NOR-3 C-0 C
Joachim Julian Klaussen

IChO
General instructions
Cover sheet

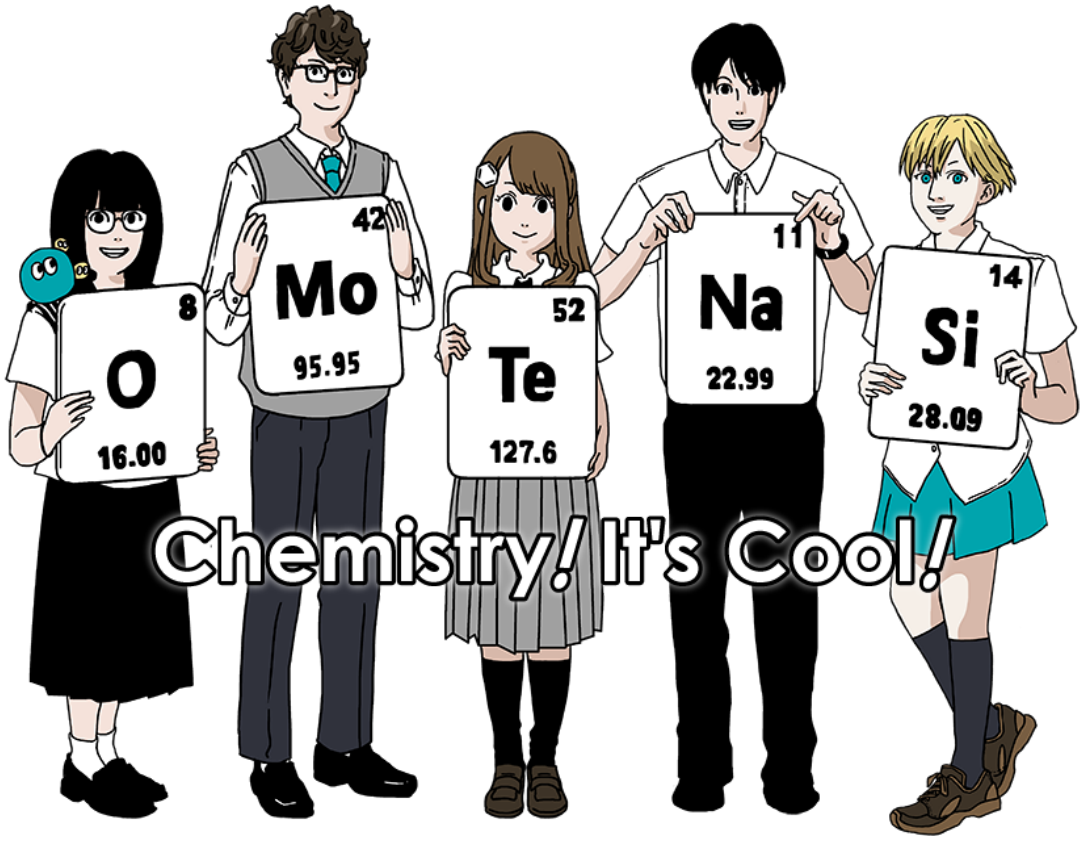
Please return this cover sheet together with all the related question sheets.

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

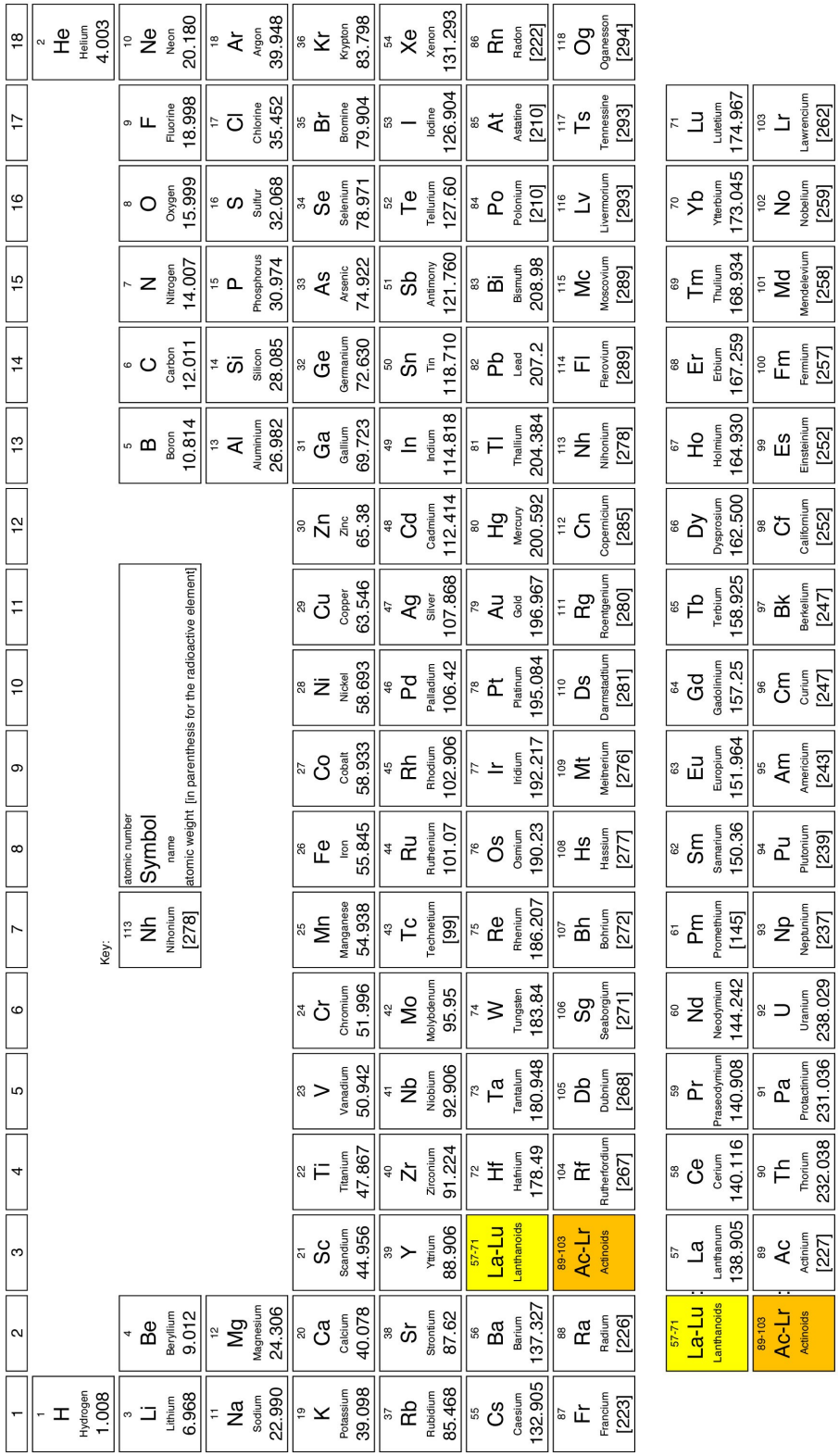
The ideal gas law	$PV = nRT$, where P is the pressure, V is the volume, n is the amount of substance, T is the absolute temperature of ideal gas.
Coulomb's law	$F = k_{\mathrm{e}} \dfrac{q_1 q_2}{r^2}$, where F is the electrostatic force, $k_{\mathrm{e}} (\simeq 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}})$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

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

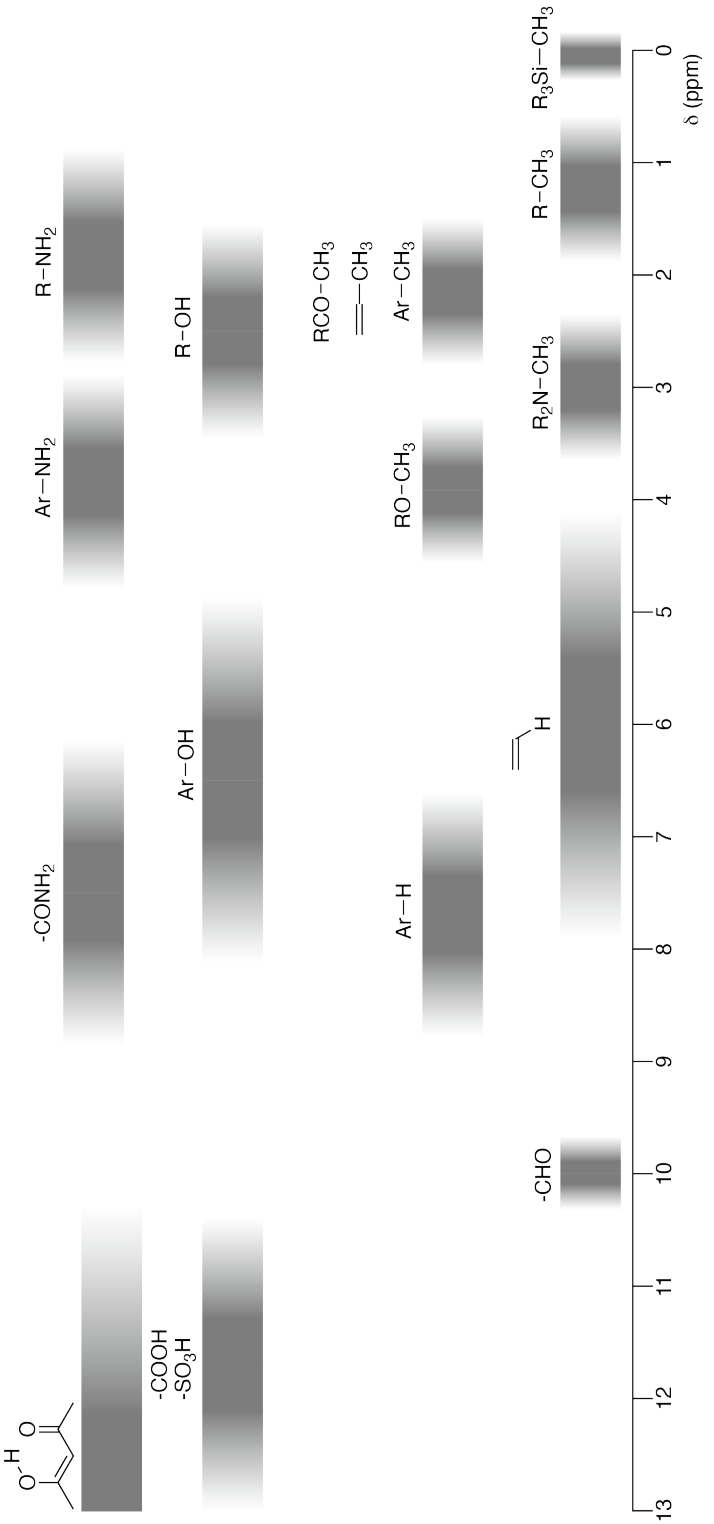
G0-6

English (Official)

Periodic Table



^{1}H NMR Chemical Shifts



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

G0-1

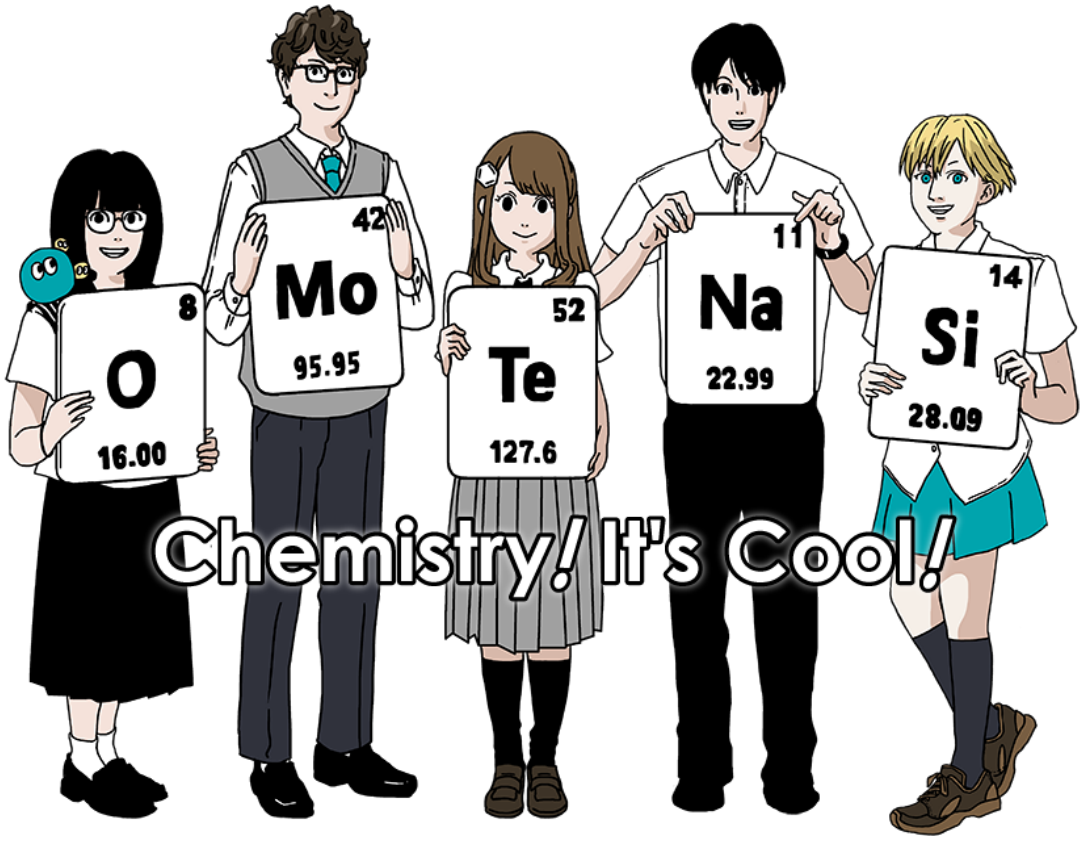
Norwegian (Norway)

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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Ligninger

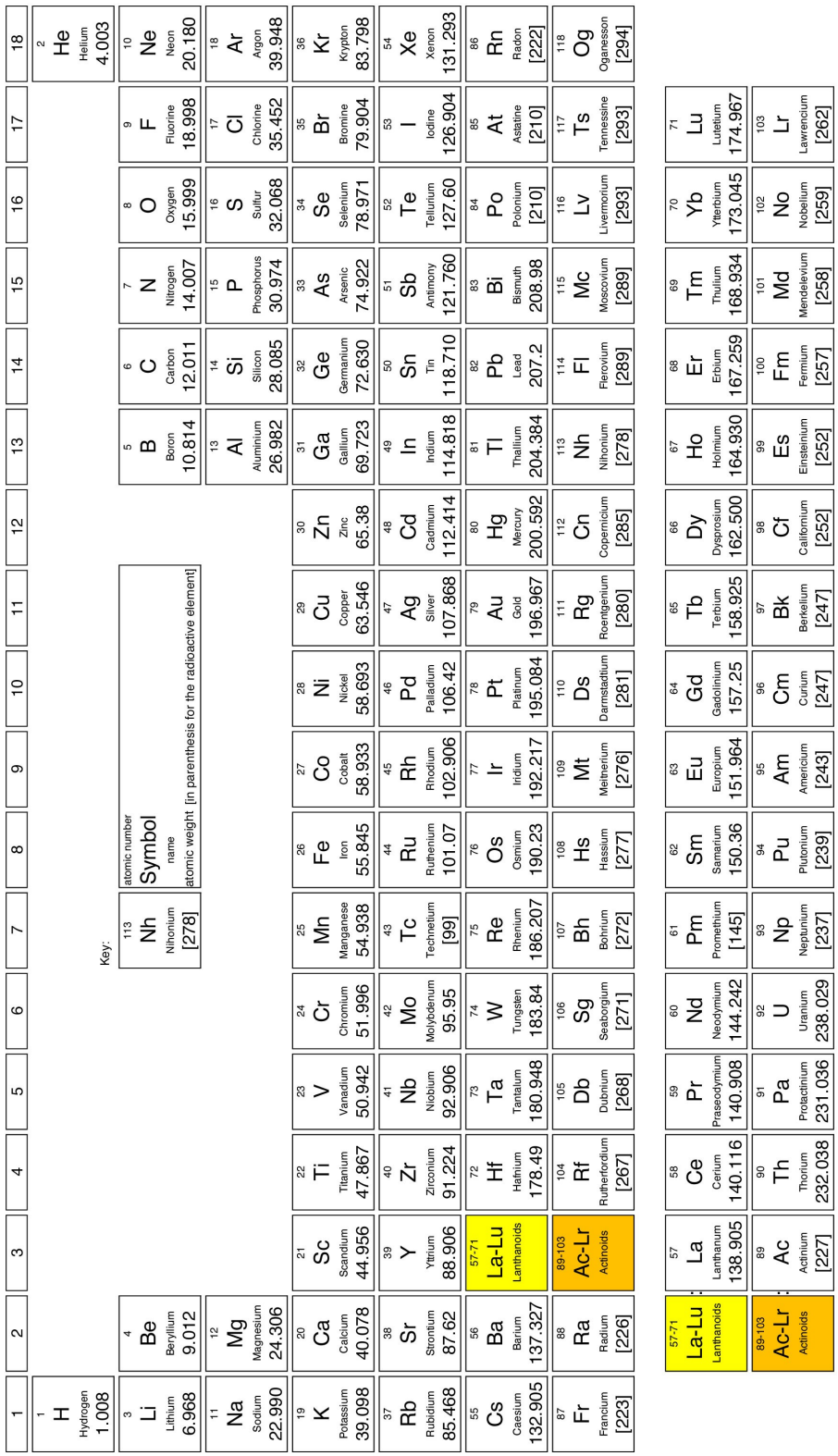
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Approximation equation that can be used to solve problems	When $x \ll 1$, $\frac{1}{1-x} \simeq 1 + x$

