



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Preparatory Problems

Finding Solutions

2023-06-02, Version 3



Preparatory Problems (Theory)



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G0-1

English (Official)

General Instructions

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Preface

We are excited to present the Preparatory Problems for the 55th International Chemistry Olympiad. These problems should serve the students in their preparation for the Olympiad and in their exploration of a variety of new topics in modern and traditional chemistry, all within our theme of "Finding Solutions". The content of this booklet is based on the IChO syllabus (see www.ichosc.org/regulations, Appendix C) and some fields of advanced difficulty which are explicitly listed below (6 for the theoretical part and 3 for the practical one). The depth of these fields is reflected in the 30 theoretical problems and 8 practical tasks whereas the number and length of these problems have only resulted from our commitment to provide interesting and well-rounded problems in a spirit as similar as possible to the final problems.

For the first time in IChO history, the preparatory problems are made available both in pdf form on our website www.icho2023.ch and in a more interactive format through OlyExams. The official solutions will be accessible by Head Mentors through OlyExams by the end of January and will be published on our website on June 1. We welcome any comments, corrections, or questions about the problems coming our way via email at exams@icho2023.ch or directly via OlyExams to encourage an open and transparent discussion within the community and with the scientific committee.

The International Chemistry Olympiad offers young people from around the world the opportunity to deepen their understanding of the wonders of chemistry and inspire one another. It also presents a great opportunity to inspire future generations to pursue a career in the fundamental sciences and positively affect public attitudes towards science, specifically chemistry. Last but not least, it is a wonderful opportunity to make friends from around the world and experience the culture and history of the host country.

Acknowledgments

We would like to express our deepest gratitude to all of the authors for their hard work in creating both preparatory and competition problems for the 55th International Chemistry Olympiad. Their dedication over many months has resulted in a booklet that will be beneficial to the young chemists participating in the Olympiad. We are also grateful to the scientific reviewers and language proofreaders, including the members of the IChO steering committee, whose precision and thoroughness greatly improved these problems. Our special thanks go to ETH Zurich, in collaboration with D-CHAB, for facilitating all organizational tasks before and during IChO 2023.

On behalf of the Scientific Committee

Prof. Dr. Wendelin J. Stark

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Fields of Advanced Difficulty

Theory

- Basics of NMR spectroscopy (chemical shifts, integrals, J couplings)
- Analysis of complex reactions using steady-state and quasi-equilibrium; Basic concept of flows
- Advanced inorganic electrochemistry: Latimer diagrams and Frost diagrams
- Radical chemistry and electrochemistry in organic synthesis
- Solid-phase peptide synthesis with common linkers and protecting groups
- Pericyclic reactions (cycloadditions, electrocyclic reactions) with regioselectivity, stereoselectivity, and stereospecificity; analysis of frontier molecular orbitals (FMO)

The following topics WILL NOT appear in the exam set:

- Application of Van 't Hoff equation or (Clausius-)Clapeyron equation
- Gas chromatography
- Organic Chemistry of Carbohydrates
- Polymer Chemistry
- Transition metal-catalysed cross-coupling reactions
- Vibrational Calculations

Practical

- Advanced separation techniques: vacuum filtration and extraction with immiscible solvents
- Thin Layer Chromatography (TLC) including the use of a staining solution
- Advanced inorganic qualitative analysis

Participants may be expected to know about the qualitative analysis of these cations:

Ag^+ , Al^{3+} , Ba^{2+} , Ca^{2+} , Co^{2+} , Cr^{3+} , Cu^+ , Cu^{2+} , Fe^{2+} , Fe^{3+} , H^+ , Mg^{2+} , Mn^{2+} , NH_4^+ , and Zn^{2+} ; and anions:
 AcO^- , Br^- , Cl^- , CO_3^{2-} , F^- , HCO_3^- , HCOO^- , I^- , MnO_4^- , NO_2^- , NO_3^- , OH^- , PO_4^{3-} , S^{2-} , SO_3^{2-} , and SO_4^{2-} .

The qualitative analysis of the following ions WILL NOT appear in the exam:

Cd^{2+} , ClO^- , Cs^+ , K^+ , Li^+ , Na^+ , Pb^{2+} , $\text{S}_2\text{O}_3^{2-}$, Sr^{2+} , Ti (any oxidation state), V (any oxidation state), WO_4^{2-} .

The following topics WILL NOT appear in the exam set:

- Use of a rotary evaporator or a simple distillation apparatus
- Recrystallization
- Use of Syringe

Preparatory Problems (Theory)



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Physical Constants and Equations

Constants

Planck constant	$h = 6.626 \cdot 10^{-34} \text{ Js}$
Boltzmann constant	$k_B = 1.381 \cdot 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
Speed of Light	$c = 299792458 \text{ m/s}$
Elementary charge	$e = 1.602 \cdot 10^{-19} \text{ C}$
Avogadro constant	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$
Universal gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Faraday constant	$F = 9.648 \cdot 10^4 \text{ C/mol}$
Standard pressure	$p_0 = 1 \cdot 10^5 \text{ Pa}$
Electronvolt	$1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$
Electric Charge & Current	$1 \text{ C} = 1 \text{ A} \cdot 1 \text{ s}$
Absolute zero	$0 \text{ K} = -273.15 \text{ }^\circ\text{C}$
Ångstrom	$1 \text{ Å} = 10^{-10} \text{ m}$
pico	$1 \text{ pm} = 10^{-12} \text{ m}$
nano	$1 \text{ nm} = 10^{-9} \text{ m}$
micro	$1 \text{ }\mu\text{m} = 10^{-6} \text{ m}$
milli	$1 \text{ mm} = 10^{-3} \text{ m}$
centi	$1 \text{ cm} = 10^{-2} \text{ m}$
deci	$1 \text{ dm} = 10^{-1} \text{ m}$
kilo	$1 \text{ km} = 10^3 \text{ m}$
mega	$1 \text{ Mm} = 10^6 \text{ m}$
giga	$1 \text{ Gm} = 10^9 \text{ m}$
tera	$1 \text{ Tm} = 10^{12} \text{ m}$
Pi (π)	$\pi = 3.141592 \dots$
Euler's number	$e = 2.718281 \dots$

Preparatory Problems (Theory)



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Equations

Ideal gas law	$pV = nRT = Nk_B T$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$ $\Delta G^\circ = -RT \ln K^\circ$ $\Delta_r G^\circ = -nFE_{cell}^\circ$ where n is the number of electrons $\Delta_r G = \Delta_r G^\circ + RT \ln Q$
Reaction quotient Q for reaction: $aA + bB \rightleftharpoons cC + dD$	$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
Nernst equation	$E = E_0 - \frac{RT}{nF} \ln Q$
Electric current	$I = Q/t$
Arrhenius law	$k = A \exp\left(\frac{-E_A}{RT}\right)$
Lambert Beer equation	$A = \epsilon lc$
Henderson-Hasselbalch equation	$\text{pH} = \text{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Integrated rate laws for ...	
... zeroth order	$[A] = [A]_0 - kt$
... first order	$\ln[A] = \ln[A]_0 - kt$
... second order	$\frac{1}{A} = \frac{1}{[A]_0} + kt$
Half life for a first order reaction	$t_{1/2} = \frac{\ln 2}{k}$
Half life for a second order process	$t_{1/2} = \frac{1}{[A]_0 k}$
Radioactivity	$A = k \cdot N$
Area of a sphere with radius R	$A = 4\pi R^2$
Volume of a sphere with radius R	$V = \frac{4\pi}{3} R^3$

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Periodic Table of the Elements

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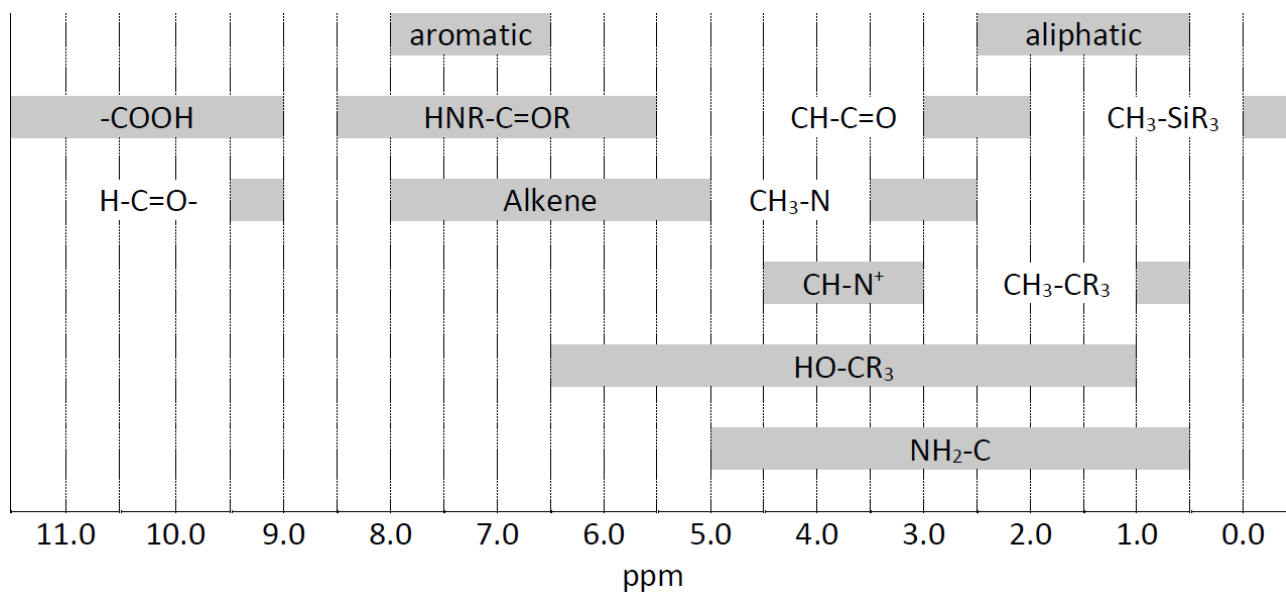
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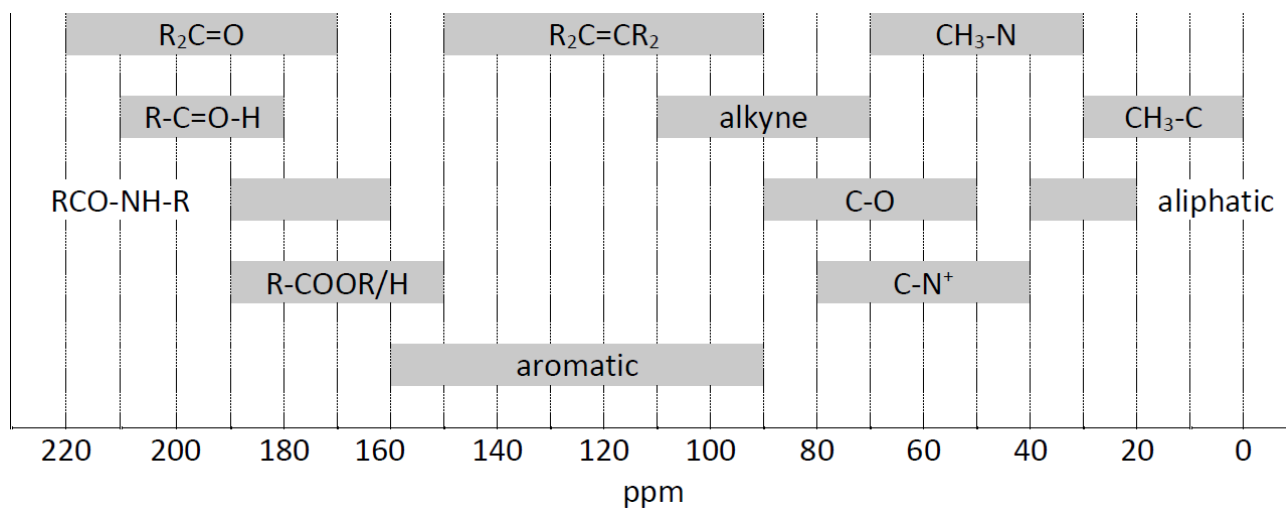
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Table of NMR Chemical Shifts

¹H NMR Chemical Shifts



¹³C NMR Chemical Shifts



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¹H NMR Coupling Constants

Type of hydrogen	$ J_6 $ (Hz)
$R_2CH_aH_b$	4-20
$R_2CH_a-CR_2H_b$	2-12
$R_2CH_a-CR_2-CR_2H_b$	If rotation free: < 0.1 Otherwise (fixed): 1-8
$RH_aC=CRH_b$	<i>cis</i> : 7-12 <i>trans</i> : 12-18
$R_2C=CH_aH_b$	0.5-3
$RH_aC=CR-CR_2H_b$	0.5-2.5

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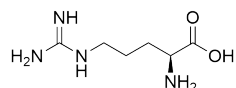
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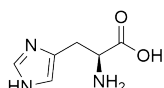
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List of Amino Acids

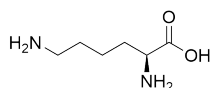
Overview of amino acids and their three- and one-letter codes



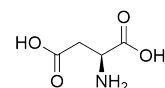
Arginine (Arg, R)



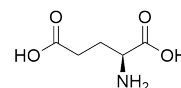
Histidine (His, H)



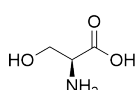
Lysine (Lys, K)



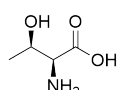
Aspartic acid (Asp, D)



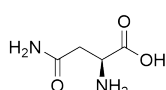
Glutamic acid (Glu, E)



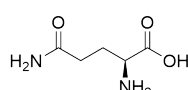
Serine (Ser, S)



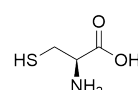
Threonine (Thr, T)



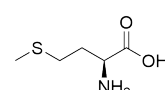
Asparagine (Asn, N)



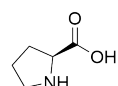
Glutamine (Gln, Q)



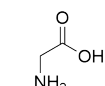
Cysteine (Cys, C)



Methionine (Met, M)



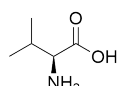
Proline (Pro, P)



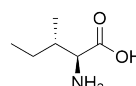
Glycine (Gly, G)



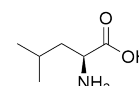
Alanine (Ala, A)



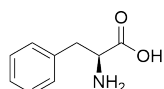
Valine (Val, V)



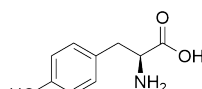
Isoleucine (Ile, I)



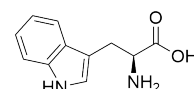
Leucine (Leu, L)



Phenylalanine (Phe, F)



Tyrosine (Tyr, Y)



Tryptophan (Trp, W)

Preparatory Problems (Theory)



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Safety

General Considerations

Participants in the IChO must be prepared to work in a chemical laboratory and be aware of all relevant rules and safety procedures. The organizers will strictly enforce the safety rules (see www.ichosc.org/regulations, Appendix A) during the event.

The Preparatory Problems are designed to be carried out in properly equipped chemical laboratories under competent supervision only. For each chemical, the GHS hazard and precautionary statements are reported. No specific and detailed safety and disposal instructions have been included as regulations may vary widely among countries. Mentors must carefully adapt the problems accordingly.

Dress code

During the examination, the students will be required to wear:

- pants covering their whole legs;
- closed and flat shoes;
- a lab coat with long sleeves;
- safety goggles fitting the contour of their face;
- if applicable, long hair and beards tied back.

Lab coats and safety goggles will be provided by the organisers. These items or a suitable alternative must be carried during the whole examination. Safety goggles are mandatory even for students wearing prescription glasses. Contact lenses are prohibited.

Any student that would fail to respect these rules will not be allowed to enter the lab and may be excluded from the competition entirely.

GHS Statements

The GHS hazard and precautionary statements associated with the materials used are indicated in the problems. Their meanings are as follows:

H-phrases Physical Hazards

H224: Extremely flammable liquid and vapour

H225: Highly flammable liquid and vapour

H226: Flammable liquid and vapour

H260: In contact with water releases flammable gases which may ignite spontaneously

H272: May intensify fire: oxidizer

H290: May be corrosive to metals

H-phrases Health Hazards

H301: Toxic if swallowed

H301+H331: Toxic if swallowed or if inhaled

H302: Harmful if swallowed

H302+H312: Harmful if swallowed or in contact with skin

H302+H312+H332: Harmful if swallowed, in contact with skin or if inhaled

H302+H332: Harmful if swallowed or inhaled

Preparatory Problems (Theory)



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H304: May be fatal if swallowed and enters airways
H311: Toxic in contact with skin
H311+H331: Toxic in contact with skin or if inhaled
H312: Harmful in contact with skin
H312+H332: Harmful in contact with skin or if inhaled
H314: Causes severe skin burns and eye damage
H315: Causes skin irritation
H317: May cause an allergic skin reaction
H318: Causes serious eye damage
H319: Causes serious eye irritation
H331: Toxic if inhaled
H332: Harmful if inhaled
H335: May cause respiratory irritation
H336: May cause drowsiness or dizziness
H351: Suspected of causing cancer
H361: Suspected of damaging fertility or the unborn child
H361d: Suspected of damaging the unborn child
H361f: Suspected of damaging fertility
H371: May cause damage to organs
H372: Causes damage to organs through prolonged or repeated exposure
H373: May cause damage to organs through prolonged or repeated exposure

H-phrases Environmental Hazards

H400: Very toxic to aquatic life
H410: Very toxic to aquatic life with long lasting effects
H411: Toxic to aquatic life with long lasting effects
H412: Harmful to aquatic life with long lasting effects
H441: Very toxic to terrestrial invertebrates

Prevention precautionary statements

P202: Do not handle until all safety precautions have been read and understood.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P220: Keep/Store away from clothing/.../combustible materials.
P223: Do not allow contact with water.
P231: Handle and store contents under inert gas/...
P232: Protect from moisture.
P233: Keep container tightly closed.

Preparatory Problems (Theory)



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P234: Keep only in original container/packaging.

P235: Keep cool.

P240: Ground and bond container and receiving equipment.

P241: Use explosion-proof electrical/ventilating/light/.../equipment.

P242: Use only non-sparking tools.

P243: Take action to prevent static discharges.

P260: Do not breathe dust/fume/gas/mist/vapours/spray.

P261: Avoid breathing dust/fume/gas/mist/vapours/spray.

P264: Wash ... thoroughly after handling.

P270: Do not eat, drink or smoke when using this product.

P271: Use only outdoors or in a well-ventilated area.

P273: Avoid release to the environment.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Response precautionary statements

P301: IF SWALLOWED:

P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

P301+P312: IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell.

P301+P330+P331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P302: IF ON SKIN:

P302+P352: IF ON SKIN: Wash with soap and water.

P303: IF ON SKIN (or hair):

P303+P361+P353: IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water [or shower].

P304: IF INHALED:

P304+P340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

P305: IF IN EYES:

P305+P351+P338: IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

P308: IF exposed or concerned:

P308+P311: IF exposed or concerned: Call a POISON CENTER or doctor/physician.

P310: Immediately call a POISON CENTER or doctor/physician.

P311: Call a POISON CENTER or doctor/physician.

P312: Call a POISON CENTER or doctor/physician if you feel unwell.

P313: Get medical advice/attention.

P314: Get Medical advice/attention if you feel unwell.

Preparatory Problems (Theory)



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P315: Get immediate medical advice/attention.

P320: Specific treatment is urgent (see ... on this label).

P330: Rinse mouth.

P331: Do NOT induce vomiting.

P332: If skin irritation occurs:

P332+P313: If skin irritation occurs: Get medical advice/attention.

P337: If eye irritation persists:

P337+P313: If eye irritation persists: Get medical advice/attention.

P338: Remove contact lenses if present and easy to do. Continue rinsing.

P340: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

P351: Rinse cautiously with water for several minutes.

P352: Wash with plenty of water.

P353: Rinse skin with water [or shower].

P361: Remove/Take off immediately all contaminated clothing.

P363: Wash contaminated clothing before reuse.

P370: In case of fire:

P370+P378: In case of fire: Use ... to extinguish.

P378: Use ... to extinguish.

P391: Collect spillage.

Storage precautionary statements

P403: Store in a well ventilated place.

P403+P233: Store in a well ventilated place. Keep container tightly closed.

P403+P235: Store in a well ventilated place. Keep cool.

P405: Store locked up.

P422: Store contents under ...

Disposal precautionary statements

P501: Dispose of contents/container to ...

Preparatory Problems (Theory)



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G0-16

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List of Theory Problems

Problem	Title
T1	The Sun-to-Fuel Project
T2	Many-faceted Oxides of Carbon
T3	What to do with CO ₂
T4	Pathways to H ₂ and Catalysts
T5	Two Transition Metals - Many Oxidation States
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Preparatory Problems (Theory)



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List of Practical Problems

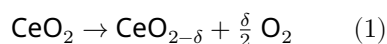
Problem	Title
P1	Essential Medicines
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P3	A Simple Aldol Condensation
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P8	Hard Water - Easy Titrations
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The Sun-to-Fuel Project

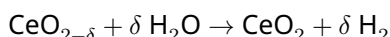
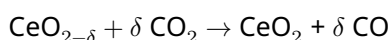
There are many approaches being investigated for the conversion of CO₂ to syngas or higher fuels, as these conversions would close the anthropogenic carbon cycle. A promising "sun-to-fuel" approach, being developed by Prof. A. Steinfeld from ETHZ, uses cerium dioxide and solar irradiation to generate syngas (a mixture of H₂, CO and CO₂) at an industrial scale. CO₂ thereby can be obtained through direct air capture (DAC). The whole approach then comprises three essential units: the DAC, the solar redox unit using non-stoichiometric CeO₂, and the gas-to-liquid (GTL) unit that produces methanol or kerosene depending on the syngas composition.

The solar redox unit relies on a two-step catalytic cycle: in the first step CeO₂ is non-stoichiometrically reduced by losing oxygen, using sunlight energy. In the second step it is re-oxidized by CO₂ to produce CO, or by H₂O to produce H₂, at far lower temperatures than the reduction step. The non-stoichiometry after reduction is denoted by δ and it contributes to the oxygen exchange capacity of CeO₂.

The process starts with the non-stoichiometric reduction of CeO₂ as well as the re-oxidation by CO₂ or by H₂O can be expressed by the equation:



This is followed by re-oxidation by CO₂ and/or H₂O:



In an initial experiment, the O₂ evolution and the syngas formation were measured after the injection of CO₂ and H₂O. The following data were obtained (with a margin of error of about 15%).

Total O ₂ release	1.52 mL g _{CeO₂} ⁻¹
Total syngas production	3.15 mL g _{CeO₂} ⁻¹
Total H ₂ production	2.21 mL g _{CeO₂} ⁻¹
Total CO production	0.94 mL g _{CeO₂} ⁻¹

- 1.1 Calculate** the δ of equation (1) per mole ceria. (Note that throughout the task, you can assume that gases have a molar volume of 22.4 L).

Later on, it became clear that complete re-oxidation is not achieved in the cyclic process. Thus, the reduction equation has to be re-written as:



where δ_{red} is the non-stoichiometry after the reduction reaction and δ_{ox} is the non-stoichiometry after re-oxidation.

α signifies the oxygen exchange capacity of CeO₂ and therefore also the fuel yield per cycle.

- 1.2 Provide** the balanced equations for i) the reduction of CeO_{2- δ_{ox}} to CeO_{2- δ_{red}} so that exactly 1 mol of O-atoms is produced and for the re-oxidation by ii) CO₂ and iii) H₂O to CeO_{2- δ_{ox}} , respectively.

α depends on the temperature and the partial pressure of O₂. $\Delta_R H$ for the reduction process is 950 kJ per mole of released O₂.

Preparatory Problems (Theory)



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1.3 **Choose** the most suitable conditions for the reduction process.

- ☐ Low O₂ partial pressure and low temperature
- ☐ Low O₂ partial pressure and high temperature
- ☐ High O₂ partial pressure and low temperature
- ☐ High O₂ partial pressure and high temperature

Using thermodynamic data, α can therefore be calculated as a function of the O₂ partial pressure at different temperatures. The relevant equations are given below:

$$\log 2\alpha_{1673\text{K}} = -(0.2105 \log p(\text{O}_2)/\text{bar} + 2.613)$$

$$\log 2\alpha_{1723\text{K}} = -(0.2168 \log p(\text{O}_2)/\text{bar} + 2.4585)$$

$$\log 2\alpha_{1773\text{K}} = -(0.2231 \log p(\text{O}_2)/\text{bar} + 2.3040)$$

1.4 **Calculate** α of the system at 1500 °C and $p(\text{O}_2) = 0.1$ mbar and **show** that its oxygen exchange capacity is bigger than for the system in question 1.

1.5 **Determine** the percentage by which α drops, when the reduction is run at 1400 °C instead of 1500 °C. Assume that $p(\text{O}_2) = 0.1$ mbar for both temperatures.

In a typical run using H₂O and CO₂ simultaneously for the re-oxidation, the following data for a 20-minute and an 8-minute run under the same conditions (1500°C and $p(\text{O}_2) = 0.1$ mbar) were obtained:

Cycle time	20.0 min	8.0 min
Collected Gas	18.5 L	9.4 L
Gas composition	40.7% H ₂ , 4.3% CO, 22.4% CO ₂ , 32.6% Ar	59.9% H ₂ , 6.0% CO, 17.2% CO ₂ , 16.9% Ar

Argon, Ar, is used to repressurize the solar redox unit to 1 bar.

1.6 For the 20.0 min run, **calculate** the H₂ : CO_x ratio where CO_x = CO + CO₂.

1.7 **Calculate** the yield of conversion of CO₂ to CO for the 20-minute run.

1.8 Depending on when the reaction is ended, different compositions are obtained. **Repeat** the calculations of questions 6 and 7 for the 8.0 min run.

The final step (Gas to Liquid, GTL) is the synthesis of methanol or of liquid alkanes according to the Fischer-Tropsch (FT) process. The FT synthesis works with CO and H₂ whereas the methanol synthesis can also process CO₂.

1.9 **Provide** the general reaction equations for the production of alkanes and for the production of alkenes, starting from syngas.

The process producing methanol works both with H₂ + CO, and with H₂ + CO₂.

Preparatory Problems (Theory)



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1.10 Provide the reaction equations for both substrate mixtures.

1.11 Comparing the 20.0 min and 8.0 min runs, decide which one is more suitable for methanol synthesis and which one for the FT process.

In a typical long run 96.2 L of syngas was collected. Its composition was 59.5% H₂ and 4.6% CO, and the rest was CO₂ and Ar. The ratio of H₂ to CO_x was 2.69. In the last step of the sun-to-fuel process, methanol can be synthesized by the processes studied above.

1.12 The yield of methanol production was 85%. Calculate how many grams of methanol were produced.

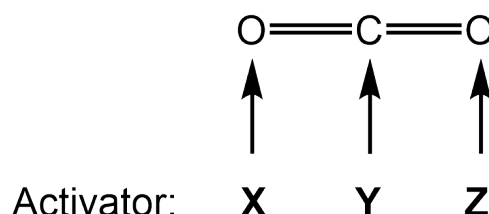
Many-faceted Oxides of Carbon

The trapping and conversion of CO₂ has become a major challenge in modern society. Whereas nature converts CO₂ elegantly into carbohydrates via the Calvin cycle with the help of solar energy, industry uses the Sabatier reaction to convert CO₂ to methane. Along this path, partially reduced products such as formic acid represent important intermediates. Conversion of CO₂ requires its activation, and modern research in homo- and heterogeneous catalysis for this reaction is steadily growing. Essentially any conversion of CO₂ requires H₂, as a co-reactant. Thus, the activation of CO₂ also requires the activation of H₂ at the same time. This leads to very interesting chemistry that includes catalyst design, mechanistic studies and biomimetic chemistry.

- 2.1** **Complete** the following reaction sequence with 2 H⁺ and 2 e⁻ in each step and the eventual side products. **Draw** the structures of **A** and **B**.



- 2.2** To activate CO₂, it must be polarized through non-covalent interactions. **Describe** the chemical properties associated with polarity of potential activators as indicated in the following scheme.



CO₂ and ammonia (NH₃) react to form urea (CO(NH₂)₂), which is a widely used fertilizer in agriculture. Before NH₃ was available in large quantities, CaCO₃ was reacted with carbon to get calcium carbide (acetylide, CaC₂). CaC₂ reacts at high temperatures with N₂ to give CaCN₂. CaCN₂ was used as a fertilizer since it forms urea with water in the soil.

- 2.3** **Draw** the full reaction sequence from CaCO₃ to urea.

- 2.4** Cyanamid H₂CN₂ exists in two tautomeric forms. **Draw** the Lewis structures of both forms.

- 2.5** Sequestering CO₂ from the atmosphere is commercially done with different trapping agents. **Draw** the products obtained from reacting CO₂ with the following compounds.
1. primary amines R-NH₂
 2. 1,2-diamines
 3. glycerol
 4. butadiene (catalyzed)

CO₂ is used by plants to eventually form sugar. The first steps of the process of CO₂ fixation are described

Preparatory Problems (Theory)



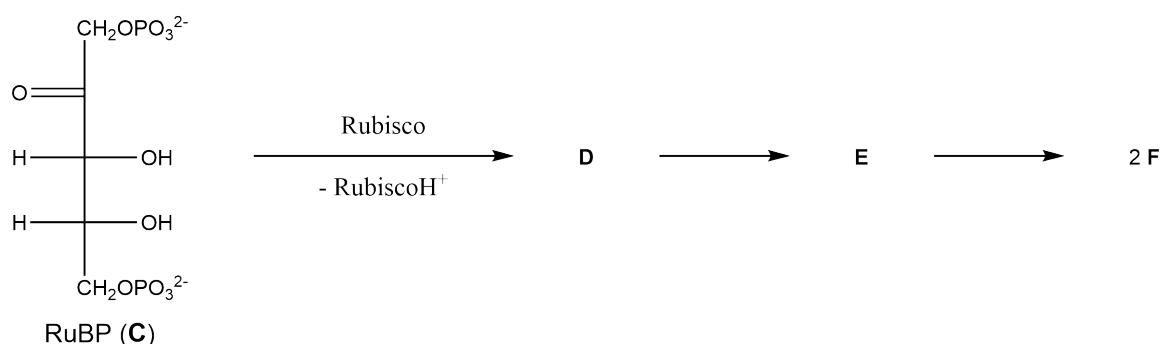
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in the following.

Starting from ribulose 1,5-bisphosphate RuBP (compound C), by action of the enzyme rubisco, a proton at C3 of RuBP is abstracted to form an enediolate D, which then in a nucleophilic attack binds CO₂. The resulting β -ketoacid E is immediately attacked by a water molecule at C3 to form a labile adduct that is split into two molecules of 3-phosphoglycerate F.



2.6 Draw the structures **D**, **E** and **F** for this reaction sequence.

Besides CO₂, there are a number of other neutral binary oxides of carbon, namely CO₃, C₃O₂, and C₁₂O₉. The latter is the anhydride of a hexacarboxylic acid.

2.7 Draw the structures of these binary carbon oxides.

1. CO₃
2. C₃O₂
3. C₁₂O₉

Carbon monoxide CO binds very well to low valent transition metals. The highest stability in such complexes is achieved when all available orbitals are filled.

2.8 Draw a complex with elementary Ni⁰ and CO. Draw its structure according to VSEPR.

2.9 Draw a complex with Fe⁰ instead of Ni⁰. Draw its structure according to VSEPR.

Squaric acid is an uncommon acid, which liberates 4 equivalents of CO after a two-electron oxidation.

2.10 Draw the structure of squaric acid.

2.11 Squaric acid is a rather strong organic acid (pK_{a1} = 1.5, pK_{a2} = 3.4). Explain this observation.

2.12 Propose a structure of a different acid that upon oxidation would liberate 5 equivalents of CO.

What to do with CO₂

The electrochemical reduction of CO₂ (in the following denoted CO₂RR) has the great potential to substantially contribute to the closing of the so-called anthropogenic carbon cycle.

What renders the CO₂RR particularly appealing is that value-added products such as high energy density fuels (e.g. methanol, ethanol, and *n*-propanol) or chemical feedstock (e.g., formic acid, ethylene, and syngas (CO/H₂)) can be produced using the surplus of renewable electricity originating from solar, hydro and wind sources. The counter reaction to the CO₂RR taking place on the anode side of the electrolysis cell is typically the oxidative oxygen evolution reaction (OER).

Key to the CO₂RR process is the use of specific catalyst materials which control both the overall CO₂RR rate and the resulting product distribution. The product distribution of an electrolysis event is typically expressed in terms of the so-called **Faradaic efficiency** ($FE_{product}$ in %). This quantity can be derived from the ratio of the charge consumed for the production of a specific electrolysis product ($Q_{product}$) and the total charge (Q_{total}) transferred at the electrode surface during the electrolysis reaction:

$$FE_{product} = \frac{Q_{product}}{Q_{tot}} \cdot 100\%$$

The sum of Faradaic efficiencies of all formed products adds to 100%.

Silver (Ag) is among the most efficient CO₂RR catalysts for the production of **carbon monoxide (CO)**. A recently developed fabrication method of high surface area catalysts is based on the simultaneous release of H₂ and the electrodeposition of metals on the cathode producing metal foam. A prime example of such novel porous catalyst material is presented at various length scales in **Figure 1a-d** for a silver catalyst.

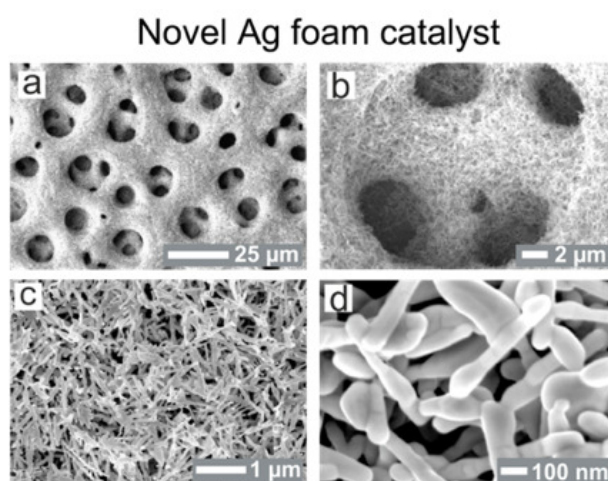


Figure 1: a-d) Scanning electron microscopy of a novel Ag foam.

The effective surface area of this foam can be calculated using electrochemical techniques. A peak current i_p in mA is measured against the potential sweep rate v in V/s. The peak current i_p is proportional to the surface area A and the potential sweep rate v measured in V/s.

This relationship is represented by the Randles-Sevcik equation valid for reversible systems at room temperature.

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$$i_p = 2.69 \cdot 10^5 \cdot n^{3/2} \cdot A \cdot c \cdot D^{1/2} \cdot v^{1/2}$$

with:

n = number of electrons transferred ; A = reactive surface area ; c = concentration D = diffusion coefficient;
 v = potential sweep rate

The constant values are:

$$c = 5 \cdot 10^{-6} \text{ mol/cm}^3 ; D = 5.50 \cdot 10^{-6} \text{ cm}^2/\text{s} ; n = 1$$

Putting together the constant values the equation can be simplified to $i_p = kA\sqrt{v}$.

3.1 Calculate k .

In a run of a silver foam after 20 seconds the following data were obtained:

Scan rate (V/s)	Peak current (mA)
0.005	0.45
0.01	0.84
0.025	1.53
0.05	2.34
0.1	4.21

3.2 Plot the graph and draw the fitting line. Then **calculate** the slope and A in cm^2 . *Hint: For this calculation you need the slope in $\text{A}/\sqrt{\text{V/s}}$ instead of $\text{mA}/\sqrt{\text{V/s}}$.*

Potentiostatic (constant electrolysis potential) CO_2 electrolysis reactions were carried out over the Ag foam and, for comparison purposes, over a planar Ag foil using a CO_2 -saturated 0.5 M KHCO_3 aqueous solution as the electrolyte. **Figure 2a-b** displays plots of the experimentally determined Faradaic efficiencies (FEs) as function of the electrolysis potential applied to the cathode (potential values are displayed versus the Reversible Hydrogen Electrode (RHE)). The comparison of panel a and b clearly demonstrates that the resulting CO_2RR product distribution is not only dependent on the chemical nature of the catalyst material (e.g., Ag) but also on its morphology on various length scales.

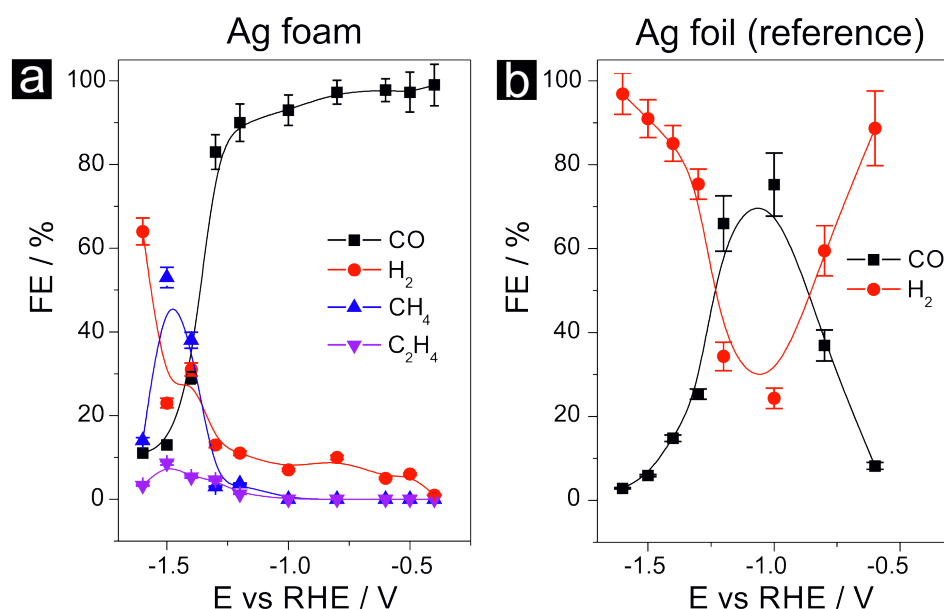


Figure 2: a) Potential-dependent product distribution of the CO₂RR carried out over the Ag foam catalyst shown in figure a-d. b) Product distribution of the CO₂RR carried out over the Ag foil catalyst (reference).

We consider a water/CO₂ co-electrolysis taking place in a classical three-electrode arrangement using a divided electrolysis cell (anolyte and catholyte compartments are separated from each other by a membrane). In the following we focus, however, only on the cathode side of the electrolysis cell where the CO₂RR takes place. As electrolyte we use a CO₂-saturated 0.5 M KHCO₃ aqueous solution. The electrolysis potential applied to the cathode was -1.0 V vs. RHE. A silver foil ($A = 10 \text{ cm}^2$) served as the catalyst (see **Figure 1a**). The only products formed over the Ag foil during electrolysis were CO ($FE_{\text{CO}} = 76\%$) and hydrogen ($FE_{\text{H}_2} = 24\%$).

3.3 **Write** the balanced equations for the production of CO from CO₂ (CO₂RR) and for the parasitic hydrogen evolution reaction (HER) through water splitting. For the CO₂RR consider water as the proton source.

3.4 **Calculate** the (total) current density (j_{tot} ; current normalized to the surface area) when 5 mmol carbon monoxide (CO) were produced within 10 hours of electrolysis.

3.5 Consider the electrolysis current density as constant. **Calculate** the partial current density for the parasitic hydrogen evolution reaction (j_{H_2}).

Consider a CO₂ reduction over the improved Ag foam electrocatalyst. A product distribution analysis revealed that the total current density of the electrolysis reaction at -1.5 V vs RHE is composed of partial current densities of methane formation ($j_{\text{CH}_4} = -18.8 \text{ mA cm}^{-2}$), ethane formation ($j_{\text{C}_2\text{H}_6} = -1.8 \text{ mA cm}^{-2}$), CO formation ($j_{\text{CO}} = -4.8 \text{ mA cm}^{-2}$), and hydrogen evolution ($j_{\text{H}_2} = -8.5 \text{ mA cm}^{-2}$).

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3.6 **Calculate** the corresponding Faradaic efficiencies (FEs). Of note, by convention cathodic currents have a negative sign.

Pathways to H₂ and Catalysts

Hydride ions and complexes

Generally speaking, there are two ways to produce H₂ from H⁺,

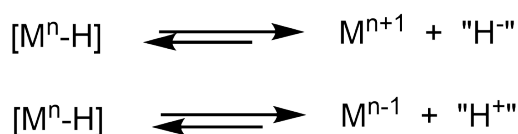
1. $2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2$ and
2. $\text{H}^+ + \text{H}^- \rightarrow \text{H}_2$

Here we focus on the second reaction using hydride ions.

In WWII the American soldiers stationed in Greenland were equipped with a survival kit that contained among others lithium hydride (LiH) in tablet form as it is a lightweight energy source to produce hydrogen gas if combined with water/ice.

4.1 State the type of this reaction (acid/base or redox reaction or both).

Hydride-containing complexes are nowadays considered direct precursors for the formation of H₂ in reaction systems meant for water splitting. Such hydride complexes can act in two ways, as proton donors (acids) or as hydride donors according to the following equations:

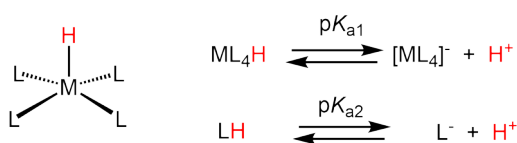


Scheme 1

4.2 Calculate the disproportionation potential of $2\text{M}^\circ \rightarrow \text{M}^+ + \text{M}^-$ as required for making the reaction $2[\text{M-H}] \rightarrow 2[\text{M}^\circ] + \text{H}_2$ possible. The bond energy M-H is 180 kJ/mol and the bond energy of H₂ is 432 kJ/mol.

4.3 The bimolecular reaction between two Co-H complexes as shown in the scheme 1 above has been proposed as a mechanistic pathway to H₂. State the final oxidation state of cobalt for which this reaction is most likely (considering the common oxidation states of cobalt).

The following scheme shows a square-pyramidal hydride complex.



Scheme 2

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- 4.4** **Choose** the correct correlation of the pK_{a2} of the ligand LH with the pK_{a1} of the complex ML_4H according to the given equations.
- ☐ If pK_{a1} goes up, pK_{a2} goes down
 - ☐ If pK_{a1} goes up, pK_{a2} goes up
 - ☐ pK_{a1} and pK_{a2} do not correlate

In photosynthesis two photosystems operate, I and II. Photosystem I needs light energy to transfer electrons to $NADP^+$ and reduce it to NADPH. In photosystem II light is used to convert water into electrons, protons and oxygen.

Thus, plastoquinone PQ (**1**, see scheme below), part of photosystem II, is reduced and protonated twice to hydroplastoquinol H₂PQ (**3**), which is then transferred to photosystem I.

Scheme 3

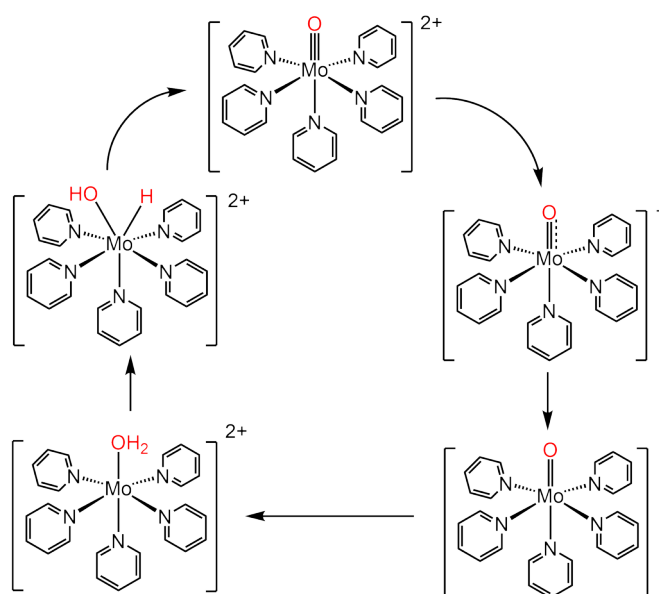
- 4.5** The standard reduction potential $\Delta E_{1/2}^\circ$ is about 0 V. **Sketch** a Frost diagram (Energy vs. oxidation state) for **1**→**3** at pH=7, taking into account that **2** disproportionates into **1** and **3**.

An alternative pathway to H_2 is thermochemical decomposition of ZnO to Zn° and O_2 . The backward reaction of Zn° with H_2O will then give H_2 and ZnO.

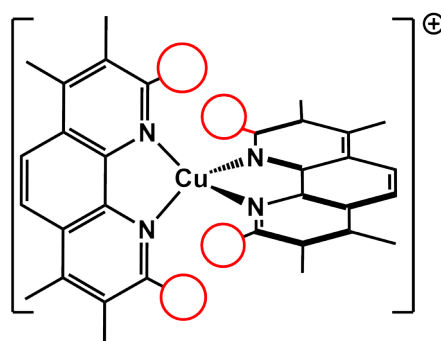
- 4.6** With the following thermodynamic data, **calculate** the temperature at which the equilibrium constant of the reaction $2 ZnO \longrightarrow 2 Zn^\circ + O_2$ is equal to 1. ($\Delta H_f^\circ(ZnO) = -348$ kJ/mol, $S^\circ(ZnO) = 43.6$; $S^\circ(O_2) = 205$; $S^\circ(Zn) = 41.6$ J·mol⁻¹·K⁻¹)

Catalysis

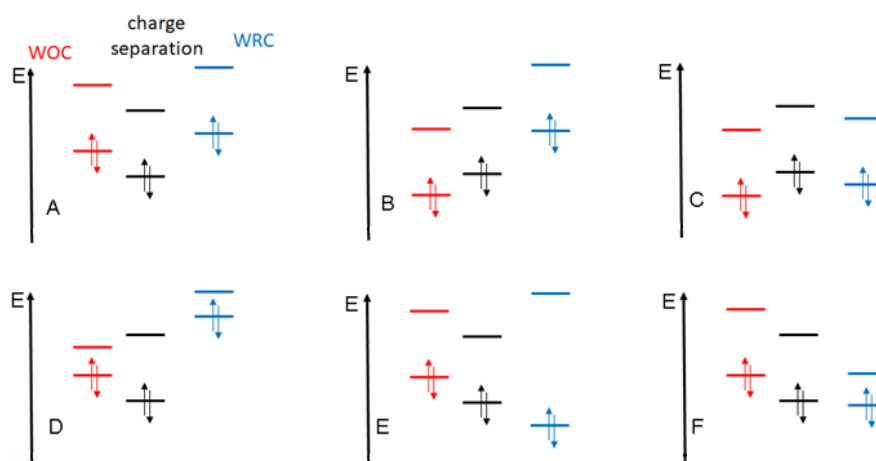
- 4.7 **Complete** the following catalytic cycle with reagents (electron and protons) and the respective oxidation states of the center metal molybdenum.



- 4.8 Copper complexes in the oxidation state +I are tetrahedral and they are square planar in the oxidation state +II. If the transition tetrahedral – square planar is hindered by substituents (red circles) on the ligands, **state** the way the standard reduction potential changes.



- 4.9** **State** which of the following thermodynamic arrangements (A-F) is able to perform a complete water splitting. WOC=water oxidizing catalyst, WRC=water reducing catalyst, black=photosensitizer.



- 4.10** **Sketch** the electron transfer processes after light excitation and the coupled reactions. Complete your scheme with the HOMO level of H_2O to the left and of the LUMO to the right.

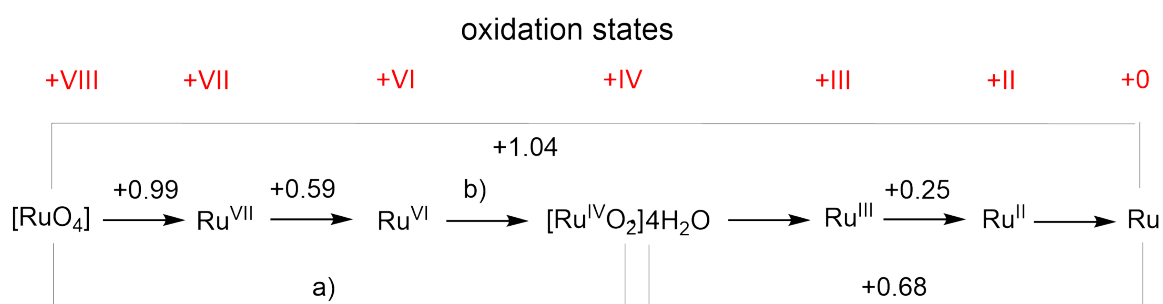
- 4.11** The standard potential for water splitting is $\Delta E^\circ = +1.23 \text{ V}$. **Calculate** the wavelength of a photon that is just able to do the reaction. ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$)

- 4.12** Assuming that the excess energy of an incident photon at 500 nm for the above reaction is not converted to heat but to a photon, **give** a general formula for calculating the wavelength of the "excess energy photon" λ_{ex} as a function of the incident wavelength λ_{inc} in general and for the 500 nm photon in particular.

Two Transition Metals - Many Oxidation States

Among the ruthenium (Ru) isotopes formed during nuclear fission there are two relatively long-lived isotopes, ^{103}Ru and ^{106}Ru , both of which form part of the Highly Active (HA) waste raffinate during spent nuclear fuel reprocessing. Especially the volatile $[\text{RuO}_4]$ is a cause for serious concern. In order to investigate the possible mobilization of this metal in nature, the redox properties are intensively studied. The figure below shows the Latimer diagram of ruthenium for acidic conditions.

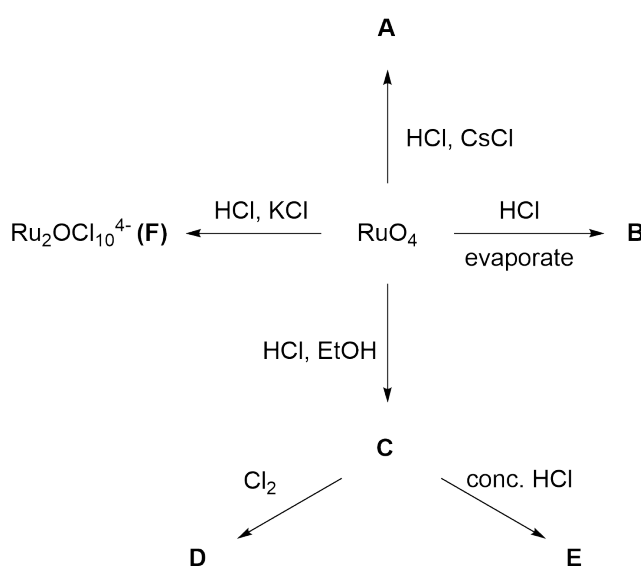
Latimer diagram of ruthenium for acidic conditions (pH 0) vs SHE.



Latimer diagram of Ru for acidic conditions (pH=0) vs SHE (standard hydrogen electrode).

5.1 Calculate the missing potentials a) and b).

Ru forms a number of well-known chloro-complexes. Scheme 2 below shows a choice of the reactions that lead to some of these chloro-complexes starting from $[\text{RuO}_4]$.



All compounds **A** to **E** have 6 ligands, either Cl or H_2O or O or a combination of them. Furthermore, the following information about the different species is given:

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Q5-2

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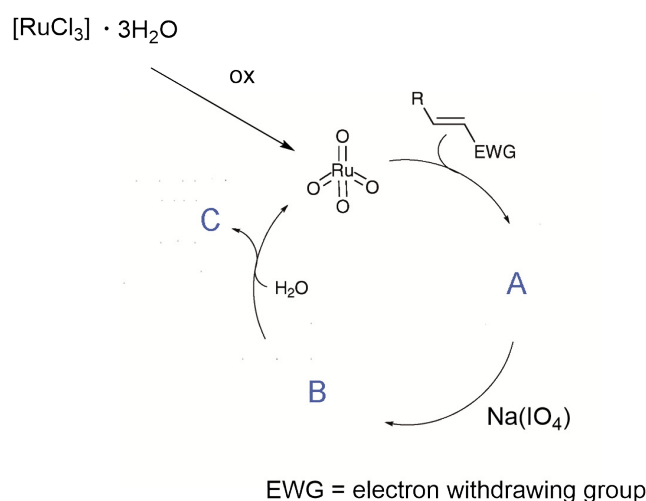
Species	Oxidation State of Ru	Charge of the complex	Molecular Mass (g/mol)
A	+VI	-2	540.69
B	+III		261.48
C	+III	-2	MM > 260
D	+IV	-2	
E	+III	-3	

5.2 Give the formula of compounds **A-E**.

5.3 **F** contains a Ru-O-Ru unit, give the structure of **F**.

5.4 Give the equation for the reaction of $[\text{RuO}_4]$ to compound **A**.

Besides the problem for nuclear waste management, ruthenium today is very important for catalysis and bioinorganic chemistry. An interesting example is the application of $[\text{RuCl}_3] \cdot 3\text{H}_2\text{O}$ in a catalytic reaction called "flash dihydroxylation" (due to its very short reaction time). Mechanistically this reaction is analogous to the very famous Sharpless dihydroxylation with $[\text{OsO}_4]$. Using $[\text{RuCl}_3] \cdot 3\text{H}_2\text{O}$ and $\text{Na}(\text{IO}_4)$ as (re)oxidant a large number of *syn*-dihydroxylation reactions of alkenes have been achieved. The general catalytic cycle of this reaction is depicted in the scheme below.



5.5 Draw the missing Lewis structures **A**, **B**, and **C**.

5.6 Determine the formal oxidation state of all metal centers.

Preparatory Problems (Theory)

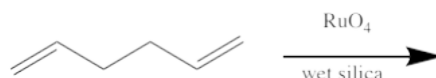


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- 5.7** Starting from a 1,5 diene, **give** the product resulting from the flash bishydroxylation. based on the fact that one equivalent of water is released during the reaction.



- 5.8** Give the product if a 1,6 diene is used instead (same conditions)?

A similar reactivity (but not catalytic) can be observed by the addition of $\text{K}[\text{MnO}_4]$ to a basic aqueous solution of an alkene. However, permanganate has a high oxidative potential and can lead to over-oxidation and oxidative cleavage. Table 1 and 2 show the half-reactions of Mn in H_2O at pH 0 and pH 14.

Redox Reactions at pH 0	E_0 / V
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	1.51
$\text{MnO}_2 + 4\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{Mn}^{3+} + 6\text{H}_2\text{O}$	0.95
$\text{H}_3\text{MnO}_4 + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{MnO}_2 + 3\text{H}_2\text{O}$	2.90
$\text{H}_2\text{MnO}_4 + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_3\text{MnO}_4 + \text{H}_2\text{O}$	1.28
$\text{MnO}_4^- + 2\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{MnO}_4 + 2\text{H}_2\text{O}$	0.92

Table 1

Redox reactions at pH 14	E_0 / V
$\text{Mn}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Mn} + 2\text{OH}^-$	-1.56
$\text{Mn}_2\text{O}_3 + 3\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Mn}(\text{OH})_2 + 2\text{OH}^-$	-0.25
$2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$	0.15
$\text{MnO}_4^{3-} + 2\text{H}_2\text{O} + \text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	0.97
$\text{MnO}_4^{2-} + \text{e}^- \rightarrow \text{MnO}_4^{3-}$	0.27
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56

Table 2

- 5.9** **Draw** the Frost diagram for **manganese in H_2O at pH 0 and pH 14** based on the data in Table 1 and 2.

- 5.10** At **what pH** does $[\text{MnO}_4]^-$ have the **lower reduction potential**: pH 0 or pH 14?

Preparatory Problems (Theory)



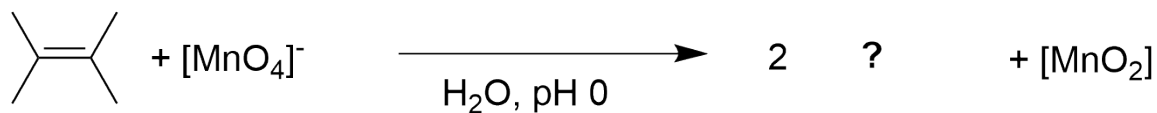
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- 5.11** Based on the Frost diagram, are the following species stable? If not **write** down their reactions in H_2O at pH 0.
- a) H_3MnO_4
 - b) Mn^{3+}
- in H_2O at pH 0?

Overoxidation of an alkene leads to the formation of the corresponding ketone (see example below).

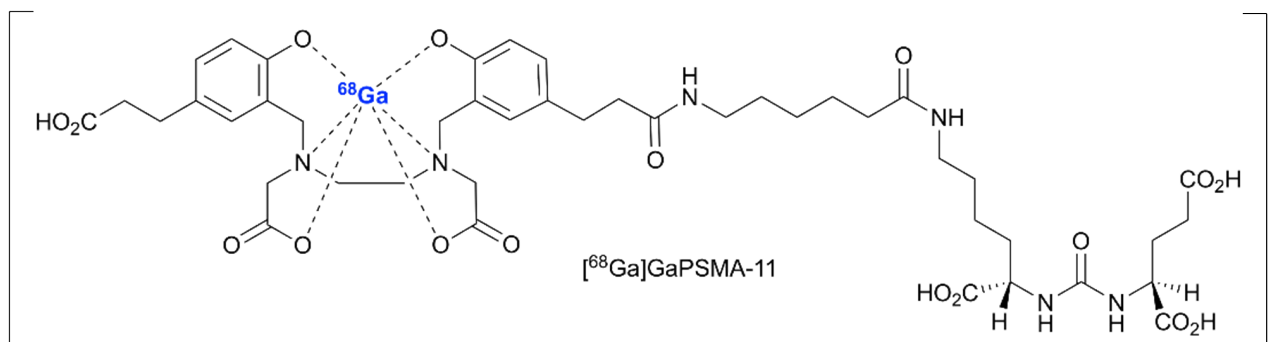


- 5.12** **Draw** the missing Lewis structure.

- 5.13** **Give** the full redox equation for this example.

Useful Radioactivity

$[^{68}\text{Ga}]\text{GaPSMA-11}$ is a radiolabelled compound used in PET imaging (PET = Positron Emission Tomography) of prostate cancer ($t_{1/2}(^{68}\text{Ga}) = 67.7 \text{ min}$).



6.1 A sample containing $[^{68}\text{Ga}]\text{GaPSMA-11}$ has an activity of 100 MBq at 10:00 in the morning.

- a) **Find** the activity at 12:00.
- b) **Find** the activity at 17:30.
- c) If the minimum activity required to record a PET image in a patient is 15 MBq at administration, **find** the latest time that the radiopharmaceutical can be injected.
- d) What is the *specific activity* (GBq/g) of ^{68}Ga ?

6.2 The figure below is a schematic representation of the Chart of the Nuclides. **Name** the decay modes of the parent nucleus that give daughter nuclides shown in the yellow squares (1), (2) and (3).

Preparatory Problems (Theory)

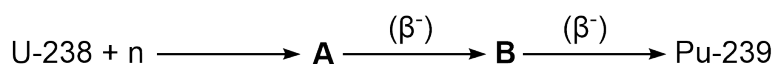


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Nuclear fuel is material used in nuclear power stations to produce heat to power turbines. Most nuclear fuels contain heavy fissile actinide elements that can undergo nuclear fission and sustain the chain reaction. The three most relevant fissile isotopes are uranium-233, uranium-235 and plutonium-239. The plutonium isotope 239 is inevitably produced in nuclear power plants operating with ^{238}U -rich isotope mixtures, due to neutron capture.



6.3 Find the isotopes **A** and **B**.

A complex enrichment process is required for U-235-based nuclear fuel. U-233, on the other hand, can be produced in a reactor by neutron capture from a naturally occurring stable element. The production follows an analogous reaction path as for Pu-239 production.

6.4 State what naturally occurring element must be added to a nuclear reactor to produce U-233. Write out all nuclear reactions and decays that are part of U-233 production.

Geochronology is the science of determining the age of rocks, fossils, and sediments using signatures in the rocks themselves. Absolute geochronology can be accomplished through radioactive isotopes such as the Rb-Sr and the Sm-Nd system. In such "chronometer" systems the amount of daughter nuclide as a function of the amount of mother nuclide and time is given by:

$$N_D = N_M \cdot (e^{\lambda \cdot t} - 1) \quad (1)$$

and can be derived from the law of radioactive decay.

6.5 Derive equation (1) from above.

An interesting chronometer system is based on the decay of K-40. In addition, K-40 (natural abundance 0.012%) has a favorable half-life (1.25×10^9 years) for radiometric dating, which corresponds to 1/4 of the age of the earth. K-40 has a nuclide with an odd proton and neutron number, which leads to special decay properties. K-40 decays by β^- decay (89.14%, $\lambda_\beta = 4.962 \times 10^{-10} \cdot \text{a}^{-1}$ (=per year)) to Ca-40 (decay energy 1.32 MeV) and by electron capture (0.2%) to Ar-40 (ground state, decay energy 1.51 MeV). Furthermore, the electron capture yields Ar-40 in an excited state (10.66%, decay energy 0.05 MeV). By γ -emission (γ -energy 1.461 MeV) the excited state of Ar-40 relaxes to the ground state. The decay constant for the overall electron capture process has been determined as $\lambda_e = 0.581 \times 10^{-10} \cdot \text{a}^{-1}$.

6.6 Draw the generic decay scheme of K-40.

The isotopic composition of Ar in rocks is not constant, but a function of their K content, age and thermal history. Provided that at time $t = 0$ (magmatic or metamorphic age), the sample contained no Ar-40 and from $t = 0$ to the present, the sample was a closed system for K and Ar, the ratio of K-40 / Ar-40 can indicate the age of the rock.

The analysis of 1 kg volcanic rock showed a total potassium content of 0.14 kg. The amount of Ar-40 has been determined as 7.638×10^{-4} mg.

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6.7 Based on the generic decay scheme of K-40, **estimate** the age of this sample.

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Heavy Metal Detoxification

2,3-dimercaptosuccinic acid (DMSA) is a medication for metal poisoning, such as lead (Pb), mercury (Hg), and arsenic (As), with the formula $\text{HO}_2\text{CCH}(\text{SH})\text{CH}(\text{SH})\text{CO}_2\text{H}$. Its mechanism of action is based on chelating by which the drug, called a chelating agent, strongly binds the metal ion, forming a water soluble 1:1 complex that is then excreted via the urinary system.

Dicarboxylicacetylene **A** is reacted with thioacetic acid to give compound **B** to yield the product DMSA.



7.1 **Write** this reaction sequence with structures of all compounds and the reagent **X**.

7.2 DMSA has several stereoisomers. **Draw** all of them, give them a number, and state the absolute configuration of each chiral center. Are there sets of enantiomers within the possible isomers? If yes, **indicate** which of them.

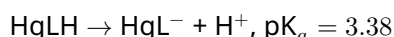
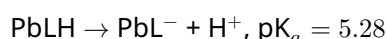
7.3 The active substance in the medication is only one isomer. This isomer reveals a rotation angle of zero under the polarimeter. **Give** the isomer that represents the active substance in the pharmaceutical.

7.4 DMSA is a tetraprotic acid. Its acid dissociation constants are:

- $\text{p}K_{a_1}$: 2.71
- $\text{p}K_{a_2}$: 3.48
- $\text{p}K_{a,\text{SH}1}$: 9.65
- $\text{p}K_{a_1,\text{SH}2}$: 12.05

Calculate the pH of a 0.1 mol/L solution of uncoordinated DMSA (The autoprotolysis of water may be neglected and the deprotonation steps can be considered decoupled).

The acid dissociation constants of the uncoordinated groups in the Pb^{2+} and Hg^{2+} chelates of mono-O-methyl DMSA are given:



The IR spectrum of HgLH shows the presence of a protonated carboxylic group, that of PbLH the presence of a carboxylate group.

7.5 **Draw** the structure of the Pb and of the Hg complex.

7.6 **Explain** the different $\text{p}K_a$ values.

A person was diagnosed with Pb-poisoning when a blood test revealed a blood lead level (BLL) of 85 $\mu\text{g/dL}$. The patient was treated with intravenously administered DMSA and the given dose corresponded

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to 5 mg/kg. Assume an average body weight of 75 kg and blood volume of 5 L.

- 7.7** Assuming that the equilibrium concentration of DMSA is 99.5% of the administered dose, **determine** the free Pb concentration after equilibrium has been reached ($t = 0$).

The clearance of the Pb(DMSA) complex was then monitored by the concentration change in free Pb over a period of 6 hours. The results are shown in the table below:

t / min	0	60	120	180	240	300	360
c / $\mu\text{mol/L}$	c from task 7	1.66	1.34	1.08	0.87	0.70	0.56

(The values are simplified)

- 7.8** **Calculate** the apparent $t_{1/2}$ and k for the clearance of free Pb from the patients blood.

- 7.9** **Calculate** how long it will take until the limiting value of 90 $\mu\text{g/L}$ free Pb is reached.

To test the interaction of the DMSA complex with Cd^{2+} , another toxic metal ion that binds to this ligand, the following experiment was carried out:

To 0.1 mmol DMSA-Pb in 1 L of neutral water, 0.05 mmol of a Cd(II) salt was added. Assume that the volume did not change and no acid/base reaction occurred.

- 7.10** **Write** the reaction equation and the expression for the resulting equilibrium.

- 7.11** **Calculate** the equilibrium constant. The stability constant for DMSA-Pb is $K_1 = 10^{17.6} \text{ M}^{-1}$ and for DMSA-Cd $K_2 = 10^{16.5} \text{ M}^{-1}$.

- 7.12** **Calculate** the equilibrium concentrations of all four species.

Vacuum-UV Modification of PDMS

Poly(dimethylsiloxane) (PDMS) is a transparent polymer used, among else, in heat-resistant tiles. Industrial synthesis starts from dichlorodimethylsilane. By vacuum-UV (VUV) irradiation in presence of oxygen, PDMS coatings can be modified to hard and transparent SiO₂-like coatings. The precursor polymer contains reactive silanol end groups.

8.1 **Draw** structures **A-C**.

8.2 **Order** the following processes by ascending energy by assigning numbers from 1 to 5.

Process	Number
x-ray photon absorption	
γ -photon absorption	
IR-photon absorption	
Electron transfer between molecules	
Ionization of a molecule	

For modification to a SiO₂-like layer, PDMS is irradiated with UV light with a wavelength of 172 nm. The bond energy is 444 kJ/mol.

8.3 **Decide**, based on a calculation, if absorption of one such photon is sufficient to break a Si-O bond.

The absorbance of a PDMS layer of some micrometer thickness for VUV light has been investigated. A 1 μm thick layer of PDMS has an absorbance of 3.5 for VUV light with a wavelength of 172 nm.

8.4 **Compute** the material depth at which 99% of the incoming VUV light has been absorbed using $A = \ln(I_0/I_s)$ to calculate the absorbance.

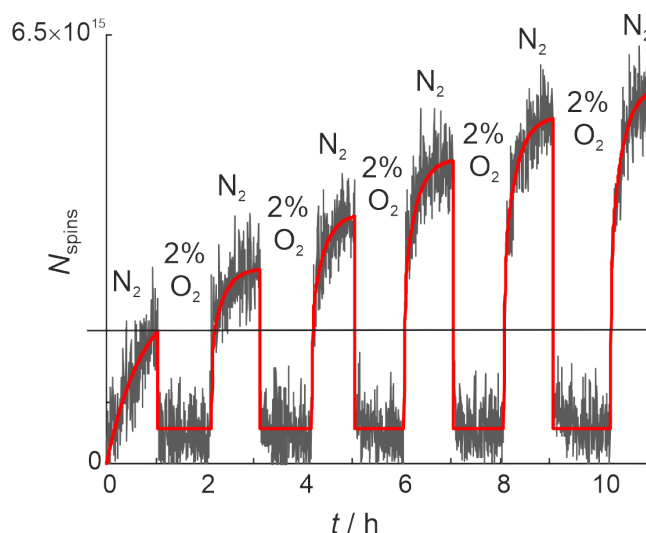


Figure 1: Evolution of the number of electron spins N_{spins} over time t in a VUV-irradiated PDMS sample. Composition of the gas stream was repeatedly switched between pure nitrogen and nitrogen with addition of 2% oxygen. The red line is a fit of radical generation and decay kinetics.

By electron paramagnetic resonance (EPR) spectroscopy, it was found that VUV irradiation of a 2 mm thick PDMS sample in absence of oxygen generates radicals of the type $\cdot\text{CH}_2\text{Si}\equiv$ and $\cdot\text{Si}\equiv$ in a 8:1 ratio. Each radical carries one electron spin. **Figure 1** shows the evolution of the number of spins in an EPR experiment performed under VUV irradiation. The gas stream was repeatedly switched between pure nitrogen and nitrogen containing 2% oxygen.

- 8.5** Assume that an equilibrium exists between the two radical types at 298 K. **Compute** the Gibbs free energy difference $\Delta G = G(\cdot\text{Si}\equiv) - G(\cdot\text{CH}_2\text{Si}\equiv)$.

EPR spectra are split into hyperfine multiplets by nuclear spins following the same rules as for NMR.

- 8.6** **Give** the number of lines of the hyperfine multiplet of the $\cdot\text{CH}_2\text{Si}\equiv$ radical.

- 8.7** **Tick** all boxes with reasonable explanations for the behavior seen in **Figure 1**.

