NOR-1 C-0 C-1

**NOR-1 C-0 C**
Abdur-Raheem Idowu

# IChO
# General instructions
## Cover sheet

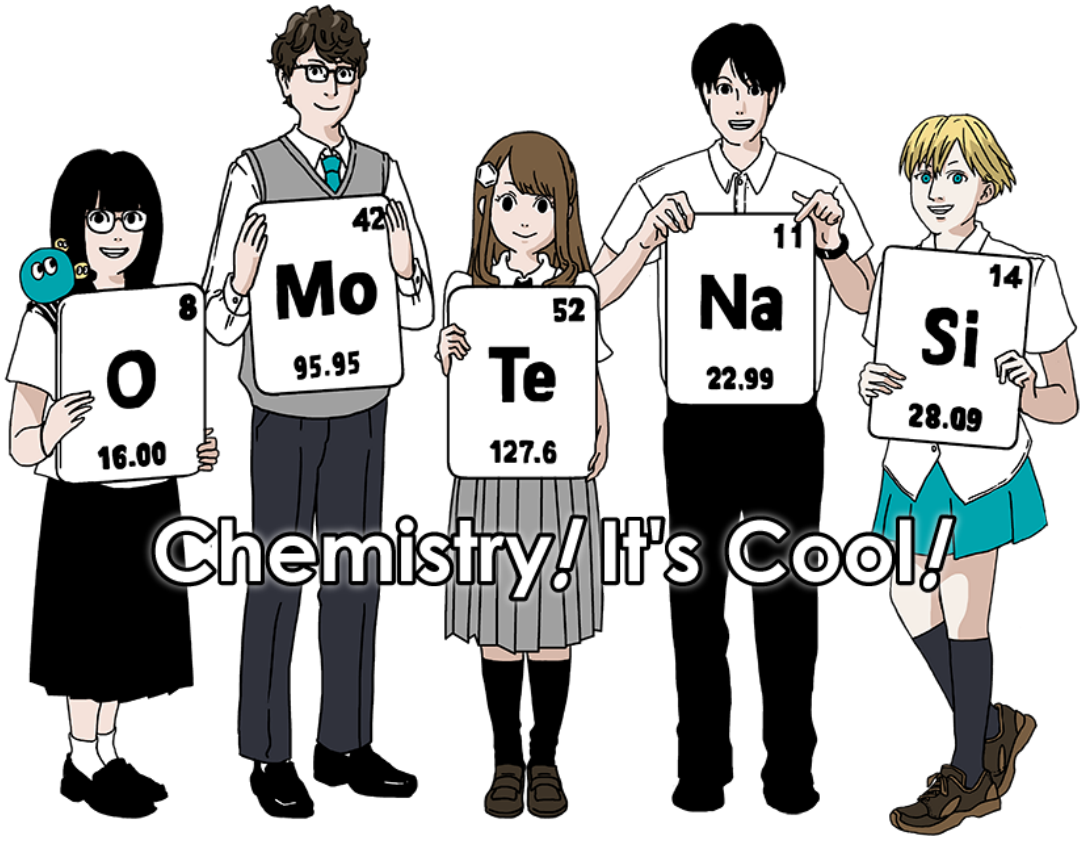
Please return this cover sheet together with all the related question sheets.

**International Chemistry Olympiad 2021 Japan**

**53rd IChO2021 Japan**

**25th July – 2nd August, 2021**

**https://www.icho2021.org**



## 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 | $c = 2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$ |
| Planck constant | $h = 6.62607015 \times 10^{-34}\ \mathrm{J\ s}$ |
| Elementary charge | $e = 1.602176634 \times 10^{-19}\ \mathrm{C}$ |
| Electron mass | $m_{\mathrm{e}} = 9.10938370 \times 10^{-31}\ \mathrm{kg}$ |
| Electric constant (permittivity of vacuum) | $\varepsilon_0 = 8.85418781 \times 10^{-12}\ \mathrm{F\ m^{-1}}$ |
| Avogadro constant | $N_{\mathrm{A}} = 6.02214076 \times 10^{23}\ \mathrm{mol^{-1}}$ |
| Boltzmann constant | $k_{\mathrm{B}} = 1.380649 \times 10^{-23}\ \mathrm{J\ K^{-1}}$ |
| Faraday constant | $F = N_{\mathrm{A}} \times e = 9.64853321233100184 \times 10^{4}\ \mathrm{C\ mol^{-1}}$ |
| Gas constant | $R = N_{\mathrm{A}} \times k_{\mathrm{B}} = 8.31446261815324\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $= 8.2057366081 \times 10^{-2}\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$ |
| Unified atomic mass unit | $u = 1\ \mathrm{Da} = 1.66053907 \times 10^{-27}\ \mathrm{kg}$ |
| Standard pressure | $p = 1\ \mathrm{bar} = 10^{5}\ \mathrm{Pa}$ |
| Atmospheric pressure | $p_{\mathrm{atm}} = 1.01325 \times 10^{5}\ \mathrm{Pa}$ |
| Zero degree Celsius | $0\ ^{\circ}\mathrm{C} = 273.15\ \mathrm{K}$ |
| Ångstrom | $1\ \text{Å} = 10^{-10}\ \mathrm{m}$ |
| Picometer | $1\ \mathrm{pm} = 10^{-12}\ \mathrm{m}$ |
| Electronvolt | $1\ \mathrm{eV} = 1.602176634 \times 10^{-19}\ \mathrm{J}$ |
| Part-per-million | $1\ \mathrm{ppm} = 10^{-6}$ |
| Part-per-billion | $1\ \mathrm{ppb} = 10^{-9}$ |
| Part-per-trillion | $1\ \mathrm{ppt} = 10^{-12}$ |
| pi | $\pi = 3.141592653589793$ |
| The base of the natural logarithm (Euler's number) | $e = 2.718281828459045$ |

**Equations**

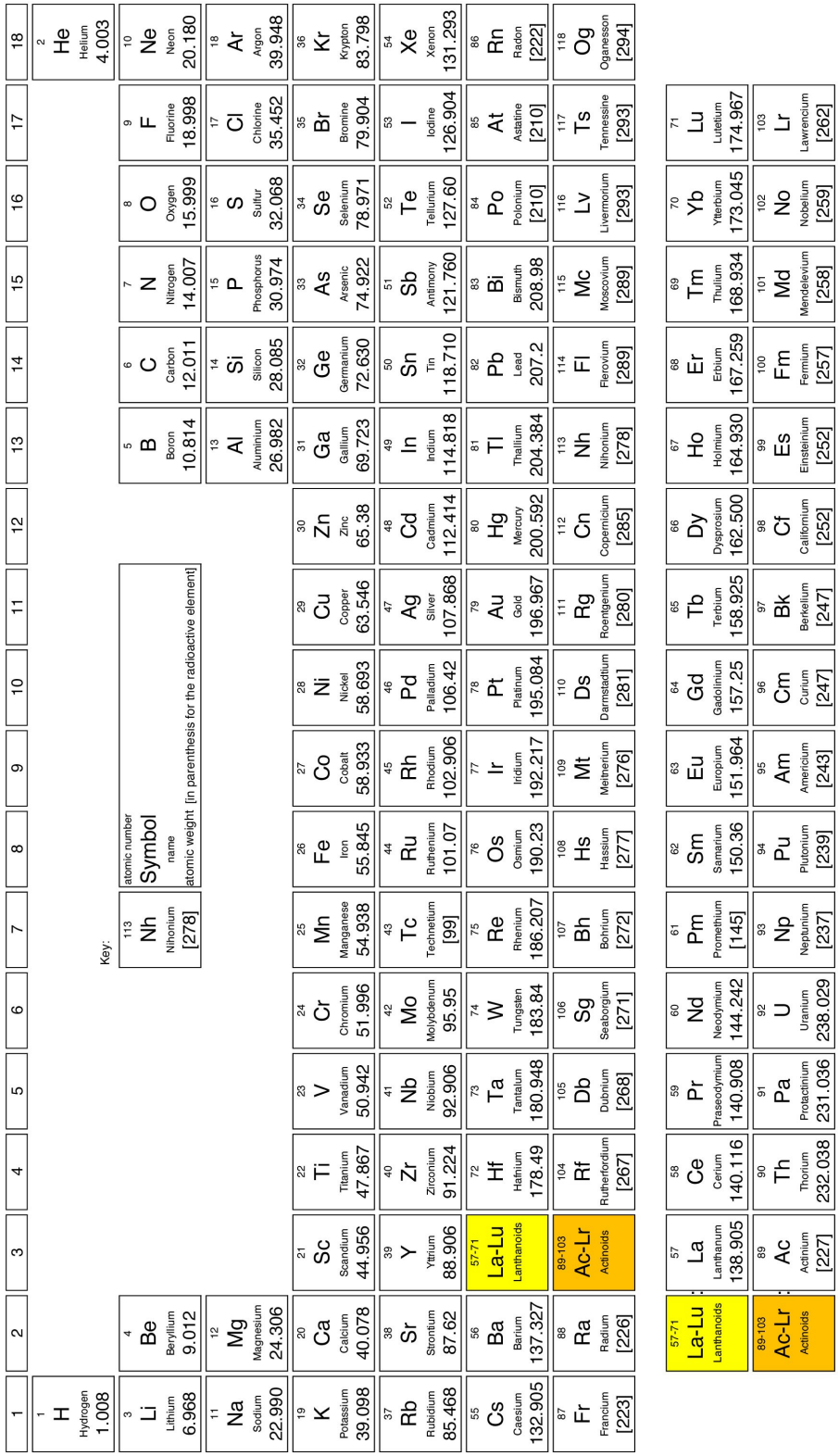
| | |
|---|---|
| The ideal gas law | $PV = nRT$<br>, where $P$ is the pressure, $V$ is the volume, $n$ is the amount of substance, $T$ is the absolute temperature of ideal gas. |
| Coulomb's law | $F = k_{\mathrm{e}} \dfrac{q_1 q_2}{r^2}$<br>, where $F$ is the electrostatic force, $k_{\mathrm{e}} (\simeq 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}})$ 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 | $\Delta U = q + w$<br>, where $\Delta U$ 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 $S$ | $S = k_{\mathrm{B}} \ln W$<br>, where $W$ is the number of microstates. |
| The change of entropy $\Delta S$ | $\Delta S = \dfrac{q_{\mathrm{rev}}}{T}$<br>, where $q_{\mathrm{rev}}$ is the heat for the reversible process. |
| Gibbs free energy $G$ | $G = H - TS$<br>$\Delta_{\mathrm{r}} G^\circ = -RT \ln K = -zFE^\circ$<br>, where $K$ is the equilibrium constant, $z$ is the number of electrons, $E^\circ$ is the standard electrode potential. |
| Reaction quotient $Q$ | $\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^\circ + RT \ln Q$<br>For a reaction<br>$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$<br>$Q = \dfrac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b}$<br>, where $[\mathrm{A}]$ is the concentration of A. |

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

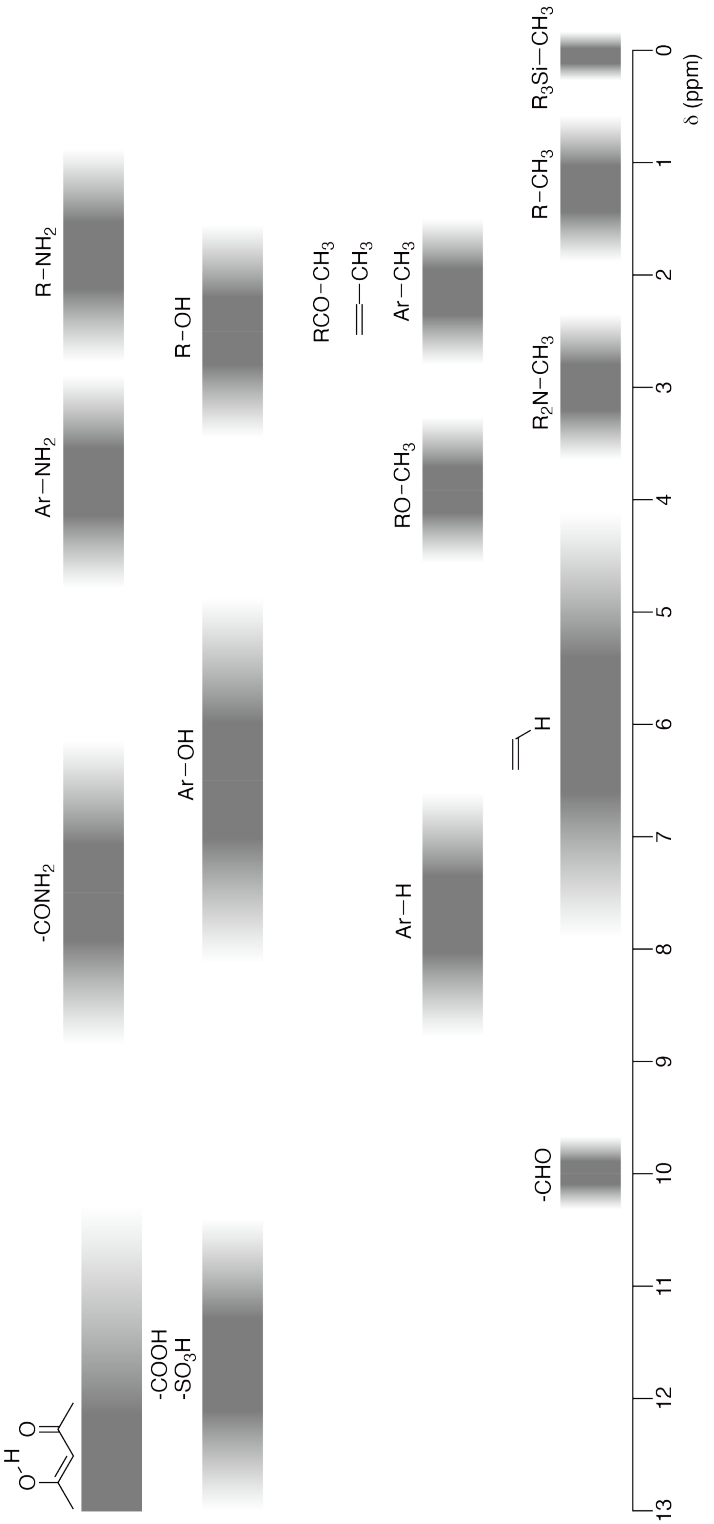
# G0-6

English (Official)

## Periodic Table



## $^1$H NMR Chemical Shifts




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

# G0-1

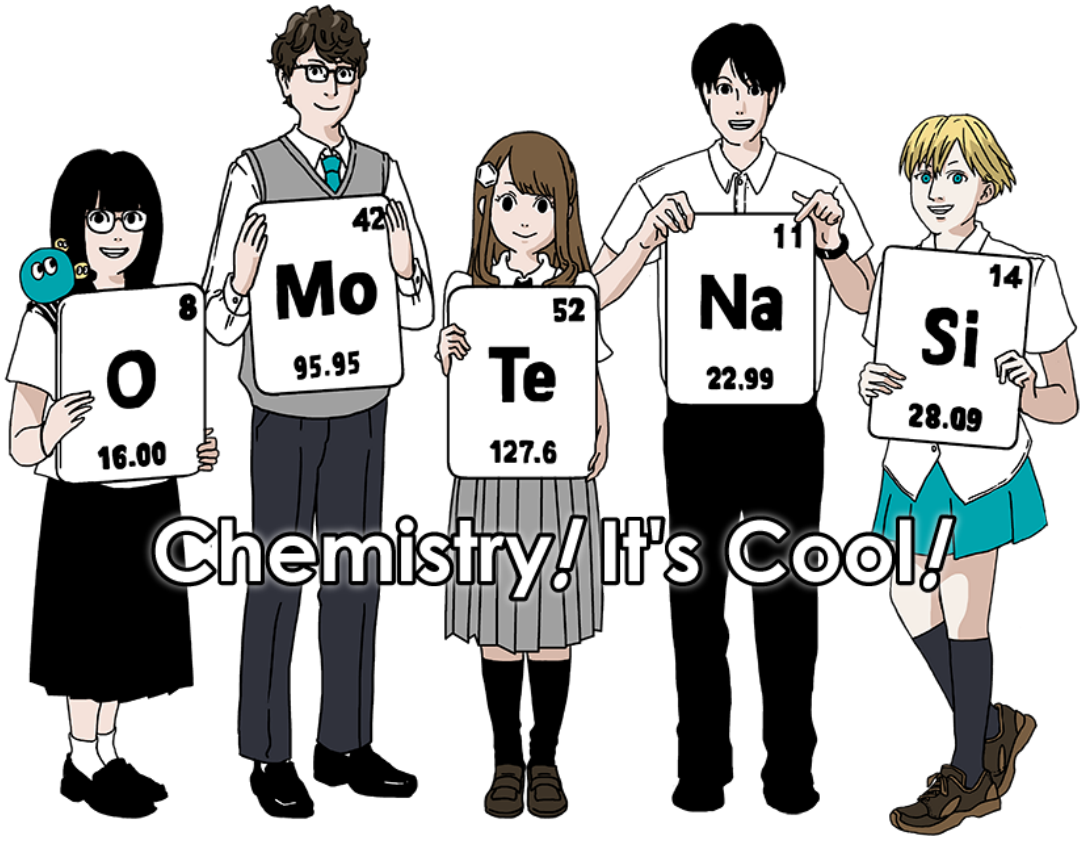
Norwegian (Norway)

**Internasjonale kjemiolympiaden 2021 Japan**

**53. IChO2021 Japan**

**25. juli – 2. august 2021**

**https://www.icho2021.org**



# G0-2

Norwegian (Norway)

## Generell informasjon

- Du har kun lov til å bruke kulepen for å skrive svarene.
- Kalkulatoren må være ikke programerbar.
- Oppgavesettet har **9 oppgaver**.
- Du kan løse oppgavene i hvilken som helst rekkefølge.
- Du har **5 timer** til å løse alle oppgavene.
- Du kan **begynne** å arbeide først etter at **START** beskjeden er gitt.
- Alle resultater må skrives i de til tilhørende svarboksene med kulepen på **svararket (answer sheets)**. Bruk baksiden av oppgavearkene hvis du trenger kladdepapir. Husk at svar skrevet utenfor boksene vil ikke bli rettet.
- Skriv relevante utregninger i de tilhørende boksene når det trengs. Full poeng for svaret gis kun når arbeidet er vist.
- Ispektøren (invigilator) vil si ifra når det er **30-minutter** igjen til **STOPP** signalet.
- Du **må stoppe** å arbeide når **STOPP** signalet er gitt. Mangel på å stoppe og skrive vil føre til kansellering av prøven..
- Den offisielle engelske versjonen er tilgjengelig på forespørsel kun for oppklaring.
- Du har ikke lov til å forlate plassen din uten tillatelse. Hvis du trenger assistanse (ødelagt kalkulator, toalettbesøk, etc) rekk opp hånda og vent til inspektøren kommer.

**LYKKE TIL!**

## Oppgave og rettingsinformasjon

| | Tittel | Total Score | Prosent |
|---|---|---|---|
| **1** | Hydrogen på en metalloverflate | **24** | **11** |
| **2** | En tidskapsel for isotoper | **35** | **11** |
| **3** | Lambert-Beers lov? | **22** | **8** |
| **4** | Redokskjemien til sink | **32** | **11** |
| **5** | Mystisk silisium | **60** | **12** |
| **6** | Kjemien til innskuddsmetallene i fast fase | **45** | **13** |
| **7** | Lek med ikke-benzenoid aromatisitet | **36** | **13** |
| **8** | Dynamiske organiske molekyler og deres kiralitet | **26** | **11** |
| **9** | Fordeler og ulemper med en kapsel | **23** | **10** |
| | | **Total** | **100** |

## Fysiske konstanter og ligninger

### Konstanter

| | |
|---|---|
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| pi | $\pi = 3.141592653589793$ |
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# G0-4

Norwegian (Norway)

**Ligninger**

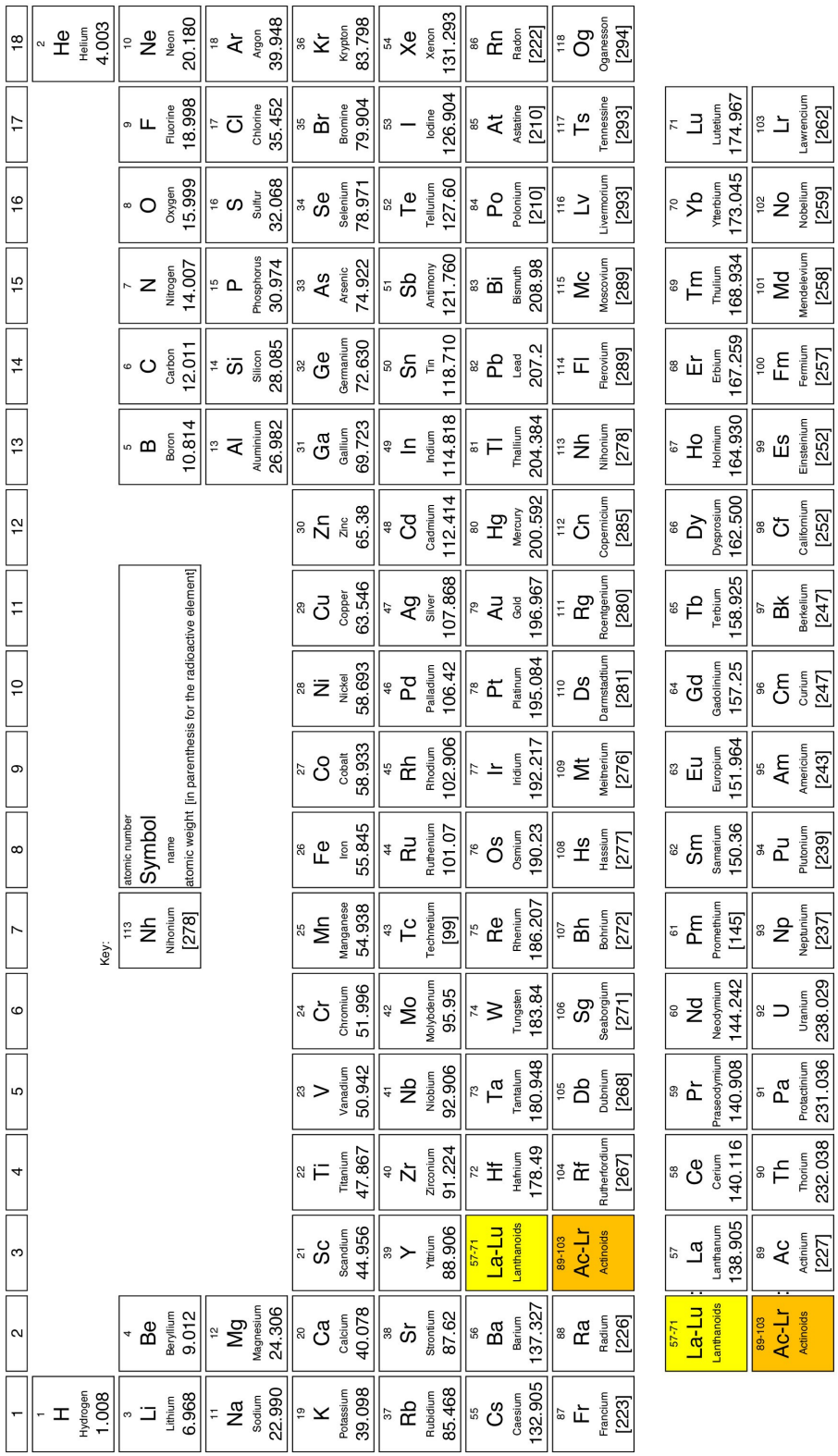
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| | |
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| Approximation equation that can be used to solve problems | When $x \ll 1$,<br>$\frac{1}{1-x} \simeq 1 + x$ |

# G0-6

Norwegian (Norway)