G0-6

Norwegian (Norway)

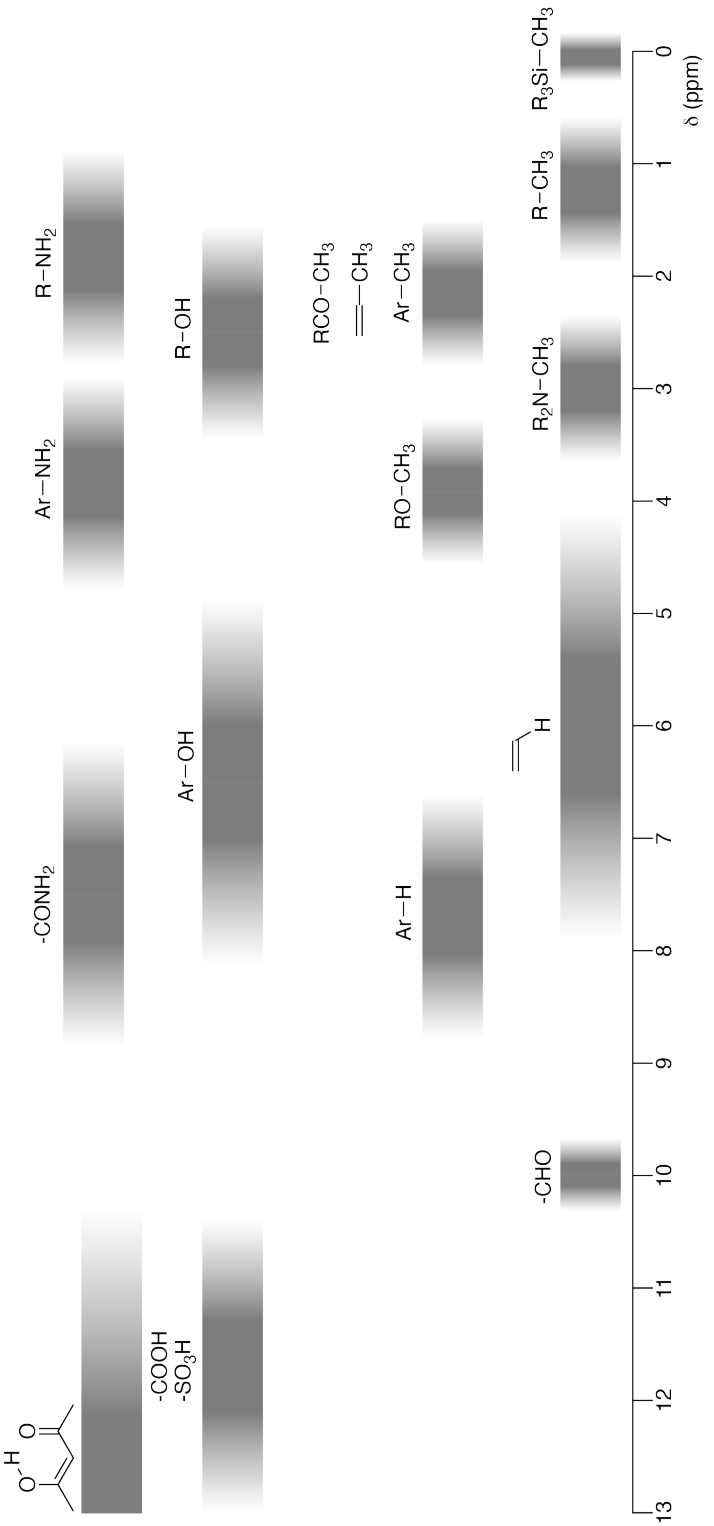
Periodesystemet



G0-7

Norwegian (Norway)

^{1}H NMR kjemiske skift



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

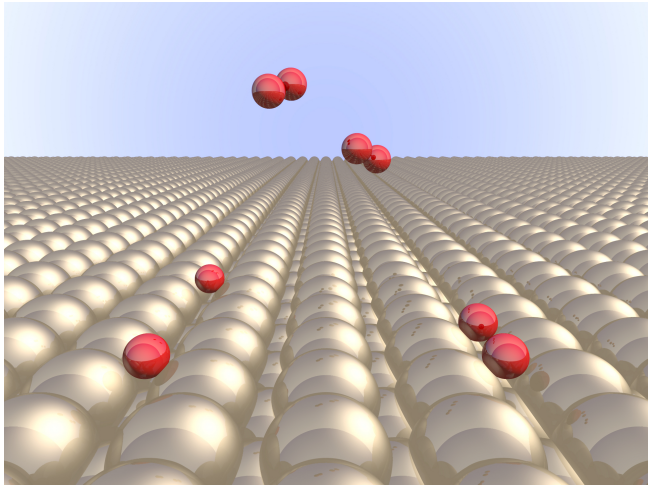
NOR-3 C-1 C
Joachim Julian Klaussen

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.

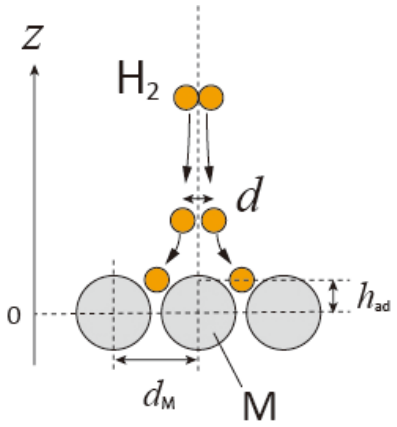


Fig.1 Definition of variables. Drawing is not in scale.

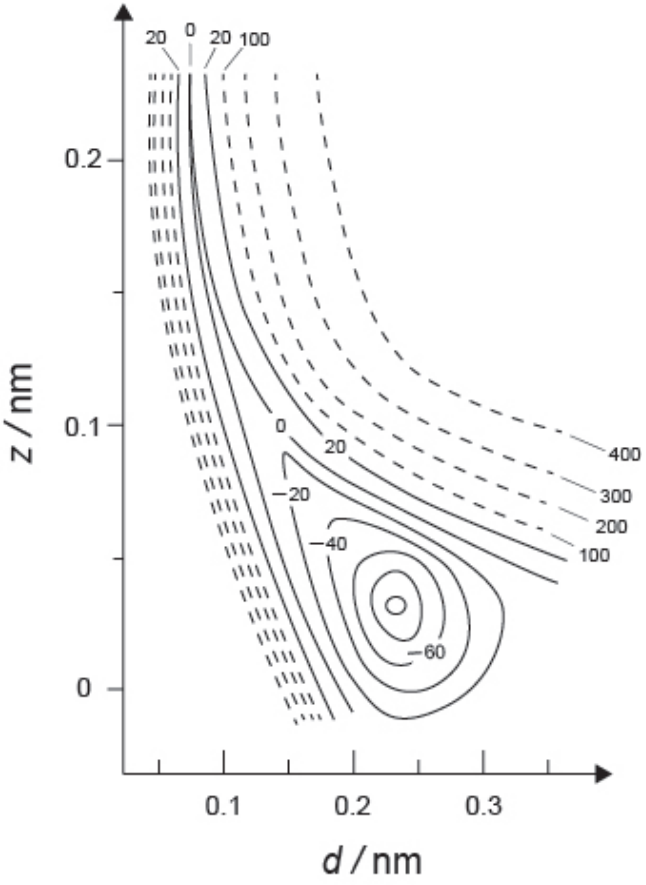


Fig.2

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

B.1 r_3 can be expressed as: 5pt

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

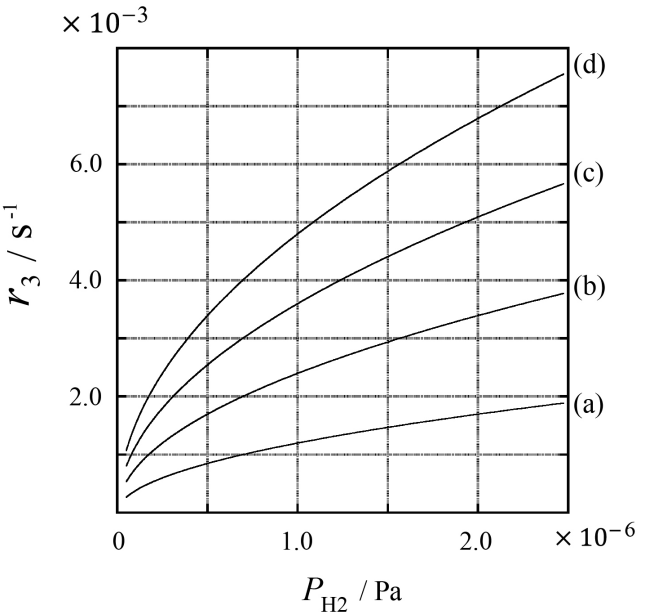
Express C using k_1 and k_2.

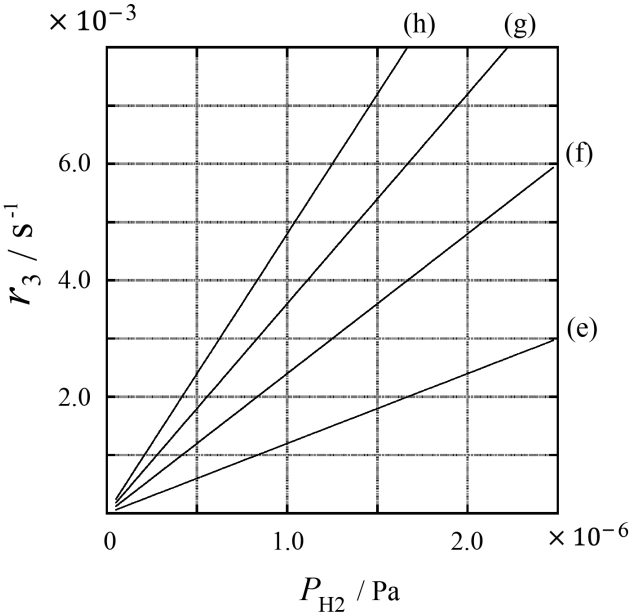
A metal sample with a surface area of $S = 1.0 \times 10^{-3}$ m^2 was placed in a container (1L = 1.0×10^{-3} m^3) with H_2 ($P_{H_2} = 1.0 \times 10^2$ Pa). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}$ m^{-2}. The surface temperature was kept at $T = 400$ 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 1.0×10^2 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

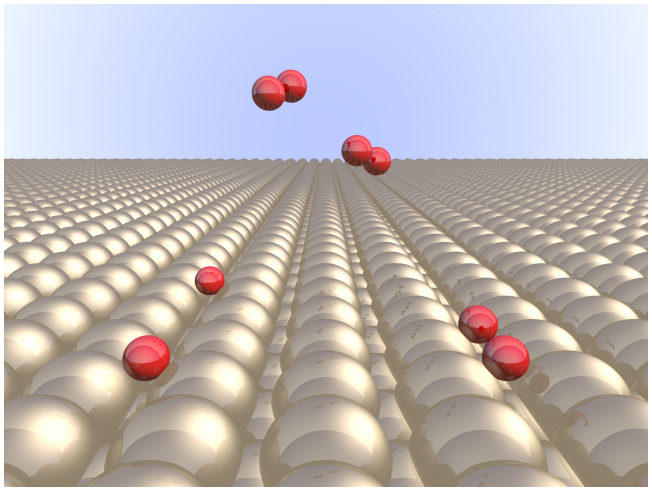
B.4 At a different T, $C = 2.5 \times 10^3$ Pa^{-1} and $k_3 = 4.8 \times 10^{-2}$ s^{-1}are given. For r_3 as a function of P_{H_2}at this temperature, **select** the correct plot from (a)–(h). 3pt





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.

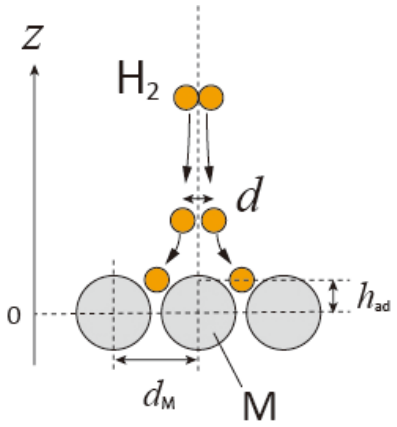


Fig. 1. Definisjon av variabler. Størrelsesforholdene er ikke riktige på tegningen.

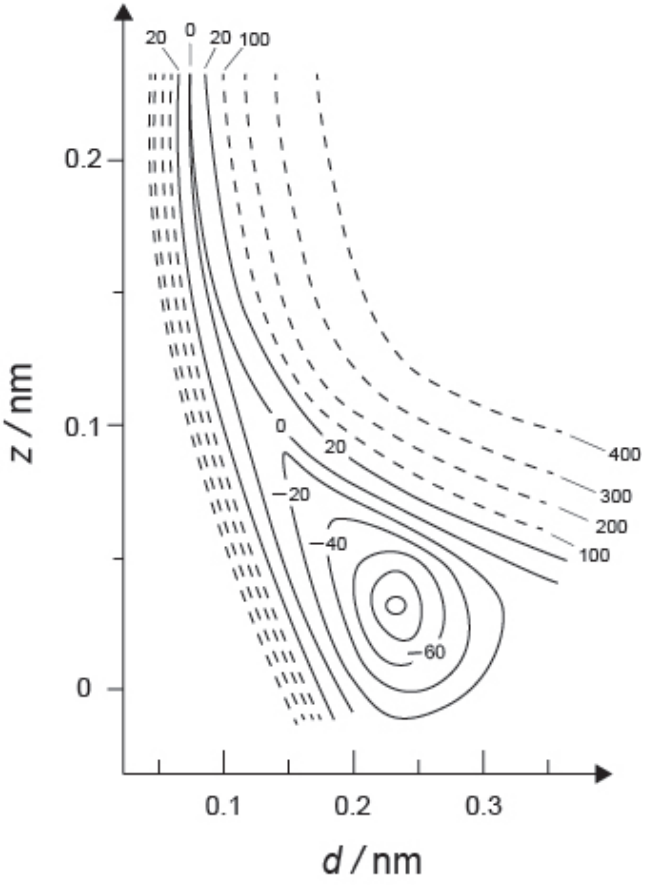


Fig.2

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.

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

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

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 [$\mathrm{s^{-1}\ Pa^{-1}}$], 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 θ forblir konstant.

B.1 r_3 kan uttrykkes som: 5pt

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

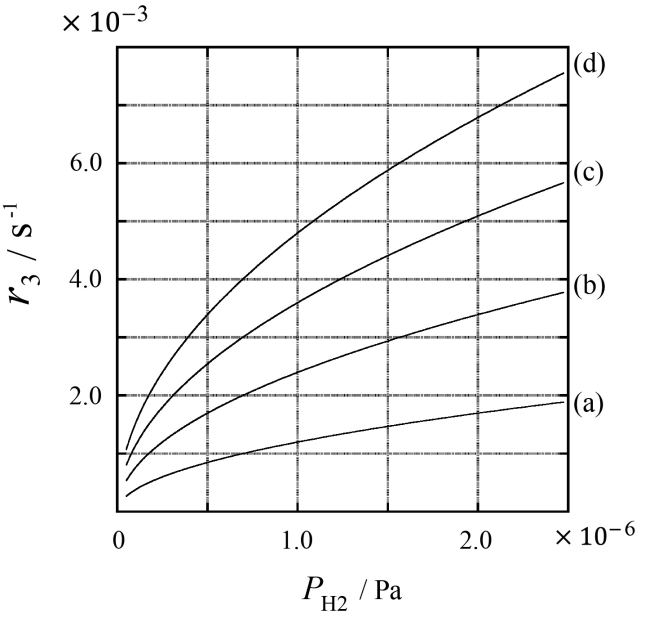
Uttrykk C ved hjelp av k_1 og k_2.

