislikes of Capsule

| 10 % of the total | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-------|
| Question | A.1 | A.2 | A.3 | A.4 | A.5 | Total |
| Points | 13 | 2 | 2 | 3 | 3 | 23 |
| Score | | | | | | |

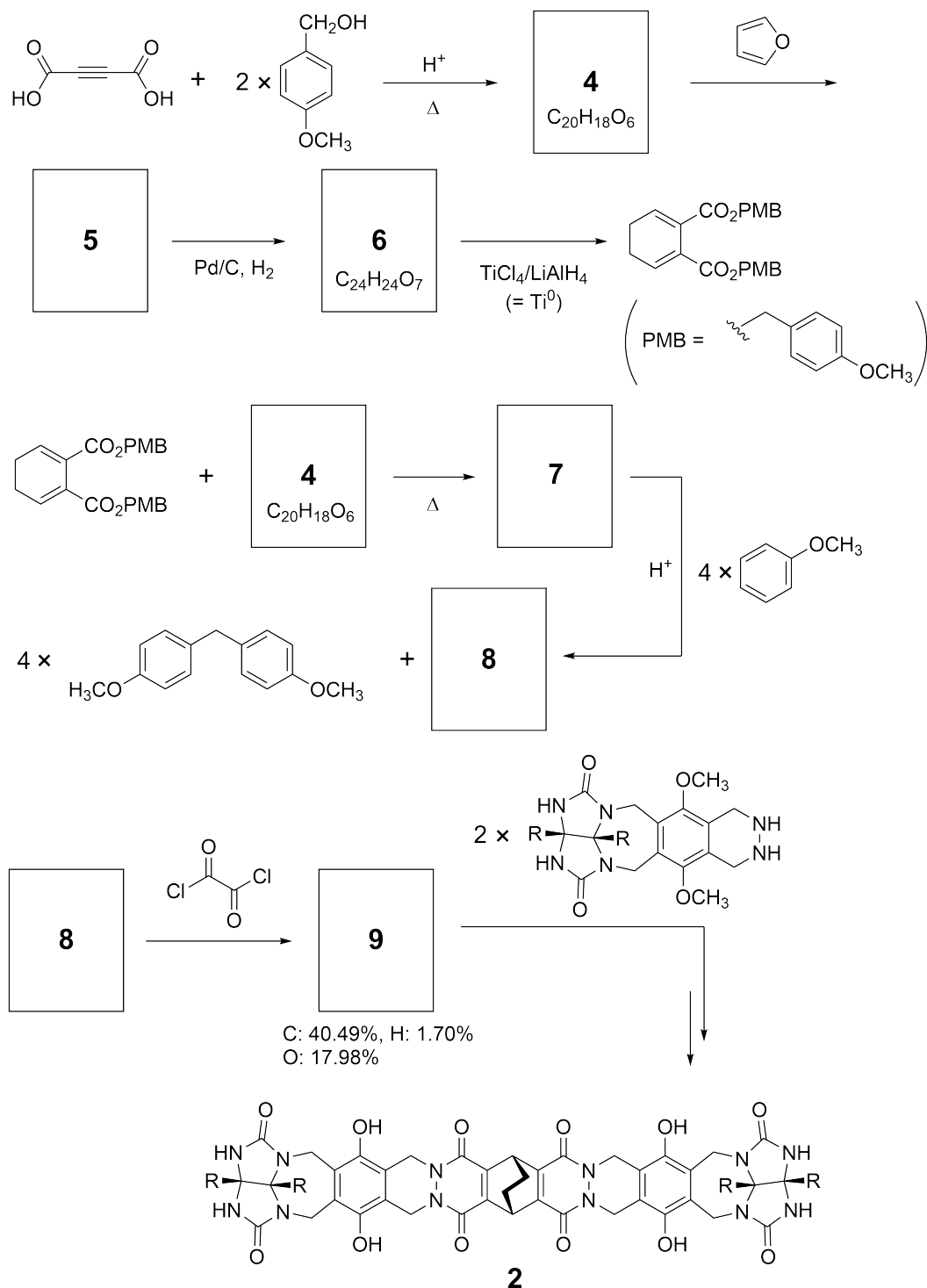
Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared 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.