- ☐ Oxidation reduces the molar extinction coefficient. Thus, more light penetrates into the sample in later pure nitrogen phases and more radicals are formed.
- ☐ During the whole experiment, radicals are formed with the same rate, but in the presence of oxygen their signal is invisible.
- ☐ Oxidation creates sites in the modified polymer that are more susceptible to forming radicals.
- ☐ Some of the formed radical sites are stable in the presence of 2% oxygen.

In this experiment, the mean penetration depth of the light was $0.26\ \mu\text{m}$ and the irradiated area $1.5\ \text{cm}^2$. PDMS has a density of $0.95\ \text{g/cm}^3$. After the first irradiation period, total radical number was 2×10^{15} .

- 8.8** Neglecting end group effects, **compute** the percentage of PDMS repeat units that had been transformed into $\cdot\text{CH}_2\text{Si}\equiv$ radicals.

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During this first irradiation period of 1 h duration under N_2 , the EPR signal increased by first-order kinetics with a rate constant of 0.48 h^{-1} .

- 8.9** **Compute** the number of radicals that would have been found by observing the time evolution while irradiating for a very long time under pure N_2 .

In subsequent irradiation periods of 1 h duration under pure nitrogen, 50% of the spins are formed with a first-order rate constant of 48 h^{-1} (A sites) and the other 50% with a first-order rate constant of 4 h^{-1} (B sites).

- 8.10** **Compute** the ratio of A-site to B-site radicals 15 min after switching the gas stream from nitrogen with 2% oxygen to pure nitrogen while the VUV irradiation is going on.

In the context of this study, a compound was characterized by elemental analysis (40.6% C, 35.6% Si, 10.2% H, remainder O), and its NMR spectra. The ^1H spectrum exhibits two singlets at 0.087 and 0.022 ppm with integral ratio 1000:334, the proton-decoupled ^{13}C NMR spectrum two singlets, and the ^{27}Si NMR spectrum also two singlets.

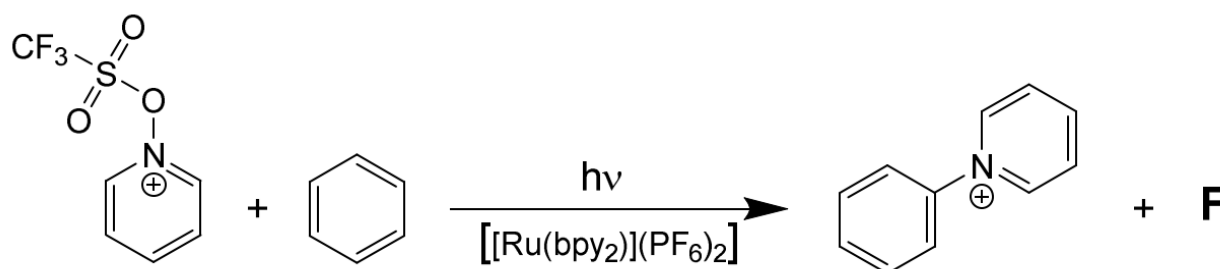
- 8.11** **Draw** the structure of this compound.

There exist symmetric cyclic siloxane oligomers. The oligomer with $n = 4$ is shown below. We consider analysis of oligomers with $n = 4$ -8.

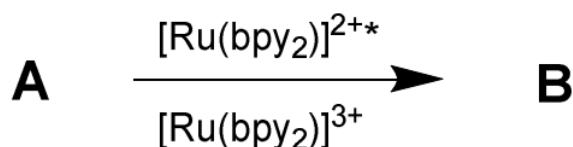
- 8.12** **Tick** the box for each analysis method that you expect to distinguish between oligomers with different n , assuming that the spectra of individual oligomers are not known beforehand.
- ☐ IR
 - ☐ ^1H NMR
 - ☐ ^{27}Si NMR
 - ☐ Determination of molecular mass
 - ☐ Elemental analysis

Exciting Arenes

After photoexcitation with visible light, Ru(II) complexes can transfer an electron to a suitable acceptor, yielding an acceptor-derived radical and a Ru(III) complex. Subsequent reduction of the Ru(III) complex completes the catalytic cycle. Such photocatalysis with an *N*-functionalized pyridinium reagent as the acceptor allows for the pyridination of arenes.



In the initial step, an electron is transferred to one of the educt molecules.



9.1 Draw the structures of **A** and **B**.

In a second step, a bond in **B** is cleaved, yielding a cationic radical **C** and an intermediate product **D**.

9.2 Draw the structures of **C** and **D**.

The cation radical **C** attacks the arene in the third step, forming **E**.

9.3 Draw the structure of **E**.

The intermediate products **D** and **E** reduce the Ru(III) complex. In this final step, compound **F** is formed.

9.4 Draw the structure of **F**.

Preparatory Problems (Theory)

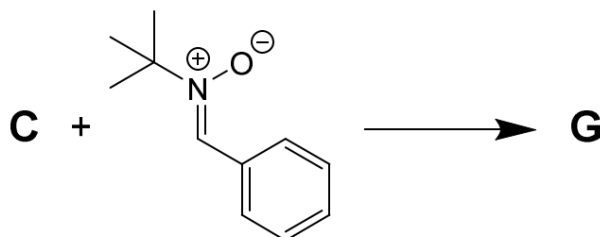


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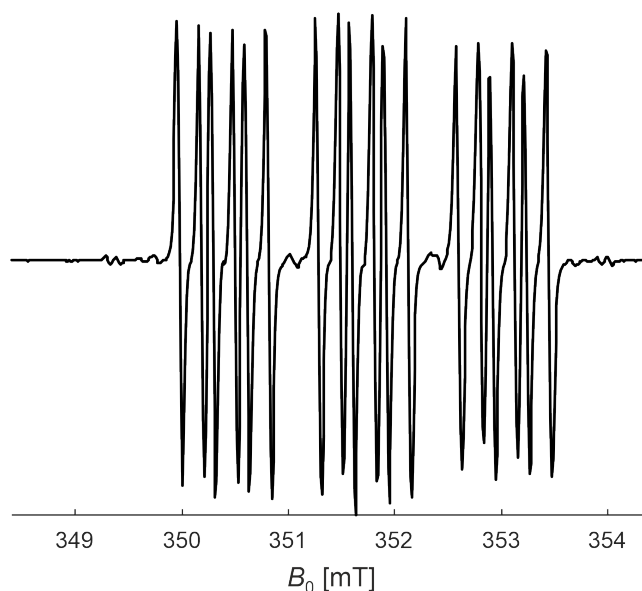
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This mechanism was elucidated by spin trapping of **C** with phenyl *N*-*t*-butylnitron and subsequent detection of the trapped cation radical **G** by electron paramagnetic resonance (EPR) spectroscopy.



9.5 Draw the structure of **G**.

EPR spectra are split into hyperfine multiplets by nuclear spins following the same rules as for NMR. Besides ^1H (spin $\frac{1}{2}$ corresponding to multiplicity 2 or d), ^{14}N (spin 1 corresponding to multiplicity 3 or t) is the only magnetic nucleus with high natural isotope abundance in **G**. The EPR spectrum is shown in Figure 1 as a function of magnetic field B_0 . Note that EPR lines are derivative absorption lines, so that each line features a positive and a negative peak.



9.6 Give the number of ^1H and ^{14}N nuclei that contribute to the resolved hyperfine structure.

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The complete catalytic cycle requires that a C-H bond in benzene with bond energy of 469 kJ/mol is cleaved. Photocatalysis works by excitation at a wavelength of 439 nm.

9.7 Tick all the boxes with true statements.

- ☐ The photon energy alone is sufficient for cleaving the C-H bond.
- ☐ The energy for breaking the C-H bond is supplied by the catalyst.
- ☐ The energy for breaking the C-H bond cannot be discussed separately from bond formation in the same reaction step.
- ☐ The energy for breaking the C-H bond must be supplied by heating the solvent.

Visible light is just one form of electromagnetic wave.

9.8 Sort the following forms of electromagnetic waves by ascending wavelength.
Microwave, green light, IR, red light, UV

The excited $\text{Ru}(\text{bpy})_3^{2+}$ complex has a reduction potential of -1.2 V vs. $\text{Fe}^{0/+}$, whereas the pyridinium reagent has a reduction potential of -0.3 V vs. $\text{Fe}^{0/+}$.

9.9 Compute the equilibrium constant for the electron transfer at 298 K.

In absence of the pyridinium reagent, the excited $\text{Ru}(\text{bpy})_3^{2+}$ complex has a lifetime of 8.55×10^{-7} s before it returns to the ground state by emitting a phosphorescence photon. At a reagent concentration of 5 mM, the intensity of the phosphorescence is half as large as in absence of the reagent.

9.10 Compute the rate constant for the oxidative quenching of the excited complex by the reagent.

In the context of this study, compound **H** was prepared and analyzed. The molar mass was 161.2 g/mol and elemental analysis provided weight percentages of 81.9% C, 8.7% N, remainder H. The ^1H NMR spectrum featured the following signals: 7.43-7.19 ppm (multiplet, 2H, signal a), 6.97 ppm (doublet of triplets, 2H, signal b), 6.90-6.71 ppm (multiplet, 1H, signal c), 3.74-2.91 ppm (multiplet, 4H, signal d), 1.87-1.67 ppm (multiplet, 4H, signal e), 1.66-1.44 ppm (multiplet, 2H, signal f).

9.11 Draw the structure of compound **H** and assign the protons to the NMR signals.

Using electron transfer catalysis, the cationic isomers **I**, **J** and **K** were synthesized, separated and analyzed. All three product cations contain C, H and N only and their ESI-MS signal is at $m/z=212.1434$. Elemental analysis of the isolated compounds including the organic counterion with the molecular formula $\text{C}_a\text{H}_b\text{F}_c\text{N}_d\text{O}_e\text{S}_f$ results in C (53.18%), H (5.02%), F (15.77%), N (3.88%).

9.12 Based on a calculation, give the molecular formula of the counter ion.

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In the following the NMR signals of the different salts containing cations **I-J** are given.

I: ^{13}C NMR δ 155.4, 147.6, 145.7, 143.9, 131.1, 129.6, 129.3, 122.8, 122.5 (counter ion), 118.3, 36.0, 31.3.

δ	Multiplicity	Integral
9.00 – 8.94	m	2H
8.69	tt, $J = 7.9, 1.3 \text{ Hz}$	1H
8.24 – 8.16	m	2H
7.79	ddd, $J = 8.0, 1.8, 1.0 \text{ Hz}$	1H
7.73	t, $J = 2.1 \text{ Hz}$	1H
7.64	t, $J = 8.0 \text{ Hz}$	1H
7.53	ddd, $J = 8.1, 2.4, 1.0 \text{ Hz}$	1H
1.39	s	9H

J: ^{13}C NMR δ 148.7, 147.9, 145.0, 141.9, 132.8, 130.9, 129.2, 129.2, 129.0, 128.6 (counter ion), 36.9, 32.0.

δ	Multiplicity	Integral
8.95 – 8.86	m	2H
8.74	tt, $J = 7.9, 1.4 \text{ Hz}$	1H
8.24 – 8.15	m	2H
7.83	dd, $J = 8.3, 1.4 \text{ Hz}$	1H
7.67	ddd, $J = 8.2, 7.3, 1.5 \text{ Hz}$	1H
7.47	ddd, $J = 7.9, 7.3, 1.4 \text{ Hz}$	1H
7.31	dd, $J = 7.9, 1.5 \text{ Hz}$	1H
1.12	s	9H

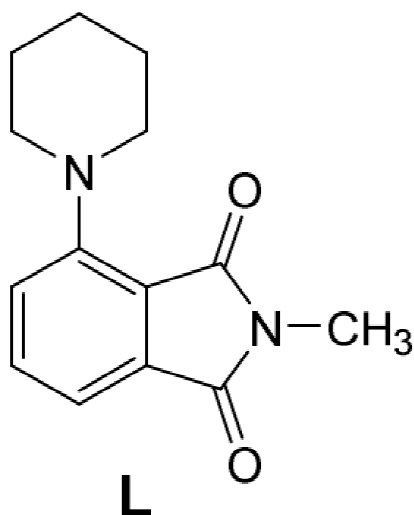
K: ^{13}C NMR δ 156.2, 147.5, 145.5, 141.5, 129.4, 128.5, 124.9, 122.1 (counter ion: d, $J = 320.9 \text{ Hz}$), 35.8, 31.3.

δ	Multiplicity	Integral
8.99 – 8.89	m	2H
8.68	tt, $J = 7.9, 1.3 \text{ Hz}$	1H
8.20	dd, $J = 7.9, 6.6 \text{ Hz}$	2H
7.80 – 7.74	m	2H
7.71 – 7.62	m	2H
1.39	s	9H

9.13 Draw the structures of **I**, **J** and **K**.

9.14 Give the number of isolated spin systems in compound **I**.

Compound **L** can be obtained after hydrogenating a pyridinated arene.



9.15 Give the numbers of signals and their multiplicities expected for compound **L** in ^1H and ^{13}C NMR.

Fluorinated Main-Group Compounds

Selenium is an essential element for humans. Its chemistry resembles that of sulfur and tellurium, with some similarities to arsenic too. Imagine compound **A** with elemental composition CFNOSe.

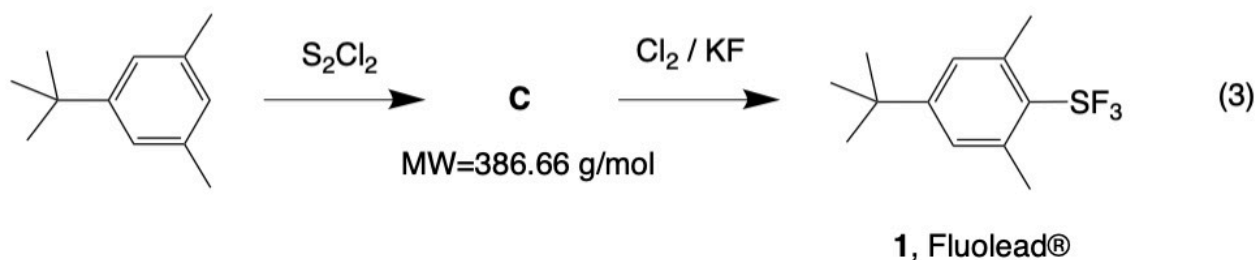
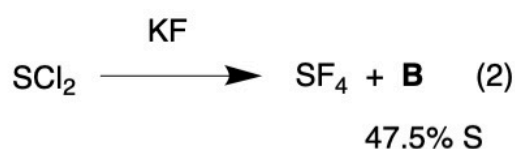
- 10.1** **Draw** a complete Lewis structure for **A** taking into account that a) the Selenium atom is bonded to three of the remaining four atoms, b) that N and O display in this compound the lowest possible oxidation number and c) that there are only two multiple bonds and d) that there are no formal charges

- 10.2** **Select** which interatomic angle $\alpha(\text{X-Se-Y})$ is the smallest in this molecule.

Since the original discovery of $\text{Xe}[\text{PtF}_6]$ by N. Bartlett in 1962, many noble gas compounds are nowadays known. Thus, Xe forms bonds not only with the most electronegative elements F and O but also with less electronegative elements such as C.

- 10.3** **Draw** the Lewis structure and **assign** a geometry to the following Xe species: XeF_2 , XeF_4 , XeOF_2 , XeO_3 , XeOF_4 , and $[\text{XeF}_2(\text{C}_6\text{F}_5)]^+$.

There are several nucleophilic fluorinating agents known. SF_4 is a highly reactive, toxic, gaseous compound that can be prepared from SCl_2 upon reaction with Cl_2 in the presence of KF, see reaction (1) below. However, it also forms when SCl_2 is reacted with KF in the absence of Cl_2 , in which case compound **B** is formed as byproduct, see reaction (2). Fluolead (**1**), a crystalline material, is a tamed form of highly reactive SF_4 and can be prepared in a two-steps sequence as shown in reaction (3).



- 10.4** **Formulate** the structure of intermediates **B** and **C** as well as balanced equations for reactions (1)-(3), knowing that **B** contains 47.5% sulfur and that the molecular weight of **C** is 386.66 g/mol.

Preparatory Problems (Theory)



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10.5 **Choose** the most appropriate description for reaction (2).

- ☐ Oxidation of SCl_2
- ☐ Nucleophilic substitution reaction
- ☐ Disproportionation
- ☐ Reduction of chlorine

10.6 **Draw** two possible Lewis structures for compound **B**.

10.7 **Draw** the structure of SF_4 and Fluolead **1**. Abbreviate the aryl substituent with Ar. **State** their geometry in terms of the arrangement of valence-shell electron-pair domains.

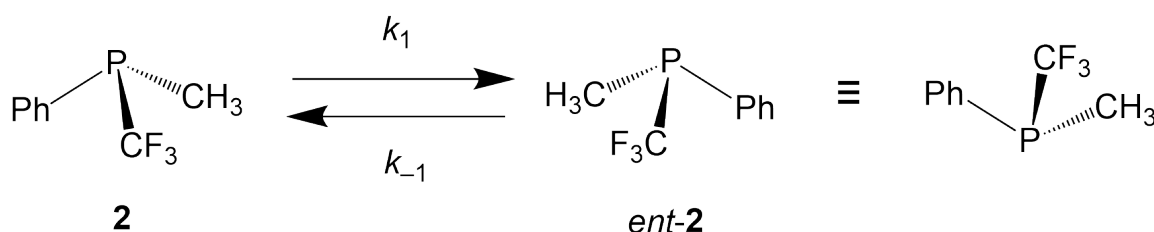
Fluolead reacts with a number of oxygen-containing functional groups, e.g. alcohols, ketones, or carboxylic acids, leading to the replacement of the oxygen atom(s) by fluorine atoms. Thus, the reaction of benzylic alcohol, PhCH_2OH , affords the corresponding primary alkyl fluoride in such a deoxyfluorination reaction.

10.8

Formulate the two reactions of PhCH_2OH with SF_4 and Fluolead (**1**), respectively, knowing that these reactions are usually not carried out in a glass apparatus, because e.g. HF reacts with glass. PhCH_2OH and SF_4 react in a 1:1 stoichiometry. **Draw** the structure of the respective sulfur-containing products for both reactions.

Dynamic Phosphorus and Arsenic Compounds

Compounds such as $\text{PhP}(\text{CH}_3)\text{CF}_3$ (**2**) are chiral. The activation barrier for the interconversion of one enantiomeric form into the other (enantiomerization process) is called inversion barrier or enantiomerization barrier, $\Delta G_{\text{en}}^\ddagger$. The calculated value for this compound in the gas phase is $\Delta G_{\text{en}}^\ddagger = 37.3 \text{ kcal}\cdot\text{mol}^{-1}$.



k_1 and k_{-1} are the rate constants for the corresponding first-order kinetics processes and are defined as follows:

$$k_1 = k_{-1} = k_{\text{en}}$$

And the racemization rate constant k_{rac} :

$$k_{\text{rac}} = k_1 + k_{-1} = 2k_{\text{en}}$$

11.1 Determine the absolute configuration of **2** and of its enantiomeric form *ent-2*.

11.2 Compute k_{en} for $T = 100^\circ\text{C}$ using the Eyring equation:

$$\Delta G_{\text{en}}^\ddagger = R \cdot T \cdot \ln \left(\frac{k_B \cdot T}{k_{\text{en}} \cdot h} \right)$$

where k_B stands for the Boltzmann constant.

11.3 Compute the half-life ($t_{1/2}$) for the racemization process of **2** at 100°C .

11.4 Assume that you have an enantiomerically pure sample of **2**. **Calculate** how long it takes until this sample displays an enantiomeric excess of 90%ee when kept in the gas phase at 100°C . Use the general form of the integrated rate law:

$$\ln \frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty} = -2 \cdot k_{\text{en}} \cdot t$$

where $[A]$ represents the concentration of any of the two enantiomers (**2** or *ent-2*), at times t , 0, and ∞ , as indicated by the subscripts.

Apicophilicity is the pronounced preference of strongly electronegative substituents to take an apical position, typically in trigonal-bipyramidal structures. Corresponding isomeric structures in which this is not the case are called *anti*-apicophilic.

Preparatory Problems (Theory)



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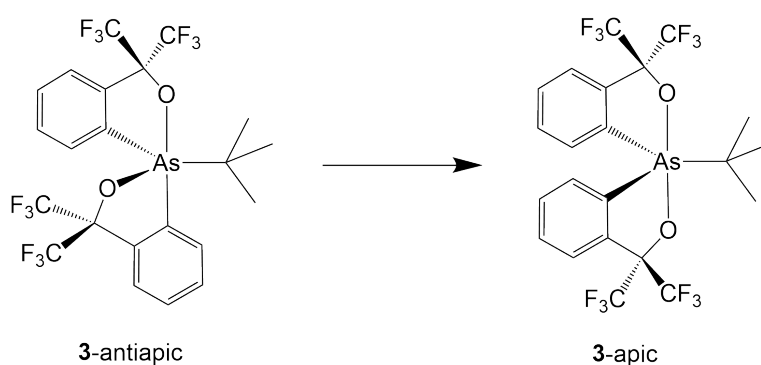
English (Official)

11.5 **Draw** the two possible geometries (isomers) of HPF_4 and mark the major one.

11.6 **State** how many ^{19}F NMR signals are displayed by these compounds.

11.7 Assume an equilibrium between the two isomers in which the minor isomer is formed from the preferred one. The calculated ΔG° is $4.24 \text{ kcal}\cdot\text{mol}^{-1}$. **Calculate** the equilibrium composition at standard conditions for such an isomerization process.

The anti-apicophilic isomer (**3-antiapic**) of the arsoranes shown below is formed as the kinetic product though it is less stable. The rate constant of thermal isomerization, also called stereomutation, to the more stable isomer (**3-apic**) has been determined at 333 K and at 363 K to be $1.78 \times 10^{-5} \text{ s}^{-1}$ and $5.47 \times 10^{-5} \text{ s}^{-1}$, respectively.



11.8 **Determine** the activation energy E_a for this process (use an Arrhenius treatment).

11.9 **Choose** which of the following options best describe the stereochemical relationship between compounds **3-antiapic** and **3-apic**.

- ☐ Enantiomers
- ☐ Rotational isomers
- ☐ Diastereomers
- ☐ *Cis-trans* isomers
- ☐ Conformational isomers

From Curves to Straight Lines

The first train in Switzerland ran from Zurich to Baden (16 km) in 1847. First-constructed railways could become curved because of the heat stress caused by temperature expansion of the steel. And it was not possible to return it to the initial linear form. Later some engineering solutions were developed to prevent this issue.



In mathematics this isn't a problem as even extremely curved graphs can sometimes be presented in linear form. Mathematical linearization is useful for analyzing big data sets in STEM as linear graphs only require two points to be defined uniquely. By linearization simple relationships can be found for even complicated equations.

A. Ideal gas law

12.1 **Obtain** a linearized equation for the ideal gas law by choosing variables composed of pressure (P) and volume (V) functions at a constant temperature.

12.2 **Find** the values of the slope and the x - and y -intercepts in this case. **State** in which direction is this graph displaced when the temperature rises.

12.3 **Explain** why deviations from the linear plot are experimentally observed at high pressures.

B. Equilibrium constant

12.4 **State** which set of axes should we use to obtain a linear plot for the equilibrium constant as a function of temperature $K = f(T)$.

- 12.5** **Select** the equations that use analogous sets of axes for their linear plots. **Give** the expression to calculate the slope for every chosen equation:
- First-order kinetics;
 - Zero-order kinetics;
 - Clausius–Clapeyron equation for phase equilibrium (liquid–gas);
 - Clapeyron equation for phase equilibrium (solid–liquid);
 - Nernst equation (for potential as a function of one of the concentrations);
 - Arrhenius equation.

- 12.6** **Define** which set of axes should we use to obtain a linear plot for the equilibrium constant as a function of pressure $K = f(P)$. **State** what is the slope in this case.

C. Example mathematical function

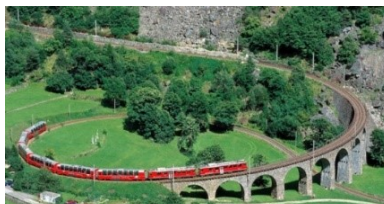
Let's take another interesting function $y = \frac{a \cdot x}{b+x}$. Three different linearization techniques could be applied to it. The first of these linearization methods gives a slope $1/a$, another gives the horizontal intercept $-1/b$, and the third gives a as the interception with the vertical axis (see table below).

No.	Linearized equation	Slope	Horizontal intercept	Vertical intercept
1		$1/a$		
2			$-1/b$	
3				a

- 12.7** **Complete** this table.

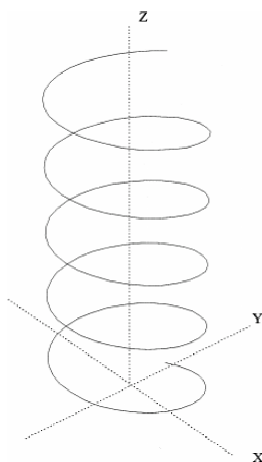
D. Helix function

In 1908, an astonishing spiral railway known as the Brusio spiral viaduct was built in the Canton of Switzerland called Graubünden. It became a World Heritage Site of UNESCO in 2008.



A well-known molecule with a similar spiral structure is DNA, which adopts a double helix form.

The mathematical three-dimensional function describing each helix in DNA is known as a circular helix with constant values of radius r and pitch p (helix height during one complete turn of the helix).



Consider a helix function with initial point at $(x = 0, y = r, z = 0)$ and a z -axis located in the center of the helix, which the helix rotates around (see the figure). The angle α is the inclination versus the horizontal XY -plane known as the helix angle. The angle β is the angle of the helix turn, e.g., $\beta = 720^\circ$ corresponds to 2 complete turns of the helix. The x - and y -coordinates can be expressed as the functions of β : $x = r \cdot \sin\beta$ and $y = r \cdot \cos\beta$.

12.8 **Derive** the expression for the dependence of the total helix height on angles α and β .

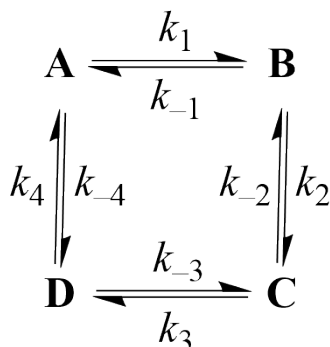
12.9 **State** under which conditions can the total height be represented as the linear function of $\alpha \cdot \beta$ product.

12.10 **Deduce** if it is possible to linearize z as a function of x or y (instead of angle β) if α is constant.

12.11 **Calculate** the total length of the molecular chain (mm) of the DNA that has 2023 turns, chain inclination $\alpha = 20^\circ$ and radius $r = 20 \text{ \AA}$.

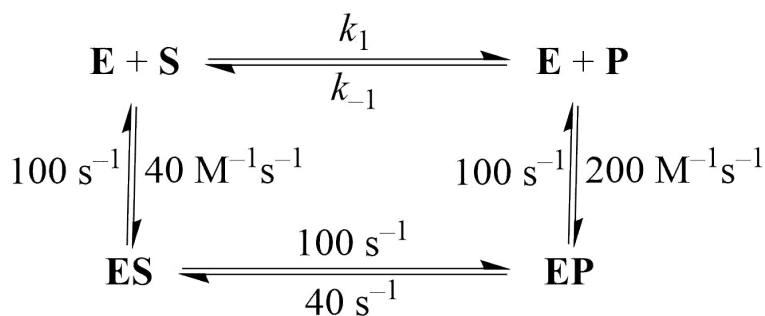
Sweet Michaelis-Menten Kinetics

A set of reactions at equilibrium can be characterized by detailed balance, in which the flow of the forward and reverse reactions of the system are equivalent. Let us start with a simple reaction scheme as follows:



13.1 Give the relationship between all the forward (k_i) and reverse (k_{-i}) rate constants.

An enzymatically catalyzed reaction can be written down in the following format, where **E** represents the enzyme:



The ratio between the free product **P** and free substrate **S** concentrations (not in equilibrium) is $\frac{[\text{P}]}{[\text{S}]} = 10$.

13.2 Choose the direction of the reaction flow.

- ☐ **S** → **P**
☐ **P** → **S**
☐ no net flow

The concept of flows can be used to derive the rate for enzymatic reactions. The absolute flow J_i is defined for each step as the difference between forward and reverse reaction rates, i.e. $J_i = v_i - v_{-i}$. The relative flow j for the enzymatic reaction is the reaction rate divided by $[\text{E}]_0$, i.e. $j = \frac{v}{[\text{E}]_0}$. Let us now consider an enzyme **E** that catalyzes the reaction **S** → **P** at a steady state according to the scheme:

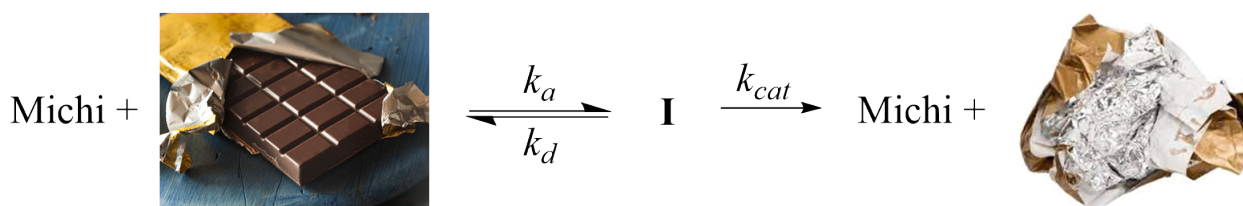
13.3 Considering the general form of the Michaelis–Menten equation, **determine** the expression for k_{cat} for the reaction scheme above using the concept of flows.

Hint: In a classical Michaelis–Menten mechanism, it follows for k_{cat} : $j = k_{cat} \frac{[S]}{K_M + [S]}$.

Switzerland is unprecedented in the production of high-quality chocolate. In that manner, Swiss children need to be able to differentiate the types of equally good chocolate.

Michi is a Swiss child who loves chocolate. His favorite brand is X chocolate. However, Y, a competitor of X, is trying to convince Michi that their chocolate is more delicious.

Michi has grown up to differentiate very well between X and Y chocolate. Let's treat Michi as the enzyme and chocolate as the substrate using Michaelis–Menten kinetics. Michi can either take chocolate (rate constant k_a , state **I**) and refuse it (rate constant k_d), or eat it (rate constant k_{cat}).



13.4 **Show** that the relative reaction flow j is proportional to the substrate concentration in case the Michaelis constant $K_M \gg [\text{chocolate}]$ and is constant in case $K_M \ll [\text{chocolate}]$.

Michi got a Magic Box as a present for his birthday with an equal and relatively big number of X and Y chocolates. After one year (ca. 52.5 weeks), Michi produced n (integer two-digit number) times more X chocolate papers than Y. The ratio between chocolates left in the Magic Box became 1.150. The sum of Michi's k_{cat} for X and Y is 2 week^{-1} . Consider that the number of chocolates can only be an integer.

13.5 **Find** how many chocolates were initially in the Magic Box and the ratio of relative flows of X and Y chocolate consumption by Michi.



Enzymes that have Everything "in Order"

Switzerland is a world-famous producer of chocolate and cheese. What is common in their processing from a chemical point of view? Fermentation is the answer! It is a process of changing the chemical composition by enzymatic reactions.

The Michaelis–Menten model is mainly used to describe the enzyme kinetics. It was originally derived for single-substrate reactions. However, approximately 60% of the known enzymatic reactions are in fact bimolecular. Here is one of the possible mechanisms for an ordered sequential reaction of substrates **A** and **B**, giving the products **P_A** and **P_B** under the catalysis of enzyme **E**:

- 14.1** a) Assuming rapid equilibrium for the formation of complex **EA** and the steady state approximation for complex **EAB**, **derive** the expressions for $[E]$ and $[EA]$ via the concentrations of **EAB**, **A**, and **B**. Use the dissociation constant:

$$K_1 = \frac{k_{-1}}{k_1} = \frac{[E] \cdot [A]}{[EA]}$$

- b) Using a mass balance for the total concentration of enzyme $[E]_0$, **express** the mole fraction of **EAB** (α_{EAB}).
c) **Derive** an expression for the initial rate of formation of **P_A** and **P_B**.

When the concentration of either substrate **A** or **B** is kept constant, the expression for the initial reaction rate takes a Michaelis–Menten form.

- 14.2** **Fill** in the gaps in the following statements:

- a) If the concentration of **A** is kept constant ($c_{A,0}$), the initial rate _____ (*increases/decreases*) with increasing $[B]$ and has a minimum value $v_{\min} =$ _____ and a maximum value ($v_{\max}$), which _____ (*depends/doesn't depend*) on $c_{A,0}$.
b) If the concentration of **B** is kept constant ($c_{B,0}$), the initial rate _____ (*increases/decreases*) with increasing $[A]$ and has a minimum value $v_{\min} =$ _____ and a maximum value ($v_{\max}$), which _____ (*depends/doesn't depend*) on $c_{B,0}$.

- 14.3** **Derive** expressions for $v_{\max}$ under conditions mentioned in both tasks **2a)** and **2b)** to confirm your statements.

- 14.4** **Express** Michaelis constants K_M of the classical Michaelis–Menten equation for both cases from tasks **2a)** and **2b)**.

In some cases, when an enzymatic reaction doesn't follow Michaelis–Menten kinetics, a more compli-

cated mechanism might be in operation. When experiments were conducted with enzyme **E**, it appeared that only in the case of a constant concentration of **A** the reaction kinetics could be described with the Michaelis–Menten mechanism. When the concentration of **B** was kept constant ($[B]_0$) and the concentration of **A** varied, the following graph was obtained:

14.5 **Complete** the mechanism of the enzymatic reaction presented at the beginning of the task with one additional step, that would explain the inhibition of the reaction at high concentrations of **A**. Note that 1 molecule of the enzyme **E** can bind only up to 2 molecules of substrates.

The maximum value for the initial rate presented on the graph can be expressed as:

$$v_{\max} = \frac{k_3 \cdot [E]_0}{\frac{\alpha}{[B]_0} \cdot (1 + 2\beta) + 1} \quad (1)$$

where α and β are some constants derived from rate (or equilibrium) constants.

14.6 Following the same steps as in task 1, **derive** the expressions for α and β and find $[A]_{\max}$ corresponding to $v_{\max}$.
Hint: The function $ax + \frac{b}{x}$ has extrema at those values of x that correspond to the intersection of functions ax and $\frac{b}{x}$.

$^{16}\text{O}/^{18}\text{O}$ isotope exchange

The Nobel Prize in Chemistry was awarded to George de Hevesy in 1943 “for his work on the use of isotopes as tracers in the study of chemical processes”. Nowadays isotope exchange reactions are widely used in organic, inorganic, physical, bio- and pharmaceutical chemistry for investigating reaction mechanisms. In such isotope exchange reactions, the isotope distribution eventually reaches an equilibrium (as expressed by mole fractions) because of the transfer of isotopically different atoms or groups.

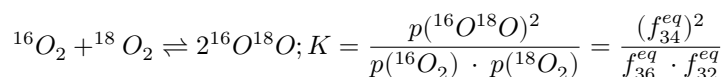
An example of isotope exchange reactions is the $^{16}\text{O}/^{18}\text{O}$ isotope exchange in molecular oxygen. Oxygen molecules that differ only in their isotopic composition, are called isotopologues, and in a system containing ^{18}O and ^{16}O isotopes there are three dioxygen isotopologues: $^{16}\text{O}_2$, $^{18}\text{O}_2$, and $^{16}\text{O}^{18}\text{O}$.

The isotopic composition of the system containing different O_2 isotopologues (not necessarily in equilibrium concentrations) may be described using the mole fractions of the isotopologues: f_{32} , f_{34} and f_{36} corresponding to the fractions of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$, respectively. The sum of all fractions is equal to unity, therefore two independent parameters are sufficient to fully describe the isotopic composition. Typically, one is the fraction of the $^{16}\text{O}^{18}\text{O}$ isotopologue, and the second is α – the fraction of the ^{18}O **atoms** in the system.

15.1 Express α in terms of the fractions of the molecular oxygen isotopologues.

15.2 Express f_{32} and f_{36} in terms of f_{34} and α .

Homogeneous isotope exchange in the gas phase is described by the following reaction:



Where $p(^x\text{O}^y\text{O})$, $x, y = 16, 18$ is the partial pressure of different oxygen isotopologues at equilibrium, f_i^{eq} , $i = 32, 34, 36$ are the mole fractions of different isotopologues at equilibrium, and K is the thermodynamic equilibrium constant.

The entropy of a system, S , is proportional to the natural logarithm of the number of possible microscopic states of a system, W .

$$S = k_b \cdot \ln W$$

where k_b is the Boltzmann constant.

For the reaction above, the number of possible microstates for the $^{16}\text{O}_2$ and $^{18}\text{O}_2$ isotopologues is equal to one. In contrast, $W = 2$ for $^{16}\text{O}^{18}\text{O}$ because the oxygen atoms are distinguishable in this molecule. In general, W for an arbitrary $^{18}\text{O}/^{16}\text{O}$ isotopologue containing n oxygen atoms in total, of which m atoms are ^{18}O , may be calculated via the following formula:

$$W = C_m^n = \frac{n!}{m!(n-m)!}, \text{ where } n! = 1 \cdot 2 \cdot \dots \cdot n; 0! = 1$$

Based on this, for the chemical reaction above standard change in entropy ($\Delta_r S^0$) may be calculated as follows:

$$\Delta_r S^0 = 2 \cdot k_b \cdot \ln 2 - k_b \cdot \ln 1 - k_b \cdot \ln 1 = 1.87 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1} \quad (11.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

Preparatory Problems (Theory)



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15.3 Calculate the change in standard Gibbs free energy at 298 K ($\Delta_r G_{298K}^0$) and the thermodynamic equilibrium constant for the reaction of homogeneous isotope exchange in the gas phase described above. **Select** how the thermodynamic equilibrium constant of this reaction depends on temperature.

- ☐ The constant increases with increasing temperature.
- ☐ The constant decreases with increasing temperature.
- ☐ Temperature has no effect on the constant.

15.4 For the closed system initially containing 0.5 mol of $^{16}\text{O}_2$ and 0.5 mol of $^{18}\text{O}_2$, **calculate** the equilibrium fractions of all isotopologues and parameter α .

The time evolution of f_{34} in closed system is described by the following equation:

$$f_{34}(t) = f_{34}^{eq} - (f_{34}^{eq} - f_{34}(0))e^{-k \cdot t}$$

15.5 Sketch how the parameter α and fractions of all isotopologues change with time in the system described above during its way towards equilibrium isotopic distribution. If you were unable to calculate the equilibrium distribution, assume that at $f_{36}^{eq} = f_{34}^{eq} = f_{32}^{eq} = \frac{1}{3}$.

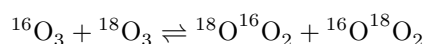
Another form of oxygen in the gas phase is ozone O_3 with possible isotopologues $^{16}\text{O}_3$, $^{18}\text{O}^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}_2$, $^{18}\text{O}_3$. For some of the ozone isotopologues there are isomers having the same number of each isotopic atom but differing in their positions in the molecule. Such isomers are called isotopomers.

15.6 Select the number of isotopomers for each isotopologue of ozone. The ozone molecule has bent (V-shape) geometry.

	number of isotopomers		
isotopologue	1	2	3
$^{16}\text{O}_3$			
$^{18}\text{O}^{16}\text{O}_2$			
$^{16}\text{O}^{18}\text{O}_2$			
$^{18}\text{O}_3$			

15.7 Calculate the number of possible microstates W for all ozone isotopologues.

15.8 For the following isotope exchange reaction between ozone molecules in gas phase,



Calculate the change in standard entropy ($\Delta_r S^0$), the change in the standard Gibbs free energy at 298 K ($\Delta_r G_{298K}^0$) and the thermodynamic equilibrium constant. If you were unable to calculate the number of possible microstates of the ozone isotopologues, assume that $W = 1$ for $^{16}\text{O}_3$ and $^{18}\text{O}_3$ and $W = 4$ for other isotopologues.

Diffusion of Oxygen Isotopes

Perovskites, a class of oxides with general formula ABO_3 , where A and B are metals, have long been proposed as cathodes in solid oxide fuel cells. One way in which perovskites are studied is through solid state isotope exchange experiments. Solid state isotope exchange is conducted by allowing perovskite to come into contact with isotopically labelled oxygen at a defined temperature for a certain period of time. After the experiment, the isotopic composition of the gas phase is studied.

In a particular experiment, 0.4860 g of SmCoO_3 with a density of $8.06 \text{ g}\cdot\text{cm}^{-3}$ were reacted with $^{18}\text{O}_2$ in a reactor with a volume of 1.500 L at a pressure of 528.56 mbar for two hours at a constant temperature of 298.0 K. After the reaction, the gas mixture consisted of three different compounds with partial pressure of $p(^{18}\text{O}_2) = 512.70 \text{ mbar}$, $p(^{16}\text{O}_2) = 2.640 \text{ mbar}$ and $m(^{18}\text{O}^{16}\text{O}) = 27.21 \text{ mg}$.

- 16.1 Calculate** how many oxygen atoms were exchanged during the reaction and **write** a stoichiometric formula of the isotope-exchanged perovskite in form of $\text{SmCo}^{16}\text{O}_x^{18}\text{O}_y$ (x, y not necessarily integers). Assume that the perovskite initially contained only ^{16}O oxygen atoms and neglect the volume of the solid.

The isotope exchange reaction between the solid and the gas phase takes place on the surface of the perovskite. In the first step of the exchange process, molecules containing ^{18}O isotopes travel, or diffuse, from the areas with a higher fraction of ^{18}O isotopes, to the area near the solid, where the ^{18}O isotope fraction is lower due to the continuous isotope exchange with the perovskite.

The rate of diffusion can be described using diffusion coefficient $D(\text{m}^2 \cdot \text{s}^{-1})$. The average time needed for a molecule in gas phase to travel to the distance L by diffusion mechanism is related to D as $t = \frac{L^2}{D}$, and for gaseous oxygen the diffusion coefficient may be calculated as follows: $D = A \cdot \frac{1}{\sqrt{M}} \cdot \frac{T^{3/2}}{p}$, where $A = 2.23 \cdot 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ mol}^{-1/2} \text{ g}^{1/2} \text{ K}^{-3/2} \text{ Pa}$, where M, T, p correspond to molar mass ($\text{g}\cdot\text{mol}^{-1}$), absolute temperature (K) and total pressure (Pa), respectively.

- 16.2 Select** the correct ratio between the diffusion coefficients of different dioxygen isotopologues.
- ☐ $D(^{16}\text{O}_2) > D(^{16}\text{O}^{18}\text{O}) > D(^{18}\text{O}_2)$
 - ☐ $D(^{18}\text{O}_2) > D(^{16}\text{O}^{18}\text{O}) > D(^{16}\text{O}_2)$
 - ☐ $D(^{16}\text{O}_2) = D(^{16}\text{O}^{18}\text{O}) = D(^{18}\text{O}_2)$

- 16.3 Calculate** the average time needed for a $^{18}\text{O}_2$ molecule to travel from the center of the reactor to the wall in the experiment described in task 1. Assume that the reactor has a spherical shape and neglect the volume of the perovskite.

Once in the vicinity of the surface, an oxygen molecule first has to adsorb to the surface before isotope exchange can take place. This adsorption can be measured via infrared vibrational spectroscopy.

When $^{16}\text{O}_2$ is contacted with a perovskite, one often observed peak in the infrared spectrum can be found at 2237 cm^{-1} , which indicates that a superoxide-anion O_2^- was formed that coordinates to a surface metal species.

- 16.4** Upon contact of $^{18}\text{O}_2$ with the metal oxide, chemically analogous superoxide species are formed. Assuming an identical vibrational force constant for different isotopologues, **calculate** the expected wave number of the above-mentioned vibration in the case of $^{18}\text{O}_2^-$ superoxide anion. Take the mass of ^{16}O isotope equal to 16 Da and mass of ^{18}O isotope equal to 18 Da.

The angular vibrational frequency can be calculated as $\omega = \sqrt{\frac{k}{\mu}}$ where k is the vibrational force constant (independent of isotopic composition) and μ is the reduced mass of the system. For a diatomic species consisting of atoms with masses of m_1 and m_2 , $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$.

In solid, diffusion of the labelled atoms from the surface to the bulk occurs. The main mechanism of oxygen diffusion in solid involves travelling of oxygen vacancies within the crystal. Vacancies are defects of the crystal which have no atom at a site where one would be expected. As oxygen vacancies are active within the diffusion mechanism, their concentration influences the rate of diffusion.

The ratio of vacancies and total atomic sites can be estimated by $\frac{N_V}{N} = \exp\left(-\frac{Q_V}{RT}\right)$, where N_V is the number of vacancies, N the number of lattice sites of a particular atom, Q_V the energy of formation of the vacancy, R the ideal gas constant and T the temperature in Kelvin.

- 16.5** For 0.4860 g of our given compound SmCoO_3 , **calculate** the number of oxygen vacancies at 298.0 K given the molar energy of vacancy formation of $1.006 \text{ eV mol}^{-1}$.

Given that diffusion takes place via oxygen vacancies, their number influences the diffusion rate, which manifests itself in a change in diffusion coefficient. The diffusion coefficient was determined for several different vacancy concentrations and the results given in the table below.

Assume that the diffusion coefficient has a polynomial dependence of the form $D = k \left(\frac{N_V}{N}\right)^x$, where D is the diffusion coefficient, k is a proportionality constant, $\frac{N_V}{N}$ is the ratio of vacancies to total atomic sites and x is the order of that dependence.

- 16.6** From this table, **determine** x and k to show the influence of the concentration of oxygen vacancies on the diffusion coefficient.

N_V/N	Diffusion coefficient $D / (\text{cm}^2 \text{ s}^{-1})$
1.225×10^{-17}	3.80×10^{-10}
2.204×10^{-17}	6.96×10^{-10}
9.062×10^{-17}	2.79×10^{-9}
1.46×10^{-16}	4.33×10^{-9}

When the diffusion coefficient is measured at several different temperatures, its temperature dependence can be approximated by an Arrhenius-type equation and thus an activation energy of the diffusion process can be estimated. For our material of interest, the diffusivity at several different temperatures is given below.

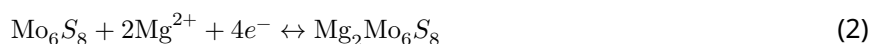


Temperature / °C	Diffusion coefficient D / (cm ² s ⁻¹)
640	1.31×10^{-8}
703	3.38×10^{-8}
740	6.46×10^{-8}
799	1.71×10^{-7}
842	3.39×10^{-7}

16.7 Calculate the activation energy of the diffusion process with the provided data and assuming an Arrhenius type behavior.

A Cheaper Storage Battery

Currently, Mg-ion batteries are gaining attention as potentially less toxic and more economical alternatives to Li-ion batteries. In Mg-ion batteries, Mg foil can be used as an anode in combination with the Chevrel phase (Mo_6S_8) cathode. The half-reactions at the anode and cathode side of the battery are as follows:



17.1 **Write** the total reaction equation of the battery and **calculate** its standard electromotive force (voltage) of the battery and the value of the standard Gibbs energy of the reaction. The standard reduction potentials of the cathode and the anode half-reactions are -1.3 V and -2.4 V, respectively.

Powerwall is a home battery designed to store energy so you can use it any time you want. Assume you would like to replace your powerwall Li-ion battery in your basement with a commercial Mg-ion battery, that can store the same amount of energy. Assume that:

1. The specific energy density of the powerwall Li-ion battery is $200 \text{ Wh} \cdot \text{kg}^{-1}$.
2. The mass of the Mg foil and Mo_6S_8 combined is 50% of the total mass of the battery.
3. The Mg foil and Mo_6S_8 are present in the appropriate stoichiometric amounts according to the total reaction equation of the battery.

The specific energy density of the battery (in $\text{Wh} \cdot \text{kg}^{-1}$) is the amount of energy (in Wh) that a battery can deliver during its discharge over the total mass of the battery (in kg).

17.2 **Calculate** how much heavier the commercial Mg-ion battery would be compared to a Li-ion battery.

Assume that the Mg-ion battery is composed of a Mg anode based on a $10 \text{ } \mu\text{m}$ -thin Mg foil and the Chevrel cathode consists of 2.5 g of Mo_6S_8 . Both electrodes have a surface area of 100 cm^2 .

17.3 **Calculate** the thickness of the Mg foil after the complete discharge of the battery. The density of magnesium is $\rho(\text{Mg}) = 1.738 \text{ g} \cdot \text{cm}^{-3}$.

17.4 The specific capacity is the amount of charge of the electrons that a material can accept/release per given mass of the material. **Calculate** the gravimetric specific capacity (in $\text{mAh} \cdot \text{g}^{-1}$) of Mo_6S_8 and Mg in accordance with the given half-reactions.

Assume that there is a commercial Mg-ion battery with a total capacity of 500 mAh.

17.5 **Calculate** the total mass of this battery assuming that:

1. The battery was assembled with 10 wt.% of excess of Mg foil over the amount needed to charge-balance Mo_6S_8 cathode and
2. The mass of the Mg foil and Mo_6S_8 is 50% of the total mass of the battery.

Preparatory Problems (Theory)



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Q17-2

English (Official)

Assume that the Mg anode in the discussed Mg-ion battery from task 5 is replaced by Mg_3Bi_2 , which is charge-balanced with a Mo_6S_8 cathode in accordance with the following half-reaction:



As opposed to task 5, there is no excess of Mg foil over the amount needed to charge-balance the Mg_3Bi_2 cathode.

17.6 **Calculate** the increase of the mass of the Mg-ion battery in case of this replacement, assuming that the mass of Mg_3Bi_2 and Mo_6S_8 is 50% of the total mass of the battery.

Magnets Going Nano

Magnetic nanoparticles, so-called “nanomagnets”, are unique materials. During their production by pyrolysis in a reductive flame, graphite-like carbon can be deposited on the magnetic core giving a core/shell architecture. The carbon coating allows for the covalent immobilization of catalysts or drugs. As such, functionalized nanomagnets prove useful in a range of applications due to their ease of separation.

Reductive flame spray pyrolysis of iron and iron carbide uses $\text{Fe}(\text{2-EHA})_3$ (2-EHA = 2-ethylhexanoate) as a suitable precursor. The precursor solution is dispersed by oxygen from a nozzle and the spray is ignited by a secondary flame of stoichiometrically premixed methane and oxygen. To control the reducing conditions, the combustion takes place in a nitrogen atmosphere. **Figure 1** shows a scheme of the process.

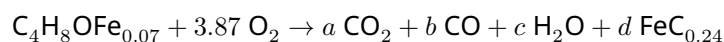
Figure 1: *Left*: Scheme of reducing flame spray pyrolysis. a: N_2 . b: $\text{CH}_4 + \text{O}_2$. c: 2.7 g/min $\text{Fe}(\text{2-EHA})_3 + 1.8$ g/min THF + O_2 . *Right*: Schematic structure of monomeric $\text{Fe}(\text{2-EHA})_3$ where Bu = butyl = C_4H_9 and Et = ethyl = C_2H_5 .

18.1 Write a balanced reaction equation for the following combustion reactions.

- $\text{Fe}(\text{2-ethylhexanoate})_3$ to CO_2 , H_2O , and $\text{Fe}(\text{0})$
- tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) to CO_2 and H_2O

18.2 Calculate how much O_2 (in L/min, at $T = 298\text{K}$ and $p = 100000\text{Pa}$) is required to run these two reactions stoichiometrically. If you could not solve task 1, assume that the combustions of $\text{Fe}(\text{2-EHA})_3$ and of THF require 30 and 6 equivalences of O_2 , respectively.

In reality, the process is run with a substoichiometric amount of O_2 to achieve reducing conditions. The following reaction shall completely summarize the overall combustion process:



Preparatory Problems (Theory)



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18.3 Calculate the expected CO_2 to CO ratio, a/b , in the exhaust gas.

The binary compound iron carbide has a carbon mass fraction of $\text{wt}\%_{\text{C}} = 6.67\%$. Particles with a lower carbon content are comprised of γ -iron and iron carbide while particles with a higher carbon content are comprised of iron carbide and elemental carbon.

18.4 Choose the correct answer for the composition of the particles produced in task 3.

- ☐ The particles are comprised of γ -iron and iron carbide.
- ☐ The particles are comprised of iron carbide only.
- ☐ The particles are comprised of iron carbide and elemental carbon.

Using a co-feed of acetylene (C_2H_2) in addition to the feed rates in **Figure 1**, even stronger reducing conditions were achieved and nanomagnets with an average carbon mass fraction $\text{wt}\%_{\text{C}} = 9.4\%$ were produced. The obtained spherical particles have an iron carbide with a radius of 30.0 nm. The density of iron carbide and graphite are 7.69 g cm^{-3} and 2.26 g cm^{-3} respectively. In bulk graphite, the distance between two graphene layers is 0.335 nm.

18.5 Calculate the total volume V_{particle} of a particle in nm^3 .

18.6 Calculate the average thickness d_{shell} of the carbon shell on a particle. Use $V_{\text{particle}} = 137300 \text{ nm}^3$ if you could not solve task 5.

18.7 Calculate the number n_{layers} of graphene layers that were on average deposited on the nanoparticles. Use $d_{\text{shell}} = 2.0 \text{ nm}$ if you could not solve task 6.

The obtained particles were functionalized to carry amine functional groups. The amine-functionalized particles were further reacted with stearoyl chloride, $\text{CH}_3(\text{CH}_2)_{16}\text{COCl}$, to demonstrate their surface reactivity. Their elemental compositions are reported below.

Element i	$\text{wt}\%_{i,\text{before}}$	$\text{wt}\%_{i,\text{after}}$
C	9.38	11.05
H	0.02	0.31
N	0.16	0.16

18.8 Write a balanced reaction equation for the amine-functionalized particles with stearoyl chloride. Use R-NH_2 to abbreviate an amine functional group on the particles' surface.

18.9 Calculate the yield for the reaction. The mass increase of a particle due to the occurred reaction can be neglected.

18.10 Calculate the average coverage of amine groups before the reaction in nm^{-2} .

Predicting Indices

Gas chromatography is an experimental technique used for analyzing mixtures of volatile substances. The mixture is injected at the entrance of a long, thin and hot glassy tube called the column. The column is internally covered by an absorbing but non-volatile substance called the stationary phase (e.g. a resin, an oil, etc.). A carrier gas is pushed through the column, and drives the injected air plus the injected substances through the column. The substances are separated while passing through the column. The more volatile a substance, the faster it passes through the column. All detection signals at the end of the column are recorded over time giving a so-called chromatogram. The time between the detection of air (i.e. the dead time) and the detection of another compound is called the reduced/adjusted retention time of the compound.

Prof. E. Kovats, working at ETH Zurich from 1955 until 1967, observed that, at constant temperature, the retention times of successive homologues in the n -alkane series form a geometric sequence with factor $f = 1.6$ (e.g. 20.0 s, 32.0 s, 51.2 s, 81.9 s, 131.1 s, ...). For a given column at a given temperature, n -hexane has the retention time $t_6 = 100$ s.

19.1 **Calculate** the retention times for the homologues series from n -hexane up to $C_{10}H_{22}$. **Transform** your data to obtain a linear relationship that gives the retention time t_n as a function of the number of carbon atoms n .

19.2 Using the linear relationship, **give** a formula that gives t_{n+1} from t_n .

If a mixture containing several successive n -alkanes and an unknown substance **X** is injected under the same conditions, the component **X** will leave the tube at a time t_X between two consecutive bracketing n -alkanes: $t_n < t_X < t_{n+1}$. In these cases, Kovats defined a retention index R_X by the expression:

$$R_X = 100n + 100 \frac{\log(t_X/t_n)}{\log(t_{n+1}/t_n)}$$

With this definition, n -alkanes have retention indices of $100n$. Experiment shows that the same considerations can be applied to any series of homologous compounds. So n -alcohols, or n -aldehydes, etc., have all consecutive retention indices which differ by a hundred: $R_{X,n+1} = R_{X,n} + 100$.

19.3 If **X** is a n -alcohol with a retention time of $t_X = 200$ s under the same experimental conditions as above, **calculate** its retention index R_X .

Kovats retention indices can also be obtained by programming the temperature of the column. If the tube is heated at a convenient constant rate (a couple of °C/min), this rate may be determined so that the n -alkanes get out at a time which is proportional to the number of C atoms n again.

These new retention indices R'_X can also be calculated by another Kovats' formula:

$$R'_X = 100n + 100 \frac{t'_X - t'_n}{t'_{n+1} - t'_n}$$

where t'_n is the retention time of the previous normal alkane with n C atoms, before t'_X .

Retention indices obtained by the isothermal method are considered as equal to those obtained by the temperature programming approach. As such, Kovats indices can be considered to be system-independent and fundamental alike to molar masses or boiling points at normal pressure.

Preparatory Problems (Theory)



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Q19-2

English (Official)

At a given heating rate, if the retention time of *n*-hexane is $t = 160$ s, it will be 180 s for *n*-heptane, 200 s for *n*-octane, 220 s for *n*-nonane, and 240 s for *n*-decane.

19.4 Calculate the expected retention time for *n*-alcohol **X** at this heating rate. Assume $R_X = 720$ if you could not solve task 3.

Based on his experiments, Prof. E. Kovats could postulate the following rules:

1. Normal alcohols with n C atoms have a retention index 280 greater than the corresponding *n*-alkane. For example, ethanol has a R' value equal to 480.
2. Ethyl *n*-carboxylates have retention indices 179 greater than the corresponding *n*-alkane (counting all C atoms in the esters). For example, ethyl stearate ($C_{17}H_{35}CO_2C_2H_5$) has a retention index equal to 2179.
3. Introduction of a double bond between two consecutive C atoms reduces the retention indices by about 30.

A vegetable oil is analyzed to determine its fatty acid content. As the naturally occurring triglycerides of fatty acids (triester of glycerol, $C_3H_8O_3$, with fatty acids) are not suitable for gas chromatography, they first have to be transformed into their volatile esters. The oil is transesterified by heating with a minimal amount of NaOH in ethanol.

19.5 Write a balanced equation of the transesterification of a fat, containing only palmitate esters ($C_{15}H_{31}CO_2R$), with ethanol (C_2H_5OH).

After adding 5 alkanes with $n = 18$ to 22 C atoms to the obtained mixture, it is analyzed by gas chromatography with temperature programming using a new constant heating rate. The result of the analysis gives peaks at the following retention times, in minutes:

16.43, 17.38, 18.13, 18.33, 19.28, 19.75, 19.99, 20.23

19.6 Determine all substances in the mixture and **assign** them to the detected peaks. Note that glycerol is not detected.



Breaking Alkanes Apart

In the 1960s in Switzerland, Prof. Tino Gäumann has studied how alkanes are decomposed by high-density gamma-ray radiolysis.

When submitted to ionizing radiations, covalent bonds in alkane molecules are randomly broken, and the alkane molecule is transformed into fragments called radicals. We will ignore the case where two or more bonds are broken in the same molecule. These radicals recombine randomly. For example, irradiated methane CH_4 is decomposed into H atoms and methyl radicals. Recombination of these fragments produces H_2 , CH_4 , and C_2H_6 .

For higher alkanes, both C-H and C-C bonds are broken, and for the scope of this problem, you can assume that all bonds break randomly with the same probability.

Let's study the radiolysis of ethane (C_2H_6) first. Assume that only one bond is broken in any molecule giving H atoms, methyl radicals ($\text{CH}_3^\bullet$), and ethyl radicals ($\text{C}_2\text{H}_5^\bullet$).

20.1 Draw all recombination products in the ethane radiolysis.

20.2 Calculate the probabilities of getting any formed radical in ethane radiolysis.

When two radicals A and B join to form molecule AB, the probability of forming molecule AB by recombination is equal to $2 \cdot p(\text{A}) \cdot p(\text{B})$. If $\text{A}=\text{B}$, the probability of forming A_2 is $p^2(\text{A})$. Recombination of the fragments in methane radiolysis therefore produces H_2 , CH_4 , and C_2H_6 in a ratio of 1:2:1.

20.3 Find the ratio of all formed products obtained in the ethane radiolysis. If you could not solve task 2, assume the probabilities of $\text{H}^\bullet$, $\text{CH}_3^\bullet$, and $\text{C}_2\text{H}_5^\bullet$ to be 1/4, 2/4, and 1/4, respectively.

The number of products and their distribution from the radiolysis of a single alkane quickly become complex with increasing length or branching of the alkane. The simple step from ethane to propane (C_3H_8) shall demonstrate this. Assume again that only one bond is broken in any molecule giving H atoms, methyl radicals ($\text{CH}_3^\bullet$), ethyl radicals ($\text{C}_2\text{H}_5^\bullet$), and two types of propyl radicals ($\text{C}_3\text{H}_7^\bullet$).

20.4 Draw all recombination products in the propane radiolysis.

20.5 Determine the least likely and most likely product(s) in the radiolysis of propane.

20.6 Find the ratio of all formed *n*-alkanes obtained in the propane radiolysis.

Preparatory Problems (Theory)



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Q21-1

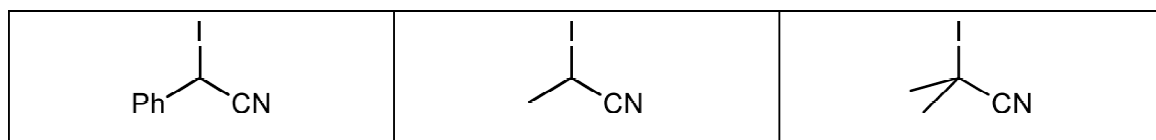
English (Official)

Quite Radical

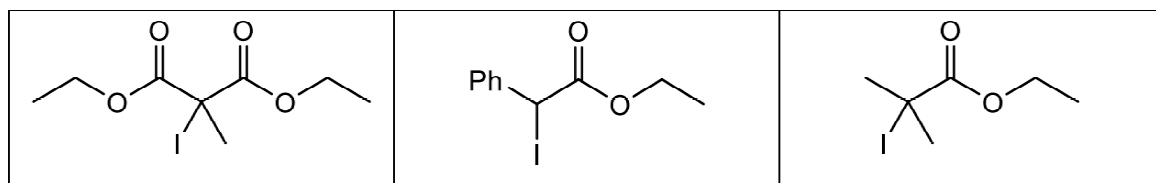
Homolysis of the carbon–iodine bond in the following compounds leads to an iodine atom and a carbon radical.

21.1 **Order** the following molecules according to their rate of radical formation (slowest to fastest).

a)

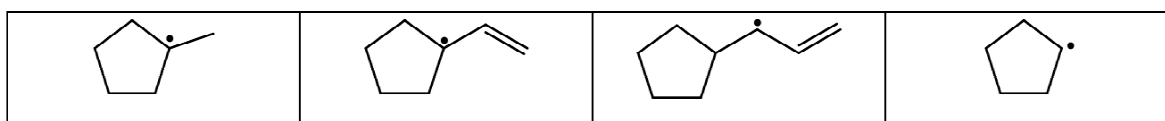


b)

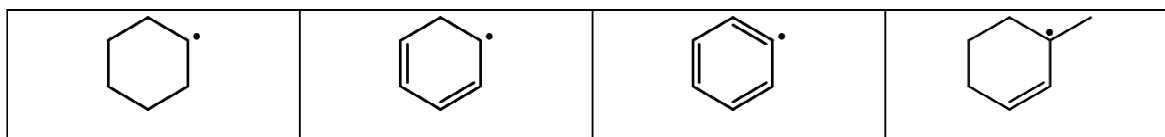


21.2 **Rank** the following radicals in order of their stability (least stable to most stable).

a)



b)



On reacting 2-methylbutane with one equivalent Cl_2 , four different monochloro isomers are obtained.

21.3 **Calculate** the percentage of each isomer. The reactivity of the C–H bond varies from tertiary > secondary > primary by the ratio 5:4:1.

Di-*tert*-butylperoxide $(\text{CH}_3)_3\text{CO}-\text{OC}(\text{CH}_3)_3$ is a stable liquid at room temperature that easily forms free radicals upon heating. A mixture of 2-methylpropane and CCl_4 is fairly stable at 130–140°C. On addition of a small amount of di-*tert*-butylperoxide this mixture mainly reacts to form *tert*-butylchloride and chloroform. *Tert*-butyl-alcohol can also be isolated, twice as much as the amount of di-*tert*-butylperoxide added.

Preparatory Problems (Theory)



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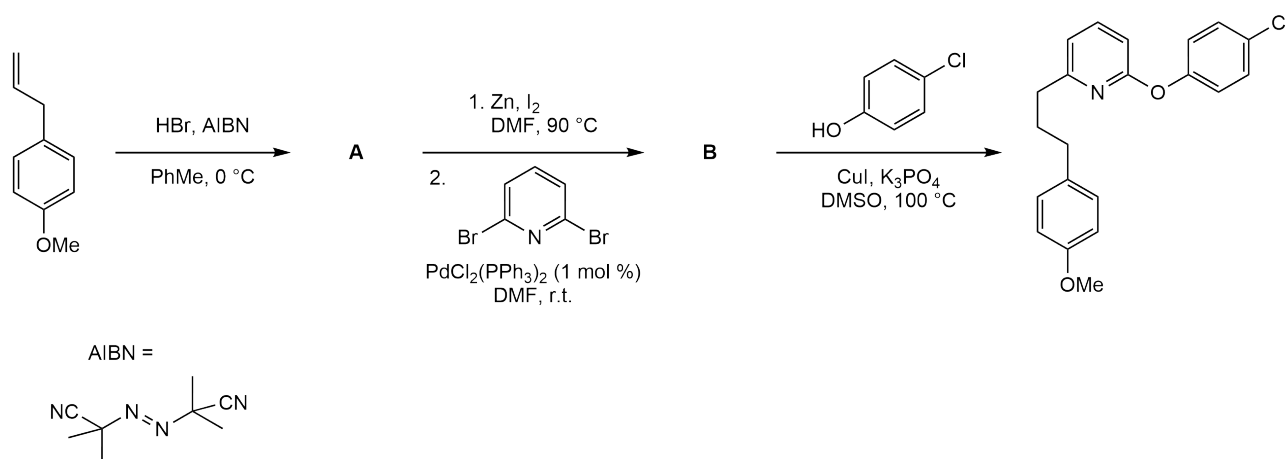
Q21-2

English (Official)

21.4 Give the initiation step and the two propagation steps for this radical chain reaction.

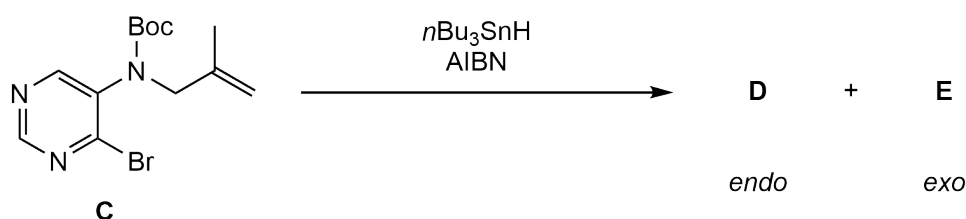
Radical reactions generally require a radical starter to be initiated. One such starter is AIBN (azo-bis-isobutyronitrile). After initiation the reaction proceeds by itself.

21.5 Provide the intermediates **A** and **B** in the following transformation.



Aryl bromide **C** can undergo radical cyclization leading to an endo and an exo product (**D** and **E**), one of which is majorly favoured over the other.

21.6 Provide the structures of two products **D** and **E**.



The bromination of *o*-xylene can be done either under light illumination or in the dark. The NMR spectrum of **F** in the aliphatic region shows a singlet at 4.56 ppm, while that of **G** shows a singlet at 4.56 ppm and a singlet at 2.29 ppm. The molecular mass of **F** is larger than that of **G**, as determined by mass spectrometry.

21.7 Provide the structures of the two main products in both reactions (**F/G** and **H/I**).

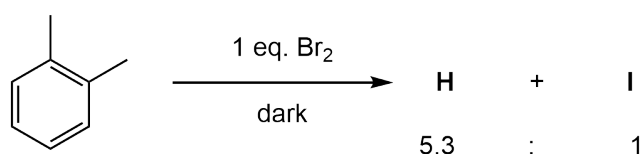
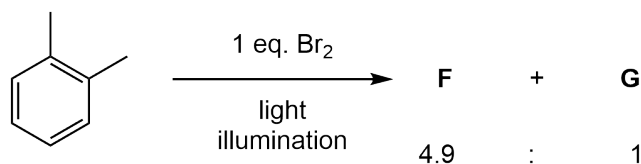
Preparatory Problems (Theory)



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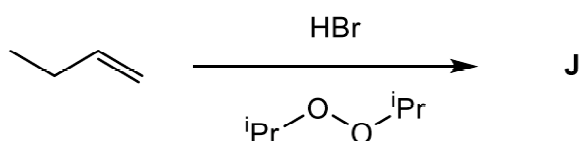
Q21-3

English (Official)



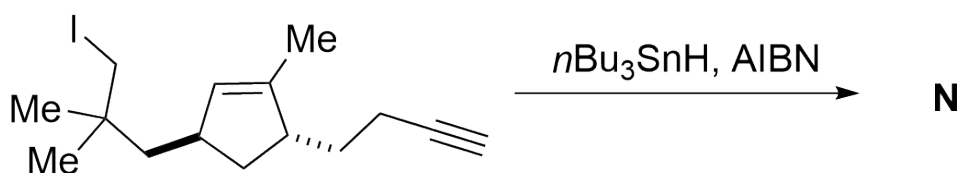
The termination of radical reactions proceeds by the recombination of two radicals.