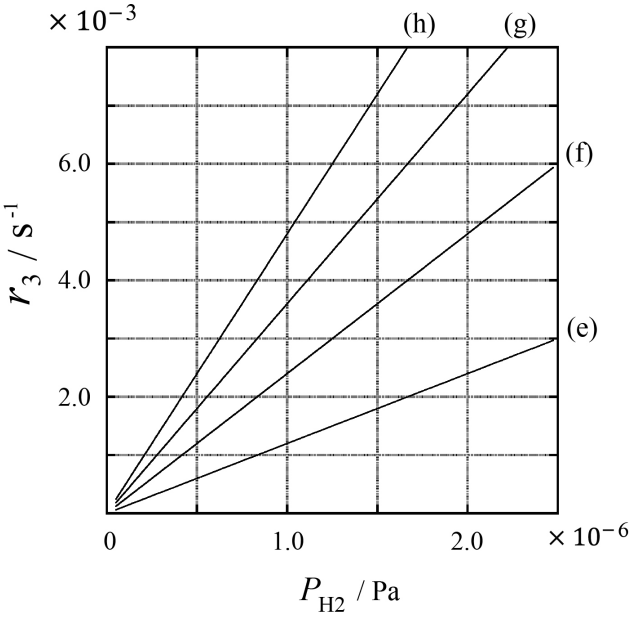
En metallbit med overflateareal $S = 1.0 \times 10^{-3}$ m^2 ble plassert i en beholder (1 L = 1.0×10^{-3} m^3) med H_2 ($P_{H_2} = 1.0 \times 10^2$ Pa). Tettheten av plasser på overflaten hvor hydrogenatomer kan adsorberes var $N = 1.3 \times 10^{18}$ m^{-2}. Overflatetemperaturen ble holdt ved $T = 400$ 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 1.0×10^2 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 på en metalloverflate

Del A

A.1 (6 pt)

(i)	(ii)	(iii)

A.2 (4 pt)

(i)	(ii)

Del 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-3 C-2 C
NOR-3 C-2 C-1 Joachim Julian Klaussen

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, ΔH, 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 ΔH 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 ν [s^{-1}] is expressed as:

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

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

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

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

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

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

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

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

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

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** Δ_{D_2} with natural D abundance when the isotopic exchange is in equilibrium at the temperature where K in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, respectively. 10pt

In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of CO_2 molecules with molecular weights of 44 and 47, which are described as $CO_2[44]$ and $CO_2[47]$ below. The quantity Δ_{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 Δ_{47} is determined as follows, where T is given as the absolute temperature in units of K:

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

A.4 The R_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-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, ΔH, 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 ΔH 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 ν [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 μ 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** ΔH 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 ΔH.
- 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 Δ_{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** Δ_{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 1.5576×10^{-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 Δ_{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

Δ_{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 4.50865×10^{-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

En tidskapsel for isotoper

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-3 C-3 C
Joachim Julian Klaussen

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

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

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.

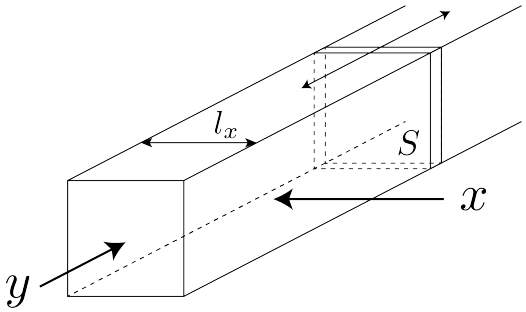
A.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. **Determine** the ratio $\varepsilon_{HA}/\varepsilon_{A^-}$, where ε_{HA} and ε_{A^-}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

Part B

Let us consider the following equilibrium in the gas phase.

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

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 ε, n, V, and l are the absorption coefficient, amount of the gas in moles, volume of the gas, and optical path length, respectively. Assume that all components of the gas mixture behave as ideal gases.



Use the following definitions if necessary.

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

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

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

Q3-1

Norwegian (Norway)

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 1.00×10^{-2} mol L^{-1}, 1.00×10^{-3} mol L^{-1}, og 1.00×10^{-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.

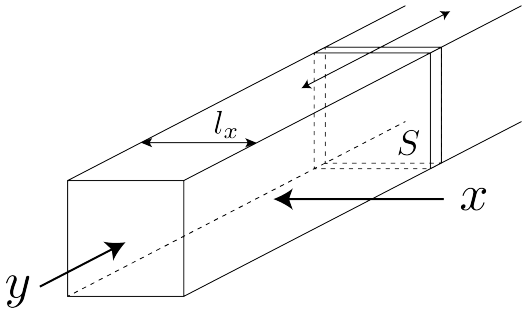
A.1 Absorbansen til **X** var A_1 ved bølgelengde λ_1. Så blir løsningen **X** fortynnet til dobbelt så stort volum ved hjelp av saltsyre med pH = 2,500. Etter fortynningen var absorbansen fortsatt A_1 ved λ_1. **Bestem** forholdet $\varepsilon_{HA}/\varepsilon_{A^-}$, hvor ε_{HA} og ε_{A^-} representerer absorpsjonskoeffisienten til henholdsvis HA og A^-, ved λ_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 ε, 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_{D}	p_{M}
Stoffmengde i mol	n_0	0	n_{D}	n_{M}
Volum	V_0		V	

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

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

Lambert-Beers lov?

Del A

A.1 (10 pt)

(Fortsetter på neste side)

A.1 (cont.)

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

Del B

B.1 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

B.2 (6 pt)

$\varepsilon_D/\varepsilon_M =$ _____

NOR-3 C-4 C
Joachim Julian Klaussen

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°.

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

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 $-38\,^{\circ}$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 $-38\,^{\circ}$C and 1 bar.

B.4 **Calculate** the Gibbs energy change for reaction (6) at $25\,^{\circ}$C. Note that the standard reduction potentials, $E^{\circ}(\mathrm{Zn/Zn^{2+}})$ and $E^{\circ}(\mathrm{O_2/H_2O})$ at $25\,^{\circ}$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°, (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 $-38\,^{\circ}$C (i februar) og høyden er 3776 m. Det atmosfæriske trykket er gitt ved 5pt

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

ved høyden h [m] og temperaturen T [°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, $E^{\circ}(\text{Zn}/\text{Zn}^{2+})$ og $E^{\circ}(\text{O}_2/\text{H}_2\text{O})$ ved $25\,^{\circ}$C og 1 bar er gitt i (10) og (11). 9pt

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

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

Redokskjemien til sink

Del A

A.1 (6 pt)

_____ < pH < _____

A.2 (5 pt)

_____ %

Del B

B.1 (4 pt)

$p_{H_2O=}$ _____ bar

B.2 (3 pt)

_____ g

B.3 (5 pt)

V

B.4 (9 pt)

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

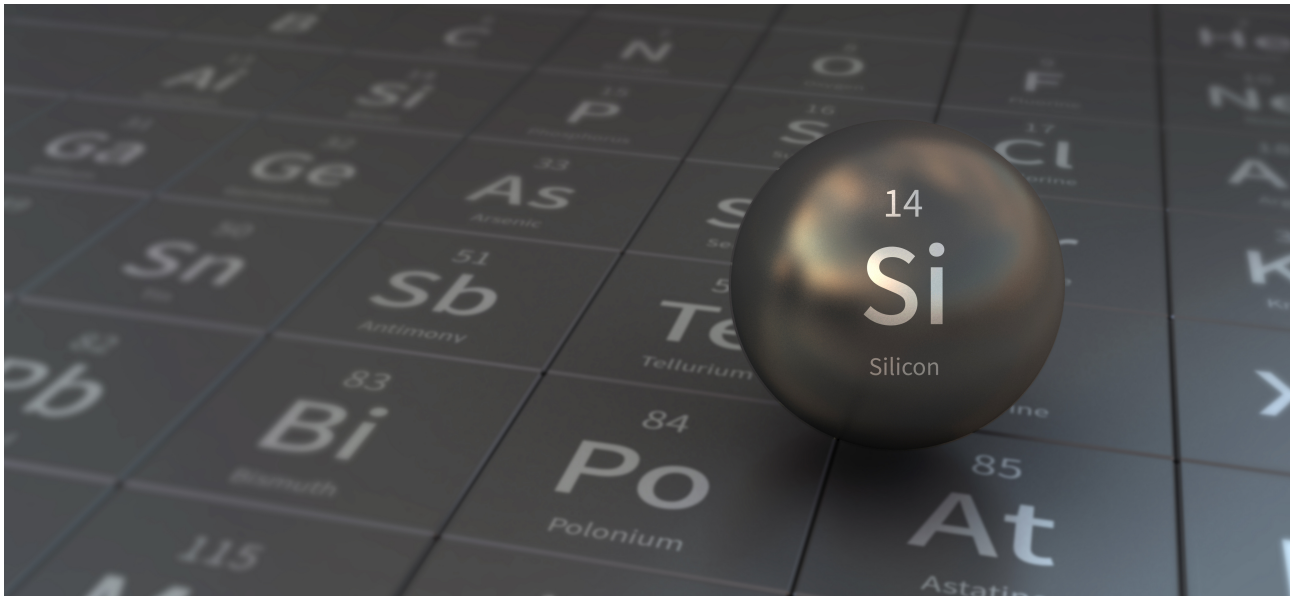
NOR-3 C-5 C
Joachim Julian Klaussen

IChO
Problem 5
Cover sheet

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

Mysterious Silicon

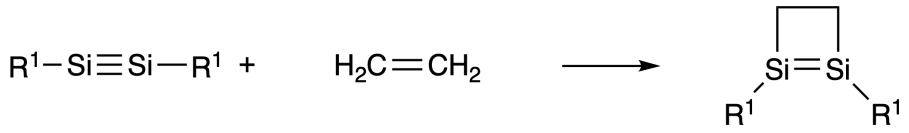
12 % of the total								
Question	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Points	9	7	6	10	5	15	8	**60**
Score								



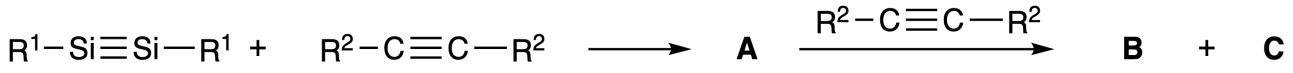
Although silicon is also a group 14 element like carbon, their properties differ significantly.

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

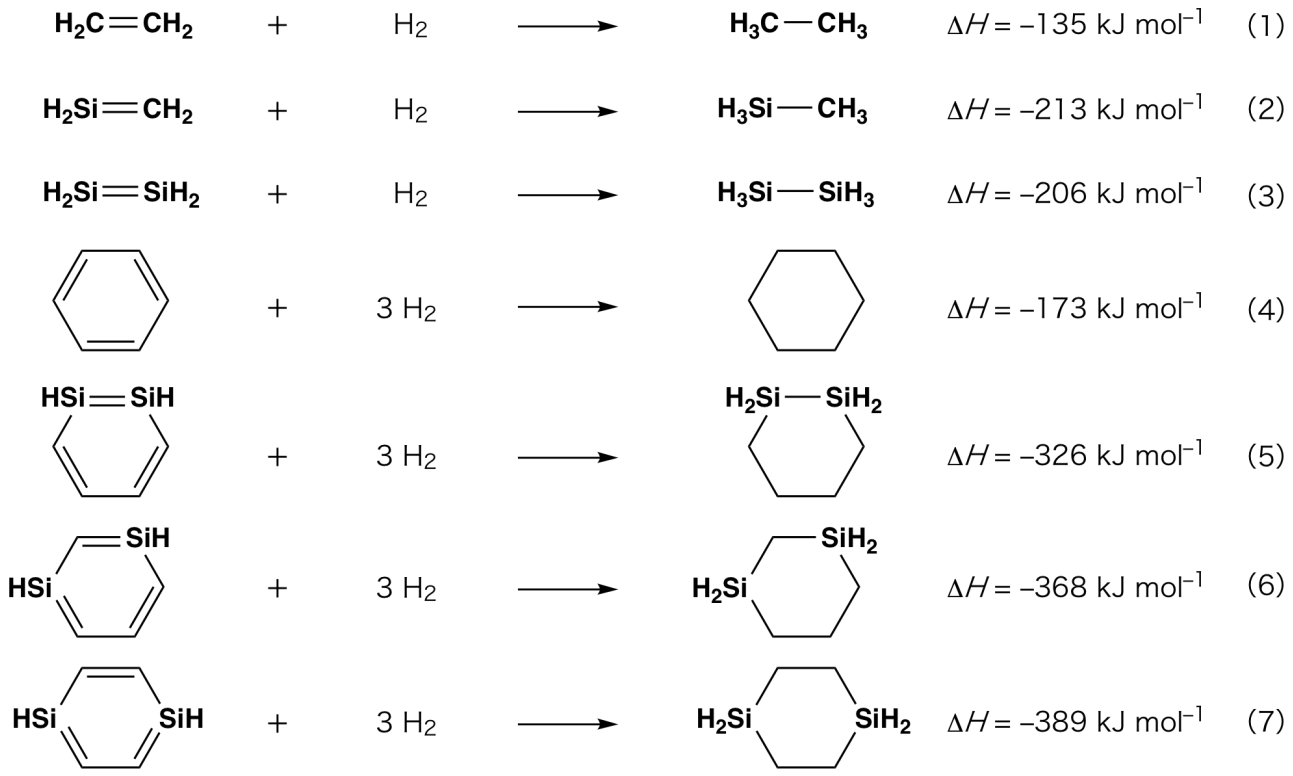


Fig. 1

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

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

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

Part B

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

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

- **Standardization of Na_2SiF_6 solution** :

· Preparation

Aqueous solution **F**: 0.855 g of Na_2SiF_6 (188.053 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.

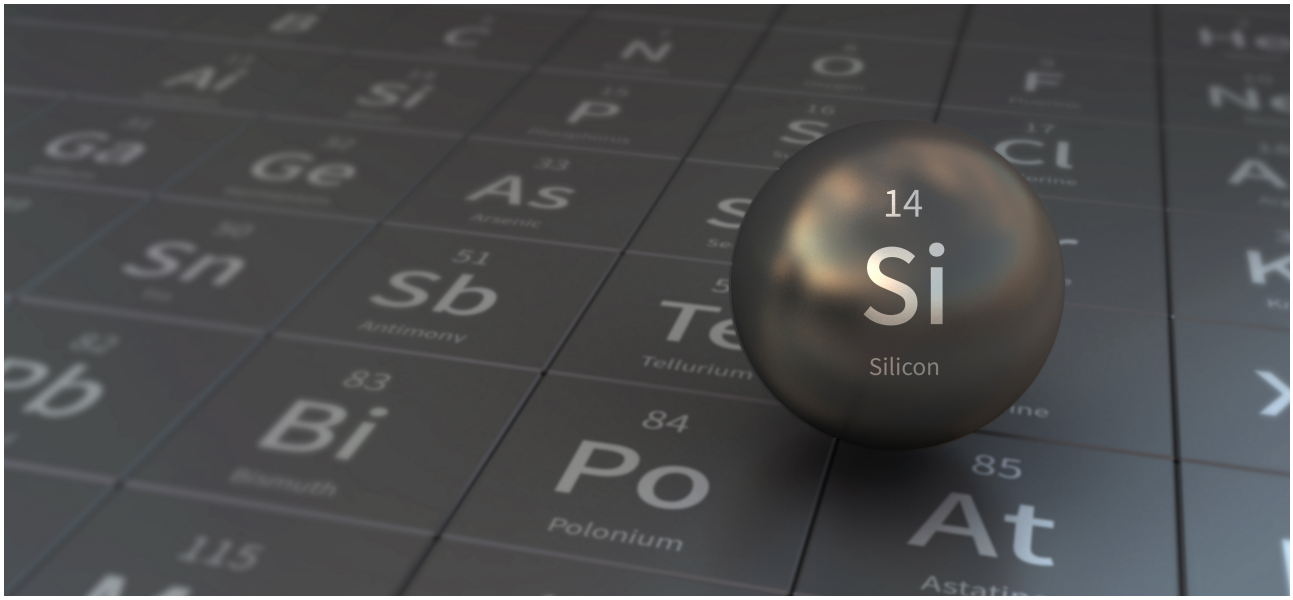
It should be noted here that the coexistence of NaCl or SiO_2 has no effect on the precipitation titration.

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

Mystisk silisium

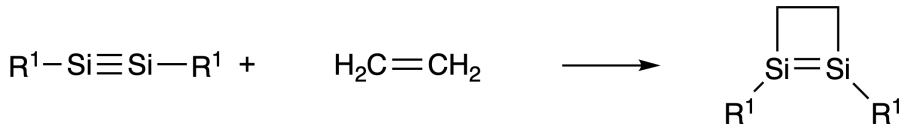
12 % av totalen								
Oppgave	A.1	A.2	A.3	A.4	B.1	B.2	B.3	**Total**
Poeng	9	7	6	10	5	15	8	**60**
Score								



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

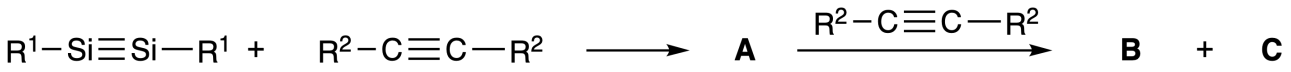
Del A

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 $(R^1–Si)_2(R^2–C)_4$.