IDN-3 C-9 Q-3

Q9-3

English (Official)

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. 13pt

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

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

A.3 **Give** the number of the hydrogen bonds in the dimeric capsule (**1₂**). 2pt

The dimeric capsule of **1** (1_2) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

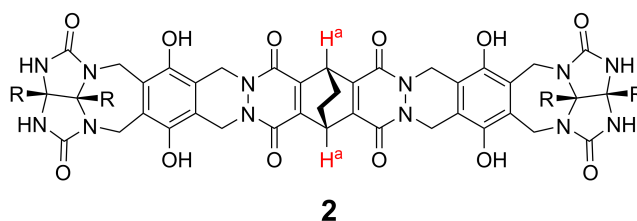


The equilibrium constant of the encapsulation of Z into 1_2 is given as below:

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

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, 1_2 in C_6D_6 gave different signals in the 1H NMR spectra before and after addition of CH_4 .

Compound **2** also forms a rigid and larger dimeric capsule (2_2). The 1H NMR spectrum of 2_2 was measured in C_6D_6 , C_6D_5F , and a C_6D_6/C_6D_5F solvent mixture, with all other conditions being kept constant. The chemical shifts for the H^a proton of **2** in the above solvents are summarized below, and no other signals from the H^a in **2**, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.



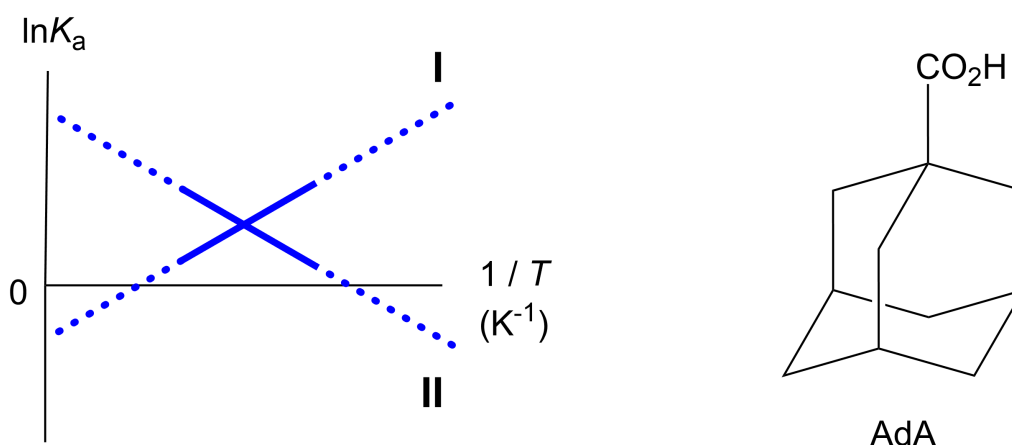
| solvent | δ (ppm) of H^a |
|--------------------|-------------------------|
| C_6D_6 | 4.60 |
| C_6D_5F | 4.71 |
| C_6D_6 / C_6D_5F | 4.60, 4.71, 4.82 |

A.4 Determine the number of C_6D_6 and C_6D_5F molecules encapsulated in 2_2 giving each H^a signal. 3pt

^1H NMR measurements in C_6D_6 revealed that $\mathbf{2}_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants (K_a) which are expressed below were determined for various temperatures. $[\text{solvent@}\mathbf{2}_2]$ denotes a species containing one or more solvent molecules.

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

Similarly, the K_a values of CH_4 and $\mathbf{1}_2$ given as eq (2) at various temperatures in C_6D_6 were also determined by ^1H NMR measurements. The plots of the two association constants (as $\ln K_a$ vs $1/T$) are shown below.



No C_6D_6 molecule is encapsulated in $\mathbf{1}_2$. In line **II**, the entropy change (ΔS) is (1) and enthalpy change (ΔH) is (2), indicating that the driving force for the encapsulation in line **II** is (3). Therefore, line **I** corresponds to (4), and line **II** corresponds to (5).