21.8 **Provide** the main product **J** and three possible termination products (**K–M**) of the following radical reaction.



In 1985 the group of D.P. Curran reported an elegant total synthesis of the racemic Hirsutene (**N**). The synthesis features a radical cascade reaction starting from the precursor shown below, in which two new five-membered rings are formed in an intramolecular fashion.

21.9 **Give** the structure of Hirsutene (**N**) (no stereochemistry required).



Preparatory Problems (Theory)



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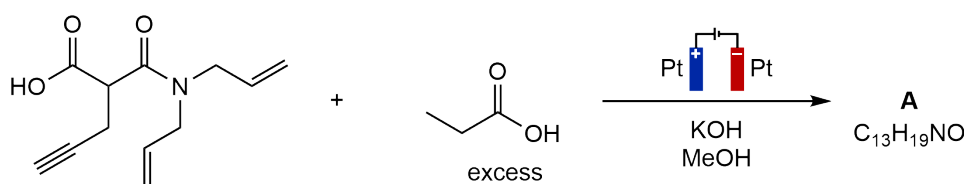
Q22-1

English (Official)

Enabling Electricity

The use of electrochemical methods can sometimes yield products that are otherwise not (easily) accessible. During these reactions, oxidised/reduced intermediates react rapidly with nucleophiles/electrophiles present in the reaction mixture. For anodic oxidation reactions, this oftentimes is the solvent.

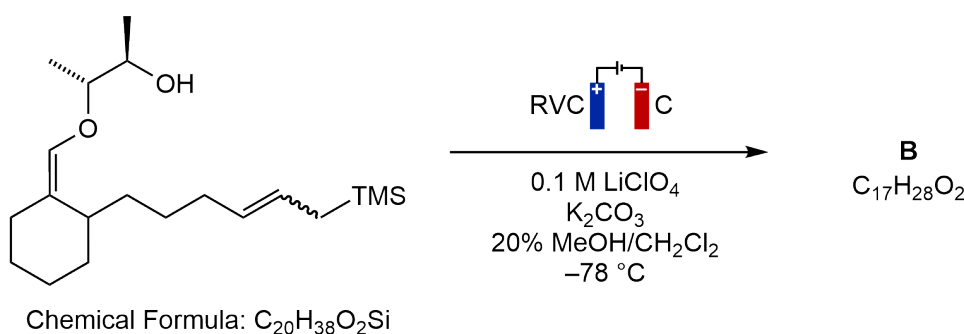
Electrolysis of carboxylic acids with relatively high current densities can lead to the formation of highly reactive carboxyl radicals and subsequent decarboxylation.



22.1 **Provide** the structural formula of product **A**. Hint: catalytic hydrogenation of product **A** consumes 3 equivalents of H_2 .

22.2 The previous reaction yields product **A** in 64% yield and with a faradaic efficiency of 29%. **Calculate** the charge accumulated (in Coulombs) over the course of the experiment if 2.80 mmol of **A** was obtained.

The RVC (reticulated vitreous carbon) anode used below is a foam made of glassy carbon that can provide high current densities.



22.3 **Provide** the structure of compound **B** (no stereochemistry required). This reaction leads to two condensed cyclohexane rings and an acetal structure.

Reactivity at the cathode can be quite different from the anode. The use of a divided cell can help to control the type of electrochemical reaction that is occurring.

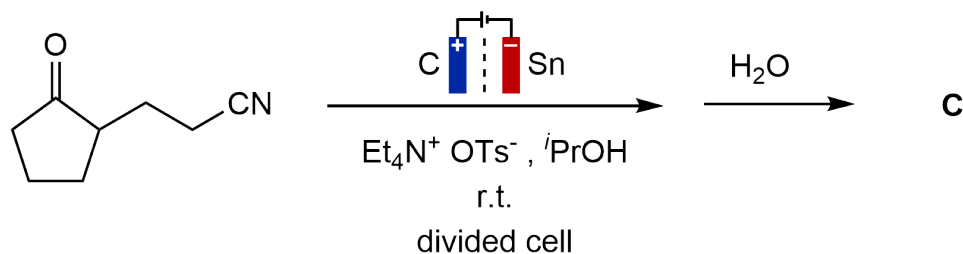
Preparatory Problems (Theory)



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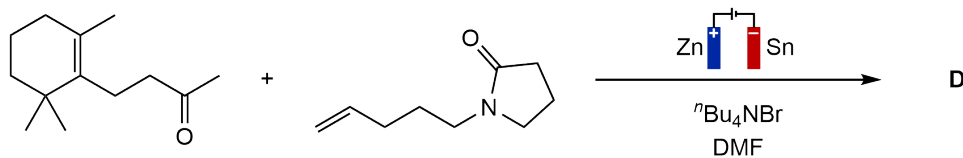
Q22-2

English (Official)

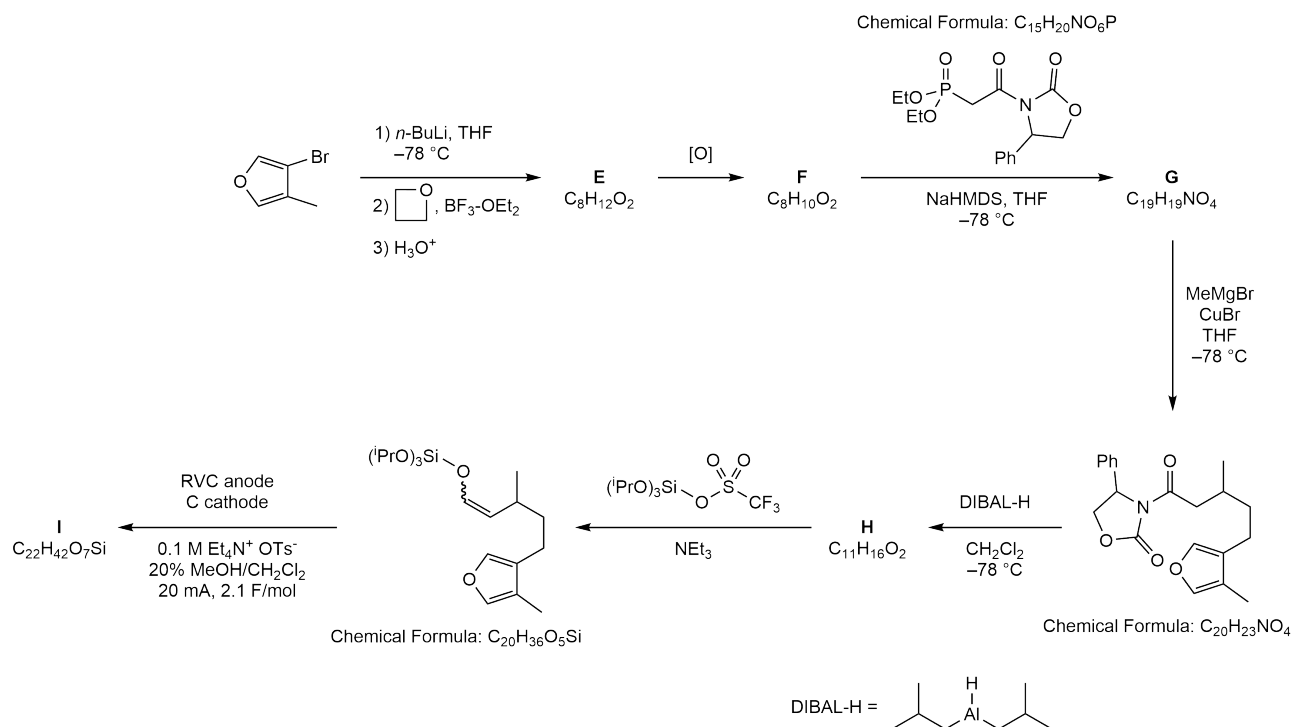


22.4 **Provide** the structure of compound **C** resulting from cathodic reduction followed by an aqueous workup. **C** contains two condensed cyclopentane rings.

Alkene-ketone coupling reactions can be achieved under electroreductive conditions.



22.5 **Provide** the structure of product **D**.



Preparatory Problems (Theory)



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Q22-3

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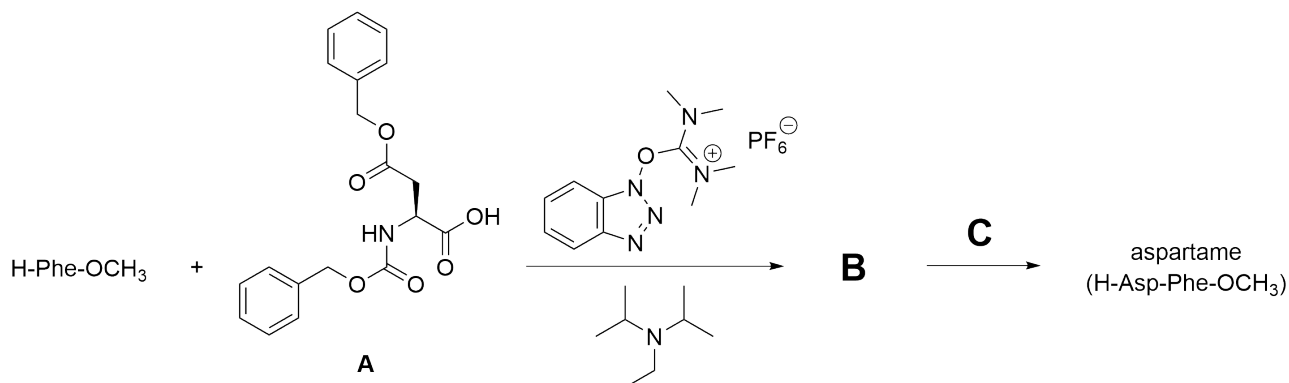
22.6 Provide the structures of compounds **E-I** (stereochemistry not required).
Hint: in the last reaction step a new six-membered ring is formed.

A Sweet Introduction to Peptides

Peptides are omnipresent chemicals with a range of biological properties and industrial applications. In nature, peptides serve as hormones (e.g., oxytocin), neurotransmitters (e.g., enkephalins), or as defense mechanisms (e.g., dendrotoxins produced by mamba snakes). Countless peptides are industrially produced in kilogram to ton quantities as medications. Switzerland is one of the World's hubs of peptide chemistry, led by companies such as the peptide giant Bachem. To take a first dive into peptide chemistry, we will look at one of the most well-known synthetic peptides – the artificial sweetener aspartame.

23.1 Draw the structure of aspartame (H-Asp-Phe-OCH₃).

Aspartame can be synthesized by amide bond formation between H-Phe-OCH₃ and protected amino acid **A**, followed by removal of the protecting groups.



23.2 Complete the scheme above: Draw the structures of H-Phe-OCH₃ and **B**. Select the correct designation of protected amino acid **A** using the three-letter amino acid notation. Select a suitable reagent **C**.

Three letter code for compound **A**:

- ☐ Boc-Asp(^tBu)-CO₂H
- ☐ Boc-Asp(^tBu)-OH
- ☐ Boc-Asp(^tBu)-H
- ☐ Cbz-Asp(Bn)-CO₂H
- ☐ Cbz-Asp(Bn)-OH
- ☐ Cbz-Asp(Bn)-H

Reagent **C**:

- ☐ 1% CF₃CO₂H in CH₂Cl₂
- ☐ H₂(g), Pd/C
- ☐ 4M aqueous HCl
- ☐ LiOH in THF
- ☐ 20% piperidine in DMF

A dipeptide like aspartame can easily be prepared by a solution-phase synthesis. The longer a peptide gets, the less practical it is to synthesize it by a sequence of solution phase steps where each step requires a workup and purification. Solid-phase peptide synthesis (SPPS) has emerged as a convenient alternative to solution-phase synthesis of long peptides. SPPS takes advantage of the immobilization of the growing peptide chain on a solid support, streamlining the repetitive sequence of coupling, washing

Preparatory Problems (Theory)

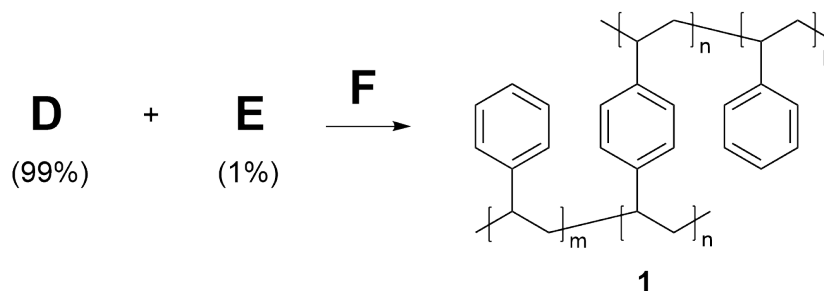


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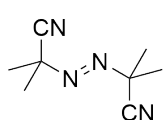
and deprotection steps. The solid support in SPPS is typically a porous organic polymer functionalized with a reactive handle. "Merrifield resin" is the traditional solid support developed by the inventor of SPPS, Robert Bruce Merrifield, which is based on functionalized polystyrene.



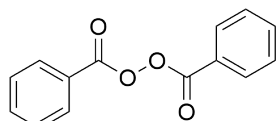
23.3 For the polystyrene (**1**) synthesis above, draw the structures of monomer **D** and cross-linker **E**. Select all suitable initiators **F**.

Initiator **F**:

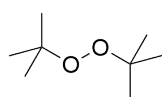
- ☐ azobis(isobutyronitrile) (AIBN)
- ☐ benzoyl peroxide (BzO_2)
- ☐ *tert*-butyl peroxide ($^t\text{BuO}_2$)
- ☐ *N,N'*-dicyclohexylcarbodiimide (DCC)
- ☐ diisopropylethylamine (DIPEA)



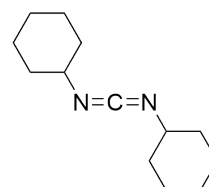
AIBN



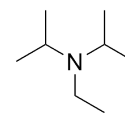
(BzO)₂



(^tBuO)₂

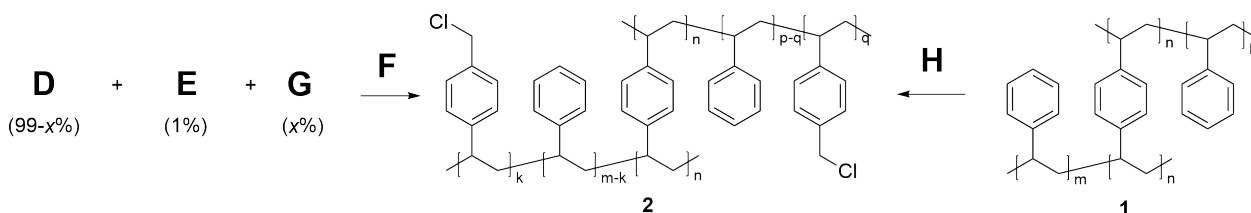


DCC



DIPEA

The Merrifield resin (**2**) contains chloromethyl substituents as functional handles. These can be introduced either via co-polymerization with a suitable monomer or by treatment of polystyrene resin with a chloromethylating agent.



Preparatory Problems (Theory)



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Q23-3

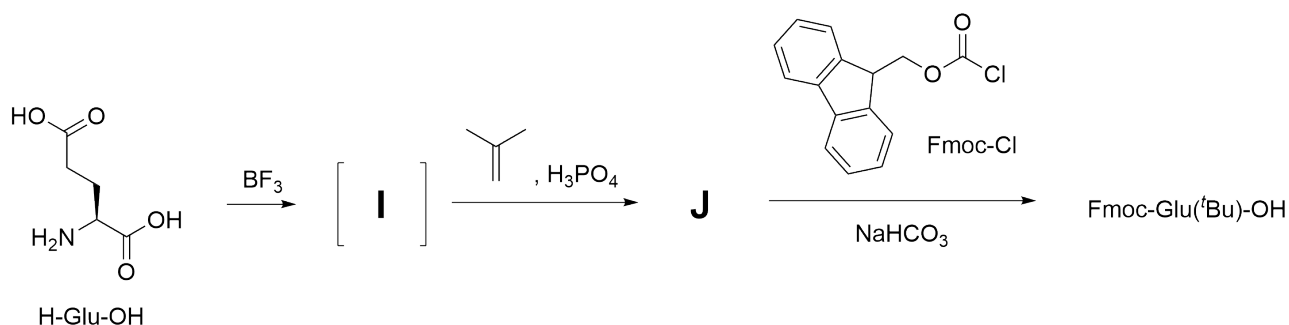
English (Official)

23.4 Draw the structure of monomer **G**. Select all suitable chloromethylating reagents **H**.

Reagent **H**:

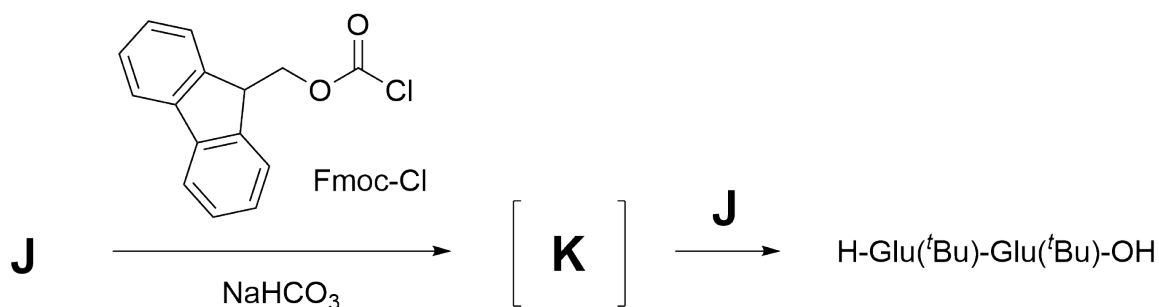
- ☐ $\text{CH}_3\text{OCH}_2\text{Cl}$, H_2SO_4
- ☐ CH_2Cl_2 , KOH
- ☐ CHCl_3 , $(^t\text{BuO})_2$
- ☐ Cl_2 , $h\nu$
- ☐ formaldehyde, HCl , ZnCl_2

SPPS is performed by an iterative sequence of coupling, washing and deprotection steps. The most common strategy used today is the so called Fmoc/ ^tBu strategy that employs amino acid building blocks with a Fmoc-protected α -amino group, a free α -carboxylic group and reactive side chains protected with acid-labile protecting groups (such as ^tBu or Boc). The synthesis of certain amino acid building blocks is not trivial. For instance, the synthesis of Fmoc-Glu(^tBu)-OH requires the selective introduction of a ^tBu protecting group on the side-chain carboxylic group in the presence of the α -carboxylic group. This issue can be solved by bidentate coordination of the α -amine and α -carboxylate to a Lewis acid, effectively blocking the two groups.



23.5 Draw the structure of intermediates **I** and **J**, and product Fmoc-Glu(^tBu)-OH.

A common side-product formed during the introduction of the Fmoc protecting group using Fmoc-Cl is the dimer of the amino acid – a dipeptide.



23.6 Draw the structure of intermediate **K** and the dimerization product H-Glu(^tBu)-Glu(^tBu)-OH.

Preparatory Problems (Theory)

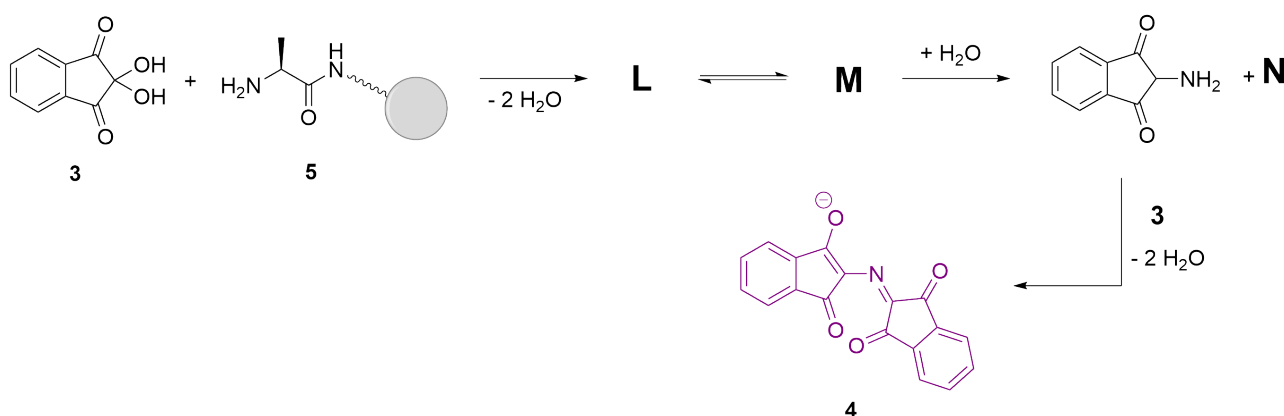


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Q23-4

English (Official)

The last piece we are missing in our SPPS toolbox before we look at a specific synthesis (in the Problem “Switzerland – the country of cheese”) is a method allowing us to monitor reactions on the resin. Unlike for solution-phase reactions, we cannot use analytical techniques such as NMR spectroscopy or chromatographic methods to follow the transformation on resin without cleaving off the peptide from the solid support. We can, however, use colorimetric methods to visualize the functional groups on a resin sample. Ninhydrin (**3**) is the most common reagent used to verify the completion of a coupling step, as it provides a colored (blue to purple) product called Ruhemann’s Purple (**4**) upon reaction with a free amino group. Purple coloration of the resin thus indicates an incomplete peptide coupling.



23.7 **Draw** structures of **L** through **N** in the scheme above showing the formation of Ruhemann's Purple (**4**) from ninhydrin (**3**) in the presence of a resin-bound alanine (**5**) with a free amino group.

23.8 **Name** the canonical amino acid that cannot provide Ruhemann's Purple according to the scheme above.

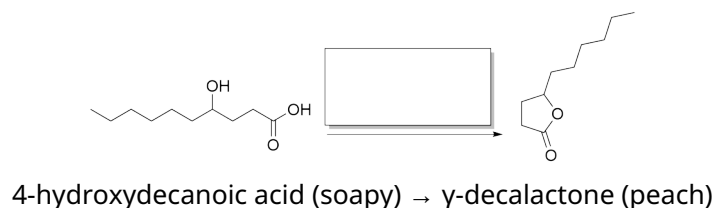
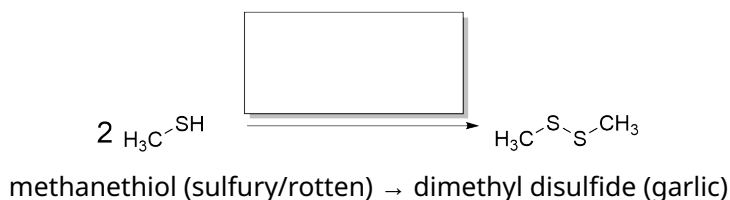
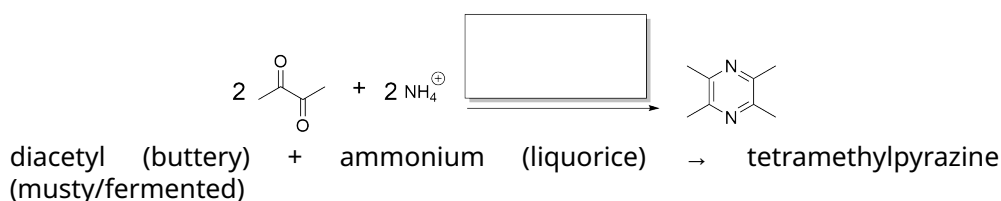
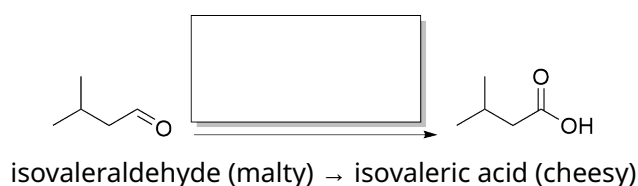


Switzerland – the country of cheese

For thousands of years milk has been a key source of nutrients for many human populations worldwide. The perishability of milk logically triggered extensive search for ways to transform this important foodstuff into a longer-life product. Next to butter and quark, cheese has become one of the main milk products developed in this regard. Several regions of contemporary Switzerland have been pioneers in cheese production and export. Already in the 1st century A.D. the Roman historian Gaius Plinius Secundus mentions caseus Helveticus (Latin for “Swiss cheese”) in his work. Many of the world-famous Swiss cheese sorts, such as Emmentaler (from the Emmental valley, canton Bern) or Gruyère (from the region of Gruyères, canton Fribourg) date back to the Middle Ages, the early days of the Swiss Confederation. During this time, cheese was so important in the Swiss Alpine region that it was used alongside coins as an alternative means of payment. Today, Switzerland produces some of the finest cheeses in the World and Swiss people themselves are passionate consumers of this aromatic milk product – Switzerland finds itself among the top 10 countries in cheese consumption per capita.

The odor and taste of cheese are caused by a wide variety of organic metabolites, both water and lipid soluble. With our nose we can sense mostly volatile compounds while our tongue then enjoys the combination of these molecules with non-volatile species. Oxidation and reduction reactions are among the key transformations between these flavor-bearing metabolites. These are often mediated enzymatically but oxidation may also occur by non-enzymatic chemistry with oxygen or other environmental oxidants, especially when promoted by light. The conditions under which cheese ripens and is stored are thus key for its final flavor.

- 24.1** All of the reactions below occur (directly or via a multistep process) during the ripening of cheese. For each reaction **decide** whether it is an oxidation, reduction, or non-redox process. For redox reactions, **indicate** how many electrons are released or accepted in the overall transformation.



One of the key components of cheese taste is its bitterness. Among the main sources of bitter taste in cheese are hydrophobic peptides that are formed as a result of the enzymatic hydrolysis of proteins from the casein family. The connection between casein and cheese is already evident from its name, which is derived from the Latin *caseus* meaning "cheese".

Preparatory Problems (Theory)



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Q24-3

English (Official)

For a well-balanced taste of cheese, a small content of bitter molecules is necessary. Nevertheless, excessive production of bitter peptides in cheese disturbs this balance and may ruin your culinary experience.

The C-terminal fragment of β -casein (termed **β -CN f193-209**) is a bitter peptide formed by the action of the aspartic protease chymosin on β -casein during cheese production. The sequence of **β -CN f193-209** is shown below.



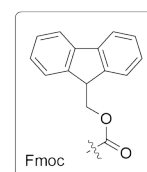
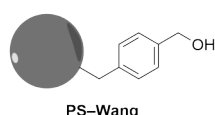
β -CN f193-209

Bitter peptide **β -CN f193-209** can be quantified in cheese by mass spectrometry. For this analysis, an internal standard of **β -CN f193-209** is required. The peptide standard is most conveniently obtained synthetically by solid-phase peptide synthesis (SPPS) via the Fmoc/^tBu strategy.

- 24.2** Polystyrene (PS) resin with the Wang linker is the standard solid phase for SPPS of peptides with a C-terminal carboxylic acid. One of the strategies to “load” (i.e., attach the first amino acid to) the Wang linker relies on creating a benzyl halide functionality followed by S_N2 substitution with a protected amino acid. **Complete** the reaction scheme below depicting Wang resin loading with Fmoc-Val-OH by **choosing** an appropriate reagent **A** and **drawing** the structure of product **B**.

Reactant **A**:

- ☐ AgOH, Br₂
- ☐ Br₂, h ν
- ☐ CBr₄, PPh₃
- ☐ KBr, acetone
- ☐ LiBr, H₃PO₂



- 24.3** **Choose** the role of CsI in the loading step above from the options below.

- ☐ Catalyst – iodide is both a better nucleophile than the carboxylate and a better leaving group than the bromide.
- ☐ Increasing ionic strength – the ionic species stabilize the charged intermediate formed during the reaction.
- ☐ Inhibitor of undesired side-reactions – the mildly acidic salt buffers the basicity of (iPr)₃NEt and prevents premature cleavage of the Fmoc protecting group.
- ☐ Solubilizer – the cesium salt of Fmoc-Val-OH is highly soluble in most organic solvents.
- ☐ Swelling agent – the charged species compete with $\pi-\pi$ interactions within the resin, improving the accessibility of all linker groups.

After resin loading, SPPS proceeds via an iterative series of Fmoc-deprotection and amino acid coupling steps. Protecting groups orthogonal to Fmoc have to be employed for certain amino acids to prevent undesired side reactions during these steps.

Preparatory Problems (Theory)

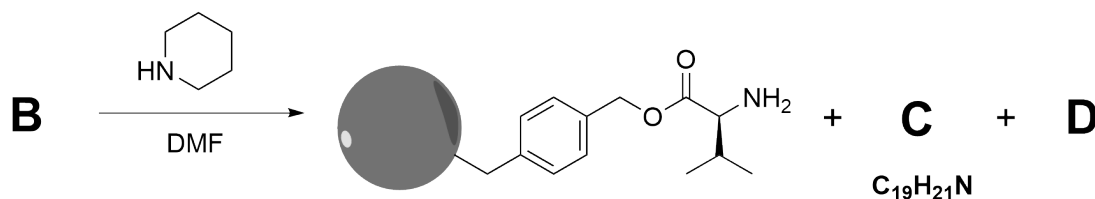


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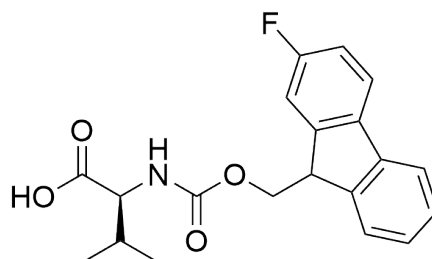
Q24-4

English (Official)

- 24.4** Fmoc deprotection is typically carried out using a 20% solution of piperidine in dimethyl formamide (DMF). **Draw** the organic byproduct (**C**) and the gaseous byproduct (**D**) that are formed next to the free amine.



- 24.5** Would cleavage of a 2-fluoro-Fmoc [Fmoc(2F)] protecting group occur slower or faster than that of the conventional Fmoc after treatment with 20% piperidine in DMF? **Choose** the option with the best possible explanation.



Fmoc(2F)-Val-OH

- ☐ Slower – a carbocation intermediate is formed during the reaction which is destabilized by the electronegative fluorine substituent.
- ☐ Slower – the sterically demanding fluorine substituent hinders the approach of the piperidine reagent.
- ☐ Faster – a carbanion intermediate is formed during the reaction which is stabilized by the electronegative fluorine substituent.
- ☐ Faster – the fluorine substituent coordinates to the piperidine reagent, thus promoting its reaction with the adjacent fluorenylmethyl group.

Preparatory Problems (Theory)

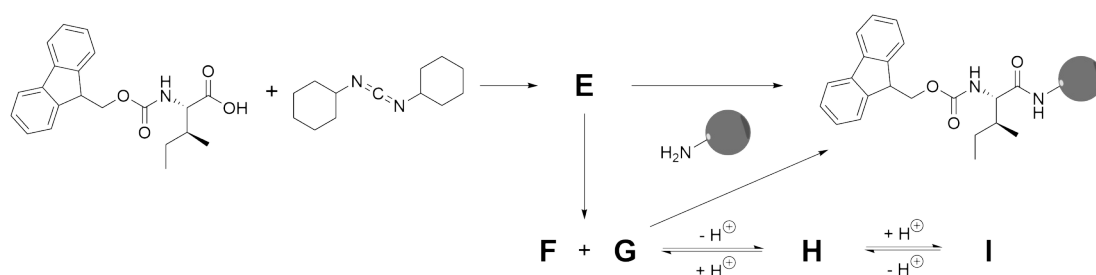


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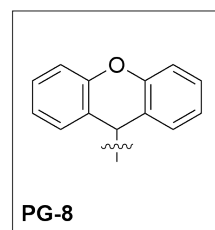
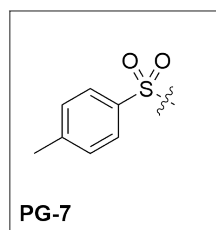
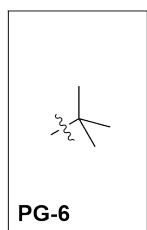
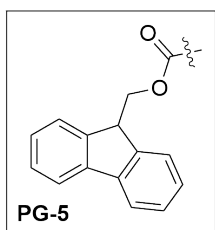
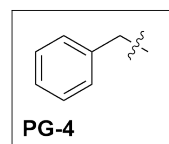
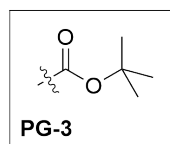
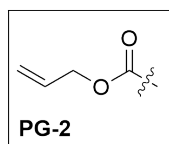
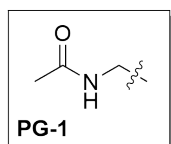
Q24-5

English (Official)

- 24.6** Dicyclohexylcarbodiimide (DCC) is a common coupling agent in peptide synthesis. However, a common undesired side reaction when using DCC as a coupling reagent is the epimerization of the amino acid at the α -carbon.
Draw the activated ester (**E**) obtained by reacting Fmoc-Ile-OH with DCC.
Draw the intermediates **F–I** of the epimerization reaction of the activated isoleucine.
Hints: F is a urea-derivative, G and I are both cyclic intermediates and are diastereomers of one another.



- 24.7** **Indicate** the amino acids in the sequence of **β -CN f193-209** that have a reactive side-chain functional group which would have to be protected during SPPS. For each of these amino acids, **choose** the most suitable, acid-labile (cleavable by treatment with 95% CF₃CO₂H) protecting group from the selection below. Note: you may use each protecting group for multiple side chains.



Protecting groups do not necessarily have to be labile under the same conditions. Using the concept of "orthogonal protecting groups", we can selectively deprotect certain residues while keeping other residues protected.

- 24.8** **Decide** whether the following pairs of protecting groups attached to amino acid side chains are orthogonal under the given conditions. If they are, **circle** the protecting group that will be cleaved.

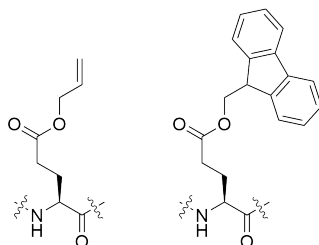
Preparatory Problems (Theory)



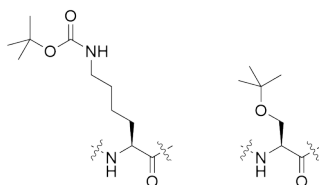
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Q24-6

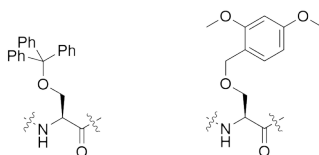
English (Official)



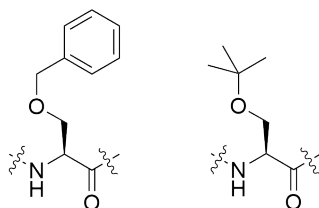
a. cleavage condition: 20% piperidine in DMF, 15 min



b. cleavage condition: 95% aq. $\text{CF}_3\text{CO}_2\text{H}$, 60 min



c. cleavage condition: 1% $\text{CF}_3\text{CO}_2\text{H}$ in CH_2Cl_2 , 15 min



d. cleavage condition: H_2 (g), Pd on charcoal, 60 min

The amide group of glutamine is unreactive enough that the amino acid can typically be coupled without sidechain protection. Without a protecting group, however, dehydration of the amide group can occur as an undesired side-reaction during the coupling step.

Preparatory Problems (Theory)

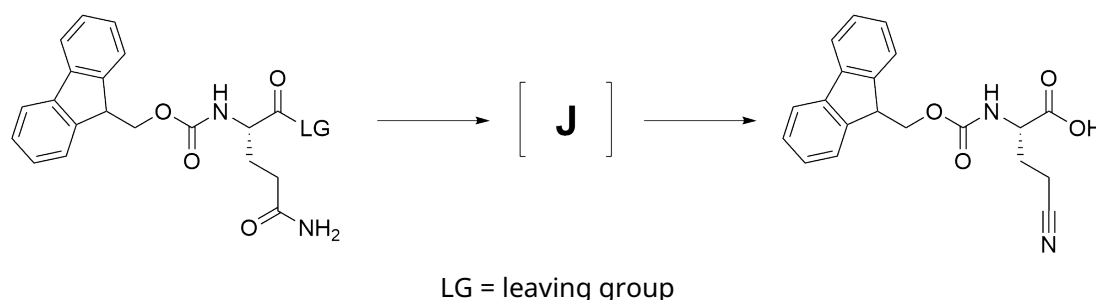


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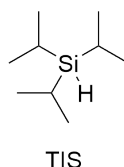
Q24-7

English (Official)

24.9 Draw the cyclic intermediate (**J**) of the dehydration reaction below.



After concluding the synthesis of the resin-bound peptide to its full length, the peptide is cleaved from the resin with concurrent removal of all protecting groups using the following cleavage solution: 95% $\text{CF}_3\text{CO}_2\text{H}$, 2.5% H_2O and 2.5% triisopropylsilane (TIS). The small amount of water and TIS are used as additives in order to prevent undesired side reactions involving reactive byproducts generated under the strongly acidic cleavage conditions.



The desired peptide provides a signal at $m/z = 1881$ (proton adduct $\text{M} + \text{H}^+$) when analyzed by mass spectrometry (MS). If cleavage of the peptide from the resin is carried out with pure $\text{CF}_3\text{CO}_2\text{H}$ (instead of the $\text{CF}_3\text{CO}_2\text{H}/\text{H}_2\text{O}/\text{TIS}$ mixture), a side product is observed which shows a signal at $m/z = 1937$ in MS.

24.10 Explain the formation of the side product. Draw a possible structure of the side product (provide at least two options).

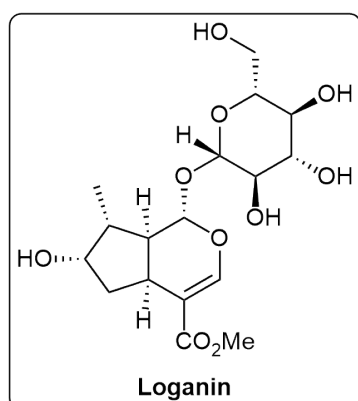
The success of SPPS depends on very high yields of each individual step of the long, iterative sequence of reactions. A yield that is considered good for a single synthetic step may become problematic for SPPS if repeated many times in the sequence.

24.11 Calculate the per-cent yield of peptide **β -CN f193-209** you would obtain considering the following yields of the individual steps:

- resin loading: 90%, Fmoc-deprotection: 90%, coupling: 90%, cleavage from resin: 90%
- resin loading: 90%, Fmoc-deprotection: 99%, coupling: 97%, cleavage from resin: 90%

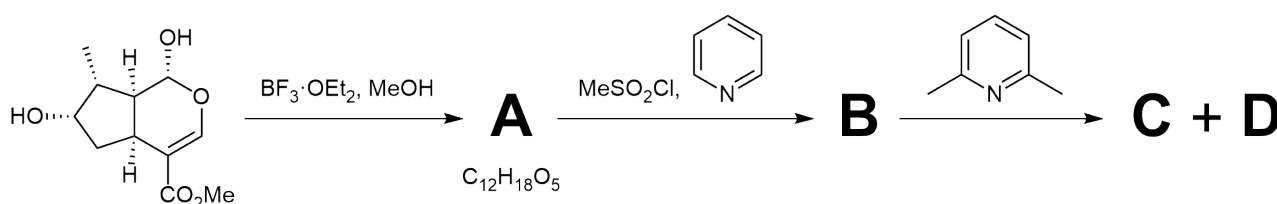
Gentian goes Chemistry

Gentian is a flowering plant occurring in mountainous habitats, which typically has violet or vivid blue trumpet-shaped flowers. Its root is used as a characteristic flavoring for distilled beverages like gentian liqueur produced in the Alps. The gentian root can also serve as feedstock for a variety of natural products. Loganin, a monoterpene glucoside occupying a central position in the biosynthetic pathway towards structurally similar alkaloids, has been isolated from natural gentian samples.



25.1 Calculate the number of possible stereoisomers of loganin. How many possible stereoisomers remain if you ignore all stereocenters at the sugar moiety?

To ascertain the structure of a newly identified natural product, especially its stereochemistry, it was a common technique to compare characteristic data (melting point, optical rotation, IR, ...) with molecules of an established structure. Degradation of the loganin aglycone to olefins **C** and **D** allowed for comparison with literature-known olefins to identify the single stereoisomer present in nature and depicted above.



25.2 Give the structures for molecules **A** to **D**. Take into consideration that the hemiacetal is more reactive towards etherification under the given conditions.

The first (formal) total synthesis of loganin was accomplished by Swiss chemist George Büchi. After an initial [2+2] cycloaddition, the central 5/6-fused bicycle was constructed via a retro-aldol reaction, the formal reverse of the aldol reaction.

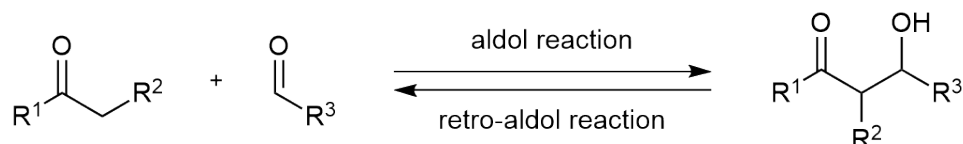
Preparatory Problems (Theory)



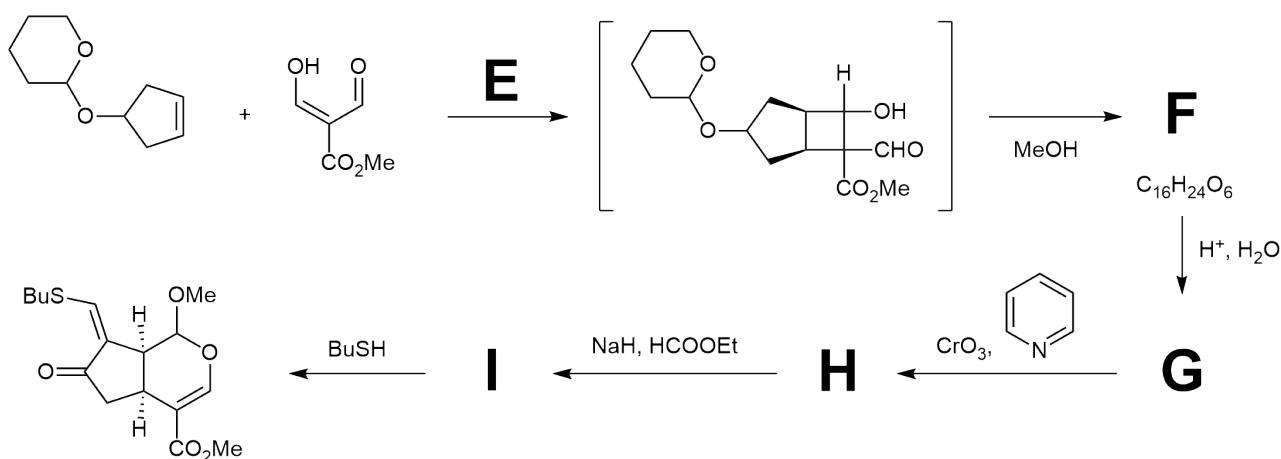
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Q25-2

English (Official)



25.3 Give structures for intermediates **F** to **I** resulting from the retro-aldol reaction of the shown intermediate. Take into consideration that THP-ethers are labile under acidic conditions.



25.4 Derive the relevant frontier molecular orbitals (FMO) of both starting materials to **explain** the stereochemistry of the shown reaction intermediate. Based on your FMO analysis, **suggest** suitable reaction conditions **E** for the desired transformation to take place.

After Nickel-catalyzed excision of the thioether, Büchi and co-workers arrived at the bicyclic ketone depicted below. It took five additional steps to synthesize the desired loganin pentaacetate, which proved to be identical to samples prepared from natural loganin.

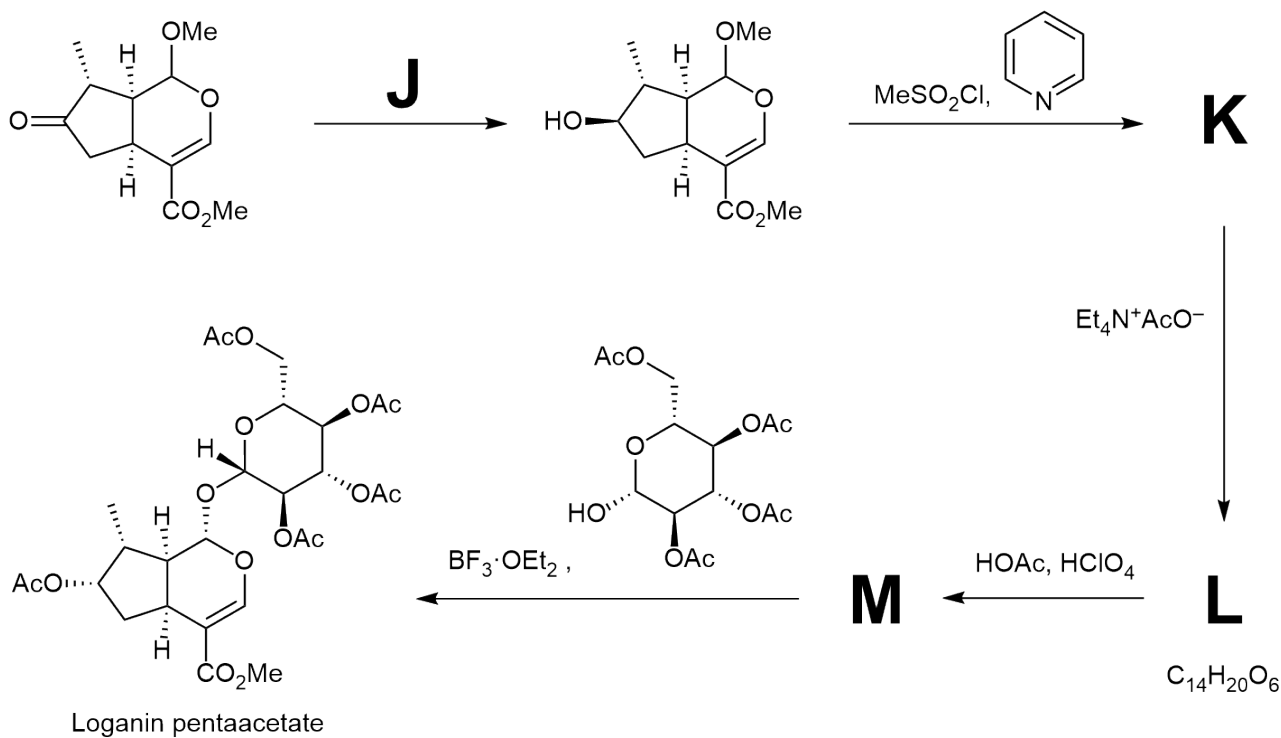
Preparatory Problems (Theory)



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Q25-3

English (Official)



25.5 **Suggest** suitable reaction conditions **J** for the shown transformation to take place. **Give** structures for intermediates **K** to **M**.



The Chemistry of Scent and Fragrance

Introductory text:

The use of odorous substances is as old as humankind. Our ancestors used herbs and spices to flavor their food, perfume oils and balms for medicinal or religious procedures or simply for enjoyment. Carvone is a monoterpene ketone that is naturally occurring in many essential oils. It is a chiral compound, and both (–)- and (+)-carvone can be isolated from natural sources. In 1841, Swiss chemist Eduard Schweizer (his surname further corroborates his Swissness) was the first to isolate (+)-carvone from caraway seed oil (Carum carvi), from which carvone has its name. (–)-Carvone, on the other hand, occurs in spearmint oil at high concentrations.

Carvone was the first compound that was used to show that the two optical isomers of the same molecule can produce different biological responses toward human olfactory receptors. While (–)-carvone has a typical sweetish minty odor, its mirror image, (+)-carvone, has a spicy aroma like caraway seeds.

26.1 **Describe** what the (+) and (–) stereodescriptors mean.

26.2 **Determine** the absolute configuration of both enantiomers of carvone using the Cahn-Ingold-Prelog (CIP) priority rules.

26.3 **Choose** the correct relationship between absolute configuration and the (+) and (–) stereodescriptors.

- ☐ (R)-isomer is always (–)
- ☐ (S)-isomer is always (–)
- ☐ (R)-isomer is always (+)
- ☐ There is no relationship between the stereodescriptors.

26.4 You have a bottle of a mixture of (+)-carvone and (–)-carvone and you want to determine the composition of the mixture. You measure the optical rotation of the mixture and obtain the value -23° (observed rotation, neat). **Find** which enantiomer is in excess. **Calculate** the ee value (formula below). The specific rotation of neat (+)-carvone is $+61^\circ$.

$$ee = \frac{(R - S)}{(R + S)}$$

Preparatory Problems (Theory)



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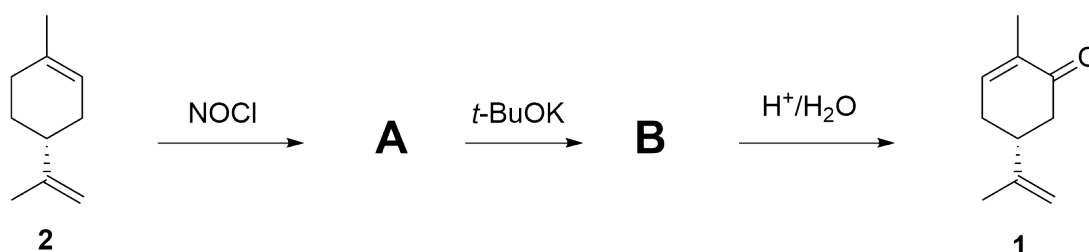
Q26-2

English (Official)

26.5 **Choose** the methods you can use to separate the two enantiomers of carvone.

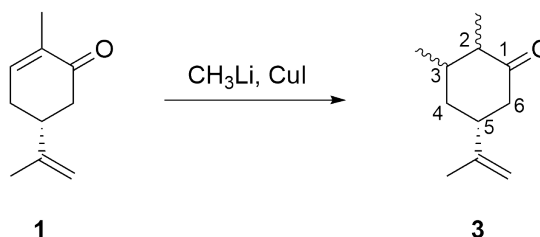
- ☐ Distillation
- ☐ Sublimation
- ☐ Chiral column chromatography
- ☐ Column chromatography on silica gel

26.6 **Draw** the products **A** and **B** in the synthesis of (–)-carvone (**1**) from (+)-limonene (**2**). Hint: NOCl reacts with the same regioselectivity as BrCl with alkenes.



Carvone does not only have interesting properties and various applications in food and flavor industry, but also rich chemistry. As an example of a molecule from the chiral pool, it is an attractive starting material for total synthesis of other complex natural products.

26.7 (–)-Carvone (**1**) undergoes conjugate addition reactions with nucleophiles, for example the addition of lithium dimethylcuprate to give product **3**. **Show** how many stereoisomers of compound **3** can form in this reaction. **Draw** the structure of the (2*R*,3*R*,5*R*) stereoisomer in the lowest energy conformation.



Introductory text:

Not all aroma compounds used for fragrances come from natural sources. In fact, Ernest Beaux, the perfumer known for creating Chanel No. 5 perfume, said, "One has to rely on chemists to find new aroma chemicals creating new, original notes. In perfumery, the future lies primarily in the hands of chemists." Indeed, flavor and fragrance (F&F) industry is a multibillion dollar industry, with several world-leading companies based in Switzerland.

Synthetic odorants are typically small, lipophilic volatile molecules that can trigger the sense of smell by interacting with the olfactory receptor neurons. The smell of each molecule that is prepared is then evaluated and categorized into the main odor families: fruity, marine, green, floral, spicy, woody, amber and musky.

Two examples of woody odorant, Ebanol® and Polysantol®, manufactured by Swiss companies Givau-

Preparatory Problems (Theory)



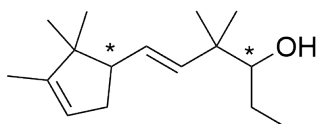
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Q26-3

English (Official)

dan and Firmenich, respectively, have both strong sandalwood odor and have been used in many fragrances.

In order to develop new odorants with possibly enhanced smells, you set out to synthesize compound **4**, and study the olfactory properties of each of the stereoisomers.



4

Preparatory Problems (Theory)



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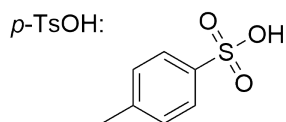
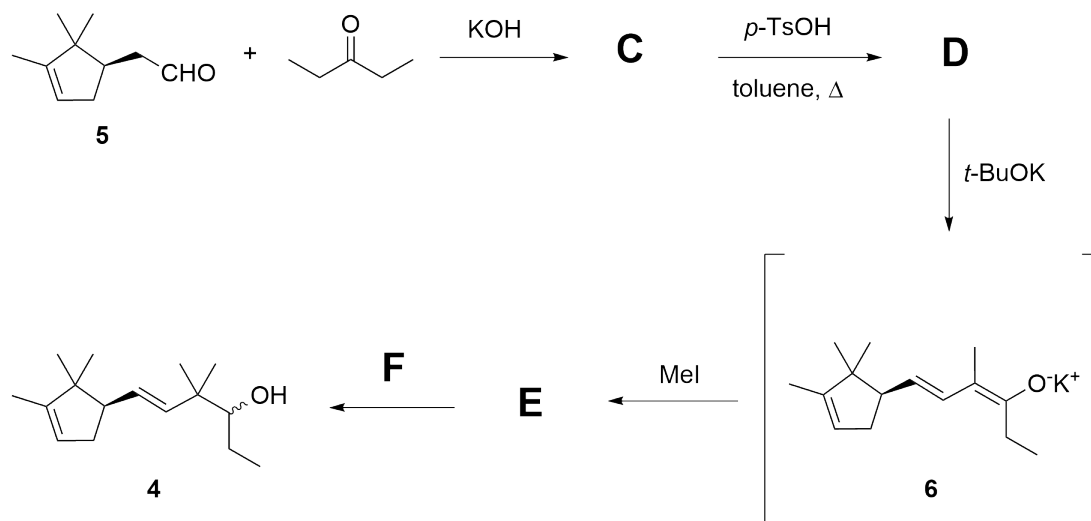
Q26-4

English (Official)

26.8 The synthesis of two stereoisomers of compound **4** starts from enantiomerically pure (*R*)-campholenic aldehyde (**5**). **Draw** the structure of **C-E** in the synthesis scheme. Choose suitable reaction conditions **F**. Stereochemical considerations are not required.

Conditions **F**:

- ☐ LiAlH_4
- ☐ NaOH
- ☐ NaBH_4
- ☐ H_2 , Pd/C



26.9 In the step from compound **C** to product **D**, the reaction is done using the Dean-Stark apparatus to remove water and drive the equilibrium towards the product **D**. **Choose** how else you could remove water from the mixture.

- ☐ Addition of 3Å molecular sieves
- ☐ Addition of zinc powder
- ☐ Using anhydrous toluene as the solvent
- ☐ Addition of anhydrous MgSO_4

Preparatory Problems (Theory)

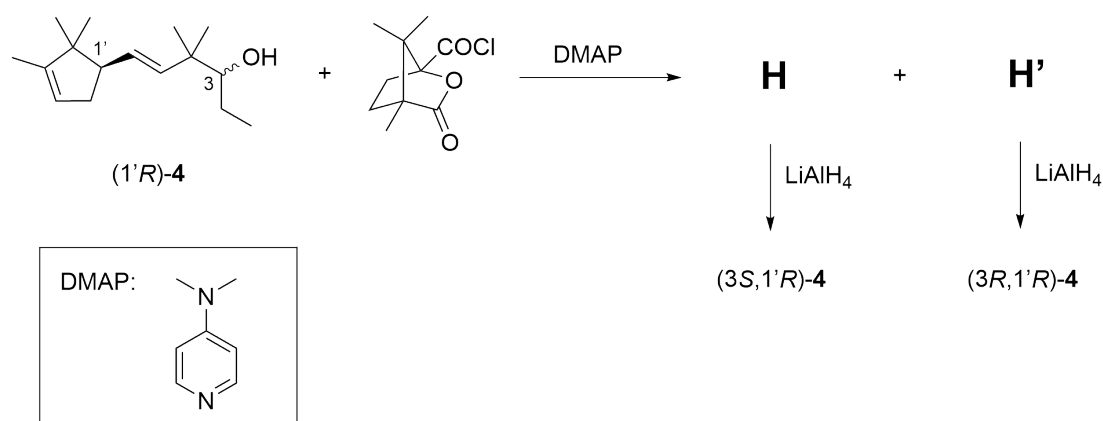


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Q26-5

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26.10 Product (1'*R*)-**4** is obtained as a mixture of two diastereomers in a 55:45 ratio. In order to separate the two diastereomers, compound (1'*R*)-**4** is transformed into the corresponding camphanoate ester derivative and the two diastereomers – **H** and **H'** – are separated by column chromatography. Reduction of the ester then affords the pure diastereomers and enantiomers of target molecule **4**. Draw the structure of products **H**, **H'** and both isomers of compound **4**, all including stereochemistry.



Having synthesized the two diastereomers of compound **4**, the last step is to evaluate their smell. The (3*S*,1'*R*)-(**4**) isomer was found to have the strongest and most substantive sandalwood odor.



Vitamin C

Vitamin C (also known as L-ascorbic acid) is an essential nutrient for humans, as our body is not able to synthesize it on its own. It has many physiological roles, e.g. it is involved in wound healing or acts as an antioxidizing agent. A deficiency of vitamin C leads to impaired collagen formation and eventually to the scurvy disease. In the search for the treatment for scurvy, vitamin C was discovered in 1912 and was given the name L-ascorbic (meaning “anti-scurvy”) acid. It was isolated in 1928 and first synthesized in the laboratory in 1933. Shortly after, Swiss chemist Tadeus Reichstein developed a method for the bulk production of vitamin C at ETH Zürich.

Note: Detailed knowledge on carbohydrate chemistry is not expected for the exam. The purpose of this problem set is the training on stereochemistry.

- 27.1** An intermediate in this so-called Reichstein process is α -L-sorbofuranose (**A**) which gets transformed to compound **1** after treatment with two equivalents of acetone under acidic conditions. **Draw** the structure of α -L-sorbofuranose (**A**).

- 27.2** In the next step, **1** is reacted with KMnO_4 to give compound **B**. Heating with aqueous acid yields 2-keto-L-gulonic acid (**C**). **Draw** the structures of **B** and **C** (in its cyclic form).

- 27.3** **Choose** the correct role of acetone in this synthesis.
- ☐ Protecting group (**a**)
 - ☐ Solubilizing group (**b**)
 - ☐ Directing group (**c**)



- 27.4** Finally, the linear form of 2-keto-L-gulonic acid (**2**) undergoes intramolecular esterification to give lactone **D** which tautomerizes to L-ascorbic acid (**3**). Draw the structure of **D**.

- 27.5** In aqueous solutions, L-ascorbic acid (**3**) has a pK_a value of 4.2. Indicate the most acidic proton. Draw a functional group with a comparable pK_a value.

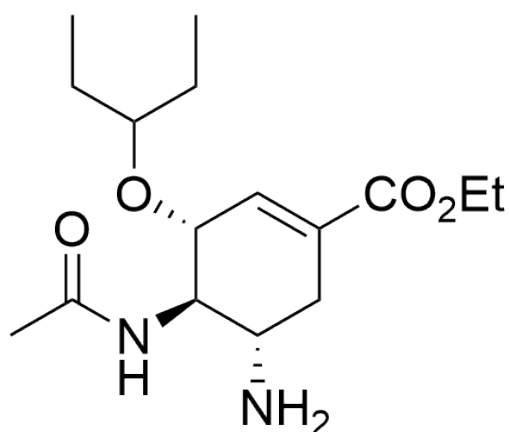
- 27.6** Vitamin C is an important antioxidant in biological systems and can be oxidized to L-dehydroascorbic acid (**E**). Draw the structure of **E**.

Antiviral Drug Tamiflu

Introductory text:

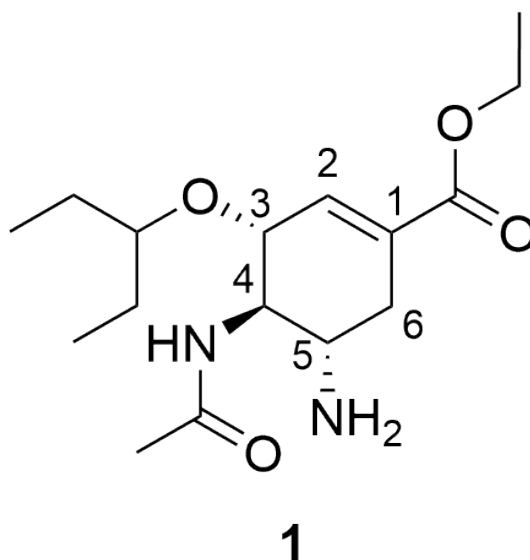
*Oseltamivir is an antiviral medicine which is sold under the brand name Tamiflu by the Swiss pharmaceutical company Roche. It inhibits the viral enzyme neuraminidase and thereby prevents the release of new viral particles from an infected human cell. Tamiflu is one of the most widely used drugs to treat and prevent influenza (flu) with more than 5 million prescriptions in the United States in 2019. There has been extensive research by numerous laboratories to develop an efficient, safe and scalable synthesis towards Oseltamivir (1). The industrial 12-step route from Roche has an overall yield of ca. 35%. It starts from (-)-shikimic acid which was originally extracted from Chinese star anise and is nowadays also produced recombinantly from genetically engineered *E. coli* bacteria.*

In 2009, Hayashi and co-workers developed an alternative efficient and low-cost synthetic route to prepare Oseltamivir. They synthesized the drug in three one-pot operations with an overall yield of 57%.



Oseltamivir (1)

28.1 **Determine** the absolute configuration of Oseltamivir (**1**) at C(4).



28.2 **Select** the relationship between substituents at C(3) and C(4).

- ☐ *cis*
- ☐ *trans*
- ☐ *syn*
- ☐ *anti*

Preparatory Problems (Theory)

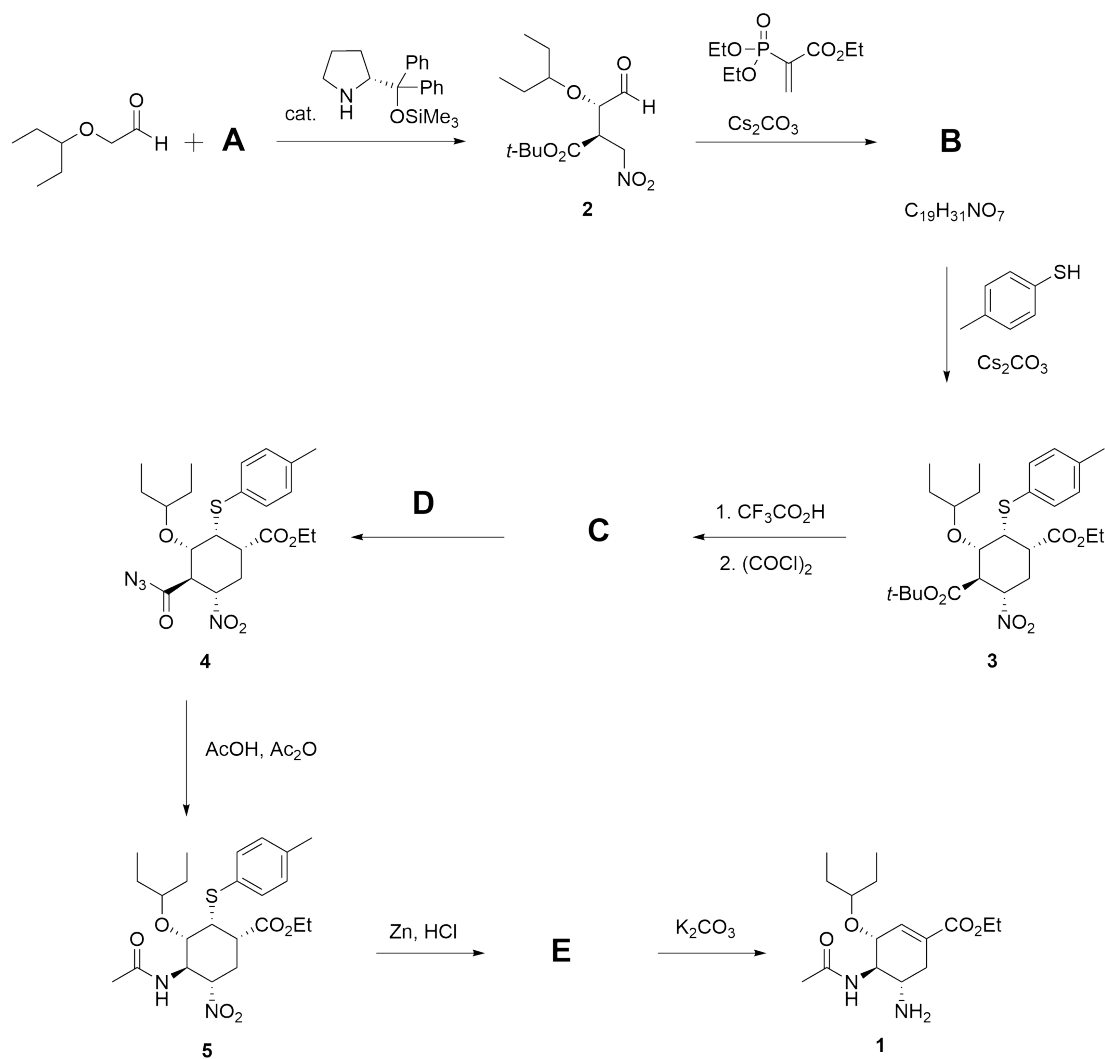


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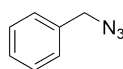
Q28-3

English (Official)

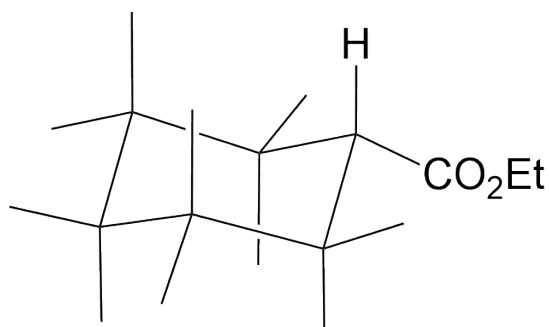
28.3 Draw the structures of compounds **A** – **C** and **E** in the synthesis of Oseltamivir (**1**). Choose a suitable reagent **D**. Draw all compounds with the correct stereochemistry. Note: Knowledge on stereochemical models of the transformation is not required. The stereochemistry can be deduced from the given structures **1-5**.



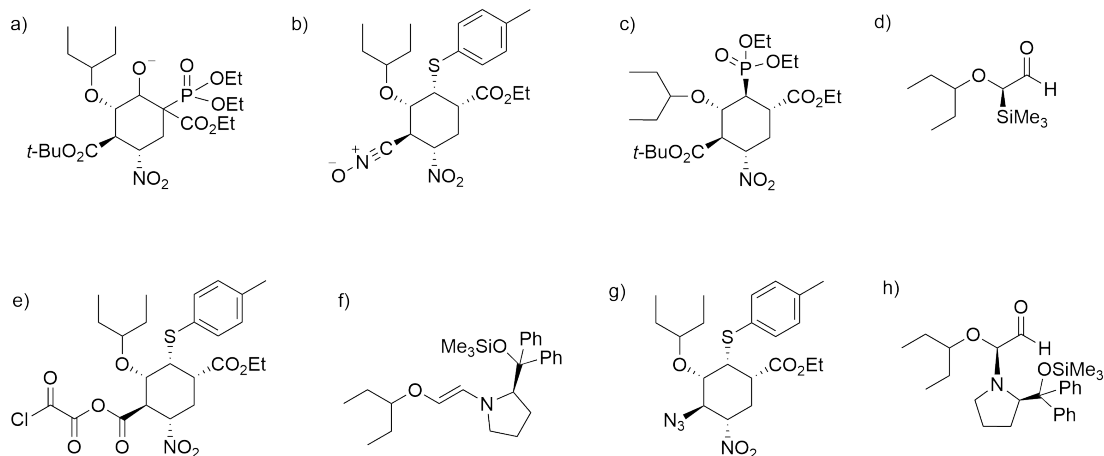
options for reagent **D**



28.4 **Draw** the chair conformation of **3** using the template below.

**3**

28.5 Which of the following intermediates is formed in the synthesis of Oseltamivir (**1**)? **Select** all correct answers.