^{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

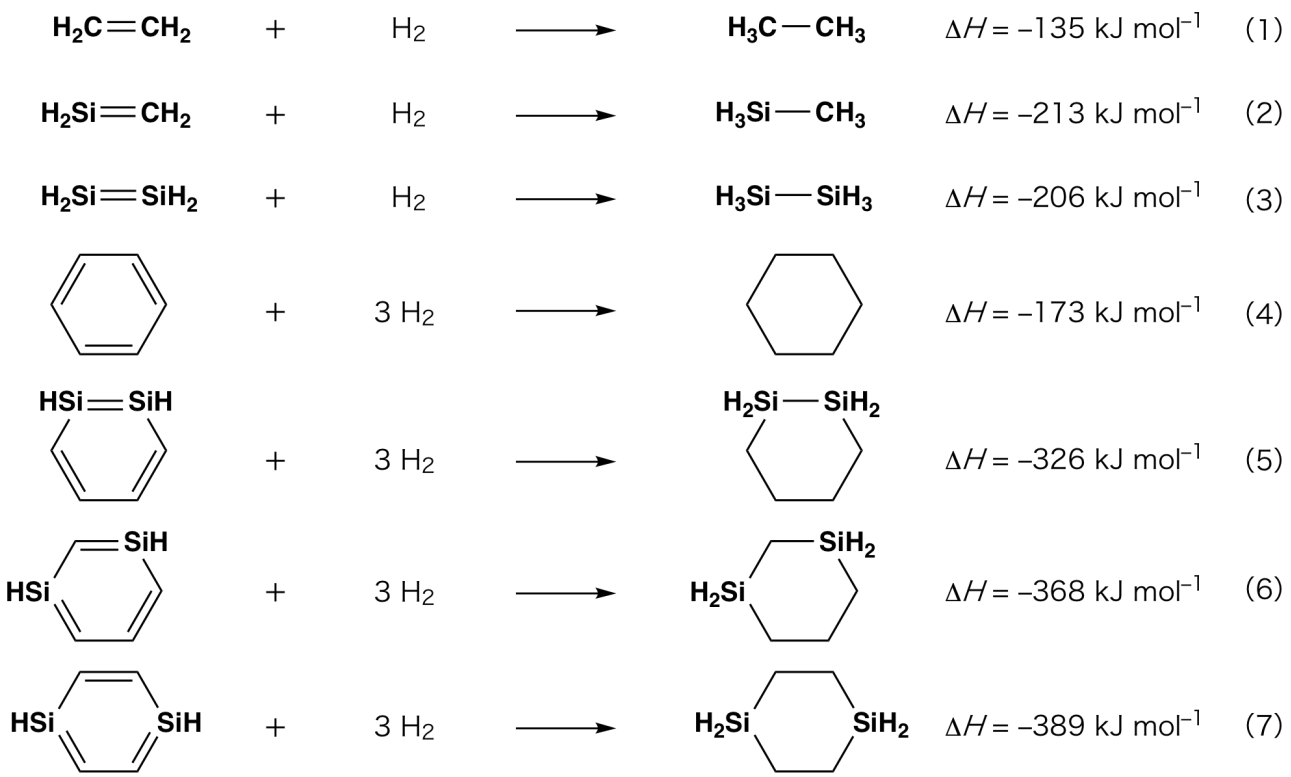


Fig. 1

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** ΔH for omdannelsen fra **D** til **E**. Anta at ΔH ikke er avhengig av temperatur. 6pt

Isomeriseringen fra **C** til **D** og **E** går gjennom en transformering av π-bindinger til σ-bindinger uten å bryte noen σ-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 ºC 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

Mystisk silisium

Del 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)

ΔH = _____ kJ mol^{-1}

A.4 (10 pt)

D (5 pt)	**E** (5 pt)

Del B

B.1 (5 pt)

B.2 (15 pt)

(Fortsetter på neste side)

B.2 (cont.)

NaCl : g, Na_2SiF_6 : g

B.3 (8 pt)

CF_3Cl : _____ g

NOR-3 C-6 C
Joachim Julian Klaussen

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:

$$D = \frac{[\mathrm{M}]_\mathrm{s}}{[\mathrm{M}]_\mathrm{l}}$$

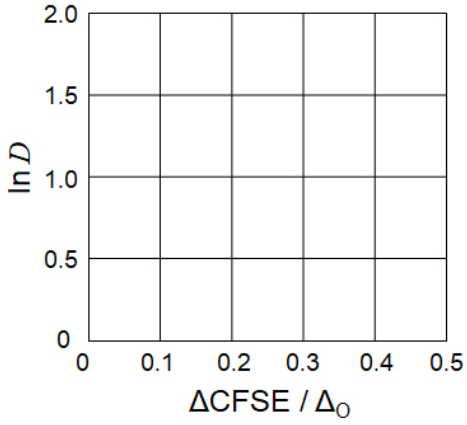
where $[M]_s$ and $[M]_l$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of $Cr^{2+}$and Mn^{2+} as examples.

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

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

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

A.2 A linear relationship is observed by plotting $\ln D$ against $\Delta CFSE / \Delta_O$ in the Cartesian coordinate system shown below. 3pt
Estimate D for Co^{2+}.



Metal oxides MO (M: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure wherein the M^{n+} adopts an O_h geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is mainly governed by the Coulomb interactions based on the radius and charge of the ions and some contributions from the CFSE of M^{n+} in the O_h field.

A.3 **Choose** the appropriate set of lattice enthalpies [kJ mol^{-1}] from one of the options (a) to (f). 3pt

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

Part B

A mixed oxide **A**, which contains La^{3+} and Cu^{2+}, crystallizes in a tetragonal unit cell shown in Fig.1. In the $[CuO_6]$ 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}).

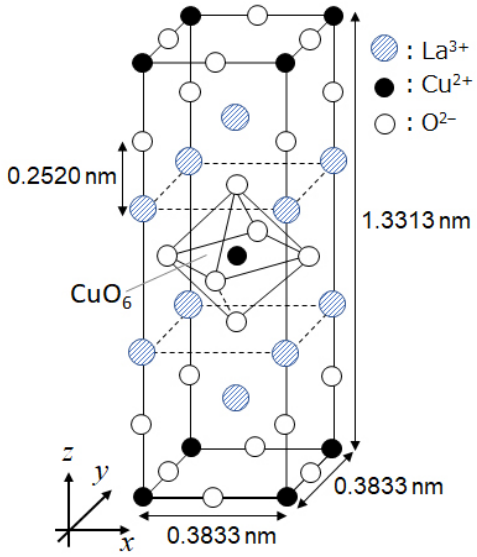


Fig. 1

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**, 2.05×10^{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 θ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The θ is 0° for **L1**. Note that hydrogen atoms are not shown in Fig. 2.

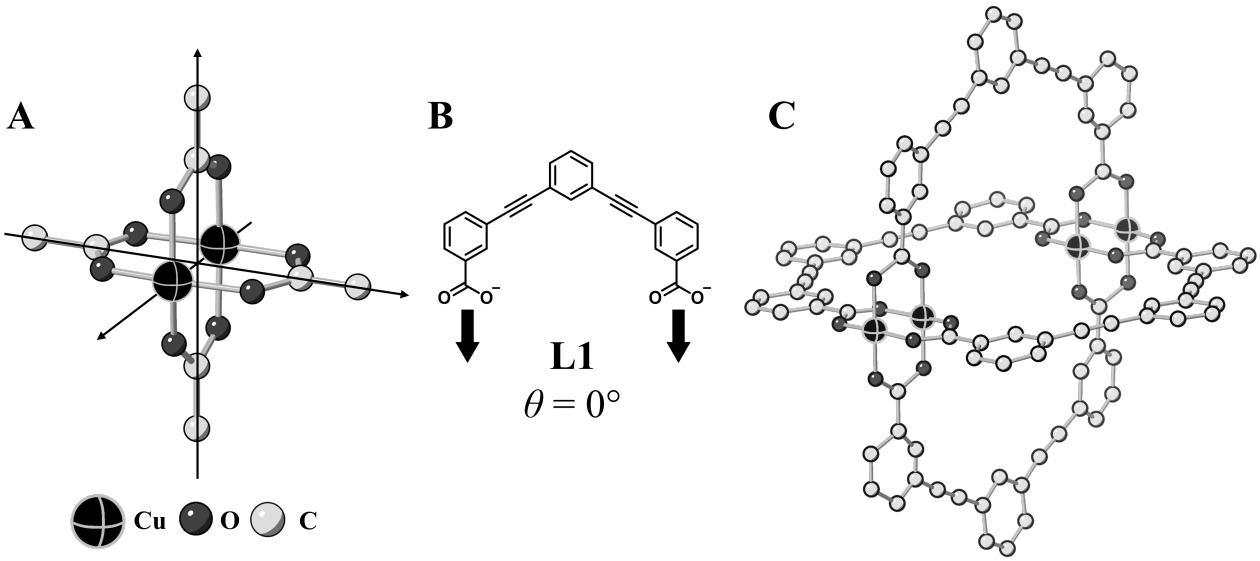
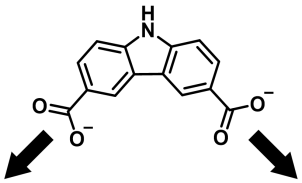


Fig. 2

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

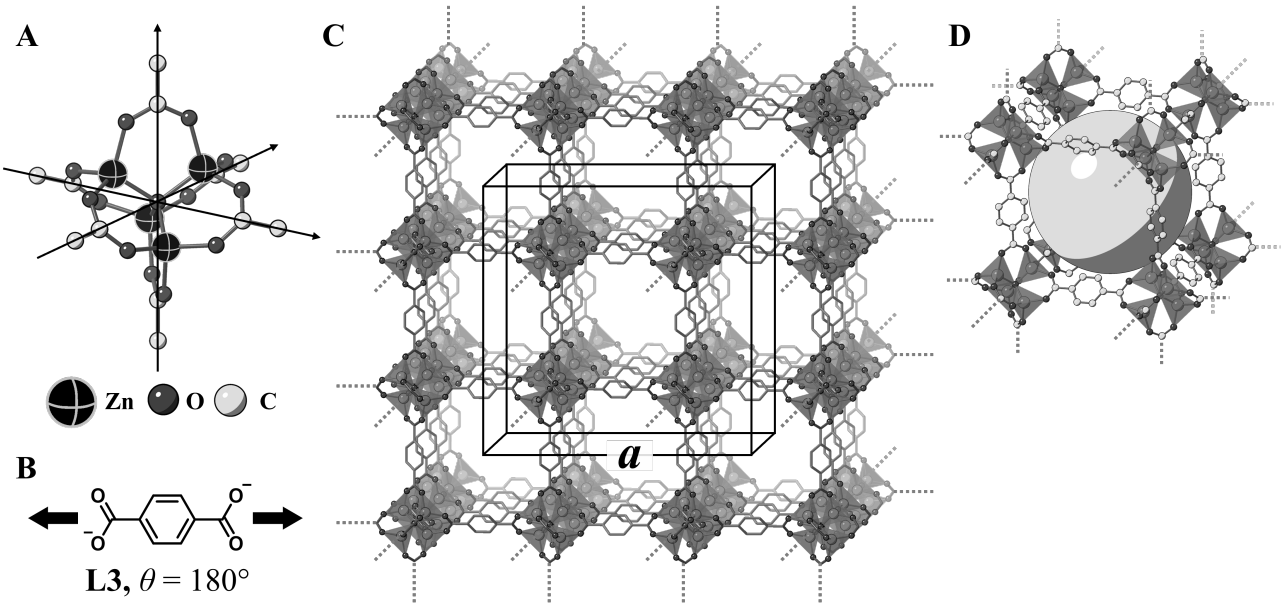


Fig. 3

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 3.0×10^2 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:

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

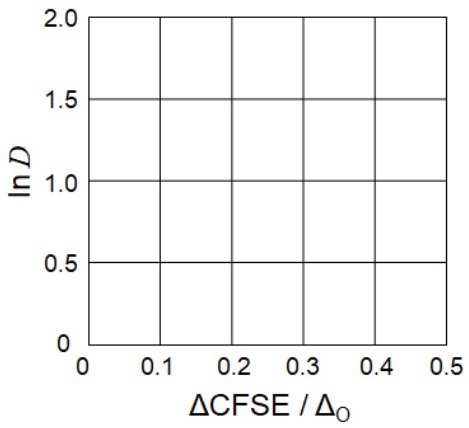
hvor $[M]_s$ og $[M]_l$ er konsentrasjonen av M^{n+} i henholdsvis silikatmineraler og magma. Tabellen under viser verdier for D for Cr^{2+} og Mn^{2+} som eksempler.

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

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

A.1 **Beregn** $|CFSE^O - CFSE^T|$ = ΔCFSE som en funksjon av Δ_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 / Δ_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

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.

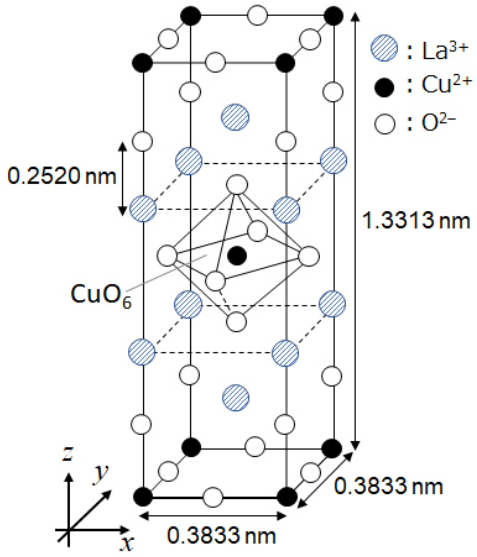


Fig. 1

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 2.05×10^{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 θ mellom koordinasjonsretningene til de to karboksylatene, vist med piler i Fig. 2B, bestemmer strukturen til bur-komplekset. Vinkelen θ er 0° for **L1**. Legg merke til at hydrogenatomene ikke er vist i Fig. 2.

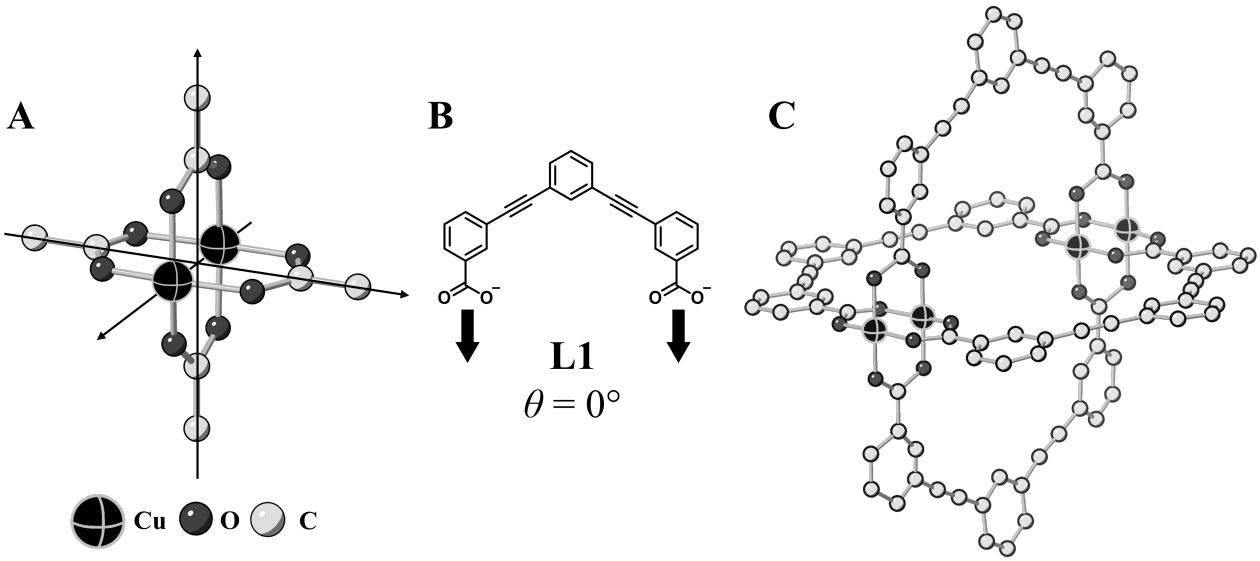
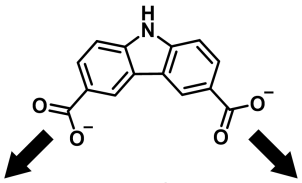


Fig. 2

Q6-5

Norwegian (Norway)

C.1 Vinkelen θ 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**, θ = 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.