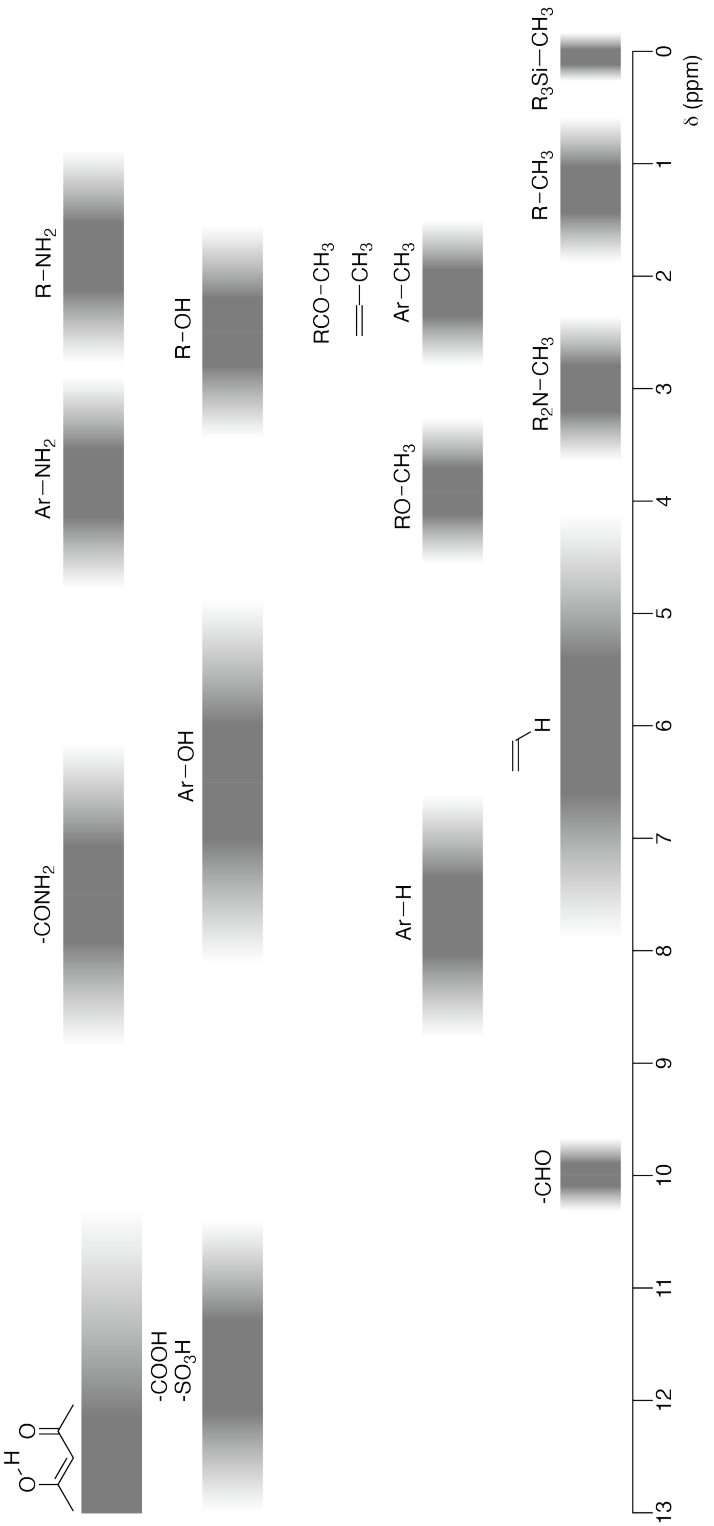
## Periodesystemet



# G0-7

Norwegian (Norway)

## $^1$H NMR kjemiske skift



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

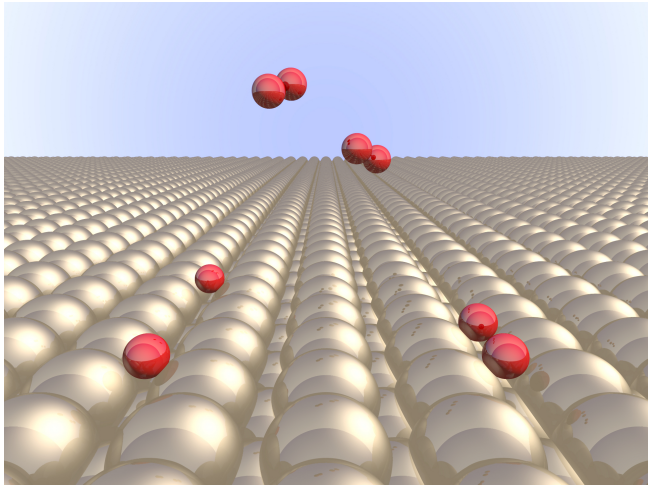
**NOR-1 C-1 C**
Abdur-Raheem Idowu

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

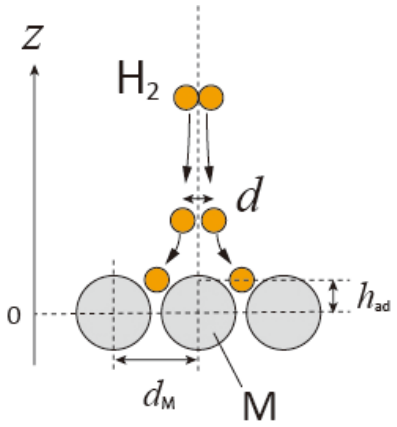



Fig.1 Definition of variables. Drawing is not in scale.

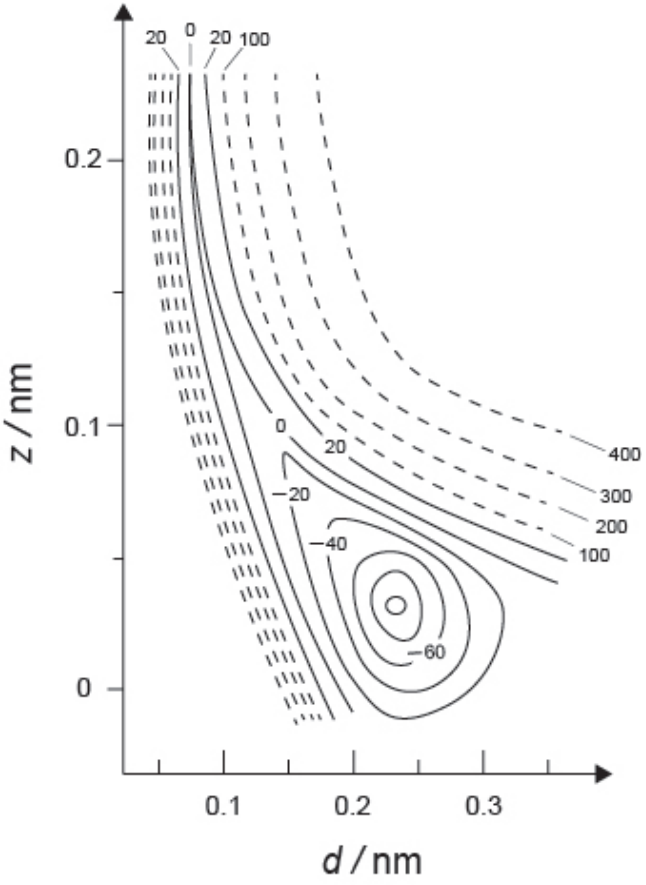



Fig.2

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

(i) The interatomic distance for a gaseous $H_2$ molecule
(ii) The interatomic distance between metal atoms ($d_M$ in Fig. 1)
(iii) The distance of adsorbed H atoms from the surface ($h_{ad}$ in Fig. 1)

| | | | |
|---|---|---|---|
| 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 $H_2$ to gaseous H [$H_2(g) \rightarrow 2H(g)$]
(ii) the energy released during the adsorption of a gaseous $H_2$ [$H_2(g) \rightarrow 2H(ad)$]

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

## Part B

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

$$\mathrm{H_2(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{2H(ad)} \tag{1a}$$

$$\mathrm{H(ad)} \xrightarrow{k_3} \mathrm{H(ab)} \tag{1b}$$

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

$$r_1 = k_1 P_{\mathrm{H_2}} (1-\theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

where $k_1\,[\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}], k_2\,[\mathrm{s}^{-1}]$ and $k_3\,[\mathrm{s}^{-1}]$ are the reaction rate constants and $P_{\mathrm{H_2}}$ is the pressure of $\mathrm{H_2}$. Among the sites available on the surface, $\theta$ ($0 \leq \theta \leq 1$) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption ($r_1, r_2 \gg r_3$) and that $\theta$ remains constant.

**B.1** $r_3$ can be expressed as: 5pt

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{1}{P_{\mathrm{H_2}} C}}} \tag{5}$$

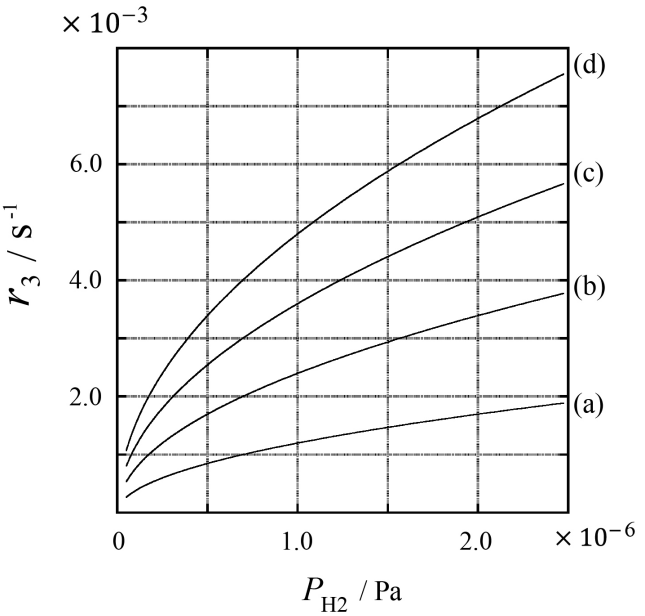
**Express** $C$ using $k_1$ and $k_2$.

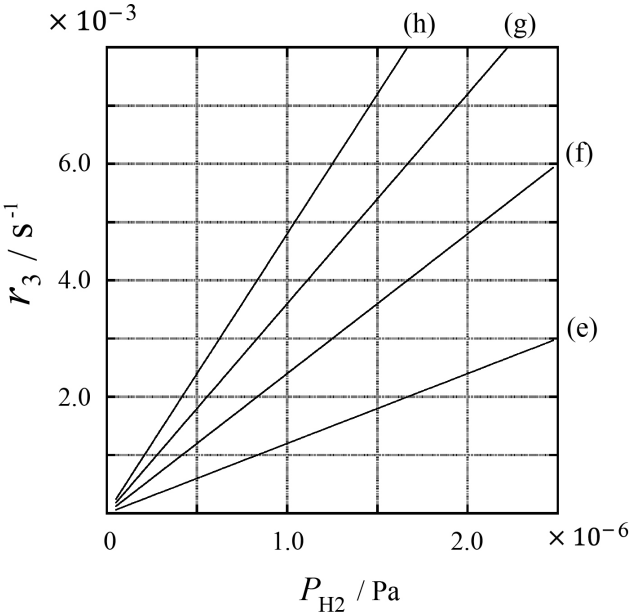
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m$^2$ was placed in a container (1L = $1.0 \times 10^{-3}$ m$^3$) with $H_2$ ($P_{H_2} = 1.0 \times 10^2$ Pa ). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m$^{-2}$. The surface temperature was kept at $T = 400$ K. As the reaction (1) proceeded, $P_{H_2}$ decreased at a constant rate of $v = 4.0 \times 10^{-4}$ 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, $A$ [mol s$^{-1}$ m$^{-2}$]. 3pt

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

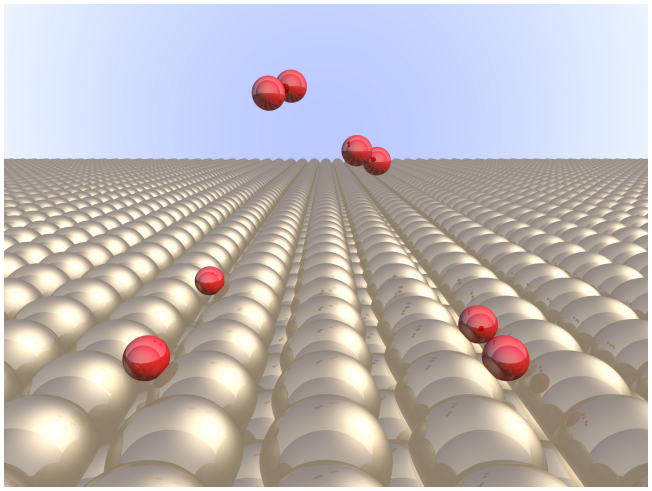
**B.4** At a different $T$, $C = 2.5 \times 10^3$ Pa$^{-1}$ and $k_3 = 4.8 \times 10^{-2}$ s$^{-1}$ are given. For $r_3$ as a function of $P_{H_2}$ at this temperature, **select** the correct plot from (a)–(h). 3pt



# Hydrogen på en metalloverflate

| 11 % av totalen | | | | | | | |
|---|---|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | B.1 | B.2 | B.3 | B.4 | **Total** |
| Poeng | 6 | 4 | 5 | 3 | 3 | 3 | **24** |
| Score | | | | | | | |



Man forventer at hydrogen i fremtiden kommer til å bli en energikilde som ikke er avhengig av fossilt brensel. I denne oppgaven skal vi se på prosessen hvor hydrogen lagres i et metall. Denne prosessen er knyttet til hydrogentransport og -lagringsteknologi.

## Del A

Når hydrogen blir absorbert til det indre av et metall via overflaten, kan vi begynne med å se på adsorpsjonen på overflaten $H_2(g) \rightarrow 2H(ad)$ hvor gassfasen og den adsorberte fasen er representert med (g) og (ad). Hydrogenmolekyler ($H_2$) som kommer i kontakt med metalloverflaten (M) dissosierer på overflaten og blir adsorbert som H-atomer (Fig. 1). I figuren er den potensielle energien til $H_2$ representert ved to variabler: avstanden mellom atomene, $d$, og høyden relativt til metallatomet på overflaten, $z$. Vi antar at aksen langs de to H-atomene er parallell med overflaten og at massesenteret alltid er på den vertikale stiplete linjen i Fig. 1. Fig. 2 viser konturplottet for den potensielle energien for dissosiering på overflaten. Tallverdien er den potensielle energien i kJ per mol $H_2$. Mellom to heltrukne linjer er forskjellen 20 kJ mol$^{-1}$, mellom to stiplete linjer er forskjellen 100 kJ mol$^{-1}$, og mellom en heltrukken og en stiplet linje er forskjellen 80 kJ mol$^{-1}$. Vibrasjonsenergien i null-tilstanden ser vi bort fra.

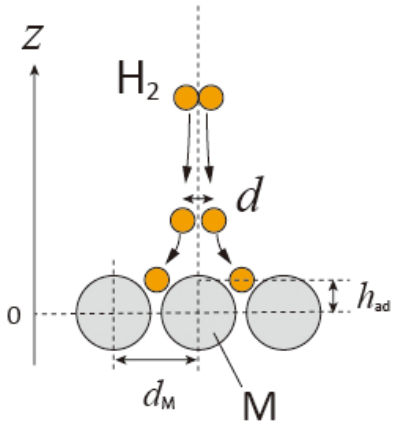



Fig. 1. Definisjon av variabler. Størrelsesforholdene er ikke riktige på tegningen.

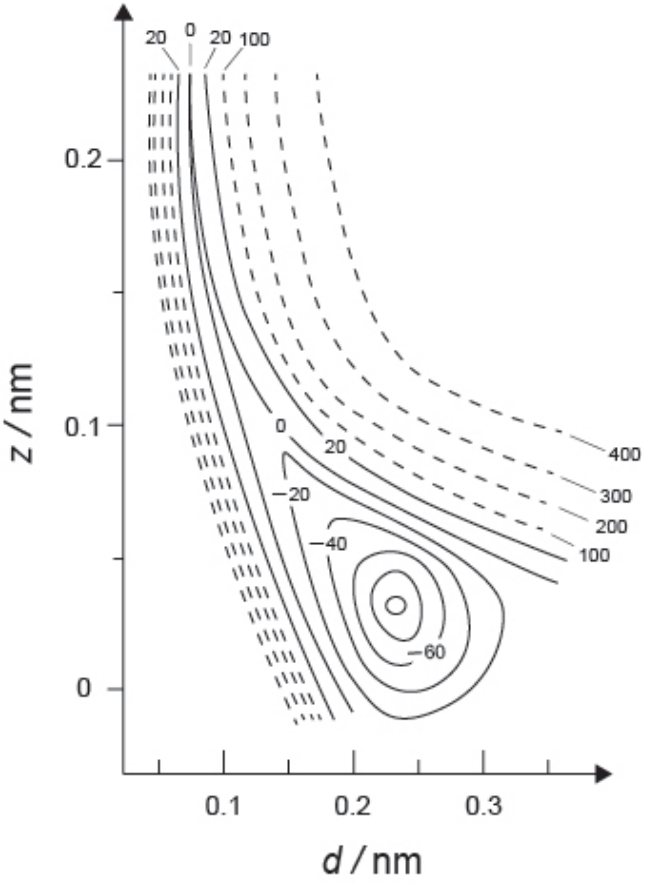



Fig.2

**A.1** For hvert av punktene (i)-(iii) **velg** den nærmeste verdien fra listen A-G. 6pt

(i) Avstanden mellom atomene i et $H_2$-molekyl i gassfase.
(ii) Avstanden mellom metallatomene ($d_M$ i Fig. 1).
(iii) Avstanden fra et adsorbert H-atom til overflaten ($h_{ad}$ i 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 hvert av punktene (i)-(ii), **velg** den nærmeste verdien fra listen A-H. 4pt

(i) Energien som er nødvendig for å dissosiere $H_2$ i gassfase til H i gassfase.
$H_2(g) \rightarrow 2H(g)$
(ii) Energien som blir frigjort når $H_2$ i gassfase blir adsorbert.
$H_2(g) \rightarrow 2H(ad)$

| | | | |
|---|---|---|---|
| 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$^{-1}$ |

## Del B

De adsorberte hydrogenatomene blir deretter enten absorbert inn i kjernen av metallet, eller slår seg sammen igjen og desorberer tilbake i gassfase, slik det vises i reaksjon (1a) og (1b). H(ab) betegner et hydrogenatom som er absorbert inn i kjernen av metallet.

$$\mathrm{H_2(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{H(ad)} \tag{1a}$$

$$\mathrm{H(ad)} \xrightarrow{k_3} \mathrm{H(ab)} \tag{1b}$$

Reaksjonshastigheten for hver plass på overflaten for adsorpsjon, desorpsjon og absorpsjon er $r_1[\mathrm{s}^{-1}], r_2[\mathrm{s}^{-1}]$ og $r_3[\mathrm{s}^{-1}]$, respektivt. De kan uttrykkes på følgende måte:

$$r_1 = k_1 P_{\mathrm{H_2}} (1-\theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

hvor $k_1$ [$\mathrm{s}^{-1}$ $\mathrm{Pa}^{-1}$], $k_2$ [$\mathrm{s}^{-1}$], og $k_3$ [$\mathrm{s}^{-1}$] er hastighetskonstantene og $P_{\mathrm{H_2}}$ er trykket av $\mathrm{H_2}$. $0 \leq \theta \leq 1$ er den andelen av tilgjengelige plasser på overflaten som er okkupert av et H-atom. Vi antar at adsorpsjonen og desorpsjonen er mye raskere enn absorpsjonen ($r_1, r_2 \gg r_3$) og at $\theta$ forblir konstant.

**B.1** $r_3$ kan uttrykkes som: 5pt

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{1}{P_{\mathrm{H_2}} C}}} \tag{5}$$

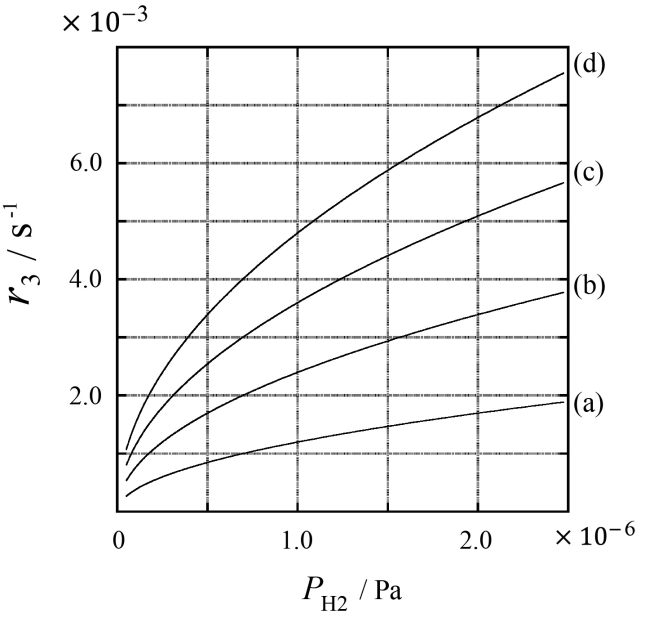
**Uttrykk** $C$ ved hjelp av $k_1$ og $k_2$.

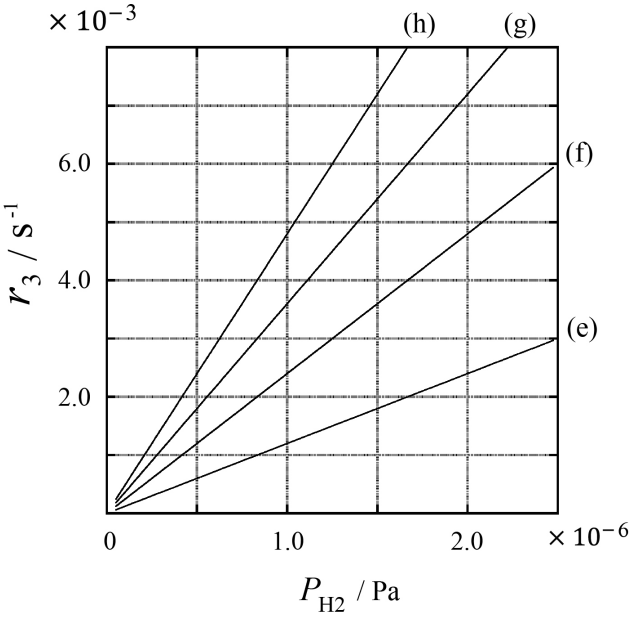
En metallbit med overflateareal $S = 1.0 \times 10^{-3}$ m$^2$ ble plassert i en beholder (1 L = $1.0 \times 10^{-3}$ m$^3$) med $H_2$ ($P_{H_2} = 1.0 \times 10^2$ Pa). Tettheten av plasser på overflaten hvor hydrogenatomer kan adsorberes var $N = 1.3 \times 10^{18}$ m$^{-2}$. Overflatetemperaturen ble holdt ved $T = 400$ K. Etter hvert som reaksjon (1) skjer, sank $P_{H_2}$ med en konstant fart $v = 4.0 \times 10^{-4}$ Pa s$^{-1}$. Anta at $H_2$ er en ideell gass og at vi kan se bort fra volumet av metallbiten.

**B.2** **Beregn** mengden H-atomer i mol som blir absorbert per arealenhet av overflaten per tidsenhet $A$ [mol s$^{-1}$ m$^{-2}$]. 3pt

**B.3** Ved $T = 400$ K, er $C$ lik $1.0 \times 10^2$ Pa$^{-1}$. **Beregn** verdien av $k_3$ ved 400 K. Hvis du ikke fant svaret i **B.2**, kan du bruke $A = 3.6 \times 10^{-7}$ mol s$^{-1}$ m$^{-2}$. 3pt

**B.4** Ved en annen temperatur $T$, er $C = 2.5 \times 10^3$ Pa$^{-1}$ og $k_3 = 4.8 \times 10^{-2}$ s$^{-1}$. **Velg** den grafen blant (a)-(h) som viser $r_3$ som en funksjon av $P_{H_2}$ ved denne temperaturen. 3pt



# Hydrogen at a Metal Surface

## Part A

**A.1** (6 pt)

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

**A.2** (4 pt)

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

## Part B

**B.1** (5 pt)

$C =$ _____

**B.2** (3 pt)

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

**B.3** (3 pt)

$k_3 =$ _____ $s^{-1}$

**B.4** (3 pt)

_____

NOR-1 C-2 C-1

**NOR-1 C-2 C**
Abdur-Raheem Idowu

# 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:

$$^{12}C^{16}O_2 + {}^{12}C^{18}O_2 \rightleftharpoons 2\,{}^{12}C^{16}O^{18}O \qquad K = \frac{[{}^{12}C^{16}O^{18}O]^2}{[{}^{12}C^{16}O_2][{}^{12}C^{18}O_2]} \tag{1}$$

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

$$S = k_B \ln W \tag{2}$$

$W = 1$ for $^{12}C^{16}O_2$ and $^{12}C^{18}O_2$. In contrast, $W = 2$ for a $^{12}C^{16}O^{18}O$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}C^{16}O^{18}O$ molecules, $W = 2^2 = 4$.