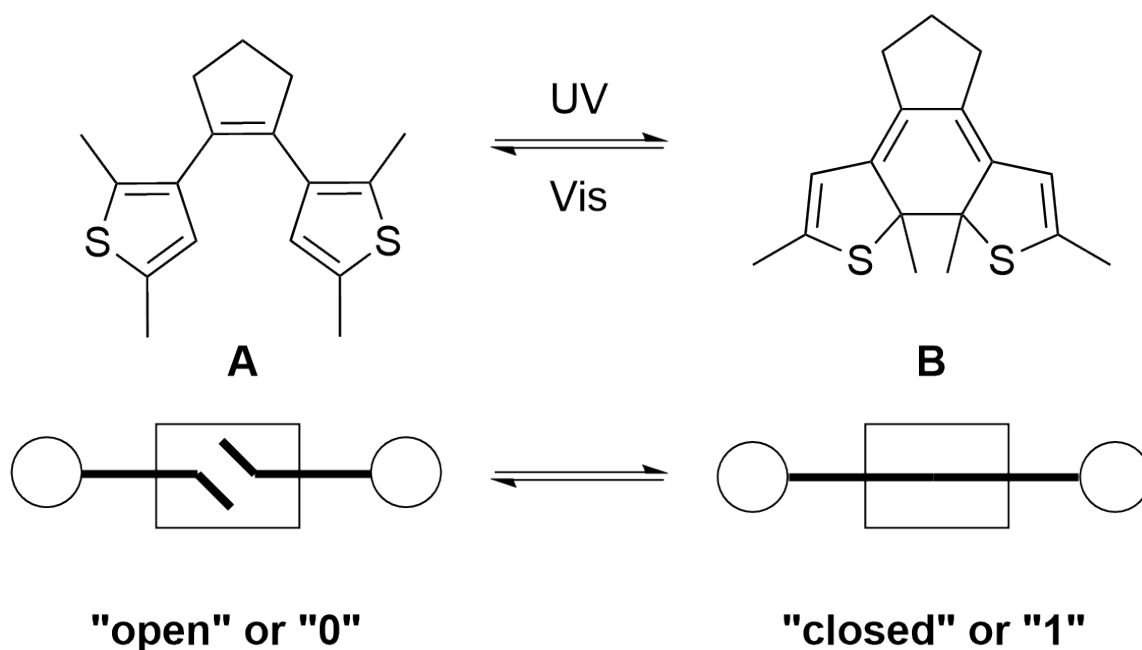


28.6 Tamiflu is a pro-drug that is converted to the active form, Oseltamivir carboxylate **F**, by hepatic esterases. **Draw** the structure of **F**.

Diarylethenes as Photoswitches

Switzerland is famous for its high-performance chronometers. These very sophisticated master pieces of top-notch engineering require very small gears and contactors. However, there are natural limits regarding the size of these macroscopic components. Chemists found a way to surpass engineers in the struggle to find even smaller switches that can be used in logic devices or implemented in smart drug molecules.

A commonly encountered class of molecular switches are diarylethenes with **A** being a rather simple example. **A** can be switched with UV-light to the closed version **B** following an electrocyclic reaction. From a logical perspective, the open state **A** could be assigned the value 0 while **B** would represent 1 in the binary system. Irradiation of **B** with visible light reverts the reaction and gives **A** via an electrocyclic ring-opening.



The photochemical reaction interconverting **A** and **B** follows general rules for chemical reactions, formulated by Robert Burns Woodward and Roald Hoffmann in the 1960s. Based on symmetry considerations of the orbitals involved in these electrocyclic reactions, a simplified version of these rules can be used to evaluate their feasibility under thermal or photochemical conditions as well as predict their stereochemical outcome.

To apply the simplified Woodward-Hoffmann rules, one first needs to determine the number of electrons (N_e) directly involved in the reaction. As a bond consists of two electrons, this number equals double the number of all breaking bonds in the starting material or all newly formed bonds (σ - and π -type bonds) in the product, respectively. Following up on that, the reaction conditions determine the rotation of the carbon cycle in the ring-closing or ring-opening reaction, as can be taken from the table below and the following figure.

Preparatory Problems (Theory)



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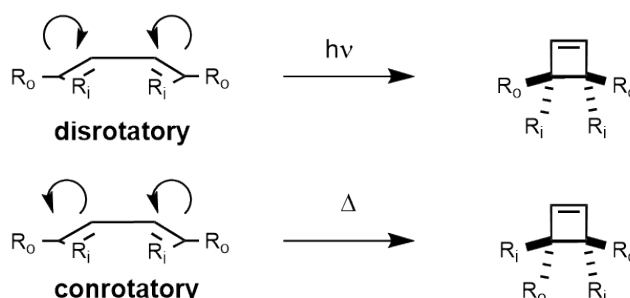
Q29-2

English (Official)

π -Electrons	Conditions	Sense of Motion
$N_e = 4n, n \in \mathbb{N}$	thermal (Δ)	conrotatory
$N_e = 4n, n \in \mathbb{N}$	photochemical ($h\nu$)	disrotatory
$N_e = 4n + 2, n \in \mathbb{N}_0$	thermal (Δ)	disrotatory
$N_e = 4n + 2, n \in \mathbb{N}_0$	photochemical ($h\nu$)	conrotatory

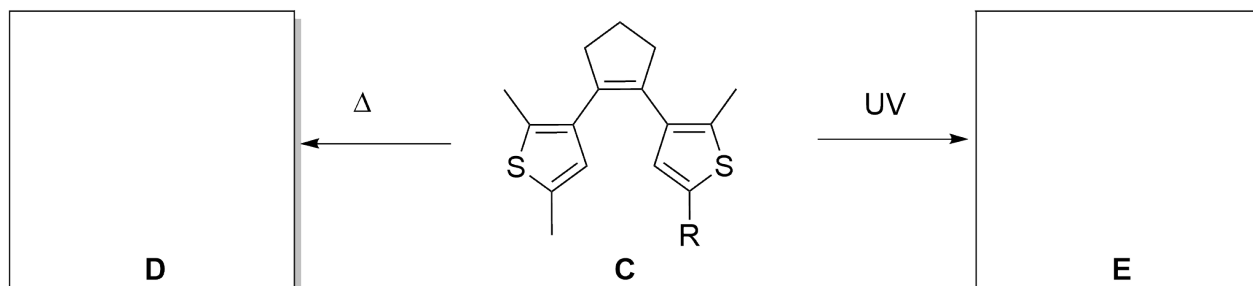
Woodward-Hoffmann rules for electrocyclic reactions.

In a disrotatory ring-closure, the substituents on the atoms that form a C-C single bond rotate in opposite directions (i.e. one clockwise and the other counterclockwise). In a conrotatory movement, the substituents move in the same direction (i.e. both clockwise or both counterclockwise). The same applies for the ring-opening reactions. Only a distinction between the clockwise or counterclockwise motion is not possible and both stereoisomeric products are usually formed in equal amounts.



29.1 How many electrons (N_e) of diarylethene **A** are directly involved in the photochemically occurring electrocyclic ring-closure to form **B**?

29.2 In what sense (disrotatory or conrotatory) do the methyl groups on the diarylethene have to move according to the Woodward-Hoffmann rules when **B** is formed?



29.3 **Draw** the products **D** and **E** of the hypothetical thermally allowed cyclization and the photochemically allowed cyclization of compound **C** with correct relative configuration.

Preparatory Problems (Theory)



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Q29-3

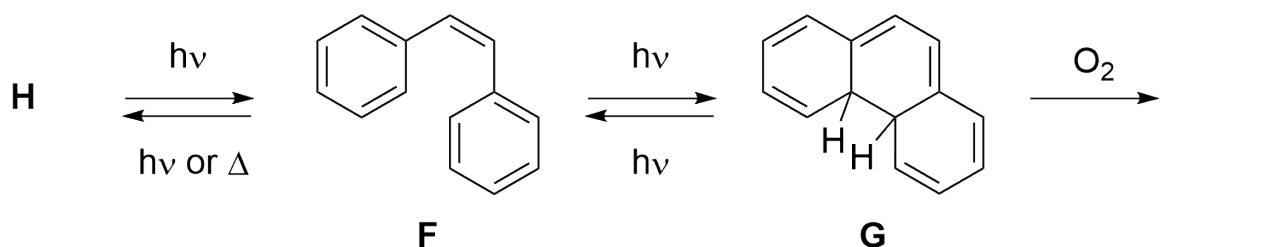
English (Official)

- 29.4** **Choose** the stereochemical relation between the resulting structures **D** and **E** ($R = \text{Me}$).
- ☐ diastereomers
 - ☐ enantiomers
 - ☐ epimers
 - ☐ constitutional isomers
 - ☐ conformational isomers

- 29.5** **State** how many products could be expected under thermal and photochemical conditions in the case that $R = \text{Et}$.

- 29.6** **Choose** the stereochemical relation between the products formed in the photochemical ring closure when $R = \text{Et}$.
- ☐ diastereomers
 - ☐ enantiomers
 - ☐ epimers
 - ☐ constitutional isomers
 - ☐ conformational isomers

For application in data storage devices, it is desirable that there are no competing reactions that lower the yield of the desired photo switching reaction. Also, the switch should possess high cycle stability, i.e. it should not undergo irreversible side reactions.



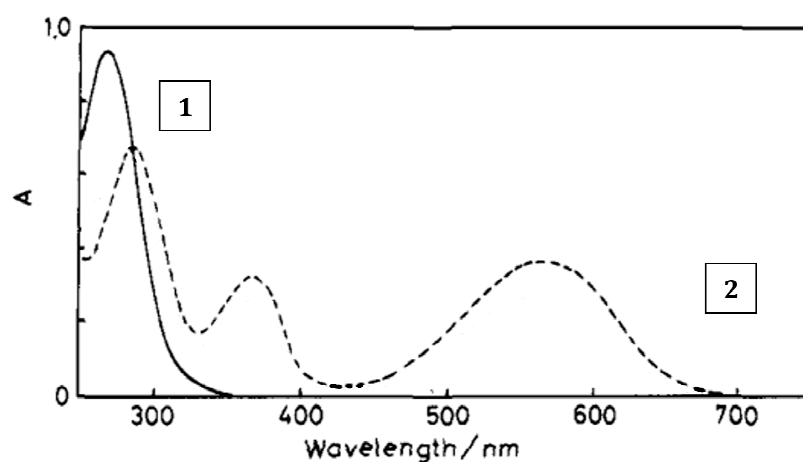
- 29.7** **Give** the structures of the reaction products **H** and **I** that might form from stilbene **F** and the electro-cyclisation product **G**.

- 29.8** **Choose** the correct answer(s) explaining the crucial modifications in **C** that prevent similar side reactivity as in case of **F** or **G**, respectively.
- ☐ Presence of methyl groups instead of H-atoms prevents irreversible oxidation to form a polycyclic aromatic system
 - ☐ Methyl groups increase the molecular weight and thus lead to a deeper energetic minimum of the structure
 - ☐ The cyclopentene backbone prevents Z to E isomerization
 - ☐ Methyl groups instead of H-atoms increase the lipophilicity of the system

In a photo-switching experiment, the thermodynamically more stable isomer is usually irradiated with light of a certain wavelength to induce the photochemical isomerization reaction. To achieve quantitative conversion in a reversible photo-switching experiment, spectral overlap of the starting material and product should be minimal at the wavelength of irradiation. This ensures the product does not revert back to the starting material under irradiation. Significant spectral overlap at the wavelength of irradiation would diminish reaction yield and would lead to an equilibrium mixture of isomers. Hence, electromagnetic radiation of different wavelengths is used in the conversion of **A** to **B** (UV light) and reversion of **B** back to **A** (visible light).

29.9 Choose the answers that apply to the system of **A** and **B**.

Hint: The A on the y-axis of the graph represents the absorbance.



- ☐ The wavelengths of the absorption maxima, relevant for photo switching between **A** and **B**, follow $\lambda_{\text{MAX,A}} > \lambda_{\text{MAX,B}}$
- ☐ The wavenumbers of the absorption maxima, relevant for photo switching between **A** and **B**, follow $\tilde{\nu}_{\text{MAX,A}} > \tilde{\nu}_{\text{MAX,B}}$
- ☐ The absorption spectrum of **A** is represented by the dashed line (2)
- ☐ The absorption spectrum of **B** is represented by the straight line (1)
- ☐ The absorption spectrum of **A** is represented by the straight line (1)
- ☐ The absorption spectrum of **B** is represented by the dashed line (2)

29.10 Estimate a reasonable wavelength to induce the transformation of **B** to **A**.

Preparatory Problems (Theory)

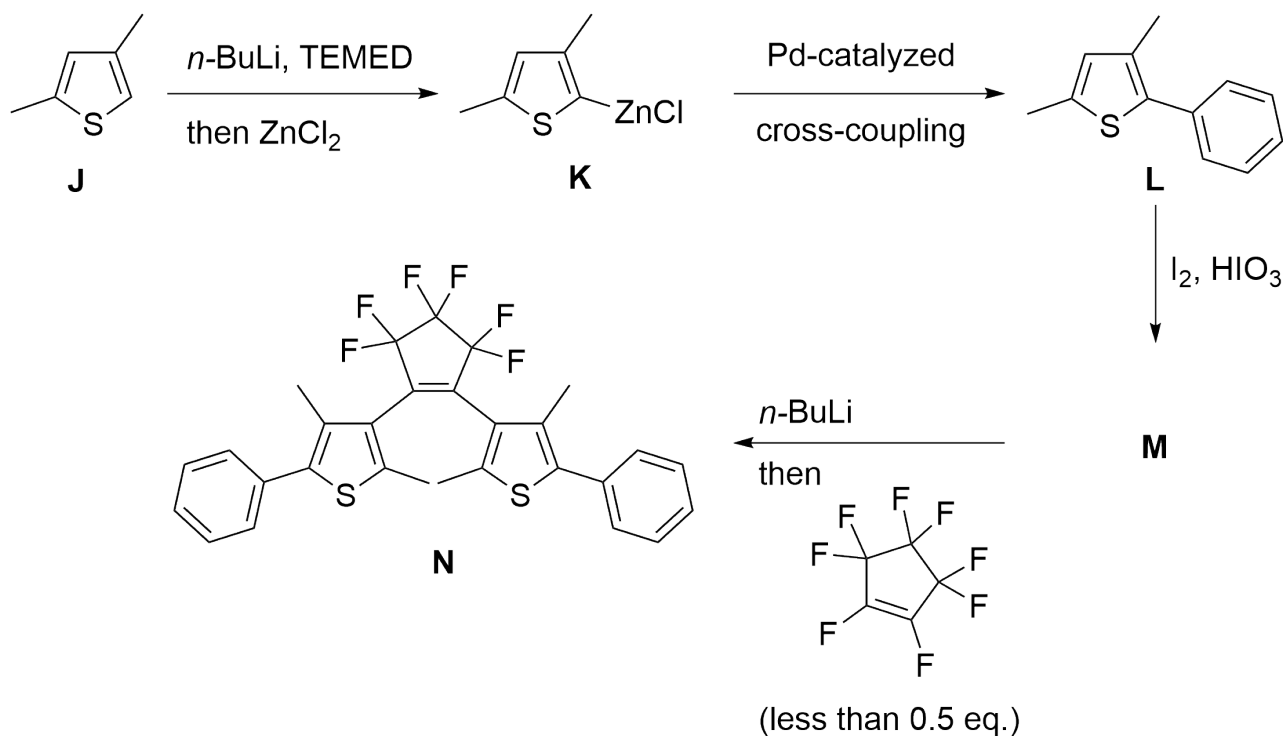


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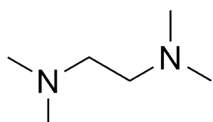
Q29-5

English (Official)

Diarylethene **N** was synthesized by Irie and co-workers in Fukuoka, Japan, through the following metal-mediated transformations.



TEMED:

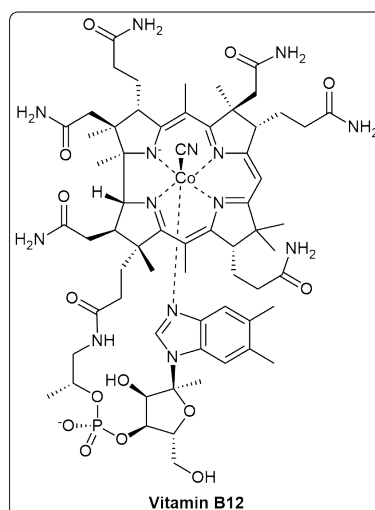


29.11 Suggest a reagent and a catalyst for the transformation of **K** to **L**.

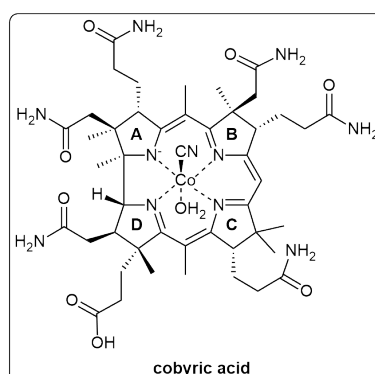
29.12 Give the structure of intermediate **M**.

29.13 Make pairs between the elementary steps and the transformations (**J** to **K**, **K** to **L**, and **M** to **N**) according to the role of the organometallic compounds involved.

- ☐ Deprotonation and transmetalation
- ☐ Metal-catalyzed cross coupling reaction
- ☐ Halogen-metal exchange
- ☐ Oxidation by stoichiometric amounts of a transition metal
- ☐ Metal-catalyzed olefin cross metathesis

Studies on Vitamin B₁₂

Vitamin B₁₂, also known as cobalamin, is a water-soluble vitamin involved in metabolism. It is the most chemically complex of all vitamins, and for humans, the only vitamin that must be sourced from animal-derived foods or supplements. The structure of B₁₂ is based on a corrin ring, which is similar to the porphyrin ring found in heme. Biochemically, the cobalt center can take part in both two-electron and one-electron reductive processes and its ability to shuttle between the +1, +2, and +3 oxidation states is responsible for the versatile chemistry of vitamin B₁₂. The complete chemical structure of the molecule was determined by Dorothy Hodgkin, based on crystallographic data in 1956, for which and other crystallographic analyses she was awarded the Nobel Prize in Chemistry in 1964. Five people have been awarded Nobel Prizes for direct and indirect studies of vitamin B₁₂.

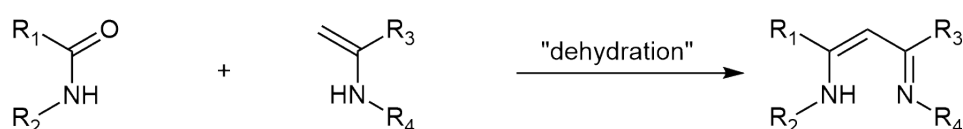


The first total synthesis of vitamin B₁₂ was accomplished in 1973 by a collaboration between Robert Burns Woodward's group at Harvard University and Albert Eschenmoser's group at the Swiss Federal Institute of Technology in Zürich and remains one of the classic feats of organic synthesis. In 1960, the ETH Zurich variant was started. Following that in 1961 the Harvard variant started, and after 1965 the work was collaboratively pursued. In terms of the amount of collaboration it required the work of 91 post-doctoral fellows, and 12 PhD students from several different nations. In the process, they achieved not only an astounding synthesis, but also opened several new fields for future investigations. The Woodward-

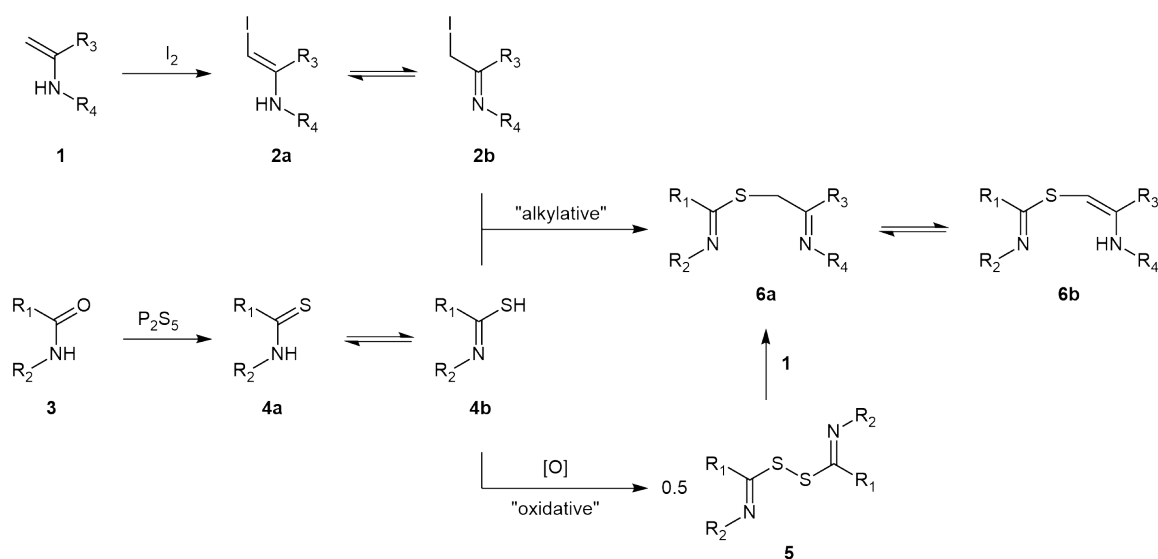
Hoffmann rules might be the most famous of the offshoots. And although there have been sporadic synthetic efforts since 1972, the Eschenmoser–Woodward synthesis remains the only completed (formal) total synthesis.

Eschenmoser Sulfide Contraction

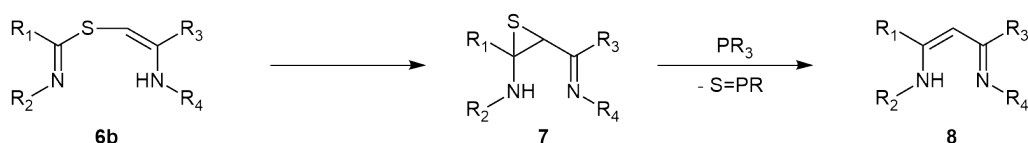
During their assembly of the B/C ring fragment, the Eschenmoser group at ETH envisioned the following hypothetical reaction to join the five membered ring fragments with a methylene bridge.



Amides and enamines do not react in this way on their own, so the researchers devised a workaround, that would enable the same overall transformation.



Amide **3** is activated as thioamide **4a** which is then coupled either via an alkylative pathway with **2b** or via an oxidative pathway with **5**, giving **6a**. Tautomerization followed by sulfur extrusion with a phosphine reagent gives the desired product **8**.



The Eschenmoser sulfide contraction proved pivotal for the construction of the macrocyclic ring system in vitamin B₁₂.

Preparatory Problems (Theory)

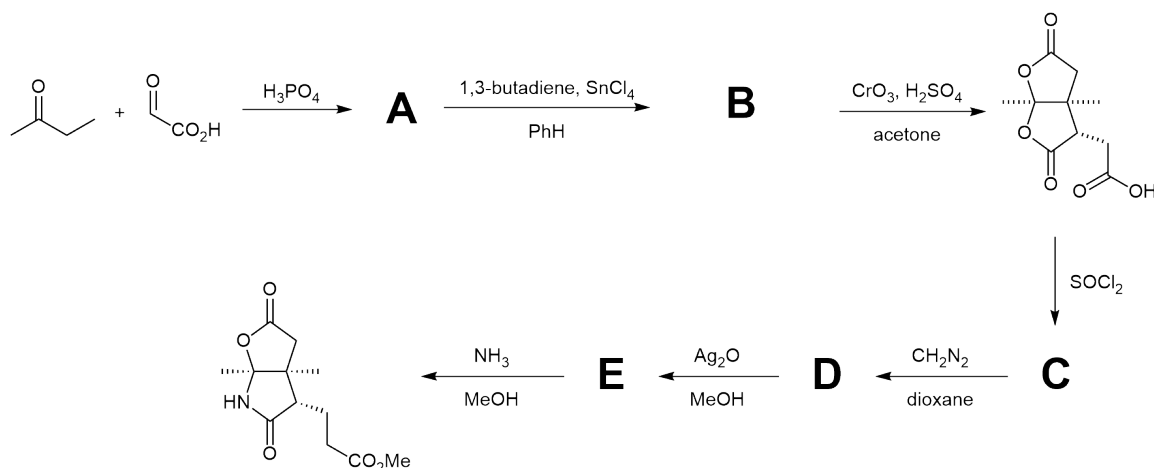


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Q30-3

English (Official)

The construction of the B/C ring fragment featured the following synthetic steps (Hint: For the problems 30.1-30.6 the stereochemistry of the products does not need to be considered):

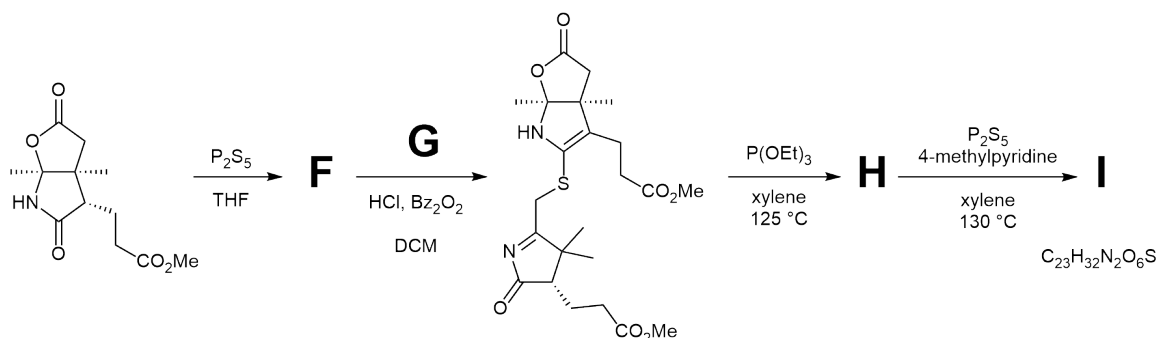


30.1 **Give** the structures of intermediate **A-E**.

(Hint: the reaction from **B** to the intermediate shown in the top right could also be carried out using different conditions, for example an ozonolysis followed by oxidative workup.)

30.2 **State** the name of the reaction from **A** to **B**. **Explain** the role of the reagent SnCl_4 in this reaction.

An Eschenmoser sulfide contraction was then used to complete the assembly of the B/C ring system in **I**:



30.3 **Give** the structures of **F-I**.

Preparatory Problems (Theory)

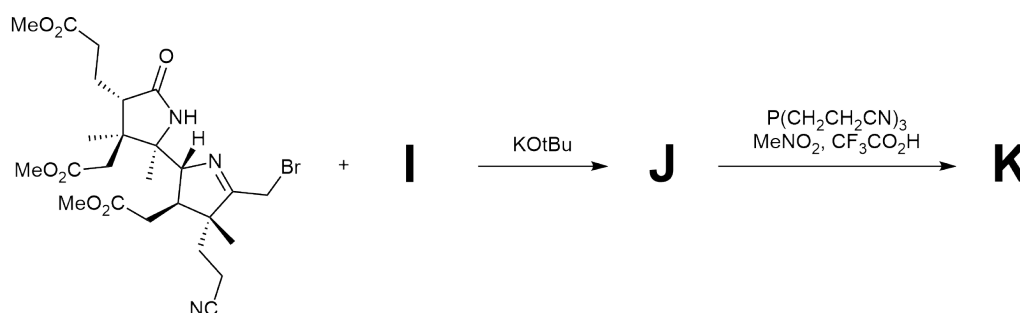


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Q30-4

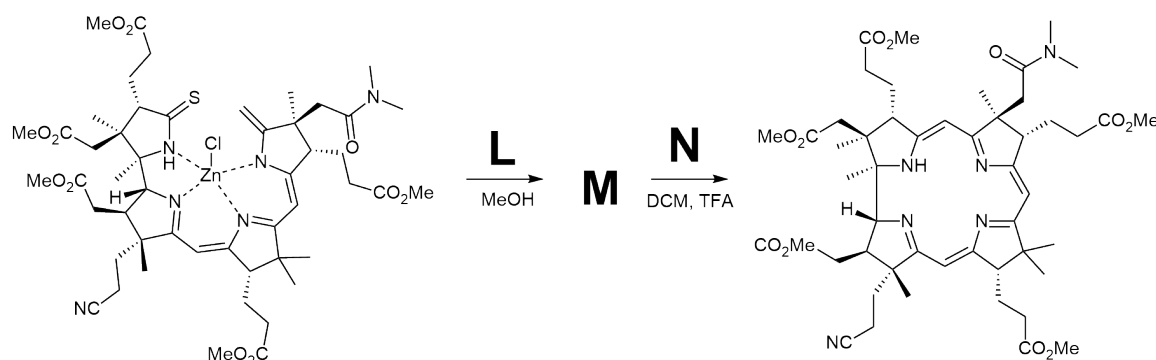
English (Official)

After similar construction of the fragment containing the A/D ring system both fragments were coupled:



30.4 Give structures for intermediates **J** and **K**.

The final intermediate after ring closure was then easily turned into cobyric acid, whose conversion to vitamin B_{12} was already known from degradation studies thereby completing the total synthesis. The synthetic steps for the ring closure are shown below:



30.5 Suggest conditions **L**, **N** and draw the structure of intermediate **M**.

30.6 State the role ZnCl_2 plays in the transformation under conditions **L**.

Frontier Molecular Orbitals

During an alternative route to the cobyric acid ring system, the Woodward group at Harvard anticipated the following Michael reaction towards constructing the A ring system. They were however unable to observe any reaction under basic conditions.

When attempting to measure the melting point of the compound they observed a reaction forging the desired connectivity, however with the wrong stereochemistry at the newly formed, quaternary center.

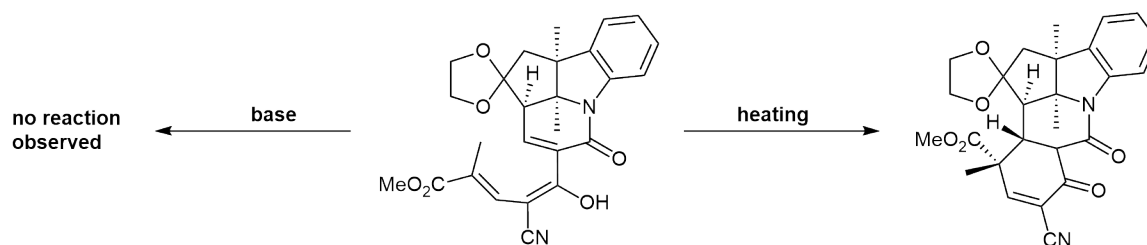
Preparatory Problems (Theory)



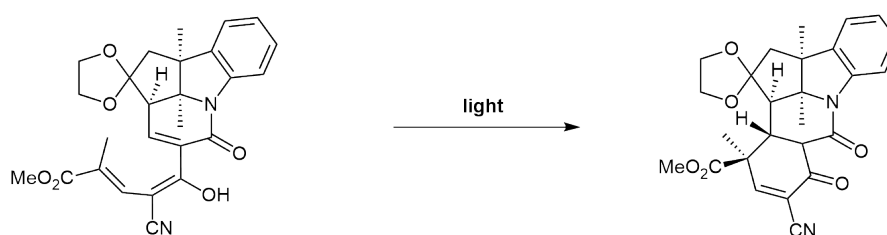
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Q30-5

English (Official)



As Woodward himself puts it: *"BUT as our investigation proceeded, it became more and more clear that our stereochemical anticipations had been dead wrong... Here was a real dilemma. I had analysed the situation very carefully in the light of what I regarded as the best contemporary theoretical principles, and I had reached an absolutely wrong conclusion. I was appalled."* Clearly, the current theoretical models were not sufficiently developed to rationalize the experimental outcome. Complicating the matter further, under photochemical conditions the opposite diastereomer was formed exclusively.



In order to explain these observations, Woodward together with Roald Hoffmann developed the Woodward-Hoffmann rules to rationalize these findings. One similar method, developed independently by Kenichi Fukui is the so-called Frontier Molecular Orbital (FMO) Theory, which is considerably more user friendly.

30.7 Derive the FMOs for (2E,4Z,6E)-octa-2,4,6-triene as a model for the reaction discussed above.

30.8 In order for a constructive reaction, orbital overlap between lobes of the same phase has to occur. Show how in the thermal reaction above this has to result in the given diastereomer. State if the reaction dis- or conrotatory.

30.9 Rationalize, with the help of FMO theory, the different stereochemical outcomes of the electrocyclisation reaction under thermal and photochemical conditions.

Preparatory Problems (Practical)



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Q1-1

English (Official)

Essential Medicines

Chemicals

Chemical	Hazards	GHS Hazard Statements
Solid 1/2/3/4	None	None
Solid 1/2/3/4	Harmful	H302, H315, H319; P264, P270, P280, P301+P312, P302+P352, P305+P351+P338
Solid 1/2/3/4	Oxidizing Corrosive Harmful Health hazard Environmental hazard	H272, H302, H314, H361d, H373, H410; P210, P260, P273, P280, P303+P361+P353, P305+P351+P338
Solid 1/2/3/4	Harmful Health hazard Environmental hazard	H302+H312+H332, H315, H319, H335, H372, H400; P273, P280, P301+P312, P302+P352+P312, P304+P340+P312, P314
Petroleum ether	Flammable Harmful Health hazard Environmental hazard	H224, H304, H315, H336, H411; P210, P233, P273, P301+P310, P331, P403+P233
Sulfuric acid, H ₂ SO ₄ , 1 M	Corrosive	H290, H315, H319; P234, P264, P280, P302+P352, P305+P351+P338, P332+P313
Solution I/II/III/IV/V	Corrosive Environmental hazard	H314, H410; P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338, P363
Solution I/II/III/IV/V	None	None
Solution I/II/III/IV/V	Toxic	H301, H315, H319; P264, P270, P280, P301+P310, P302+P352, P305+P351+P338
Solution I/II/III/IV/V	Oxidizing Toxic Environmental hazard	H272, H301, H319, H400; P210, P220, P264, P273, P301+P310, P305+P351+P338
Solution I/II/III/IV/V	None	None
Solution A/B/C	Corrosive Harmful Environmental hazard	H302, H318, H410; P264, P270, P273, P280, P301+P312, P305+P351+P338
Solution A/B/C	Harmful Health hazard	H302, H319, H372; P260, P264, P270, P280, P301+P312, P305+P351+P338, P314, P337+P313, P501
Solution A/B/C	Harmful	H319; P264, P280, P305+P351+P338, P337+P313

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q1-2

English (Official)

The mass of each solid is ca. 200 mg. The volume of each solution is ca. 20 ml. The encoded solutions have a concentration of ca. 1 wt%.

Glassware and Equipment

Item	Quantity
Test tube rack	1
Permanent marker	1
Closed vials with solids 1-4	4
Closed vials with solutions I-V	5
Closed vials with solutions A-C	3
Closed vials with petroleum ether and H ₂ SO ₄ solution	2
Test tubes	At least 15
Plastic Pasteur pipettes	12
Wash bottle with distilled water	1

Switzerland is a globally known centre of the pharmaceutical industry. Many pharmaceutical companies are located here, including very big corporations, such as *Novartis* and *Hoffmann-La Roche* in the Basel area. Chemicals are taking leading positions among export products of the country. Switzerland is also the home of the *World Health Organization* (WHO), which is a specialized agency of the United Nations, with the headquarter in Geneva.

In 1977 WHO published an Essential Medicines List (EML), which is updated every 2 years. Currently, it contains almost 500 medications, which are considered to be the most effective and safe to cover the principal needs of the health system. In this task, you will have to determine the compounds from this list and learn, for which properties they were included in the EML.

Note: knowledge of the medical use of compounds won't be necessary for the practical exam. Here, the questions about medical use are given only to improve your erudition.

Part A

Preparatory Problems (Practical)



55TH INTERNATIONAL
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SWITZERLAND 2023

Q1-3

English (Official)

- 1.1** In each of the vials **1–4** there is only one solid from the list: BaSO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $[\text{Ag}(\text{NH}_3)_2]\text{F}$, KMnO_4 , $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, C , As_2O_3 , I_2 , $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$. **Fill in** the table with the formulas of corresponding medications.

Formula	Trade name (example)	Medical use
	<i>CharcoAid</i>	Poisonings (non-specific antidote)
	<i>Radiogardase</i>	Thallium and radioactive caesium poisonings
	<i>Trisenox</i>	Cancer
	<i>Feosol</i>	Iron deficiency
	<i>Nipride</i>	Hypertensive crisis (high blood pressure)
	<i>Permitabs</i>	Dermatological infections
	<i>Varibar</i>	X-ray imaging (radiocontrast agent)
	<i>Iodosorb</i>	Iodine deficiency, antiseptic
	<i>Saforide</i>	Dental caries prevention, antimicrobial

- 1.2** **Identify** the compounds in vials **1–4** by analyzing their appearance, solubility in water and petroleum ether, as well the colours of formed solutions.

Vial	Compound	Reasoning
1		
2		
3		
4		

- 1.3** **Find** which two compounds from **1–4** can react with each other in an aqueous solution. **Perform** this reaction without and with the addition of acid (H_2SO_4). **Specify** the observations and **write down** the equations of the reactions. Use “↓” for precipitates and “↑” for gases.

Conditions	Reaction equation with observations
without H_2SO_4	
with H_2SO_4	

Part B

In vials **I–V** there are five solutions of sodium salts also from EML: fluoride, hypochlorite, nitrite, hydrogen carbonate and thiosulfate.

Preparatory Problems (Practical)



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SWITZERLAND 2023

Q1-4

English (Official)

1.4 **Assign** the medical use of the compounds with the letter of corresponding medical use:

- **A** – Severe metabolic acidosis
- **B** – Dental caries prevention
- **C** – Cyanide poisoning
- **D** – Cyanide poisoning and fungal skin infections
- **E** – Disinfectant

Formula	Letter
NaNO ₂	
NaHCO ₃	
Na ₂ S ₂ O ₃	
NaF	
NaClO	

1.5 **Identify** the compounds **I–V**. You can use the solution of H₂SO₄ and the compounds **1–4**. For each compound, **write** at least one chemical reaction, which helped you explicitly identify the compounds. **Specify** the observations clearly: formation of precipitate (↓), gas evolution (↑) or other effects.

Compound	Formula	Reaction(s) equation(s) with observations
I		
II		
III		
IV		
V		

Part C

In vials **A–C** there are 3 solutions of mixtures of 2 compounds from the list: Li₂CO₃, ZnSO₄, KI, CH₃COOH, MgSO₄, CaCl₂. All these compounds are also listed as important medicines in EML. Each of them is used to prepare a mixture and is used only once.

Preparatory Problems (Practical)



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SWITZERLAND 2023

Q1-5

English (Official)

- 1.6** **Find** the only possible compositions of the 3 mixtures. **Arrange** them with the medical use of the compounds.

Compound	Medical use
	Bipolar disorders
	Hyperthyroidism, radiation accidents, fungal infections

Mixture 1

Compound	Medical use
	Anticonvulsant
	Diarrhoea

Mixture 2

Compound	Medical use
	Corresponding metal supplement
	Infections of the ear canal

Mixture 3

- 1.7** **Perform** the cross-reactions between mixtures **A–C** and **fill in** the following table of observations with the symbols: "↓" – precipitate, "↑" – gas, "–" if there are no visible observations. Be aware that the result of some reactions can depend on the ratio of reagents used.

Mixtures	A	B	C
A			
B			
C			

Preparatory Problems (Practical)



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Q1-6

English (Official)

- 1.8** Based on the observations, **determine** the composition of each mixture. **Write down** the ionic equations of performed reactions. Use "↓" for precipitates and "↑" for gases.

--	--

Mixture **A**

--	--

Mixture **B**

--	--

Mixture **C**

Combination	Ionic equation(s)
A+B	
A+C	
B+C	

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q2-1

English (Official)

Cantons of Switzerland

Chemicals

Chemical	Hazards	GHS Hazard Statements
Solution 1/2/3/4/5	Harmful Environmental hazard	H302, H319, H410; P264, P280, P301+P330+P331, P312, P337+P313
Solution 1/2/3/4/5	Harmful	H302; P280, P301+P312, P303+P361+P353, P305+P351+P338
Solution 1/2/3/4/5	Corrosive	H314; P280, P301+P330+P331, P303+P361+P353, P305+P351+P338, P310
Solution 1/2/3/4/5	Toxic Corrosive Environmental hazard	H290, H301, H314, H332, H400; P260, P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338
Solution 1/2/3/4/5	Corrosive	H314; P260, P280, P301+P330+P331, P303+P361+P353, P304+P340+P310, P305+P351+P338
Ammonia solution, NH ₃ , 1 M	Corrosive Environmental hazard	H315, H318, H410; P264, P273, P280, P302+P352, P305+P351+P338, P332+P313
Sulfuric acid, H ₂ SO ₄ , 1 M	Corrosive	H290, H315, H319; P234, P264, P280, P302+P352, P305+P351+P338, P332+P313
Solution CH-1/CH-2/CH-3	Harmful Health hazard	H302, H319, H371, H373; P301+P312+P330, P305+P351+P338, P308+P311
Solution CH-1/CH-2/CH-3	Toxic Health hazard Environmental hazard	H301+H331, H351, H373, H410; P202, P260, P264, P273, P301+P310, P304+P340+P311
Solution CH-1/CH-2/CH-3	Corrosive	H318; P280, P305+P351+P338+P310
Zinc dust, Zn	Environmental hazard	H410; P273, P391, P501
Solution A/B	Harmful Corrosive Environmental hazard	H302, H315, H318, H335, H410 P280, P301+P330+P331, P302+P352, P304+P340, P305+P351+P338, P310, P332+P313
Solution A/B	Toxic Environmental hazard	H301, H411 P264, P270, P273, P301+P310, P391, P405
Potassium permanganate solution, KMnO ₄ , 1 wt%	Oxidizing Corrosive Harmful Health hazard Environmental hazard	H272, H302, H314, H361d, H373, H410; P210, P260, P273, P280, P303+P361+P353, P305+P351+P338

The volume of each solution is ca. 20 ml. The encoded solutions have a concentration of 1–5 wt%. Some ions that do not participate in identification reactions could have been substituted with other inert ions. Solutions of some encoded compounds could have been simulated using a mixture of compounds of targeted ions with inert counterions. Ask your mentors if these changes were implemented.

Preparatory Problems (Practical)



55TH INTERNATIONAL
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SWITZERLAND 2023

Q2-2

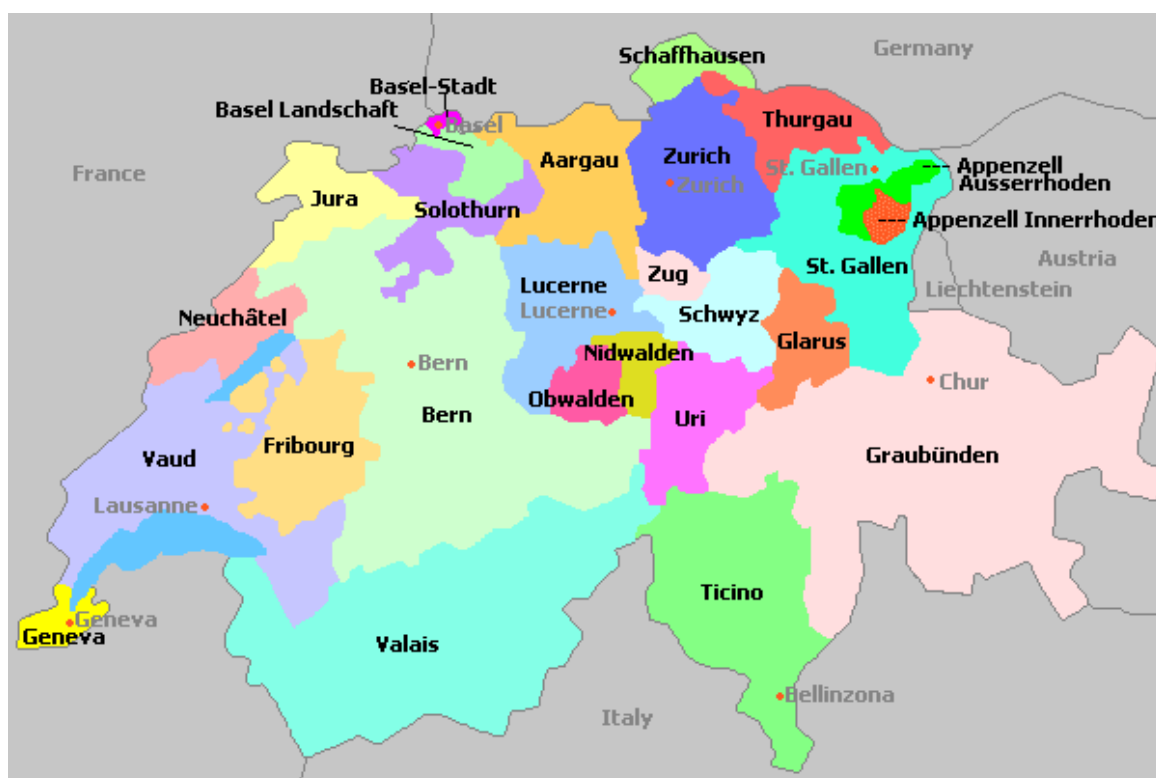
English (Official)

Glassware and Equipment

Item	Quantity
Test tube rack	1
Permanent marker	1
Closed vials with solutions 1–5	5
Closed vials with solutions CH-1, CH-2, CH-3	3
Closed vials with solutions A, B	2
Closed vials with NH_3 , H_2SO_4 , KMnO_4 solutions	3
Closed vial with Zn dust	1
Test tubes	At least 20
Plastic Pasteur pipettes	13
Wash bottle with distilled water	1
Small spatula for Zn dust	1

Switzerland, or officially the Swiss Confederation, is a federal republic consisting of 26 cantons. Interestingly, it does not have an official capital, although the parliament sits in Bern. Despite being a “federal city”, it is not the most populated in Switzerland, the first place belongs to Zurich.

Switzerland has a code **CH**, abbreviated from the Roman name of the region *Confœderatio Helvetica*. You can find “.ch” as a top-level domain for Swiss websites. Also, each of the cantons has a two-letter abbreviation, listed below. They are used, for example, on car license plates.



Preparatory Problems (Practical)



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CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q2-3

English (Official)

Coat of arms	Code	Name	Coat of arms	Code	Name
	ZH	Zurich		SH	Schaffhausen
	BE	Bern		AR	Appenzell Ausserrhoden
	LU	Lucerne		AI	Appenzell Innerrhoden
	UR	Uri		SG	St. Gallen
	SZ	Schwyz		GR	Graubünden
	OW	Obwalden		AG	Aargau
	NW	Nidwalden		TG	Thurgau
	GL	Glarus		TI	Ticino
	ZG	Zug		VD	Vaud
	FR	Fribourg		VS	Valais
	SO	Solothurn		NE	Neuchâtel
	BS	Basel-Stadt		GE	Geneva
	BL	Basel-Landschaft		JU	Jura

Part A

In vials **1–5** there are five colourless solutions of individual ionic compounds. Each compound corresponds to one of Switzerland's cantons by its code: the first letter of the code is the starting letter for the metal cation formula and the second letter of the code is the starting letter for the anion formula. For example, **SH** (Schaffhausen) can correspond to **SrHPO₄** and **BS** (Basel-Stadt) to **BaSO₃**. The solutions **1–5** contain the compounds with the following anions: *formate* (**HCOO⁻**), *hydroxide* (**OH⁻**), *iodide* (**I⁻**), *sulphide* (**S²⁻**) and *tungstate* (**WO₄²⁻**).

*Note: the chemistry of tungsten (W) and titanium (Ti) won't be a part of the practical exam. The tungstate (WO₄²⁻) could have been substituted with phosphate (PO₄³⁻) by your mentors. In this case, proceed as if it would correspond to the second letter **W** in the canton's code.*

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q2-4

English (Official)

- 2.1** For each anion from compounds **1–5**, **specify** possible cation code(s) and water-soluble compounds that could correspond to them. Note that some cation code(s) may have no examples of water-soluble compounds. Do not consider the compounds of *f*-block elements.

Anion	Cation code(s)	Example of the compound
<i>formate</i> (HCOO^-)		
<i>hydroxide</i> (OH^-)		
<i>iodide</i> (I^-)		
<i>sulphide</i> (S^{2-})		
<i>tungstate</i> (WO_4^{2-}) or <i>phosphate</i> (PO_4^{3-} , letter W)		

- 2.2** **Perform** the cross-reactions between solutions **1–5** as well as reactions with NH_3 and H_2SO_4 solutions and **fill in** the following table of observations with the symbols: “↓” for precipitation, “↑” for gas evolution, and “–” if there are no visible observations. Note the colours of precipitates.

Solution	1	2	3	4	5
1					
2					
3					
4					
5					
NH_3					
H_2SO_4					

- 2.3** Based on the observations and above-mentioned information, **identify** the compounds **1–5**.

1	2	3	4	5

Preparatory Problems (Practical)



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Q2-5

English (Official)

- 2.4** Write down the ionic equations of the performed reactions. Use “↓” for precipitates and “↑” for gases.

Combination	Ionic equation(s)
1+2	
1+3	
1+4	
1+5	
2+3	
2+4	
2+5	
3+4	
3+5	
4+5	
1+NH ₃	
1+H ₂ SO ₄	
2+NH ₃	
2+H ₂ SO ₄	
3+NH ₃	
3+H ₂ SO ₄	
4+NH ₃	
4+H ₂ SO ₄	
5+NH ₃	
5+H ₂ SO ₄	

Part B

In vials **CH-1**, **CH-2** and **CH-3** there are three colourless solutions of different formates (HCOO⁻), which correspond to the code for Switzerland **CH** according to the rule described before.

- 2.5** Provide 3 examples of each of the formates that form colourless and coloured solutions. Do not consider the compounds of *f*-block elements.

Colourless			
Coloured			

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q2-6

English (Official)

- 2.6** **Identify** the compounds in test tubes **CH-1**, **CH-2** and **CH-3** by conducting reactions with NH_3 and H_2SO_4 . **Write down** the ionic equations and **specify** the observations: formation of precipitate ($\downarrow$) and its colour, gas evolution ($\uparrow$), or other effects. Use “–” if there are no visible observations.

Vial	Compound	Ionic equation(s) with observations
CH-1		
CH-2		
CH-3		

- 2.7** **Specify** the combination of two anions from compounds **1–5**, which could also be used to identify the cations in **CH-1**, **CH-2** and **CH-3**. **Check** your suggestion, if possible, by performing the reactions with chosen anion. **Write** down the corresponding ionic equations and **specify** the observations: formation of precipitate ($\downarrow$) and its colour, gas evolution ($\uparrow$) or other effects. Use “–” if there are no visible observations.

Chosen anions		
---------------	--	--

Vial	Ionic equation(s) with observations
CH-1	
CH-2	
CH-3	

Part C

In vials **A** and **B** there are two solutions of salts of different shades of blue. Following the rule described above, the formula of each salt corresponds either to the code for Switzerland or cantons.

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q2-7

English (Official)

- 2.8** **Perform** the reactions of **A** and **B** with: a) variable quantities of NH_3 solution; b) Zn with the addition of H_2SO_4 solution. Based on observations, **identify** the cations of given salts and specify possible associated code(s) of cantons or Switzerland. **Write down** the ionic equations of conducted reactions, indicating precipitates ($\downarrow$), gas evolution ($\uparrow$), or other effects, including colour changes.

Vial	Cation	Associated code(s)
A		
B		

Combination	Ionic equation(s)
A+ NH_3	
A+ $\text{Zn}(\text{H}^+)$	
B+ NH_3	
B+ $\text{Zn}(\text{H}^+)$	

- 2.9** **Suggest** the anions in **A** and **B**. **Check** your suggestion by performing the reaction(s) with any reagent or encoded solution. **Write down** the corresponding chemical equations and **specify** the observations: formation of precipitate ($\downarrow$) and its colour, gas evolution ($\uparrow$), or other effects.

Vial	Anion	Reaction equation(s) with observation(s)
A		
B		

- 2.10** *Bonus question:* The complex formed by one of the salts in the excess of ammonia is called Schweizer's reagent. It is named after the Swiss chemist Matthias Eduard Schweizer (1818–1860), who discovered its property to dissolve a common substance. **Choose** the name of this substance:

- ☐ polyethylene
- ☐ proteins
- ☐ fats
- ☐ starch
- ☐ cellulose

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q3-1

English (Official)

A Simple Aldol Condensation

Chemicals:

Chemical	State & Properties	Comment	GHS Statements
Acetone	Liquid, b.p. 56.08 °C, MW 58.08 g/mol, ρ 0.784 g/mL	Flammable	H225, H319, H336; P210, P240, P241, P242, P305+P351+P338
Cinnamaldehyde	Liquid, MW 132.16 g/mol, ρ 1.05 g/mL		H315, H315, H317, H319, H335; P261, P264, P271, P280, P302+P352, P305+P351+P338
Ethanol (EtOH)	Liquid, b.p. 78.2 °C, MW 46.07 g/mol	Flammable	H225, H319; P210, P233, P240, P241, P242, P305, P351+P338
Ethyl acetate (EtOAc)	Liquid, b.p. 77.1 °C, MW 88.11 g/mol	Flammable	H225, H319, H336; P210, P233, P240, P305+P351+P338, P403+P235
Hexane	Liquid, b.p. 68.73 °C, MW 86.18 g/mol	Flammable	H225, H304, H315, H336, H361f, H373, H411; P201, P210, P273, P301+P310, P303+P361+P353, P331
Sodium hydroxide (NaOH)	Solid, MW 40.00 g/mol	Corrosive	H290, H314; P234, P260, P280, P303+P361+P355, P304+P340+P310, P305+P351+P338
Water (de-ionized)	Liquid, b.p. 100 °C, MW 18.02 g/mol		Not a hazardous sub- stance or mixture accord- ing to Regulation (EC) No. 1272/2008

Preparatory Problems (Practical)



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SWITZERLAND 2023

Q3-2

English (Official)

Glassware and Equipment:

Item	Count
Ice-water bath	1
Round-bottom flask, 100 mL	2
Laboratory stand	1
Clamp	3
Cork ring (for round-bottom flasks)	2
Magnetic stir bar	2
Measuring cylinder, 20 mL	2
Measuring cylinder, 50 mL	1
Glass Pasteur pipette	5
Rubber bulb for Pasteur pipette	1
Glass rod	1
Volumetric pipette, 5 mL	1
Volumetric pipette, 1 mL	1
Pipette balloon	1
Magnetic stir bar remover	1
Büchner funnel	1
Filter paper	2
Suction flask with rubber adapter and vacuum hose to vacuum supply	1
Reflux condenser with 2 water hoses for cooling	1
Hotplate with magnetic stirring	1
Water bath	1
TLC chamber	1
Vial for samples	3
TLC capillary	2
TLC plate (ca. 10 cm x 4 cm)	1
Tweezers	1
Pencil	1
Felt pen (waterproof)	1
Ruler	1
Spatula	1
Thermometer	1
UV lamp	1 (shared among students)

Preparatory Problems (Practical)



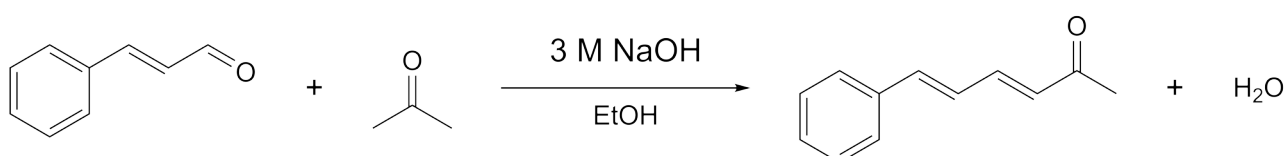
55TH INTERNATIONAL
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SWITZERLAND 2023

Q3-3

English (Official)

Introduction:

Aldol condensations are important reactions in organic chemistry, as they are a reliable tool to form carbon-carbon bonds. The resulting β -hydroxy aldehydes or ketones (aldehyde and alcohol functionalities serve as the reaction's namesakes) and α,β -unsaturated aldehydes or ketones (after elimination of water) are found in many natural products and pharmaceuticals, while also allowing for further transformation to more complex molecules. In this task, you will carry out the aldol condensation of two simple molecules.



Procedure:

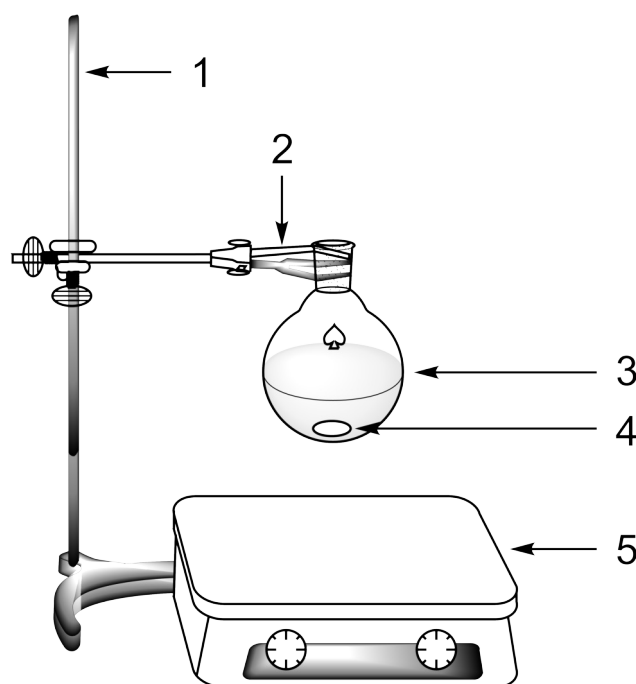


Figure 1: 1 = laboratory stand, 2 = clamp, 3 = round-bottom flask, 4 = magnetic stir bar, 5 = hotplate with magnetic stirring.

1. **Clamp** a 100 mL round-bottom flask to the stand and add a stir bar.
2. In this flask, **dissolve** cinnamaldehyde (1.3 mL) in ethanol (20 mL).
3. **Set aside** a small sample (1 drop) of cinnamaldehyde in a vial for thin layer chromatography (TLC) analysis (to be carried out later).
4. **Cool** the ethanol (EtOH) bottle in an ice-water bath and **store** it in this bath throughout the preparation.

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q3-4

English (Official)

5. While stirring, **add** acetone (0.74 mL) to the cinnamaldehyde solution.
6. **Add** an aqueous NaOH solution (20 mL, 3 M solution) using a measuring cylinder.
7. **Stir** for 20 minutes at room temperature to allow complete precipitation of the product.
8. Meanwhile, **prepare** a mixture of cold ethanol and de-ionized water in a 1:2 ratio (total 50 mL).
9. **Add** this solution to the reaction mixture to stop the reaction.
10. **Stop** the stirring and **remove** the stir bar with the magnetic stir bar remover.
11. **Set up** a vacuum filtration apparatus according to the general procedure given in the Appendix (Section A) and **filter** the crude product.
12. **Wash** the solid collected on the Büchner funnel thoroughly with cold ethanol (ca. 10 mL).
13. **Let** air suck through the precipitate for 3 minutes to dry the product. **Disconnect** the vacuum source. **Use** the spatula to transfer the crude product to a fresh 100 mL round-bottom flask.
14. **Wash** both the suction flask and the Büchner funnel first with ethanol and then with water.
15. **Analyze** the crude product by TLC (thin layer chromatography):
 - (a) **Take** the vial set aside with 1 drop of cinnamaldehyde (see above, step 3) and **prepare** a dilute solution by adding 1 mL of EtOAc. **Prepare** a separate dilute solution of your crude product in another vial (small spatula tip in 1 mL of EtOAc).
 - (b) **Perform** the TLC analysis according to the general scheme provided in the Appendix, section B ("starting material" = cinnamaldehyde), using a mixture of hexane and EtOAc in a 97:3 ratio as the eluent.
 - (c) After developing and drying the TLC plate, **visualize** it under the UV lamp. With a pencil, gently **circle** all the visible spots.

Preparatory Problems (Practical)



55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q3-5

English (Official)

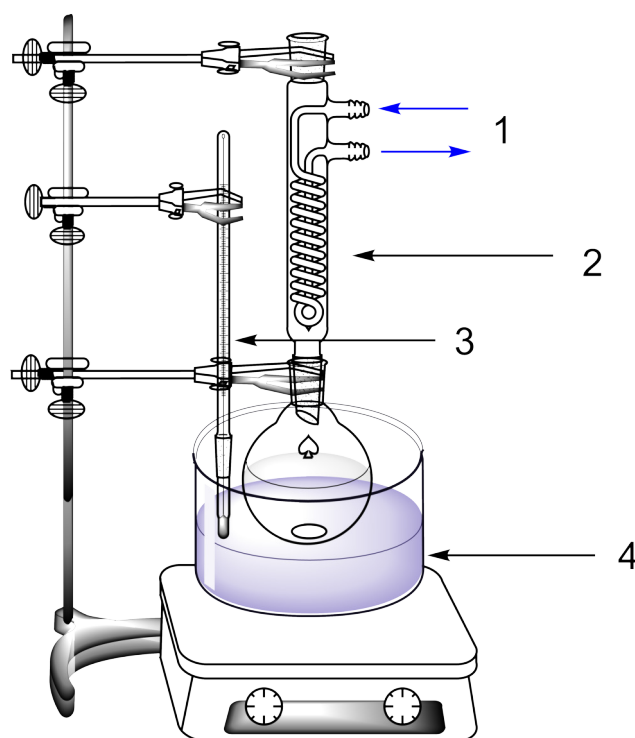


Figure 2: 1 = cooling water, 2 = reflux condenser, 3 = thermometer, 4 = water bath.

16. **Add** ethanol (40 mL) and a stir bar to the flask containing the crude product while stirring.
17. **Attach** a reflux condenser to the round-bottom flask.
18. **Connect** the condenser through hoses to a water source and **turn on** the cooling water.
19. **Heat** the mixture to the boiling point of EtOH (78 °C) using a water bath. **Insert** a thermometer into the water bath to control its temperature.
20. **Continue** the slow addition of EtOH until the solid is completely dissolved (note: dissolving substances may take some time; therefore, add the solvent portionwise and wait until the mixture boils between additions). Once the solid is completely dissolved, slowly add water with a Pasteur pipette until a precipitate starts to appear. Wait between additions of water until the mixture boils again. Once the precipitate persists, add just enough EtOH to dissolve it again (ca. 5 mL). This may take some time.
21. **Turn off** the stirring, **raise** the flask above the water bath by adjusting the position of the clamp, and **turn off** the cooling water.
22. **Let** the flask cool down to room temperature without disturbance. Crystallization of the product should be observed. If not, you may scratch the side of the flask with a glass rod to induce crystallization.
23. After the suspension of crystals has reached room temperature, **remove** the reflux condenser and **place** the flask into an ice-water bath to complete crystallization (make sure to **clamp** the flask to the stand).
24. **Remove** the stir bar with a magnetic stir bar remover.
25. **Filter** the recrystallized product by suction filtration according to the general procedure given in the

Preparatory Problems (Practical)



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Q3-6

English (Official)

Appendix (Section A) and **wash** the crystals collected on the Büchner funnel with a small amount of cold ethanol.

26. **Let** air suck through the crystals for 2-3 minutes. **Disconnect** the vacuum source. **Let** the purified product air-dry for at least 15 minutes.
27. **Repeat** the TLC analysis (as described in step 15) with your recrystallized product.
28. **Transfer** the recrystallized product into a vial with a spatula. **Label** the vial "Final product".

Questions:

1. Based on the TLC analysis of the crude product, were impurities present? **Choose** the correct answer.
☐ yes
☐ no
2. Based on the TLC analysis of the recrystallized product, were impurities present? **Choose** the correct answer.
☐ yes
☐ no
3. **Calculate** the theoretical product yield (mass, in grams) based on the amount of cinnamaldehyde used in the experiment.
4. In the above reaction, 6 equivalents of NaOH have been added in relation to the starting materials cinnamaldehyde and acetone. Would the reaction work, in principle, also with 3 equivalents of NaOH? **Choose** the correct answer.
☐ yes
☐ no
5. In the above aldol condensation, an initial C—C bond-forming step leading to an 'aldol' (i.e. a β -hydroxy ketone) intermediate is followed by an elimination of H₂O, which affords the final (isolated) product. **Draw** the structure of the β -hydroxy ketone intermediate.

Preparatory Problems (Practical)



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Q4-1

English (Official)

Dihydroxylation of Oleic Acid

Chemicals:

Chemical	State & Properties	Comment	GHS Statements
Ethanol (EtOH)	Liquid, b.p. 78.2 °C, MW 46.07 g/mol	Flammable	H225, H319; P210, P233, P240, P241, P242, P305+P351+P338
Ethyl Acetate (EtOAc)	Liquid, b.p. 77.1 °C, MW 88.11 g/mol	Flammable	H225, H319, H336; P210, P233, P240, P305+P351+P338, P403+P235
Hexane	Liquid, b.p. 68.73 °C, MW 86.18 g/mol	Flammable	H225, H304, H315, H336, H361f, H373, H411; P201, P210, P273, P301+P310, P303+P361+P353, P331
Hydrochloric acid (HCl, 6 M in H ₂ O)	Liquid	Corrosive	H290, H314, H335; P260, P280, P303+P361+P353, P305+P351+P338
Oleic Acid (technical, 85%)	Liquid, m. p. 16.3 °C, MW 282.49 g/mol, ρ 0.887 g/mL	Purity and density of commercial oleic acid are variable	Not a hazardous sub- stance or mixture accord- ing to Regulation (EC) No. 1272/2008
Potassium perman- ganate (KMnO ₄)	Solid, MW 158.03 g/mol	Strong oxidizer	H272, H302, H314, H361d, H373, H410; P210, P220, P280, P301+P330+P331, P303+P361+P353, P305+P351+P338, P310
Sodium hydroxide (NaOH)	Solid, MW 40.00 g/mol	Corrosive	H290, H314; P234, P260, P280, P303+P361+P355, P304+P340+P310, P305+P351+P338
Sodium sulfite (Na ₂ SO ₃)	Solid, MW 126.04 g/mol		Not a hazardous sub- stance or mixture accord- ing to Regulation (EC) No. 1272/2008
Water (de-ionized)	Liquid, b.p. 100 °C, MW 18.02 g/mol		Not a hazardous sub- stance or mixture accord- ing to Regulation (EC) No. 1272/2008

Preparatory Problems (Practical)



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Q4-2

English (Official)

Glassware and Equipment:

Item	Count
Ice-water bath	1
Beaker, 500 mL	2
Erlenmeyer flask, 250 mL	1
Volumetric flask, 250 mL	1
Magnetic stir bar	1
Magnetic stir bar remover	1
Hotplate with magnetic stirring	1
Laboratory stand	1
Clamp	1
Measuring cylinder, 50 mL	2
Measuring cylinder, 25 mL	1
Volumetric pipette, 1 mL	1
Pipette balloon	1
Thermometer	1
Glass Pasteur pipette	5
Rubber bulb for Pasteur pipette	1
Spatula	2
Büchner funnel	1
Filter paper	1
Suction flask with rubber adapter and vacuum hose to vacuum supply	1
TLC chamber	1
Vial for samples	3
TLC capillary	2
TLC plate (ca. 10 cm x 4 cm)	1
Weighing paper	2
Tweezers	1
Pencil	1
Felt pen (waterproof)	1
Ruler	1
Heat gun	1 (shared among students)
Weighing balance	1 (shared among students)

Preparatory Problems (Practical)



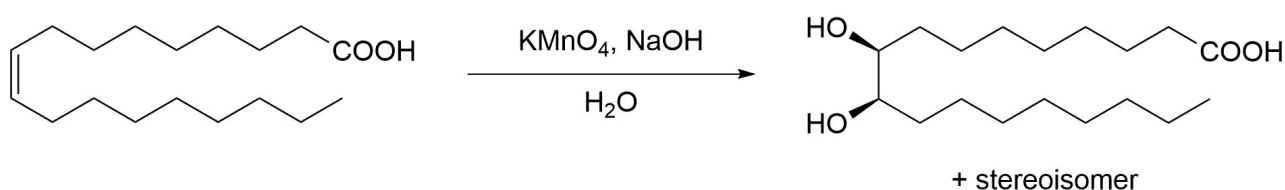
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Q4-3

English (Official)

Introduction:

The catalytic conversion of compounds with full control of installed stereogenic centers is a crucial aspect in synthesis and has already been awarded two Nobel prizes (2001 and 2021). While the full control of absolute stereochemistry can be challenging, the relative configuration of jointly generated stereogenic centers is often a direct result of the underlying reaction mechanism. In this task, you will carry out the *cis*-dihydroxylation of oleic acid.



Scheme 1: *cis*-Dihydroxylation of oleic acid, yielding two stereoisomers.

Procedure:

1. **Set aside** a small sample (1 drop) of oleic acid in a vial for thin layer chromatography (TLC) analysis (to be carried out later).
2. **Take** a 500 mL beaker, **add** 250 mL of water and **cool** it in an ice-water bath.
3. **Take** a second 500 mL beaker (no. 2), **add** a stir bar and **place** the beaker on a hotplate.
4. **Add** water (32 mL) to beaker no. 2.
5. While stirring, **add** NaOH (0.32 g) to beaker no. 2.
6. Then **add** oleic acid (0.37 mL, 85% pure) to beaker no. 2.

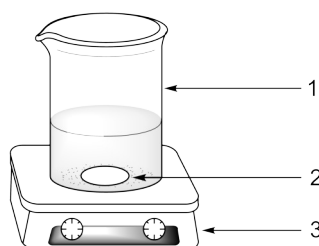


Figure 1: 1 = beaker, 2 = magnetic stir bar, 3 = hotplate with magnetic stirring.