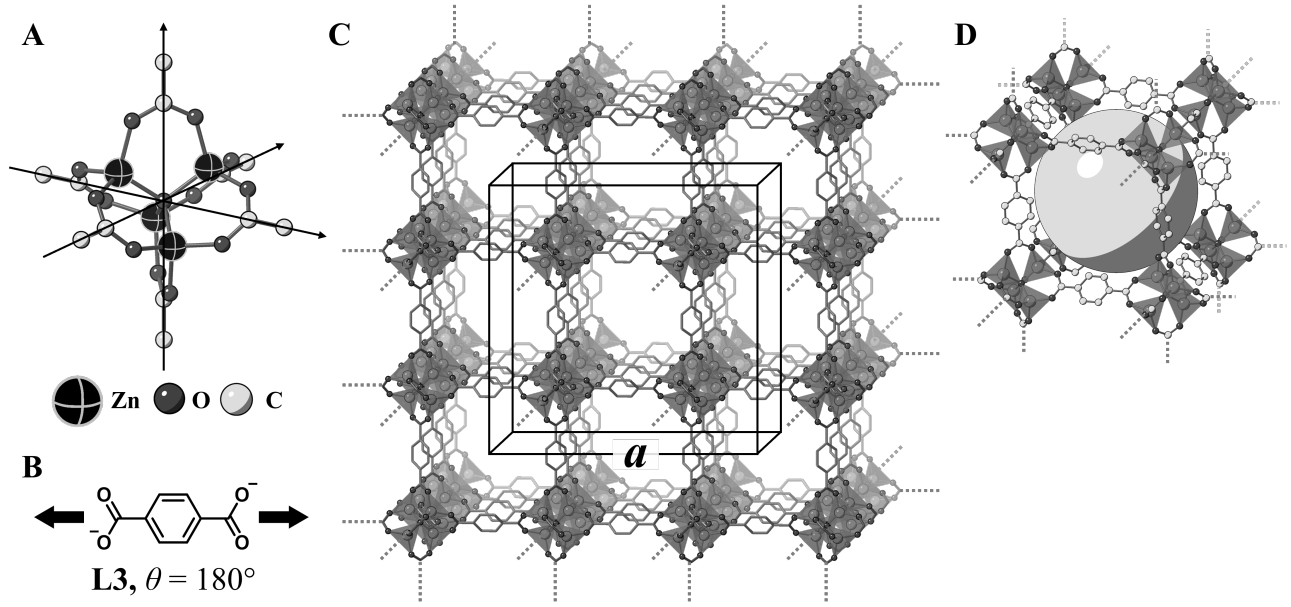


Fig. 3

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 3.0×10^2 mL CO_2-gass i porene ved 1 bar og 25 °C. **Beregn** det gjennomsnittlige antallet CO_2-molekyler per pore.	5pt

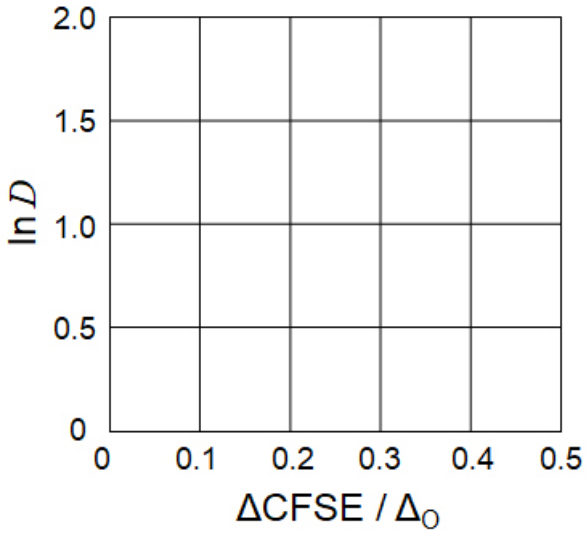
Kjemien til innskuddsmetallene i fast fase

Del A

A.1 (6 pt)

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

A.2 (3 pt)



D : _____

A.3 (3 pt)

_____

Del B

B.1 (6 pt)

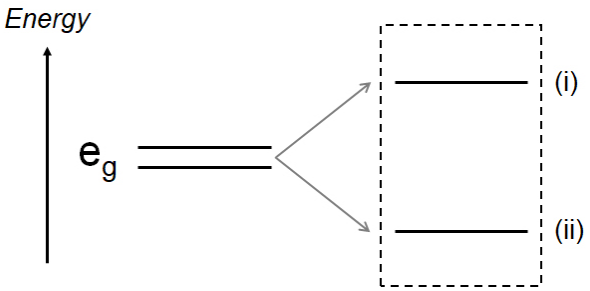
A : _____, B : _____

B.2 (4 pt)

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

B.3 (4 pt)

(i) : _____ , (ii) : _____



B.4 (4 pt)

_____ %

Del C

C.1 (5 pt)

$n =$ _____, $m =$ _____

C.2 (5 pt)

$a =$ _____ cm

C.3 (5 pt)

NOR-3 C-7 C
Joachim Julian Klaussen

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.



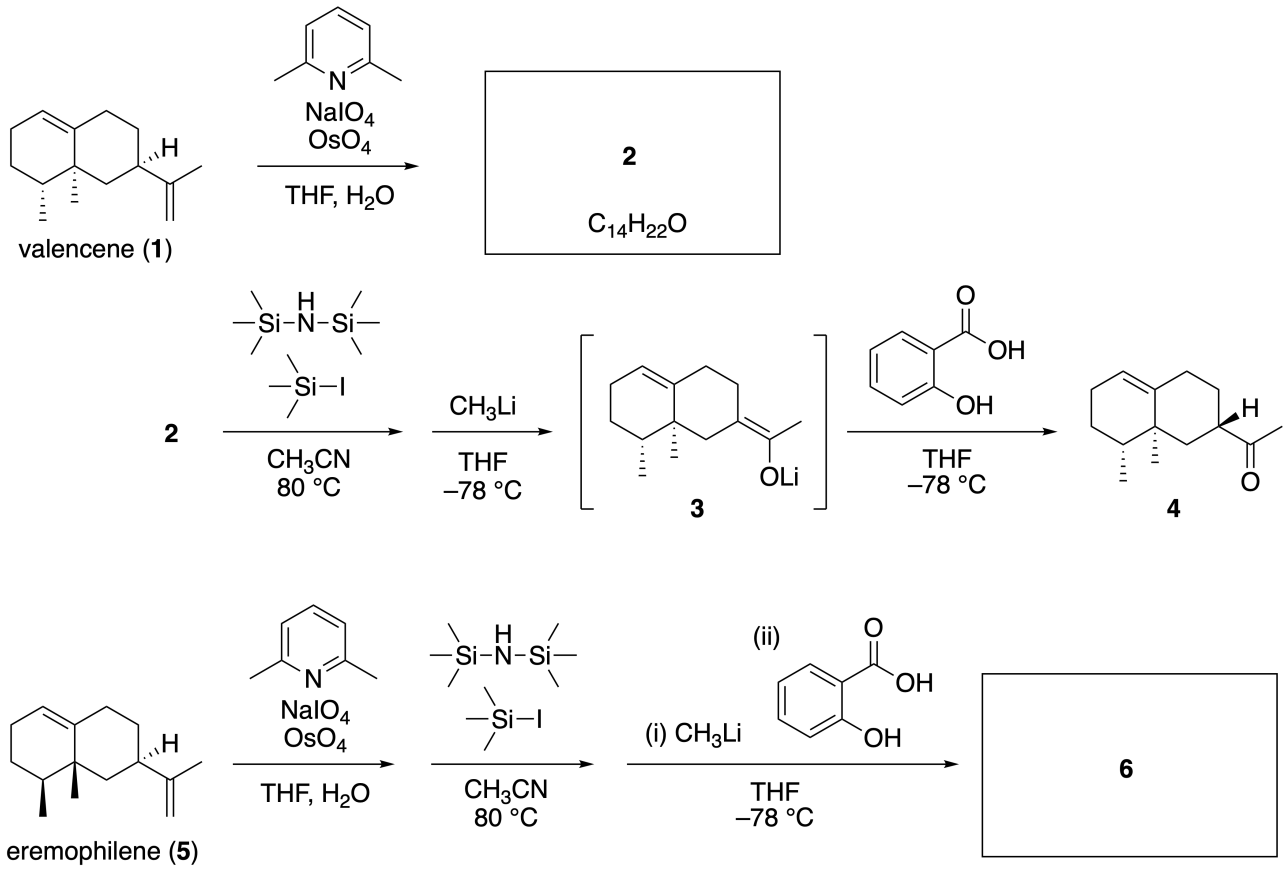
Photo courtesy: Tohoku Univ.

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.



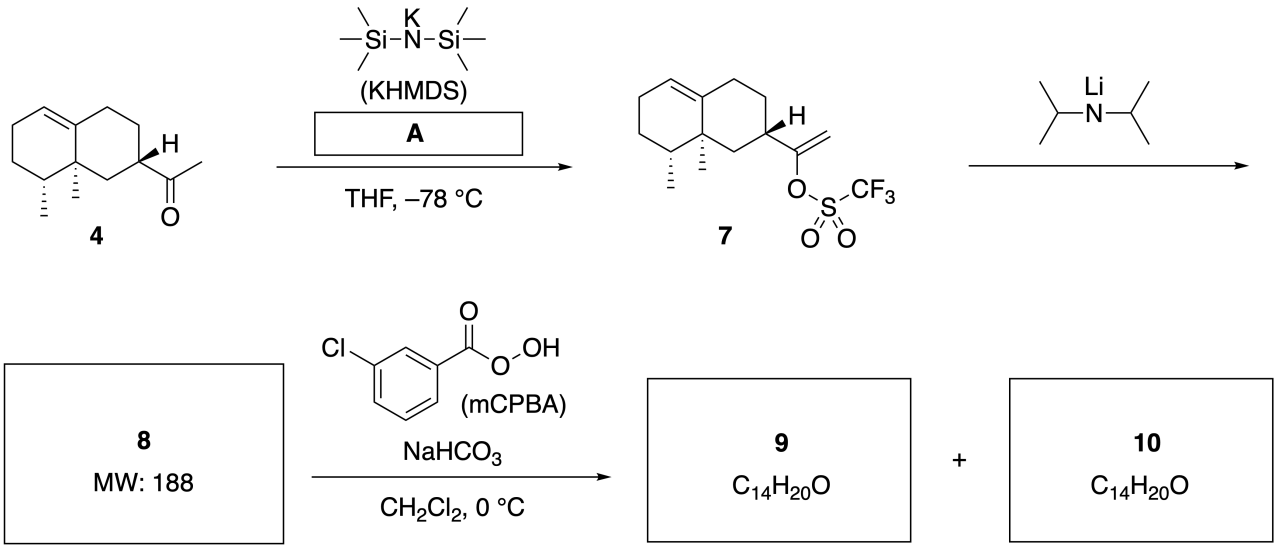
Inula linariifolia

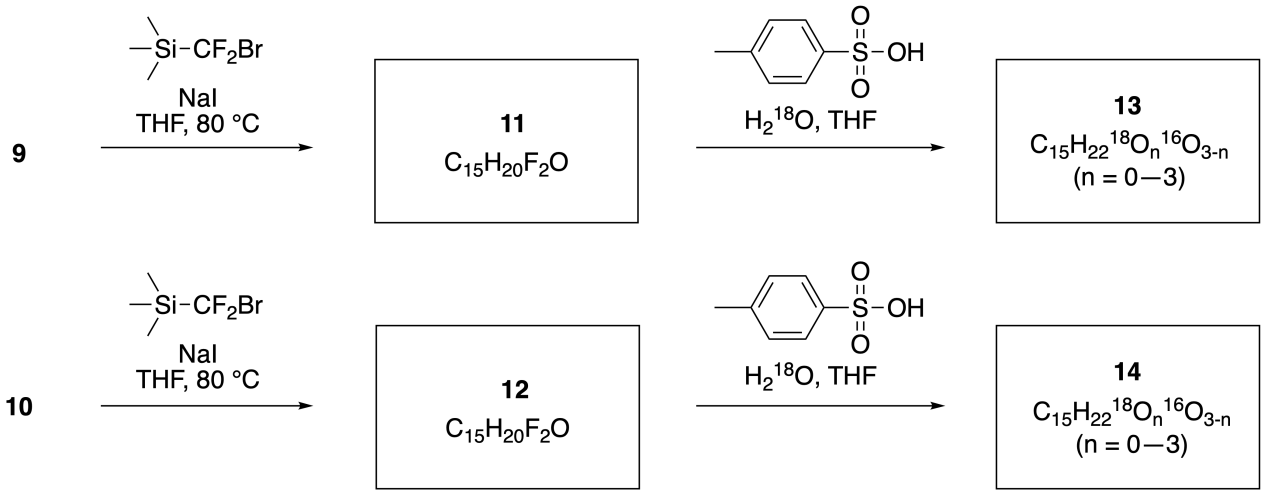


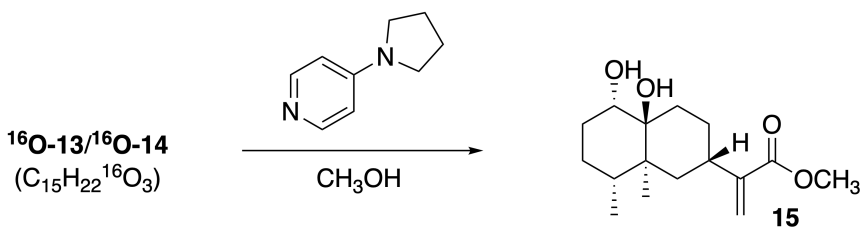
A.1 **Draw** the structures of **2** and **6** and clearly identify the stereochemistry where necessary. 5pt

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

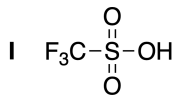
that $H_2{}^{18}O$ is used instead of $H_2{}^{16}O$ for the synthesis of ^{18}O-labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are ^{18}O-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product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

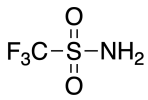


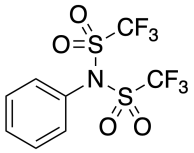


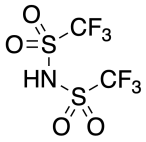


A.2 **Choose** the appropriate structure for **A**. 2pt

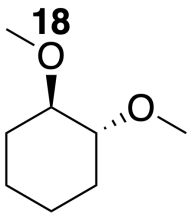
I 

II 

III 

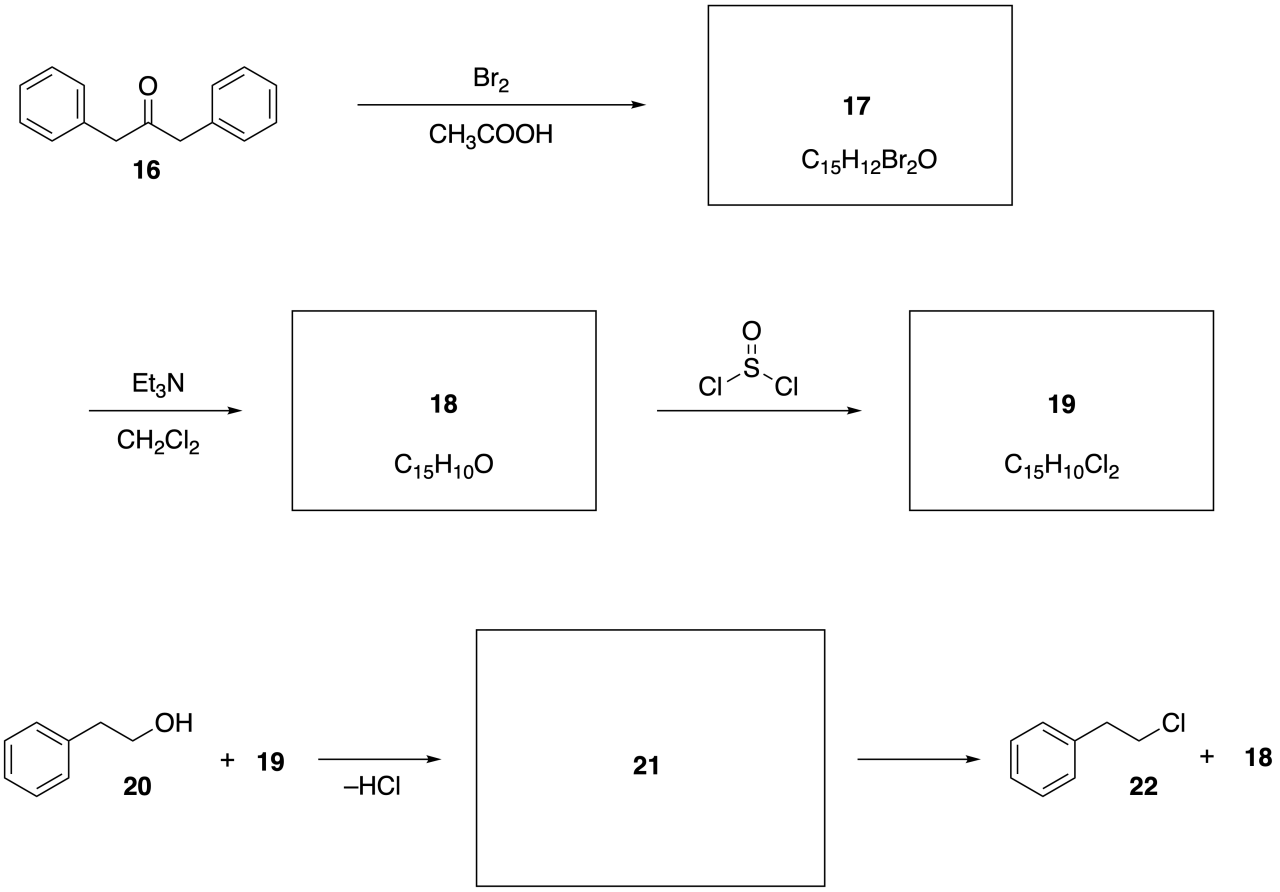
IV 

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**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

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

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.