**A.1** The enthalpy change, $\Delta H$, of eq. 3 is positive regardless of the temperature. 8pt

$$H_2 + DI \rightleftharpoons HD + HI \quad (3)$$

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

The Δ*H* of the following process can be explained by molecular vibrations.

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

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

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

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

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

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

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

$$2HD \to H_2 + D_2 \quad (8)$$

Assume that:
- only the vibrational energy contributes to the $\Delta H$.
- the $k$ values for $H_2$, HD, and $D_2$ are identical.
- the mass of H to be 1 Da and the mass of D to be 2 Da.

The molar ratio of $H_2$, HD, and $D_2$ depends on the temperature in a system in equilibrium. Here, $\Delta_{D_2}$ is defined as the change of the molar ratio of $D_2$.

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 \tag{9}$$

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

**A.3** **Calculate** $\Delta_{D_2}$ with natural D abundance when the isotopic exchange is in equilibrium at the temperature where $K$ in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are $1.5576 \times 10^{-4}$ and $1 - 1.5576 \times 10^{-4}$, respectively. 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 $CO_2$ molecules with molecular weights of 44 and 47, which are described as $CO_2[44]$ and $CO_2[47]$ below. The quantity $\Delta_{47}$ is defined as:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \tag{10}$$

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

| | $^{12}C$ | $^{13}C$ |
|---|---|---|
| natural abundance | 0.988888 | 0.011112 |

| | $^{16}O$ | $^{17}O$ | $^{18}O$ |
|---|---|---|---|
| natural abundance | 0.997621 | 0.0003790 | 0.0020000 |

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

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

**A.4** The $R_{47}$ of fossil plankton obtained from the Antarctic seabed was $4.50865 \times 10^{-5}$. **Estimate** the temperature using this $R_{47}$. This temperature is interpreted as the air temperature during the era in which the plankton lived. Consider only the most common isotopologue of $CO_2[47]$ for the calculation. 9pt

# En tidskapsel for isotoper

| 11 % av totalen | | | | | |
|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | A.3 | A.4 | **Total** |
| Poeng | 8 | 8 | 10 | 9 | **35** |
| Score | | | | | |



Molekyler som bare skiller seg fra hverandre ved sammensetningen av isotoper, sånn som $CH_4$ og $CH_3D$, kalles isotopologer. Isotopologer antas i utgangspunktet å ha de samme kjemiske egenskapene. I virkeligheten er det likevel små forskjeller.

Anta at alle stoffene i denne oppgaven er i gassfase.

La oss betrakte følgende likevekt:

$$^{12}C^{16}O_2 + {}^{12}C^{18}O_2 \rightleftharpoons 2\,{}^{12}C^{16}O^{18}O \qquad K = \frac{[{}^{12}C^{16}O^{18}O]^2}{[{}^{12}C^{16}O_2][{}^{12}C^{18}O_2]} \tag{1}$$

Entropien, $S$, øker når antall mikroskopiske tilstander i systemet, $W$, øker:

$$S = k_B \ln W \tag{2}$$

$W = 1$ for $^{12}C^{16}O_2$ og $^{12}C^{18}O_2$. Men $W = 2$ for et molekyl av typen $^{12}C^{16}O^{18}O$ fordi det nå er mulig å skille de to oksygenatomene i molekylet. Fordi høyresiden i likevekten vist i ligning (1) har to $^{12}C^{16}O^{18}O$-molekyler, er $W = 2^2 = 4$.

**A.1** Entalpiendringen, $\Delta H$, for ligning 3 er positiv ved alle temperaturer. 8pt

$$H_2 + DI \rightleftharpoons HD + HI \quad (3)$$

**Beregn** likevektskonstanten, $K$, for ligning 3 ved veldig lav (altså $T \to 0$) og veldig høy (altså $T \to +\infty$) temperatur. Anta at reaksjonen fortsetter å skje på samme måte ved disse temperaturene og at $\Delta H$ konvergerer til en konstant verdi ved høye temperaturer.

Δ*H* for den følgende prosessen kan forklares ved hjelp av molekylære vibrasjoner.

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

Ved $T$ = 0 K, kan den vibrasjonelle energien til et diatomært molekyl med vibrasjonsfrekvens $\nu$ [$s^{-1}$] uttrykkes som:

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

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

Hvor $k$ er kraftkonstanten og $\mu$ er den reduserte massen, som kan uttrykkes ved hjelp av massen til de to atomene i det diatomære molekylet $m_1$, og $m_2$, på følgende måte:

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

**A.2** Vibrasjonen til $H_2$ er ved 4161,0 $cm^{-1}$ når den blir oppgitt som bølgetall. **Beregn** $\Delta H$ for den følgende ligningen ved $T$ = 0 K i J $mol^{-1}$. 8pt

$$2HD \to H_2 + D_2 \quad (8)$$

Anta at:

- bare vibrasjonsenergi bidrar til $\Delta H$.
- verdien for $k$ for $H_2$, HD, og $D_2$ er identiske.
- massen til H er 1 Da og massen til D er 2 Da.

Molforholdet mellom $H_2$, HD, og $D_2$ er avhengig av temperaturen i systemet ved likevekt. Vi definerer $\Delta_{D_2}$ som endringen av molforholdet for $D_2$.

$$\Delta_{D_2} = \frac{R_{D_2}}{R^*_{D_2}} - 1 \tag{9}$$

Her lar vi $R_{D_2}$ være $\frac{[D_2]}{[H_2]}$ i prøven og $R^*_{D_2}$ være $\frac{[D_2]}{[H_2]}$ når $T \to +\infty$. Vær klar over at distribusjonen av isotoper blir vilkårlig ved $T \to +\infty$.

| | | |
|---|---|---|
| **A.3** | **Beregn** $\Delta_{D_2}$ med en naturlig forekomst av D når utbyttingen av isotoper er ved likevekt ved den temperaturen som gjør at $K$ i ligning 4 er 0,300. Anta at den naturlige forekomsten av D og H er $1.5576 \times 10^{-4}$ og $1 - 1.5576 \times 10^{-4}$, respektivt. | 10pt |

Generelt øker molforholdet av den dobbelt substituerte isotopologen som har to atomer av den tunge isotopen, ved lavere temperaturer. Vi ser på molforholdet for $CO_2$-molekyler med molekylmasse 44 og 47, som vi betegner $CO_2[44]$ og $CO_2[47]$ nedenfor. Størrelsen $\Delta_{47}$ er definert på følgende måte:

$$\Delta_{47} = \frac{R_{47}}{R_{47}^*} - 1 \tag{10}$$

$R_{47}$ er $\frac{[CO_2[47]]}{[CO_2[44]]}$ i prøven og $R_{47}^*$ er $\frac{[CO_2[47]]}{[CO_2[44]]}$ når $T \to +\infty$. Den naturlige forekomsten av karbon og oksygen er vist nedenfor. Se bort fra isotoper som ikke er i tabellen.

| | $^{12}C$ | $^{13}C$ |
|---|---|---|
| Naturlig forekomst | 0,988888 | 0,011112 |

| | $^{16}O$ | $^{17}O$ | $^{18}O$ |
|---|---|---|---|
| Naturlig forekomst | 0,997621 | 0,0003790 | 0,0020000 |

$\Delta_{47}$ er avhengig av temperaturen på følgende måte, hvor $T$ er den absolutte temperaturen oppgitt i K:

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

**A.4** $R_{47}$ for et fossilt plankton som ble funnet på havbunnen ved Sydpolen, ble målt til $4.50865 \times 10^{-5}$. **Estimer** temperaturen ved å bruke denne verdien for . Denne temperaturen kan tolkes som lufttemperaturen ved det tidspunktet planktonet var levende. I beregningen skal du bare ta hensyn til den mest vanlige isotopologen av $CO_2[47]$. 9pt

# Isotope Time Capsule

**A.1** (8 pt)

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

**A.2** (8 pt)

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

**A.3** (10 pt)

$\Delta_{D_2}$ = _____

**A.4** (9 pt)

$T =$ _____ K

NOR-1 C-3 C-1

**NOR-1 C-3 C**
Abdur-Raheem Idowu

# 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 $1.00 \times 10^{-2}$ mol $L^{-1}$, $1.00 \times 10^{-3}$ mol $L^{-1}$, and $1.00 \times 10^{-4}$ mol $L^{-1}$, respectively, which are correlated via the following acid-base equilibrium:

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

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

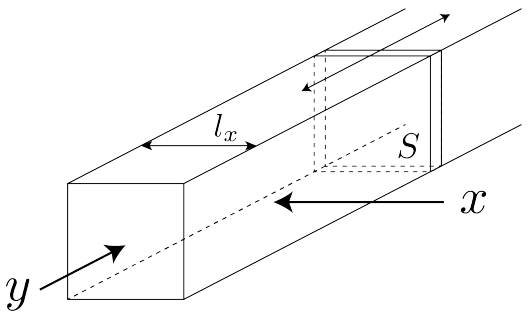
**A.1** The absorbance of **X** was $A_1$ at a wavelength of $\lambda_1$. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still $A_1$ at $\lambda_1$. **Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where $\varepsilon_{HA}$ and $\varepsilon_{A^-}$ represent the absorption coefficients of HA and of $A^-$, respectively, at $\lambda_1$. 10pt

## Part B

Let us consider the following equilibrium in the gas phase.

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \tag{2}$$

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




Use the following definitions if necessary.

| | Initial state | | After equilibrium | |
|---|---|---|---|---|
| | D | M | D | M |
| Partial pressure | $P$ | $0$ | $p_{\mathrm{D}}$ | $p_{\mathrm{M}}$ |
| Amount in moles | $n_0$ | $0$ | $n_{\mathrm{D}}$ | $n_{\mathrm{M}}$ |
| Volume | $V_0$ | | $V$ | |

**B.1** The absorbance of the gas at $\lambda_{\mathrm{B1}}$ measured from direction $x$ ($l = l_x$) was $A_{\mathrm{B1}}$ both at the initial state and after the equilibrium. **Determine** the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at $\lambda_{\mathrm{B1}}$, where $\varepsilon_{\mathrm{D}}$ and $\varepsilon_{\mathrm{M}}$ represent the absorption coefficients of D and of M, respectively. 6pt

**B.2** The absorbance of the gas at $\lambda_{\mathrm{B2}}$ measured from direction $y$ was $A_{\mathrm{B2}}$ both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). **Determine** the ratio $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ at $\lambda_{\mathrm{B2}}$. 6pt

# Lambert-Beers lov?

| 8 % av totalen | | | | |
|---|---|---|---|---|
| Oppgave | A.1 | B.1 | B.2 | **Total** |
| Poeng | 10 | 6 | 6 | **22** |
| Score | | | | |

I denne oppgaven kan du se bort fra absorpsjon i cellen og løsemiddelet. Temperaturen til alle løsninger og gasser holdes konstant lik 25 °C.

## Del A

En vandig løsning **X** ble laget av HA og NaA. Konsentrasjonen av $[A^-]$, $[HA]$, og $[H^+]$ i løsning **X** er $1.00 \times 10^{-2}$ mol $L^{-1}$, $1.00 \times 10^{-3}$ mol $L^{-1}$, og $1.00 \times 10^{-4}$ mol $L^{-1}$, respektivt. Stoffene deltar i følgende syre-base-likevekt:

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

Den optiske veilengden er $l$ i del A. Se bort fra endringer i tetthet ved fortynning. Anta at det ikke skjer andre kjemiske reaksjoner enn den i ligning 1.

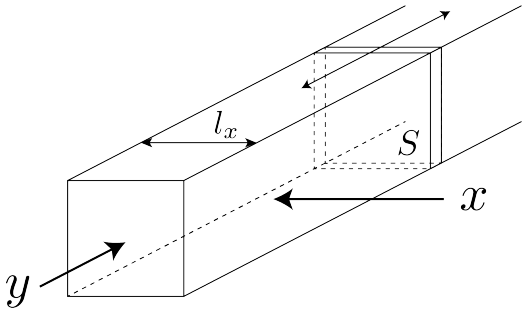
**A.1** Absorbansen til **X** var $A_1$ ved bølgelengde $\lambda_1$. Så blir løsningen **X** fortynnet til dobbelt så stort volum ved hjelp av saltsyre med pH = 2,500. Etter fortynningen var absorbansen fortsatt $A_1$ ved $\lambda_1$. **Bestem** forholdet $\varepsilon_{HA}/\varepsilon_{A^-}$, hvor $\varepsilon_{HA}$ og $\varepsilon_{A^-}$ representerer absorpsjonskoeffisienten til henholdsvis HA og $A^-$, ved $\lambda_1$. 10pt

## Del B

La oss betrakte følgende likevekt i gassfase.

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \tag{2}$$

Ren gass D blir fylt i en beholder som er et rektangulært prisme, og som har en bevegelig vegg med overflate $S$ (se figuren nedenfor). Trykket er $P$, og likevekten innstiller seg mens totaltrykket hele tiden holdes ved $P$. Absorbansen til gassen er $A = \varepsilon(n/V)l$, hvor $\varepsilon$, $n$, $V$, og $l$ er henholdsvis absorpsjonskoeffisienten, stoffmengden gass i mol, volumet av gassen og den optiske veilengden. Anta at alle stoffene i gassblandingen oppfører seg som ideelle gasser.




Bruk følgende definisjoner om nødvendig.

| | Ved start | | Ved likevekt | |
|---|---|---|---|---|
| | D | M | D | M |
| Partielt trykk | $P$ | $0$ | $p_{\mathrm{D}}$ | $p_{\mathrm{M}}$ |
| Stoffmengde i mol | $n_0$ | $0$ | $n_{\mathrm{D}}$ | $n_{\mathrm{M}}$ |
| Volum | $V_0$ | | $V$ | |

**B.1** Absorbansen til gassen ved $\lambda_{\mathrm{B1}}$ målt i retning $x$ ($l = l_x$) var $A_{\mathrm{B1}}$ både ved start og ved likevekt. **Bestem** forholdet $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ ved $\lambda_{\mathrm{B1}}$, hvor $\varepsilon_{\mathrm{D}}$ og $\varepsilon_{\mathrm{M}}$ absorpsjonskoeffisienten til henholdsvis D og M. 6pt

**B.2** Absorbansen til gassen ved $\lambda_{\mathrm{B2}}$ målt i retning $y$ var $A_{\mathrm{B2}}$ både ved start ($l = l_{y0}$) og ved likevekt ($l = l_y$). **Bestem** forholdet $\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{M}}$ ved $\lambda_{\mathrm{B2}}$. 6pt

# Lambert–Beer Law?

## Part A

**A.1** (10 pt)

(Continued on the next page)

**A.1 (cont.)**

$\varepsilon_{HA}/\varepsilon_{A^-}$ = _____

## Part B

**B.1** (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

**B.2** (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

**NOR-1 C-4 C**
Abdur-Raheem Idowu

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

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

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

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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14} \tag{4}$$

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

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

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

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

## Part B

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

$$\mathrm{Zn(OH)_2(s)} \rightarrow \mathrm{ZnO(s)} + \mathrm{H_2O(l)} \tag{6}$$

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

$$\mathrm{ZnO(s)} + \mathrm{H_2(g)} \rightarrow \mathrm{Zn(s)} + \mathrm{H_2O(g)} \tag{7}$$

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

$$\mathrm{Zn(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{ZnO(s)} \qquad E^\circ = 1.65\,\mathrm{V} \tag{8}$$

**B.2** A zinc–air battery was discharged at 20 mA for 24 hours. **Calculate** the change in mass of the negative electrode (anode) of the battery. 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 $-38\,^{\circ}\mathrm{C}$ (February) and 3776 m, respectively. The atmospheric pressure is represented by 5pt

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

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

**B.4** **Calculate** the Gibbs energy change for reaction (6) at $25\,^{\circ}\mathrm{C}$. Note that the standard reduction potentials, $E^{\circ}(\mathrm{Zn/Zn^{2+}})$ and $E^{\circ}(\mathrm{O_2/H_2O})$ at $25\,^{\circ}\mathrm{C}$ and 1 bar are given as (10) and (11), respectively. 9pt

$$\mathrm{Zn^{2+} + 2e^- \rightarrow Zn} \qquad E^{\circ}(\mathrm{Zn^{2+}/Zn}) = -0.77\,\mathrm{V} \tag{10}$$

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \qquad E^{\circ}(\mathrm{O_2/H_2O}) = 1.23\,\mathrm{V} \tag{11}$$

# Redokskjemien til sink

| 11 % av totalen | | | | | | | |
|---|---|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | B.1 | B.2 | B.3 | B.4 | **Total** |
| Poeng | 6 | 5 | 4 | 3 | 5 | 9 | **32** |
| Score | | | | | | | |



Sink har lenge blitt brukt i legeringer av messing og stål. Sink i avfallsvannet fra industrien blir fjernet ved utfelling for å gjøre vannet ufarlig, og bunnfallet samles og og reduseres slik at man kan gjenbruke sinkmetallet.

## Del A

Likevekten for sinkhydroksid $Zn(OH)_2(s)$ ved 25 °C og de relevante likevektskonstantene er gitt i ligning 1-4.

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

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

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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14} \tag{4}$$

Løseligheten, $S$, til sink (konsentrasjonen av sink i en mettet vandig løsning) er gitt i ligning 5.

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

**A.1** Når alle likevektene i ligning 1-4 er innstilt, **beregn** det pH-intervallet hvor $[\mathrm{Zn(OH)_2(aq)}]$ er størst blant $[\mathrm{Zn^{2+}(aq)}]$, $[\mathrm{Zn(OH)_2(aq)}]$ og $[\mathrm{Zn(OH)_4^{2-}(aq)}]$. 6pt

**A.2** En mettet løsning av $\mathrm{Zn(OH)_2(s)}$ med pH = 7,00 ble laget og filtrert. NaOH ble tilsatt til filtratet slik at pH økte til 12,00. **Beregn** molprosenten av sink som ble felt ut når pH økte fra 7,00 til 12,00. Se bort fra endringer i volum og temperatur. 5pt

## Del B

Så blir sinkhydroksid som man har fått dannet, varmet opp slik at det dannes sinkoksid etter følgende ligning:

$$\mathrm{Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(l)} \tag{6}$$

Sinkoksid blir så redusert til metallisk sink i en reaksjon med hydrogen:

$$\mathrm{ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g)} \tag{7}$$

**B.1** For at reaksjon (7) skal fortsette mens hydrogentrykket holdes ved 1 bar, er det nødvendig å redusere partialtrykket av vanndampen som dannes. **Beregn** den øvre grensen for partialtrykket av vanndamp slik at reaksjon (7) fortsetter ved 300 °C. Gibbs dannelsesenergien til sinkoksid og vanndamp ved 300 °C og 1 bar for stoffene i gassfase er henholdsvis $\Delta G_{\mathrm{ZnO}}(300^{\circ}\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ og $\Delta G_{\mathrm{H_2O}}(300^{\circ}\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\,mol^{-1}}$. 4pt

Metallisk sink blir brukt som negativ elektrode (anode) i metall-luft-batterier. Elektroden består av Zn og ZnO. Den benytter følgende redoksreaksjon til å generere elektrisitet med en spenning, $E^{\circ}$, (elektromotorisk spenning, e.m.f.) ved 25 °C og 1 bar trykk.

$$\mathrm{Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)} \qquad E^{\circ} = 1.65\,\mathrm{V} \tag{8}$$

**B.2** Et sink-luft-batteri ble utladet med 20 mA i 24 timer. **Beregn** endringen i masse til den negative elektroden (anoden) i batteriet. 3pt



Mt. Fuji

**B.3** Vi skal se på hvordan spenningen til sink-luft-batteriet er avhengig av omgivelsene. **Beregn** spenningen (e.m.f.) på toppen av Fuji-fjellet hvor temperaturen er $-38\,^{\circ}\mathrm{C}$ (i februar) og høyden er 3776 m. Det atmosfæriske trykket er gitt ved 5pt

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

ved høyden $h\,[\mathrm{m}]$ og temperaturen $T\,[^{\circ}\mathrm{C}]$. Molprosenten av oksygen i atmosfæren er 21 %. Endringen i Gibbsenergien til reaksjon (8) er ved og 1 bar.

**B.4** **Beregn** endringen i Gibbsenergi for reaksjon (6) ved 25 °C. Standard reduksjonspotensial, $E^{\circ}(\mathrm{Zn/Zn^{2+}})$ og $E^{\circ}(\mathrm{O_2/H_2O})$ ved $25\,^{\circ}\mathrm{C}$ og 1 bar er gitt i (10) og (11). 9pt

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

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \qquad E^{\circ}(\mathrm{O_2/H_2O}) = 1.23\,\mathrm{V} \qquad (11)$$

# The Redox Chemistry of Zinc

## Part A

**A.1** (6 pt)

$<$ pH $<$ _____

**A.2** (5 pt)

_____ %

## Part B

**B.1** (4 pt)

$p_{H_2O=}$ _____ bar

**B.2** (3 pt)

_____ g

**B.3** (5 pt)

V

**B.4** (9 pt)

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

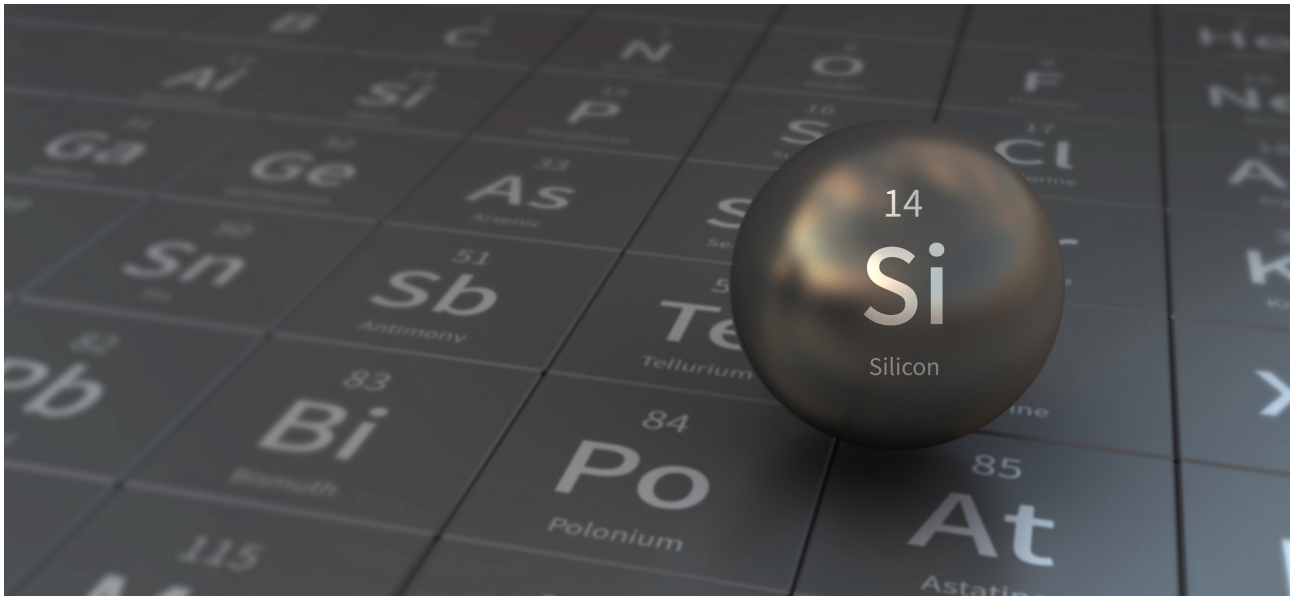
**NOR-1 C-5 C**
Abdur-Raheem Idowu

# IChO
# Problem 5
## Cover sheet

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

# Mysterious Silicon

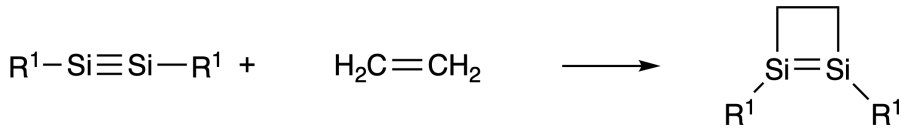
| 12 % of the total | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Question | A.1 | A.2 | A.3 | A.4 | B.1 | B.2 | B.3 | **Total** |
| Points | 9 | 7 | 6 | 10 | 5 | 15 | 8 | **60** |
| Score | | | | | | | | |



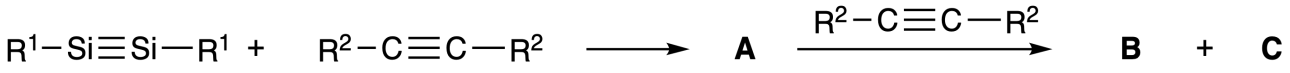

Although silicon is also a group 14 element like carbon, their properties differ significantly.