7. Slowly **heat** the mixture until a clear solution is obtained.
8. **Remove** beaker no. 2 from the hotplate and **add** cold water (250 mL) from beaker no. 1.
9. **Measure** the temperature of the solution with a thermometer. If it is $>10\text{ }^{\circ}\text{C}$, **cool** beaker no. 2 to $10\text{ }^{\circ}\text{C}$ using an ice-water bath (**do not** put the ice-water bath onto the stirrer when it is still hot).

Preparatory Problems (Practical)



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Q4-4

English (Official)

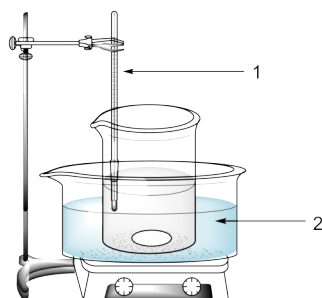


Figure 2: 1 = thermometer, 2 = ice-water bath.

10. While stirring, **add** KMnO_4 (aq) solution (1% KMnO_4 in water, 25 mL) over a period of 1 minute.
11. **Stir** at 10 °C for 5 minutes.
12. **Add** solid sodium sulfite (1.26 g).
13. Carefully **add** 6 M HCl (aq) (19 mL). If the solution is still colored, carefully **continue adding** small portions of 6 M HCl (aq) until the solution turns colorless.
14. **Filter** the colorless, flocculent precipitate by suction filtration according to the general procedure given in the Appendix (Section A) and **wash** it with ice-cold water (20 mL).
15. **Wash** the product collected on the Büchner funnel with hexane (30 mL) and **let** air suck through the solid for 3 minutes to dry it. **Disconnect** the vacuum source.
16. **Perform** a TLC analysis with the dried product:
 - (a) **Take** the vial set aside with a small sample (1 drop) of oleic acid (see above, step 1) and **prepare** a dilute solution by adding EtOAc (1 mL).
 - (b) **Transfer** a small sample (1 small spatula tip) of the product from the Büchner funnel to another vial and **dissolve** it in EtOAc (1 mL).
 - (c) **Perform** the TLC analysis according to the general scheme provided in the Appendix, section B ("starting material" = oleic acid, "product" = product sample collected from the Büchner funnel), using EtOAc as the eluent.
 - (d) After developing and drying the TLC plate, **use** tweezers and briefly **immerse** the plate (with the starting line facing down) into the KMnO_4 staining solution (**caution**: the staining solution is not the same as the KMnO_4 (aq) solution used in step 10 of the reaction). **Stain** the plate up to the eluent front, then **take** it **out** of the staining solution.
 - (e) **Heat** the TLC plate with a heat gun (**caution**: always **point** the heat gun into the fume hood, away from yourself and others, and **remove** flammable objects and compounds beforehand). With a pencil, gently **circle** all the visible spots.
17. **Transfer** the dried product from the Büchner funnel to a vial with a spatula. **Label** the vial "Final Product" with a felt pen.

Preparatory Problems (Practical)



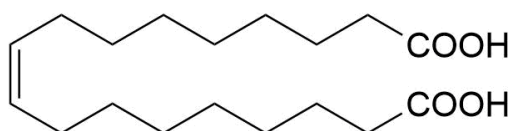
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SWITZERLAND 2023

Q4-5

English (Official)

Questions:

- Based on the TLC analysis of the product, were impurities present? **Choose** the correct answer.
☐ yes
☐ no
- Provide** a reason for the TLC plate being visualized with a staining solution and not under a UV lamp.
- Provide** a reason for the addition of sodium sulfite (Na_2SO_3) in the above procedure.
- In the above reaction, the product is obtained in the form of two stereoisomers. What is their stereochemical relationship? **Choose** the correct answer.
☐ enantiomeric
☐ diastereomeric
- How many stereoisomers are formed in the *cis*-dihydroxylation of the dicarboxylic acid shown below? **Choose** the correct answer.
☐ 1
☐ 2
☐ 4



Preparatory Problems (Practical)



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Q5-1

English (Official)

Synthesis of Lidocaine

Chemicals:

Chemical	State & Properties	Comment	GHS Statements
Diethylamine	Liquid, b.p. 55.5 °C, ρ 0.706 g/mL, MW 73.14 g/mol	Flammable, corro- sive	H225, H302+H332, H311, H314, H335; P210, P280, P301+P312, P303+P361+P353, P304+P340+P310, P305+P351+P338
Ethanol (EtOH)	Liquid, b.p. 78.2 °C, MW 46.07 g/mol	Flammable	H225, H319; P210, P233, P240, P241, P242, P305, P351+P338
Ethyl acetate (EtOAc)	Liquid, b.p. 77.1 °C, MW 88.11 g/mol	Flammable	H225, H319, H336; P210, P233, P240, P305+P351+P338, P403+P235
Hexane	Liquid, b.p. 68.73 °C, MW 86.18 g/mol	Flammable	H225, H304, H315, H336, H361f, H373, H411; P201, P210, P273, P301+P310, P303+P361+P353, P331
Hydrochloric acid (HCl, 3 M in H ₂ O)	Liquid	Corrosive	H290, H314, H335, P260, P280, P303+P361+P353, P305+P351+P338
<i>N</i> -(2,6-Dimethylphenyl)- chloroacetamide	Solid, MW 197.66 g/mol		H315, H319, H335; P261, P264, P271, P280, P302+P352, P305+P351+P338
Sodium hydroxide (NaOH)	Solid, MW 40.00 g/mol	Corrosive	H290, H314; P234, P260, P280, P303+P361+P355, P304+P340+P310, P305+P351+P338
Toluene (PhMe)	Liquid, b.p. 110.6 °C, MW 92.14 g/mol	Flammable	H225, H304, H315, H336, H361d, H373, H412; P202, P210, P273, P301+P310, P303+P361+P353, P331
Water (de-ionized)	Liquid, b.p. 100 °C, MW 18.02 g/mol		Not a hazardous sub- stance or mixture accord- ing to Regulation (EC) No. 1272/2008

Preparatory Problems (Practical)



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Q5-2

English (Official)

Glassware and Equipment:

Item	Count
Round-bottom flask, 50 mL	1
Round-bottom flask, 25 mL	1
Magnetic stir bar	2
Magnetic stir bar remover	1
pH paper	unspecified
Volumetric pipette, 2.5 mL	2
Pipette balloon	1
Measuring cylinder, 15 mL	1
Measuring cylinder, 10 mL	3
Spatula	1
Weighing balance	1 (shared among students)
Weighing paper	1
Reflux condenser with 2 water hoses for cooling	1
Oil bath	1
Thermometer	1
Hotplate with magnetic stirring	1
Laboratory stand	1
Clamp	3
Separatory funnel, 100 mL, with stopper	1
Glass funnel	1
Erlenmeyer flask, 250 mL	2
Glass Pasteur pipette	4
Rubber bulb for Pasteur pipette	1
Büchner funnel	1
Filter paper	1
Suction flask with rubber adapter and vacuum hose to vacuum supply	1
Ice-water bath	1
TLC chamber	1
Vial for samples	4
TLC capillary	2
TLC sheet (ca. 10 cm x 4 cm)	4
Tweezers	1
Pencil	1
Felt pen (waterproof)	1
Ruler	1
UV lamp	1 (shared among students)

Preparatory Problems (Practical)



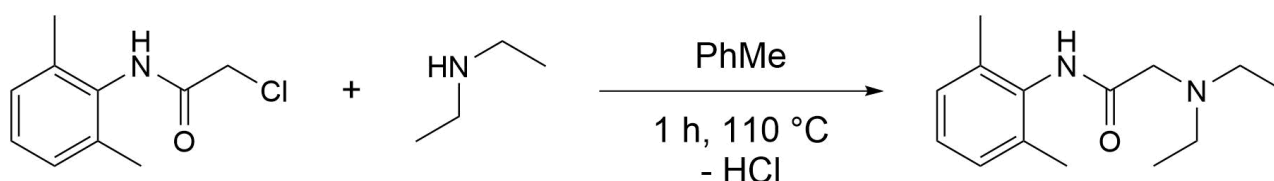
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Q5-3

English (Official)

Introduction:

Lidocaine is a local anesthetic and has been put on the 'List of Essential Medicines' by the World Health Organization. In this task, you will carry out the final step of the synthesis of lidocaine and perform a simple reaction monitoring.



Procedure:

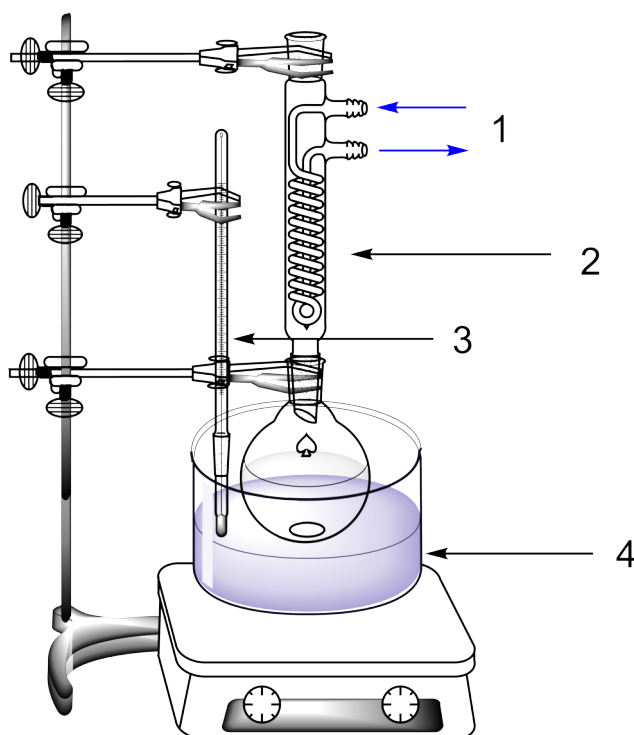


Figure 1: 1 = cooling water, 2 = reflux condenser, 3 = thermometer, 4 = oil bath.

1. **Cool** the ethanol (EtOH) bottle in an ice-water bath and **store** it in this bath throughout the preparation.
2. **Set aside** a small sample (1 small spatula tip) of *N*-(2,6-dimethylphenyl)chloroacetamide in a vial for thin layer chromatography (TLC) analysis (to be carried out later).
3. **Clamp** a 50 mL round-bottom flask to the stand and add a stir bar to the flask.
4. In this flask, **dissolve** diethylamine (2.1 mL) in toluene (13 mL) while stirring. Next, **add** *N*-(2,6-dimethylphenyl)chloroacetamide (1.0 g).

Preparatory Problems (Practical)



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SWITZERLAND 2023

Q5-4

English (Official)

5. **Attach** a reflux condenser to the flask. **Connect** it through hoses to a water source and **turn on** the cooling water.
6. **Place** the flask in an oil bath, **turn on** the hotplate and **heat** the reaction mixture to reflux (ca. 110 °C, check the bath temperature with a thermometer, see **Figure 1**) for 1 h. After that time, **raise** the flask above the oil bath by adjusting the position of the clamp.
7. **Follow** the reaction progress by TLC (thin layer chromatography).
 - (a) **Take** the vial set aside with a small sample (1 small spatula tip) of *N*-(2,6-dimethylphenyl)chloroacetamide (see above, step 2) and **prepare** a dilute solution by adding 1 mL of EtOAc.
 - (b) **Take** a sample of your crude product directly from the reaction mixture: After it has stopped boiling, **lift off** the reflux condenser for a moment, **withdraw** a few drops of the reaction mixture with a Pasteur pipette and **put** them into a fresh vial.
 - (c) **Perform** the TLC analysis according to the general scheme provided in the Appendix, section B ("starting material" = *N*-(2,6-dimethylphenyl)chloroacetamide, "product" = sample withdrawn from reaction mixture), using a mixture of hexane and EtOAc in a 2:1 ratio as the eluent.
 - (d) After developing and drying the TLC plate, **visualize** it under the UV lamp. With a pencil, gently **circle** all the visible spots.
8. If the reaction is complete, **proceed** with step 11. If the reaction is not complete yet, **heat** the reaction mixture to reflux for another 0.5 h.
9. **Perform** another TLC analysis (see step 7) to check for completeness of the reaction.
10. If the reaction is complete, **proceed** with step 11. If the reaction is not complete yet, **heat** the reaction mixture to reflux for another 0.5 h, after which you **perform** another TLC analysis (see step 7).
11. To terminate the reaction, **raise** the flask above the oil bath by adjusting the position of the clamp and **let** the reaction mixture cool to room temperature. Then, **remove** the reflux condenser and **turn off** the cooling water.
12. **Clamp** a 100 mL separatory funnel to the stand and **fit** it with a glass funnel.
13. **Transfer** the reaction mixture to the separatory funnel. **Add** water (20 mL) and **seal** the separatory funnel with a stopper. **Shake** it vigorously for a while, making sure to interrupt shaking and to vent the funnel from time to time, with its spout pointing into the hood. **Stop** shaking, **vent** the funnel one more time and **clamp** it to the stand. **Remove** the stopper and **wait** until the bottom (aqueous) layer separates fully from the top (organic) layer. **Drain** the aqueous layer through the bottom valve into an Erlenmeyer flask (the washing water should not be discarded immediately), and **keep** the top, organic layer in the funnel. **Repeat** this washing of the organic layer with water (20 mL) 3 more times.
14. Then **wash** the organic layer in the separatory funnel with 3 M aqueous hydrochloric acid (7 mL) in the same way as described above. **Make sure** to collect the acidic aqueous extract in a fresh Erlenmeyer flask (no. 2). **Wash** the organic layer once more with water (10 mL) and **drain** the aqueous layer into the same Erlenmeyer flask (no. 2).
15. **Add** a stir bar to the Erlenmeyer flask (no. 2) and **clamp** it to the stand. **Place** an ice-water bath onto the stirrer and **lower** the Erlenmeyer flask into the bath by adjusting the position of the clamp. **Cool** the content of the flask by stirring for 5 minutes before proceeding to the next step.
16. While stirring, slowly **add** sodium hydroxide (3 M solution of NaOH in water) dropwise with a Pasteur pipette until the first indication of a precipitate appears. **Make sure** to keep the temperature of the solution low during the entire addition. **Interrupt** the addition of NaOH (aq) at regular intervals to

Preparatory Problems (Practical)



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Q5-5

English (Official)

check the pH of the solution, which should be adjusted to ca. 10 using pH paper strips. To do so, **use** a separate Pasteur pipette to take a small aliquot of the solution and **drip** it onto a strip, **do not dip** the strips directly into the aqueous solution. At pH 10, the product separates as a granular white solid, which is isolated by vacuum filtration.

17. **Remove** the stir bar with a magnetic stir bar remover.
18. **Filter** the solid by suction filtration according to the general procedure given in the Appendix (Section A), and **wash** the product collected on the Büchner funnel with 10 mL of an ice-cold 1:1 mixture of water and ethanol.
19. **Let** air suck through the filtered product for 2-3 minutes. **Disconnect** the vacuum source. **Let** the product air-dry for at least 15 minutes.
20. **Repeat** the TLC analysis (see step 7) with the dried product.
21. **Transfer** the product into a vial with a spatula. **Label** the vial "Final product".

Questions:

1. Has the reaction run to completeness after 1.0 h? **Choose** the correct answer.
☐ yes
☐ no
2. Has the reaction run to completeness after 1.5 h (if applicable)? **Choose** the correct answer.
☐ yes
☐ no
3. Has the reaction run to completeness after 2.0 h (if applicable)? **Choose** the correct answer.
☐ yes
☐ no
4. **Provide** a reason why the reaction mixture is washed multiple times with pure water after completion of the reaction.
5. In the above procedure, an excess of diethylamine is used in relation to *N*-(2,6-dimethylphenyl)-chloroacetamide.
 - (a) **Calculate** the number of equivalents of diethylamine used in relation to *N*-(2,6-dimethylphenyl)-chloroacetamide.
 - (b) **Provide** a reason why an excess of diethylamine (in relation to *N*-(2,6-dimethylphenyl)-chloroacetamide) is necessary in this reaction to obtain a good product yield.
6. After the reaction, when the organic layer is washed with 3 M aqueous hydrochloric acid in the separatory funnel, the product molecule (lidocaine) is protonated by HCl. **Draw** the structure of the resulting salt (protonated lidocaine molecule and counter-ion).

Preparatory Problems (Practical)



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Q6-1

English (Official)

Transformation of Vanillin to Vanillyl Alcohol

Chemicals

Preparatory Problems (Practical)



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SWITZERLAND 2023

Q6-2

English (Official)

Chemical	Sate & Properties	Comment	GHS Statements
Diethyl ether (Et ₂ O)	Liquid, b.p. 34.6 °C, MW 74.12 g/mol	Flammable	H224, H302, H336; P210, P233, P240, P241, P242, P243, P261, P264, P270, P271, P280, P301+P312, P303+P361+P353, P304+P340, P312, P330, P370+P378, P403+P233, P403+P235, P405, P501
Ethanol (EtOH)	Liquid, b.p. 78.2 °C, MW 46.07 g/mol	Flammable	H225, H319; P210, P233, P240, P241, P242, P305, P351+P338
Ethyl acetate (EtOAc)	Liquid, b.p. 77.1 °C, MW 88.11 g/mol	Flammable	H225, H319, H336; P210, P233, P240, P305+P351+P338, P403+P235
Hexane	Liquid, b.p. 68.73 °C, MW 86.18 g/mol	Flammable	H225, H304, H315, H336, H361f, H373, H411; P201, P210, P273, P301+P310, P303+P361+P353, P331
Hydrochloric acid (HCl, 6 M in H ₂ O)	Liquid	Corrosive	H290, H314, H335; P260, P280, P303+P361+P353, P305+P351+P338
Magnesium sulfate (MgSO ₄)	Solid	Hygroscopic	Not a hazardous substance or mixture according to Regulation (EC) No. 1221/2021
Sodium borohydride (NaBH ₄)	Solid, MW 37.84 g/mol	Flammable, corrosive	H260, H301, H311, H314; P223, P231, P232, P280, P301+P310, P370+P378, P422
Sodium chloride (saturated solution of NaCl in water)	Liquid		Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008
Sodium hydroxide (NaOH)	Solid, MW 40.00 g/mol	Corrosive	H290, H314; P234, P260, P280, P303+P361+P355, P304+P340+P310, P305+P351+P338
Vanillin	Solid, MW 152.15 g/mol		H302, H317, H319; P280, P305+P351+P338
Water (deionized)	Liquid, b.p. 100 °C, MW 18.02 g/mol		Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008

Preparatory Problems (Practical)



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Q6-3

English (Official)

Glassware and Equipment

Item	Count
Separatory funnel, 100 mL, with stopper	1
Round-bottom flask, 50 mL	1
Round bottom flask, 100 mL	1
Magnetic stir bar	2
Magnetic stir bar remover	1
pH paper	unspecified
Glass funnel	2
Cotton plug	2
Measuring cylinder, 10 mL	3
Spatula	3
Weighing balance	1 (shared among students)
Weighing paper	2
Beaker, 25 mL	1
Hotplate with magnetic stirring	1
Laboratory stand	1
Clamp	1
Cork ring (for 50 mL round-bottom flask)	1
Glass Pasteur pipette	4
Rubber bulb for Pasteur pipette	1
Büchner funnel	1
Filter paper	1
Suction flask with rubber adapter and vacuum hose to vacuum supply	1
Ice-water bath	1
TLC chamber	1
Vial for samples	3
TLC capillary	2
TLC sheet (ca. 10 cm x 4 cm)	1
Tweezers	1
Pencil	1
Felt pen (waterproof)	1
Ruler	1
UV lamp	1 (shared among students)

Preparatory Problems (Practical)



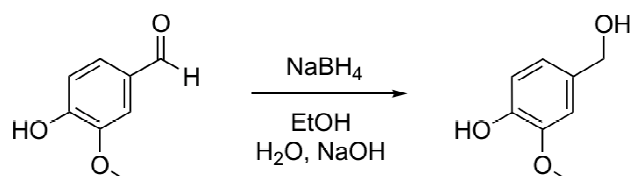
55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Q6-4

English (Official)

Introduction:

The flavoring agent vanillin is found in the capsule fruits of spice vanilla (*Vanilla planifolia*), an orchid plant in which vanillyl alcohol, the product of the present reaction, occurs as well. In this task, you will use sodium borohydride to convert the aldehyde function of vanillin into an alcohol function.



Preparation:

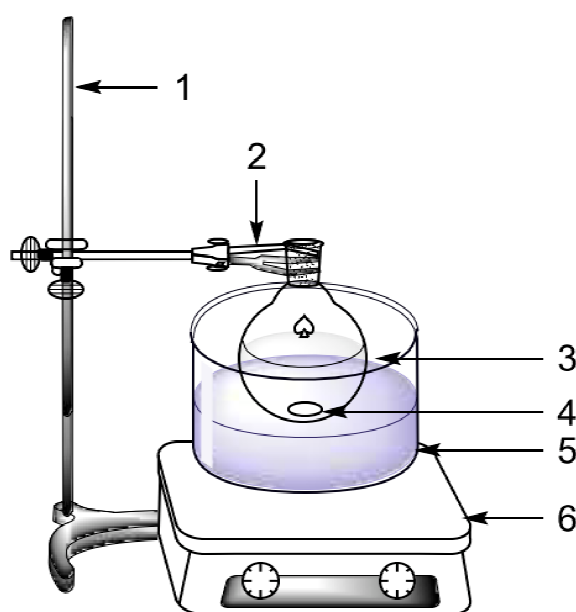


Figure 1: 1 = laboratory stand, 2 = clamp, 3 = round-bottom flask, 4 = stir bar, 5 = ice-water bath, 6 = hotplate with magnetic stirring.

1. **Set aside** a small sample (1 small spatula tip) of vanillin in a vial for thin layer chromatography (TLC) analysis (to be carried out later).
2. **Clamp** a 50 mL round-bottom flask to the stand and **add** a stir bar to the flask.
3. **Add** vanillin (2.0 g) to the round-bottom flask, then **add** ethanol (8 mL).
4. **Stir** the mixture until vanillin has completely dissolved. This may take several minutes.
5. **Raise** the flask by adjusting the position of the clamp, **put** an ice-water bath underneath and **cool** the solution by lowering the flask into the bath (**adjust** the position of the clamp).
6. **Take** a 25 mL beaker and **add** 4 mL of an aqueous NaOH solution (1 M) with a Pasteur pipette.

Preparatory Problems (Practical)



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Q6-5

English (Official)

7. **Add** NaBH_4 (0.5 g) and **dissolve** it by gentle agitation of the beaker.
8. Using a Pasteur pipette, **add** the NaBH_4 solution dropwise to the vanillin solution over a period of 10 minutes.
9. **Remove** the ice-water bath from the reaction flask and **stir** the reaction mixture for 10 minutes.
10. **Put back** the ice-water bath and **cool** the reaction mixture again.
11. While stirring, **add** hydrochloric acid (6 M aq) dropwise with a Pasteur pipette until the evolution of gas stops (ca. 5 mL).
12. **Withdraw** a tiny sample of the mixture with a Pasteur pipette and **drip** a drop onto a pH paper strip to check the pH range. If the mixture is acidic ($\text{pH} < 7$), **stop** adding HCl. If it is still basic, **continue** adding HCl until the mixture is slightly acidic.
13. **Add** distilled water (20 mL) to the mixture and stir for 1 minute.
14. **Clamp** a 100 mL separatory funnel to the stand and **fit** it with a glass funnel. **Put** a small plug of adsorbent cotton into the narrow part of the funnel.
15. **Pour** the reaction mixture into the funnel, thereby filtering it through the cotton plug into the separatory funnel.
16. **Rinse** the round-bottom flask with EtOAc (20 mL) and **flush** the rinsing solvent into the funnel as well.
17. **Seal** the separatory funnel with a stopper and **shake** it vigorously for a while. **Make sure** to interrupt shaking and to vent the funnel from time to time, with its spout pointing into the hood.
18. **Stop** shaking, **vent** the funnel one more time and **clamp** it to the stand. **Remove** the stopper and **let** the layers separate. This may take some time.
19. **Drain** the lower (aqueous) layer into the used round-bottom flask and **pour** the organic layer (EtOAc) into a 50 mL beaker.
20. **Repeat** steps 15-19 twice, using 5 mL of EtOAc each time (instead of the initial 20 mL).
21. **Pour** the combined EtOAc extracts back into the separatory funnel and **add** a saturated aqueous solution of NaCl (20 mL). **Repeat** steps 17-19, then **proceed** with step 22.
22. **Add** 2-3 spatula tips of MgSO_4 to the beaker with the combined EtOAc extracts containing the product. **Add** a stir bar and stir the suspension for 5 minutes. Then **remove** the stir bar with a magnetic stir bar remover.
23. **Clamp** a 100 mL round-bottom flask to the stand and **fit** it with a fresh glass funnel. **Put** a small plug of adsorbent cotton into the narrow part of the funnel.
24. **Filter** the solution of the product in EtOAc into the round-bottom flask. Rinse the beaker with EtOAc (5 mL) and **flush** the rinsing solvent into the funnel as well.
25. **Distil off** the solvents (EtOAc and EtOH) using a rotary evaporator or a simple distillation apparatus.
26. After the solvents have been evaporated, **place** the round-bottom flask containing the crude product in an ice-water bath until it crystallizes.
27. **Add** 5 mL of diethyl ether (Et_2O) to the crystallized product and **triturate** it well with a spatula. **Filter** the product by suction filtration according to the general procedure given in the Appendix (Section A).
28. **Wash** the product collected on the Büchner funnel three times with Et_2O (3 x 5 mL) and **let** air suck through the solid for 2-3 minutes to dry it. **Disconnect** the vacuum source.

Preparatory Problems (Practical)



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29. **Perform** a TLC analysis with the dried product:
- (a) **Take** the vial set aside with a small sample (1 small spatula tip) of vanillin (see above, step 1) and **prepare** a dilute solution by adding EtOAc (1 mL).
 - (b) **Transfer** a small sample (1 small spatula tip) of the product from the Büchner funnel to another vial and **dissolve** it in EtOAc (1 mL).
 - (c) **Perform** the TLC analysis according to the general scheme provided in the Appendix, section B ("starting material" = vanillin, "product" = product sample collected from the Büchner funnel), using a mixture of hexane and EtOAc in a 2:1 ratio as the eluent.
 - (d) After developing and drying the TLC plate, **visualize** it under the UV lamp. With a pencil, gently **circle** all the visible spots.
30. **Transfer** the dried product from the Büchner funnel to a vial with a spatula. **Label** the vial "Final Product" with a felt pen.

Questions:

1. Based on the TLC analysis of the product, were impurities present? **Choose** the correct answer.
☐ yes
☐ no
2. In the above experiment, is vanillin oxidized, reduced, or not subject to a redox reaction? **Choose** the correct answer.
☐ oxidized
☐ reduced
☐ not a redox reaction
3. After the completion of the reaction, HCl (aq) is added, resulting in gas evolution. **Provide** the molecular formula of the gas that is formed.
4. In the above procedure, equimolar amounts of vanillin and NaBH₄ were used. If only 0.5 equivalent of NaBH₄ was used in relation to vanillin, could the reaction still come to completion? **Choose** the correct answer.
☐ yes
☐ no

Preparatory Problems (Practical)



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Q7-1

English (Official)

Colourful Copper

Chemicals:

Chemical	State	Comment	GHS Hazard Statements
Solid X	Solid	An anhydrous inorganic Cu(II) salt	H302-H312, H315, H318, H410; P264, P273, P280, P301+P3012, P320+P352+P312, P305+P315+P338
1.0 M NH ₃ solution	Liquid		H314, H318, H410; P264, P273, P280, P302+P352, P305+P351+P338, P332+P313
K ₂ C ₂ O ₄ ·H ₂ O	Solid		H302+H312, H319; P264, P270, P280, P301+P312, P302+P352+P312, P305+P351+P338
Acetylacetone	Liquid	Flammable	H226, H302, H311+H331; P210, P233, P280, P301+P312, P303+P361+P353, P304+P340+P311
2.0 M AcOH solution	Liquid		H315, H319; P264, P280, P302+P352, P305+P351+P338
Salicylaldoxime	Solid		H302, H315, H319, H335; P301+P312+P330, P302+P352, P305+P351+P338
0.010 M EDTA standard solution	Liquid		H332, H373, H412; P260, P271, P273, P304+P340+P312, P314, P501
1.0 M NH ₄ Cl solution	Liquid		H302, H319; P264, P270, P280, P301+P312, P305+P351+P338, P337+P313
Murexide (1 wt% in NaCl)	Solid		Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.
De-ionised water	Liquid		Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.

Preparatory Problems (Practical)



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Q7-2

English (Official)

Glassware and Equipment:

Item	Count
Beaker, 25 mL	1
Beaker, 50 mL	1
Stir bar	1
Spatula	1
Weighing paper	2
Plastic pipette	3
Graduated cylinder, 10 mL	1
Watch glass	1
Hotplate with magnetic stirrer	1
Ice bath	1
Glass rod	1
Syringe, 1 mL	1
Fritted glass funnel	1
Suction flask with rubber adapter	1
Volumetric flask, 500 mL	1
Erlenmeyer flask, 250 mL	3
Burette, 25 mL	1
Laboratory stand with burette holder	1
Funnel, fitting the burette	1
Volumetric pipette, 25.00 mL	1
Pipette bulb	1
H ₂ O wash bottle	1
pH-indicator strip	1
Oven	1 (shared among students)
Balance	1 (shared among students)

Introduction:

Copper, usually with an oxidation state of +1 or +2, can form a variety of colourful compounds. These complexes catalyse numerous reactions both in chemical and biological processes. In this experiment, the metal content of an anhydrous inorganic Cu(II) salt **X** will be identified by two methods and a series of Cu(II) complexes will be prepared. Since it is possible to perform the preparations of these complexes in a one-pot procedure, only a minimal amount of the copper salt is needed.

Procedure:

I. Preparation of complexes A and B:

- In a 25 mL beaker, **add** approximately 225 mg **X** with a spatula and **add** a stir bar. **Record** the exact weight m_{prep} below.
- Add** 2.0 mL of de-ionised water with a graduated cylinder. **Start** stirring.

Preparatory Problems (Practical)



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English (Official)

3. Once completely dissolved, **report** the colour of the formed complex **A** in the table in section VI.
4. **Add** 8.0 mL of 1.0 M NH_3 solution with a graduated cylinder while stirring. A clear solution of a new colour is obtained. If necessary, **add** a few more drops of 1.0 M NH_3 solution with a plastic pipette.
5. **Report** the colour of the formed complex **B** in the table in section VI.

Sample mass, m_{prep} / mg	
-------------------------------------	--

II. Preparation of complex C:

1. **Add** 650 mg $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ with a weighing paper while stirring.
2. **Cover** the beaker with a watch glass.
3. **Set** the hotplate to 120 °C and **start** heating.
4. **Boil** the mixture for 1 min while stirring.
5. **Stop** stirring and heating. **Let** the mixture cool to room temperature.
6. **Place** the beaker in an ice bath for 30 min. If necessary, **use** a glass rod to induce crystallization.
7. **Report** the colour of the formed solid complex **C** in the table in section VI.

III. Preparation of complex D:

1. **Let** the mixture warm to room temperature.
2. **Add** 470 μL acetylacetone with a 1 mL syringe to the beaker while stirring on the cooled hotplate.
3. **Keep** stirring for 10 min.
4. **Report** the colour of the formed solid complex **D** in the table in section VI.

IV. Preparation and isolation of complex E:

1. **Add** 15 mL of 2 M AcOH with a graduated cylinder to the beaker while stirring. The pH value should be between 3 and 5. **Check** the pH of your solution with a pH-indicator strip and **add** more AcOH with a plastic pipette as necessary.
2. **Add** 700 mg salicylaldehyde with a weighing paper to the beaker while stirring.
3. **Keep** stirring for 30 min.
4. **Report** the colour of the formed solid complex **E** in the table section VI.
5. **Tare** a fritted glass funnel. **Report** its exact weight m_{tared} below.
6. **Pour** the suspension into the funnel mounted on a suction flask with a rubber adapter and **apply** vacuum.
7. **Rinse** the beaker with de-ionised water to transfer all of the solid to the funnel.
8. **Wash** your solid with at least 3x10 mL de-ionised water. **Dry** your solid on the funnel by letting air suck through the funnel. **Turn** off the vacuum when done drying on the funnel.
9. **Dry** your solid further in an oven at 100 °C for 2 h or until its weight remains constant.
10. **Report** the final weight m_{total} of your fritted glass funnel with your solid and **calculate** the exact mass m_{isol} of your isolated solid below.

Preparatory Problems (Practical)



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Q7-4

English (Official)

Item	Weight / mg
Fritted glass funnel, m_{tared}	
Fritted glass funnel with solid E , m_{total}	
Solid E , m_{isol}	

V. Titration of X:

- In a 500 mL volumetric flask, **add** approximately 100 mg **X**. **Record** the exact weight m_{titr} below.
- Dissolve** the compound in de-ionised water and **bring** the solution to the mark with de-ionised water.
- Fill** your burette with 0.010 M EDTA standard solution using a funnel and a 50 mL beaker.
- In a 250 mL Erlenmeyer flask, **add** 50.00 mL of your sample solution containing **X** with a volumetric pipette, 10.0 mL of 1.0 M NH_4Cl solution with a graduated cylinder, a drop of 1.0 M NH_3 solution with a plastic pipette, and a small amount of murexide with a spatula to obtain a yellow solution.
- Titrate** the solution while swirling constantly. The equivalence point is reached when the colour has changed to violet. **Record** your titration volume V_{titr} .
- Repeat** the titration (steps 3-6) as necessary.

Sample mass, m_{titr} / mg	
------------------------------	--

Analysis No.	V_{titr} / mL
1	
2	
3	
Reported value V_{titr} / mL	

VI. Questions:

Complex	A	B	C	D	E
Colour					
Molecular formula	$[\text{CuH}_{12}\text{O}_6]^{2+}$	$[\text{CuH}_{16}\text{N}_4\text{O}_2]^{2+}$	$\text{K}_2[\text{CuC}_4\text{H}_4\text{O}_{10}]$	$[\text{CuC}_{10}\text{H}_{18}\text{O}_6]$	$[\text{CuC}_{14}\text{H}_{12}\text{N}_2\text{O}_4]$

The structures of the organic ligands used in the syntheses are shown in their protonated form below:

Preparatory Problems (Practical)



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Q7-5

English (Official)

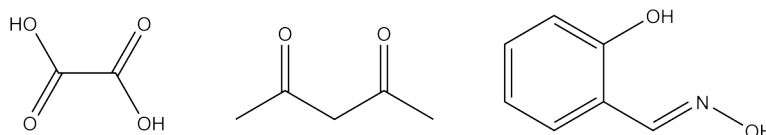


Figure 1, from left to right: Structures of oxalic acid ($C_2H_2O_4$), acetylacetonate ($C_5H_8O_2$), and salicylaldehyde oxime ($C_7H_7NO_2$).

7.1 Draw the structures of complexes **A** – **E**.

7.2 What happens during the preparation of **B** from **A**? Choose the correct answer.

- ☐ Precipitation of $Cu(OH)_2$
- ☐ Reduction of $Cu(II)$ to insoluble $Cu(0)$
- ☐ Precipitation of the anion from **X** upon reaction with NH_3

7.3 Based on your solid **E**, calculate the metal content of **X**.

7.4 Based on your titrations, calculate the metal content of **X**.

7.5 Write the chemical formula of **X**. The solid has a theoretical metal content of 47.3%.

7.6 Which method gave the more accurate result? Choose the correct answer.

- ☐ Gravimetry
- ☐ Titration

Preparatory Problems (Practical)



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SWITZERLAND 2023

Q8-1

English (Official)

Hard Water – Easy Titrations

Chemicals:

Chemical	State	Comment	GHS Hazard Statements
Water Sample W	Liquid	Containing Ca^{2+} , Mg^{2+} , HCO_3^- , and Cl^- In volumetric flask, 500 mL	H319; P264, P280, P305+P351+P338, P337+P313
0.010 M HCl standard solution	Liquid	In bottle, 100 mL	Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.
1.0 M HCl solution	Liquid	Corrosive In bottle, 50 mL	H290; P234, P390
Methyl orange solution (10 g/L in EtOH)	Liquid	Flammable In vial, 10 mL	H225, H301, H319; P210, P233, P240, P241, P242, P264, P270, P301+P310, P305+P351+P338, P405, P501
0.010 M EDTA standard solution		In bottle, 200 mL	H332, H373, H412; P260, P271, P273, P304+P340+P312, P314, P501
1.0 M NaOH	Liquid	Corrosive In bottle, 50 mL	H290; P234, P390
Buffer solution (pH = 10, $c_{\text{HB}^+} + c_{\text{B}} = 8.8 \text{ M}$)	Liquid	Containing NH_4Cl and NH_3 In bottle, 50 mL	H302, H314, H319, H335, H410; P261, P264, P270, P271, P273, P280, P303+P361+P353, P305+P351+P338, P310+P312, P337+P313
Eriochrome [®] Black T (1 wt% in NaCl)	Solid	In vial, 10 mL	H319, H441; P264, P273, P280, P305+P351+P338, P337+P313, P391
Murexide (1 wt% in NaCl)	Solid	In vial, 10 mL	Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.

Preparatory Problems (Practical)



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Q8-2

English (Official)

Item	Count
Beaker, 50 mL	1
pH-indicator strips	10
Burette, 25 mL	1
Laboratory stand with burette holder	1
Funnel, fitting the burette	1
Erlenmeyer flask, 250 mL	3
Volumetric pipette, 25.00 mL	1
Pipette bulb	1
Plastic pipette	3
Hotplate	1
Thermometer	1
Spatula	1
H ₂ O wash bottle	1

Introduction:

The drinking water in Switzerland meets high standards and is regularly analysed by authorities. All tap water in Switzerland is therefore drinkable and it has a better ecological balance than bottled water.

With the largest part of Swiss drinking water coming from Alpine rivers and lakes, it contains a variety of dissolved salts. Thereof, Ca²⁺ and Mg²⁺ are the most prevalent cations. While they are non-toxic to humans, they can cause problems to infrastructures by precipitation as hydroxides or carbonates. As such, it is meaningful to monitor the total hardness (i.e. the sum of the molar concentration of Ca²⁺ and Mg²⁺) and the carbonate hardness (i.e. the fraction of Ca²⁺ and Mg²⁺ balanced by HCO₃⁻ and CO₃²⁻) of tap water.

The analysis of water hardness by titration has been among the first complexometric titrations and has been well-established by Swiss chemist and former ETH Prof. G. Schwarzenbach (1904 – 1978). In this task, you will analyse a simulated water sample as if you would take it directly from a tap in Zurich.

Procedure:

I. Determination of Carbonate Hardness

1. You are given a sample of 500 mL “Zurich tap water”, labelled as **W**. Keep it well closed and perform this analysis as quickly as possible to avoid CO₂ absorption from the air!
2. In a 50 mL beaker, **check** the pH of **W** with a pH-indicator strip.
3. **Fill** a 25 mL burette with 0.010 M HCl standard solution using a funnel and a 50 mL beaker.
4. In a 250 mL Erlenmeyer flask, **add** 50.00 mL of **W** with a volumetric pipette and a few drops of methyl orange with a plastic pipette.
5. **Titrate** the solution while swirling constantly. At the equivalence point, the colour will change from yellow to orange. **Record** the titration volume V_1 .
6. **Repeat** the titration (steps 3-5) as needed.

Preparatory Problems (Practical)



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Q8-3

English (Official)

Analysis No.	V_1 / mL
1	
2	
3	
Reported Value V_1 / mL	

II. Determination of Total Calcium and Magnesium Content:

1. **Fill** a 25 mL burette with 0.010 M EDTA standard solution using a funnel and a 50 mL beaker.
2. In a 250 mL Erlenmeyer flask, **add** 50.00 mL of **W** with a volumetric pipette and 3.0 mL of 1.0 M HCl solution with a plastic pipette.
3. On a hotplate set to 90°C, **heat** the solution for 10 min.
4. **Let** the solution cool to room temperature. **Neutralize** the solution with approximately 3.0 mL of 1.0 M NaOH solution with a plastic pipette. **Add** the last few drops slowly and, intermittently, **check** the pH of your solution with a pH-indicator strip until pH = 7 is reached.
5. **Add** 1.0 mL of pH buffer with a plastic pipette and a small amount of Eriochrome® Black T with a spatula.
6. **Titrate** the solution while swirling constantly. A colour change from red to blue occurs. The equivalence point is reached when the last hue of red disappears. **Record** the titration volume V_2 .
7. **Repeat** the titration (steps 1-6) as needed.

Analysis No.	V_2 / mL
1	
2	
3	
Reported value V_2 / mL	

III. Determination of Calcium Content:

1. **Fill** a 25 mL burette with 0.010 M EDTA standard solution using a funnel and a 50 mL beaker.
2. In a 250 mL Erlenmeyer flask, **add** 50.00 mL of **W** with a volumetric pipette and 5.0 mL of 1.0 M NaOH solution with a plastic pipette. Perform the following steps quickly to avoid the precipitation of magnesium salts.
3. **Check** the pH of the solution with a pH-indicator strip. If the pH is below 12, **add** 1.0 M NaOH dropwise until pH $\geq$ 12.
4. **Add** a small amount of murexide with a spatula.

Preparatory Problems (Practical)



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Q8-4

English (Official)

5. **Titrate** the solution while swirling constantly. A colour change from red to violet occurs. The equivalence point is reached when the last hue of red will disappear. **Record** the titration volume V_3 .
6. **Repeat** the titration (steps 1-5) as needed.

Analysis No.	V_3 / mL
1	
2	
3	
Reported value V_3 / mL	

Questions:

8.1 **Write** the balanced chemical equation for the titration in part I. The $pK_{a,1}$ and $pK_{a,2}$ values of carbonic acid (H_2CO_3) are 3.5 and 10.5, respectively.

8.2 **Calculate** the carbonate hardness of **W** in mM.

8.3 **Calculate** the total hardness of **W** in mM.

8.4 **Calculate** the ratio of Ca^{2+} to Mg^{2+} in **W**.

8.5 How could the total hardness be lowered? **Choose** the correct answer(s).

- ☐ Addition of $Ca(OH)_2$
- ☐ Pass through ion exchange resin (NaCl-regenerated)
- ☐ Application of magnetic field
- ☐ Addition of HCl
- ☐ Boiling

Appendix

A. Vacuum Filtration

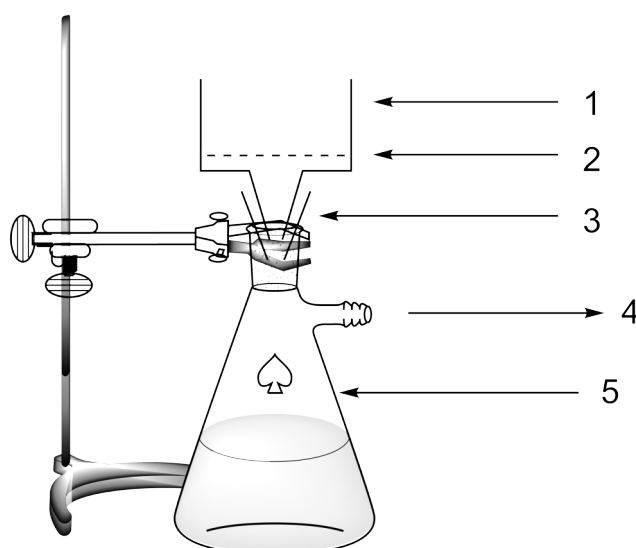


Figure 1: 1 = Büchner funnel, 2 = filter paper, 3 = rubber adapter, 4 = towards vacuum, 5 = suction flask.

Procedure:

1. **Set up** a vacuum filtration apparatus using a Büchner funnel, a filter paper, and a suction flask which is secured to the laboratory stand with a clamp (see Figure).
2. **Connect** the suction flask with a vacuum hose to the vacuum source.
3. **Wet** the filter paper with an appropriate solvent (typically the solvent containing the suspension to be filtered) and ensure that it covers all the holes of the Büchner funnel.
4. **Apply** vacuum and **pour** the suspension of the solid to be filtered into the Büchner funnel.
5. **Close** the vacuum when done.

B. Thin Layer Chromatography (TLC) Analysis

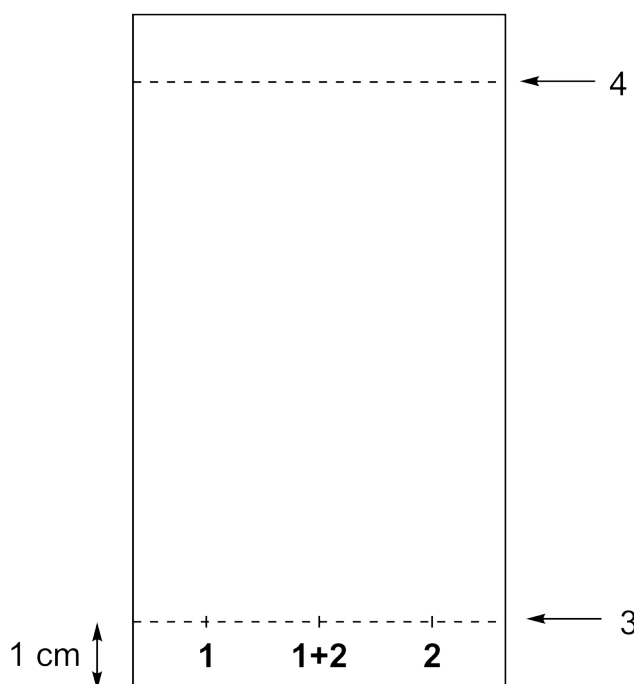


Figure 2: 1 = starting material, 2 = product, 1+2 = co-spot of both the starting material and the product, 3 = starting line, 4 = eluent front.

1. **Prepare** the elution chamber: **Load** it to a height of ca. 0.5 cm with the eluent and **cover** it with a lid.
2. With a pencil, gently **draw** the starting line ca. 1 cm above the bottom of the plate.
3. **Spot** the TLC plate on the starting line with your starting material (left), product (right) and co-spot of both (center) (see Figure).
4. **Develop** the TLC plate: Using tweezers, **insert** the TLC plate into the elution chamber and **cover** it with the lid. Let the eluent reach approximately 1 cm below the top of the plate. Using tweezers, **remove** the plate from the chamber, **mark** the eluent front gently with a pencil and **let** the plate air-dry.



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Solutions Preparatory Problems

Finding Solutions

2023-06-02, Version 3



Solution: The Sun-to-Fuel Project

1.1.

$$M_{CeO_2} = 172.12 \text{ g/mol}$$

Thus:

$$O_2 \text{ release} = 0.0117 \text{ mol mol}_{CeO_2}^{-1}$$

$$H_2 \text{ production} = 0.0158 \text{ mol mol}_{CeO_2}^{-1}$$

$$CO \text{ production} = 0.0067 \text{ mol mol}_{CeO_2}^{-1}$$

The amount of syngas produced equals the amount of "O" released within the margin of error and δ is calculated to be:

$$\delta = 2 * (O_2 \text{ release}) = 0.0234$$

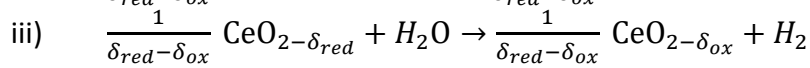
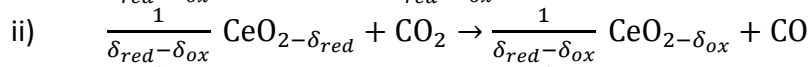
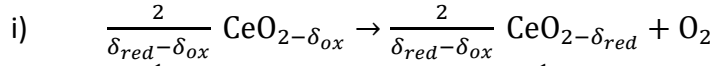
1.2.

Based on the oxygen balance, α can be determined:

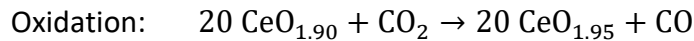
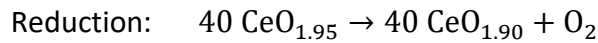
$$2 - \delta_{ox} = 2 - \delta_{red} + 2 * \alpha$$

$$\alpha = \frac{\delta_{red} - \delta_{ox}}{2}$$

Thus:



To help understand this equation, assume $\delta_{ox} = 0.05$ and $\delta_{red} = 0.10$. Then:



1.3.

α increases with increasing temperature and with decreasing O_2 partial pressure during the reduction process. High temperature and low O_2 partial pressure are the most suitable conditions.

1.4.

$$2 \alpha_{1773} = \exp \left(-0.2231 \log \left(\frac{0.1 \cdot 10^{-3} \text{ bar}}{1 \text{ bar}} \right) - 2.3040 \right) = 0.0388$$

$$\alpha_{1773 K} = \frac{\delta_{red} - \delta_{ox}}{2} \cong \frac{\delta_{red, 1773 K}}{2} = 0.0194$$

For the system in question 1, $\alpha = \frac{\delta}{2} = 0.0117 < \alpha_{1773 K}$. This means that for the release of one O-atom, the system in question 1 requires $\frac{1}{0.0117} = 42.7$ CeO_2 units while the system here requires $\frac{1}{0.0388} = 25.8$ CeO_2 units only.

5.

$$2 \alpha_{1673} = \exp \left(-0.2105 \log \left(\frac{0.1 \times 10^{-3} \text{ bar}}{1 \text{ bar}} \right) - 2.613 \right) = 0.0169$$

$$\alpha_{1673 K} = \frac{\delta_{red} - \delta_{ox}}{2} \cong \frac{\delta_{red,1773 K}}{2} = 0.0085$$

$$\frac{\alpha_{1673 K} - \alpha_{1773 K}}{\alpha_{1773 K}} = \frac{0.0085 - 0.0194}{0.0194} = -0.562$$

The oxygen exchange capacity drops by 56.2%.

6.

$$\frac{n_{H_2}}{n_{CO_x}} = \frac{n_{H_2}}{n_{CO} + n_{CO_2}} = \frac{40.7}{4.3 + 22.4} = 1.52$$

7.

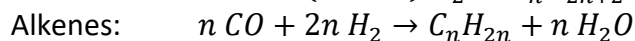
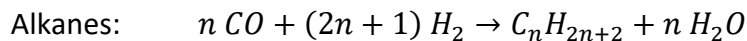
$$conv = \frac{n_{CO}}{n_{CO} + n_{CO_2}} = \frac{4.3}{4.3 + 22.4} = 0.16$$

8.

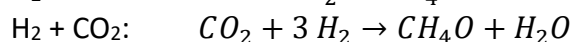
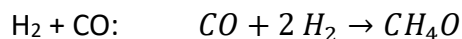
$$\frac{n_{H_2}}{n_{CO_x}} = \frac{n_{H_2}}{n_{CO} + n_{CO_2}} = \frac{59.9}{6.0 + 17.2} = 2.58$$

$$conv = \frac{n_{CO}}{n_{CO} + n_{CO_2}} = \frac{6.0}{6.0 + 17.2} = 0.26$$

9.



10.



11.

Liquid alkane/alkene production requires a H_2 to CO ratio of about 2, whereas the methanol production requires a H_2 to CO_x ratio of 2.5 – 2.8. Thus the 20 minute run is not ideal for either process, the short run is well suitable for the production of methanol.

12.

$$n_{H_2} = 59.5\% * \frac{96.2 L}{22.4 L} = 2.55 \text{ mol}$$

$$n_{CO} = 4.6\% * \frac{96.2 L}{22.4 L} = 0.20 \text{ mol}$$

$$n_{CO_2} = \frac{n_{H_2} - 2.69 * n_{CO}}{2.69} = 0.75 \text{ mol}$$

Judging from the stoichiometries in **10**, full conversion requires $2 * 0.20 \text{ mol} + 3 * 0.75 \text{ mol} = 2.65 \text{ mol } H_2$. As such H_2 is the limiting component and the theoretical maximum amount of methanol produced is:

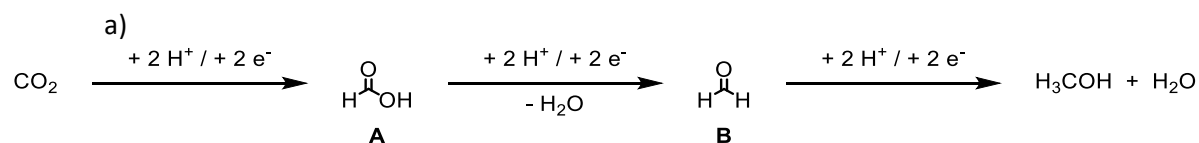
$$\frac{2.55 \text{ mol}}{2.65 \text{ mol}} * (0.20 \text{ mol} + 0.75 \text{ mol}) = 0.91 \text{ mol}$$

The mass of produced MeOH is then:

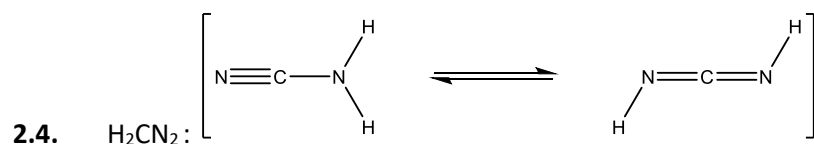
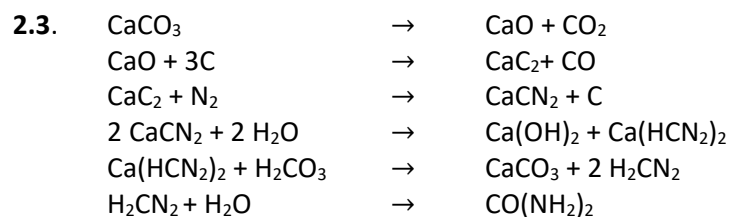
$$m_{\text{MeOH}} = 0.85 * 0.91 \text{ mol} * 32.04 \frac{\text{g}}{\text{mol}} = 24.8 \text{ g}$$

Solution: Many-faceted Oxides of Carbon

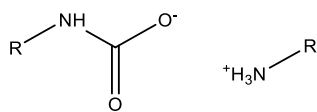
2.1.



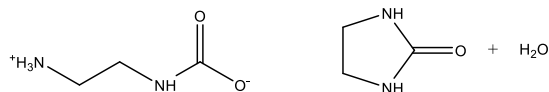
2.2. O activators: $X^{\delta+}$, $Z^{\delta+}$; C activators: $Y^{\delta-}$ or X = Lewis acid and Y = Lewis base



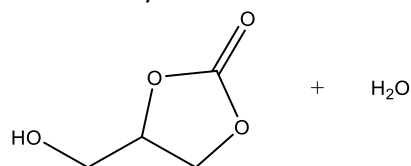
2.5. i) - Ammonium Carbamate:



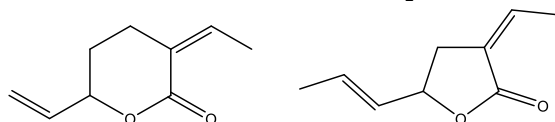
ii- Carbamate or dicarbamate:



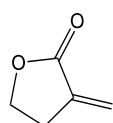
iii- cyclic ester:



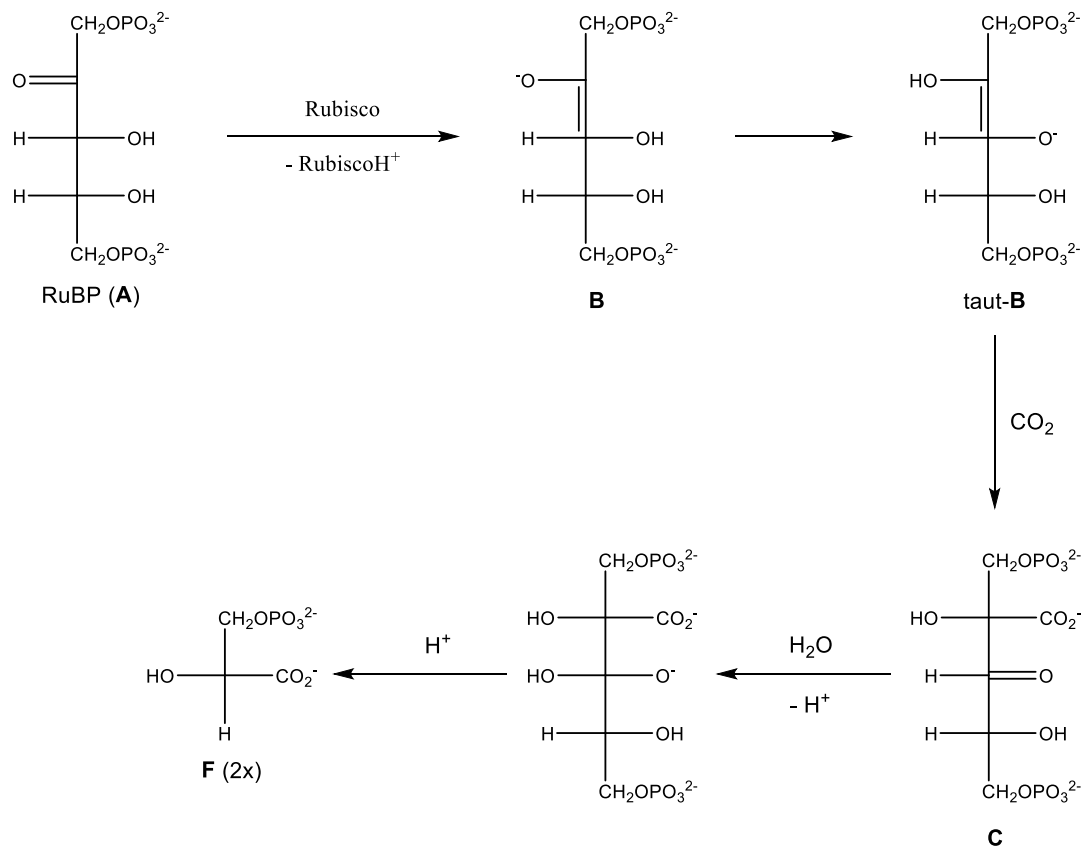
iv- Lactone from 2 butadien + CO₂ or 1 Butadien + CO₂:



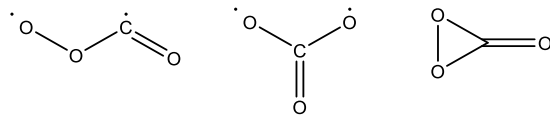
or



2.6.

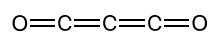


2.7.

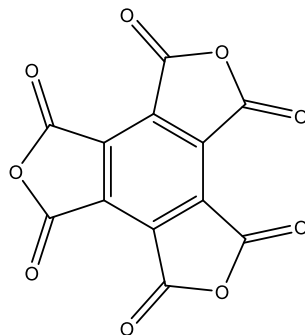


1. CO_3 , carbontrioxide

2. C_3O_2 , carbonsuboxide

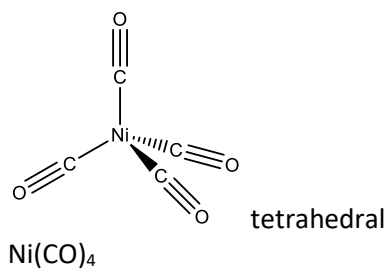


3.

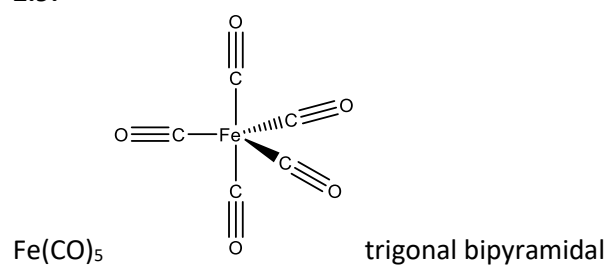


C_{12}O_9 , mellitic anhydride

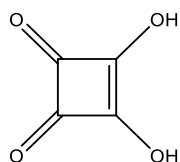
2.8.



2.9.



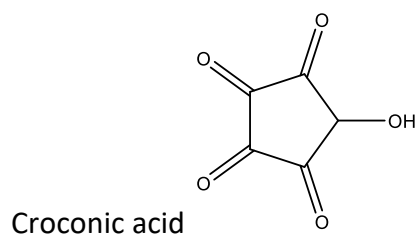
2.10.



2.11

The dianion is resonance stabilized and the mono anion is stabilized by intramolecular hydrogen bonding.

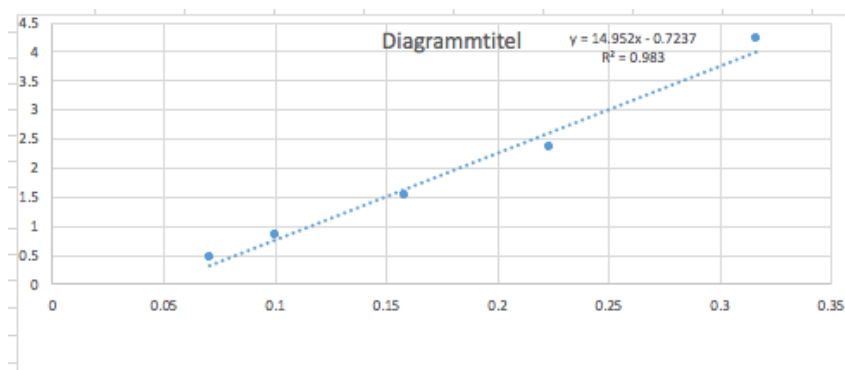
2.12.



Solutions - What to do with CO₂

- 3.1** The constant value k adds up to $2.69 \cdot 10^5 \cdot 1 \cdot 5 \cdot 10^{-6} \cdot 2.35 \cdot 10^{-3} = 3.15 \cdot 10^{-3}$ unit of k is C ($V^{-1/2} \text{ cm}^{-2} \text{ s}^{-1/2}$)

3.2



y-axis: peak current in mA

x-axis: potential sweep rate in $(V/s)^{1/2}$

The plotted graph shows a slope of $14.94 \pm 0.5 \text{ mA}/(V/s)^{1/2} = 14.94 \cdot 10^{-3} \text{ A}/(V/s)^{1/2}$. Since $k \cdot A = \text{slope}$ we have $A = \text{slope}/k$ and thus $A = 14.94/3.15 = 4.74 \pm 0.2 \text{ cm}^2$.

- 3.3** $\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{OH}^-$
 $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$

- 3.4** $n = \frac{Q}{z} \cdot F = I \frac{t}{z} F \Rightarrow I = nz \frac{F}{t} \Rightarrow I_{\text{CO}} = -(0.005 \text{ mol} \cdot 2 \cdot 96485 \text{ A s}) / (36000 \text{ s}) = -0.0268 \text{ A} \Rightarrow I_{\text{tot}} = -0.0268 \text{ A} / 0.76 = -0.0352 \text{ A} \Rightarrow j_{\text{tot}} = -0.0352 \frac{\text{A}}{10 \text{ cm}^2} = -0.00352 \text{ A cm}^{-2}$
 $n = \frac{Q}{z} \cdot F = I \frac{t}{z} F \Rightarrow I = nz \frac{F}{t} \Rightarrow I_{\text{CO}} = -(0.005 \text{ mol} \cdot 2 \cdot 96485 \text{ A s}) / (36000 \text{ s}) = -0.0268 \text{ A} \Rightarrow I_{\text{tot}} = -0.0268 \text{ A} / 0.76 = -0.0352 \text{ A} \Rightarrow j_{\text{tot}} = -0.0352 \frac{\text{A}}{10 \text{ cm}^2} = -0.00352 \text{ A cm}^{-2}$

- 3.5** $j_{\text{H}_2} = j_{\text{tot}} \cdot FE_{\text{H}_2} = -0.00352 \text{ A cm}^{-2} \cdot 0.24 = -0.00084 \text{ A cm}^{-2}$ (of note, by convention cathodic currents have a negative sign.)



3.6

$$j_{tot} = -33.9 \text{ mA cm}^{-2}$$

$$FE_{product} = j_{product}/j_{tot} \rightarrow FE_{CO} = 14.1\%$$

$$FE_{H_2} = 25.1\%$$

$$FE_{CH_4} = 55.5\%$$

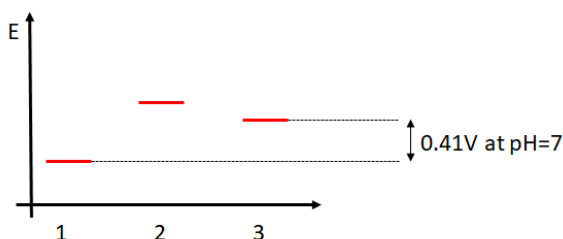
$$FE_{C_2H_6} = 5.3\%$$

Solution - Pathways to H₂ and catalysts

Hydrides

- 4.1. It is both, an acid base reaction, a proton is transferred from water to the hydride ion, and a redox reaction since it is a comproportionation: $-I + +I \rightarrow 0$
- 4.2. The overall ΔG° of this reaction is $-432+360=-72\text{kJ/mol}$. Thus, the disproportionation may not be higher than $+72\text{kJ/mol}$. According to $\Delta G^\circ=-n \cdot F \cdot \Delta E^\circ$, this corresponds to a disproportionation potential of -0.75V .
- 4.3. The most common oxidation states of Co are +I (d^8), +II (d^7) and +III (d^6). Thus, Co-H is in the oxidation state +I as a hydride and +III as an acid. Formal comproportionation to +II.
- 4.4. If pK_{a1} goes up, pK_{a2} goes up: The ligand donates electrons to the metal center, making it electron rich. The more electron density is localized on the metal center, the more the pK_{a1} increases and the H becomes less acidic and more "hydridic".

4.5.



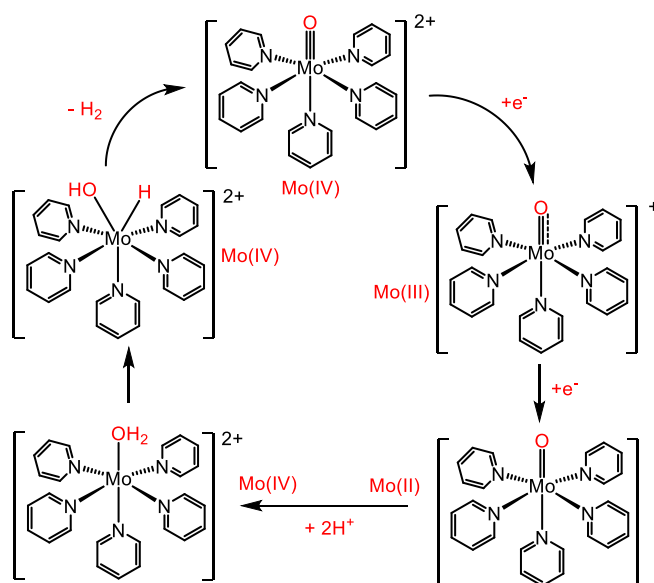
Since 2 disproportionates, its level must be above the line between 1 and 3. If the standard potential is about 0V, the potential at pH=7 is about -0.41V .

- 4.6. With the given data, the $T\Delta S^\circ_r$ can be calculated: $T\Delta S^\circ_r = 298 \cdot (205 + 2 \cdot 41.6 - 2 \cdot 43.6)/2 = 29.9\text{kJ/mol}$. With the Gibbs formula, ΔG°_r is thus -318kJ/mol .

For $K=1$, ΔG°_r is 0 or $\Delta H^\circ_r = T\Delta S^\circ_r$, or $348 = T \cdot 29.9$ and $T = 3462\text{K}$ assuming that ΔH°_r is temperature independent.

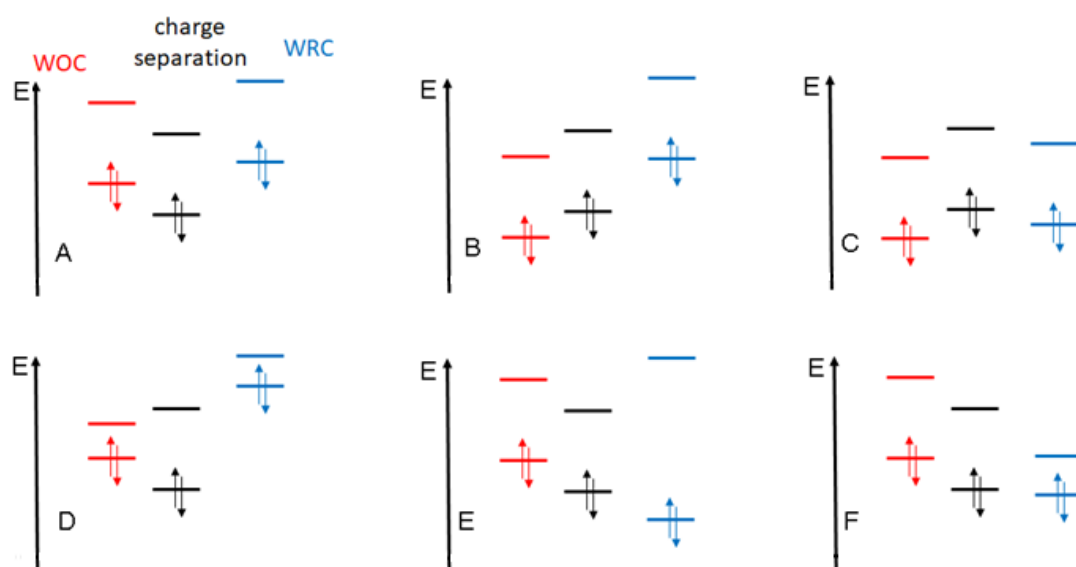
Catalysts

4.7.