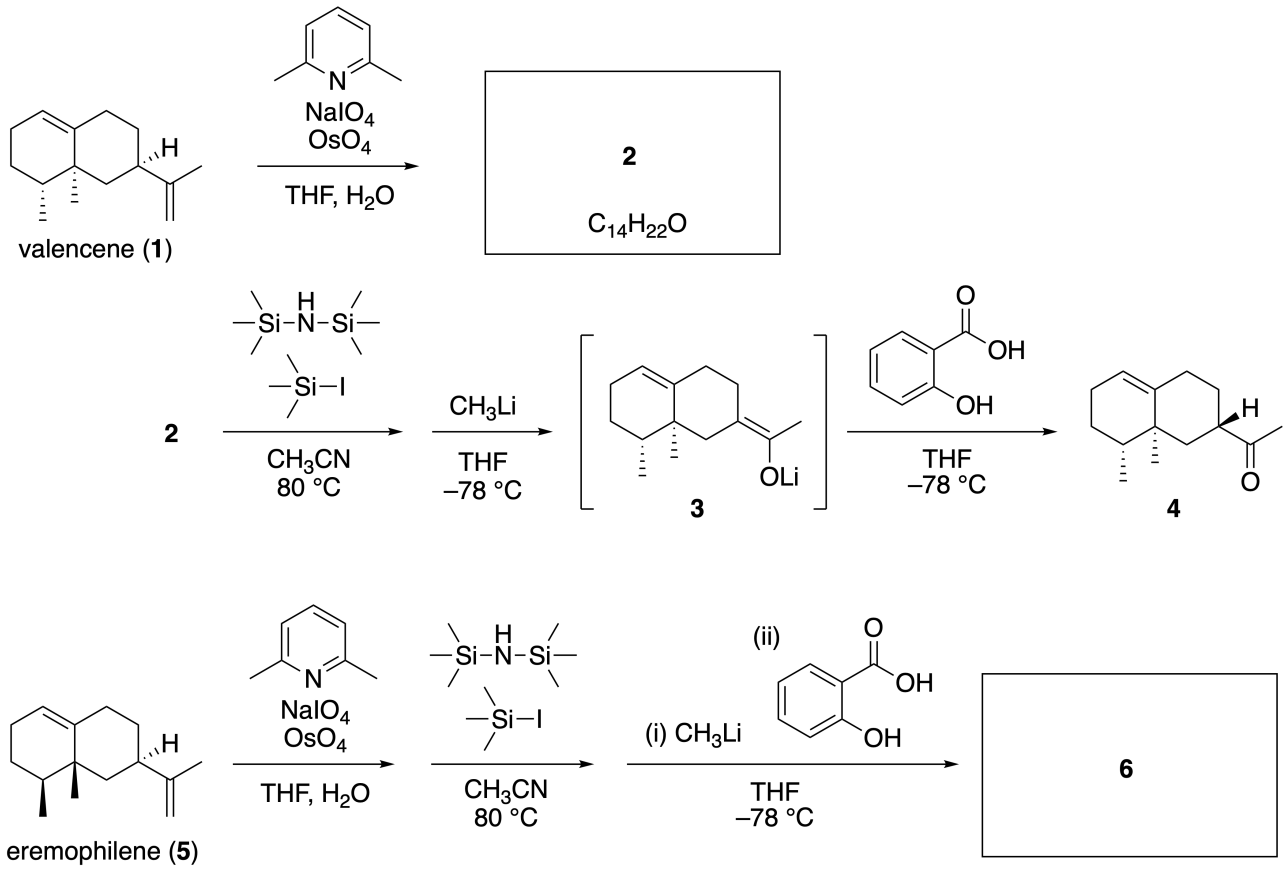
Rettigheter: Universitetet i Tohoku

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.



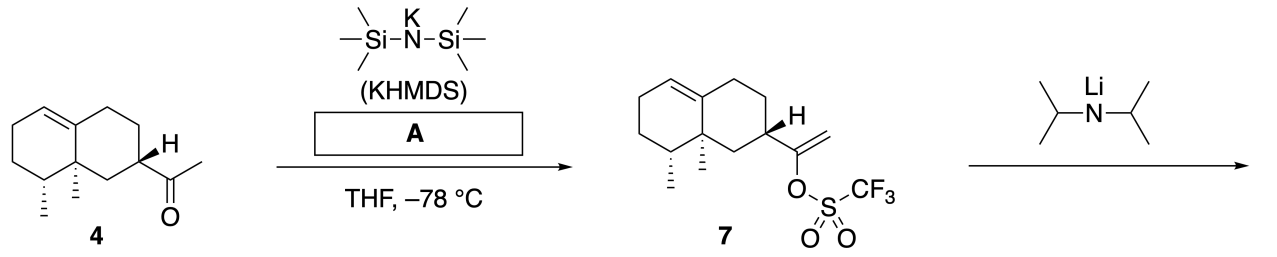
Inula linariifolia

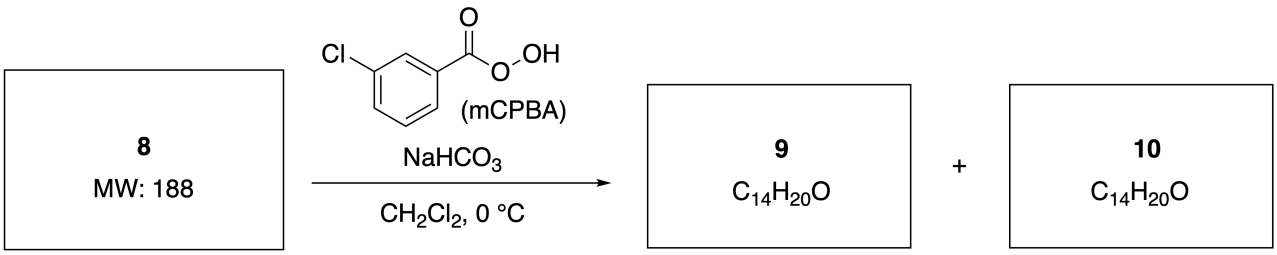


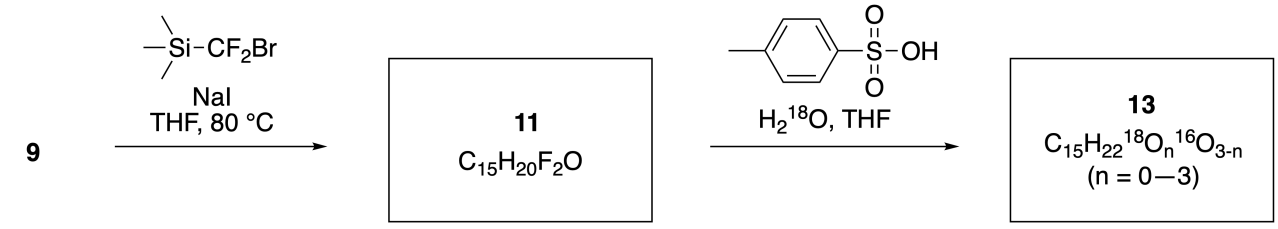
A.1	**Tegn** strukturen til **2** og **6** og marker stereokjemien tydelig der det er nødvendig.	5pt

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

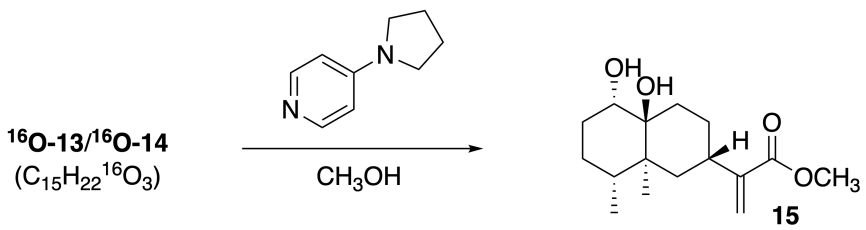
brukt istedenfor $H_2{}^{16}O$ for å syntetisere ^{18}O-merket lineariifolianonene **13** og **14** fra henholdsvis **11** og **12**. Forbindelsene **13** og **14** er ^{18}O-merkede isotopomerer. Bortsett fra isotopmerkingen gir både **13** og **14** det samme produktet **15** med identisk stereokjemi.



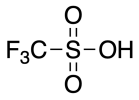


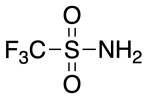


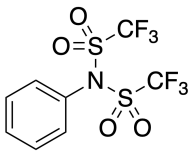


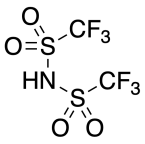


A.2 **Velg** den riktige strukturen for **A**. 2pt

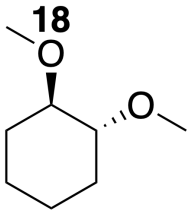
I 

II 

III 

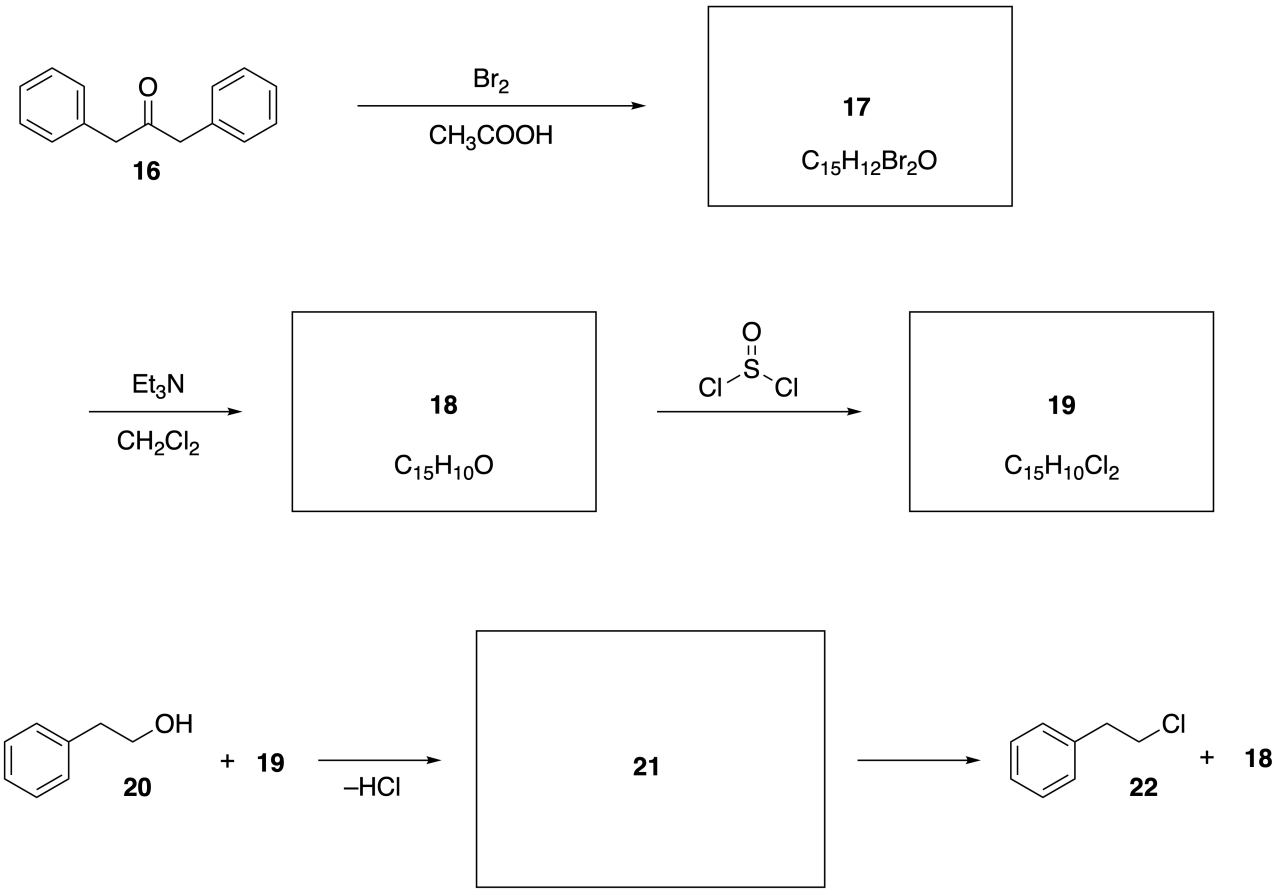
IV 

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**: δ 7.4–7.2 (5H), 3.7 (2H), 2.8 (2H), 2.2 (1H)
21: δ 8.5–7.3 (15H), 5.5 (2H), 3.4 (2H)

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

Lek med ikke-benzenoid aromatisitet

Del 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)

Del B

B.1 (10 pt)

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

NOR-3 C-8 C
Joachim Julian Klaussen

IChO
Problem 8
Cover sheet

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

Q8-1

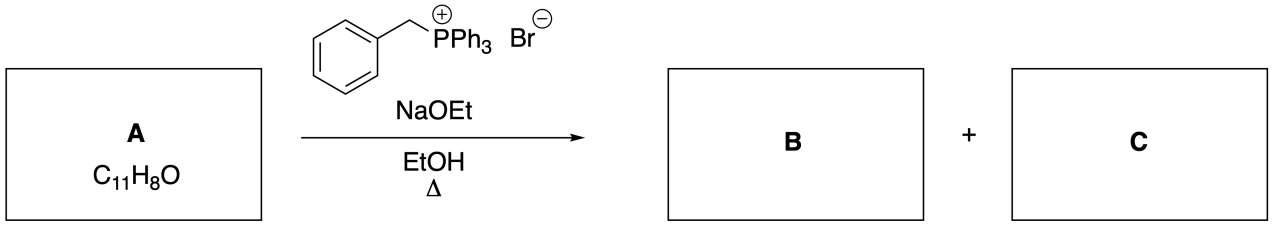
English (Official)

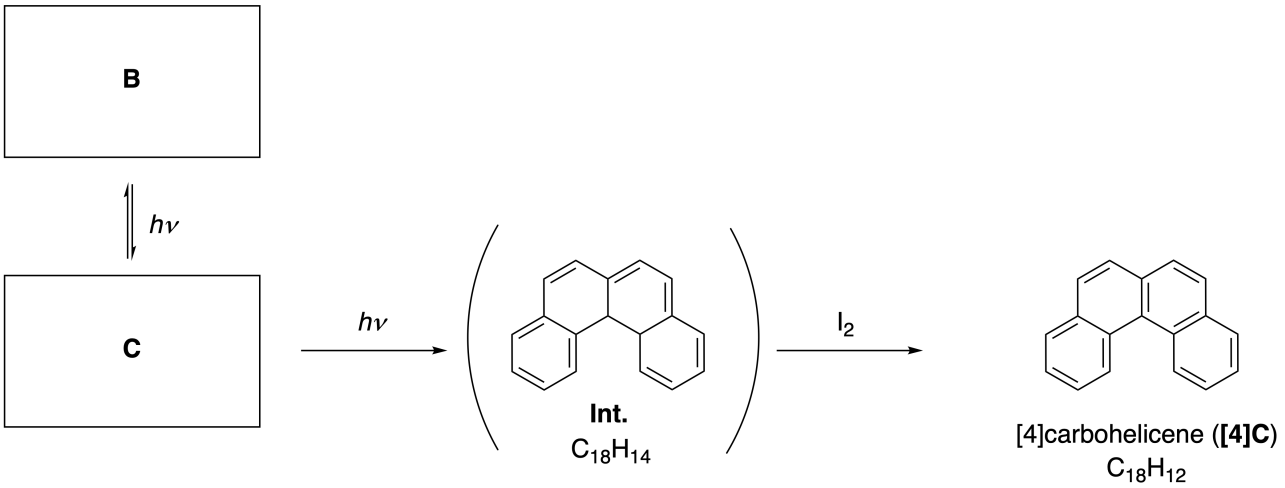
Dynamic Organic Molecules and Their Chirality

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

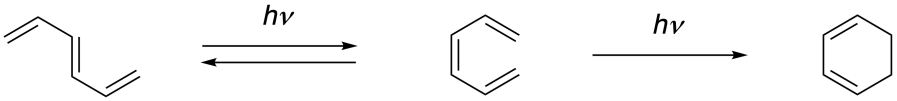
Part A

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.