## Part A

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




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

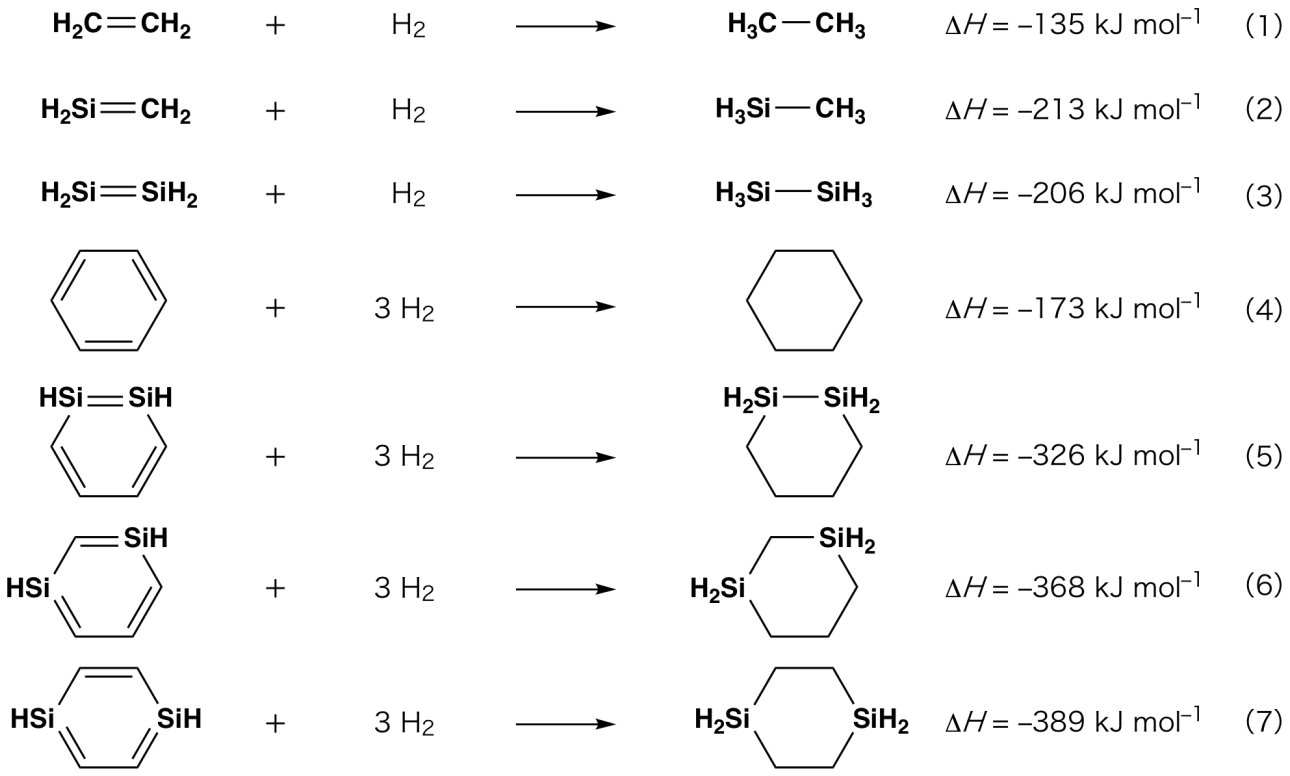



Fig. 1

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** $\Delta H$ for the transformation of **D** to **E**. Assume that $\Delta H$ does not depend on temperature. | 6pt |

The isomerization from **C** to **D** and to **E** proceeds via transformations of $\pi$-bonds into $\sigma$-bonds without breaking any $\sigma$-bonds. A $^{13}C$ NMR analysis revealed one signal for the $Si_2C_4$ 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 g mol$^{-1}$) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ (568.424 g mol$^{-1}$) dissolved in water (total volume: 200 mL).

· Procedure

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

| | | |
|---|---|---|
| **B.1** | **Write** the balanced equation for the reaction of $Na_2SiF_6$ with $Ce_2(SO_4)_3$. | 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:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \quad (8)$$

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 |

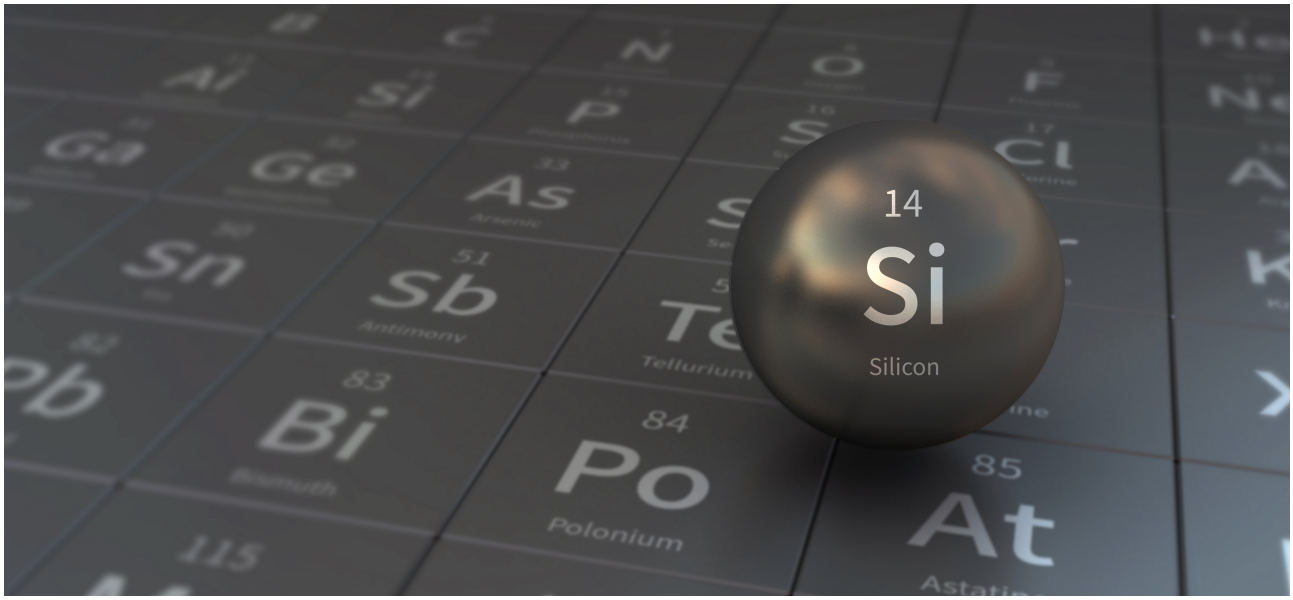
| | | |
|---|---|---|
| **B.3** | 77.8% of the $CCl_4$ used as a starting material was unreacted. **Calculate** the mass of $CF_3Cl$ generated. | 8pt |

# Q5-1

Norwegian (Norway)

## Mystisk silisium

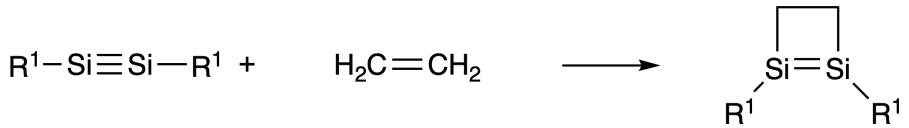
| 12 % av totalen | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | A.3 | A.4 | B.1 | B.2 | B.3 | **Total** |
| Poeng | 9 | 7 | 6 | 10 | 5 | 15 | 8 | **60** |
| Score | | | | | | | | |




Selv om silisium også er i gruppe 14 sammen med grunnstoffet karbon, er egenskapene svært forskjellige.

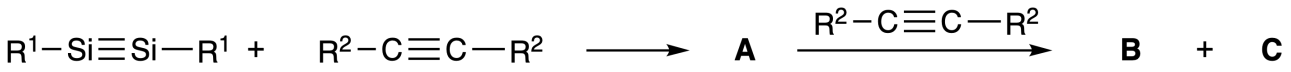
### Del A

Til forskjell fra en karbon-karbon trippelbinding, er silisium-silisium trippelbindingen, $R^1–Si \equiv Si–R^1$ (R: en organisk substituent) ekstremt reaktiv. For eksempel reagerer den med eten (etylen) og danner et syklisk produkt som inneholder er ring med fire atomer.




Når $R^1–Si \equiv Si–R^1$ reagerer med et alkyn ($R^2–C \equiv C–R^2$), dannes først en ring med fire atomer, forbindelse **A**, som et mellomprodukt. **A** reagerer videre med et nytt molekyl $R^2–C \equiv C–R^2$ og gir de to isomerene **B** og **C**; begge disse har en benzen-lignende syklisk, konjugert struktur, såkalt 'disilabenzen', som inneholder

en ring med seks atomer, og som kan skrives slik $(R^1\text{–}Si)_2(R^2\text{–}C)_4$.




$^{13}$C-NMR analyse for ringen med seks atomer, $Si_2C_4$, viser to signaler for forbindelse **B** og ett signal for **C**.

| | | |
|---|---|---|
| **A.1** | **Tegn** strukturformel for **A**, **B** og **C** ved å bruke $R^1$, $R^2$, Si, og C, for en av de mulige resonansstrukturene. | 9pt |

| | | |
|---|---|---|
| **A.2** | **Beregn** den aromatiske stabiliseringsenergien (ASE) for benzen og **C** (for tilfellet $R^1 = R^2 = H$) som positive verdier, når du tar hensyn til entalpiendringene i noen av hydrogeneringsreaksjonene for umettede systemer vist nedenfor (Fig. 1). | 7pt |

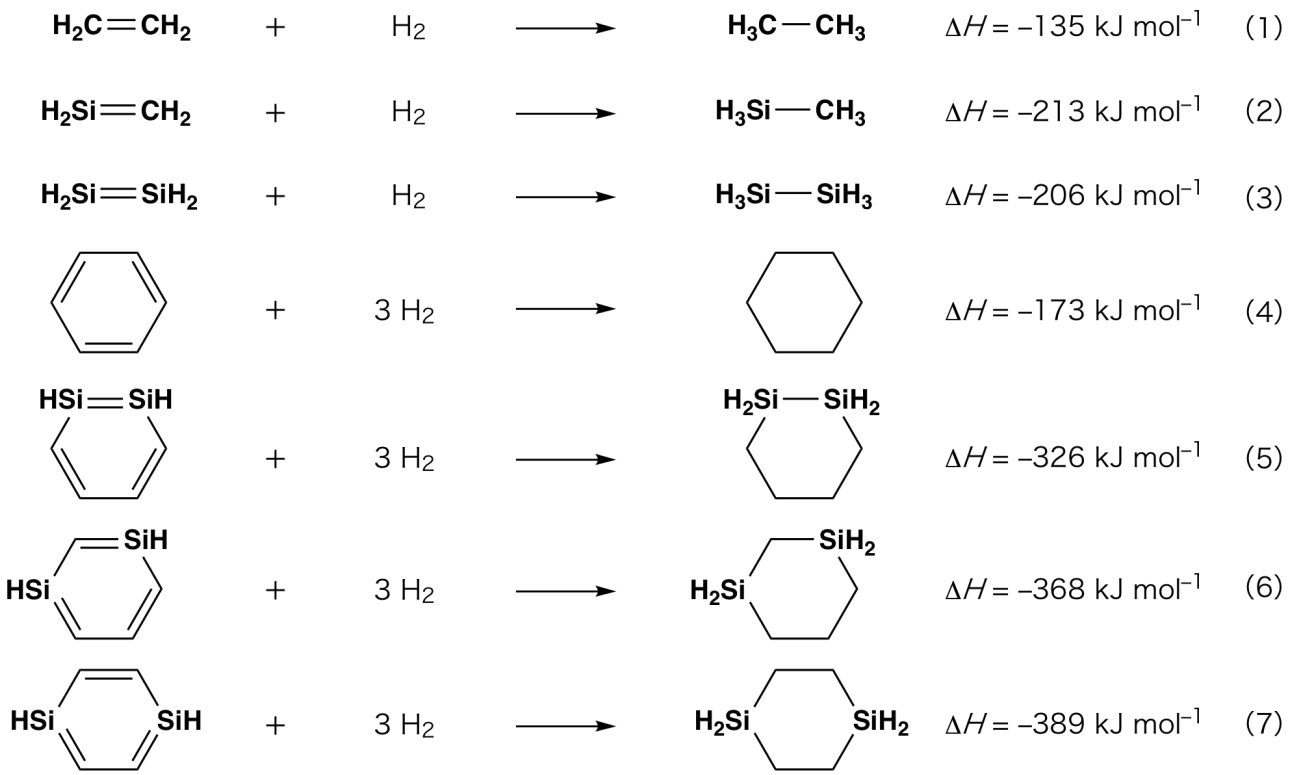



Fig. 1

Når en løsning av **C** i xylen varmes opp, skjer det en isomerisering som gir en likevekt av de to forbindelsene **D** og **E**. Molforholdet er **D** : **E** = 1 : 40,0 ved 50,0 ˚C og **D** : **E** = 1 : 20,0 ved 120,0 ˚C.

| | | |
|---|---|---|
| **A.3** | **Beregn** $\Delta H$ for omdannelsen fra **D** til **E**. Anta at $\Delta H$ ikke er avhengig av temperatur. | 6pt |

Isomeriseringen fra **C** til **D** og **E** går gjennom en transformering av $\pi$-bindinger til $\sigma$-bindinger uten å bryte noen $\sigma$-bindinger. $^{13}$C-NMR analyse viser ett signal for $Si_2C_4$-skjelettet til **D** og to signaler for **E**. Skjelettet til **D** inneholder ikke noen ringer med tre atomer, mens **E** inneholder to ringer med tre atomer, og ringene har en felles kant.

| | | |
|---|---|---|
| **A.4** | **Tegn** strukturformelen til **D** og **E** ved å bruke $R^1$, $R^2$, Si og C. | 10pt |

## Del B

Silisium kan danne forbindelser med høyt koordinasjonstall (> fire substituenter) med elektronegative grunnstoffer som fluor. Metallfluorider brukes ofte som reagens i fluoreringsreaksjoner. Silisiumfluorider med høyt koordinasjonstall kan også brukes i slike reaksjoner.

Fluorering av $CCl_4$ ved hjelp av $Na_2SiF_6$ ble gjort på følgende måte.

- **Standardisering av $Na_2SiF_6$-løsning:**

Tillaging

Vandig løsning **F**: 0,855 g $Na_2SiF_6$ (188,053 g mol$^{-1}$) ble løst i vann (Totalvolum: 200 mL).

Vandig løsning **G**: 6,86 g $Ce_2(SO_4)_3$ (568,424 g mol$^{-1}$) ble løst i vann (Totalvolum: 200 mL).

Fremgangsmåte

Fellingstitrering med løsning **F** (50,0 mL) ved dråpevis tilsetting av løsning **G** med xylenol-oransj, som koordinerer til $Ce^{3+}$, som indikator. Etter tilsetting av 18,8 mL av løsning **G**, endret løsningen farge fra gul til magenta. Bunnfallet som dannes er et binært stoff som inneholder $Ce^{3+}$, og det eneste produktet med silisium er $Si(OH)_4$.

| | | |
|---|---|---|
| **B.1** | **Skriv** balansert ligning for reaksjonen mellom $Na_2SiF_6$ og $Ce_2(SO_4)_3$. | 5pt |

- **Reaksjon mellom $CCl_4$ og $Na_2SiF_6$:**

(Massetap, f. eks. ved fordampning kan neglisjeres i de neste trinnene.)

$Na_2SiF_6$ ($x$ [g]) ble tilsatt til $CCl_4$ (500,0 g) og varmet opp til 300 °C i en forseglet, trykksikker beholder. Ureagert $Na_2SiF_6$ og det dannede NaCl ble fjernet ved filtrering. Filtratet ble fortynnet til et totalvolum på 1,00 L med $CCl_4$ (løsning **H**). $^{29}$Si- og $^{19}$F-NMR-spektre av løsning **H** viser at $SiF_4$ er det eneste stoffet med sillisium. $^{19}$F-NMR-spektret, viser i tillegg til $SiF_4$, signaler som stemmer med $CFCl_3$, $CF_2Cl_2$, $CF_3Cl$, og $CF_4$ (jf. Table 1). Forholdet mellom integralene i $^{19}$F-NMR-spekteret er proporsjonalt til antall fluor-kjerner.

Table 1

| $^{19}$F NMR data | $CFCl_3$ | $CF_2Cl_2$ | $CF_3Cl$ | $CF_4$ |
|---|---|---|---|---|
| Forholdet mellom integralene | 45.0 | 65.0 | 18.0 | 2.0 |

$SiF_4$ blir hydrolysert til $H_2SiF_6$ slik det er vist i ligning 8:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \quad (8)$$

Løsning **H** (10 mL) ble helt oppi et overskudd av vann, slik at $SiF_4$ ble fullstendig hydrolysert. Etter separasjon, ble $H_2SiF_6$ fra hydrolysen nøytralisert og fullstendig omdannet til $Na_2SiF_6$ (vandig løsning **J**).

Bunnfallet av ureagert $Na_2SiF_6$ og NaCl, som ble fjernet i filtreringen i det første trinnet (understreket), ble fullstendig løst i vann, og gav en vandig løsning (løsning **K**; 10,0 L).

Flere fellingstitreringer med løsning **G** ble gjennomført, og ekvivalenspunktet (endepunktet) for titreringen med **G** var som følger:

- For løsning **J** (hele volumet): 61,6 mL.
- For 100 mL av løsning **K**: 44,4 mL.

Merk deg at tilstedeværelsen av NaCl og $SiO_2$ ikke påvirker fellingstitreringen.

| | | |
|---|---|---|
| **B.2** | **Beregn** massen av NaCl som dannes i reaksjonsbeholderen (understreket informasjon), og **beregn** massen ( $x$ [g]) av $Na_2SiF_6$ som ble brukt som startmateriale. | 15pt |

| | | |
|---|---|---|
| **B.3** | 77,8 % av den mengden $CCl_4$ som ble brukt som startmateriale var ureagert. **Beregn** massen av $CF_3Cl$ som ble dannet. | 8pt |

# Mysterious Silicon

## Part 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$^{-1}$

**A.3** (6 pt)

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

**A.4** (10 pt)

| **D** (5 pt) | **E** (5 pt) |
|---|---|
| | |

## Part B

**B.1** (5 pt)

**B.2** (15 pt)

(Continued on the next page)

**B.2 (cont.)**

NaCl : g, $Na_2SiF_6$ : g

**B.3** (8 pt)

$CF_3Cl$ : _____ g

**NOR-1 C-6 C**
Abdur-Raheem Idowu

# 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:

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

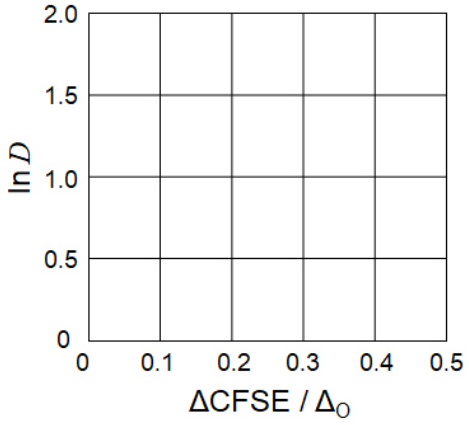
where $[M]_s$ and $[M]_l$ are the concentrations of $M^{n+}$ in the silicate minerals and the magma, respectively. The table below shows the $D$ values of $Cr^{2+}$and $Mn^{2+}$ as examples.

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

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

**A.1** **Calculate** $|CFSE^O - CFSE^T| = \Delta CFSE$ in terms of $\Delta_O$ for $Cr^{2+}$, $Mn^{2+}$, and $Co^{2+}$; assume $\Delta_T = 4/9\Delta_O$. 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 $[CuO_6]$ octahedron, the Cu–O length along the *z*-axis ($l_z$) is longer than that of the *x*-axis ($l_x$), and $[CuO_6]$ is distorted from the regular $O_h$ geometry. This distortion removes the degeneracy of the $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$).

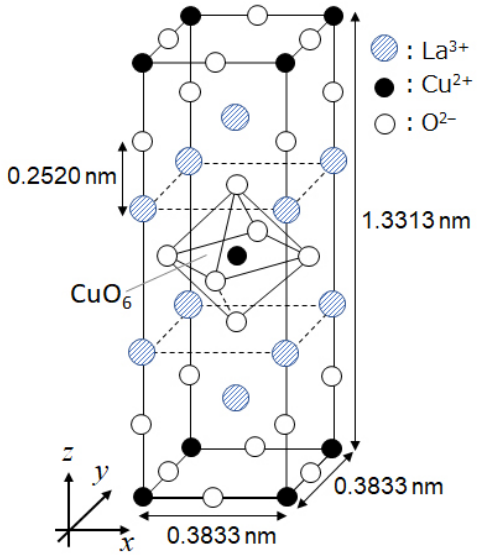



Fig. 1

**A** can be synthesized by thermal decomposition (pyrolysis) of complex **B**, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid $C_4H_2O_4$, i.e., a diacid. The pyrolysis behavior of **B** in dry air shows a weight loss of 29.1% up to 200 °C due to the loss of crystallization water, followed by another weight loss up to 700 °C due to the release of $CO_2$. 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 $[CuO_6]$ octahedron in **A** of Fig. 1, **write** the names of the split $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$) in (i) and (ii), and **draw** the electron configuration in the dotted box in your answer sheet. | 4pt |

**A** is an insulator. When one $La^{3+}$ is substituted with one $Sr^{2+}$, one hole is generated in the crystal lattice that can conduct electricity. As a result, the $Sr^{2+}$-doped **A** shows superconductivity below 38 K. When a substitution reaction took place for **A**, $2.05 \times 10^{27}$ holes $m^{-3}$ were generated.

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

## Part C

$Cu_2(CH_3CO_2)_4$ is composed of four $CH_3CO_2^-$ coordinated to two $Cu^{2+}$ (Fig. 2A). $Cu_2(CH_3CO_2)_4$ 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 $Cu_4(\mathbf{L1})_4$ is composed of planar dicarboxylate **L1** (Fig. 2B) and $Cu^{2+}$ (Fig. 2C). The angle $\theta$ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The $\theta$ is 0° for **L1**. Note that hydrogen atoms are not shown in Fig. 2.