A.5 **Choose** the correct options in gaps (1)-(5) in the following paragraph from A 3pt and B.

| | A | B |
|-----|----------------------------------|------------------------|
| (1) | positive | negative |
| (2) | positive | negative |
| (3) | ΔS | ΔH |
| (4) | $\mathbf{1}_2$ and CH_4 | $\mathbf{2}_2$ and AdA |
| (5) | $\mathbf{1}_2$ and CH_4 | $\mathbf{2}_2$ and AdA |

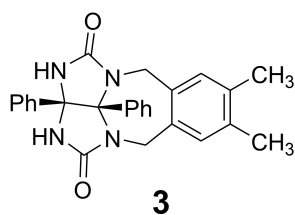
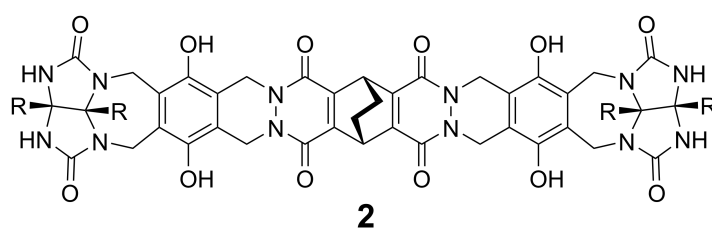
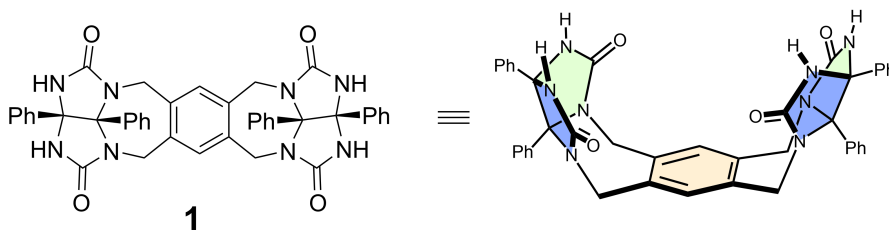
Kapsul Suka dan Benci

| 10 % dari total poin | | | | | | |
|----------------------|-----|-----|-----|-----|-----|-----------|
| Pertanyaan | A.1 | A.2 | A.3 | A.4 | A.5 | Total |
| Poin | 13 | 2 | 2 | 3 | 3 | 23 |
| Nilai | | | | | | |