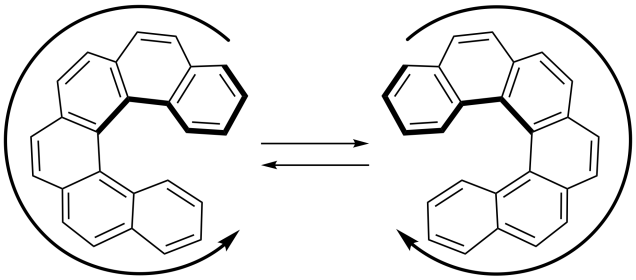


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

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

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

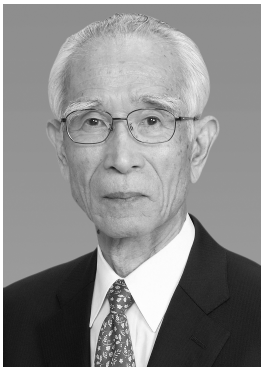
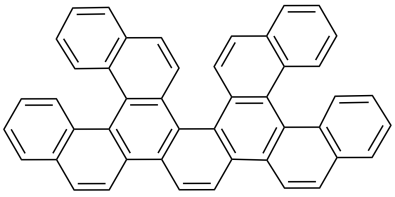
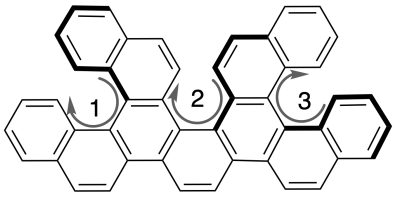


Photo courtesy: The Japan Prize Foundation

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.

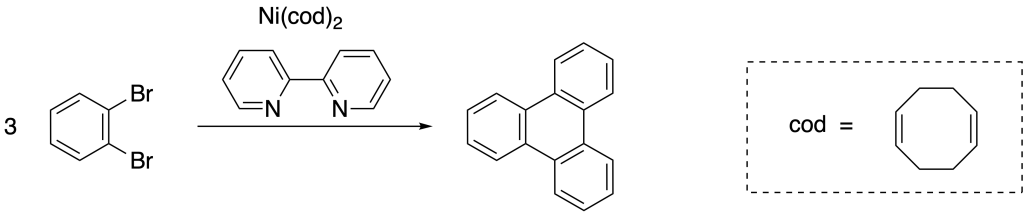


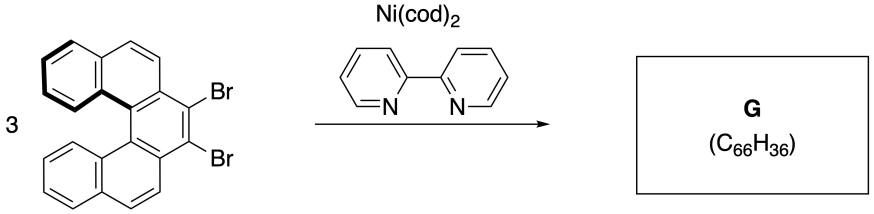
E



(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

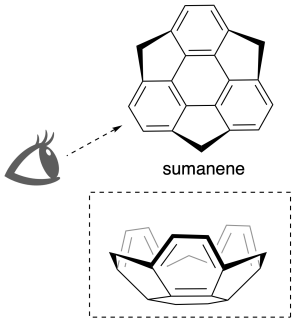




(*P*)-**F**

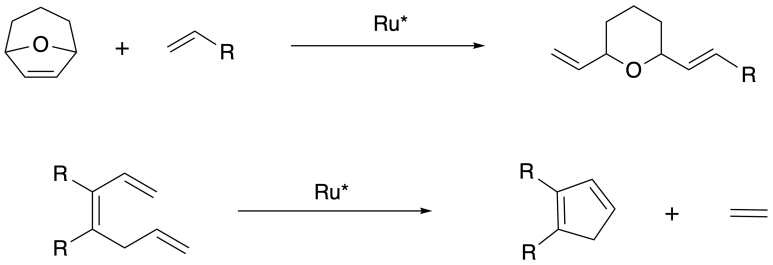
Part B

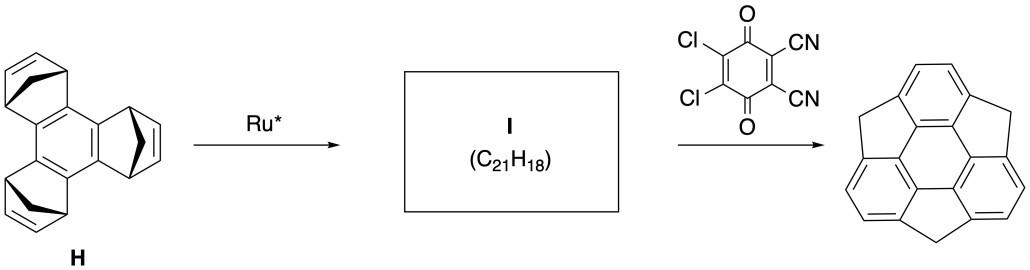
Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.



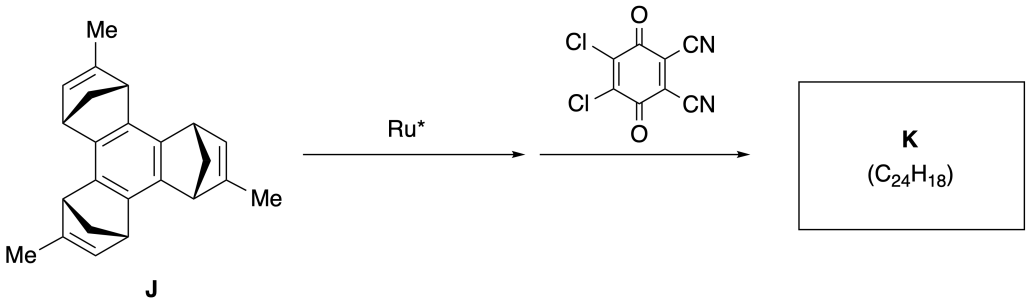


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru*) are shown below.





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

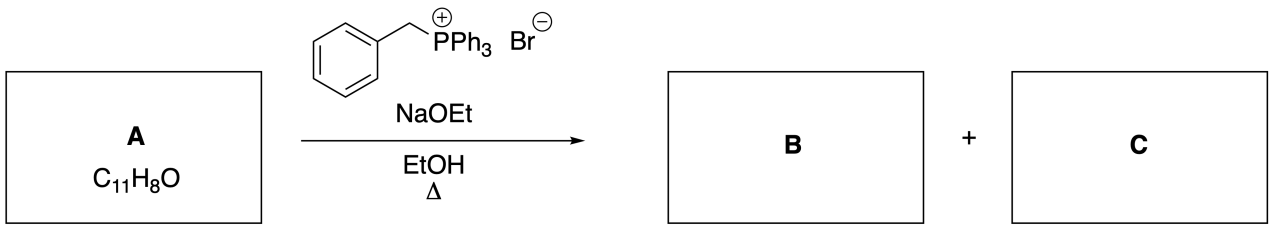
Norwegian (Norway)

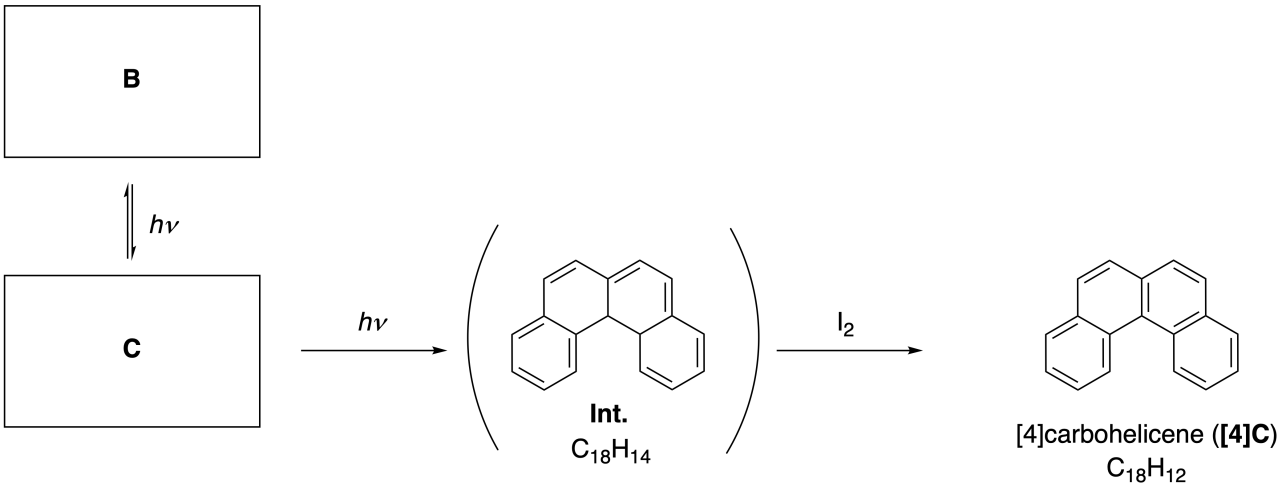
Dynamiske organiske molekyler og deres kiralitet

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

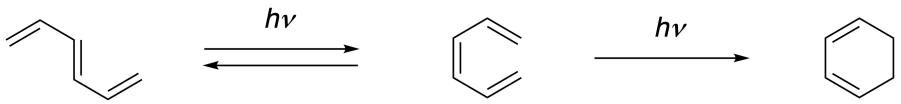
Del A

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:

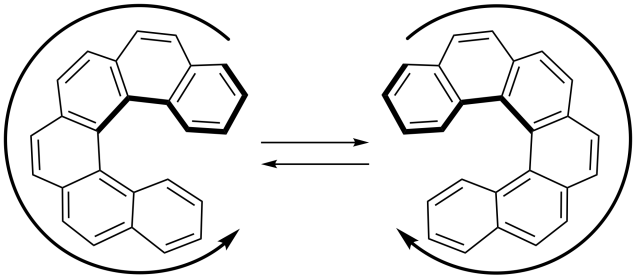


Merk: For alle Oppgave 8 oppgavene, tegn alternerende enkelt og dobbelbindinger i svaret ditt som vist i eksempelet for carbohelicene. Bruk ikke sirkler for konjungerte π systemer.

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

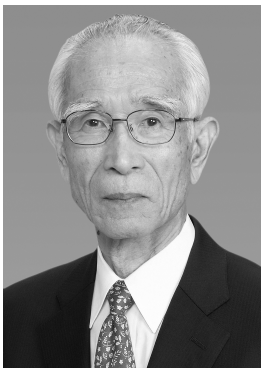
A.2	Forsøk på å syntetisere [5]carbohelicene fra samme fosfoniumsalt og en passende utgangsforbindelse resulterte kun i veldig små mengder (spormengder) av [5]carbohelicene. Istedet ble produktet **D** dannet med molekylvekt 2 Da lavere enn det til [5]carbohelicene. ^{1}H NMR kjemiske skift til **D**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

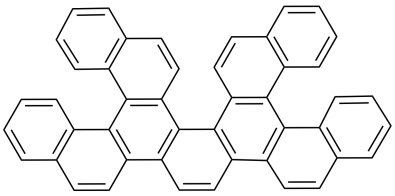


Fototilatelse: The Japan Prize Foundation

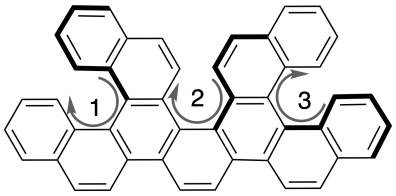
Q8-3

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.

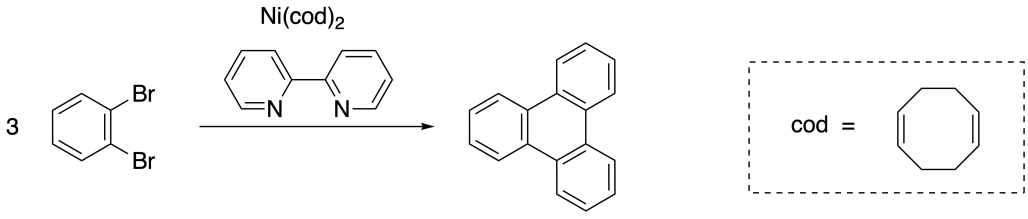


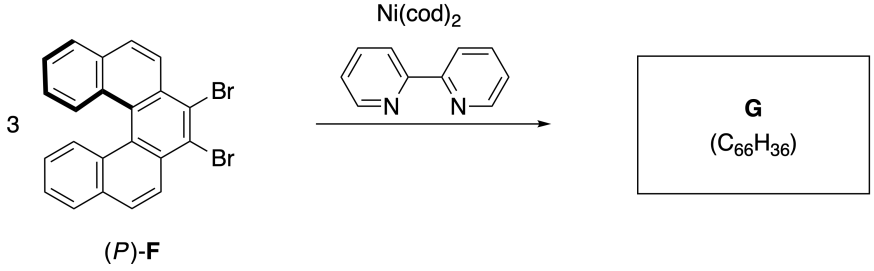
E



(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

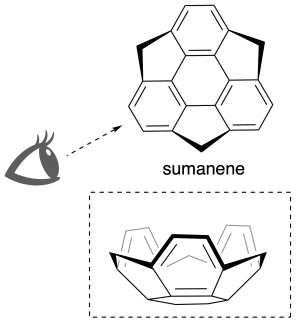




(*P*)-**F**

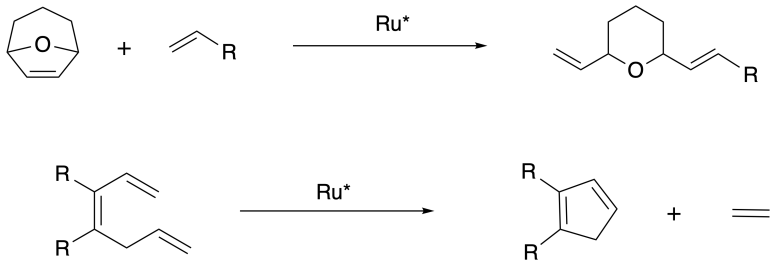
Del B

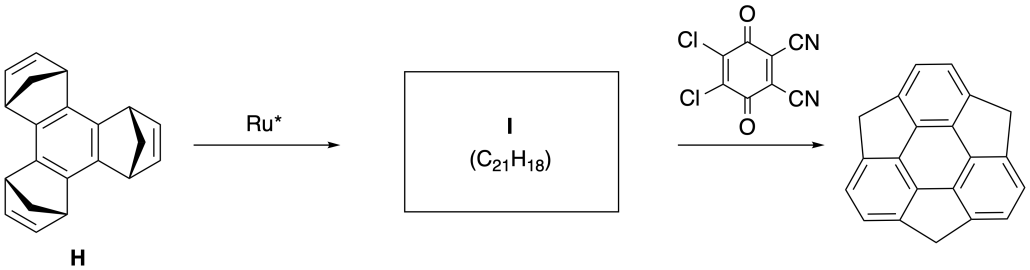
Sumanene er en bolle-formet hydrokarbon som ble først rapportert i Japan i 2003. Navnet "sumanene" kommer fra et Sanskrit-Hindi ord "suman" som betyr solsikke. Syntesen av sumanene skjer via en sekvens av reaksjoner som består av ring-åpnende og ring-lukkende metateser.



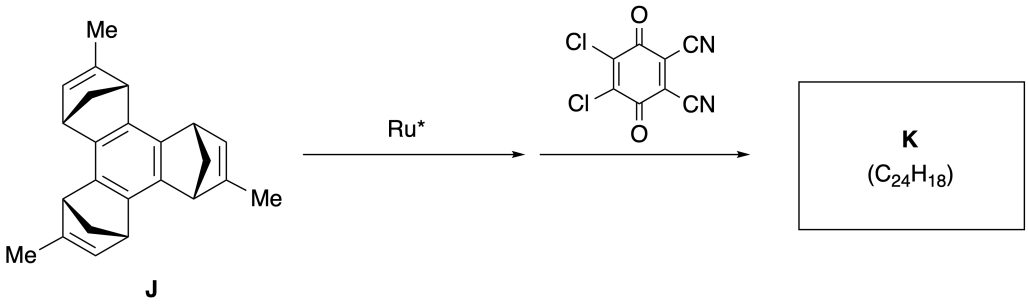


Under er det vist representative metatesereaksjoner som katalyseres av en ruteniumkatalysator (Ru*).