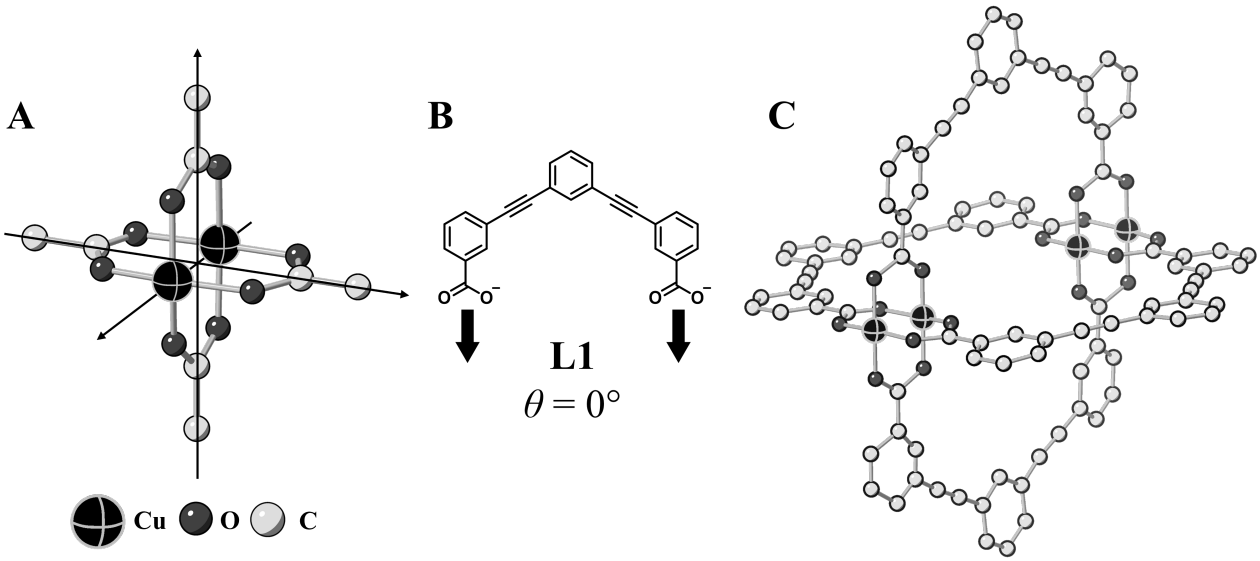
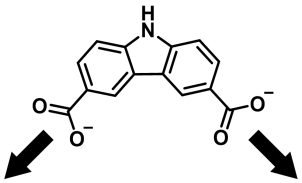



Fig. 2

**C.1** The $\theta$ of the planar dicarboxylate **L2** below is fixed to 90˚. If the composition of the cage complex formed from **L2** and $Cu^{2+}$ is $Cu_n(\mathbf{L2})_m$, **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




**L2**

$\theta = 90°$

A zinc complex, $Zn_4O(CH_3CO_2)_6$, contains four tetrahedral $Zn^{2+}$, six $CH_3CO_2^-$, and one $O^{2-}$ (Fig. 3A). In $Zn_4O(CH_3CO_2)_6$, 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°) 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 $[Zn_4O(\mathbf{L3})_3]_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral $Zn^{2+}$ is represented as dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

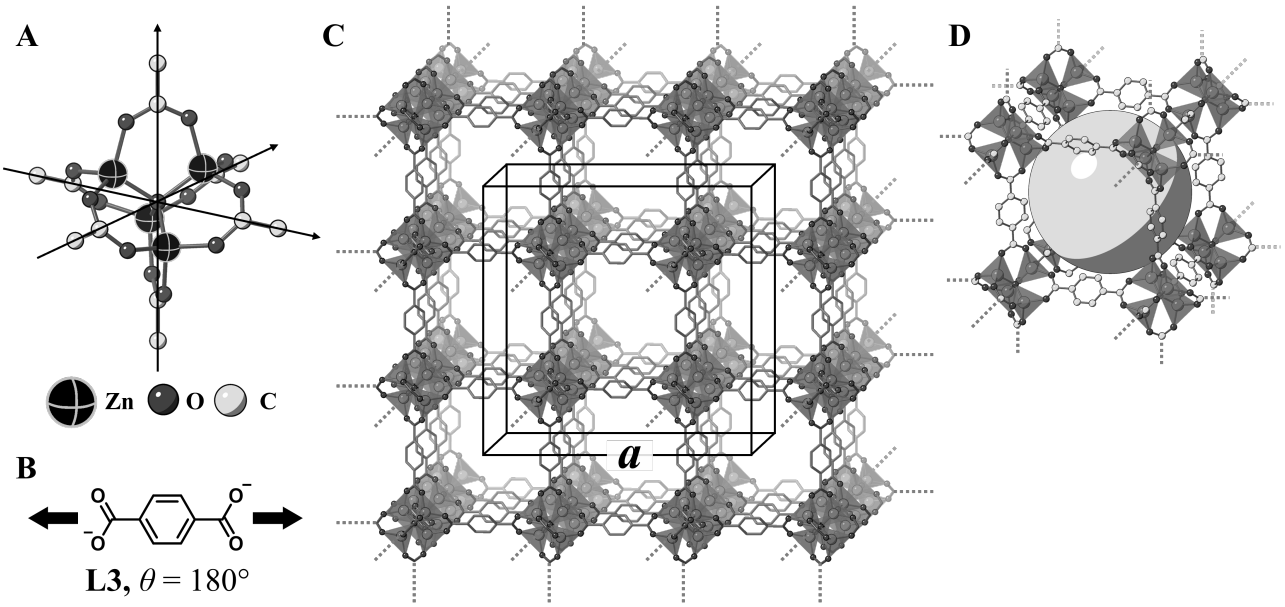



Fig. 3

| | | |
|---|---|---|
| **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 $3.0 \times 10^2$ 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 |

# Q6-1

Norwegian (Norway)

## Kjemien til innskuddsmetallene i fast fase

| 13 % av totalen | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | A.3 | B.1 | B.2 | B.3 | B.4 | C.1 | C.2 | C.3 | **Total** |
| Poeng | 6 | 3 | 3 | 6 | 4 | 4 | 4 | 5 | 5 | 5 | **45** |
| Score | | | | | | | | | | | |



Vulkan på Sakurajima-øya

### Del A

Japan er et av landene i verden med flest vulkaner. Når silikatmineraler krystalliserer fra magma, blir en del ioner av innskuddsmetaller ($M^{n+}$) i magma inkorporert i silikatmineralene. De $M^{n+}$ vi ser på i denne oppgaver er koordinert til oksidioner ($O^{2-}$) og har fire-koordinert tetrahedral ($T_d$) geometri i magma og seks-koordinert oktahedral ($O_h$) geometri i silikatmineralene. I begge tilfeller med høy-spinn elektronkonfigurasjon. Fordelingskoeffisienten til $M^{n+}$ mellom silikatmineraler og magma, $D$, kan uttrykkes slik:

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

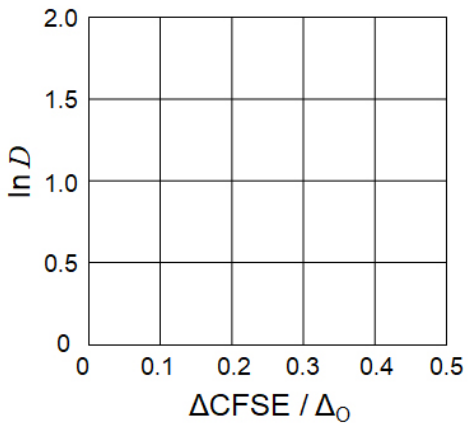
hvor $[M]_s$ og $[M]_l$ er konsentrasjonen av $M^{n+}$ i henholdsvis silikatmineraler og magma. Tabellen under viser verdier for $D$ for $Cr^{2+}$ og $Mn^{2+}$ som eksempler.

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

La $\Delta_O$ være energiforskjellen mellom d-orbitalene i $M^{n+}$ og $CFSE^O$ være krystallfeltstabiliseringsenergien i et $O_h$-felt. La $\Delta_T$ og $CFSE^T$ være tilsvarende verdier for et $T_d$-felt.

**A.1** **Beregn** $|CFSE^O - CFSE^T|$ = ΔCFSE som en funksjon av $\Delta_O$ for $Cr^{2+}$, $Mn^{2+}$, and $Co^{2+}$; anta $\Delta_T = 4/9\Delta_O$. 6pt

**A.2** En lineær sammenheng blir tydelig når vi plotter ln $D$ mot ΔCFSE / $\Delta_O$ i koordinatsystemet nedenfor. **Estimer** $D$ for $Co^{2+}$. 3pt




Metalloksider MO (M: Ca, Ti, V, Mn, eller Co) krystalliserer i steinsalt-struktur hvor $M^{n+}$ får en $O_h$-geometri med høyspinn elektronkonfigurasjon. Gitterentalpien for disse oksidene er hovedsakelig bestemt av coulomb-interaksjonene basert på radius og ladning for ionene, og noe bidrag fra CFSE til $M^{n+}$ i $O_h$-feltet.

**A.3** **Velg** den riktige kombinasjonen av gitterentalpier [kJ mol$^{-1}$] fra alternativene (a) til (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 |

# Q6-3

Norwegian (Norway)

## Del B

Et blandet oksid, **A**, som inneholder $La^{3+}$ og $Cu^{2+}$, krystalliserer i en tetragonal enhetscelle vist i Fig. 1. I $[CuO_6]$-oktahederet, er Cu-O lengden langs z-aksen ($l_z$) lengre enn langs x-aksen ($l_x$), og $[CuO_6]$ blir fordreid (distorted) fra den regulære $O_h$-geometrien. Denne fordreielsen (distortion) gjør at $e_g$-orbitalene ($d_{x^2-y^2}$ og $d_{z^2}$) ikke lenger er degenererte.

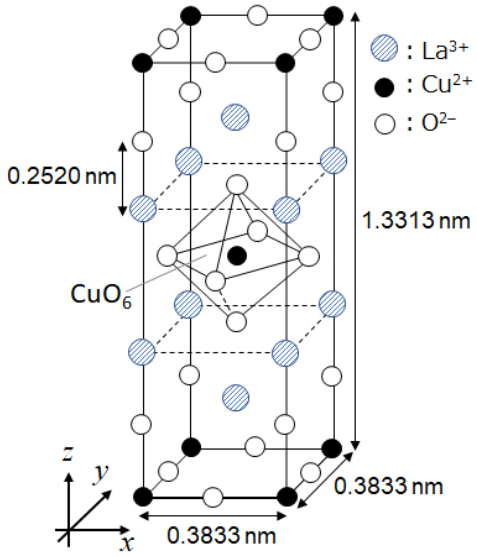



Fig. 1

**A** kan syntetiseres ved termisk dekomponering (pyrolyse) av kompleks **B**, som blir dannet ved å blande metallklorider i fortynnet ammoniakk blandet med squaric acid (kvadratsyre) $C_4H_2O_4$, altså en disyre. Når **B** pyrolyserer i tørr luft, skjer det først et massetap på 29,1 % opp til 200 °C fordi krystallvannet fordamper; deretter skjer et nytt massetap opp til 700 °C fordi det frigjøres $CO_2$. Det totale massetapet når **A** dannes fra **B** er 63,6 %. Det er bare vann og $CO_2$ som frigjøres i pyrolysereaksjonen.

| | | |
|---|---|---|
| **B.1** | **Skriv** kjemisk formel for **A** og **B**. | 6pt |
| **B.2** | **Beregn** $l_x$ og $l_z$ ved hjelp av Fig. 1. | 4pt |
| **B.3** | For i det fordreide $[CuO_6]$-oktahederet i **A** i Fig. 1, **skriv** navnet på de splittede $e_g$-orbitalene ($d_{x^2-y^2}$ og $d_{z^2}$) i (i) og (ii), og **tegn** elektronkonfigurasjonen i den stiplede boksen på svararket. | 4pt |

**A** er isolerende. Når en $La^{3+}$ blir substituert med en $Sr^{2+}$, dannes det et hull i krystallgitteret som nå kan lede strøm. Som et resultat, er $Sr^{2+}$-dopet **A** superledende under 38 K. Når man gjorde denne substitusjonsreaksjonen for **A**, ble det dannet $2.05 \times 10^{27}$ hull $m^{-3}$.

| | | |
|---|---|---|
| **B.4** | **Beregn** prosentandelen $Sr^{2+}$ som har substituert $La^{3+}$ basert på molforholdet i substitusjonsreaksjonen. Valensen til ionene som deltar og krystallstrukturen blir ikke endret i substitusjonsreaksjonen. | 4pt |

## Del C

$Cu_2(CH_3CO_2)_4$ består av fire $CH_3CO_2^-$ koordinert til to $Cu^{2+}$ (Fig. 2A). $Cu_2(CH_3CO_2)_4$ har stor grad av struktursymmetri, med to akser som går gjennom karbonatomene på de fire $CH_3CO_2^-$ og en akse som går gjennom de to $Cu^{2+}$. Alle aksene står vinkelrett på hverandre. Når en dikarboksylat brukes som ligand istedenfor $CH_3CO_2^-$, dannes et "bur"-kompleks. Bur-komplekset $Cu_4(\mathbf{L1})_4$ består av det plane dikarboksylatet **L1** (Fig. 2B) og $Cu^{2+}$ (Fig. 2C). Vinkelen $\theta$ mellom koordinasjonsretningene til de to karboksylatene, vist med piler i Fig. 2B, bestemmer strukturen til bur-komplekset. Vinkelen $\theta$ er 0° for **L1**. Legg merke til at hydrogenatomene ikke er vist i Fig. 2.

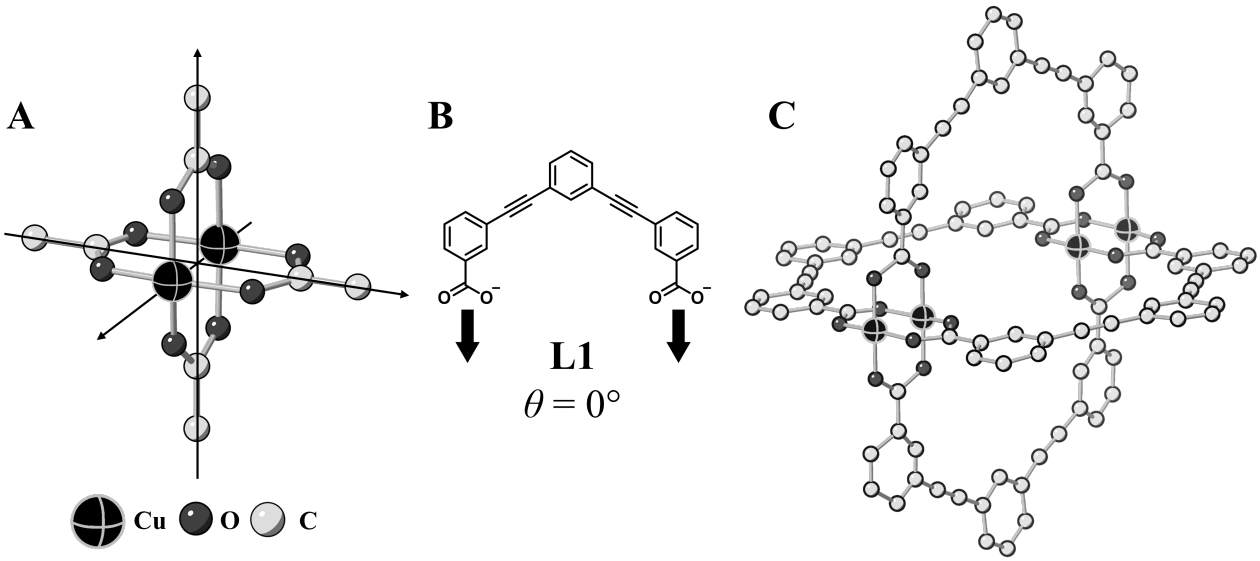
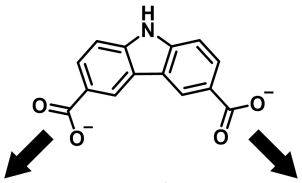



Fig. 2

# Q6-5

Norwegian (Norway)

**C.1** Vinkelen $\theta$ til det plane dikarboksylatet **L2** nedenfor er låst til 90°. Hvis sammensetningen av bur-komplekset som dannes av **L2** og $Cu^{2+}$ er $Cu_n(\mathbf{L2})_m$, **oppgi** den minste heltallige kombinasjonen av *n* og *m*. Anta at bare $CO_2^-$-gruppene i **L2** danner koordinerende bindinger til $Cu^{2+}$-ionene. 5pt



**L2**

$\theta = 90°$

# Q6-6

Norwegian (Norway)

Et sinkkompleks, $Zn_4O(CH_3CO_2)_6$, består av fire tetrahedrale $Zn^{2+}$, seks $CH_3CO_2^-$, og ett $O^{2-}$ (Fig. 3A). I $Zn_4O(CH_3CO_2)_6$ er $O^{2-}$ plassert i origo, og de tre aksene som passer gjennom karbonatomene i $CH_3CO_2^-$ står vinkelrett på hverandre. Når *p*-benzendikarboksylat (Fig. 3B, **L3**, $\theta$ = 180°) blir brukt istedenfor $CH_3CO_2^-$, blir $Zn^{2+}$-klusterne koblet til hverandre og danner et krystallinsk, fast stoff (**X**) som kalles en "porøs koordinasjonspolymer" (Fig. 3C). Sammensetningen til **X** er $[Zn_4O(\mathbf{L3})_3]_n$, og stoffet har en kubisk krystallstruktur med porer i nano-størrelse. Én pore er representert med en kule i Fig. 3D, og hver tetrahedral $Zn^{2+}$ er representert med et mørk grå polyheder i Fig. 3C og 3D. Hydrogene er ikke tegnet i Fig. 3.

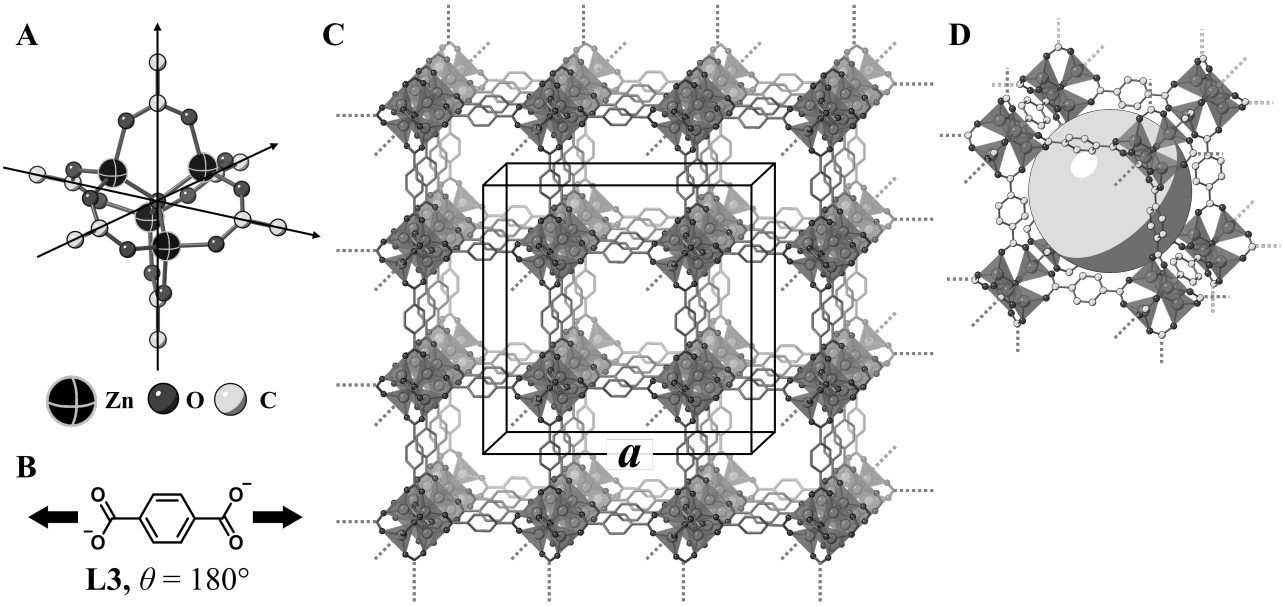



Fig. 3

| | | |
|---|---|---|
| **C.2** | **X** har en kubisk enhetscelle med sidelengde $a$ (Fig. 3C) og en tetthet på 0,592 g cm$^{-3}$. **Beregn** $a$ i [cm]. | 5pt |

| | | |
|---|---|---|
| **C.3** | **X** inneholder en stor mengde porer, og 1 g **X** kan inneholde $3.0 \times 10^2$ mL $CO_2$-gass i porene ved 1 bar og 25 °C. **Beregn** det gjennomsnittlige antallet $CO_2$-molekyler per pore. | 5pt |

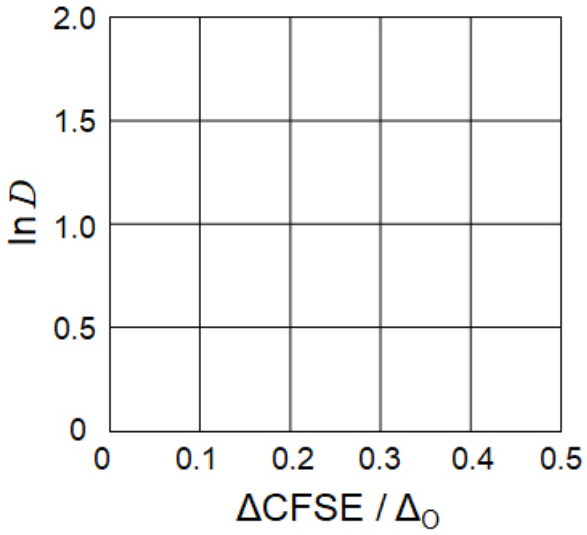
# The Solid-State Chemistry of Transition Metals

## Part A

**A.1** (6 pt)

$Cr^{2+}$ : _____ $\Delta_O$, $Mn^{2+}$ : _____ $\Delta_O$, $Co^{2+}$ : _____ $\Delta_O$

**A.2** (3 pt)




$D$ : _____

**A.3** (3 pt)

_____

## Part B

**B.1** (6 pt)

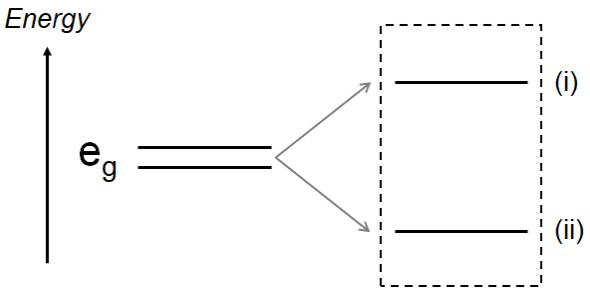
A : _____, B : _____

**B.2** (4 pt)

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

**B.3** (4 pt)

(i) : _____ , (ii) : _____




**B.4** (4 pt)

_____ %

## Part C

**C.1** (5 pt)

$n =$ _____, $m =$ _____

**C.2** (5 pt)

$a =$ _____ cm

**C.3** (5 pt)

**NOR-1 C-7 C**
Abdur-Raheem Idowu

# 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.



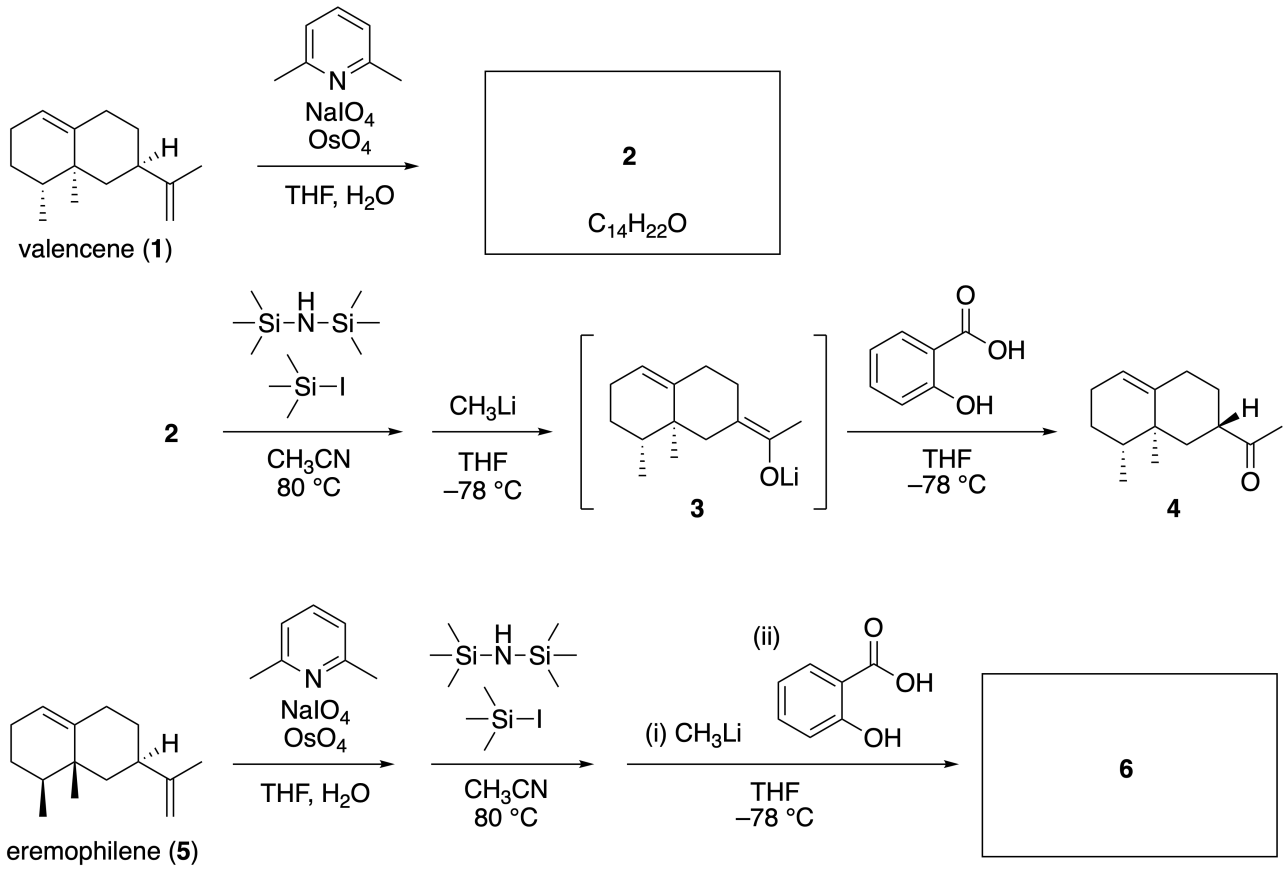
Photo courtesy: Tohoku Univ.