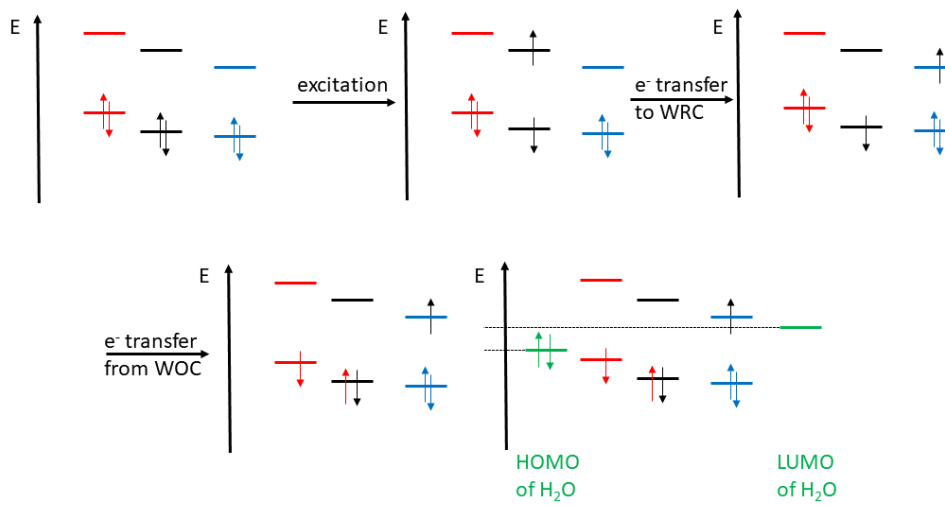
4.8. The $\Delta E_{1/2}^\circ$ for the reaction $[CuL_2]^{2+} + 1e^- \rightarrow [CuL_2]^+$ becomes more positive the bulkier the red groups are.

4.9.



F is the only possibility. After excitation, the electron is in a higher level than the LUMO of the WRC and can be transferred. The "hole" of the sensitizer can be filled with an electron from the HOMO of the WOC. These three processes lead to charge separation.

4.10.



Water transfers an electron from its highest occupied energy level to WOC and is thereby oxidized and WRC gives an electron from its lowest unoccupied energy level into the lowest unoccupied energy level of water.

4.11. ΔE° corresponds to 1.23eV per electron and thus to $1.97 \cdot 10^{-19}$ J. With $E = h \cdot \nu = h \cdot c / \lambda$, we get for $\lambda = 1003.8$ nm

4.12. $E_{\text{tot}} = E_{\text{ps}} + E_{\text{ex}}$ thus $h \cdot c / \lambda_{\text{inc}} = h \cdot c / \lambda_{\text{ex}} + h \cdot c / (1003)$ or $\lambda_{\text{ex}} = (\lambda_{\text{inc}} \cdot \lambda_{\text{ps}}) / (\lambda_{\text{ps}} - \lambda_{\text{inc}})$

For the 500nm photon, the excess energy would thus correspond to a photon of 994nm

Solution – Two Transition Metals – Many Oxidation States

5.1.

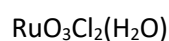
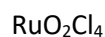
a) 1.4 V b) 2.0 V

The following information about the different species is given:

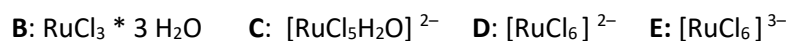
Species	Oxidation State of Ru	Charge of complex	Molecular Mass (g/mol)
A	+VI	-2	540.69
B	+III	none	261.42
C	+III	-2	> 260
D	+IV	-2	
E	+III	-3	

5.2 A $\text{Cs}_2[\text{RuO}_2\text{Cl}_4]$; calculation example:

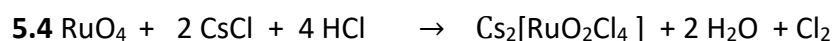
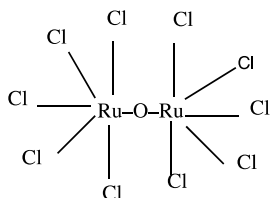
oxidation state and anion charge require 8 neg. charges; counterion can only be Cs
possible composition of the anion (without charges)



Only RuO_2Cl_4 is 6 coordinate and fits together with 2 Cs the MM of 540.69

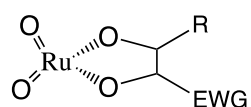


5.3 F contains a Ru-O-Ru unit:

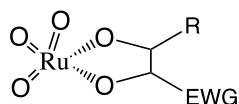


5.5 Draw the missing structures A, B, and C.

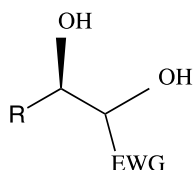
A Ester:



B oxidized ester



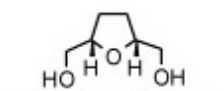
C dihydroxy compound



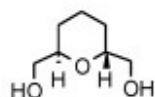
5.6. Ox states: RuO_4 : VIII, A : +VI, B: +VIII,

5.7. tetrahydrofuran derivative

(a tetrahydropyran derivative is also possible)



5.8. tetrahydropyran derivative



5.9.

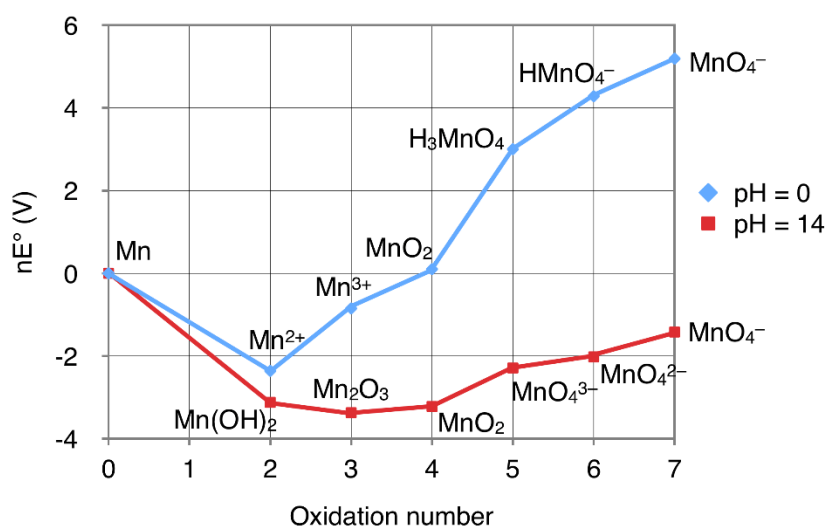
Table 1

Redox reactions at pH 0	E_0 / V
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	1.51
$\text{MnO}_2 + 4\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{Mn}^{3+} + 6 \text{H}_2\text{O}$	0.95
$\text{H}_3\text{MnO}_4 + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{MnO}_2 + 3 \text{H}_2\text{O}$	2.90
$\text{H}_2\text{MnO}_4 + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_3\text{MnO}_4 + \text{H}_2\text{O}$	1.28
$\text{MnO}_4^- + 2\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{MnO}_4 + 3 \text{H}_2\text{O}$	0.92

Table 2

Redox reactions at pH 14	E_0 / V
$\text{Mn}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Mn} + 2\text{OH}^-$	-1.56
$\text{Mn}_2\text{O}_3 + 3\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Mn}(\text{OH})_2 + 2\text{OH}^-$	-0.25
$2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$	0.15
$\text{MnO}_4^{3-} + 2\text{H}_2\text{O} + \text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	0.97
$\text{MnO}_4^{2-} + \text{e}^- \rightarrow \text{MnO}_4^{3-}$	0.27
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56

Frost diagram for manganese

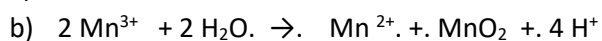


5.10. pH 14

5.11.

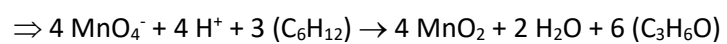
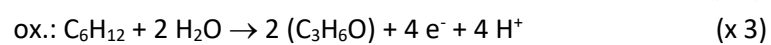
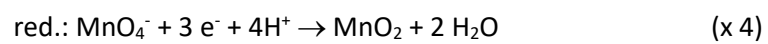
a) and b)

In both cases disproportionation; they are above the line that connects their neighbours.



5.12. 2 molecules of acetone.



5.13.

Solutions - Useful Radioactivity

6.1.

a) $\ln A - \ln A_0 = -\lambda \cdot t$
 $A = 29 \text{ MBq}$

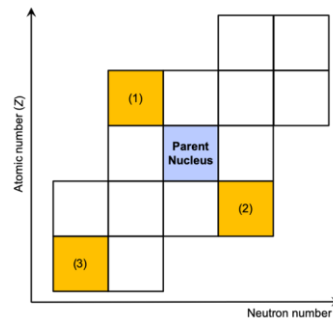
b) 1.02 MBq

c) $13:05:20$

d) $T_{1/2} = \ln 2 / \lambda \quad \lambda = 0.0001706 \text{ s}^{-1}$
 $A = \lambda N$
 $1 \text{ g} = x \text{ N}$

$1 \text{ g } ^{68}\text{Ga} = 8.855 \cdot 10^{21} \text{ Teile}$
 $A = 0.0001706 \text{ s}^{-1} \times 8.855 \cdot 10^{21} = 1.51 \cdot 10^{18} \text{ Bq / gr} = 1.51 \cdot 10^9 \text{ GBq / gr}$

6.2 (1) β^- , (2) β^+ , (3) α

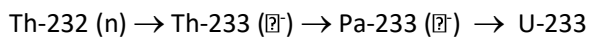


6.3.

What are the isotopes **A** and **B**?

$A = \text{U-239} \quad B = \text{Np-239}$

6.4.



6.5.

$N = N_0 e^{-\lambda t} \quad (1)$

N_0 can be replaced when the number of daughter nuclides (D) is taken into account:

$N_0 = N + D$

Equation (1) can then be written as

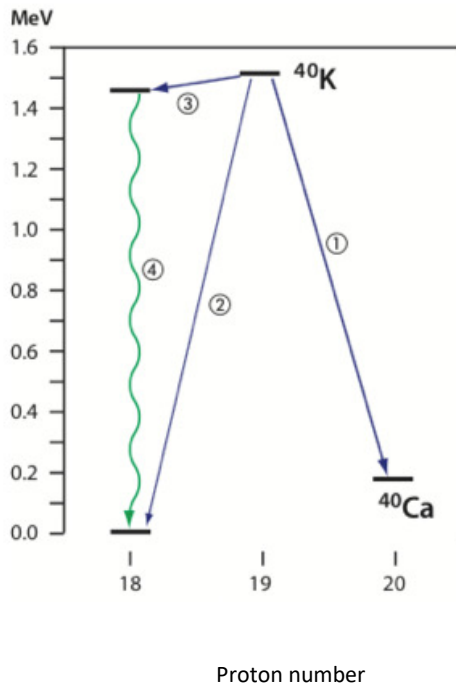
$N = (N + D) \cdot e^{-\lambda t}$

$N \cdot e^{\lambda t} = N + D$

$D = N \cdot (e^{\lambda t} - 1)$ or, D being N_D and $N = N_M$, you get the above equation

$$N_D = N_M \cdot (e^{\lambda t} - 1)$$

6.6.



1) 89.14% undergo a β -decay to the ground state of ^{40}Ca .

2) 0.2% undergo an electron capture to the ground state of ^{40}Ar

1) 10.66% undergo an electron capture to the excited state of ^{40}Ar

Decay of the excited state of ^{40}Ar to the ground state under γ -emission

6.7.

$$\lambda_{\text{tot}} = \lambda_{\beta} + \lambda_{\epsilon} = 5.543 \cdot 10^{-10} \text{ a}^{-1} \quad N_{\text{K-40}} = 0.012\% \text{ of } 0.14 \text{ kg} \cdot 40/39 = 0.0172 \text{ mg}$$

$$N_D = N_M \cdot (e^{\lambda t} - 1)$$

$$N_{\text{Ar-40}} + N_{\text{Ca-40}} = N_{\text{K-40}} \cdot (e^{\lambda t} - 1)$$

$$N_{\text{Ar-40}} + N_{\text{Ca-40}} = (\lambda_{\beta} + \lambda_{\epsilon}) / \lambda_{\text{tot}} \cdot N_{\text{K-40}} \cdot (e^{\lambda t} - 1)$$

$$N_{\text{Ar-40}} + N_{\text{Ca-40}} = \lambda_{\epsilon} / \lambda_{\text{tot}} \cdot N_{\text{K-40}} \cdot (e^{\lambda t} - 1) + \lambda_{\beta} / \lambda_{\text{tot}} \cdot N_{\text{K-40}} \cdot (e^{\lambda t} - 1)$$

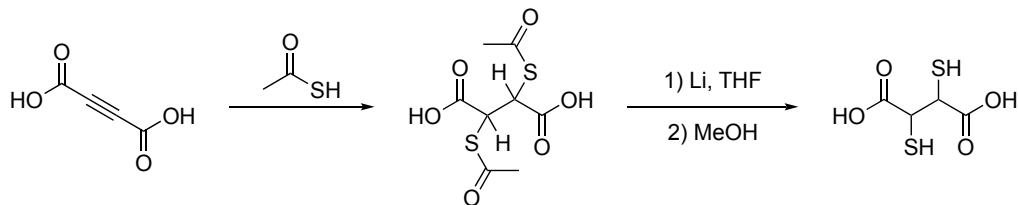
$$\Rightarrow N_{\text{Ar-40}} = \lambda_{\epsilon} / \lambda_{\text{tot}} \cdot N_{\text{K-40}} \cdot (e^{\lambda t} - 1)$$

$$t = 1 / \lambda_{\text{tot}} \cdot \ln(N_{\text{Ar-40}} / N_{\text{K-40}} \cdot \lambda_{\text{tot}} / \lambda_{\epsilon} + 1)$$

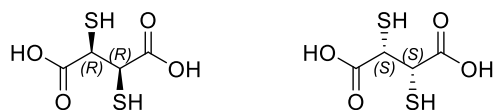
$$t = 755 \cdot 10^3 \text{ a}$$

Solution – Heavy Metal Detoxification

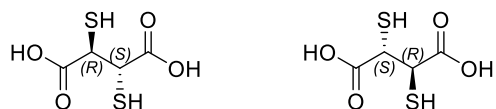
7.1.



7.2.



Enantiomers



meso

7.3. The meso form

7.4.

First Proton:



$$0.1 - x \quad \quad x \quad \quad x$$

The resulting quadratic equation renders $c(\text{H}^+) = c(\text{RCOO}^-) = x = 0.013 \text{ mol/L}$.

pH = 1.886

Second proton

initial	R'-COOH	H ⁺	+	R'-COO ⁻
change	- y	+ y		+ y
equilibrium	0.013 - y	0.013 + y		y

The resulting quadratic equation renders $y = 0.000262$

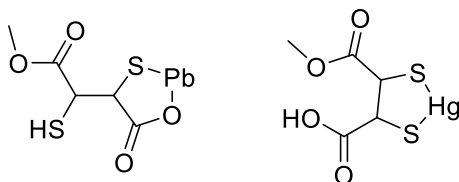
Thus $c(\text{H}^+) = 0.013 + y = 0.013 + 0.000262 = 0.01326$

pH = 1.877

The S-H protons can be neglected. Also, the approximation of decoupling the two dissociation steps is justified, since the difference is small and otherwise the algebra would be much more complicated.

7.5.

Pb (and Cd): bonding through O and S; Hg bonding through the two S since the Hg IR spectrum shows no -COO^- band.



7.6. The Hg complex has two free carboxylic acid group; when losing a proton the resulting carboxylate anion is stabilized by an additional hydrogen bond from the other carboxylic group. This reaction is similar to malonic acid.

The Pb complex has only one carboxylic group, the pka is in the range of acetic acid.

7.7.

	DMSA [mol/L]	Pb [mol/L]	Pb(DMSA)
Initial	4.12 E-4	4.12E-6	0
End	$4.12\text{E-}4 - 0.995 = 4.0994 \text{ E-}4$	$4.12\text{E-}6 - (4.12 \text{ E-}4 \cdot 0.005) = 2.06 \text{ E-}6$	$(4.12\text{E-}4 \cdot 0.005) = 2.06 \text{ E-}6$

7.8.

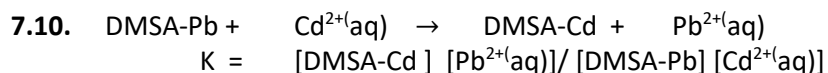
We test for a first order reaction mechanism:

t in min	0	60	120	180	240	300	360
$\ln c$ ($\mu\text{mol/L}$)	0.722	0.507	0.293	0.074	-0.140	-0.356	-0.580

It gives a linear graph; thus:

a) $t_{1/2} = 192.5 \text{ min}$; $k = -0.0036 \mu\text{mol L}^{-1}\text{min}^{-1}$

7.9. $90 \mu\text{g/L} = 0.494 \mu\text{mol/l}$ thus: 396.7 min

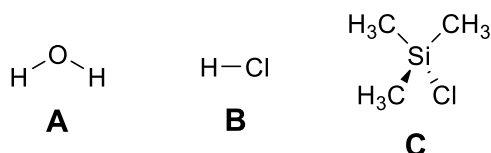


7.11. $K = K_{\text{Cd}} : K_{\text{Pb}} = 10^{16.5} : 10^{17.6} = 10^{-1.1}$

7.12. $[\text{Pb-DMSA}] = 0.0847 \text{ mol/L}$; $[\text{Cd-DMSA}] = 0.0153 \text{ mol/L}$
 $[\text{Pb}^{2+}] = 0.0153 \text{ mol/L}$; $[\text{Cd}^{2+}] = 0.0347 \text{ mol/L}$

Vacuum-UV Modification of PDMS

8.1



8.2

Process	Number
x-ray photon absorption	4
γ-photon absorption	5
IR-photon absorption	1
Electron transfer between molecules	2
Ionization of a molecule	3

8.3

$$E_{\text{photon}} = h \nu = h c / \lambda = 6.6261 \cdot 10^{-34} \text{ J s} \cdot 3 \cdot 10^8 \text{ m s}^{-1} / 172 \cdot 10^{-9} \text{ m} = 1.155 \cdot 10^{-18} \text{ J}$$

For 1 mol photons: $E_m = N_A \cdot E_{\text{photon}} = 6.0221 \cdot 10^{23} \text{ mol}^{-1} = 695.4 \text{ kJ/mol}$. Hence, the absorption of one photon is sufficient to break the bond.

8.4

Lambert-Beer law: $A = \epsilon l c$. We have $3.5 = 1 \text{ cm} \cdot \epsilon c$, hence $\epsilon c = 3.5 \cdot 10^6 \text{ m}^{-1}$. $A = \ln(I_0/I_s)$. If 99% of the light is absorbed, $A = \ln(1/0.01) = 4.605$. The material depth is $l = A/(\epsilon c) = 4.605/3.5 \cdot 10^6 = 1.32 \text{ cm}$.

8.5

$$\Delta G = G(\cdot\text{Si}\equiv) - G(\cdot\text{CH}_2\text{Si}\equiv) = -RT \ln K = -8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K} \cdot \ln(1/8) = 5.152 \text{ kJ/mol}.$$

8.6

Since ^{13}C and ^{29}Si have low natural abundance, hyperfine splitting from only the protons with spin $I = \frac{1}{2}$ is observed. Two protons lead to three lines.

8.7

☐ Oxidation reduces the molar extinction coefficient. Thus, more light penetrates into the sample in later pure nitrogen phases and more radicals are formed.

(this cannot be the case, as the light is completely absorbed in all cases, see task 1.4)

☐ During the whole experiment, radicals are formed with the same rate, but in the presence of oxygen their signal is invisible.

(this cannot be the case, since the signal is not immediately restored after switching back to nitrogen and since some signal is seen in the presence of oxygen).

☒ Oxidation creates sites in the modified polymer that are more susceptible to forming radicals.

(this is likely, since radicals are formed faster after the first oxidation period and more radicals are formed at this fast rate after additional oxidation periods)

☒ Some of the formed radical sites are stable in the presence of 2% oxygen.

(there is clearly a non-zero spin count during the oxidation periods)

8.8

The irradiated volume is $V = 0.26 \cdot 10^{-6} \text{ m} \cdot 1.5 \cdot 10^{-4} \text{ m}^2 = 3.9 \cdot 10^{-11} \text{ m}^3$. The polymer mass is thus $m = 950 \text{ kg} \cdot \text{m}^{-3} \cdot 3.9 \cdot 10^{-11} \text{ m}^3 = 3.705 \cdot 10^{-8} \text{ kg}$. The molar mass of the PDMS repeat unit is $M = (28.09 \text{ g/mol} + 16.00 \text{ g/mol} + 2 \cdot 12.01 \text{ g/mol} + 6 \cdot 1.0079 \text{ g/mol}) = 74.16 \cdot 10^{-3} \text{ kg/mol}$. The number of irradiated repeat units is thus $N = N_A \cdot 3.705 \cdot 10^{-8} \text{ kg} / 74.16 \cdot 10^{-3} \text{ kg/mol} = 6.0221 \cdot 10^{23} \text{ mol}^{-1} \cdot 5.00 \cdot 10^{-7} \text{ mol} = 3.01 \cdot 10^{17}$. The number of $\cdot\text{CH}_2\text{Si}\equiv$ radicals is $2 \cdot 10^{15} \cdot (8/9) = 1.78 \cdot 10^{15}$. Hence, the percentage of PDMS repeat units that had been that had been transformed into $\cdot\text{CH}_2\text{Si}\equiv$ radicals is $100 \% \cdot 1.78 \cdot 10^{15} / 3.01 \cdot 10^{17} = 0.6 \%$.

8.9

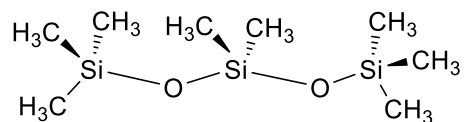
With $n(t) = n_\infty (1 - e^{-kt})$ we have $n_\infty = n(t) / (1 - e^{-kt})$. We insert $n(t) = 2 \cdot 10^{15}$ and $kt = 0.48$ and obtain $n_\infty = 5.25 \cdot 10^{15}$.

8.10

From $n_A(1 \text{ h}) = n_{A,\infty} [1 - \exp(-48)] = n_B(1 \text{ h}) = n_{B,\infty} [1 - \exp(-4)]$ we obtain $n_{B,\infty} = 1.019 \cdot n_{A,\infty}$. After 15 min, we have $n_A(0.25 \text{ h}) = n_{A,\infty} [1 - \exp(-12)] \approx n_{A,\infty}$ and $n_B(0.25 \text{ h}) = 1.019 \cdot n_{A,\infty} [1 - \exp(-1)] = 0.644 \cdot n_{A,\infty}$. Hence, the ratio is $R_{AB} = 1/0.644 = 1.55$.

8.11

The ratio C:Si:H:O is $0.406/12.01:0.356/28.09:0.102/1.0079:0.136/16.00 = 3.98:1.49:11.9:1$. We can thus expect an elemental formula $(\text{C}_8\text{Si}_3\text{H}_{24}\text{O}_2)_n$. All protons are aliphatic and, given the chemical shifts, probably methyl protons. The number of protons per heavy atoms excludes multiple bonds or a ring. We have $18n$ protons of one type and $6n$ protons of the other type. The $18n$ equivalent protons must be attached to carbon atoms ($6n$ equivalent methyl groups). With $n > 1$, it is impossible to realize that many equivalent methyl groups. Since there are no splittings in the ^1H NMR spectrum, the heavy atoms to which the hydrogen atoms are bound, must be separated by more than one bond. The 6 equivalent methyl groups can be bound only to two silicon atoms. The remaining 6 equivalent protons then must belong to two more methyl groups. Thus, only the following structure is consistent with the spectra and elemental composition:



8.12

☐ IR

☐ ¹H NMR

☐ ²⁷Si NMR

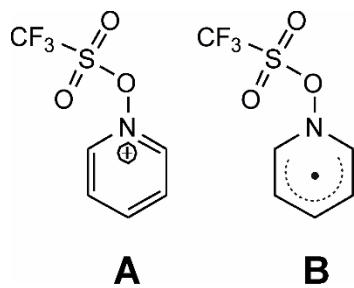
☒ Determination of molecular mass

☐ Elemental analysis

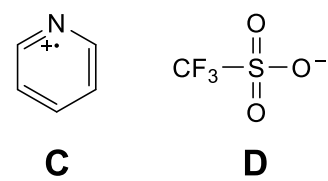
The two NMR methods will show only a single signal for any n . The IR spectra may differ in the fingerprint region. However, this region can be interpreted only if the spectra of individual members are already known. Elemental analysis gives the same result for all n . Only determination of molecular mass will distinguish the different oligomers.

Exciting Arenes

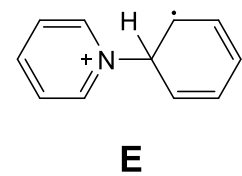
9.1



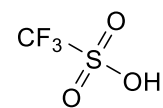
9.2



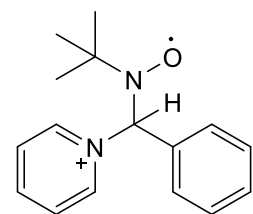
9.3



9.4



9.5



9.6

Isotope	Number of nuclei
^1H	1
^{14}N	2

One counts $18 = 2 \cdot 3 \cdot 3$ lines. The number of lines is $\prod_i (2 k_i I_i + 1)$, where index i runs over all groups of equivalent nuclei, k_i is the number of equivalent nuclei in a group, and I_i is the nuclear spin. The nuclear spins are $I = \frac{1}{2}$ for ^1H and $I = 1$ for ^{14}N . The factor 2 can only arise from a single ^1H . Factors 3 can arise either from a single ^{14}N or from two equivalent ^1H . In the former case, the three lines have the same intensity, in the latter one, they have intensity ratio 1:2:1, which is not observed. Factors 6 or 9 from several equivalent ^1H or ^{14}N are also excluded by the intensity ratios.

9.7

- ☐ The photon energy alone is sufficient for cleaving the C-H bond.
- ☐ The energy for breaking the C-H bond is supplied by the catalyst.
- ☒ The energy for breaking the C-H bond cannot be discussed separately from bond formation in the same reaction step.
- ☐ The energy for breaking the C-H bond must be supplied by heating the solvent.

$$E_{\text{photon}} = h \nu = h c / \lambda = 6.6261 \cdot 10^{-34} \text{ J s} \cdot 3 \cdot 10^8 \text{ m} \cdot \text{s}^{-1} / 439 \cdot 10^{-9} \text{ m} = 4.53 \cdot 10^{-19} \text{ J}$$

For 1 mol photons: $E_m = N_A \cdot E_{\text{photon}} = 6.0221 \cdot 10^{23} \text{ mol}^{-1} = 273 \text{ kJ/mol}$. Hence, the absorption of one photon is not sufficient to break the bond. The catalyst cannot supply the energy, because it is reformed in the catalytic cycle. Indeed, total energy of bond breaking and formation must be considered, which means that we cannot conclude without further information whether the step is endothermic.

9.8

$$\nu(\text{UV}) < \nu(\text{green light}) < \nu(\text{red light}) < \nu(\text{IR}) < \nu(\text{microwave})$$

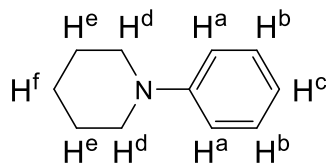
9.9

$$\Delta_R G^\circ = -z F U^\circ = -RT \ln K \Rightarrow K = \exp[(z F U^\circ / (RT))] = \exp[96485 \text{ C} \cdot \text{mol}^{-1} \cdot (-0.3 + 1.2) \text{ V} / (298 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K})] = 1.666 \cdot 10^{15}.$$

9.10

If phosphorescence is half as large und quenching conditions, quenching has the same rate as emission. Thus, we have $\nu = k [R] = 1/(8.55 \cdot 10^{-7} \text{ s})$ with $[R] = 5 \cdot 10^{-3} \text{ M}$. We find $k = 2.34 \cdot 10^8 \text{ s}^{-1} \cdot \text{M}^{-1}$.

9.11



9.12

The elemental analysis is normalized to the element with lowest content: N

element	Mol. mass	EA	$M_{EA_N}/M_N EA$
C	12.000	53.18%	16
H	1.008	5.02%	18
F	18.998	15.77%	3
N	14.007	3.88%	1
O	15.999		
S	32.06		

Mono isotopic mass of the compound is 212.1434. It only contains C,H and N. OR structure in 2.11 solved. The only suitable molecular formula is $C_{15}H_{18}N$. That leaves $C_1F_3O_eS_f$ for the counter ion.

$$(O+S)=100\%-53.18\%-5.02\%-15.77\%-3.88\%=22.15\%$$

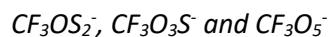
$f=$	expected % in EA	result
1	8.88	possible
2	17.76	possible
3	26.64	impossible

$$f < 3$$

$e=$		
1	4.43	possible
2	8.86	possible
3	13.30	possible
4	17.73	possible
5	21.16	possible

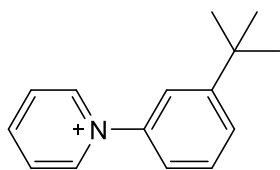
$$e < 6$$

The sum of both elements must be 21.15%. This is true for

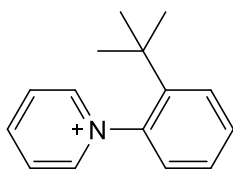


$CF_3O_3S^-$ is known as triflate, $CF_3O_5^-$ has no possible structure and $CF_3OS_2^-$ is not a common organic counter ion

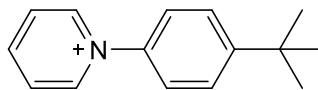
9.13



I



J



K

9.14

3

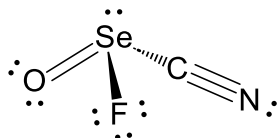
9.15

^1H NMR: 7: CH₃ s; piperidine ring: CH₂ multi, CH₂ multi; phenyl ring: CH d, CH dd, CH d

^{13}C NMR: 12

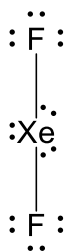
Unusual Fluorine Compounds

10.1.

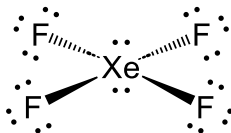


10.2. The angle C-Se-F is smallest due to the strong repulsion by the Se=O electron-pairs domain (calculated angles: C-Se-F = 90.6°; O-Se-F = 106.3°; C-Se-O = 103.9°)

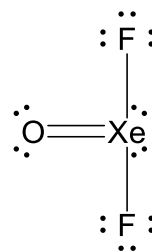
10.3. The geometry is given with respect to the arrangement of atoms. The geometry with respect to electron-pair domains is given in parentheses.



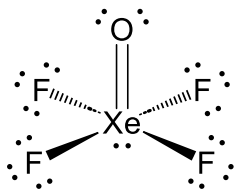
linear
(trigonal bipyramidal)



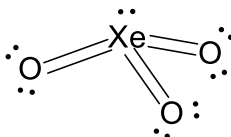
square planar
(octahedral)



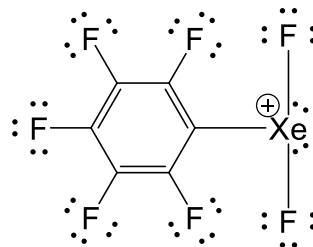
T-shaped
(trigonal bipyramidal)



square pyramidal
(octahedral)



trigonal pyramidal
(tetrahedral)



octahedral
(trigonal bipyramidal)

10.4. For **B**, the smallest multiple of the molecular weight MW_n is computed as

$$MW_n = \frac{M(S)}{\omega(S)} = \frac{32.06 \text{ g mol}^{-1}}{0.4748} = 67.51 \text{ g mol}^{-1},$$

subtracting the molecular weight of the known element sulfur, we draw the conclusion that the remaining weight corresponds to one equivalent of chlorine:

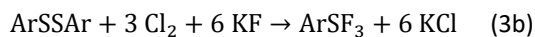
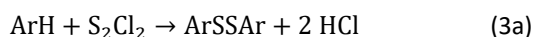
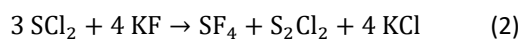
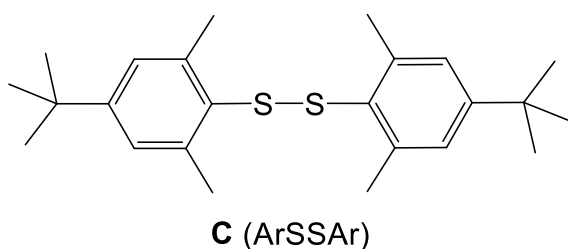
$$67.51 \text{ g mol}^{-1} - 32.06 \text{ g mol}^{-1} = 35.45 \text{ g mol}^{-1} \Rightarrow (\text{SCl})_n$$

Now, we can formulate formulae for each n until we find a chemically feasible structure (i.e. the Lewis structure can be drawn in a way to obtain a theoretically stable molecule):

$n = 1$: SCl not feasible

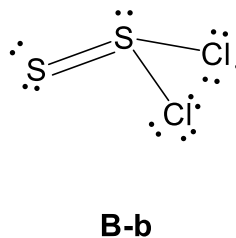
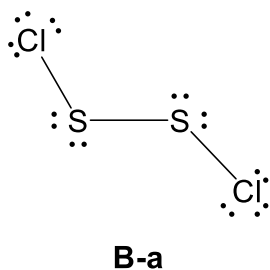
$n = 2$: S_2Cl_2 is a chemically feasible structure (see also 6.)

For **C**, the molecule must contain sulfur. With the given molecular weight small reasonable products can be excluded:

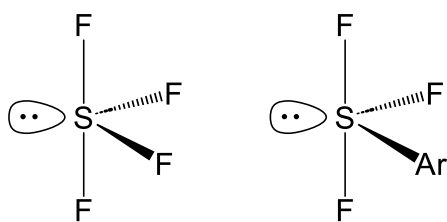


10.5. Disproportionation (sulfur is both oxidized, S(+II) to S(+IV), and reduced, S(+II) to S(+I))

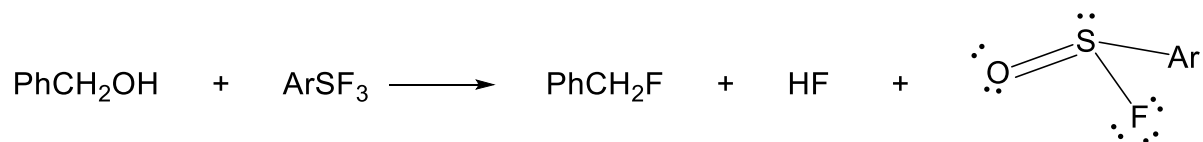
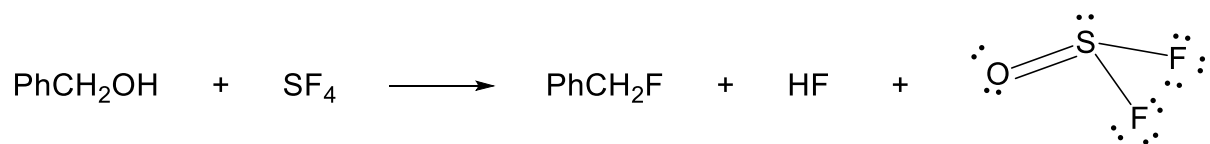
10.6. Structure **B-b** is known only in the case of S_2F_2 :



10.7. Both compounds have a trigonal bipyramidal geometry with respect to the valence-shell electron-pair domains. The non-bonding electron pair at the sulfur atom in both compounds as well as the Aryl substituent in Fluolead are in an equatorial position.



10.8.



Dynamic Phosphorus and Arsenic Compounds

11.1. (S)-2, (R)-ent-2

11.2. The Arrhenius equation is used to describe the dependence of the reaction rate constant as a function of temperature and the activation energy and is an empirical law. The Eyring equation is similar to that but uses a statistical mechanical treatment and transition-state model to find an expression for the temperature-dependence of a rate constant. In the exam, it will be clearly stated which treatment should be used (Eyring or Arrhenius):

$$\Delta G_{en}^{\ddagger} = RT \ln \left(\frac{k_B T}{k_{en} h} \right) \Leftrightarrow \frac{k_B T}{k_{en} h} = e^{\frac{\Delta G_{en}^{\ddagger}}{RT}} \Leftrightarrow k_{en} = \frac{k_B T}{h e^{\frac{\Delta G_{en}^{\ddagger}}{RT}}}$$

with $T = 100 + 273.15 = 373.15 \text{ K}$ and $\Delta G_{en}^{\ddagger} = 37.3 \text{ kcal mol}^{-1} \cdot 4.184 \text{ kJ kcal}^{-1} \cdot 1000 \text{ J kJ}^{-1} = 156000 \text{ J mol}^{-1}$:

$$k_{en} = \frac{k_B T}{h e^{\frac{\Delta G_{en}^{\ddagger}}{RT}}} = k_{en} = \frac{1.38 \cdot 10^{-23} \text{ J K}^{-1} 373.15 \text{ K}}{6.63 \cdot 10^{-34} \text{ J s}^{-1} e^{\frac{156000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 373.15 \text{ K}}}} = 1.13 \cdot 10^{-9} \text{ s}^{-1}$$

k_{en} is thus equal to $1.13 \cdot 10^{-9} \text{ s}^{-1}$.

11.3. For first order kinetics, the rate law is described as:

$$v_{rac} = -k_{rac} \cdot [2] \cdot t = \frac{d[2]}{dt} \Leftrightarrow \ln([2](t)) = \ln([2]_0) - k_{rac} \cdot t$$

for the half-life, $\ln([2](t_{1/2})) = \ln\left(\frac{[2]_0}{2}\right)$ and thus

$$\ln\left(\frac{[2]_0}{2}\right) = \ln([2]_0) - k_{rac} \cdot t_{1/2} \Leftrightarrow t_{1/2} = \frac{\ln(2)}{k_{rac}} = \frac{\ln(2)}{2 k_{en}}$$

with this, the half-life is computed from the rate constant calculated in II. (the temperature stays the same) as

$$t_{1/2} = \frac{\ln(2)}{2 \cdot 1.13 \cdot 10^{-9} \text{ s}^{-1}} = 3.07 \cdot 10^8 \text{ s} = 3560 \text{ d} = 9.74 \text{ a}$$

The half-life for the racemization process is thus equal to 9.74 years.

11.4. The enantiomeric excess is described as $ee(\%) = \frac{[S] - [R]}{[S] + [R]} \cdot 100\%$, where $[S]$ and $[R]$ stands for the concentration of the enantiomers. In equilibrium, i.e. when $t \rightarrow \infty$, we obtain a racemic mixture of 50% $[S]$ and 50% ($ee = 0$). In other words, when the concentration of the enantiomerically pure $[S]$ sample was $[A]_0$, in equilibrium, $[A]_{\infty} = \frac{1}{2} [A]_0$.

To determine $[A]_t$, we express $[S]$ as $[A]_t$ and $[R]$ as $[A]_0 - [A]_t$, so that

$$ee = \frac{|[S] - [R]|}{[S] + [R]} = \frac{|[A]_t - ([A]_0 - [A]_t)|}{[A]_0 - [A]_t + [A]_t} = \frac{|2[A]_t - [A]_0|}{[A]_0}$$

$$\Leftrightarrow [A]_t = \frac{[A]_0}{2}(1 + ee)$$

Inserting this into the original expression for the integrated rate law yields

$$\begin{aligned} \ln\left(\frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty}\right) &= \ln\left(\frac{\frac{[A]_0}{2}(1 + ee) - \frac{1}{2}[A]_0}{[A]_0 - \frac{1}{2}[A]_0}\right) = \ln\left(\frac{\frac{1}{2}[A]_0(1 + ee - 1)}{\frac{1}{2}[A]_0}\right) \\ &= \ln(ee) = -2 \cdot k_{en} \cdot t_{ee} \end{aligned}$$

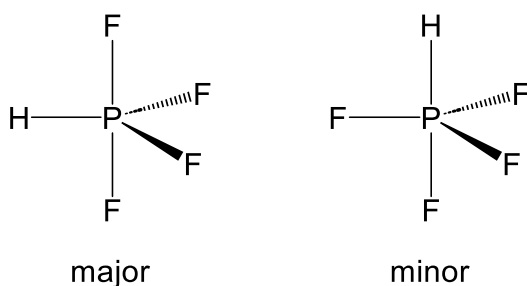
The rate constant is the same as derived in 2., as the temperature remains constant.

With that, we obtain

$$t_{ee(\%)} = \frac{\ln(ee)}{-2 \cdot k_{en}} \Rightarrow t_{90} = \frac{\ln(0.9)}{-2 \cdot 1.13 \cdot 10^{-9} \text{ s}^{-1}} = 4.66 \cdot 10^7 \text{ s} = 539 \text{ d} = 1.48 \text{ a}$$

The time required to get to an ee of 90%, therefore, is equal to 539 days. This is in accordance with our previous result in V., as $t_{90} < t_{1/2}$.

11.5.



- 11.6.** Two signals for both isomers. However, the relative intensities and multiplicities (if recorded without decoupling) differ.

11.7. $\Delta G^0 = -R \cdot T \cdot \ln(K) \Leftrightarrow K = e^{-\frac{\Delta G^0}{R \cdot T}}$

with $T = 298.15 \text{ K}$ (standard conditions), $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ and $\Delta G^0 = 4.24 \text{ kcal mol}^{-1} \cdot 4.184 \text{ kJ kcal}^{-1} \cdot 1000 \text{ J kJ}^{-1} = 17740 \text{ J mol}^{-1}$:

$$K = e^{-\frac{\Delta G^0}{R \cdot T}} = e^{-\frac{17740 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \cdot 298.15 \text{ K}}} = 7.80 \cdot 10^{-4}$$

The equilibrium constant of such an isomerization process is thus equal to $7.80 \cdot 10^{-4}$.

The equilibrium composition could be calculated starting from only the preferred isomer:

Isomer	Major	Minor
Initial	1	0
Final	1-x	x

With the definition $K = [\text{minor}]/[\text{major}]$, it follows that:

$K = \frac{x}{1-x} \rightarrow x = \frac{K}{1+K} \cong K = 7.80 \cdot 10^{-4}$. Given the small K, the minor isomer makes up for only 0.08 mol% in equilibrium under standard conditions.

11.8. For the Arrhenius treatment, we use the relation $\ln(k) = \ln(A) - \frac{E_a}{RT}$, where $E_a = \Delta G^\ddagger$.

With two data points accessible, we can describe the difference as

$$\ln(k_1) - \ln(k_2) = \ln\left(\frac{k_1}{k_2}\right) = -\frac{\Delta G^\ddagger}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and thus

$$\begin{aligned} \Delta G^\ddagger &= -R \cdot \ln\left(\frac{k_1}{k_2}\right) \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \\ &= -8.314 \text{ J mol}^{-1}\text{K}^{-1} \cdot \ln\left(\frac{1.78}{5.47} \cdot \frac{10^{-5}\text{s}^{-1}}{10^{-5}\text{s}^{-1}}\right) \left(\frac{1}{333 \text{ K}} - \frac{1}{363 \text{ K}}\right)^{-1} \\ &= 37.6 \text{ kJ mol}^{-1} \end{aligned}$$

As the rate constant is expressed in units of s^{-1} , the reaction follows a first-order rate law.

11.9. Diastereoisomers

Solution – From Curves to Straight Lines

A. Ideal gas law

12.1

Ideal gas law: $PV = nRT$. Thus, the linear graph would be $P = nRT \cdot \frac{1}{V}$ with coordinates P vs. $\frac{1}{V}$.

As the other solution, the logarithmic form is also a linear function: $\ln P = \ln(nRT) - \ln V$ with the coordinates $\ln P$ vs. $\ln V$.

12.2

For the linear equation, $P = nRT \cdot \frac{1}{V}$ the slope is $\text{tg}\alpha = nRT$. For abscissa and ordinate, we have the interception at (0;0). If T rises, $\text{tg}\alpha$ also increases, so the graph keeps the same interception at (0;0) while rotating counterclockwise.

For the logarithmic function, $\ln P = \ln(nRT) - \ln V$ the slope is $\text{tg}\alpha = -1$. The x- and y-intercepts are both $\ln(nRT)$. At higher temperatures, the slope remains unchanged, while the graph lifts up due to higher values of intercepts.

12.3

At high pressure, the molecules are close enough to each other, thus, a model of an ideal gas (i.e., non-interacting molecules) is not applicable. And real gas equation cannot be linearized.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

B. Equilibrium constant

12.4

The Van't Hoff equation: $\ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$. In short temperature ranges, when enthalpy and entropy changes are practically independent of temperature, the linear form is $\ln K = f\left(\frac{1}{T}\right)$.

12.5

The correct answers are:

c) Clausius–Clapeyron equation for phase equilibrium (liquid–gas):

$$\ln P = -\frac{\Delta H_{\text{vap}}^\circ}{R} \left(\frac{1}{T}\right) + C, \text{tg}\alpha = -\frac{\Delta H_{\text{vap}}^\circ}{R}$$

f) Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right), \text{tg}\alpha = -\frac{E_a}{R}$$

12.6

Indeed, as K depends directly on ΔG° which is defined at constant pressure, $\frac{dK}{dP} = 0$, thus

$K = f(P)$ is itself a linear function with the slope $\tan \alpha = 0$. In fact, any other set of axes, where y -axis is a function of K and x -axis is the function of P , can be chosen in this case to represent a linear graph with the slope 0 as well.

C. Example mathematical function

12.7

The completed table:

No.	Linearized equation	Slope	Horizontal intercept	Vertical intercept
1	$\frac{x}{y} = \frac{1}{a} \cdot x + \frac{b}{a}$	$1/a$	$-b$	b/a
2	$\frac{1}{y} = \frac{b}{a} \cdot \frac{1}{x} + \frac{1}{a}$	b/a	$-1/b$	$1/a$
3	$y = -b \cdot \frac{y}{x} + a$	$-b$	a/b	a

D. Helix function

12.8

The helix height is the z value as the initial point of the function has $z = 0$. When the helix completes one turn the length projection on the horizontal XY -plane is a complete circle with the radius r and, thus, circumference $2\pi r$. Having the helix angle α as a parameter, we could find the height of one turn (known as pitch): $p = 2\pi r \cdot \tan \alpha$. If the helix has N turns ($N = \theta/2\pi$), the total height is $z = N \cdot p = \theta \cdot r \cdot \tan \alpha$.

12.9

As $\tan \alpha \approx \alpha$ for very small values of α , the height z will be a linear function of $\alpha \cdot \theta$ at any θ values and very small values of α .

12.10

The linearization of z as a function of x or y is not possible: z depends linearly on θ , while $x = r \cdot \sin \theta$ represents a periodic function (similarly for y). We can write that $\theta = \arcsin(x/r)$ and $z = \arcsin(x/r) \cdot r \cdot \tan \alpha$, but we will obtain multiple possible values of z for any given value of $x \leq r$ (or $y \leq r$), which can also be seen directly from the figure. Therefore, we can't perform this linearization as for any linear function, only one value corresponds to one argument (and *vice versa*).

12.11

The height of the DNA molecule is $z = N \cdot p = N \cdot 2\pi \cdot r \cdot \operatorname{tg} \alpha$. The length L of one DNA chain is $L = z / \sin \alpha = N \cdot 2\pi \cdot r / \cos \alpha = 2023 \cdot 2\pi \cdot 20 / \cos(20^\circ) = 270533 \text{ (\AA)}$. Having two helices in the DNA molecule, the total length is $2L = 541066 \text{ \AA}$, i.e., ca. 0.054 mm.

Solution – Sweet Michaelis-Menten Kinetics

13.1

Let us write down the concentrations of the intermediates and reaction rate constants as follows:

$$[B] = \frac{k_1}{k_{-1}}[A]; \quad [C] = \frac{k_2}{k_{-2}}[B]; \quad [D] = \frac{k_3}{k_{-3}}[C]; \quad [A] = \frac{k_4}{k_{-4}}[D]$$

Deriving $[A]$, we obtain:

$$[A] = \frac{k_4}{k_{-4}}[D] = \frac{k_4}{k_{-4}} \frac{k_3}{k_{-3}}[C] = \frac{k_4}{k_{-4}} \frac{k_3}{k_{-3}} \frac{k_2}{k_{-2}}[B] = \frac{k_4}{k_{-4}} \frac{k_3}{k_{-3}} \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}}[A]$$

From this, it follows that the product of the rate constants clockwise is equal to the product of the rate constants anti-clockwise:

$$k_1 k_2 k_3 k_4 = k_{-1} k_{-2} k_{-3} k_{-4}$$

13.2

From the detailed balance property, it follows that:

$$\begin{aligned} k_1 \cdot 200 \text{ M}^{-1} \text{ s}^{-1} \cdot 40 \text{ s}^{-1} \cdot 100 \text{ s}^{-1} &= k_{-1} \cdot 40 \text{ M}^{-1} \text{ s}^{-1} \cdot 100 \text{ s}^{-1} \cdot 100 \text{ s}^{-1} \\ k_1 \cdot 800\,000 \text{ M}^{-1} \text{ s}^{-3} &= k_{-1} \cdot 400\,000 \text{ M}^{-1} \text{ s}^{-3} \\ \frac{k_1}{k_{-1}} &= \frac{400\,000 \text{ M}^{-1} \text{ s}^{-3}}{800\,000 \text{ M}^{-1} \text{ s}^{-3}} = \frac{1}{2} \end{aligned}$$

To calculate the equilibrium constant from the detailed balance, we have the following:

$$K_{eq} = \frac{[P]_{eq}}{[S]_{eq}} = \frac{k_1}{k_{-1}} = \frac{1}{2}$$

As $K_{eq} < 1$, the reverse rate constant is higher than the forward: $k_{-1} > k_1$. Thus, the equilibrium lies towards the formation of the substrate, i.e., the backward reaction.

The given ratio $\frac{[P]_{free}}{[S]_{free}} = 10$ with respect to K_{eq} indicates only that according to Le Chatelier's principle, in order to keep $K_{eq} = 0.5$, the same will decrease, i.e., the net flow will be $\mathbf{P} \rightarrow \mathbf{S}$.

13.3

Using steady-state approximation, we can write the following expressions for the absolute flows at each step:

$$\begin{aligned} J_0 &= k_a[E][S] - k_d[ES_1] \\ J_1 &= k_1[ES_1] \end{aligned}$$

$$J_2 = k_2[ES_2]$$

$$J_3 = k_3[ES_3]$$

At steady state, individual absolute flows J_i are equal to the general absolute flow J :

$J_0 = J_1 = J_2 = J_3 = J$. Each intermediate can be expressed as $[ES_i] = \frac{J}{k_i}$ ($i=1-3$). For the

considered reaction $\mathbf{S} \rightarrow \mathbf{P}$ under the given conditions, the general flow has the same value as the reaction rate v , which is defined as the rate of formation of product $\mathbf{P}$, thus,

$$j = \frac{v}{[E]_0} = \frac{J}{[E]_0} = k_{cat} \frac{[S]}{K_M + [S]}.$$

The concentration of an enzyme can be expressed as follows:

$$J = J_0 = k_a[E][S] - k_d[ES_1] = k_a[E][S] - k_d \frac{J}{k_1}$$

$$[E] = \frac{J + k_d \frac{J}{k_1}}{k_a[S]} = \frac{J}{k_a[S]} \left(\frac{k_1 + k_d}{k_1} \right)$$

From mass balance, it follows that:

$$[E]_0 = [E] + [ES_1] + [ES_2] + [ES_3]$$

$$[E]_0 = \frac{J}{k_a[S]} \left(\frac{k_1 + k_d}{k_1} \right) + \frac{J}{k_1} + \frac{J}{k_2} + \frac{J}{k_3} = J \left(\frac{1}{k_a[S]} \left(\frac{k_1 + k_d}{k_1} \right) + \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3} \right)$$

$$j = \frac{J}{[E]_0} = \frac{1}{\frac{1}{k_a[S]} \left(\frac{k_1 + k_d}{k_1} \right) + \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}} = \frac{\frac{1}{\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}} [S]}{\frac{k_1 + k_d}{k_a k_1} + [S]}$$

Considering the general form of the MM rate equation as:

$$j = \frac{J}{[E]_0} = k_{cat} \frac{[S]}{K_M + [S]}$$

It follows that:

$$k_{cat} = \frac{1}{\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}}$$

13.4

In case $K_M \gg [\text{chocolate}]$, the relative flow is the product of substrate concentration and catalytic efficiency ε :

$$j = k_{cat} \frac{[S]}{K_M + [S]} \approx k_{cat} \frac{[S]}{K_M} = \varepsilon[S]$$

In case $K_M \ll [\text{chocolate}]$, e.g., when Michi as the enzyme is completely “saturated” with chocolates as substrates, the relative flow becomes equal to the k_{cat} , i.e., turnover number (TON):

$$j = k_{cat} \frac{[S]}{K_M + [S]} \approx k_{cat} \frac{[S]}{[S]} = k_{cat} = \text{TON}$$

13.5

As there was a relatively big number of chocolates in the Magic Box, Michi can be treated as completely “saturated” with chocolates. Thus, the ratio of relative flows is equal to the ratio of $k_{cat,i}$. The fact that Michi produced n times more X chocolate papers than Y in one year implies that the ratio of flows is n as well:

$$\frac{j_X}{j_Y} = \frac{k_{cat,X}}{k_{cat,Y}} = n$$

The sum of Michi’s k_{cat} for X and Y is 2 week^{-1} , or $2 \cdot 52.5 = 105 \text{ year}^{-1}$, which means that he ate 105 chocolates in total in one year: $k_{cat,X} + k_{cat,Y} = 105 \text{ year}^{-1}$. Knowing that n is an integer two-digit number, there are only 3 valid options: a) $n = 102/3 = 34$; b) $n = 100/5 = 20$; c) $n = 98/7 = 14$.

Let’s consider that initially, there were $2m$ chocolates in the Magic Box, i.e., m chocolates of each brand. Considering the first option, the ratio between chocolates left in the Magic Box after one year:

$$\frac{N_Y}{N_X} = \frac{m-3}{m-102} = 1.150$$

From this equation, we obtain $m = 762$. Thus, the total initial number of chocolates in the Magic Box was $2m = 1524$. Other options don’t give integer values of m . That means that the ratio of chocolate papers and, therefore, flows is $n = 34$.

Solution - Enzymes that have Everything “in Order”

14.1

a) Rapid equilibrium for the formation of **EA**: $K_1 = \frac{[E][A]}{[EA]} \Rightarrow [E] = \frac{K_1}{[A]}[EA]$

Steady state for complex **EAB**:

$$\frac{d[EAB]}{dt} = 0 = k_2[EA][B] - (k_{-2} + k_3)[EAB]$$

$$[EAB] = \frac{k_2[EA][B]}{k_{-2} + k_3} \Rightarrow [EA] = \frac{k_{-2} + k_3}{k_2[B]}[EAB] \Rightarrow [E] = \frac{K_1(k_{-2} + k_3)}{k_2[A][B]}[EAB]$$

b) Using mass balance for enzyme:

$$[E]_0 = [E] + [EA] + [EAB] = \left(\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} + 1 \right) [EAB]$$

$$\alpha_{EAB} = \frac{[EAB]}{[E]_0} = \frac{1}{\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} + 1}$$

c) Initial rate of products formation:

$$v = k_3[EAB] = k_3\alpha_{EAB}[E]_0 = \frac{k_3[E]_0}{\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} + 1}$$

14.2

The statements:

a) If the concentration of **A** is kept constant (c_0), the initial rate increases with increasing $[B]$ and has a minimum value $v_{\min} = \underline{0 \text{ M}\cdot\text{s}^{-1}}$ and a maximum value ($v_{\max}$), which doesn't depend on c_0 .

b) If the concentration of **B** is kept constant (c_0), the initial rate increases with increasing $[A]$ and has a minimum value $v_{\min} = \underline{0 \text{ M}\cdot\text{s}^{-1}}$ and a maximum value ($v_{\max}$), which depends on c_0 .

14.3

Deriving the expressions for $v_{\max}$:

a) If $[A]$ is kept constant ($c_{A,0}$):

$$v = \frac{k_3[E]_0}{\frac{K_1(k_{-2} + k_3)}{k_2 c_{A,0}[B]} + \frac{k_{-2} + k_3}{k_2[B]} + 1} = \frac{k_3[E]_0}{\frac{k_{-2} + k_3}{k_2[B]} \left(\frac{K_1}{c_{A,0}} + 1 \right) + 1}$$

$$v_{\max} = v([B] \rightarrow \infty) = k_3[E]_0$$

b) If $[B]$ is kept constant ($c_{B,0}$):

$$v = \frac{k_3[E]_0}{\frac{K_1(k_{-2} + k_3)}{k_2[A]c_{B,0}} + \frac{k_{-2} + k_3}{k_2 c_{B,0}} + 1}$$

$$v_{\max} = v([A] \rightarrow \infty) = \frac{k_3[E]_0}{\frac{k_{-2} + k_3}{k_2 c_{B,0}} + 1}$$

14.4

Classical Michaelis–Menten equation for a substrate **S**:

$$v = \frac{v_{\max}[S]}{K_M + [S]} = \frac{v_{\max}}{\frac{K_M}{[S]} + 1}$$

a) Michaelis constant K_M if $[A]$ is kept constant (c_0):

$$v = \frac{k_3[E]_0}{\frac{k_{-2} + k_3}{k_2[B]} \left(\frac{K_1}{c_{A,0}} + 1 \right) + 1} = \frac{v_{\max}}{\frac{k_{-2} + k_3}{k_2[B]} \left(\frac{K_1}{c_{A,0}} + 1 \right) + 1} = \frac{v_{\max}}{\frac{K_M}{[B]} + 1}$$

$$K_M = \frac{k_{-2} + k_3}{k_2} \left(\frac{K_1}{c_{A,0}} + 1 \right)$$

b) From 3b follows: $k_3[E]_0 = v_{\max} \left(\frac{k_{-2} + k_3}{k_2 c_{B,0}} + 1 \right)$

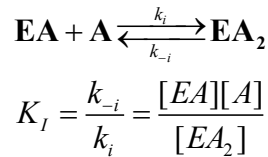
Michaelis constant K_M if $[B]$ is kept constant (c_0):

$$\begin{aligned}
v &= \frac{k_3[E]_0}{\frac{K_1(k_{-2} + k_3)}{k_2[A]c_{B,0}} + \left(\frac{k_{-2} + k_3}{k_2c_{B,0}} + 1\right)} = \frac{v_{\max} \left(\frac{k_{-2} + k_3}{k_2c_{B,0}} + 1\right)}{\frac{K_1(k_{-2} + k_3)}{k_2[A]c_{B,0}} + \left(\frac{k_{-2} + k_3}{k_2c_{B,0}} + 1\right)} = \frac{v_{\max}}{\frac{K_1(k_{-2} + k_3)}{k_2[A]c_{B,0}} \bigg/ \left(\frac{k_{-2} + k_3}{k_2c_{B,0}} + 1\right) + 1} = \\
&= \frac{v_{\max}}{\frac{K_1(k_{-2} + k_3)}{k_2[A]c_{B,0}} \bigg/ \frac{k_{-2} + k_3 + k_2c_{B,0}}{k_2c_{B,0}} + 1} = \frac{v_{\max}}{\frac{K_1(k_{-2} + k_3)}{k_2[A]c_{B,0}} \cdot \frac{k_2c_{B,0}}{k_{-2} + k_3 + k_2c_{B,0}} + 1} = \frac{v_{\max}}{\frac{K_1(k_{-2} + k_3)}{(k_{-2} + k_3 + k_2c_{B,0})[A]} + 1} = \frac{v_{\max}}{\frac{K_M}{[A]} + 1} \\
K_M &= \frac{K_1(k_{-2} + k_3)}{k_{-2} + k_3 + k_2c_{B,0}}
\end{aligned}$$

14.5

Substrate inhibition of **EA** with another molecule of **A** takes place (equilibrium is also assumed)

– one additional step:



14.6

Derivation of initial rate in case of substrate inhibition:

$$\begin{aligned}
[E] &= \frac{K_1(k_{-2} + k_3)}{k_2[A][B]}[EAB]; \quad [EA] = \frac{k_{-2} + k_3}{k_2[B]}[EAB]; \quad [EA_2] = \frac{[EA][A]}{K_I} \\
[E]_0 &= [E] + [EA] + [EA_2] + [EAB] = [EAB] \left(\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} \left(1 + \frac{[A]}{K_I} \right) + 1 \right) \\
\alpha_{EAB} &= \frac{[EAB]}{[E]_0} = \frac{1}{\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} \left(1 + \frac{[A]}{K_I} \right) + 1} \\
v &= k_3[EAB] = k_3\alpha_{EAB}[E]_0 = \frac{k_3[E]_0}{\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} \left(1 + \frac{[A]}{K_I} \right) + 1} = \frac{k_3[E]_0}{\frac{k_{-2} + k_3}{k_2[B]} \left(\frac{K_1}{[A]} + 1 + \frac{[A]}{K_I} \right) + 1}
\end{aligned}$$

In the case of a constant concentration of **B** ($[B]_0$), the expression for v has a maximum when

the denominator and, hence, $\frac{K_1}{[A]} + \frac{[A]}{K_I}$ is at a minimum. With a given hint, this happens when:

$$\frac{K_1}{[A]_{\max}} = \frac{[A]_{\max}}{K_I} \Rightarrow [A]_{\max} = \sqrt{K_1 K_I}$$

Thus, the maximum rate is:

$$v_{\max} = \frac{k_3[E]_0}{\frac{k_{-2} + k_3}{k_2[B]_0} \left(1 + 2\sqrt{\frac{K_1}{K_I}} \right) + 1}$$

And the constants:

$$v_{\max} = \frac{k_3[E]_0}{\frac{k_{-2} + k_3}{k_2[B]_0} \left(1 + 2\sqrt{\frac{K_1}{K_I}} \right) + 1} = \frac{k_3[E]_0}{\frac{\alpha}{[B]_0} (1 + 2\beta) + 1}$$

$$\alpha = \frac{k_{-2} + k_3}{k_2}, \quad \beta = \sqrt{\frac{K_1}{K_I}}$$

$^{16}\text{O}/^{18}\text{O}$ Isotope Exchange

15.1.

α is number of ^{18}O atoms divided by total number of all oxygen atoms

$$\alpha = \frac{f_{36} + \frac{1}{2}f_{34}}{f_{36} + f_{34} + f_{32}} = f_{36} + \frac{1}{2}f_{34}$$

15.2.

From $\alpha = f_{36} + \frac{1}{2}f_{34}$ can get $f_{36} = \alpha - \frac{1}{2}f_{34}$. Since $f_{36} + f_{34} + f_{32} = 1$,
 $f_{32} = 1 - f_{36} - f_{34} = 1 - \left(\alpha - \frac{1}{2}f_{34}\right) - f_{34} = 1 - \alpha - \frac{1}{2}f_{34}$

15.3.

$$\Delta_r G_{298}^0 = \Delta H_{298}^0 - 298 \cdot \Delta S_{298}^0 = -298 \text{ K} \cdot 11.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -3.43 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K = e^{\frac{-\Delta_r G_{298}^0}{RT}} = e^{\frac{-\Delta_r H_{298}^0}{RT}} \cdot e^{\frac{\Delta_r S_{298}^0}{R}} = e^0 \cdot e^{2\ln 2} = 4$$

The change in enthalpy is equal to zero. Therefore, at any temperature $K = e^{\frac{\Delta_r S_{298}^0}{R}} = 4$. Same conclusion originates from Chatelier's principle.

- ☐ The constant increases with increase in temperature.
- ☐ The constant decreases with increase in temperature.
- ☒ Temperature has no effect on the constant.

15.4.

In the course of reaction x mole of both $^{16}\text{O}_2$ and $^{18}\text{O}_2$ are transformed into $2 \cdot x$ mole of $^{16}\text{O}^{18}\text{O}$.

The total amount of oxygen remains constant and equal to 1 mole, therefore at equilibrium fraction of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ are equal to $0.5 - x$, fraction of $^{16}\text{O}^{18}\text{O}$ is equal to $2x$.

$$K = \frac{(f_{34}^{eq})^2}{f_{36}^{eq} \cdot f_{32}^{eq}} = \frac{(2x)^2}{(0.5 - x) \cdot (0.5 - x)} = 4$$

Taking square roots from both sides

$$2 = \frac{2x}{0.5 - x}; x = 0.25$$

$$f_{36} = f_{32} = 0.5 - 0.25 = 0.25; f_{34} = 0.25 \cdot 2 = 0.5$$

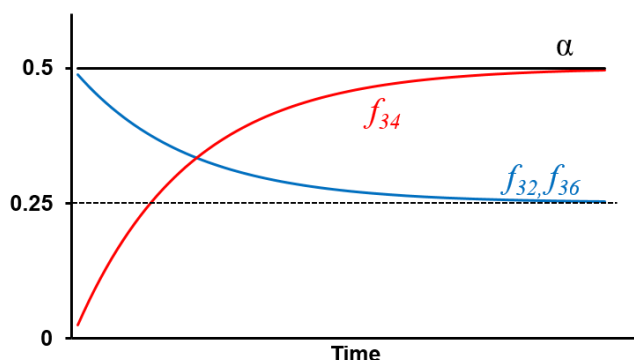
$$\alpha = \frac{N(^{18}\text{O})}{N(^{18}\text{O}) + N(^{16}\text{O})} = \frac{N(^{18}\text{O})}{N(^{18}\text{O}) + N(^{16}\text{O})} = \frac{0.25 \cdot 2 + 0.5 \cdot 1}{(0.25 \cdot 2 + 0.5 \cdot 1) + (0.5 \cdot 1 + 0.25 \cdot 2)} = 0.5$$

System at equilibrium contains 50% of $^{16}\text{O}^{18}\text{O}$, 25% of $^{16}\text{O}_2$ and 25% of $^{18}\text{O}_2$, $\alpha = 0.5$.

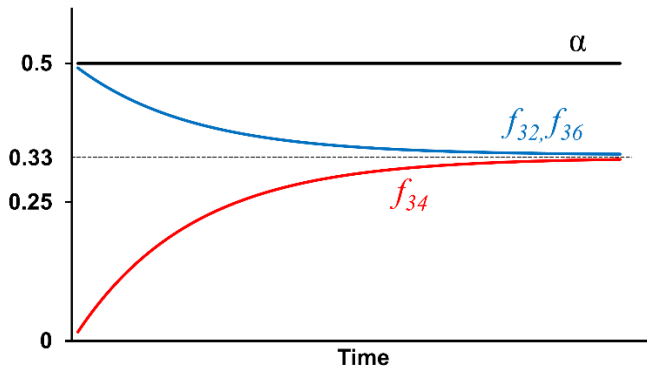
15.5.

α is constant during the experiment, while the second is differential equation for the first-order reaction and indicates that parameter f_{34} tends to f_{34}^{eq} exponentially. Simultaneously, f_{32} and f_{36} are exponentially decreasing to f_{32}^{eq} and f_{36}^{eq} .

For $f_{36} = f_{32} = 0.25$; $f_{34} = 0.5$ graph is the following:



For $f_{36}^{eq} = f_{34}^{eq} = f_{32}^{eq} = \frac{1}{3}$ the schematic graph will be the following:



15.6.

For the isotopologues containing exclusively one type of isotope in composition ($^{16}\text{O}_3$ and $^{18}\text{O}_3$) the only distribution of atoms in the structure exists, therefore the number of isotopomers is equal to one. For the isotopologues containing two isotopes of one sort and one isotope of another sort ($^{18}\text{O}^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}_2$) the “lonely” isotope can occupy position either in the center or on the edge. Therefore, for such isotopologues the number of possible isotopomers is equal to two.