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

Dynamiske organiske molekyler og deres kiralitet

Del A

A.1 (9 pt)

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

A.2 (3 pt)

A.3 (7 pt)

Del B

B.1 (3 pt)

B.2 (4 pt)

NOR-3 C-9 C
Joachim Julian Klaussen

IChO
Problem 9
Cover sheet

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

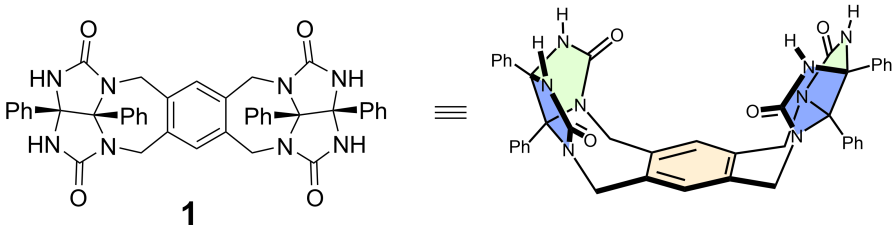
Likes and Dislikes of Capsule

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

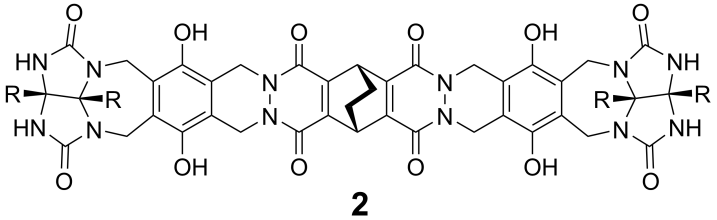
Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



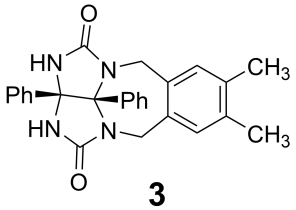
Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



1

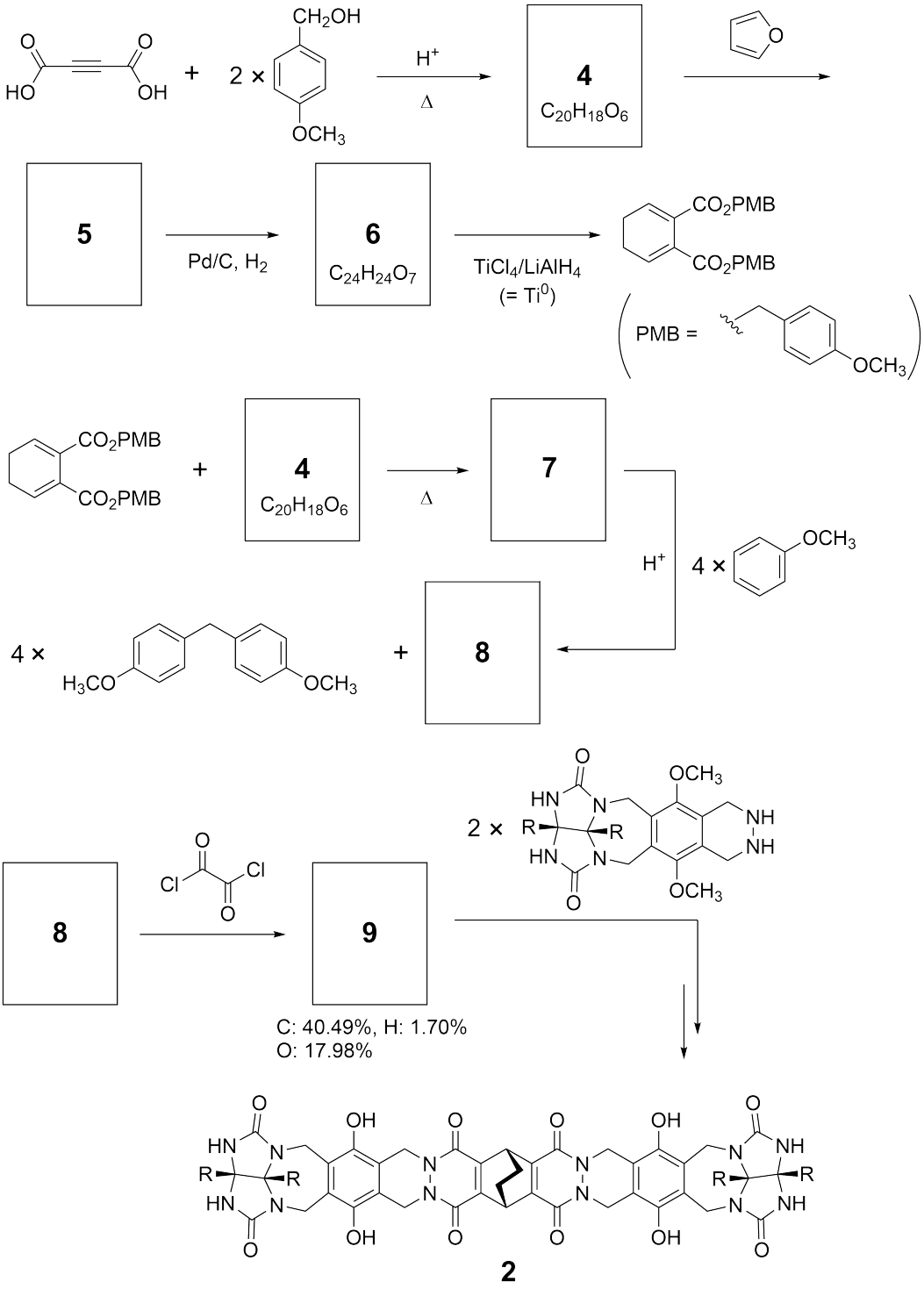


2



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:

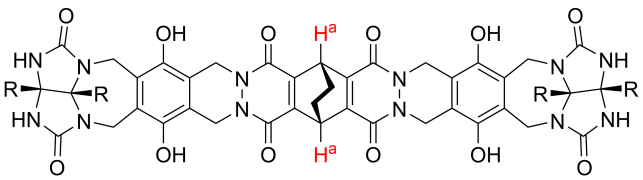
$$\mathrm{Z} + \mathbf{1}_2 \rightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

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

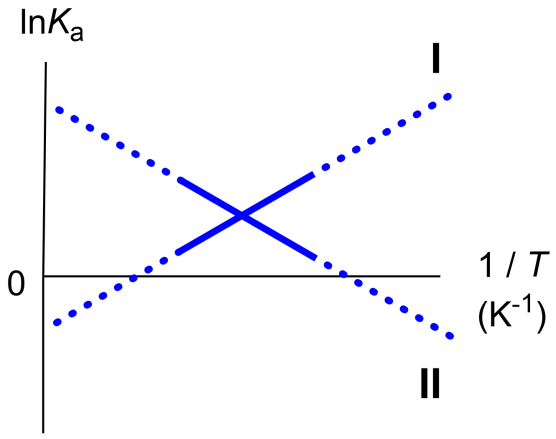
solvent	δ (ppm) of H^a
C_6D_6	4.60
C_6D_5F	4.71
C_6D_6 / C_6D_5F	4.60, 4.71, 4.82

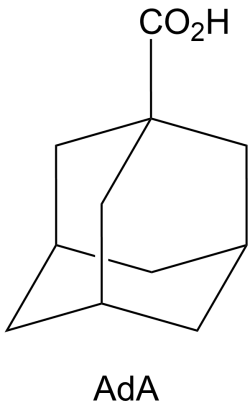
A.4 **Determine** the number of C_6D_6 and C_6D_5F molecules encapsulated in $\mathbf{2}_2$ giving each H^a signal. 3pt

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

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

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

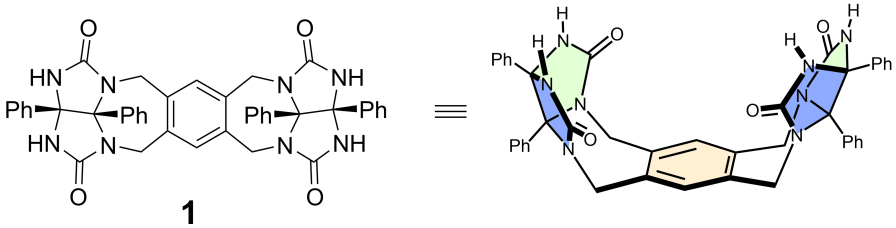
Fordeler og ulemper med en kapsel

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

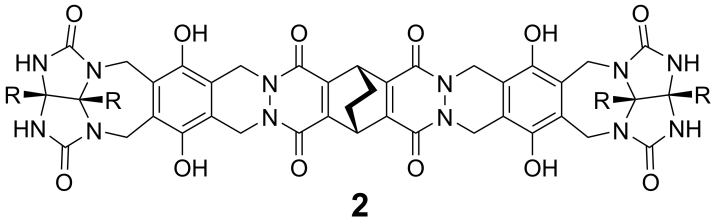
Snille barn gjør ikke dette, men hvis du løsner sømmen på en tennisball så kan du få to U-formede deler.



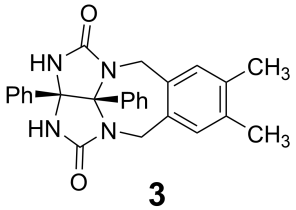
Basert på denne ideen ble forbindelse **1** og **2** syntetisert som U-formede molekyler med forskjellig størrelse. Forbindelse **3** ble laget som en sammenligning med **1,** og innkapslingsegenskapen (encapsulation behavior) til disse forbindelsene ble undersøkt.



1



2

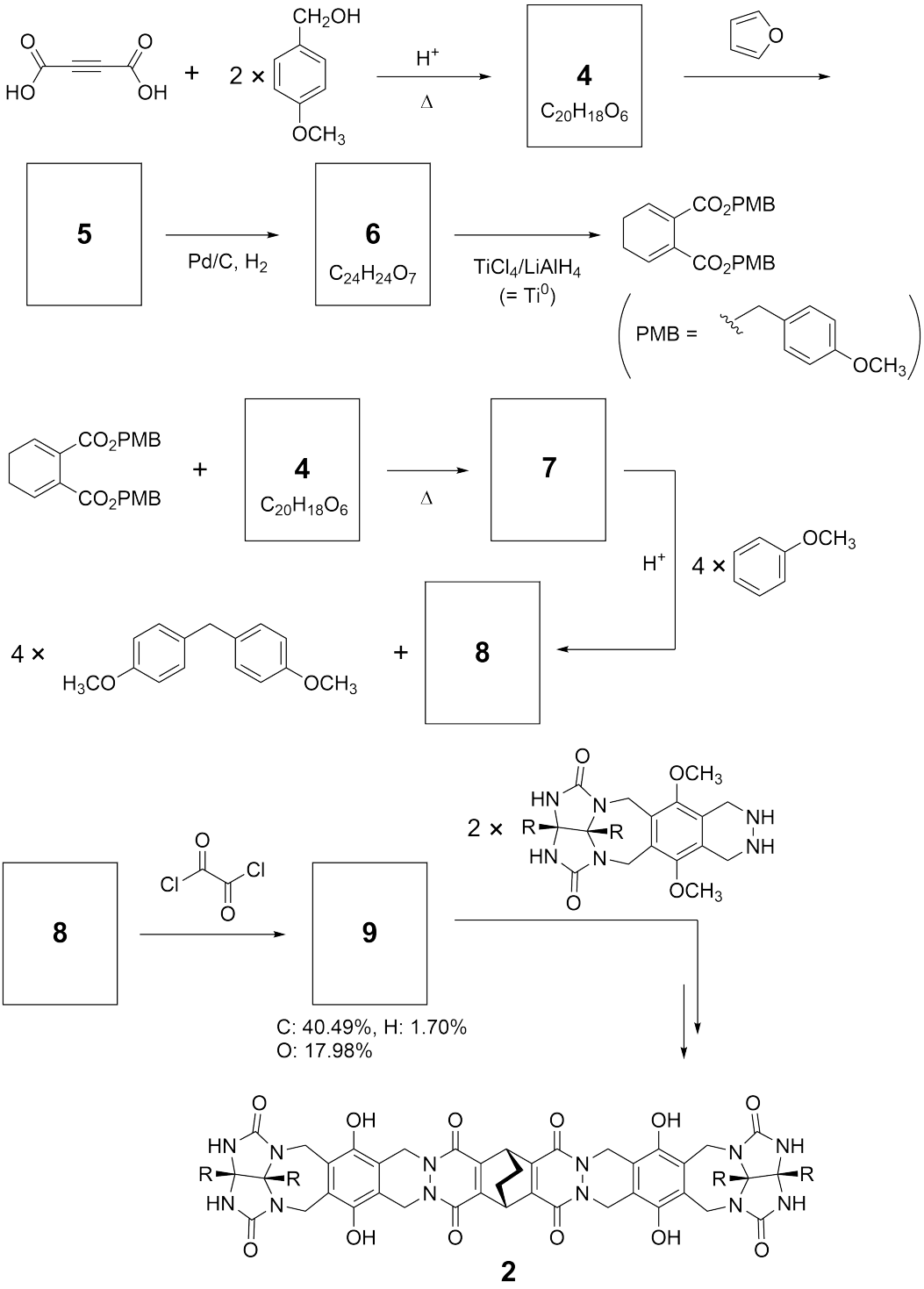


3

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:

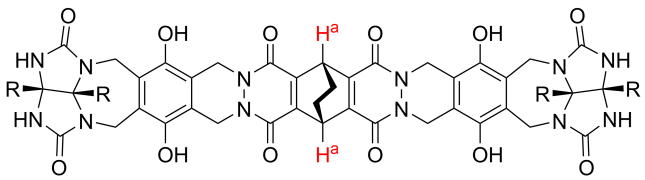
$$Z + \mathbf{1}_2 \rightarrow Z@\mathbf{1}_2 \tag{1}$$

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 ^{1}H NMR spektre før og etter tilsetning av CH_4.

Forbindelse **2** danner også en rigid og større dimerisk kapsel ($\mathbf{2}_2$). ^{1}H 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

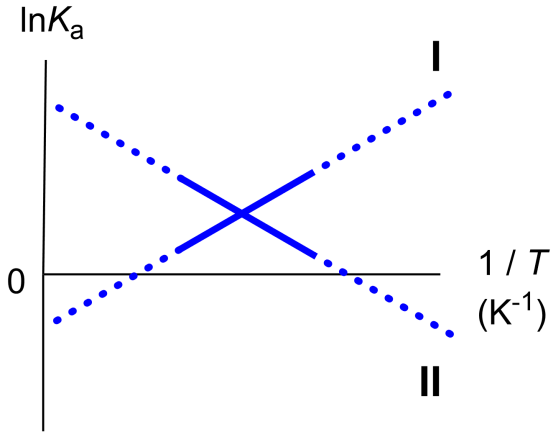
løsningsmiddel (solvent)	δ (ppm) til H^a
C_6D_6	4,60
C_6D_5F	4,71
C_6D_6 / C_6D_5F	4,60; 4,71; 4,82

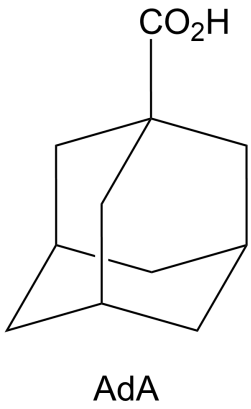
A.4 **<u>Bestem</u>** antallet av C_6D_6 og C_6D_5F molekyler innkapslet i $\mathbf{2}_2$ gitt hvert H^a signal. 3pt

^{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 (ΔS) er (1) og entalpiendringen (ΔH) 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

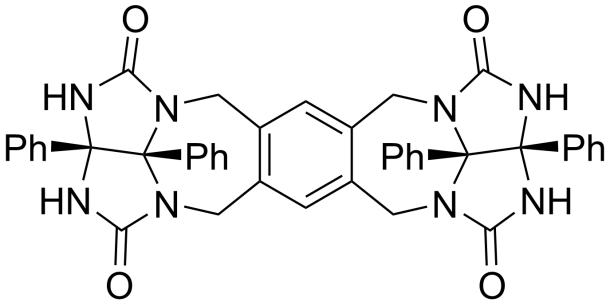
	A	B
(1)	positiv	negativ
(2)	positiv	negativ
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ og CH_4	$\mathbf{2}_2$ og AdA
(5)	$\mathbf{1}_2$ og CH_4	$\mathbf{2}_2$ og AdA

Fordeler og ulemper med en kapsel

A.1 (13 pt)

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

A.2 (2 pt)



A.3 (2 pt)

A.4 (3 pt)

δ (ppm) til H[a]	antall C_6D_6	antall C_6D_5F
4,60 ppm		
4,71 ppm		
4,82 ppm		

A.5 (3 pt)

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

(4) : (5) :