## 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.



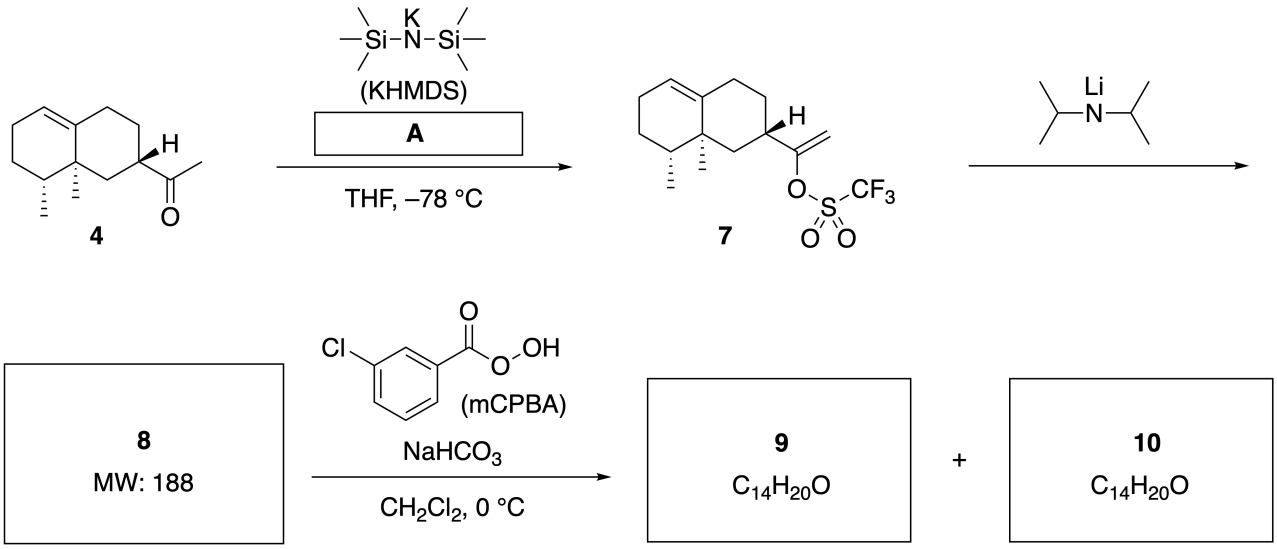
*Inula linariifolia*

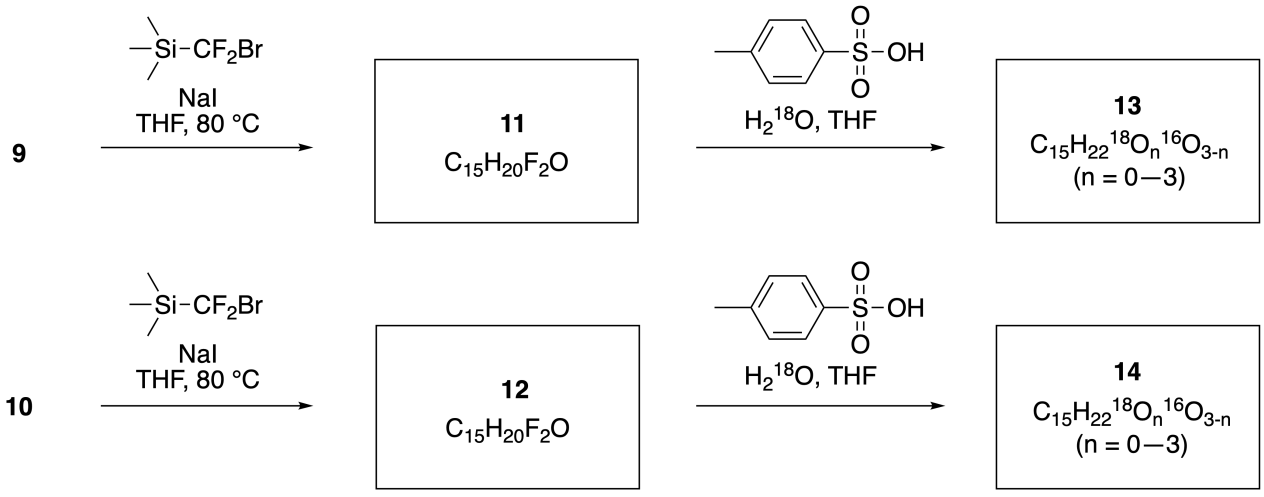


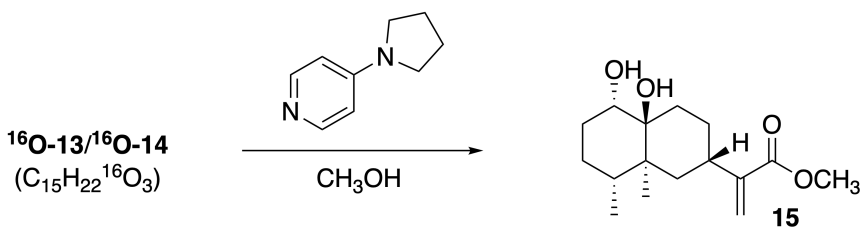

**A.1** **Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary. 5pt

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

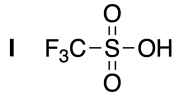
that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of $^{18}O$-labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are $^{18}O$-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product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

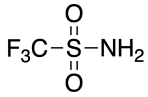


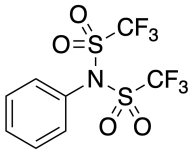



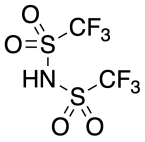



**A.2** **Choose** the appropriate structure for **A**. 2pt

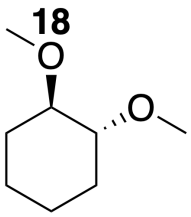
**I** 

**II** 

**III** 

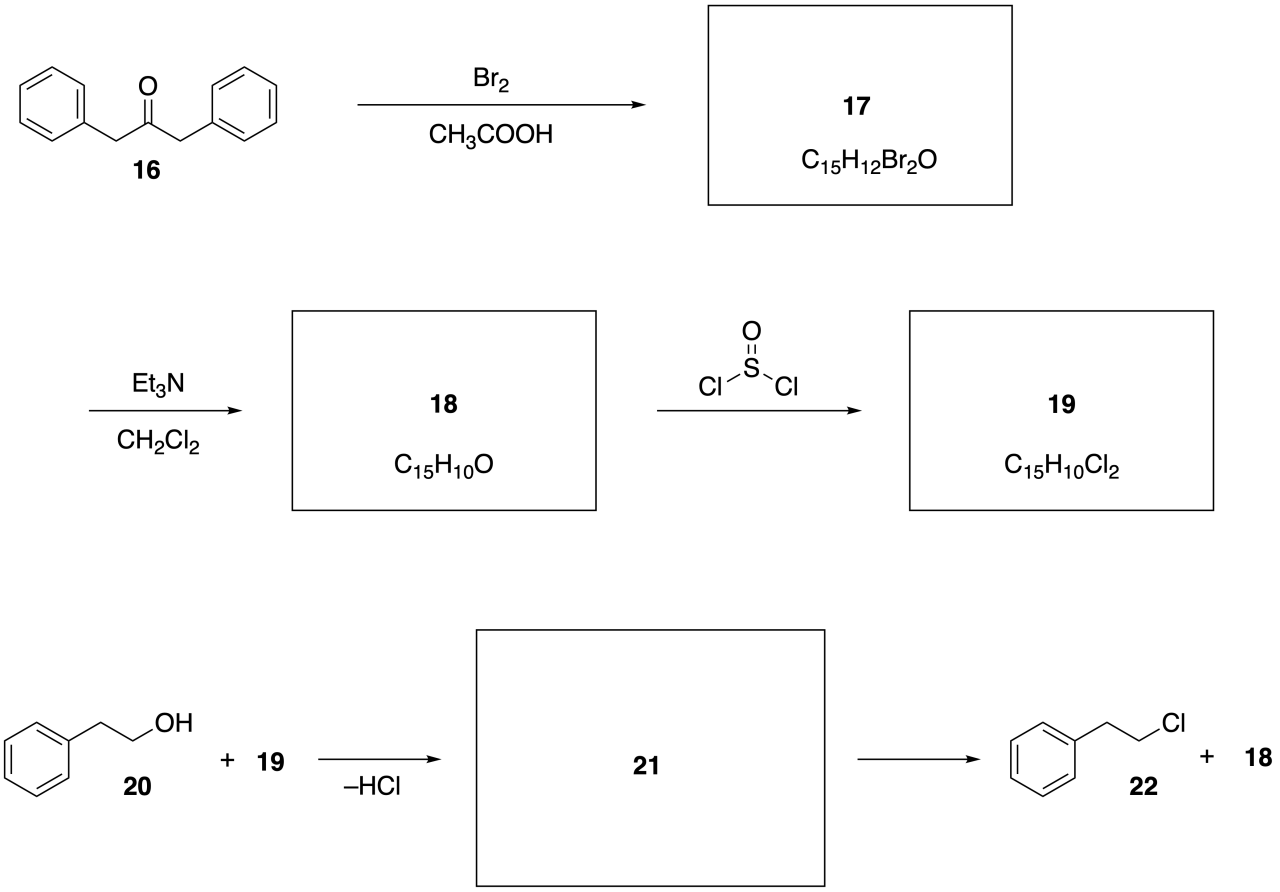
**IV** 

**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**.




$^1$H NMR ($CD_3CN$, ppm) **20**: $\delta$ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
**21**: $\delta$ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

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

# Lek med ikke-benzenoid aromatisitet

| 13 % av totalen | | | | | |
|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | A.3 | B.1 | **Total** |
| Poeng | 5 | 2 | 19 | 10 | **36** |
| Score | | | | | |

Professor Nozoe (1902-1996) started forskningen på ikke-benzenoide aromatiske forbindelser, stoffer som i dag er sentrale i organisk kjemi.



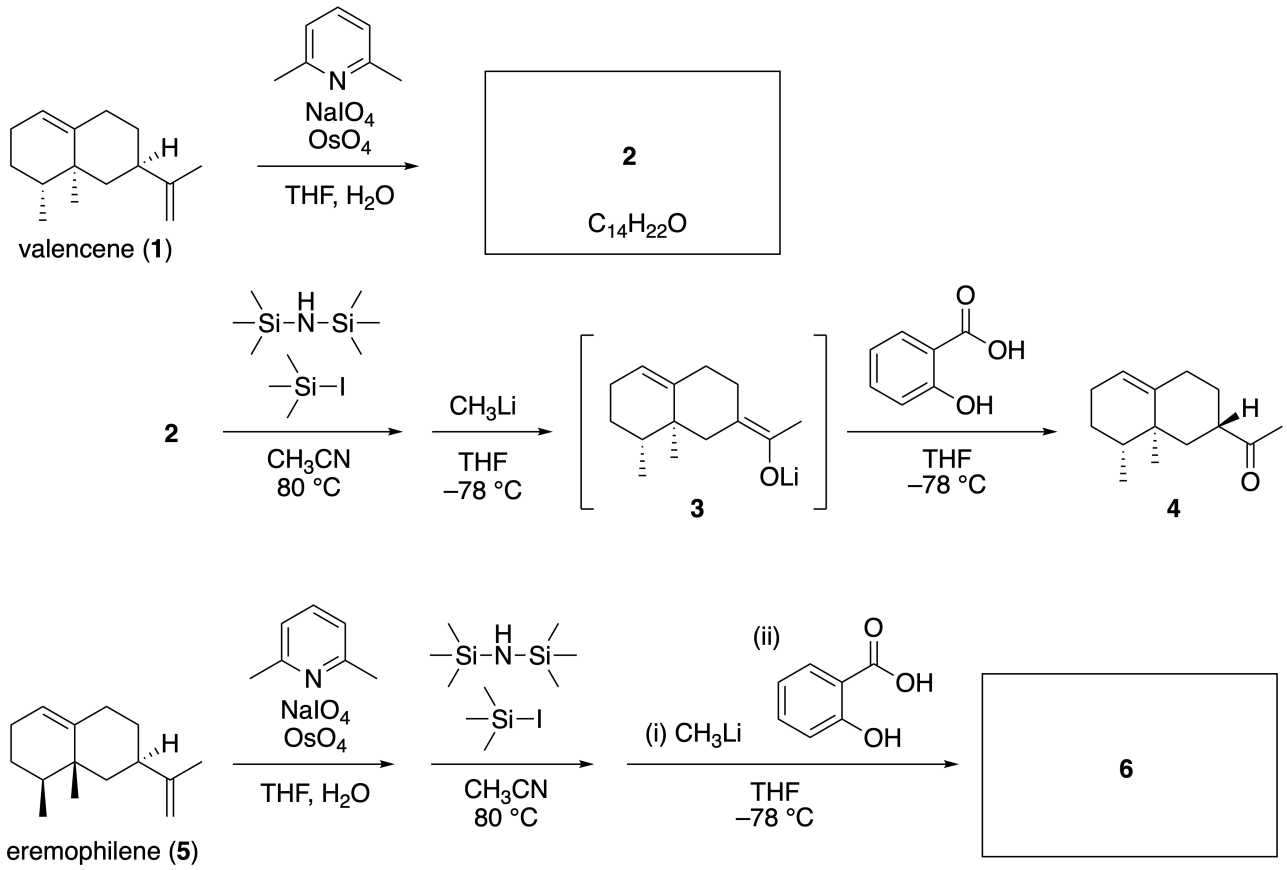
Rettigheter: Universitetet i Tohoku

## Del A

Lineariifolianone er et naturprodukt med en unik struktur. Stoffet ble isolert fra *Inula linariifolia*. Fra valencene (**1**), kan man i ett trinn danne **2**, før en tretrinns reaksjon via **3** gir ketonet **4**. Eremophilene (**5**) blir omdannet til **6** gjennom de samme fire trinnene.



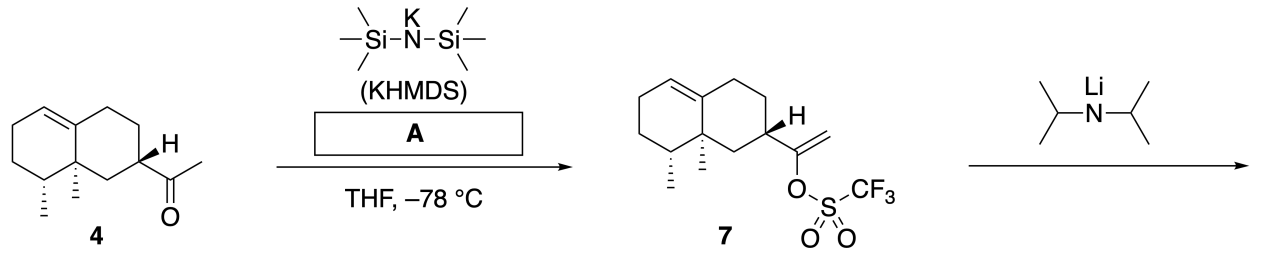
*Inula linariifolia*

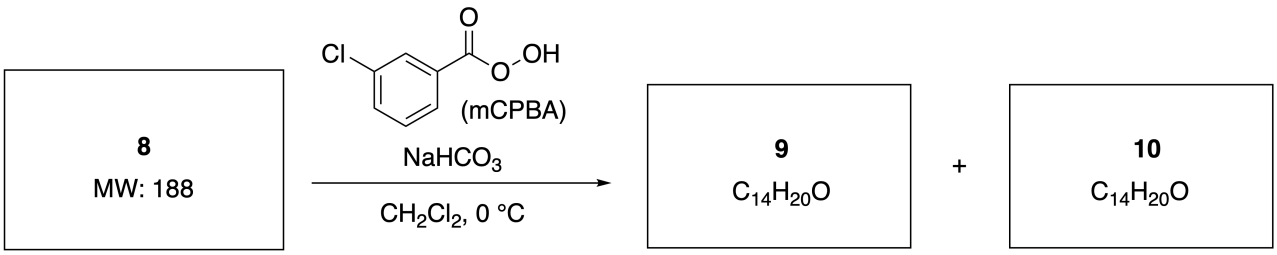


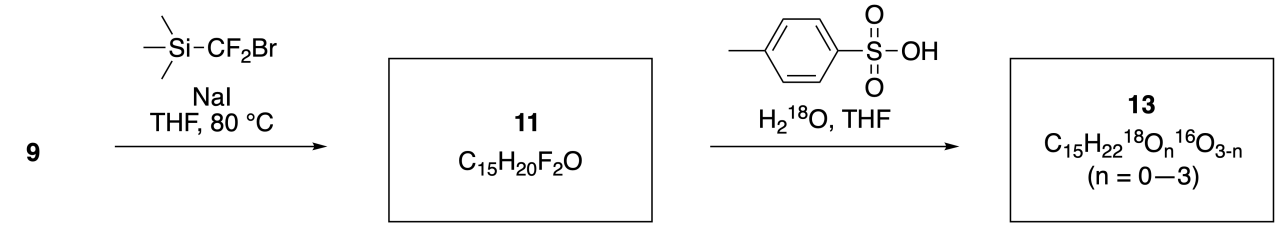

| | | |
|---|---|---|
| **A.1** | **Tegn** strukturen til **2** og **6** og marker stereokjemien tydelig der det er nødvendig. | 5pt |

Så blir keton **4** omdannet til ester **15**. Forbindelse **8** (molar masse: 188) beholder alle stereosenterne i **7**. Forbindelse **9** og **10** har fem stereosentre og ingen karbon-karbon dobbeltbindinger. Anta at $H_2{}^{18}O$ blir

brukt istedenfor $H_2{}^{16}O$ for å syntetisere $^{18}O$-merket lineariifolianonene **13** og **14** fra henholdsvis **11** og **12**. Forbindelsene **13** og **14** er $^{18}O$-merkede isotopomerer. Bortsett fra isotopmerkingen gir både **13** og **14** det samme produktet **15** med identisk stereokjemi.

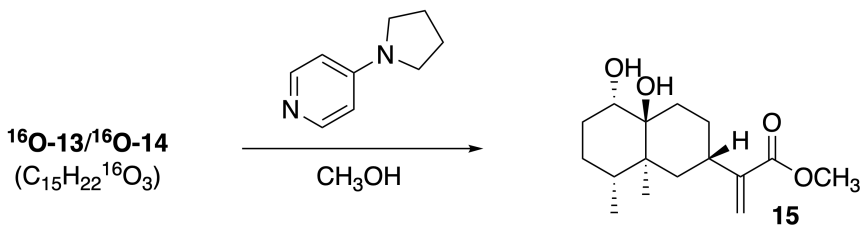


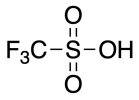



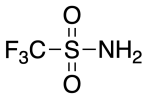


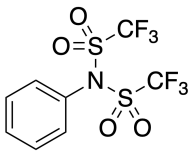


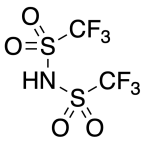


**A.2** **Velg** den riktige strukturen for **A**. 2pt

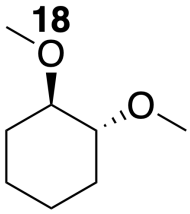
**I** 

**II** 

**III** 

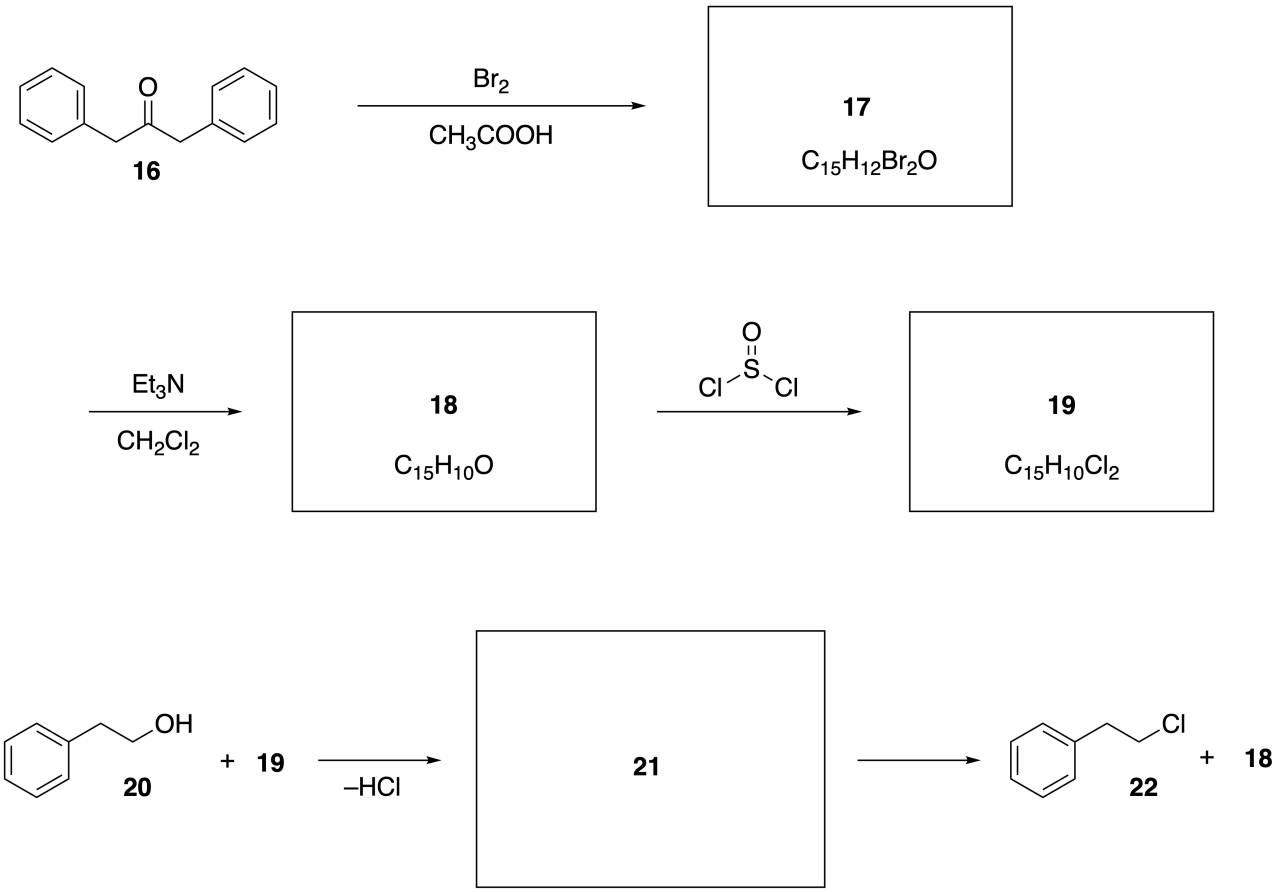
**IV** 

**A.3** **Tegn** strukturene **8**-**14** og marker stereokjemien tydelig der det er nødvendig. **Marker** også $^{18}O$-atomene i forbindelse **13** og **14** slik det er vist i eksemplet under. 19pt



## Del B

Forbindelse **19** blir syntetisert som vist under. I sammenheng med ikke-benzenoid aromatisitet, kan **19** bli brukt som en aktivator for alkoholer, og **20** ble omdannet til **22** via mellomproduktet **21** som er et ione-par. Selv om dannelsen av **21** kan bli observert med NMR, vil **21** gradvise dekomponere og gi **18** og **22**.