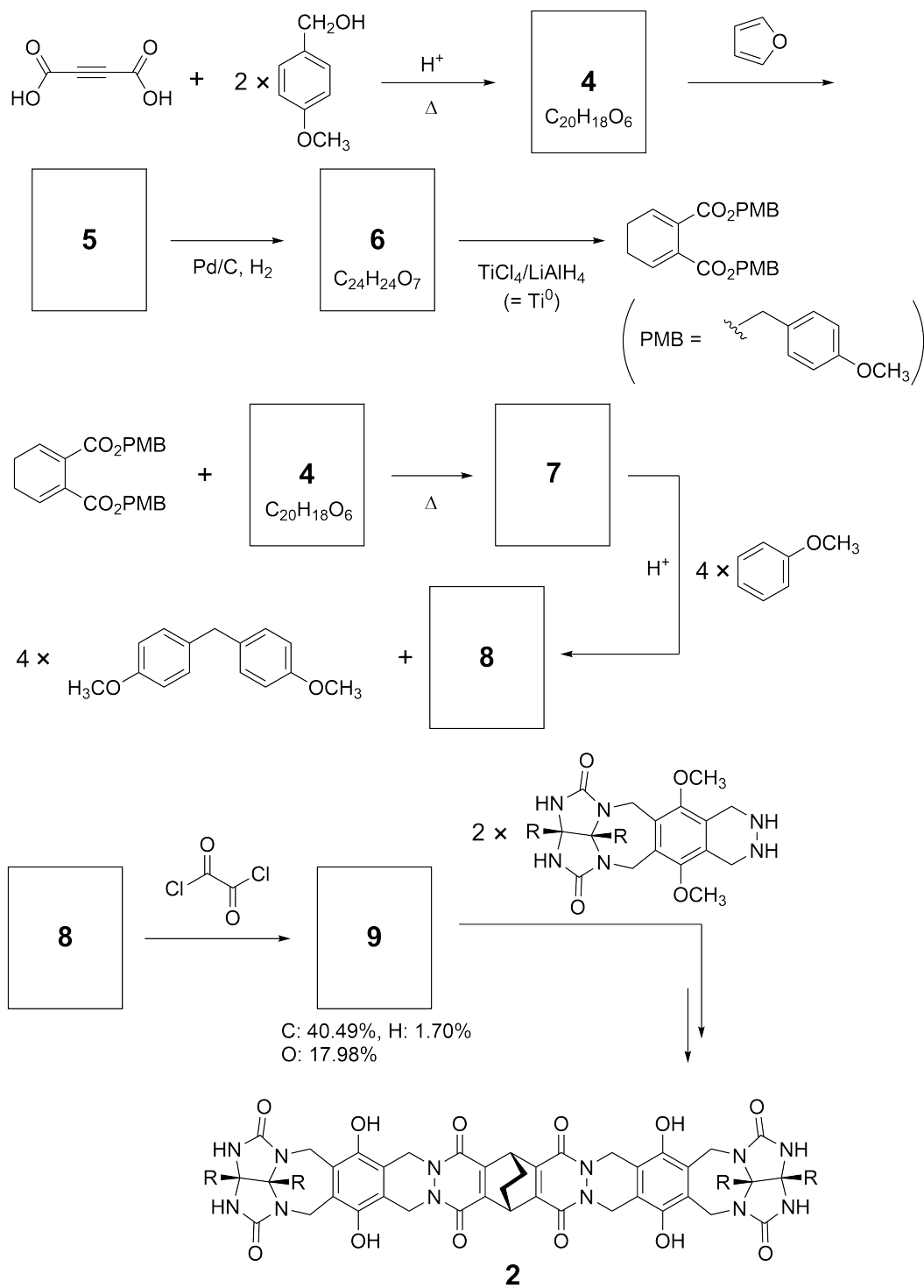
Anak yang baik tidak melakukan ini, tetapi jika Anda membuka jahitan bola tenis, Anda dapat membongkarnya menjadi dua bagian berbentuk-U.



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. 13pt



IDN-3 C-9 Q-4

Q9-4

Indonesia (Indonesia)

Pada spektrum massa **1**, puncak ion yang mewakili dimernya (1_2) jelas teramati, sedangkan puncak ion untuk 3_2 tidak teramati pada spektrum **3**. Pada spektrum ^1H NMR larutan 1_2 , semua proton NH yang berasal dari **1** teramati memiliki lingkungan kimia yang ekuivalen, 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 (1_2). | 2pt |
|------------|--|-----|

Kapsul dimer **1** (1_2) memiliki ruang internal tempat suatu molekul kecil Z dapat dienkapsulasi. Fenomena ini dinyatakan dengan persamaan berikut:

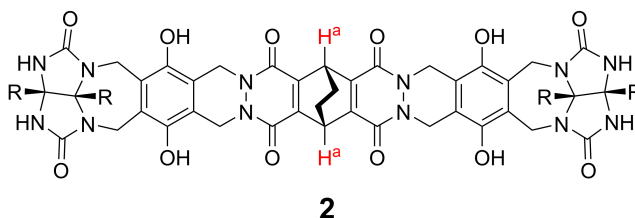


Tetapan kesetimbangan enkapsulasi Z ke dalam 1_2 dinyatakan sebagai berikut:

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

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 1H NMR.

Senyawa **2** juga membentuk kapsul dimer (2_2) yang kaku dan lebih besar. Spektrum 1H NMR 2_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.