$^{16}\text{O}_3$ -1, $^{18}\text{O}^{16}\text{O}_2$ -2, $^{16}\text{O}^{18}\text{O}_2$ -2, $^{18}\text{O}_3$ -1

isotopologue	number of isotopomers		
	1	2	3
$^{16}\text{O}_3$	x		
$^{18}\text{O}^{16}\text{O}_2$		x	
$^{16}\text{O}^{18}\text{O}_2$		x	
$^{18}\text{O}_3$	x		

15.7.

for $^{16}\text{O}_3$ $n = 3; m = 0; W(^{16}\text{O}_3) = C_0^3 = \frac{3!}{0!(3-0)!} = 1$

for $^{18}\text{O}^{16}\text{O}_2$ $n = 3; m = 1; W(^{18}\text{O}^{16}\text{O}_2) = C_1^3 = \frac{3!}{1!(3-1)!} = 3$

for $^{16}\text{O}^{18}\text{O}_2$ $n = 3; m = 2; W(^{16}\text{O}^{18}\text{O}_2) = C_2^3 = \frac{3!}{2!(3-2)!} = 3$

for $^{18}\text{O}_3$ $n = 3; m = 3; W(^{18}\text{O}_3) = C_3^3 = \frac{3!}{3!(3-3)!} = 1$

15.8.

$$\Delta_r S^0 = k_b \cdot \ln 3 + k_b \cdot \ln 3 - k_b \cdot \ln 1 - k_b \cdot \ln 1 = 2.97 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1} (17.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - 298 \cdot \Delta_r S_{298}^0 = -298 \text{ K} \cdot 17.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -5.33 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K = e^{\frac{-\Delta_r G_{298}^0}{RT}} = e^{\frac{-\Delta_r H_{298}^0}{RT}} \cdot e^{\frac{\Delta_r S_{298}^0}{R}} = e^0 \cdot e^{2 \ln 3} = 9$$

For calculation where $W=1$ for $^{16}\text{O}_3$ and $^{18}\text{O}_3$ and $W=4$ for other isotopologues

$$\Delta_r S^0 = k_b \cdot \ln 4 + k_b \cdot \ln 4 - k_b \cdot \ln 1 - k_b \cdot \ln 1 = 3.74 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1} (22.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - 298 \cdot \Delta_r S_{298}^0 = -298 \text{ K} \cdot 17.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -6.86 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K = e^{\frac{-\Delta_r G_{298}^0}{RT}} = e^{\frac{-\Delta_r H_{298}^0}{RT}} \cdot e^{\frac{\Delta_r S_{298}^0}{R}} = e^0 \cdot e^{2 \ln 4} = 16$$

Diffusion of Oxygen Isotopes

16.1.

$$\text{Before reaction: } n_{^{18}\text{O}_2} = \frac{pV}{RT} = \frac{0.52856 \cdot 10^5 \text{ Pa} \cdot 0.00150 \text{ m}^3}{8.3146 \frac{\text{J}}{\text{mol K}} \cdot 298.0 \text{ K}} = 0.03200 \text{ mol}; \rightarrow 0.06400 \text{ mol } ^{18}\text{O} \text{ present}$$

$$n_{\text{SmCoO}_3} = m / M = 0.4860 \text{ g} / 257.29 \text{ g/mol} = 0.001889 \text{ mol} \rightarrow 0.005667 \text{ mol Oxygen atoms present}$$

$$\text{After reaction: } n_{^{18}\text{O}_2} = \frac{pV}{RT} = \frac{0.5127 \cdot 10^5 \text{ Pa} \cdot 0.00150 \text{ m}^3}{8.3146 \frac{\text{J}}{\text{mol K}} \cdot 298.0 \text{ K}} = 0.03104 \text{ mol};$$

$$n_{^{16}\text{O}_2} = \frac{pV}{RT} = \frac{0.002640 \cdot 10^5 \text{ Pa} \cdot 0.00150 \text{ m}^3}{8.3146 \frac{\text{J}}{\text{mol K}} \cdot 298.0 \text{ K}} = 0.0001598 \text{ mol}; n_{^{18}\text{O}^{16}\text{O}} = \frac{m}{M} = \frac{0.02721 \text{ g}}{34 \frac{\text{g}}{\text{mol}}} = 0.0008003 \text{ mol};$$

$$\text{Number of exchanged oxygen atoms} = 0.06400 - 2 \cdot 0.03104 - 0.00080 = 0.00112 \text{ mol}$$

$$\text{Stoichiometric formula: } 0.00112 \text{ mol} / 0.001889 \text{ mol} = 0.593 \rightarrow \text{SmCo}^{16}\text{O}_{2.407}^{18}\text{O}_{0.593}$$

$$x = 2.407, y = 0.593$$

16.2.

Diffusion coefficient is proportional to $\frac{1}{\sqrt{M}}$, therefore heavier isotopologues have lower diffusion coefficients.

$$\checkmark \quad D(^{16}\text{O}_2) > D(^{16}\text{O}^{18}\text{O}) > D(^{18}\text{O}_2).$$

$$\square \quad D(^{18}\text{O}_2) > D(^{16}\text{O}^{18}\text{O}) > D(^{16}\text{O}_2).$$

$$\square \quad D(^{16}\text{O}_2) = D(^{16}\text{O}^{18}\text{O}) = D(^{18}\text{O}_2).$$

16.3.

$$t = \frac{L^2}{D} = \frac{\left(\sqrt[3]{\frac{3V}{4\pi}}\right)^2}{A \cdot \frac{1}{\sqrt{M}} \cdot \frac{T^{\frac{3}{2}}}{p}} = \frac{\left(\sqrt[3]{\frac{3 \cdot 1.5 \cdot 10^{-3}}{4\pi}}\right)^2 \text{ m}^2}{2.23 \cdot 10^{-3} \frac{1}{\sqrt{36}} \cdot \frac{298^{\frac{3}{2}}}{52856} \text{ m}^2 \cdot \text{s}^{-1}} = 1.96 \cdot 10^3 \text{ s}$$

16.4.

Wavenumber $\tilde{\nu} = \frac{\nu}{c} = \frac{\omega}{2\pi c}$, where c is the speed of light and ν the vibrational frequency in Hz

$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \rightarrow$ with k being equal for vibrations of both $^{16}\text{O}_2$ and $^{18}\text{O}_2$ and π and c being constants, one obtains:

$$\tilde{\nu}_{^{18}\text{O}_2} = \tilde{\nu}_{^{16}\text{O}_2} \cdot \sqrt{\frac{\mu_{^{16}\text{O}_2}}{\mu_{^{18}\text{O}_2}}} = \tilde{\nu}_{^{16}\text{O}_2} \cdot 0.9428$$

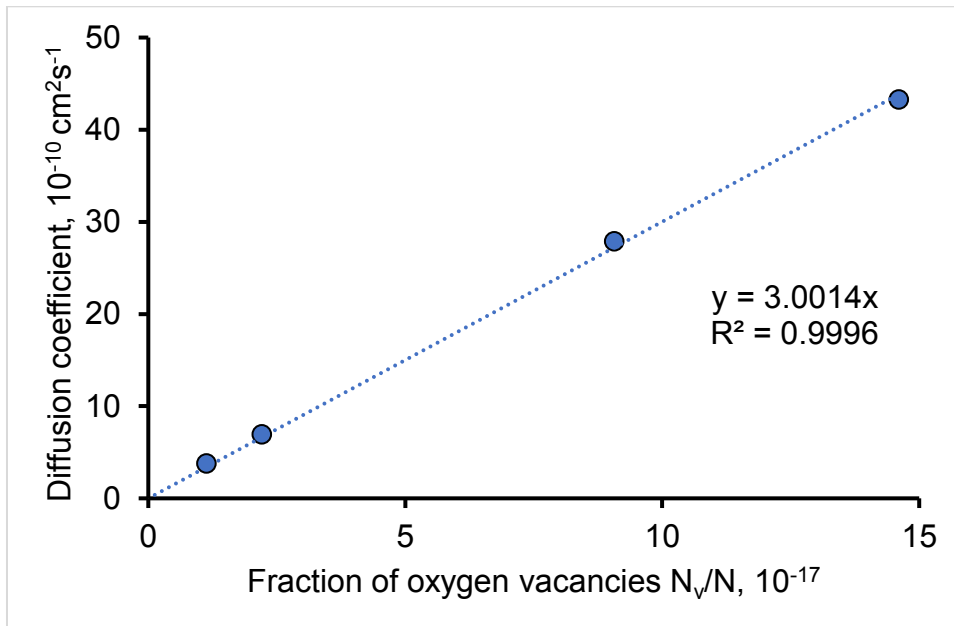
$$2237 \text{ cm}^{-1} \rightarrow 2109 \text{ cm}^{-1}$$

16.5.

$$0.005667 \text{ mol O atoms} = N \text{ (see exercise a). } N_v = N \cdot \exp\left(-\frac{Q_v}{RT}\right) = 3.308 \cdot 10^4 \text{ vacancies}$$

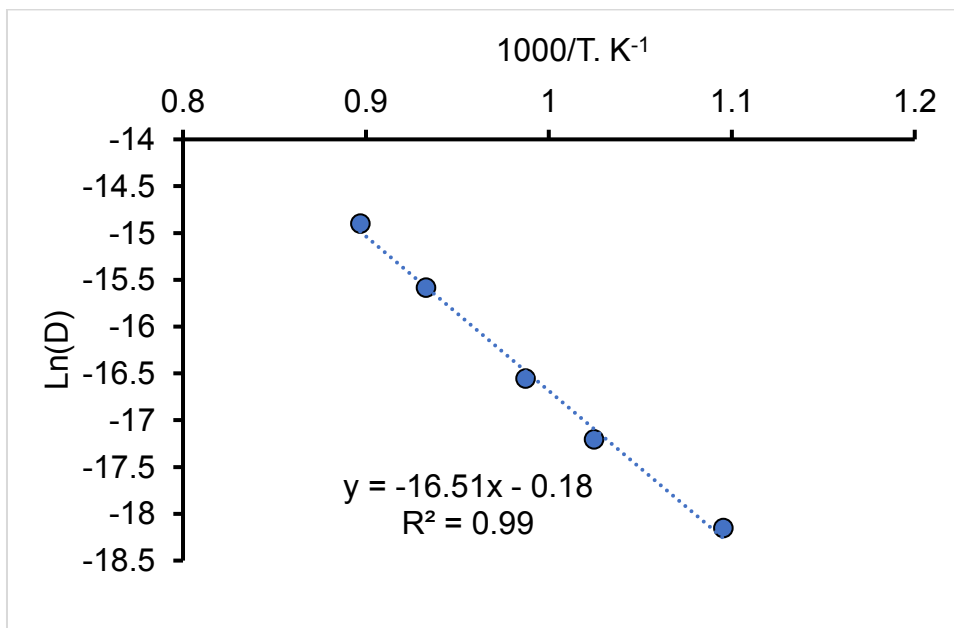
16.6.

First row to second, N_v / N increases by a factor of 1.799 and D by 1.83; first row to third – N_v / N increases by factor 7.398, D by 7.34; first row to fourth – N_v / N increases by factor 11.92, D by 11.4 → linear increase



Diffusion coefficient: $D = 3 \cdot 10^7 * \left(\frac{N_v}{N}\right)^1$

16.7.

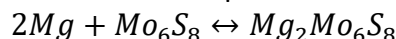


A linear regression of $\ln(D)$ with $1/T$ (in Kelvin) gave -16510.7 as a slope. $E_A = -\text{slope} * R = 137 \text{ kJ/mol}$.

Solution – A Cheaper Storage Battery

17.1

Total reaction equation:



The standard electromotive force (voltage) of the battery:

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0 = -1.3 V - (-2.4 V) = 1.1 V$$

The standard Gibbs energy of the reaction:

$$\Delta G^0 = -nFE_{cell}^0 = -4 \times 96485 C mol^{-1} \times 1.1 V = -424 kJ mol^{-1}$$

17.2

To answer the second part of the question, one should calculate the specific energy density of the described Mg-ion battery (in Wh kg⁻¹).

Let's assume that the battery is composed of 1 mol of Mo₆S₈ and 2 mol of Mg, which can deliver 4 mol of electrons (4 mol of electrons moves from Magnesium anode to Mo₆S₈ cathode). Therefore, the charge (in Ah), which can be delivered by this battery can be calculated as follows (considering that 1 Ah = 3600 C):

$$\frac{96485 C mol^{-1} \times 4 mol \times 1 Ah}{3600 C} = 107.2 Ah$$

Taking into account that the sum of masses of the Mg foil and Mo₆S₈ takes 50% of the total mass of the battery, one can calculate the mass of this battery:

$$\frac{M(Mg) g mol^{-1} \times 2 mol + M(Mo_6S_8) g mol^{-1} \times 1 mol}{0.5} = \frac{24.3 g mol^{-1} \times 2 mol + 832.1 g mol^{-1} \times 1 mol}{0.5} = 1761.44 g$$

$$= 1.76144 kg$$

Thus, the specific capacity of the discussed Mg-ion battery is $\frac{107.2 Ah \times 1 kg}{1.76144 kg} = 60.86 Ah kg^{-1}$ and its specific energy density is $60.86 Ah kg^{-1} \times 1.1 V = 66.95 Wh kg^{-1}$

Considering that energy density of Tesla powerwall Li-ion battery is 200 Wh kg⁻¹, the Mg-ion battery (which can store the same amount of energy) will be $\frac{200 Wh kg^{-1}}{60.86 Wh kg^{-1}} =$

3 times heavier.

17.3

$$\begin{aligned} & m(Mg \text{ foil used during discharge}) \\ &= \frac{m(Mo_6S_8) g}{M(Mo_6S_8) g mol^{-1}} \times M(Mg) g mol^{-1} \\ & \times n mol (\text{moles of Mg per 1 mol of } Mo_6S_8) \\ &= \frac{2.5 g}{832.12 g mol^{-1}} \times 24.3 g mol^{-1} \times 2 = 0.146 g \end{aligned}$$

$$V(Mg \text{ foil used during discharge}) = \frac{0.146 g}{1.738 g cm^{-3}} = 0.084 cm^3$$

$$\begin{aligned} & \text{Thickness (Mg foil used during discharge assuming that surface area of foil is } 100 cm^2) \\ &= \frac{0.084 cm^3}{100 cm^2} = 0.00084 cm = 8.4 \mu m \end{aligned}$$

Therefore, the thickness of the Mg foil, left after complete discharge of Mg-ion battery is 10 μm – 8.4 μm = 1.6 μm

17.4

Gravimetric specific capacity (in mAh g⁻¹) of Mo₆S₈

Considering that 1 mol of Mo₆S₈ can accept 4 mol of electrons, the electric charge, which can be accepted by 1 mol of Mo₆S₈ equals $4 \times F = 4 \text{ mol} \times 96485 \text{ C mol}^{-1} = 385940 \text{ C}$

1 Ah = 3600 C, thus the electric charge in Ah equals $\frac{1 \text{ Ah} \times 385940 \text{ C}}{3600 \text{ C}} = 107.2 \text{ Ah}$

Since $M(\text{Mo}_6\text{S}_8) = 832.12 \text{ g mol}^{-1}$, gravimetric specific capacity (in mAh g⁻¹) of Mo₆S₈ can be calculated as follows: $\frac{107.2 \text{ Ah mol}^{-1}}{832.12 \text{ g mol}^{-1}} = 0.129 \text{ Ah g}^{-1} = 129 \text{ mAh g}^{-1}$

Gravimetric specific capacity (in mAh g⁻¹) of Mg

Considering that 1 mol of Mg can release 2 mol of electrons, the electric charge, which can be released by 1 mol of Mg equals $2 \times F = 2 \text{ mol} \times 96485 \text{ C mol}^{-1} = 192970 \text{ C}$

1 Ah = 3600 C, thus, the electric charge in Ah equals $\frac{1 \text{ Ah} \times 385940 \text{ C}}{3600 \text{ C}} = 53.6 \text{ Ah}$

Since $M(\text{Mg}) = 24.3 \text{ g mol}^{-1}$, gravimetric specific capacity (in mAh g⁻¹) of Mg can be calculated as follows: $\frac{53.6 \text{ Ah mol}^{-1}}{24.3 \text{ g mol}^{-1}} = 2.206 \text{ Ah g}^{-1} = 2206 \text{ mAh g}^{-1}$

17.5

Solution 1:

Mg-ion battery has a total capacity of 500 mAh. This means that during discharge of this battery, 500 mAh of charge of electrons moves from Magnesium anode to Mo₆S₈ cathode. Considering that 1 Ah = 3600 C, one can calculate moles of electrons, which moves from anode to cathode:

$$\frac{3600 \text{ C} \times 0.5 \text{ Ah}}{1 \text{ Ah} \times F} = \frac{3600 \text{ C} \times 0.5 \text{ Ah}}{1 \text{ Ah} \times 96485 \text{ C mol}^{-1}} = 0.0187 \text{ mol}$$

Taking into account that 1 mol of Mg releases 2 moles of electrons and 1 mol of Mo₆S₈ accepts 4 moles of electrons, masses of Mg and Mo₆S₈ can be calculated as follows:

$$m(\text{Mg}) = \frac{0.0187 \text{ mol}}{2} \times M(\text{Mg}) \text{ g mol}^{-1} = \frac{0.0187 \text{ mol}}{2} \times 24.3 \text{ g mol}^{-1} = 0.227 \text{ g}$$

$$m(\text{Mo}_6\text{S}_8) = \frac{0.0187 \text{ mol}}{4} \times M(\text{Mo}_6\text{S}_8) \text{ g mol}^{-1} = \frac{0.0187 \text{ mol}}{4} \times 832.12 \text{ g mol}^{-1} = 3.9 \text{ g}$$

Since the battery was assembled with 10 wt% of excess of Mg, thus, the mass of Mg used in the battery is $0.227 + 0.227 \times 0.1 = 0.25 \text{ g}$

Total mass of the Mo₆S₈ and Mg is $3.9 \text{ g} + 0.25 \text{ g} = 4.15 \text{ g}$

Total mass of the battery = $4.15 / 0.5 = 8.3 \text{ g}$

Solution 2 (using previously calculated specific capacities of Mg and Mo₆S₈):

$$m(\text{Mo}_6\text{S}_8) = \frac{\text{Capacity of battery mAh}}{\text{specific capacity of Mo}_6\text{S}_8 \text{ mAh g}^{-1}} = \frac{500 \text{ mAh}}{129 \text{ mAh g}^{-1}} = 3.9 \text{ g}$$

To charge-balance the cathode half-reaction, one should take $m(\text{Mg}) = \frac{\text{Capacity of battery mAh}}{\text{specific capacity of Mg}} = \frac{500 \text{ mAh}}{2206 \text{ mAh g}^{-1}} = 0.227 \text{ g}$

Since the battery was assembled with 10 wt% of excess of Mg, thus, the mass of Mg used in the battery is $0.227 + 0.227 \times 0.1 = 0.25 \text{ g}$

Total mass of the Mo₆S₈ and Mg is $3.9 \text{ g} + 0.25 \text{ g} = 4.15 \text{ g}$

Total mass of the battery = $4.15 / 0.5 = 8.3 \text{ g}$

17.6

The analyzed Mg-ion battery has a total capacity of 500 mAh. This means that during discharge of this battery, 500 mAh of charge of electrons moves from Mg₃Bi₂ anode to Mo₆S₈ cathode.

Considering that $1\text{ Ah} = 3600\text{ C}$, one can calculate moles of electrons, which moves from anode to cathode:

$$\frac{3600\text{ C} \times 0.5\text{ Ah}}{1\text{ Ah} \times F} = \frac{3600\text{ C} \times 0.5\text{ Ah}}{1\text{ Ah} \times 96485\text{ C mol}^{-1}} = 0.0187\text{ mol}$$

Taking into account that 1 mol of Mg_3Bi_2 releases 6 moles of electrons and 1 mol of Mo_6S_8 accepts 4 moles of electrons, masses of Mg_3Bi_2 and Mo_6S_8 can be calculated as follows:

$$m(\text{Mg}) = \frac{0.0187\text{ mol}}{6} \times M(\text{Mg}_3\text{Bi}_2)\text{ g mol}^{-1} = \frac{0.0187\text{ mol}}{2} \times 490.88\text{ g mol}^{-1} = 1.53\text{ g}$$

$$m(\text{Mo}_6\text{S}_8) = \frac{0.0187\text{ mol}}{4} \times M(\text{Mo}_6\text{S}_8)\text{ g mol}^{-1} = \frac{0.0187\text{ mol}}{4} \times 832.12\text{ g mol}^{-1} = 3.9\text{ g}$$

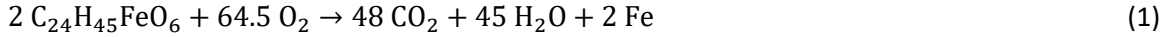
Total mass of the Mo_6S_8 and Mg_3Bi_2 is $3.9\text{ g} + 1.53\text{ g} = 5.43\text{ g}$

Total mass of the battery = $5.43 / 0.5 = 10.9\text{ g}$

Mass increase = $10.9\text{ g} - 8.3\text{ g} = 2.6\text{ g}$

Magnets Going Nano

18.1.



18.2. We first calculate the molecular weights and the amounts of both compounds fed into the flame:

$$\begin{aligned} M_{\text{Fe(2-EHA)}_3} &= 24 * M_{\text{C}} + 45 * M_{\text{H}} + M_{\text{Fe}} + 6 * M_{\text{O}} \\ &= 24 * 12.01 \frac{\text{g}}{\text{mol}} + 45 * 1.008 \frac{\text{g}}{\text{mol}} + 55.85 \frac{\text{g}}{\text{mol}} + 6 * 16.00 \frac{\text{g}}{\text{mol}} \\ &= 485.45 \frac{\text{g}}{\text{mol}} \end{aligned}$$

$$M_{\text{THF}} = 4 * M_{\text{C}} + 8 * M_{\text{H}} + M_{\text{O}} = 4 * 12.01 \frac{\text{g}}{\text{mol}} + 8 * 1.008 \frac{\text{g}}{\text{mol}} + 16.00 \frac{\text{g}}{\text{mol}} = 72.10 \frac{\text{g}}{\text{mol}}$$

$$\dot{n}_{\text{Fe(2-EHA)}_3} = \frac{\dot{m}_{\text{Fe(2-EHA)}_3}}{M_{\text{Fe(2-EHA)}_3}} = \frac{2.7 \text{ g/min}}{485.45 \text{ g/mol}} = 5.56 * 10^{-3} \text{ mol/min}$$

$$\dot{n}_{\text{THF}} = \frac{\dot{m}_{\text{THF}}}{M_{\text{THF}}} = \frac{1.8 \text{ g/min}}{72.10 \text{ g/mol}} = 25.0 * 10^{-3} \text{ mol/min}$$

The stoichiometric amount of O_2 based on feeds and reaction equations in task 1 are:

$$\dot{n}_{\text{O}_2,(1)} = \frac{\nu_{\text{O}_2,(1)}}{\nu_{\text{Fe(2-EHA)}_3,(1)}} * \dot{n}_{\text{Fe(2-EHA)}_3} = \frac{64.5}{2} * 5.56 * 10^{-3} \text{ mol/min} = 0.179 \text{ mol/min}$$

$$\dot{n}_{\text{O}_2,(2)} = \frac{\nu_{\text{O}_2,(2)}}{\nu_{\text{THF,(2)}}} * \dot{n}_{\text{THF}} = \frac{5.5}{1} * 25.0 * 10^{-3} \text{ mol/min} = 0.138 \text{ mol/min}$$

$$\dot{n}_{\text{O}_2} = \dot{n}_{\text{O}_2,(1)} + \dot{n}_{\text{O}_2,(2)} = 0.317 \text{ mol/min}$$

Using the hint, the same total is found:

$$\dot{n}_{\text{O}_2,(1)} = \frac{\nu_{\text{O}_2,(1)}}{\nu_{\text{Fe(2-EHA)}_3,(1)}} * \dot{n}_{\text{Fe(2-EHA)}_3} = 30 * 5.56 * 10^{-3} \text{ mol/min} = 0.167 \text{ mol/min}$$

$$\dot{n}_{\text{O}_2,(2)} = \frac{\nu_{\text{O}_2,(2)}}{\nu_{\text{THF,(2)}}} * \dot{n}_{\text{THF}} = 6 * 25.0 * 10^{-3} \text{ mol/min} = 0.150 \text{ mol/min}$$

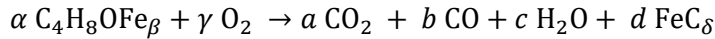
$$\dot{n}_{\text{O}_2} = \dot{n}_{\text{O}_2,(1)} + \dot{n}_{\text{O}_2,(2)} = 0.317 \text{ mol/min}$$

The required volume feed of oxygen can then be calculated from the ideal gas law:

$$\dot{V}_{\text{O}_2} = \frac{\dot{n}_{\text{O}_2} * R * T}{p} = \frac{0.317 \text{ mol/min} * 8.3145 \text{ J/mol/K} * 298 \text{ K}}{10^5 \text{ Pa}} = 7.85 * 10^{-3} \frac{\text{m}^3}{\text{min}} = 7.85 \frac{\text{L}}{\text{min}}$$

The same result can be obtained by performing the calculation for a fixed time interval, e.g. 1 min.

18.3. To formulate the solution, four variables $\alpha = 1$, $\beta = 0.07$, $\gamma = 3.87$, and $\delta = 0.24$ are introduced:



This defines the following systems of equations based on the atom balance and the hint:

$$4 * \alpha = a + b + d * \delta \quad \text{C balance}$$

$$8 * \alpha = 2 * c \quad \text{H balance}$$

$$\alpha + 2 * \gamma = 2 * a + b + c \quad \text{O balance}$$

$$\alpha * \beta = d \quad \text{Fe balance}$$

The system of equations can unambiguously be solved:

$$c = \frac{8}{2} * \alpha = \frac{8}{2} * 1 = 4 \quad \text{By H balance}$$

$$d = \alpha * \beta = 1 * 0.07 = 0.07 \quad \text{By Fe balance}$$

$$\begin{aligned} a &= -3 * \alpha + 2 * \gamma - c + d * \delta \\ &= -3 * 1 + 2 * 3.87 - 4 + 0.07 * 0.24 = 0.757 \quad \text{By subtracting C balance from O balance} \end{aligned}$$

$$b = 4 * \alpha - a - d * \delta = 4 * 1 - 0.757 - 0.07 * 0.24 = 3.23 \quad \text{By C balance}$$

The CO_2 to CO ratio is then calculated as:

$$a/b = 0.757/3.23 = 0.234$$

which corresponds to $\text{CO}_2 : \text{CO} = 19 : 81$.

The same result may be obtained by omitting the particles since their contribution to the C balance ($0.07 * 0.24 = 0.02$) is negligible.

18.4. The stoichiometric of the particles produced in task 3 is $\text{FeC}_{0.24}$. Its carbon mass fraction is calculated as:

$$\text{wt}\%_{\text{C}} = \frac{0.24 * MW_{\text{C}}}{MW_{\text{Fe}} + 0.24 * MW_{\text{C}}} = \frac{0.24 * 12.01 \frac{\text{g}}{\text{mol}}}{55.85 \frac{\text{g}}{\text{mol}} + 0.24 * 12.01 \frac{\text{g}}{\text{mol}}} = 4.90\%$$

Therefore, the correct answer is: "The particles are comprised of γ -iron and iron carbide."

- 18.5. Based on the information provided for task 4, $wt\%_{C,avg} = 9.4 \%$ corresponds to carbon-coated iron carbide particles. The core volume is calculated as:

$$V_{core} = \frac{4}{3} \cdot \pi \cdot r_{core}^3 = \frac{4}{3} \cdot \pi \cdot (30.0 \text{ nm})^3 = 113100 \text{ nm}^3$$

The average carbon mass fraction of the whole particles can be expressed as:

$$wt\%_{C,avg} = \frac{wt\%_{C,core} \cdot \rho_{core} \cdot V_{core} + wt\%_{C,shell} \cdot \rho_{shell} \cdot V_{shell}}{\rho_{core} \cdot V_{core} + \rho_{shell} \cdot V_{shell}}$$

Solving for V_{shell} gives:

$$V_{shell} = \frac{\rho_{core}}{\rho_{shell}} \cdot \frac{wt\%_{C,avg} - wt\%_{C,core}}{wt\%_{C,shell} - wt\%_{C,avg}} \cdot V_{core} = \frac{7.69 \frac{g}{cm^3}}{2.26 \frac{g}{cm^3}} \cdot \frac{0.094 - 0.067}{1.000 - 0.094} \cdot 113100 \text{ nm}^3 = 11500 \text{ nm}^3$$

The total volume of a particle is then:

$$V_{particle} = V_{core} + V_{shell} = 113100 \text{ nm}^3 + 11500 \text{ nm}^3 = 124600 \text{ nm}^3$$

- 18.6. The carbon shell thickness can be obtained by subtracting the core radius from the radius of the total particle:

$$r_{total} = \sqrt[3]{\frac{V_{particle}}{\frac{4}{3}\pi}} = \sqrt[3]{\frac{124600 \text{ nm}^3}{\frac{4}{3}\pi}} = 31.0 \text{ nm}$$

$$d_{shell} = r_{total} - r_{core} = 31.0 \text{ nm} - 30.0 \text{ nm} = 1.0 \text{ nm}$$

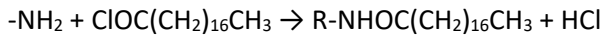
Using the hint, $r_{total} = 32.0 \text{ nm}$ and $d_{shell} = 2.0 \text{ nm}$ is obtained.

- 18.7. The number of graphene layers is obtained as:

$$n_{layer} = \frac{d_{shell}}{d_{graphite}} = \frac{1.0 \text{ nm}}{0.335 \text{ nm}} = 3.0$$

Using the hint on either task 6 or 7, $n_{layer} = 6.0$ is obtained.

- 18.8.



R

18.9. The loading of H and N before and after the reaction can be calculated as:

$$q_{NH_2,before} = \frac{wt\%_{N,before}}{MW_N} = \frac{1.6 \frac{mg}{g}}{14.01 \frac{g}{mol}} = 0.11 \frac{mmol}{g}$$

$$q_{H,before} = \frac{wt\%_{H,before}}{MW_H} = \frac{0.2 \frac{mg}{g}}{1.01 \frac{g}{mol}} = 0.20 \frac{mmol}{g}$$

$$q_{H,after} = \frac{wt\%_{H,before}}{MW_H} = \frac{3.1 \frac{mg}{g}}{1.01 \frac{g}{mol}} = 3.07 \frac{mmol}{g}$$

Using the reaction equation found in task 8, the yield can be calculated based on the increase in the loading of H due to bound stearyl amide:

$$\begin{aligned} yield &= \frac{q_{amide,after}}{q_{NH_2,before}} = \frac{(q_{H,after} - q_{H,before})/34}{q_{NH_2,before}} \\ &= \frac{\left(3.07 \frac{mmol}{g} - 0.20 \frac{mmol}{g}\right)/34}{0.11 \frac{mmol}{g}} = 77 \% \end{aligned}$$

18.10. The specific surface area of the particles prior to functionalization is:

$$\begin{aligned} SSA &= \frac{A_{particle}}{m_{particle}} = \frac{4 \cdot \pi \cdot r_{total}^2}{\rho_{core} \cdot V_{core} + \rho_{shell} \cdot V_{shell}} \\ &= \frac{4 \cdot \pi \cdot (31.0 \text{ nm})^2}{7.69 \frac{g}{cm^3} \cdot \left(\frac{1 \text{ cm}}{10^7 \text{ nm}}\right)^3 \cdot 113100 \text{ nm}^3 + 2.26 \frac{g}{cm^3} \cdot \left(\frac{1 \text{ cm}}{10^7 \text{ nm}}\right)^3 \cdot 11500 \text{ nm}^3} \\ &= 1.35 \cdot 10^{19} \text{ nm}^2/\text{g} \end{aligned}$$

Accordingly, the amine loading can be expressed as a coverage instead:

$$\alpha_{NH_2} = \frac{q_{NH_2,before} \cdot N_A}{SSA} = \frac{0.11 \cdot 10^{-3} \frac{mol}{g} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1}}{1.35 \cdot 10^{19} \frac{nm^2}{g}} = 4.91 \text{ nm}^{-2}$$

Predicting Indices

- 19.1. Starting from $t_6 = 100$ s, all retention times can be calculated by iterative multiplication with factor $f = 1.6$:

$$t_7 = 1.6 * t_6 = 1.6 * 100 \text{ s} = 160 \text{ s}$$

$$t_8 = 1.6 * t_7 = 1.6 * 160 \text{ s} = 256 \text{ s}$$

$$t_9 = 1.6 * t_8 = 1.6 * 256 \text{ s} = 410 \text{ s}$$

$$t_{10} = 1.6 * t_9 = 1.6 * 410 \text{ s} = 655 \text{ s}$$

Given the multiplicative nature, the formula $\log(t_n) = a * n + b$ can be assumed. Using any two data points, the following relationship can be found:

$$\log(t_n) = 0.204 * n + 0.775$$

- 19.2. Subtracting two consecutive data points, the following formula can be found:

$$\log(t_{n+1}) = \log(t_n) + 0.204$$

- 19.3. Based on the retention time, the leading and trailing n -alkanes are C_7H_{16} and C_8H_{18} , respectively. Using the formula, the retention index can be calculated:

$$R_X = 100 * n + \frac{\log(t_X/t_7)}{\log(t_8/t_7)} = 100 * 7 + \frac{\log(200 \text{ s}/160 \text{ s})}{\log(256 \text{ s}/160 \text{ s})} = 747.5$$

- 19.4. Using the formula, the retention time can be calculated:

$$t'_X = \frac{t'_8 - t'_7}{100} * (R'_X - 100 * n) + t'_7 = \frac{200 \text{ s} - 180 \text{ s}}{100} * (747.5 - 100 * 7) + 180 \text{ s} = 189.5 \text{ s}$$

Using the hint, $t_X = 184.0$ s is found instead.

- 19.5. $(C_{15}H_{31}CO_2)_3C_3H_5 + 3 C_2H_5OH \rightarrow 3 C_{15}H_{31}CO_2C_2H_5 + C_3H_8O_3$

- 19.6. The linear series is 16.43, 17.38, 18.33, 19.28, and 20.23 min where the retention times correspond to the formula: $t''_{n+1} = t''_n + 0.95$. They correspond to the n -alkanes with C_{18} to C_{22} .

Thus, the retention indices of the three other peaks are:

$$18.13 \text{ min: } R'' = 1900 + 100 * (18.13 - 17.33)/(18.33 - 17.38) = 1979$$

$$19.75 \text{ min: } R'' = 2100 + 100 * (19.75 - 19.28)/(20.23 - 19.28) = 2149$$

$$19.99 \text{ min: } R'' = 2100 + 100 * (19.99 - 19.28)/(20.23 - 19.28) = 2175$$

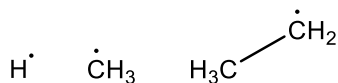
The peaks at 18.13 min and at 19.99 min have retention indexes 1979 and 2175, which are "exactly" 200 in difference: they belong to the same family of saturated ethyl n -carboxylates. Using rule 2), they are ethyl palmitate ($C_{15}H_{31}CO_2C_2H_5$) and ethyl stearate ($C_{17}H_{35}CO_2C_2H_5$).

Based on rules 1) and 2), the peak at 19.75 min is neither an n -alkane nor a saturated ethyl n -carboxylate. As its retention index is 29 less than ethyl stearate, it corresponds to ethyl oleate ($(CH_3(CH_2)_7CH=CH(CH_2)_7CO_2C_2H_5$, exact location of double bond not important) based on rule 3).

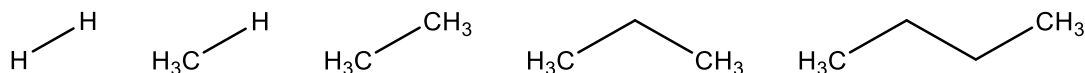
Breaking Alkanes Apart

20.1. As the three possible fragments are $\text{H}^\bullet$, $\text{CH}_3^\bullet$, and $\text{C}_2\text{H}_5^\bullet$, four new molecules can be produced by recombination in the ethane radiolysis. Ethane can also be reformed.

Fragments:



Products:



20.2. As ethane contains 6 C–H bonds and 1 C–C bond, the probability of forming $\text{H}^\bullet + \text{C}_2\text{H}_5^\bullet$ is $6/7$ and the probability of forming $2 \text{CH}_3^\bullet$ is $1/7$. For a large number n of molecules, the number of radicals and their probability can be calculated:

Species	Number	Probability
$\text{H}^\bullet$	$6n/7$	$(6n/7)/2n = 3/7$
$\text{CH}_3^\bullet$	$2n/7$	$(2n/7)/2n = 1/7$
$\text{C}_2\text{H}_5^\bullet$	$6n/7$	$(6n/7)/2n = 3/7$
Total	$14n/7 = 2n$	1

20.3. Using the provided formulae, the product distribution can be calculated by accounting for all recombination possibilities:

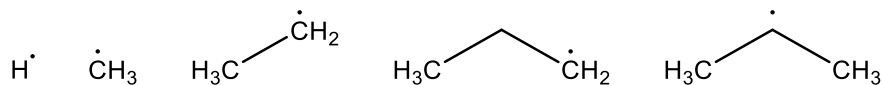
Product	Recombination of	Probability	Using hint
H_2	$\text{H}^\bullet + \text{H}^\bullet$	$(3/7) * (3/7) = 9/49$	$(1/4) * (1/4) = 1/16$
CH_4	$\text{H}^\bullet + \text{CH}_3^\bullet$	$2 * (3/7) * (1/7) = 6/49$	$2 * (1/4) * (2/4) = 4/16$
C_2H_6	$\text{H}^\bullet + \text{C}_2\text{H}_5^\bullet$	$2 * (3/7) * (3/7) = 18/49$	$2 * (1/4) * (1/4) = 2/16$
C_2H_6	$\text{CH}_3^\bullet + \text{CH}_3^\bullet$	$(1/7) * (1/7) = 1/49$	$(2/4) * (2/4) = 4/16$
C_3H_8	$\text{CH}_3^\bullet + \text{C}_2\text{H}_5^\bullet$	$2 * (1/7) * (3/7) = 6/49$	$2 * (2/4) * (1/4) = 4/16$
C_4H_{10}	$\text{C}_2\text{H}_5^\bullet + \text{C}_2\text{H}_5^\bullet$	$(3/7) * (3/7) = 9/49$	$(1/4) * (1/4) = 1/16$
Total		1	1

Thus, the ratio of all formed products is obtained by adding the recombination pathways for individual products and dividing by the lowest probability:

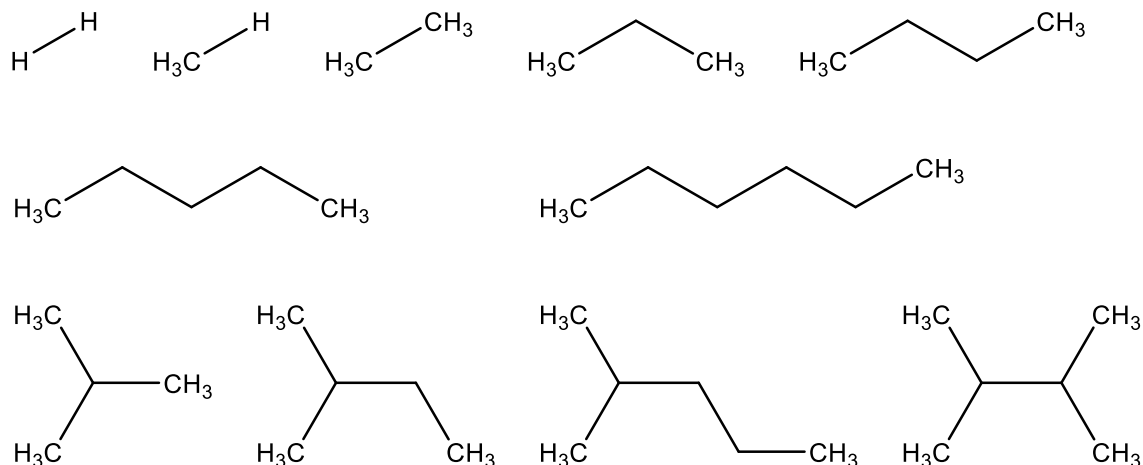
Product	Ratio	Using hint
H_2	9	1
CH_4	6	4
C_2H_6	19	6
C_3H_8	6	4
C_4H_{10}	9	1

- 20.4. As the five possible fragments are $\text{H}^\bullet$, $\text{CH}_3^\bullet$, $\text{C}_2\text{H}_5^\bullet$, $1\text{-C}_3\text{H}_7^\bullet$, and $2\text{-C}_3\text{H}_7^\bullet$, 10 new molecules can be produced by recombination in the propane radiolysis. Propane can also be reformed.

Fragments:



Products:



- 20.5. It can be deduced that the least likely product must result from the symmetric combination of one of the least likely radicals. This leaves only C_2H_6 , C_4H_{10} , and $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ as candidates. Since C_2H_6 and C_4H_{10} can also be obtained by other pathways, the most branched product $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ is the least likely product.

It can be concluded that the reformation of propane gives the most likely product. The same conclusions can be reached by explicit calculation (see below).

- 20.6. As propane contains 6 $\text{C}_{\text{prim}}\text{-H}$ bonds, 2 $\text{C}_{\text{sec}}\text{-H}$ bonds, and 2 C-C bonds, their ruptures produced 20 fragments (assuming equal probability):

Rupture	Number of ... radicals formed				
	$\text{H}^\bullet$	$\text{CH}_3^\bullet$	$\text{C}_2\text{H}_5^\bullet$	$1\text{-C}_3\text{H}_7^\bullet$	$2\text{-C}_3\text{H}_7^\bullet$
6 $\text{C}_{\text{prim}}\text{-H}$	6	0	0	6	0
2 $\text{C}_{\text{sec}}\text{-H}$	2	0	0	0	2
2 C-C	0	2	2	0	0

For a large number n of molecules, the number of radicals and their probability can be calculated:

Species	Number	Probability
$\text{H}^\bullet$	$8n/10$	$(8n/10)/2n = 4/10$
$\text{CH}_3^\bullet$	$2n/10$	$(2n/10)/2n = 1/10$
$\text{C}_2\text{H}_5^\bullet$	$2n/10$	$(2n/10)/2n = 1/10$
$1\text{-C}_3\text{H}_7^\bullet$	$6n/10$	$(6n/10)/2n = 3/10$
$2\text{-C}_3\text{H}_7^\bullet$	$2n/10$	$(2n/10)/2n = 1/10$

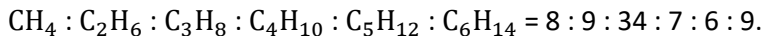
Total	$20n/10 = 2n$	1
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Similar to task 3, the product distribution can be calculated by accounting for all recombination possibilities:

Product	Recombination of	Probability
H ₂	H [•] + H [•]	$(4/10) * (4/10) = 16/100$
CH ₄	H [•] + CH ₃ [•]	$2 * (4/10) * (1/10) = 8/100$
C ₂ H ₆	H [•] + C ₂ H ₅ [•]	$2 * (4/10) * (1/10) = 8/100$
C ₃ H ₈	H [•] + 1-C ₃ H ₇ [•]	$2 * (4/10) * (3/10) = 24/100$
C ₃ H ₈	H [•] + 2-C ₃ H ₇ [•]	$2 * (4/10) * (1/10) = 8/100$
C ₂ H ₆	CH ₃ [•] + CH ₃ [•]	$(1/10) * (1/10) = 1/100$
C ₃ H ₈	CH ₃ [•] + C ₂ H ₅ [•]	$2 * (1/10) * (1/10) = 2/100$
C ₄ H ₁₀	CH ₃ [•] + 1-C ₃ H ₇ [•]	$2 * (1/10) * (3/10) = 6/100$
(CH ₃) ₂ CHCH ₃	CH ₃ [•] + 2-C ₃ H ₇ [•]	$2 * (1/10) * (1/10) = 2/100$
C ₄ H ₁₀	C ₂ H ₅ [•] + C ₂ H ₅ [•]	$(1/10) * (1/10) = 1/100$
C ₅ H ₁₂	C ₂ H ₅ [•] + 1-C ₃ H ₇ [•]	$2 * (1/10) * (3/10) = 6/100$
(CH ₃) ₂ CHCH ₂ CH ₃	C ₂ H ₅ [•] + 2-C ₃ H ₇ [•]	$2 * (1/10) * (1/10) = 2/100$
C ₆ H ₁₄	1-C ₃ H ₇ [•] + 1-C ₃ H ₇ [•]	$(3/10) * (3/10) = 9/100$
(CH ₃) ₂ CHCH ₂ CH ₂ CH ₃	1-C ₃ H ₇ [•] + 2-C ₃ H ₇ [•]	$2 * (3/10) * (1/10) = 6/100$
(CH ₃) ₂ CHCH(CH ₃) ₂	2-C ₃ H ₇ [•] + 2-C ₃ H ₇ [•]	$(1/10) * (1/10) = 1/100$
Total		1

Product	Ratio
H ₂	16
CH ₄	8
C ₂ H ₆	9
C ₃ H ₈	34
C ₄ H ₁₀	7
C ₅ H ₁₂	6
C ₆ H ₁₄	9
(CH ₃) ₂ CHCH ₃	2
(CH ₃) ₂ CHCH ₂ CH ₃	2
(CH ₃) ₂ CHCH ₂ CH ₂ CH ₃	6
(CH ₃) ₂ CHCH(CH ₃) ₂	1

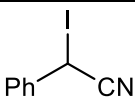
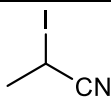
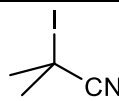
The formed *n*-alkanes are in the proportions:



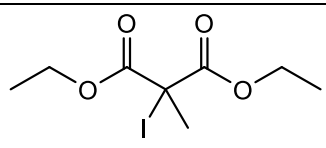
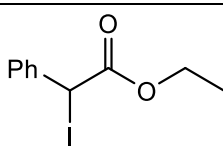
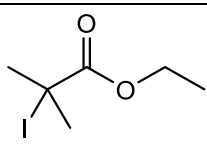
Solution: Quite Radical

21.1

a)

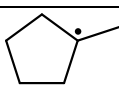
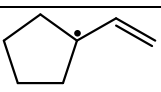
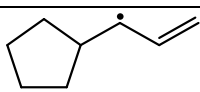
		
3	1	2

b)

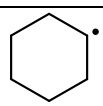
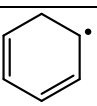
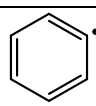
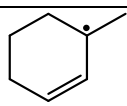
		
3	2	1

21.2

a)

			
2	4	3	1

b)

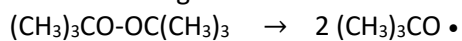
			
2	4	1	3

21.3

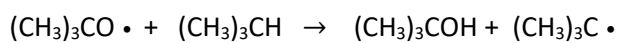
The reactivity of tert., sec. and prim. H-atoms decreases in the order tert > sec > prim with the ratio 5:4:1. Thus by multiplying the reactivity with the number of H atoms of the four different types you can calculate the product ratio. Thus: 1-chloro-2-methylbutane 27.3; 2-chloro-2-methylbutane 22.7 %; 2-chloro-3-methylbutane. 36.4%; and 1-chloro-3-methylbutane 13.6%.

21.4

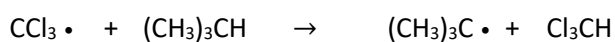
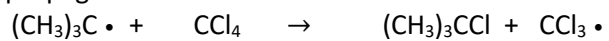
1. step: radical forming



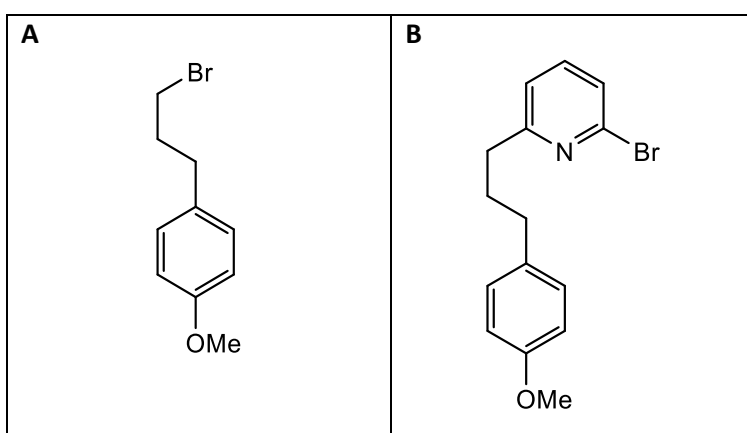
2. step:



3. step: propagation



21.5

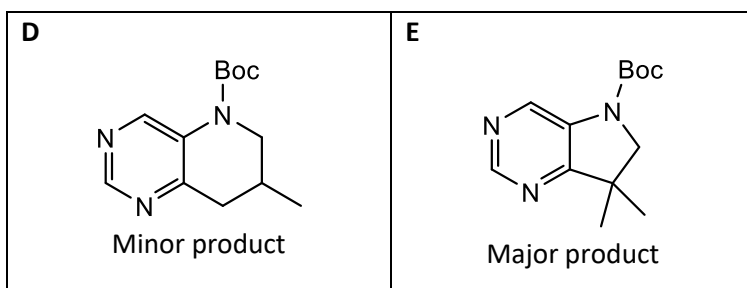


Starting molecule to **A**: radical hydrobromination

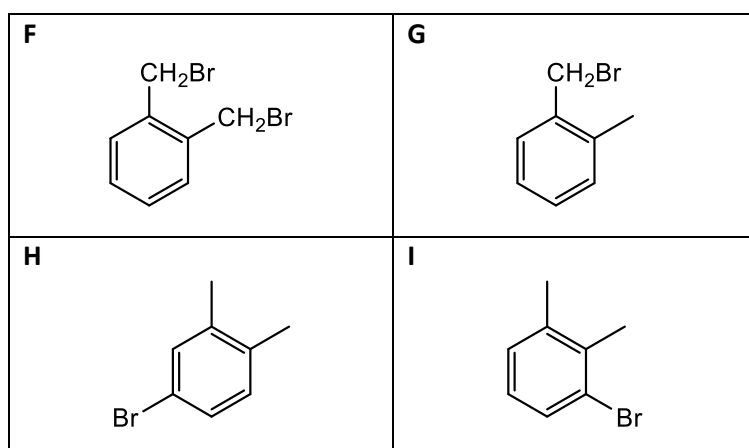
A to **B**: formation of alkyl zinc bromide (RZnBr), cross coupling (Negishi reaction)

B to final product: transition metal catalyzed C-O coupling (Ullmann type reaction), – HBr

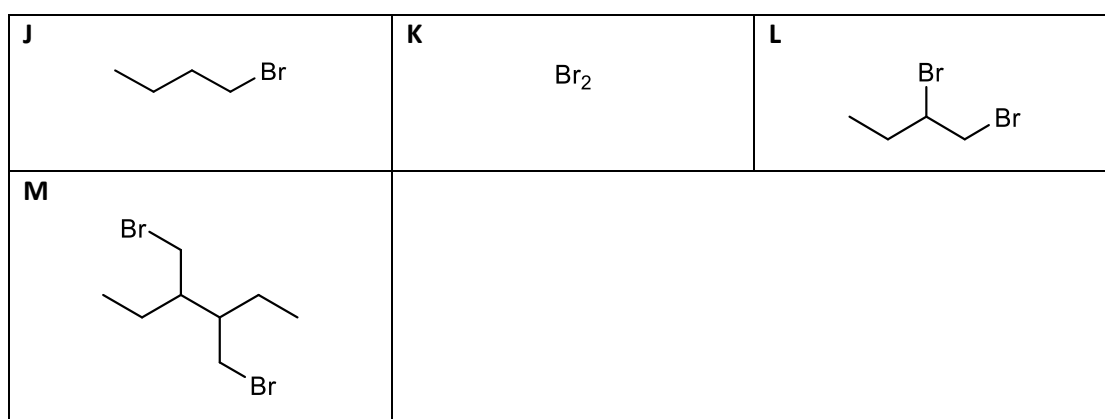
21.6



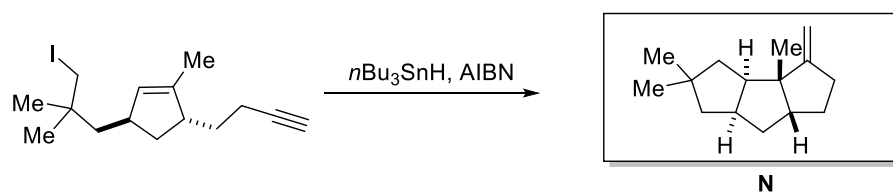
21.7



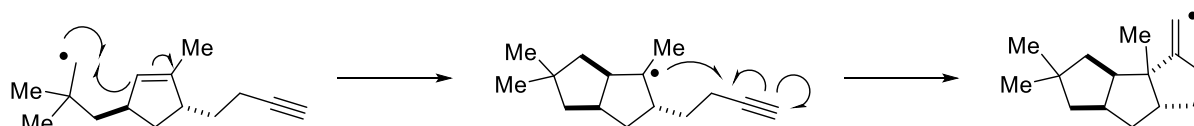
21.8



21.9



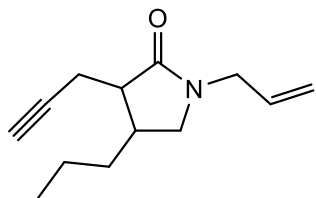
via



Solution - Enabling Electricity

22.1

A

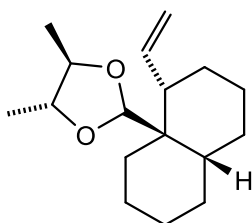


22.2

$$\text{moles of } e^- = x * 2 * \frac{100\%}{29\%} = 0.0028 \text{ mol} * 2 * \frac{100}{29} = 0.0193 \text{ mol}$$
$$Q = F * 0.00193 \text{ mol} = 96485.33 \frac{\text{C}}{\text{mol}} * 0.00193 \text{ mol} = 1863.16 \text{ C}$$

22.3

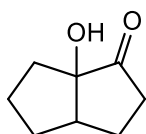
B



cyclisation by anodic oxidation

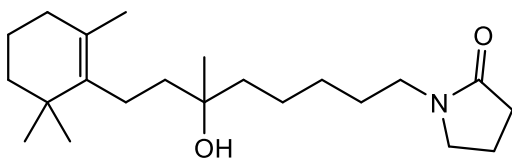
22.4

C

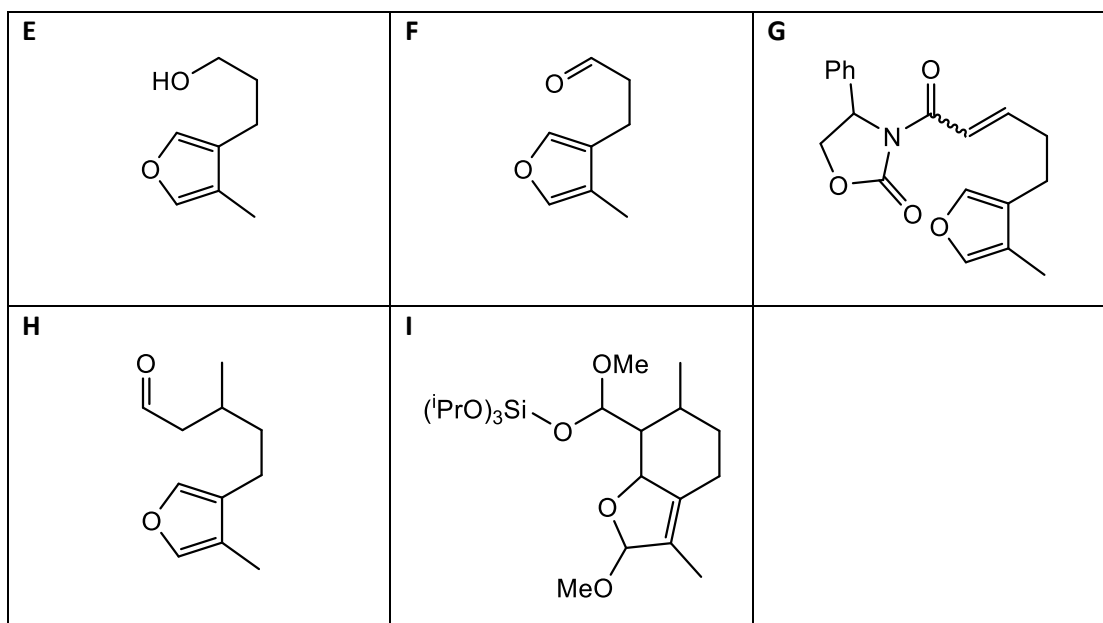


22.5

D



22.6



Reaction from **F** to **G** is a Wittig type reaction (HWE-reaction)

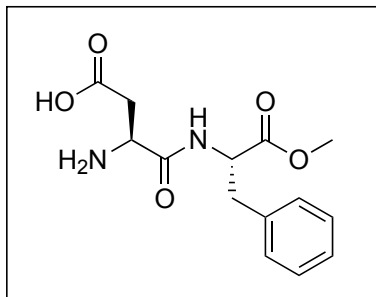
To **H**: splitting of the amide bond by DIBAL-H

H to the given formula is a protective silylation of the enol

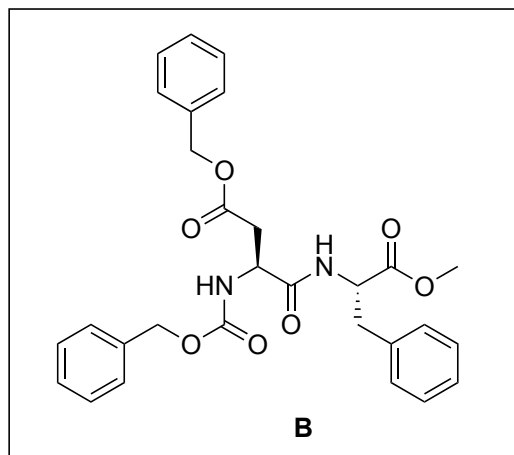
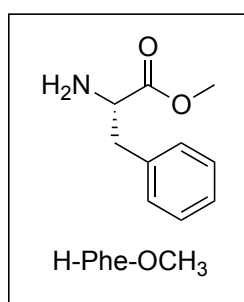
Final step: oxidative ring closure and radical capture by methanol

Solution – A Sweet Introduction to Peptides

23.1



23.2



Code for compound **A** using the three-letter amino acid notation:

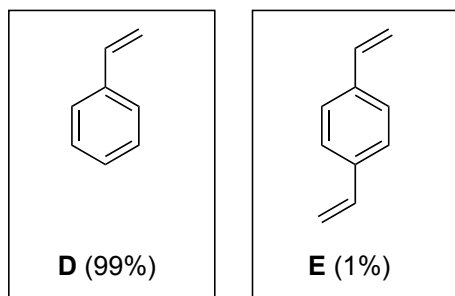
- ☐ Boc-Asp(^tBu)-CO₂H
- ☐ Boc-Asp(^tBu)-OH
- ☐ Boc-Asp(^tBu)-H
- ☐ Cbz-Asp(Bn)-CO₂H
- ☒ **Cbz-Asp(Bn)-OH**
- ☐ Cbz-Asp(Bn)-H

Reagent **C**:

- ☐ 1% CF₃CO₂H in CH₂Cl₂
- ☒ **H₂ (g), Pd/C**
- ☐ 4M aqueous HCl

- ☐ LiOH in THF
- ☐ 20% piperidine in DMF

23.3

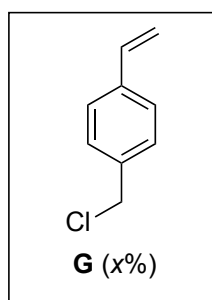


Initiator **F**:

- ☒ **azobis(isobutyronitrile) (AIBN)**
- ☒ **benzoyl peroxide (BzO)₂**
- ☐ *tert*-butyl peroxide (*t*BuO)₂
- ☐ *N,N'*-dicyclohexylcarbodiimide (DCC)
- ☐ diisopropylethylamine (DIPEA)

Note: *tert*-butyl peroxide is not a suitable radical initiator for styrene polymerization as oxygen-centered radicals are not prone to radical addition but rather hydrogen abstraction.

23.4

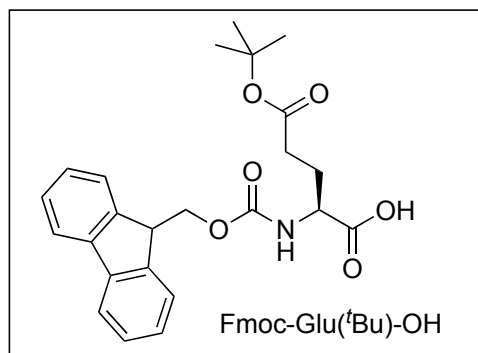
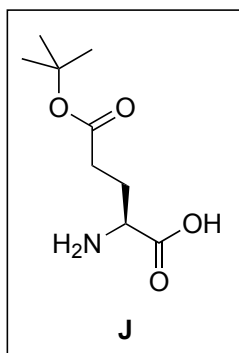
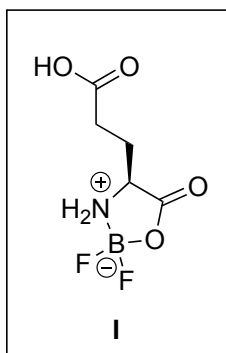


Reagent **H**:

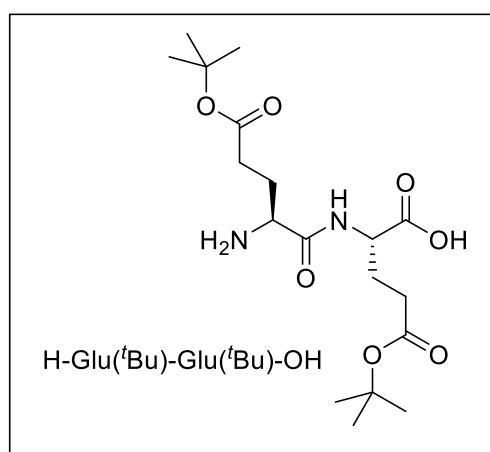
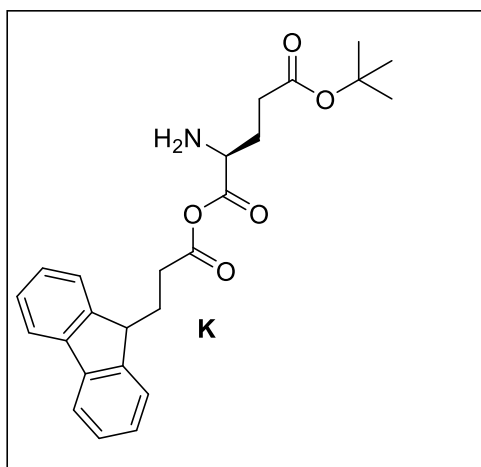
- ☒ **CH₃OCH₂Cl, H₂SO₄**
- ☐ CH₂Cl₂, KOH
- ☐ CHCl₃, (*t*BuO)₂
- ☐ Cl₂, *hν*

☒ formaldehyde, HCl, ZnCl₂

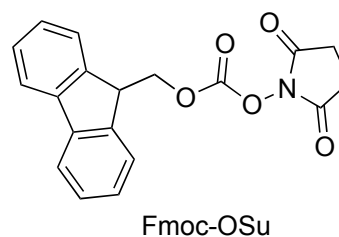
23.5



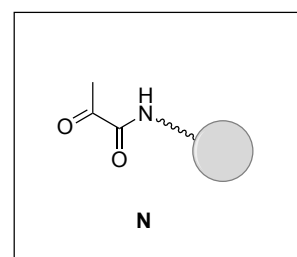
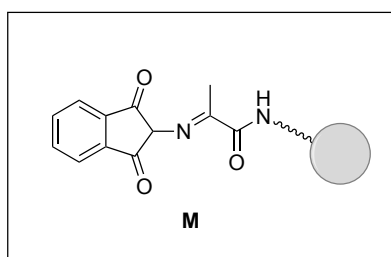
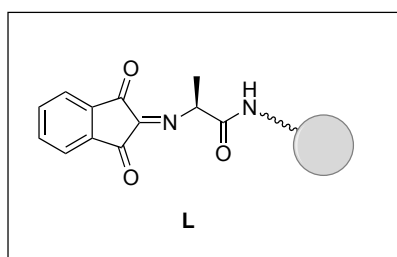
23.6



Note: The intermediate **K** is a mixed anhydride, an activated derivative of the carboxylic acid which readily reacts with another molecule of **J**. To prevent the dimerization, Fmoc-OSu (NHS ester) is often preferred.



23.7

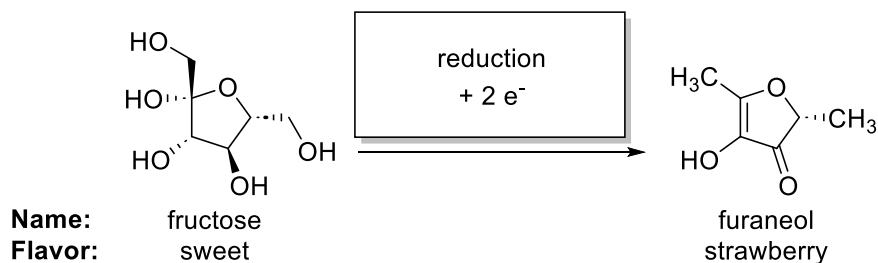
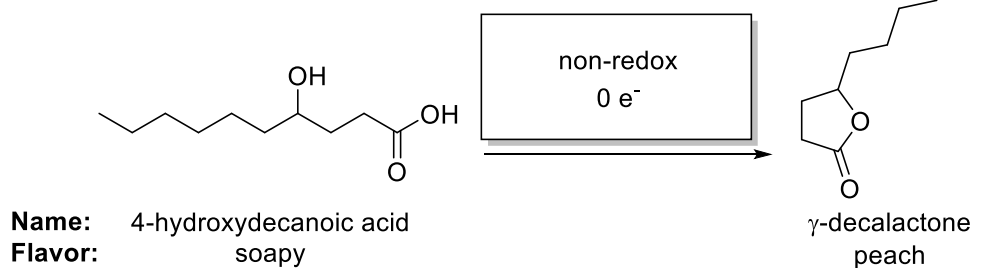
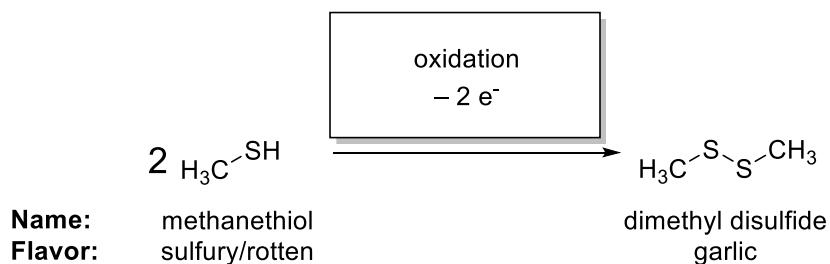
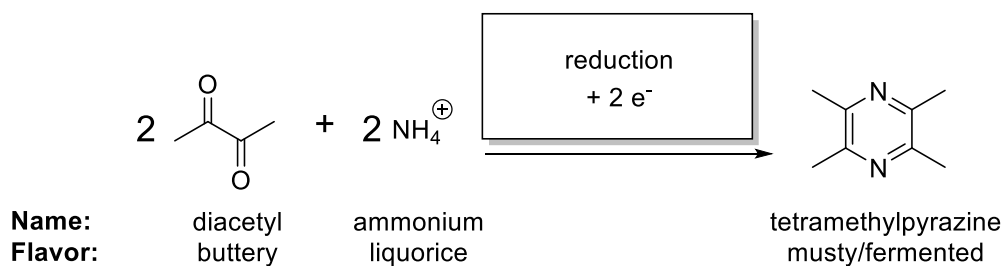
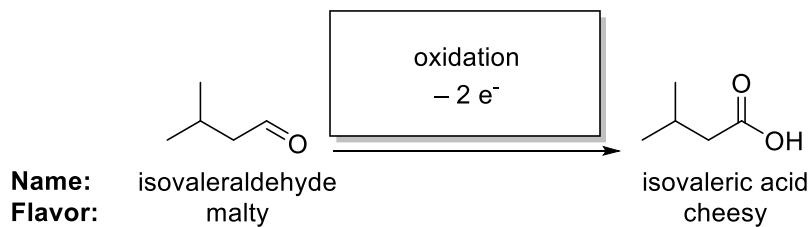


23.8

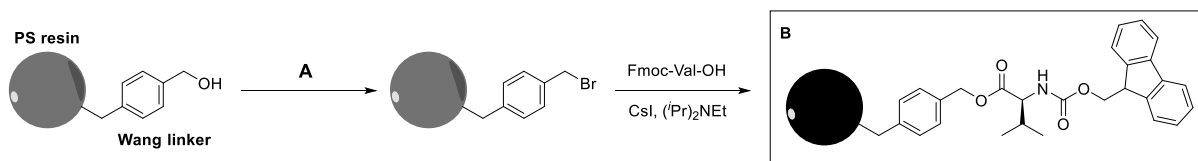
Proline

Solution - Switzerland – the country of cheese

24.1



24.2



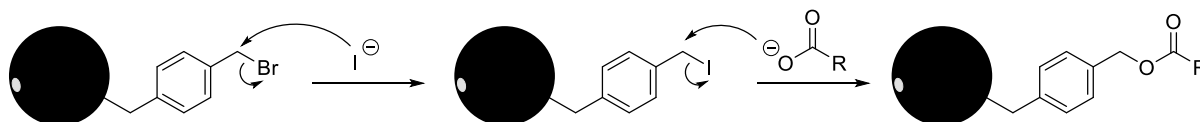
Reagent A:

- ☐ AgOH, Br₂
- ☐ Br₂, *hn*
- ☒ CBr₄, PPh₃
- ☐ KBr, acetone
- ☐ LiBr, H₃PO₂

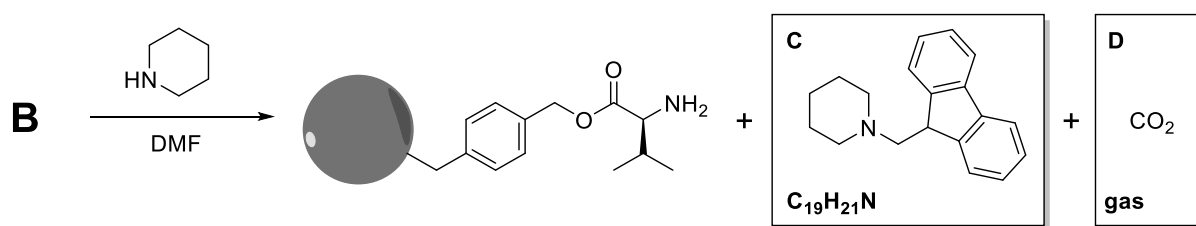
24.3

- ☒ Catalyst – iodide is both a better nucleophile than the carboxylate and a better leaving group than the bromide.
- ☐ Increasing ionic strength – the ionic species stabilize the charged intermediate formed during the reaction.
- ☐ Inhibitor of undesired side-reactions – the mildly acidic salt buffers the basicity of (iPr)₂NEt and prevents premature cleavage of the Fmoc protecting group.
- ☐ Solubilizer – the cesium salt of Fmoc-Val-OH is highly soluble in most organic solvents.
- ☐ Swelling agent – the charged species compete with π - π interactions within the resin, improving the accessibility of all linker groups.