$^1$H NMR ($CD_3CN$, ppm) **20**: $\delta$ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
**21**: $\delta$ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

| | | |
|---|---|---|
| **B.1** | **Tegn** strukturen til **17**-**19** og **21**. Du trenger ikke å tegne stereokjemi. | 10pt |

# Playing with Non-benzenoid Aromaticity

## Part 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)

## Part B

**B.1** (10 pt)

| | |
|---|---|
| **17** (2 pt) | **18** (2 pt) |
| **19** (3 pt) | **21** (3 pt) |

**NOR-1 C-8 C**
Abdur-Raheem Idowu

# IChO
# Problem 8
## Cover sheet

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

# Q8-1

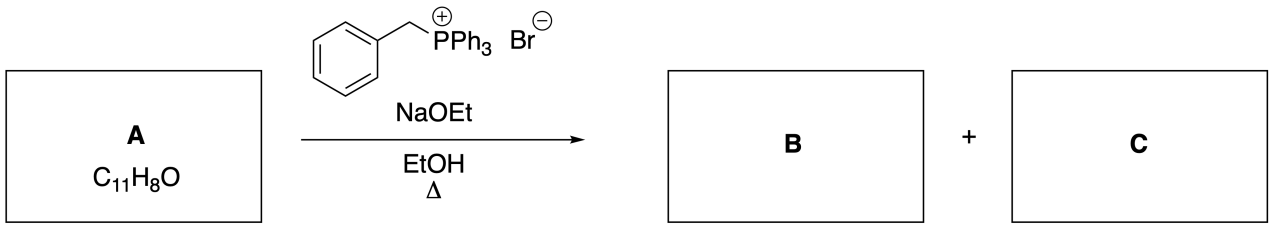
English (Official)

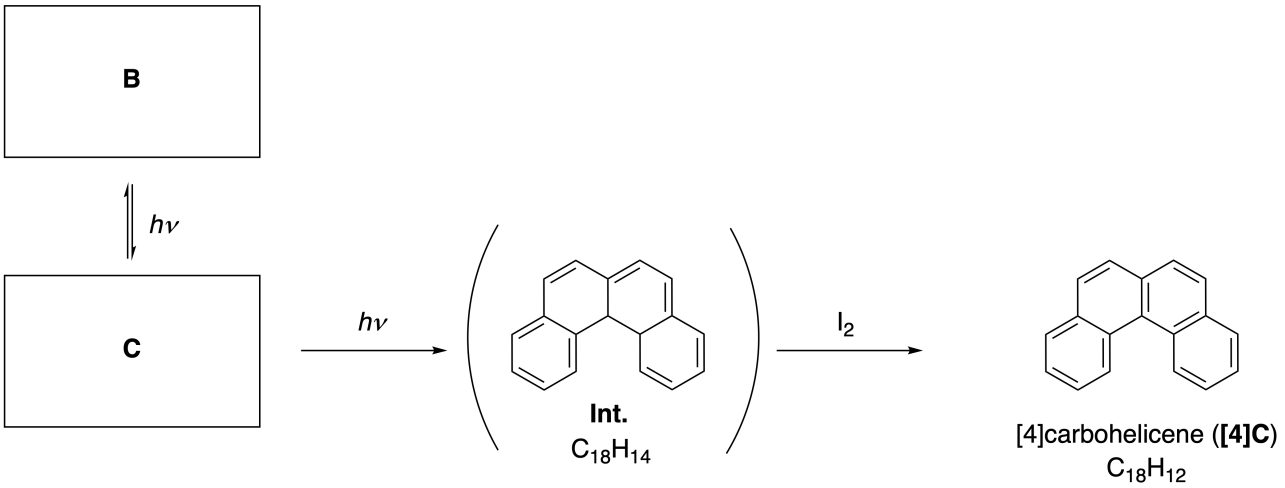
# Dynamic Organic Molecules and Their Chirality

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

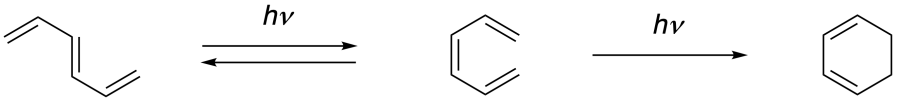
## Part A

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.

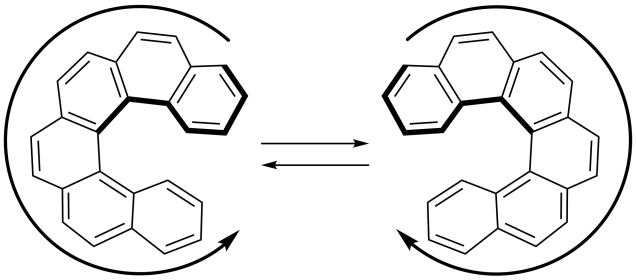


**Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated $\pi$ systems.**

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

| | | |
|---|---|---|
| **A.2** | Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product **D** whose molecular weight was 2 Da lower than that of [5]carbohelicene. The $^1$H NMR chemical shifts of **D** are listed below. **Draw** the structure of **D**.<br>**[D** ($\delta$, ppm in $CS_2$, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)**]** | 3pt |

[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.



(*M*) (*P*)

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

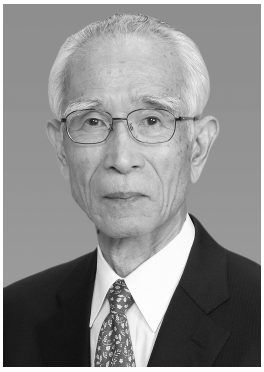
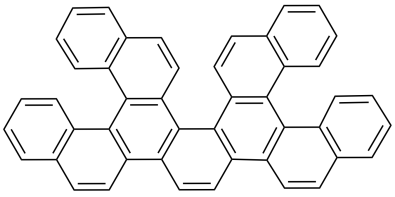
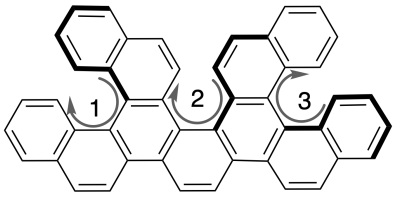


Photo courtesy: The Japan Prize Foundation

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.

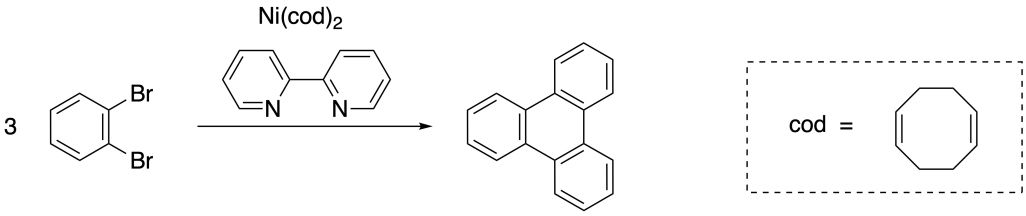


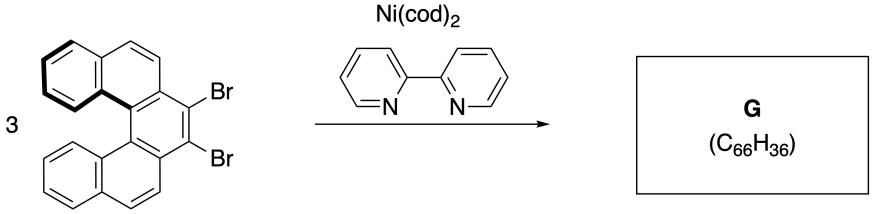
**E**




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

**A.3** The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (*P*)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, **identify all** the possible stereoisomers of **G** formed in this process, without duplication. As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and *M* and *P* labels according to the same numbering. For instance, the other stereoisomers of **E** should be listed as (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *M*, *P*), (*M*, *P*, *P*), and (*M*, *P*, *M*). 7pt

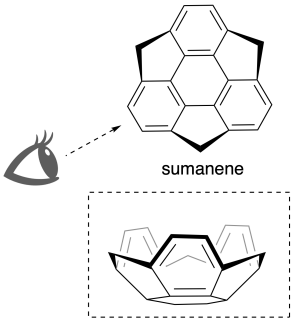



(*P*)-**F**

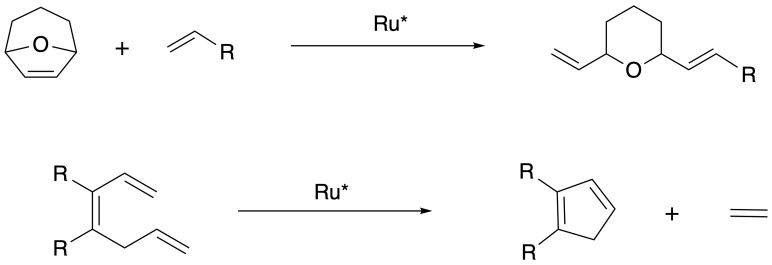
## Part B

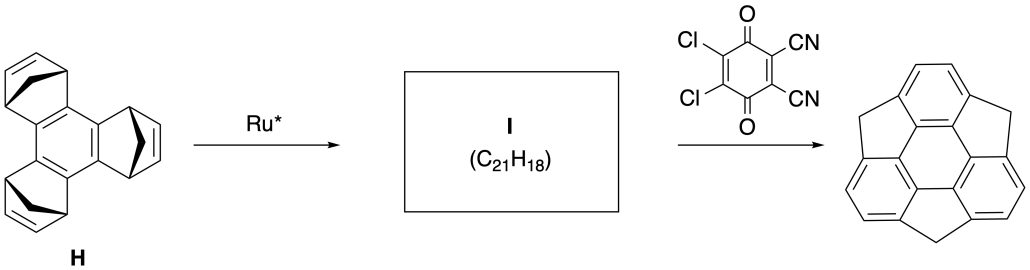
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



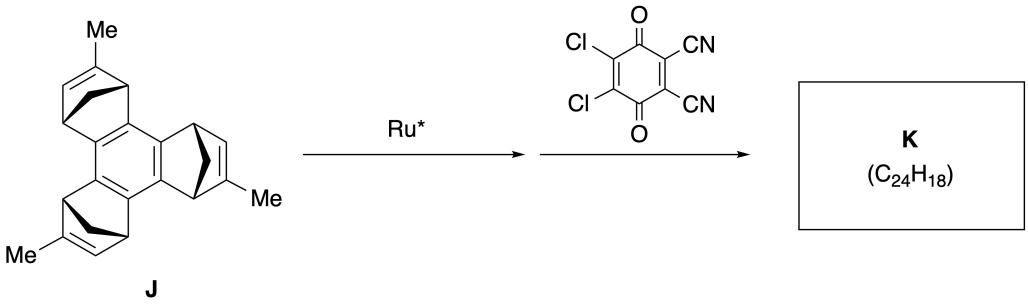



Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.




| | | |
|---|---|---|
| **B.1** | **Draw** the structure of intermediate **I** (its stereochemistry is not required). | 3pt |




**J**

| | | |
|---|---|---|
| **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 |

# Q8-1

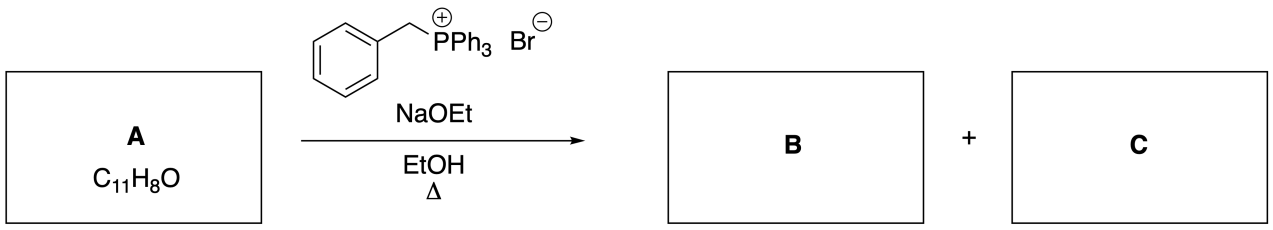
Norwegian (Norway)

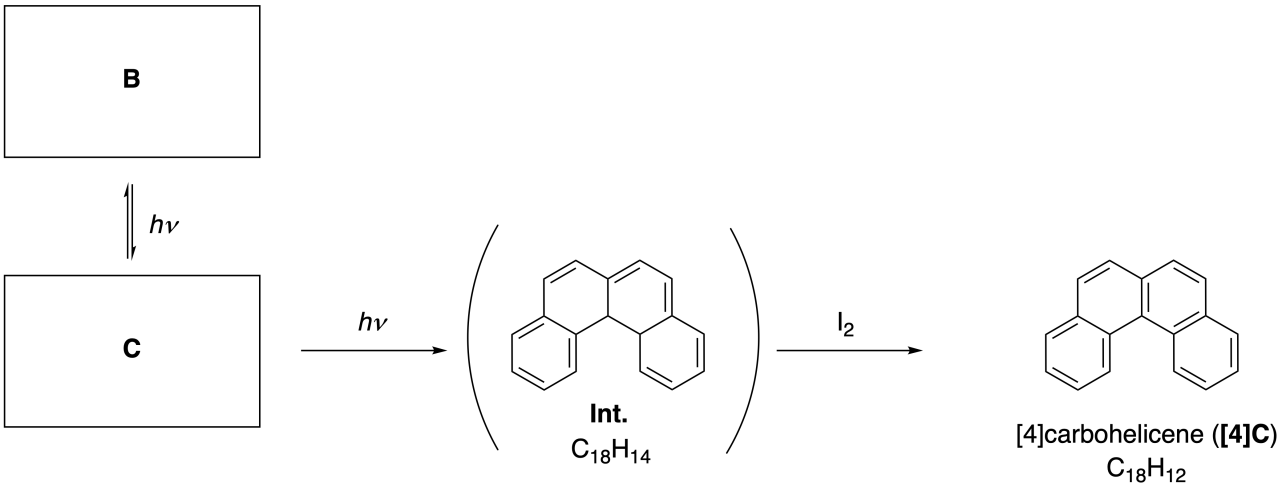
# Dynamiske organiske molekyler og deres kiralitet

| 11 % av totalen | | | | | | |
|---|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | A.3 | B.1 | B.2 | **Total** |
| Poeng | 9 | 3 | 7 | 3 | 4 | **26** |
| Score | | | | | | |

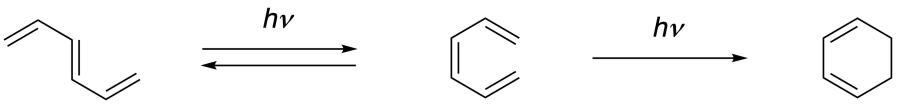
## Del A

Polysykliske aromatiske hydrokarboner med påfølgende orto-koblinger kalles [n]carbohelicenes (n angir antallet seksringer) (se under). [4]Carbohelicene (**[4]C**) lages effektivt i en reaksjonsvei som bruker en fotoreaksjon som vist under via et mellomprodukt (intermediate **Int.**) som lett oksideres av jod (iodine).




Fotoreaksjonen foregår på en lignende måte som følgende eksempel:



# Q8-2

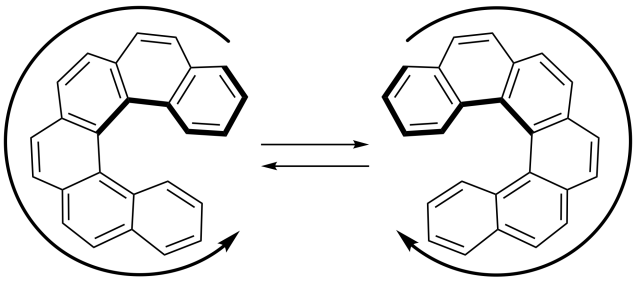
Norwegian (Norway)

**Merk: For alle Oppgave 8 oppgavene, tegn alternerende enkelt og dobbelbindinger i svaret ditt som vist i eksempelet for carbohelicene. Bruk ikke sirkler for konjungerte $\pi$ systemer.**

| | | |
|---|---|---|
| **A.1** | **Tegn** strukturene til **A**–**C**. Skill på stereoisomere. | 9pt |

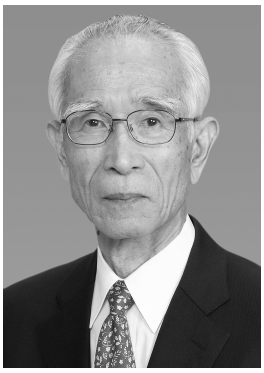
| | | |
|---|---|---|
| **A.2** | Forsøk på å syntetisere [5]carbohelicene fra samme fosfoniumsalt og en passende utgangsforbindelse resulterte kun i veldig små mengder (spormengder) av [5]carbohelicene. Istedet ble produktet **D** dannet med molekylvekt 2 Da lavere enn det til [5]carbohelicene. $^1$H NMR kjemiske skift til **D** er oppgitt under. **Tegn** strukturen til **D**.<br>**[D** ($\delta$, ppm in $CS_2$, r.t.), 8,85 (2H), 8,23 (2H), 8,07 (2H), 8,01 (2H), 7,97 (2H), 7,91 (2H)**]** | 3pt |

[5]- og større [n]carbohelicenes har heliks (helical) kiralitet og omdannelsen mellom enantiomerene til disse helicenes er signifikant sakte ved romtemperatur. Kiraliteten til [n]carbohelicenes er definert som (*M*) eller (*P*) som vist under.



(*M*) (*P*)

[n]Carbohelicenes med n større enn 4 kan separeres enantiomerisk med kiral kolonnekromatografi som ble utviklet av professor Yoshio Okamoto.

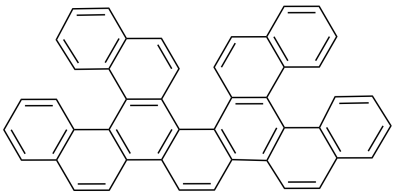


Fototilatelse: The Japan Prize Foundation

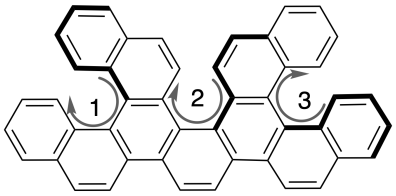
# Q8-3

Norwegian (Norway)

Multiple helicenes er molekyler som inneholder to eller flere helicene-lignende strukturerer. Hvis man tar hensyn til den heliske kirkalitet, så eksisterer det flere stereoisomere i en multiple helicene. For eksempl, forbindelse **E** inneholder tre [5]carbohelicene-lignende deler (moieties) i et molekyl. En av stereoisomerene beskrives som (*P*, *P*, *P*) som vist under.

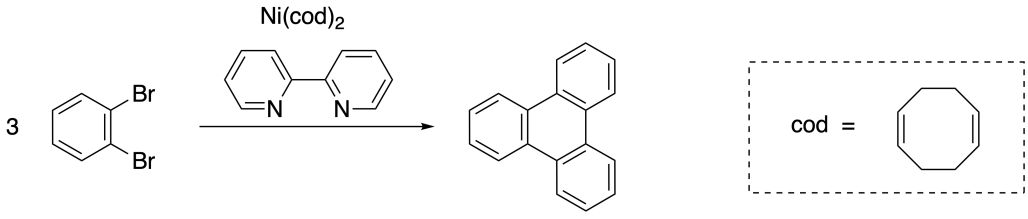


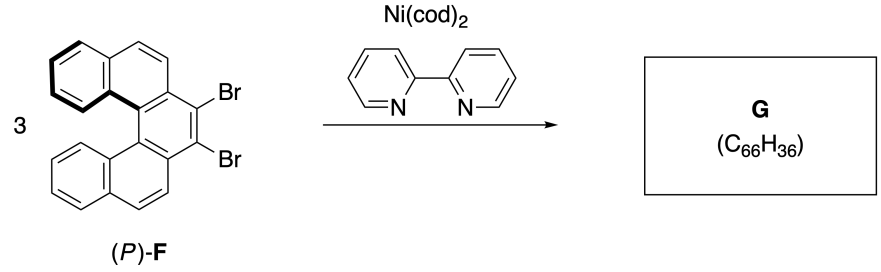
**E**




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

**A.3** Nikkel-mediert trimerisering av 1,2-dibrombenzen genererer trifenylen. Når den samme reaksjonen benyttes for en enantiomer av **F**, (*P*)-**F**, får man multiple helicene **G** ($C_{66}H_{36}$). Gitt at omdanning mellom stereoisomere ikke skjer under reaksjon, **identifiser alle** mulige stereoisomere av **G** som dannes i denne prosessen, uten dupliseringer. Som referanse skal en isomer tegnes fullstendig med kiraliteten angitt som i eksemplet over, med tallangivelse (numerical labels); de andre stereoisomerene skal angis med tall (location number) og *M* og *P* merkelapp i henhold til samme nummering. For eksempel: de andre stereoisomerene til **E** vil angis som (1, 2, 3) = (*P*, *M*, *P*), (*P*, *M*, *M*), (*P*, *P*, *M*), (*M*, *M*, *M*), (*M*, *M*, *P*), (*M*, *P*, *P*), og (*M*, *P*, *M*). 7pt

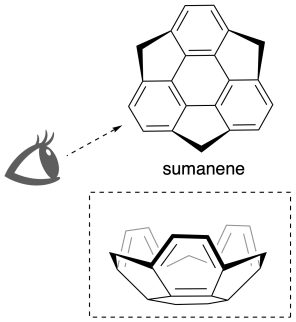



(*P*)-**F**

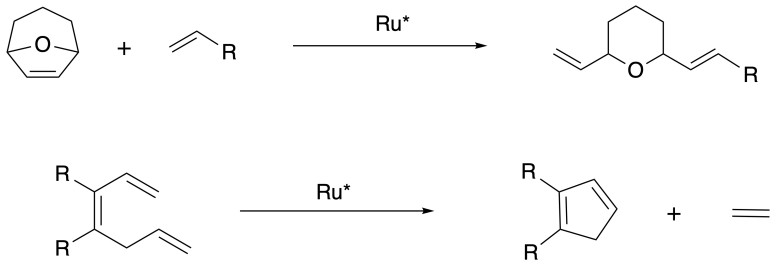
## Del B

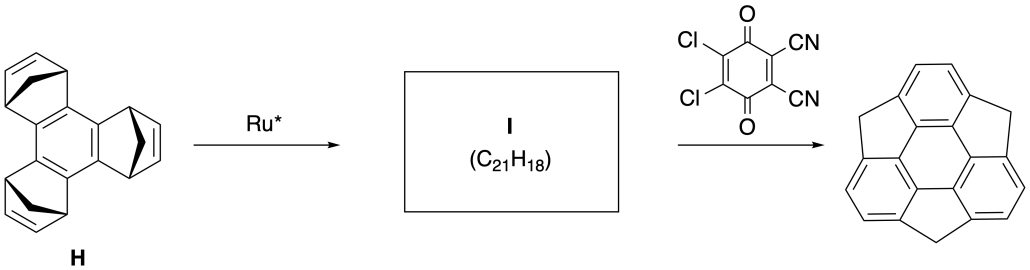
Sumanene er en bolle-formet hydrokarbon som ble først rapportert i Japan i 2003. Navnet "sumanene" kommer fra et Sanskrit-Hindi ord "suman" som betyr solsikke. Syntesen av sumanene skjer via en sekvens av reaksjoner som består av ring-åpnende og ring-lukkende metateser.