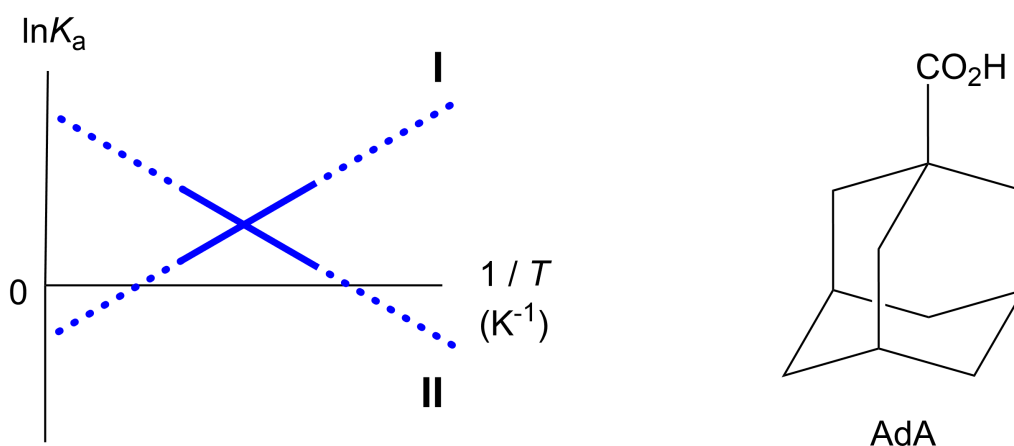
| pelarut | δ (ppm) H^a |
|--------------------|----------------------|
| C_6D_6 | 4.60 |
| C_6D_5F | 4.71 |
| C_6D_6 / C_6D_5F | 4.60, 4.71, 4.82 |

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 ^1H NMR dalam C_6D_6 menunjukkan bahwa $\mathbf{2}_2$ dapat memuat satu molekul 1-adamantanecarboxylic acid (AdA), dan tetapan kesetimbangan asosiasi (K_a) yang dinyatakan berikut ditentukan pada berbagai temperatur. $[\text{solvent@}\mathbf{2}_2]$ adalah spesi yang mengandung satu atau lebih molekul pelarut.

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

Demikian pula, nilai K_a CH_4 dan $\mathbf{1}_2$ yang dinyatakan dengan persamaan (2) pada berbagai temperatur dalam C_6D_6 juga ditentukan melalui pengukuran ^1H NMR. Aluran dua tetapan asosiasi (sebagai $\ln K_a$ vs $1/T$) ditunjukkan di bawah ini.



Tidak ada molekul C_6D_6 yang terenkapsulasi di dalam $\mathbf{1}_2$. Pada garis **II**, perubahan entropi (ΔS) adalah (1) dan perubahan entalpi (ΔH) 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. 3pt

| | A | B |
|-----|----------------------------------|------------------------|
| (1) | positif | negatif |
| (2) | positif | negatif |
| (3) | ΔS | ΔH |
| (4) | $\mathbf{1}_2$ dan CH_4 | $\mathbf{2}_2$ dan AdA |
| (5) | $\mathbf{1}_2$ dan CH_4 | $\mathbf{2}_2$ dan AdA |



IDN-3 C-9 A-1

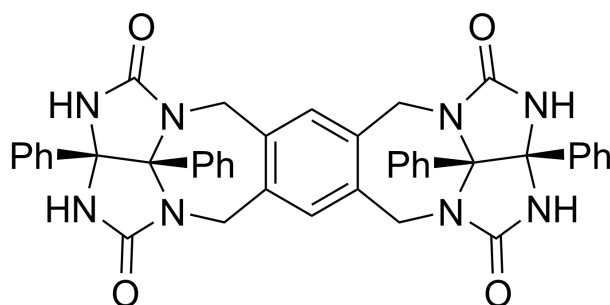
A9-1
Indonesia (Indonesia)

Kapsul Suka dan Benci

A.1 (13 pt)

| | |
|-----------------|-----------------|
| 4 (2 pt) | 5 (3 pt) |
| 6 (2 pt) | 7 (2 pt) |
| 8 (2 pt) | 9 (2 pt) |

A.2 (2 pt)



A.3 (2 pt)

A.4 (3 pt)

| δ (ppm) H ^a | jumlah C ₆ D ₆ | jumlah C ₆ D ₅ F |
|-------------------------------|--------------------------------------|--|
| 4.60 ppm | | |
| 4.71 ppm | | |
| 4.82 ppm | | |

A.5 (3 pt)

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

(4) : _____ (5) : _____