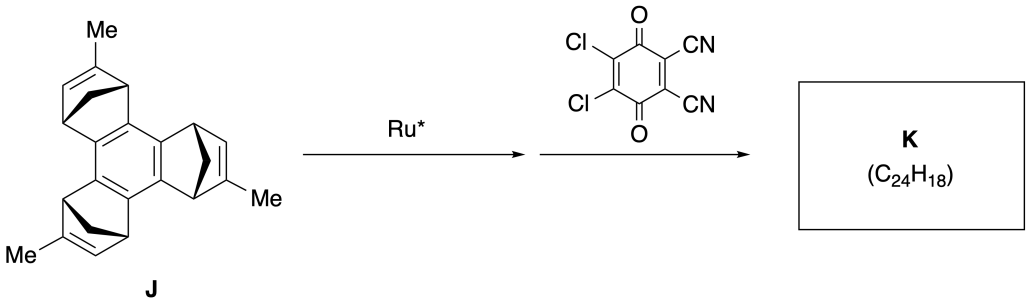



Under er det vist representative metatesereaksjoner som katalyseres av en ruteniumkatalysator (Ru*).




| | | |
|---|---|---|
| **B.1** | **Tegn** strukturen av mellomprodukt **I** (du trenger ikke å tegne stereokjemien). | 3pt |




**J**

| | | |
|---|---|---|
| **B.2** | Ved å starte fra den optisk aktive forløperen **J** så gir den samme reaksjonssekvensen her det optisk aktive sumanene derivatet **K**. Stereosenteret i **J** opplever ingen inversjon i metatesereaksjonen. **Tegn** strukturen til **K** med den passende stereokjemien. | 4pt |

# Dynamic Organic Molecules and Their Chirality

## Part A

**A.1** (9 pt)

| **A** (3 pt) | **B** (3 pt) | **C** (3 pt) |
|---|---|---|
| | | |

**A.2** (3 pt)

**A.3** (7 pt)

## Part B

**B.1** (3 pt)

**B.2** (4 pt)

**NOR-1 C-9 C**
Abdur-Raheem Idowu

# IChO
# Problem 9
## Cover sheet

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

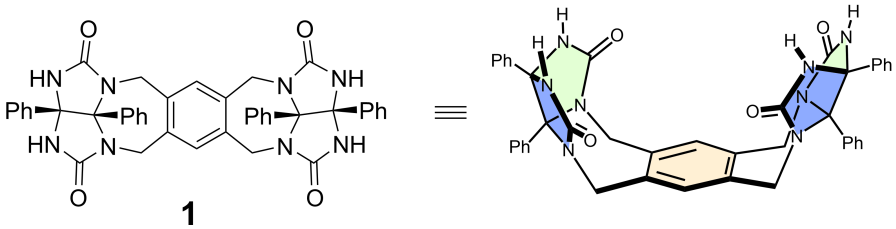
# Likes and Dislikes of Capsule

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

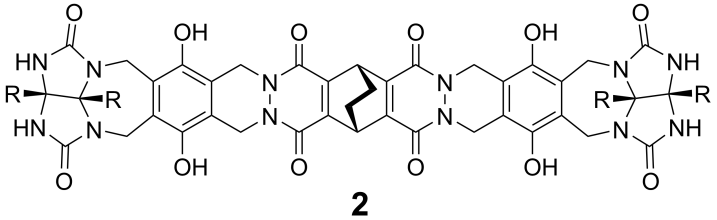
Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



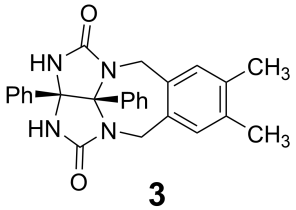
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



**1**

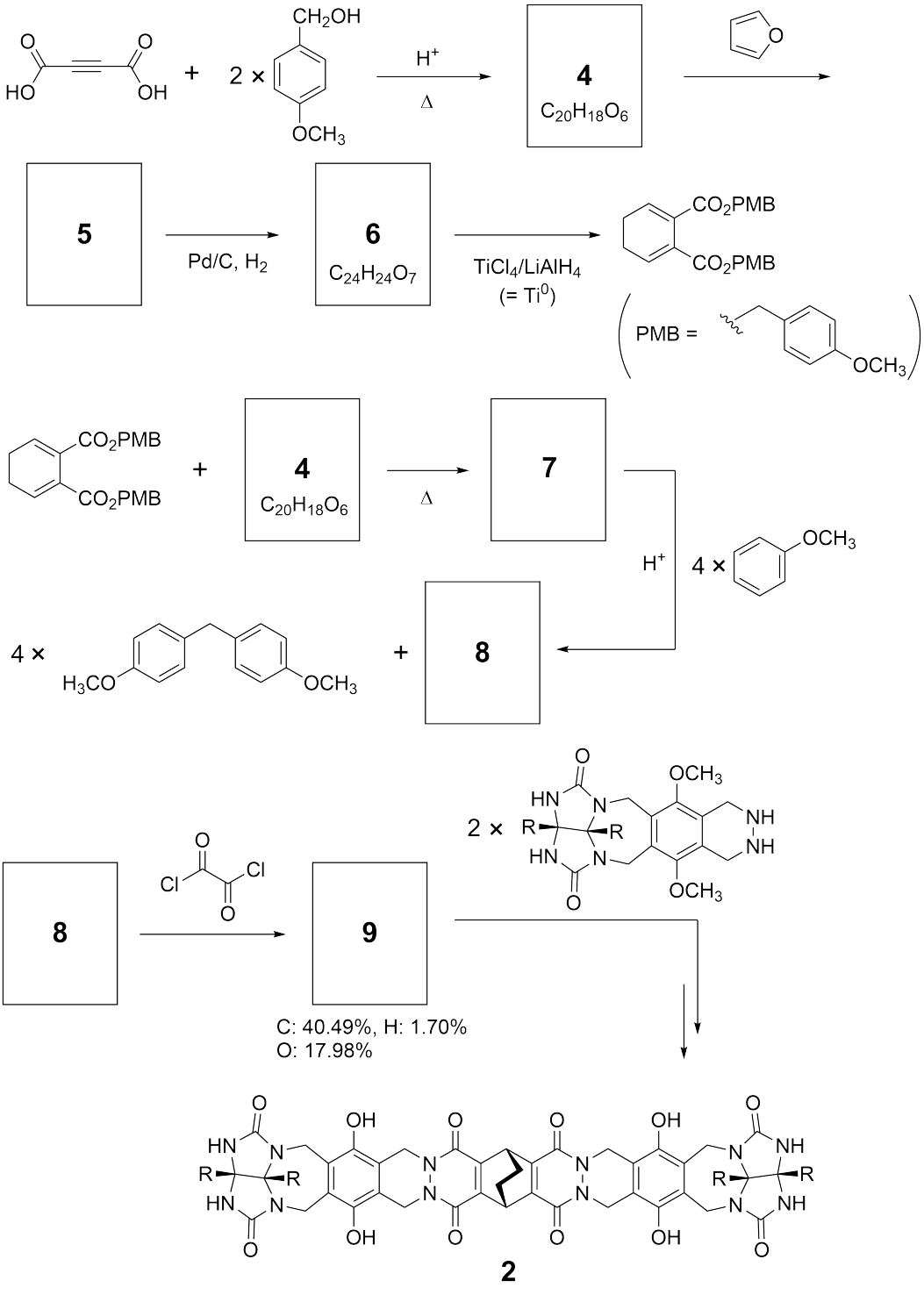


**2**



**3**

The synthetic route to **2** is shown below. The elemental composition of compound **9**: C; 40.49%, H; 1.70%, and O; 17.98% by mass.



| | | |
|---|---|---|
| **A.1** | **Draw** the structures of **4**–**9**; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above. | 13pt |

In the mass spectrum of **1**, the ion peak corresponding to its dimer ($\mathbf{1}_2$) was clearly observed, whereas an ion peak for $\mathbf{3}_2$ was not observed in the spectrum of **3**. In the $^1$H NMR spectra of a solution of $\mathbf{1}_2$, all the NH protons derived from **1** were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of **3**. These data indicate that hydrogen bonds are formed between the NH moieties of **1** and atoms **X** of another molecule of **1** to form the dimeric capsule.

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

| | | |
|---|---|---|
| **A.3** | **Give** the number of the hydrogen bonds in the dimeric capsule ($\mathbf{1}_2$). | 2pt |

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

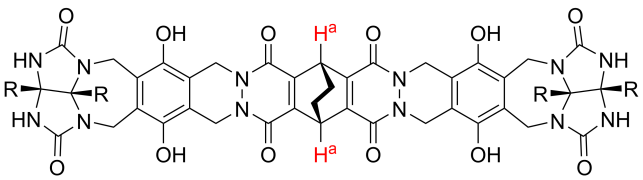
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

The equilibrium constant of the encapsulation of Z into $\mathbf{1}_2$ is given as below:

$$K_\mathrm{a} = \frac{[\mathrm{Z}@\mathbf{1}_2]}{[\mathrm{Z}][\mathbf{1}_2]} \tag{2}$$

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

Compound **2** also forms a rigid and larger dimeric capsule ($\mathbf{2}_2$). The $^1$H NMR spectrum of $\mathbf{2}_2$ 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.




**2**

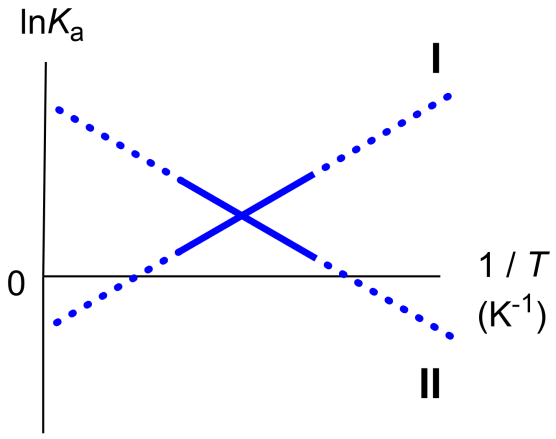
| solvent | $\delta$ (ppm) of $H^a$ |
|---|---|
| $C_6D_6$ | 4.60 |
| $C_6D_5F$ | 4.71 |
| $C_6D_6$ / $C_6D_5F$ | 4.60, 4.71, 4.82 |

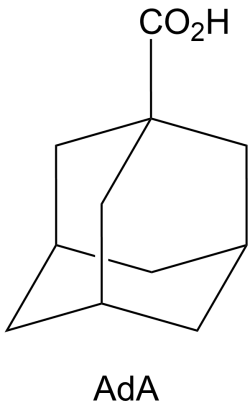
**A.4** **Determine** the number of $C_6D_6$ and $C_6D_5F$ molecules encapsulated in $\mathbf{2}_2$ giving each $H^a$ signal. 3pt

$^1$H 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.

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

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 $^1$H 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 ($\Delta S$) is ( 1 ) and enthalpy change ($\Delta H$) is ( 2 ), indicating that the driving force for the encapsulation in line **II** is ( 3 ). Therefore, line **I** corresponds to ( 4 ), and line **II** corresponds to ( 5 ).

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

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

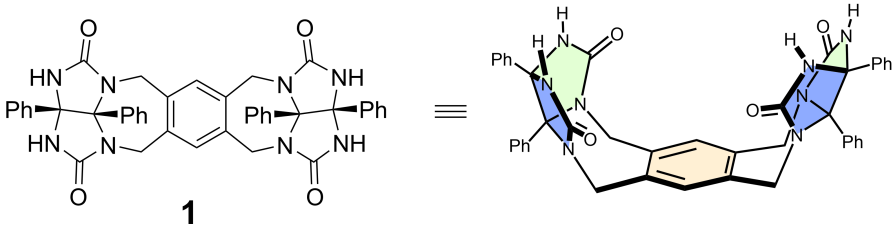
# Fordeler og ulemper med en kapsel

| 10 % av totalen | | | | | | |
|---|---|---|---|---|---|---|
| Oppgave | A.1 | A.2 | A.3 | A.4 | A.5 | **Total** |
| Poeng | 13 | 2 | 2 | 3 | 3 | **23** |
| Score | | | | | | |

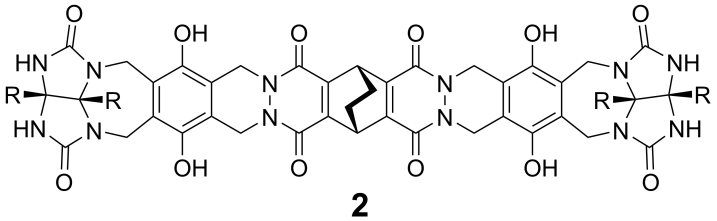
Snille barn gjør ikke dette, men hvis du løsner sømmen på en tennisball så kan du få to U-formede deler.



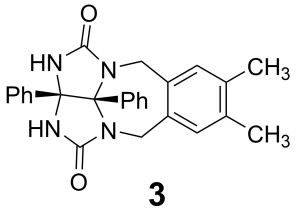
Basert på denne ideen ble forbindelse **1** og **2** syntetisert som U-formede molekyler med forskjellig størrelse. Forbindelse **3** ble laget som en sammenligning med **1,** og innkapslingsegenskapen (encapsulation behavior) til disse forbindelsene ble undersøkt.



**1**



**2**

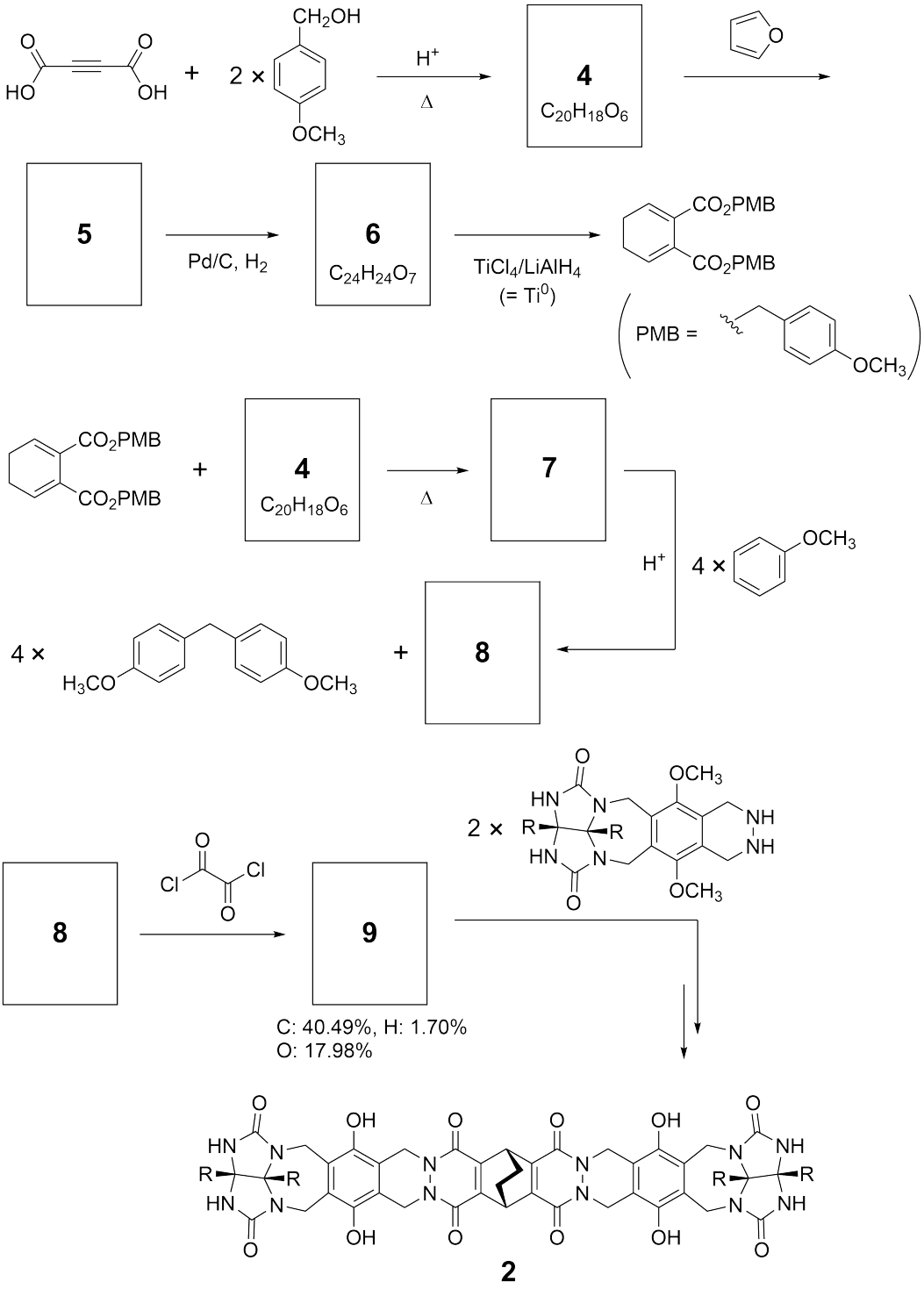


**3**

# Q9-2

Norwegian (Norway)

Den syntetiske veien for dannelse av **2** er vist under. Grunnstoffanalyse av forbindelse **9**: C; 40.49%, H; 1.70%, og O; 17.98% ved masse



| | | |
|---|---|---|
| **A.1** | **Tegn** strukturene til **4**–**9**; du behøver ikke ta med stereokjemien . Bruk ”PMB” istedenfor å tegne hele strukturen til *p*-metoksybenzyl gruppen vist i skjemaet over. | 13pt |

I massespekteret til **1** ble ionetoppen som korresponderer til dimeren ($\mathbf{1}_2$) tydelig observert, mens ionetoppen til $\mathbf{3}_2$ ble ikke observert i spektret til **3**. I $^1$H NMR spektre til en løsning av $\mathbf{1}_2$, ble alle NH protonene fra **1** observert å være kjemisk ekvivalente, og de kjemiske skiftene var signifikant forskjellig fra NH protonene til **3**. Disse dataene indikerer at det er dannet hydrogenbindinger mellom NH deler (moieties) i **1** og atom **X** i et annet molekyl av **1** som danner en dimerisk kapsel.

| | | |
|---|---|---|
| **A.2** | **Tegn sirkel/sirkler** rundt alle fornuftige atom(er) **X** i **1**. | 2pt |

| | | |
|---|---|---|
| **A.3** | **Angi** antallet hydrogenbindinger i den dimeriske kapselen ($\mathbf{1}_2$). | 2pt |

Den dimeriske kapselen av **1** ($\mathbf{1}_2$) har et indre rom hvor et passende lite molekyl Z kan bli innkapslet (encapsulated). Dette fenomenet beskrives med med følgende ligning:

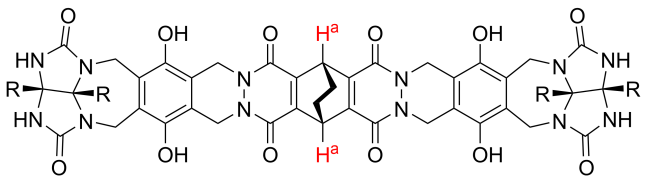
$$Z + \mathbf{1}_2 \rightarrow Z@\mathbf{1}_2 \tag{1}$$

Likevektskonstanten for innkapslingen av Z i $\mathbf{1}_2$ er gitt under:

$$K_a = \frac{[Z@\mathbf{1}_2]}{[Z][\mathbf{1}_2]} \tag{2}$$

Innkapslingen av et molekyl i en kapsel kan studeres med NMR spektroskopi. For eksempel, $\mathbf{1}_2$ i $C_6D_6$ gav forskjellige signaler i $^1H$ NMR spektre før og etter tilsetning av $CH_4$.

Forbindelse **2** danner også en rigid og større dimerisk kapsel ($\mathbf{2}_2$). $^1H$ NMR spektret til $\mathbf{2}_2$ ble målt i $C_6D_6$, $C_6D_5F$, og en $C_6D_6$/$C_6D_5F$ løst blanding, mens alle andre betingelser ble holdt konstant. De kjemiske skiftene til $H^a$ protonene til **2** i løsningsmidlene angitt ovenfor er oppsummert under, og ingen andre signaler fra $H^a$ i **2** ble observert utenom de som er oppført i tabellen. Anta at det indre av kapselen alltid er fylt med det maksimale antallet løsningsmiddelmolekyler og at hvert signal hører til en specie i den fylte kapselen.




**2**

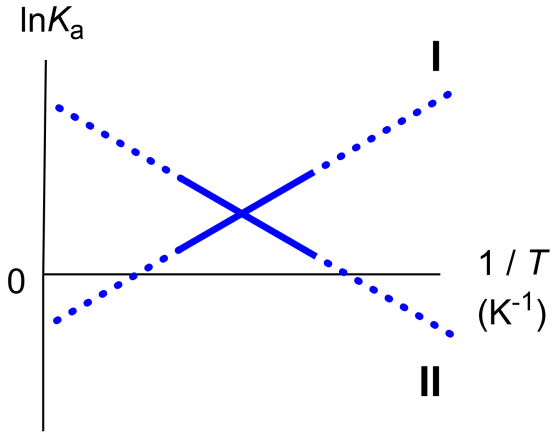
| løsningsmiddel (solvent) | $\delta$ (ppm) til $H^a$ |
|---|---|
| $C_6D_6$ | 4,60 |
| $C_6D_5F$ | 4,71 |
| $C_6D_6$ / $C_6D_5F$ | 4,60; 4,71; 4,82 |

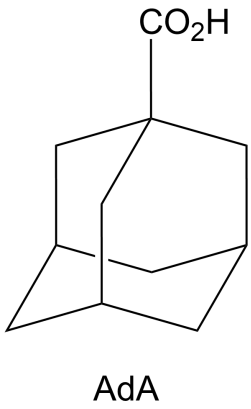
**A.4** **<u>Bestem</u>** antallet av $C_6D_6$ og $C_6D_5F$ molekyler innkapslet i $\mathbf{2}_2$ gitt hvert $H^a$ signal. 3pt

$^1$H NMR målingene i $C_6D_6$ gav at $\mathbf{2}_2$ kan inkorporere/ta opp et molekyl av 1-adamantanecarboxylic acid (AdA), og at assosiasjonskonstanten ($K_a$) som er angitt under ble bestemt for forskjellige temperaturer.

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

Tilsvarende ble $K_a$ verdiene for $CH_4$ og $\mathbf{1}_2$, gitt som ligning (2) ved forskjellige temperaturer i $C_6D_6$, også bestemt fra $^1$H NMR målinger. Plottene av de to assosiasjonskonstantene (som ln $K_a$ vs 1/$T$) er gitt under.




Ingen $C_6D_6$ molekyler er innkapslet i $\mathbf{1}_2$. I linje **II**, entropiendringen ($\Delta S$) er ( 1 ) og entalpiendringen ($\Delta H$) er ( 2 ), som indikerer at drivkraften for innkapslingen i linje i **II** er ( 3 ). Derfor hører linje **I** til ( 4 ) og linje **II** til ( 5 ).

**A.5** **Velg** det korrekte alternativet A eller B for hver av (1)–(5) i tabellen under. 3pt

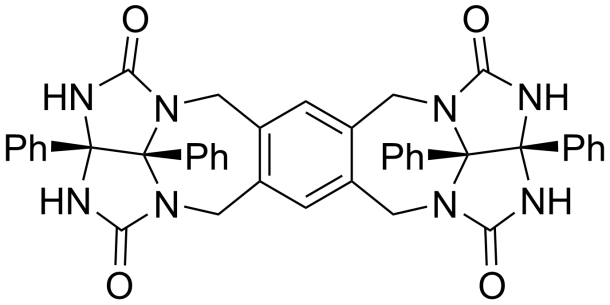
| | A | B |
|---|---|---|
| (1) | positiv | negativ |
| (2) | positiv | negativ |
| (3) | $\Delta S$ | $\Delta H$ |
| (4) | $\mathbf{1}_2$ og $CH_4$ | $\mathbf{2}_2$ og AdA |
| (5) | $\mathbf{1}_2$ og $CH_4$ | $\mathbf{2}_2$ og AdA |

# Likes and Dislikes of Capsule

**A.1** (13 pt)

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

**A.2** (2 pt)




**A.3** (2 pt)

**A.4** (3 pt)

| $\delta$ (ppm) of $H^a$ | numbers of $C_6D_6$ | numbers of $C_6D_5F$ |
|---|---|---|
| 4.60 ppm | | |
| 4.71 ppm | | |
| 4.82 ppm | | |

**A.5** (3 pt)

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

(4) : (5) :