Mechanism of the catalyzed, two-step process:



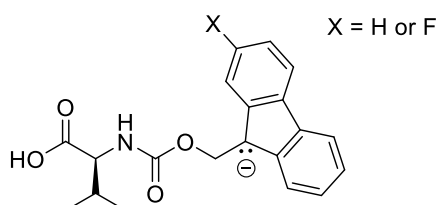
24.4



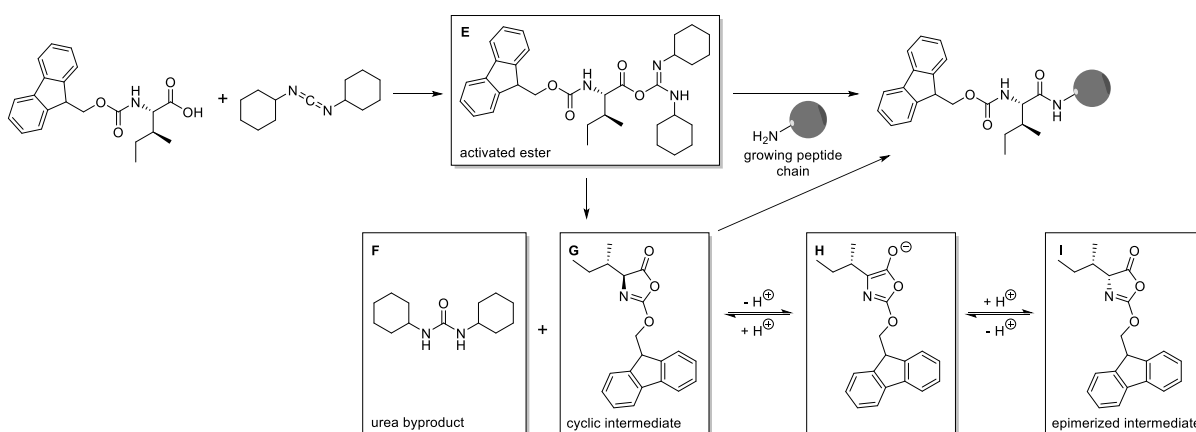
24.5

- ☐ Slower – a carbocation intermediate is formed during the reaction which is destabilized by the electronegative fluorine substituent.
- ☐ Slower – the sterically demanding fluorine substituent hinders the approach of the piperidine reagent.
- ☒ Faster – a carbanion intermediate is formed during the reaction which is stabilized by the electronegative fluorine substituent.
- ☐ Faster – the fluorine substituent coordinates to the piperidine reagent, thus promoting its reaction with the adjacent fluorenylmethyl group.

The reaction runs via an E1cB mechanism. Structure of the intermediate:



24.6



24.7

Tyr **PG-6**

Gln **PG-8** (no PG is also a valid answer here)

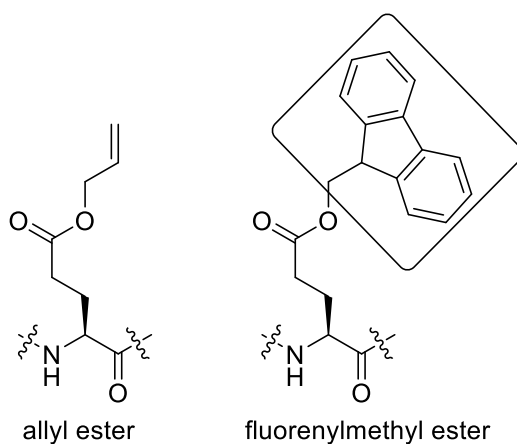
Glu **PG-6**

Arg **PG-3**

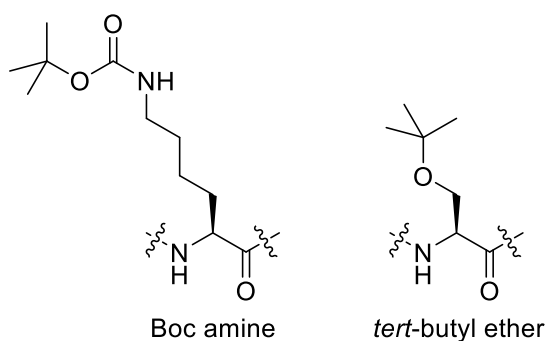
Note: **PG-8** (Xan) is not a common protecting group but the students should be able to deduce its lability and deprotection mechanism by associating it with the common *p*-methoxybenzyl (PMB) protecting group.

24.8

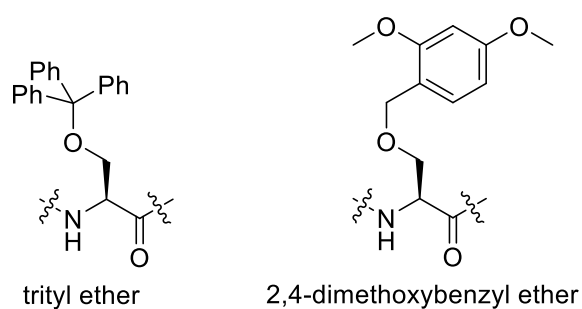
a. *cleavage condition:* 20% piperidine in DMF, 15 min YES



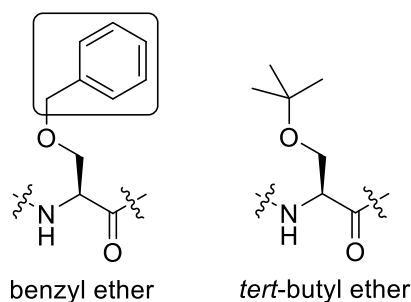
b. *cleavage condition:* 95% CF₃CO₂H, 60 min NO



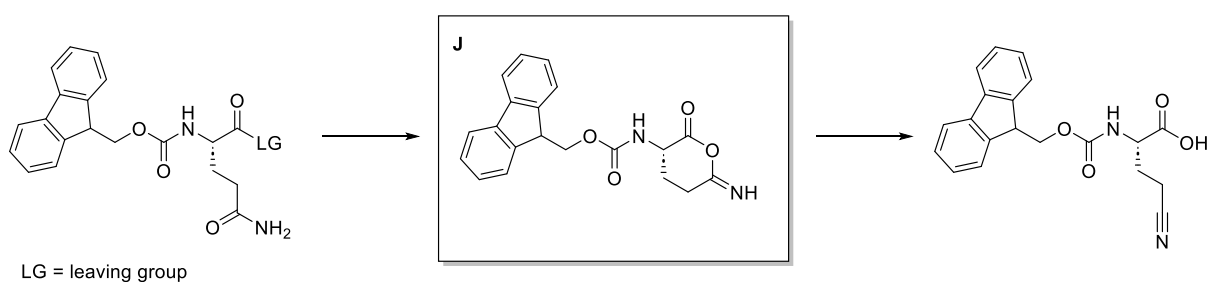
c. *cleavage condition:* 1% CF₃CO₂H in CH₂Cl₂, 15 min NO



d. *cleavage condition*: H₂ (g), Pd on charcoal, 60 min YES



24.9

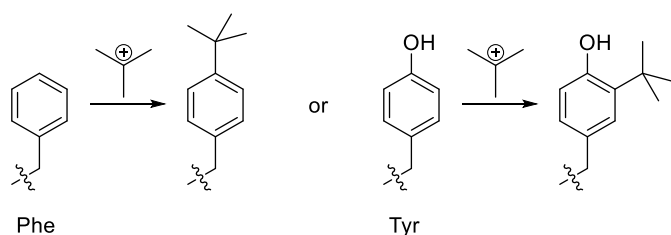


24.10

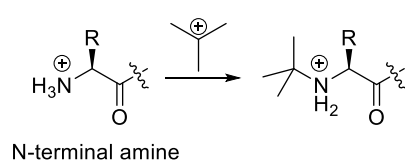
$$\Delta m/z = 1937 - 1881 = 56$$

The increase in mass by 56 amu corresponds to a *tert*-butyl group. The *tert*-butyl carbocation is formed as an intermediate during removal of Boc a ^tBu protecting groups. In the absence of additives, the *tert*-butyl carbocation may react with nucleophilic groups present in the peptide. The most probable sites of attachment are aromatic sidechains of Phe and Tyr via electrophilic aromatic substitution. Attachment to the N-terminal amino group of the peptide is less likely as this functionality is fully protonated under the strongly acidic conditions.

More likely:



Less likely:



24.11

General strategy: multiply yields for each step raised to the power corresponding to the number of repetitions of this step

$$\text{Yield} = \text{loading} \times \text{deprotection}^{17} \times \text{coupling}^{16} \times \text{cleavage}$$

$$\text{a. Yield} = 0.9 \times 0.9^{17} \times 0.9^{16} \times 0.9 = 0.9^{35} = 0.025 \Rightarrow \mathbf{2.5\%}$$

b. $Yield = 0.9 \times 0.99^{17} \times 0.97^{16} \times 0.9 = 0.42 \Rightarrow \mathbf{42\%}$

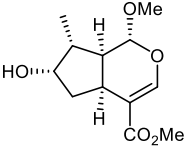
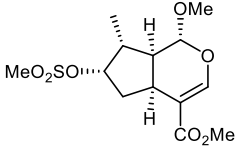
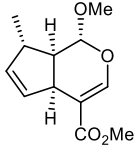
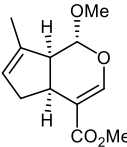
Solution: Gentian goes chemistry

25.1

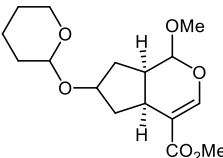
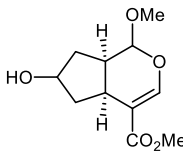
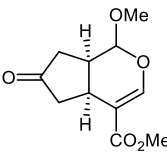
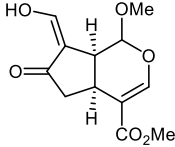
with sugar moiety: 10 stereocenters $\rightarrow 2^{10} = 1024$ possible stereoisomers

without sugar moiety: 5 stereocenters $\rightarrow 2^5 = 32$ possible stereoisomers

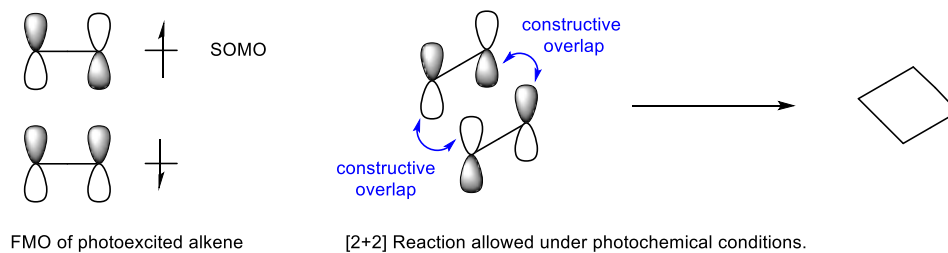
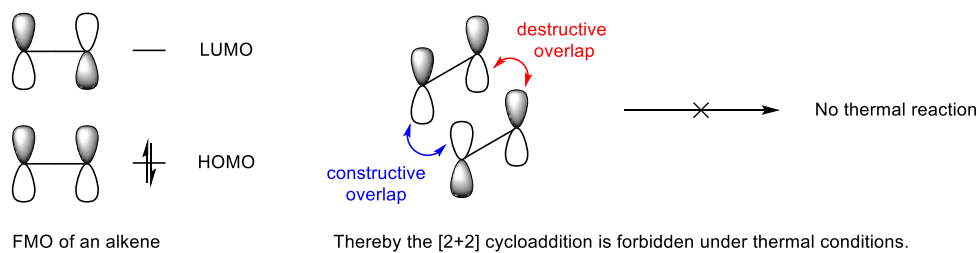
25.2

A	B	C
		
D		
		

25.3

F	G	H
		
I		
 or tautomers		

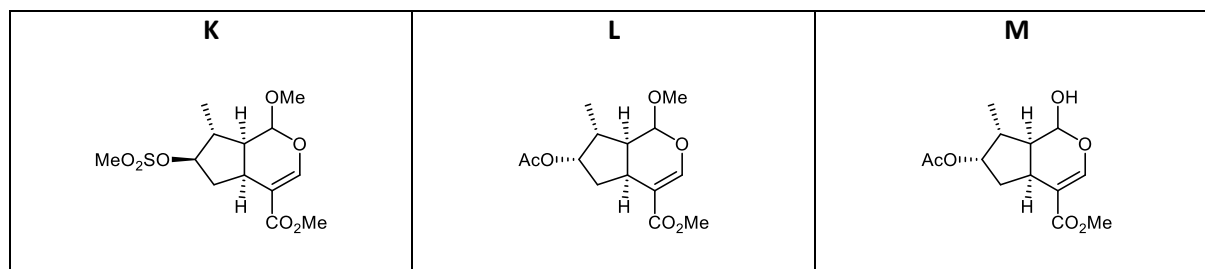
25.4



conditions **E**: Considering the FMO-interactions, the desired reaction must be conducted under photochemical conditions.

25.5

conditions **J**: NaBH_4 at 0°C in MeOH

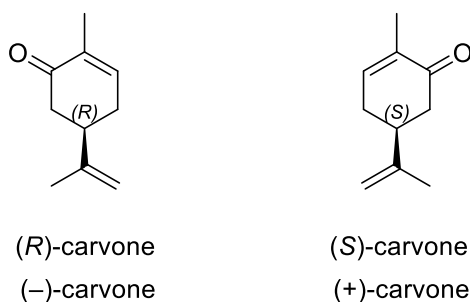


Solution - The Chemistry of Scent and Fragrance

26.1

The signs indicate in which direction the enantiomer rotates the plane of polarized light in a polarimetry experiment. By convention, the (+) sign is dextrorotatory (clockwise), the (–) sign is for compounds that have levorotatory (counter-clockwise) optical rotation.

26.2



26.3

- a) (*R*)-isomer is always (–)
- b) (*S*)-isomer is always (–)
- c) (*R*)-isomer is always (+)
- d) **There is no relationship between the stereodescriptors.**

The (*R*) and (*S*) designation describes the absolute configuration of a specific stereocenter in the molecule, whereas the (+) and (–) prefixes describe a property of the molecule as a whole. There is no relationship between the *R/S* designation and the sign of its specific rotation, (+) or (–). We have to experimentally measure the optical rotation by polarimetry.

26.4

The measured optical rotation is -23° , which means it is levorotary. The major enantiomer in the mixture therefore has to be the (–)-carvone (the *R*-enantiomer).

$$\text{Rotation}(\text{mix}) = [\text{Fraction}(S) \times \text{Rotation}(S)] + [\text{Fraction}(R) \times \text{Rotation}(R)]$$

If we set $\text{Fraction}(S) = x$, then $\text{Fraction}(R) = 1 - x$ and

$$\text{Rotation}(\text{mix}) = [x \times \text{Rotation}(S)] + [(1-x) \times \text{Rotation}(R)]$$

We obtain:

$$-23 = [x \times (+61)] + [(1-x) \times (-61)]$$

Solve for x :

$$x = 0.3114$$

$$(1 - x) = 0.6885$$

The mixture consists of 69% of (*R*)-carvone and 31% of (*R*)-carvone.

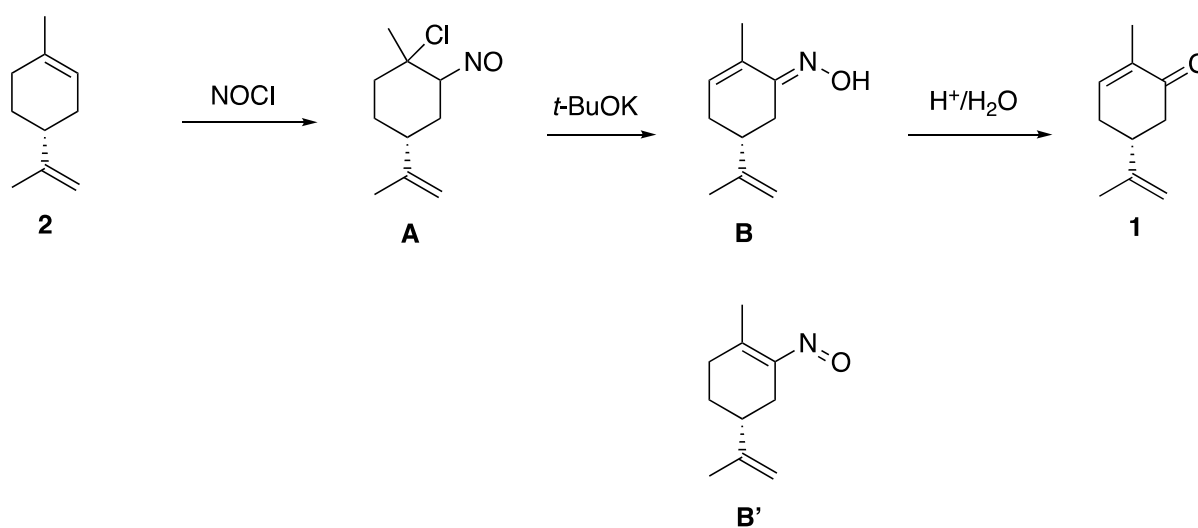
The enantiomeric excess is of the mixture is 37.8%:

$$\% ee = \frac{(R - S)}{(R + S)} = \frac{(69 - 31)}{(100)} = 38\%$$

26.5

- a) Distillation
- b) Sublimation
- c) **Chiral column chromatography**
- d) Column chromatography on silica gel

26.6

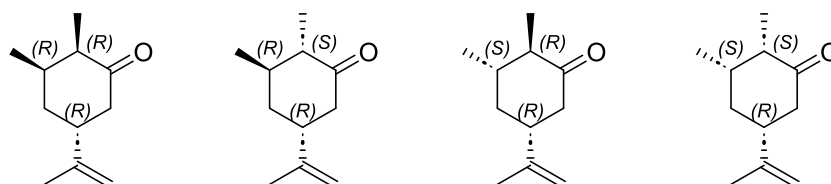


Compound A – (+)-limonene nitrosochloride

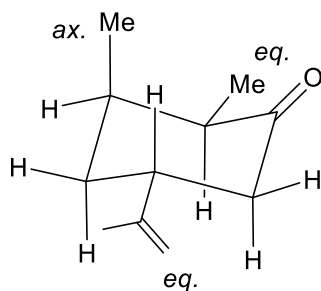
Compound B – (–)-carvone oxime (the tautomer B' also correct)

26.7

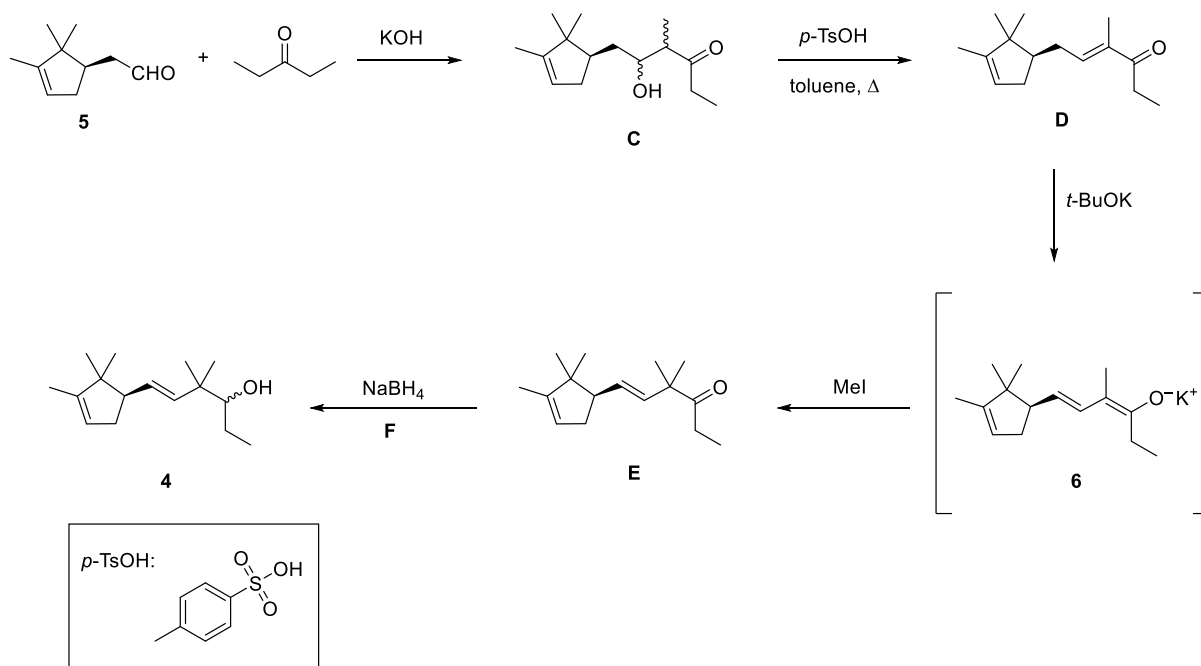
Since we start from an optically pure (–)-carvone, there are 4 possible stereoisomers that can form: (2*R*,3*R*,5*R*), (2*S*,3*R*,5*R*), (2*R*,3*S*,5*R*), (2*S*,3*S*,5*R*).



The lowest energy conformation of (2*R*,3*R*,5*R*) isomer is the chair conformation with two substituents in the equatorial position and one in the axial.



26.8



Note: Deprotonation of **D** to give **6** is performed under thermodynamic conditions, while alkylation of **6** with MeI under kinetic control.

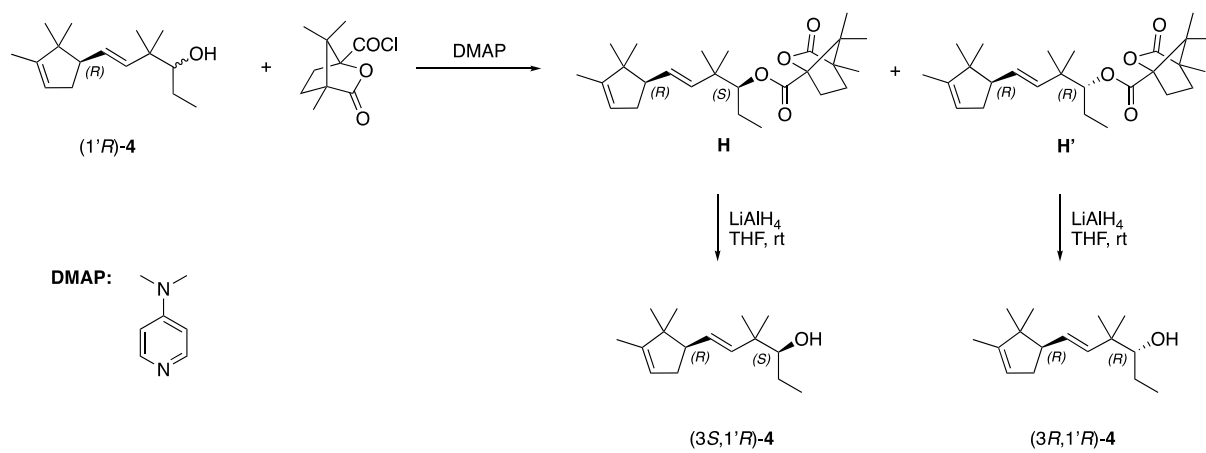
Conditions **F**:

- a) LiAlH_4
- b) NaOH
- c) NaBH_4
- d) H_2 , Pd/C

26.9

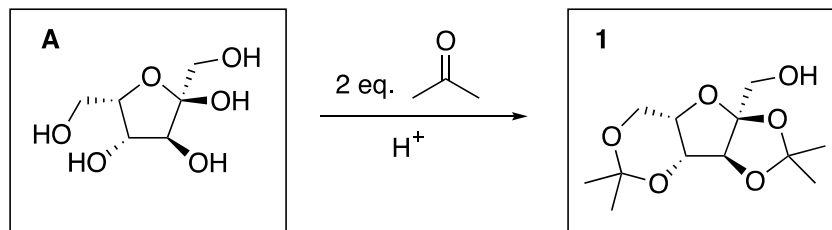
- a) Addition of 3Å molecular sieves
- b) Addition of zinc powder
- c) Using anhydrous toluene as solvent
- d) Addition of anhydrous MgSO_4

26.10

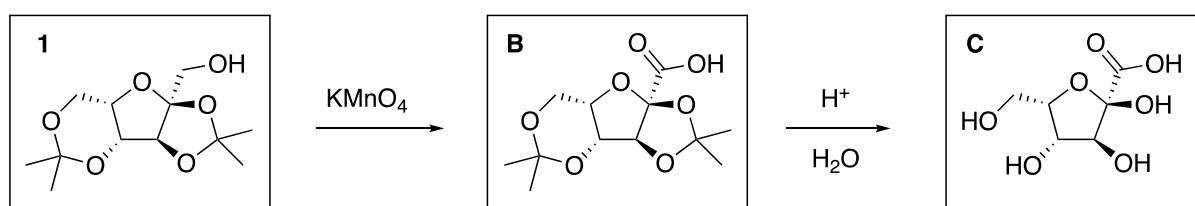


Solution – Vitamin C

27.1



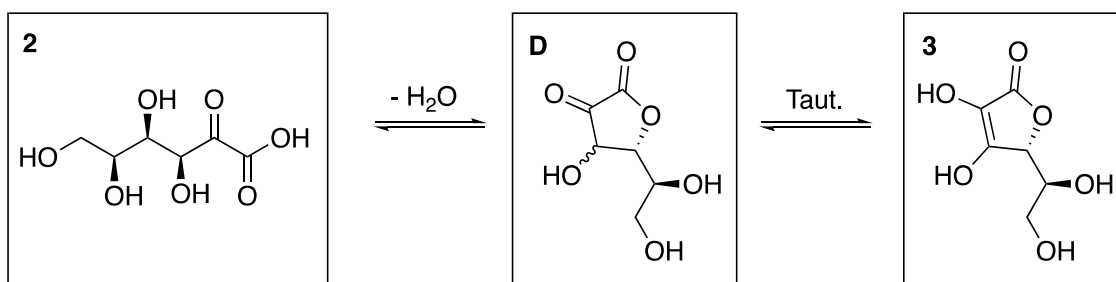
27.2



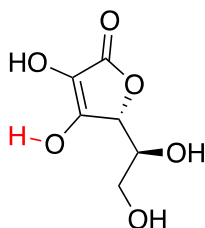
27.3

- ☒ Protecting group (a)
- ☐ Solubilizing group (b)
- ☐ Directing group (c)

27.4

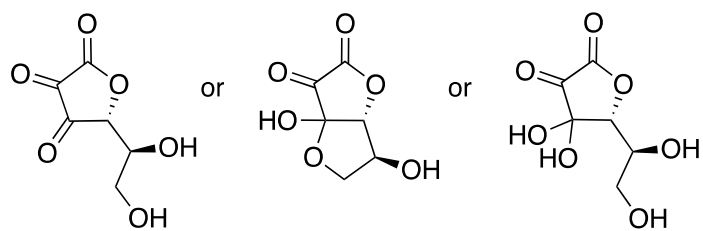


27.5



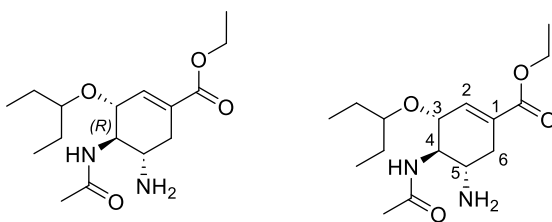
Similar to *e.g.* a carboxylic acid RCOOH

27.6



Solution: Antiviral Drug Tamiflu

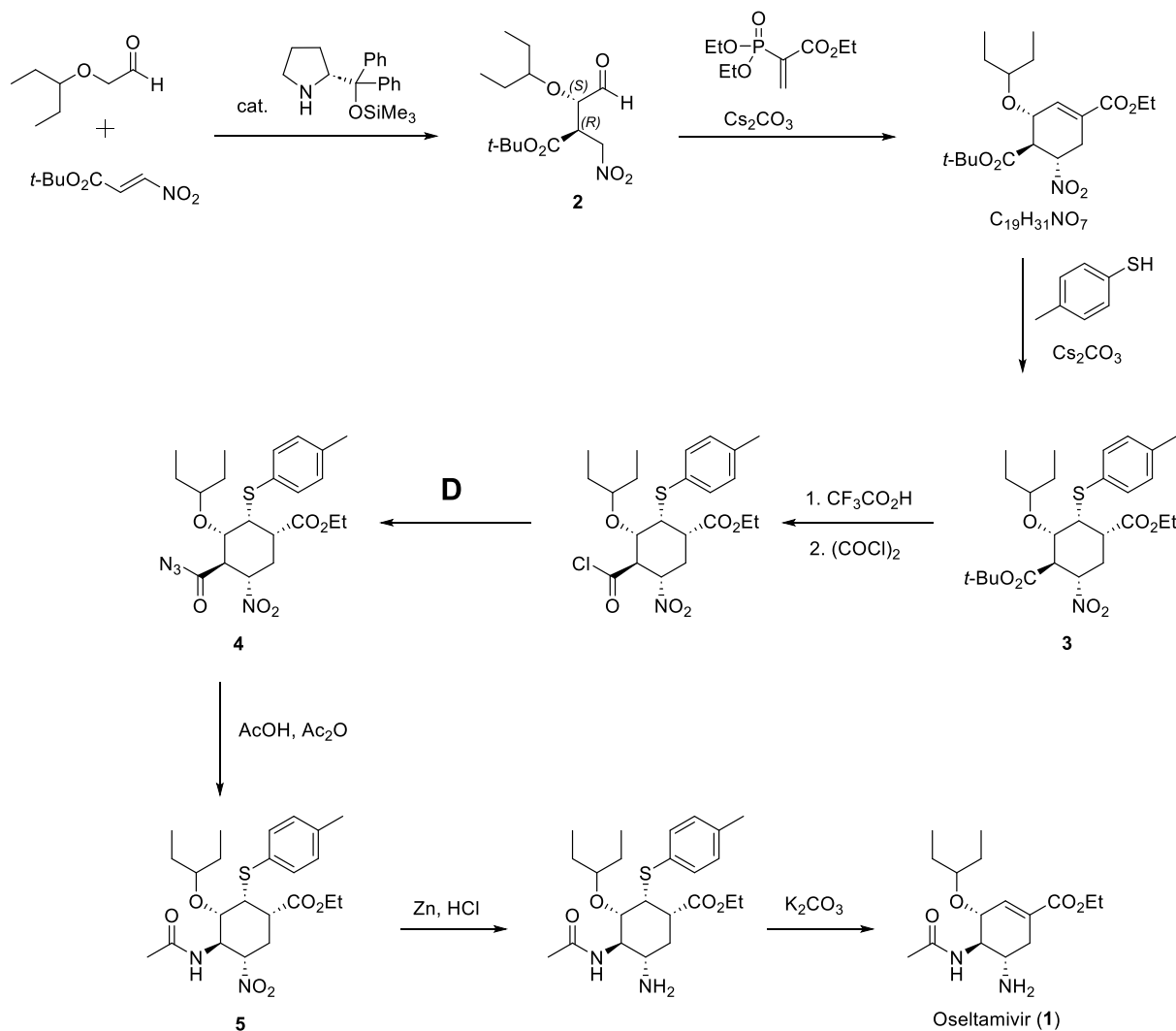
28.1



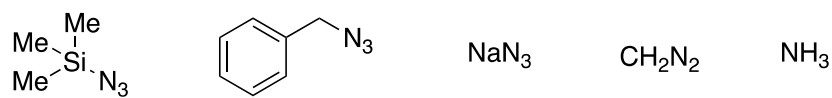
28.2

- a. *Cis*
- b. *Trans*
- c. *Syn*
- d. *Anti*

28.3

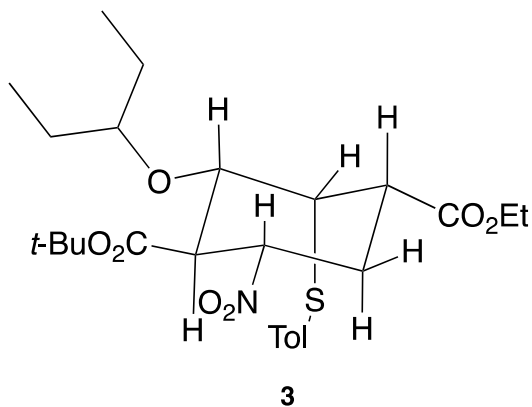


Reagent **D**:

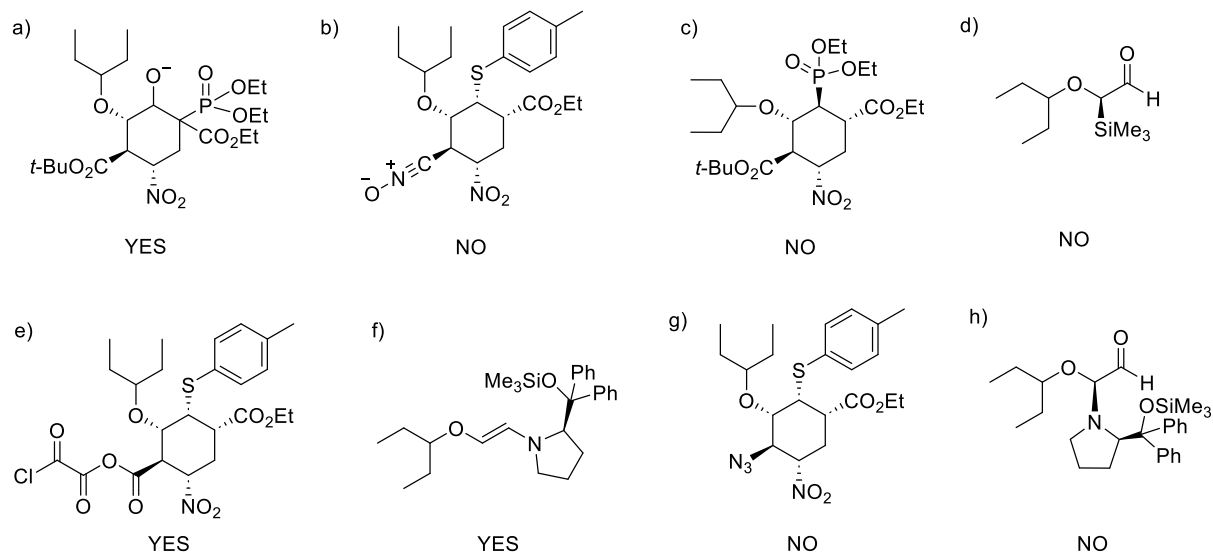


S £ S £ £

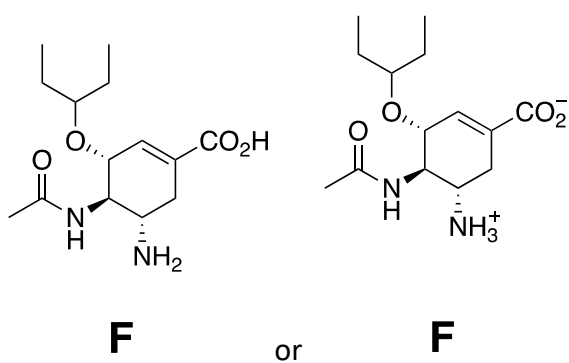
28.4



28.5



28.6



Solution: Diarylethenes as Photoswitches

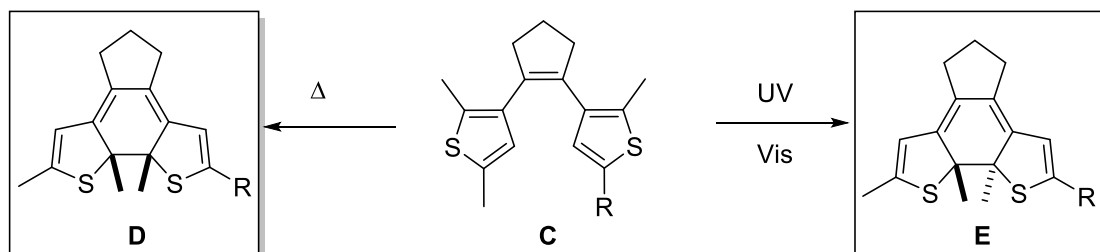
29.1

6 π -electrons

29.2

conrotatory

29.3



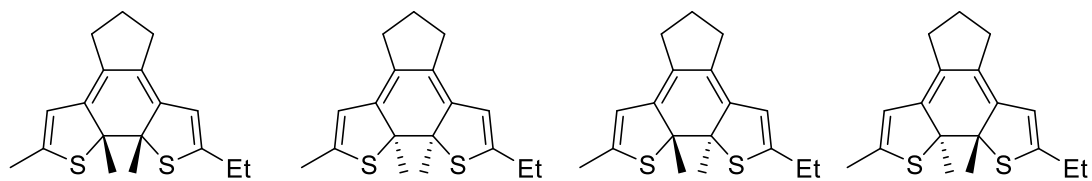
29.4

a) diastereomers

c) epimers

29.5

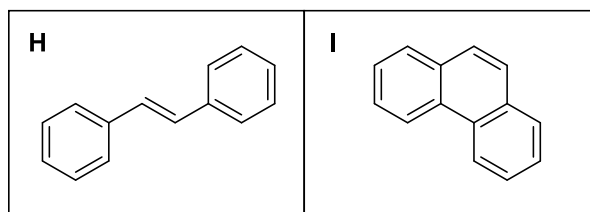
4 products



29.6

b) enantiomers

29.7



29.8

- a) presence of methyl groups instead of H-atoms prevents irreversible oxidation to form a polycyclic aromatic system
- c) the cyclopentene backbone prevents *Z* to *E* isomerization

29.9

- b) the wavenumbers of the absorption maxima, relevant for photo switching between **A** and **B**, follow

$$\tilde{\nu}_{MAX,A} > \tilde{\nu}_{MAX,B}$$

- e) the absorption spectrum of **A** is represented by the straight line
- f) the absorption spectrum of **B** is represented by the dashed lines

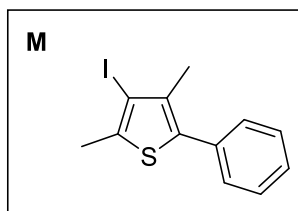
29.10

500 - 650 nm

29.11

Appropriate Pd⁰ catalyst or precursor *e.g.* [Pd(PPh₃)₄] and an aryl halide *e.g.* PhI

29.12

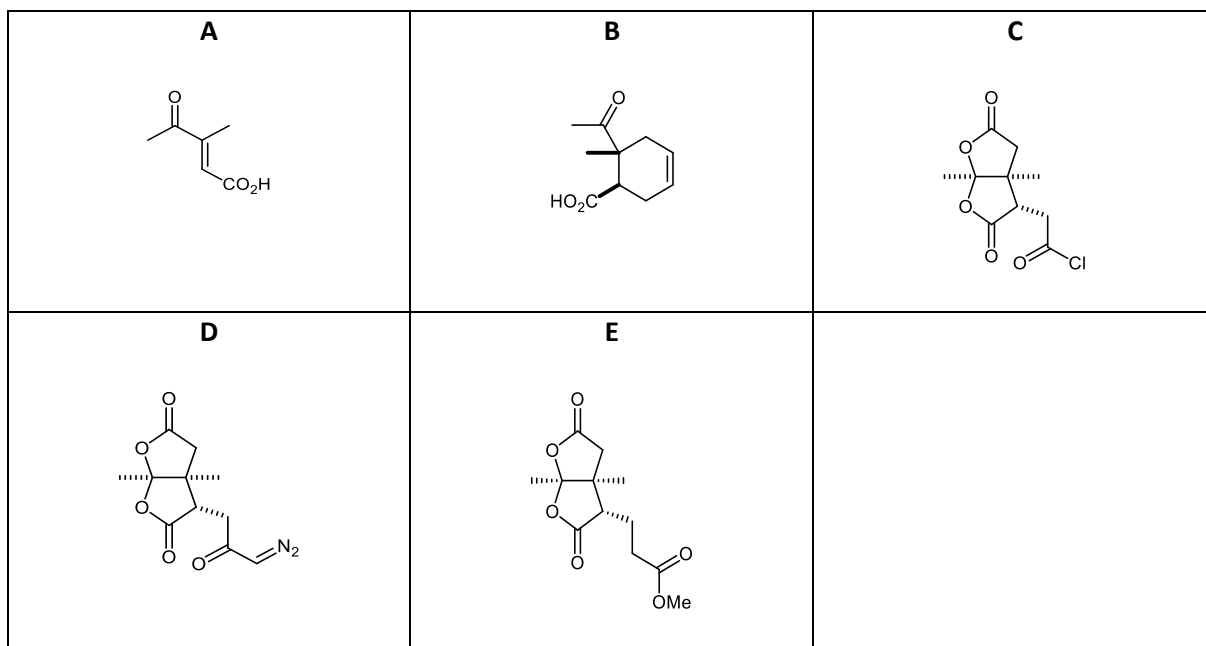


29.13

- a) deprotonation and transmetalation (**J to K**)
- b) metal-catalysed cross coupling reaction (**K to L**)
- c) halogen-metal exchange (**M to N**)
- d) oxidation by stoichiometric amounts of a transition metal
- e) olefin cross-metathesis

Solution: Studies on Vitamin B₁₂

30.1



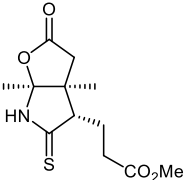
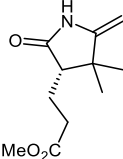
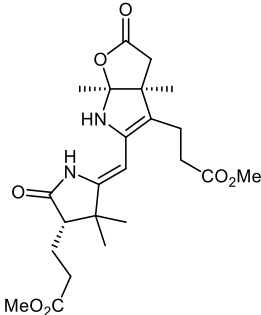
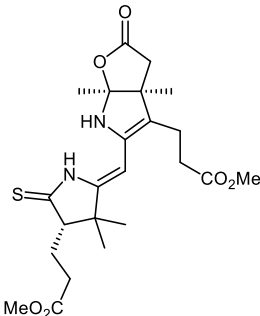
The sequence from the carboxylic acid intermediate to **E** is known as Arndt-Eistert homologation.

30.2

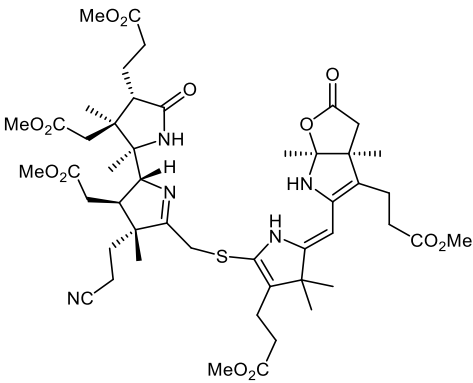
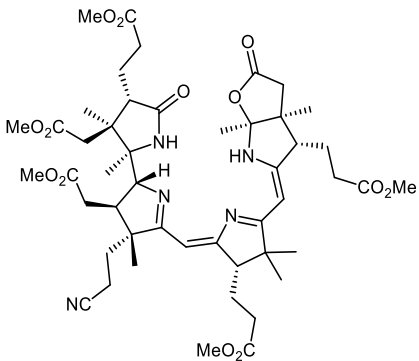
Intermediate **A** takes part in a Diels-Alder reaction. SnCl₄ acts as Lewis acid, lowering the energy of the LUMO orbital and facilitating reactivity. A more complete explanation can be given via FMOs.

30.3

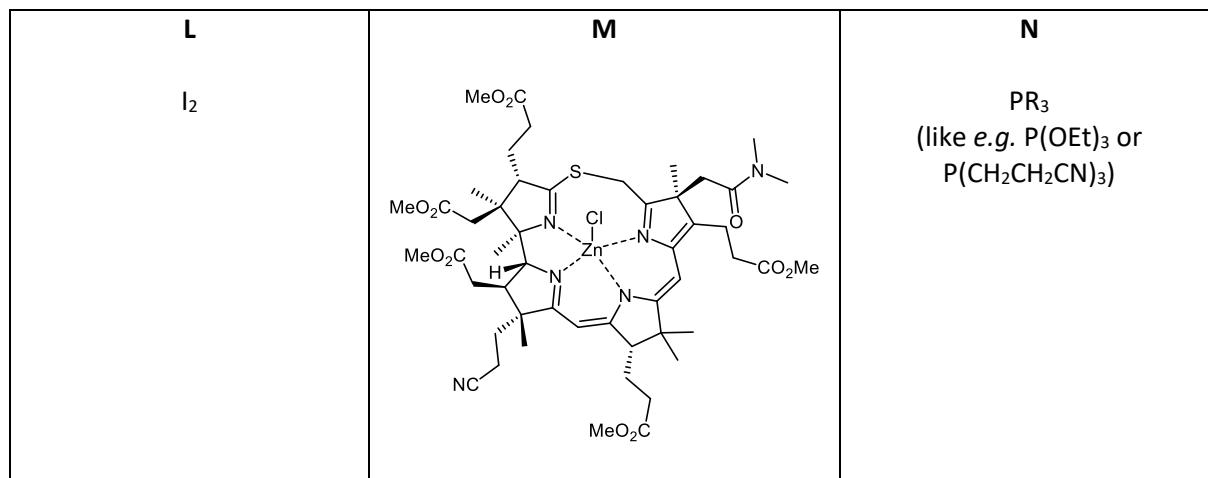
Note that in the following structures (especially **G**, **H**, **I**, **M** and **N**) various tautomers are in principle valid answers. The structures presented here are what was observed by the researchers, more broadly If there are no additional hints given (*i.e.* spectroscopic data) the students are not required to know whether a given structure (*i.e.* **H**) exists as the Imine, the enamine, or a mixture thereof.

F 	G 	H 
I 		

30.4

J 	K 
---	--

30.5



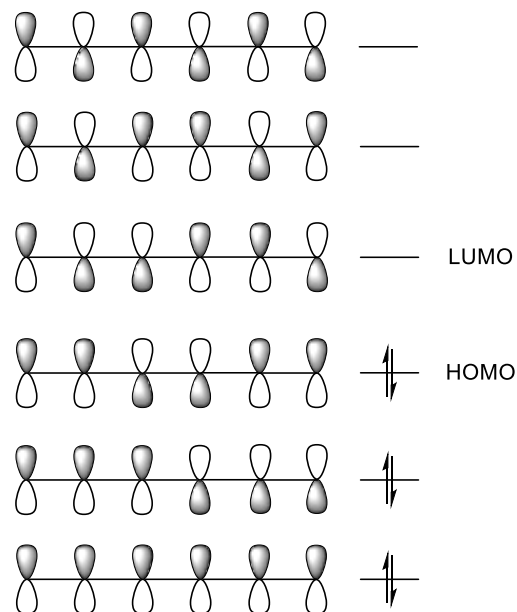
30.6

The coordination of the Zn(II) brings together the reacting termini – thereby accelerating the reaction (preorganization).

30.7

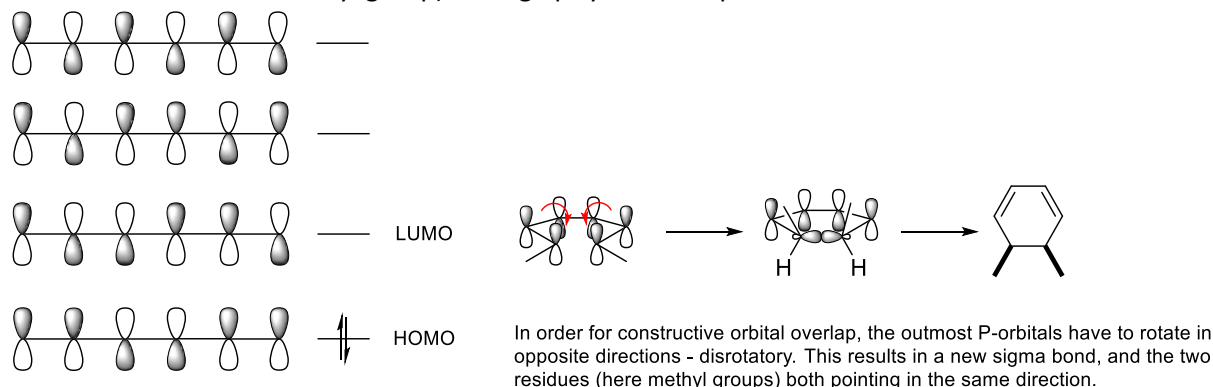


FMO's for the triene are given to the right - important are the orientation of the lobes of the HOMO and LUMO



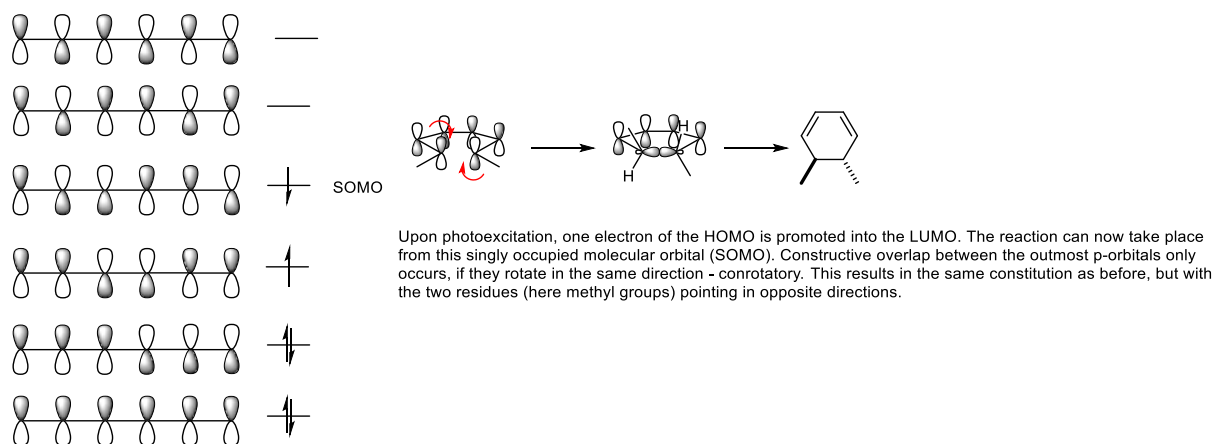
30.8

Under thermal conditions, the reaction is disrotatory, with both residues (in the example from Vitamin B₁₂ The H and methyl group) ending up syn with respect to each other.



30.9

Under photochemical conditions, an electron is promoted into the SOMO, resulting in a conrotatory ring closure:



Solution: Essential Medicines

Part A

1.1.

Formula	Trade name (example)	Medical use
C	<i>CharcoAid</i>	Poisonings (non-specific antidote)
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	<i>Radiogardase</i>	Thallium and radioactive caesium poisonings
As_2O_3	<i>Trisenox</i>	Cancer
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	<i>Feosol</i>	Iron deficiency
$\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$	<i>Nipride</i>	Hypertensive crisis (high blood pressure)
KMnO_4	<i>Permitabs</i>	Dermatological infections
BaSO_4	<i>Varibar</i>	X-ray imaging (radiocontrast agent)
I_2	<i>Iodosorb</i>	Iodine deficiency, antiseptic
$[\text{Ag}(\text{NH}_3)_2]\text{F}$	<i>Saforide</i>	Dental caries prevention, antimicrobial

1.2.

Vial	Compound	Reasoning
1	C	Black powder, insoluble in water and petroleum ether
2	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Blue-green crystals, colourless to light-green solution in water depending on the concentration, insoluble in petroleum ether
3	KMnO_4	Purple-black crystals, purple solution in water, insoluble in petroleum ether
4	I_2	Grey solid, slightly and slowly dissolves in water to form a light-brown solution, purple solution in petroleum ether

1.3.

Conditions	Reaction equation with observations
without H_2SO_4	$3\text{FeSO}_4 + \text{KMnO}_4 + 2\text{H}_2\text{O} = 3\text{Fe}(\text{OH})\text{SO}_4 + \text{KOH} + \text{MnO}_2 \downarrow$ or $6\text{FeSO}_4 + 2\text{KMnO}_4 + 4\text{H}_2\text{O} = [\text{Fe}(\text{OH})_2]_2\text{SO}_4 + 4\text{Fe}(\text{OH})\text{SO}_4 + \text{K}_2\text{SO}_4 + 2\text{MnO}_2 \downarrow$ (disappearance of purple colour, brown precipitate, colourless solution)
with H_2SO_4	$10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 = 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O}$ (disappearance of purple colour, colourless solution)

Part B

1.4.

Formula	Letter	Medical use
NaNO_2	C	Cyanide poisoning
NaHCO_3	A	Severe metabolic acidosis
$\text{Na}_2\text{S}_2\text{O}_3$	D	Cyanide poisoning and fungal skin infections
NaF	B	Dental caries prevention
NaClO	E	Disinfectant

1.5.

Compound	Formula	Reaction(s) equation(s) with observations
I	NaClO	$4\text{NaClO} + 2\text{H}_2\text{SO}_4 = 2\text{Na}_2\text{SO}_4 + \text{Cl}_2 \uparrow + \text{O}_2 \uparrow + 2\text{H}_2\text{O}$ (green solution, gas) $\text{NaClO} + 2\text{FeSO}_4 + \text{H}_2\text{O} = \text{NaCl} + 2\text{Fe}(\text{OH})\text{SO}_4 \downarrow$ (brown precipitate) $5\text{NaClO} + \text{I}_2 (\text{org}) + \text{H}_2\text{O} = 5\text{NaCl} + 2\text{HIO}_3$ (disappearance of the purple colour of the organic phase)

II	NaHCO ₃	$2\text{NaHCO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2\uparrow$ (odourless colourless gas) $2\text{NaHCO}_3 + \text{FeSO}_4 = \text{FeCO}_3\downarrow + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2\uparrow$ (green precipitate which turns brown with time due to oxidation on air, the formation of gas is hardly visible)
III	NaF	$2\text{NaF} + \text{FeSO}_4 = \text{FeF}_2\downarrow + \text{Na}_2\text{SO}_4$ (pale yellow opaque solution, slow formation of precipitate)
IV	NaNO ₂	$2\text{NaNO}_2 + 4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + 8\text{H}_2\text{O} = 2[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4$ (brown solution due to formation of nitrosyl complex) $5\text{NaNO}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = 5\text{NaNO}_3 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$ (purple colour disappearance, colourless solution)
V	Na ₂ S ₂ O ₃	$\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{SO}_2\uparrow + \text{S}\downarrow + \text{H}_2\text{O}$ (colloidal precipitate, odorous gas) $3\text{Na}_2\text{S}_2\text{O}_3 + 8\text{KMnO}_4 + \text{H}_2\text{O} = 3\text{K}_2\text{SO}_4 + 8\text{MnO}_2\downarrow + 3\text{Na}_2\text{SO}_4 + 2\text{KOH}$ (purple colour disappearance, dark-brown precipitate) $5\text{Na}_2\text{S}_2\text{O}_3 + 8\text{KMnO}_4 + 7\text{H}_2\text{SO}_4 = 4\text{K}_2\text{SO}_4 + 8\text{MnSO}_4 + 5\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$ (purple colour disappearance, colourless solution) $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2(\text{org}) = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$ (disappearance of the purple colour of the organic phase)

Part C

1.6.

Mixture	Compound	Medical use
1	Li ₂ CO ₃	Bipolar disorders
	KI	Hyperthyroidism, radiation accidents, fungal infections
2	MgSO ₄	Anticonvulsant
	ZnSO ₄	Diarrhoea
3	CaCl ₂	Corresponding metal supplement
	CH ₃ COOH	Infections of the ear canal

1.7.

Mixtures	A	B	C
+A		white ↓	–
+B	white ↓		colourless ↑, then white ↓ (excess of B)
+C	–	colourless ↑	

1.8.

A	
MgSO ₄	ZnSO ₄

B	
Li ₂ CO ₃	KI

C	
CaCl ₂	CH ₃ COOH

Combination	Ionic equation(s)
A+B	$2\text{Mg}^{2+} + 3\text{CO}_3^{2-} + 2\text{H}_2\text{O} = (\text{MgOH})_2\text{CO}_3\downarrow + 2\text{HCO}_3^-$ $2\text{Zn}^{2+} + 3\text{CO}_3^{2-} + 2\text{H}_2\text{O} = (\text{ZnOH})_2\text{CO}_3\downarrow + 2\text{HCO}_3^-$
A+C	If recommended concentrations are used, there are no visible observations. However, if calcium salt is prepared with a higher concentration, then the white precipitate can be observed upon mixing with sulfates: $\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4\downarrow$
B+C	When C is added to B dropwise: $\text{CO}_3^{2-} + 2\text{CH}_3\text{COOH} = \text{CO}_2\uparrow + 2\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$ When B is added to C dropwise: $2\text{CH}_3\text{COOH} + \text{CO}_3^{2-} = \text{CO}_2\uparrow + 2\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$, then: $\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3\downarrow$ (when the excess of B is used)

Solution: Cantons of Switzerland

Chemicals

Chemical	Hazards	GHS Hazard Statements
Zinc formate, $\text{Zn}(\text{HCOO})_2$ (557-41-5)	Harmful Environmental hazard	H302, H319, H410 P264, P280, P301+P330+P331, P312, P337+P313
Sodium tungstate dihydrate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (10213-10-2)	Harmful	H302 P280, P301+P312, P303+P361+P353, P305+P351+P338
Strontium hydroxide octahydrate, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (1311-10-0)	Corrosive	H314 P280, P301+P330+P331, P303+P361+P353, P305+P351+P338, P310
Barium sulfide, BaS (21109-95-5)	Toxic Corrosive Environmental hazard	H290, H301, H314, H332, H400 P260, P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338
Aluminium iodide, AlI_3 (7784-23-8)	Corrosive	H314 P260, P280, P301+P330+P331, P303+P361+P353, P304+P340+P310, P305+P351+P338
Ammonia solution, NH_3 , 1 M (1336-21-6)	Corrosive Environmental hazard	H315, H318, H410 P264, P273, P280, P302+P352, P305+P351+P338, P332+P313
Sulfuric acid, H_2SO_4 , 1 M (7664-93-9)	Corrosive	H290, H315, H319 P234, P264, P280, P302+P352, P305+P351+P338, P332+P313
Cesium formate, CsHCOO (3495-36-1)	Harmful Health hazard	H302, H319, H371, H373 P301+P312+P330, P305+P351+P338, P308+P311
Cadmium formate, $\text{Cd}(\text{HCOO})_2$ (4464-23-7)	Toxic Health hazard Environmental hazard	H301+H331, H351, H373, H410 P202, P260, P264, P273, P301+P310, P304+P340+P311
Calcium formate, $\text{Ca}(\text{HCOO})_2$ (544-17-2)	Corrosive	H318 P280, P305+P351+P338+P310
Zinc dust, Zn (7440-66-6)	Environmental hazard	H410 P273, P391, P501
Copper(II) formate tetrahydrate, $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$, (5893-61-8)	Harmful Corrosive Environmental hazard	H302, H315, H318, H335, H410 P280, P301+P330+P331, P302+P352, P304+P340, P305+P351+P338, P310, P332+P313
Vanadyl sulfate hydrate, $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ (123334-20-3)	Toxic Environmental hazard	H301, H411 P264, P270, P273, P301+P310, P391, P405
Potassium permanganate solution, KMnO_4 , 1 wt% (7722-64-7)	Oxidizing Corrosive Harmful Health hazard Environmental hazard	H272, H302, H314, H361d, H373, H410 P210, P260, P273, P280, P303+P361+P353, P305+P351+P338

*It is recommended to prepare 1–5 wt% solutions (at least 20 ml per student) of the encoded compounds. The 5 wt% solutions of salts containing WO_4^{2-} , Al^{3+} , Cd^{2+} , Ca^{2+} , Cu^{2+} , and VO^{2+} ions provide more clear observations in comparison with 1 wt% solutions. Some ions that do not participate in identification reactions could be substituted with other inert ions (see suggestions further). Solutions of some encoded compounds could be simulated using a mixture of compounds of targeted ions with inert counterions (see suggestions further). Warn the students about the implemented changes. Recommended amount for Zn dust – at least 100 mg per student.

Glassware and Equipment

Item	Quantity
Test tube rack	1
Permanent marker	1
Closed vials with solutions 1–5	5
Closed vials with solutions CH-1, CH-2, CH-3	3
Closed vials with solutions A, B	2
Closed vials with NH_3 , H_2SO_4 , KMnO_4 solutions	3
Closed vial with Zn dust	1
Test tubes	At least 20
Plastic Pasteur pipettes	13
Wash bottle with distilled water	1
Small spatula for Zn dust	1

Part A

Note: the chemistry of tungsten (W) and titanium (Ti) won't be a part of the practical exam.

*The tungstate (WO_4^{2-}) could be substituted with phosphate (PO_4^{3-}). In this case, proceed as if it would correspond to the second letter **W** in the canton's code. Warn the students which anion they are working with.

2.1.

Anion	Canton code(s)	Example of the compound
<i>formate</i> (HCOO^-)	ZH SH	$\text{Zn}(\text{HCOO})_2$ $\text{Sr}(\text{HCOO})_2$
<i>hydroxide</i> (OH^-)	SO	$\text{Sr}(\text{OH})_2$
<i>iodide</i> (I^-)	AI TI	AlI_3 TiI_3 (violet solution)
<i>sulphide</i> (S^{2-})	BS VS	BaS no example of soluble salt
<i>tungstate</i> (WO_4^{2-}) or <i>phosphate</i> (PO_4^{3-} , letter W)	NW OW	Na_2WO_4 or Na_3PO_4 no example of soluble salt

2.2.

Solution	1 $\text{Zn}(\text{HCOO})_2$	2 Na_2WO_4 or Na_3PO_4	3 $\text{Sr}(\text{OH})_2$	4 BaS	5 AlI_3
+1 $\text{Zn}(\text{HCOO})_2$		white ↓	white ↓ (no dissolution in excess of 1)	white ↓	–
+2	white ↓		white ↓	white ↓	white ↓

Na_2WO_4 or Na_3PO_4					
+3 $\text{Sr}(\text{OH})_2$	white ↓ (no dissolution in excess of 3)	white ↓		white ↓ (small amount of precipitate)	white ↓, then solution (excess of 3)
+4 BaS	white ↓	white ↓	white ↓ (small amount of precipitate)		white ↓ (opacity) (+ odorous ↑)*
+5 AlI_3	–	white ↓	solution, then white ↓ (excess of 5)	white ↓ (+ odorous ↑)*	
+NH₃	white ↓, then solution (excess of NH ₃)	–	–	–	white ↓
+H₂SO₄	–	If Na_2WO_4 : yellow ↓ (opacity, can be slow if low concentrations of WO_4^{2-} are used) If Na_3PO_4 : –	white ↓	white ↓ (+ odorous ↑)*	–

*The formation of H_2S as a gas is hardly observable. However, it can be confirmed by the characteristic smell or a test with paper soaked in Pb^{2+} , Ag^+ , or Cd^{2+} salt solution.

2.3.

1	2	3	4	5
$\text{Zn}(\text{HCOO})_2$	Na_2WO_4	$\text{Sr}(\text{OH})_2$ Saturated solution. Filtration may be required. Use it freshly prepared and store it in a closed bottle.	BaS Filtration may be required depending on the quality of the chemical. Use it freshly prepared and store it in a closed bottle.	AlI_3 Carefully dissolve the salt in small portions. It may form a pale yellow solution due to contamination with iodine.

* If these chemicals are not available, the following substitutes can be used:

1	2	3	4	5
$\text{Zn}(\text{CH}_3\text{COO})_2$ $\text{Zn}(\text{NO}_3)_2$ ZnCl_2 $\text{Na}(\text{HCOO})$ can also be added, but formate ion is not necessary here.	Na_3PO_4 Analogous to Na_2WO_4 , it gives white precipitates with Zn^{2+} , Sr^{2+} , Ba^{2+} , and Al^{3+} , but no precipitate with H^+ .	$\text{Sr}(\text{CH}_3\text{COO})_2 + \text{NaOH}$ $\text{Sr}(\text{NO}_3)_2 + \text{NaOH}$ $\text{SrCl}_2 + \text{NaOH}$ (filtration may be required)	$\text{Ba}(\text{CH}_3\text{COO})_2 + \text{Na}_2\text{S}$ $\text{Ba}(\text{NO}_3)_2 + \text{Na}_2\text{S}$ $\text{BaCl}_2 + \text{Na}_2\text{S}$	$\text{Al}(\text{NO}_3)_3$ AlCl_3 KI can also be added, but iodide ion is not necessary here.

2.4.

Combination	Ionic equation(s)
1+2	$\text{Zn}^{2+} + \text{WO}_4^{2-} = \text{ZnWO}_4\downarrow$ If Na_3PO_4 is used as 2: $3\text{Zn}^{2+} + 2\text{PO}_4^{3-} = \text{Zn}_3(\text{PO}_4)_2\downarrow$ (or hydroxyphosphate)
1+3	$\text{Zn}^{2+} + 2\text{OH}^- = \text{Zn}(\text{OH})_2\downarrow$ (saturated solution of $\text{Sr}(\text{OH})_2$ is not basic enough to completely dissolve $\text{Zn}(\text{OH})_2$ and form the hydroxo complex: $\text{Zn}(\text{OH})_2 + 2\text{OH}^- = [\text{Zn}(\text{OH})_4]^{2-}$)
1+4	$\text{Zn}^{2+} + \text{S}^{2-} = \text{ZnS}\downarrow$
1+5	–
2+3	$\text{Sr}^{2+} + \text{WO}_4^{2-} = \text{SrWO}_4\downarrow$ If Na_3PO_4 is used as 2: $3\text{Sr}^{2+} + 2\text{PO}_4^{3-} = \text{Sr}_3(\text{PO}_4)_2\downarrow$ (or hydroxyphosphate)
2+4	$\text{Ba}^{2+} + \text{WO}_4^{2-} = \text{BaWO}_4\downarrow$ If Na_3PO_4 is used as 2: $3\text{Ba}^{2+} + 2\text{PO}_4^{3-} = \text{Ba}_3(\text{PO}_4)_2\downarrow$ (or hydroxyphosphate)
2+5	$2\text{Al}^{3+} + 3\text{WO}_4^{2-} = \text{Al}_2(\text{WO}_4)_3\downarrow$ If Na_3PO_4 is used as 2: $\text{Al}^{3+} + \text{PO}_4^{3-} = \text{AlPO}_4\downarrow$ (or hydroxyphosphate)
3+4	$\text{Sr}^{2+} + \text{S}^{2-} = \text{SrS}\downarrow$ (small amount of precipitate as it is slightly soluble)
3+5	$\text{Al}^{3+} + 3\text{OH}^- = \text{Al}(\text{OH})_3\downarrow$ In excess of 3: $\text{Al}(\text{OH})_3 + \text{OH}^- = [\text{Al}(\text{OH})_4]^-$ (or $[\text{Al}(\text{OH})_6]^{3-}$)
4+5	$2\text{Al}^{3+} + 3\text{S}^{2-} + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3\downarrow + 3\text{H}_2\text{S}\uparrow$
1+ NH_3	$\text{Zn}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2\downarrow + 2\text{NH}_4^+$ In excess of NH_3 : $\text{Zn}(\text{OH})_2 + 4\text{NH}_3 = [\text{Zn}(\text{NH}_3)_4]^{2+} + 2\text{OH}^-$
1+ H_2SO_4	–
2+ NH_3	–
2+ H_2SO_4	$2\text{H}^+ + \text{WO}_4^{2-} = \text{WO}_3 \cdot \text{H}_2\text{O}\downarrow$ If Na_3PO_4 is used as 2: $\text{H}^+ + \text{PO}_4^{3-} = \text{HPO}_4^{2-}$ (or H_2PO_4^- , or H_3PO_4) – no visible observations
3+ NH_3	–
3+ H_2SO_4	$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ $\text{Sr}^{2+} + \text{SO}_4^{2-} = \text{SrSO}_4\downarrow$
4+ NH_3	–
4+ H_2SO_4	$2\text{H}^+ + \text{S}^{2-} = \text{H}_2\text{S}\uparrow$ $\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4\downarrow$
5+ NH_3	$\text{Al}^{3+} + 3\text{NH}_3 + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3\downarrow + 3\text{NH}_4^+$ (no dissolution in excess of NH_3)
5+ H_2SO_4	–

Part B

2.5.

Colourless	$\text{Ca}(\text{HCOO})_2$	$\text{Cd}(\text{HCOO})_2$	CsHCOO
Coloured	$\text{Cr}(\text{HCOO})_3$	$\text{Co}(\text{HCOO})_2$	$\text{Cu}(\text{HCOO})_2$

2.6.

Vial	Compound	Ionic equation(s) with observations
CH-1	CsHCOO	–
CH-2	Cd(HCOO) ₂	$\text{Cd}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} = \text{Cd}(\text{OH})_2\downarrow + 2\text{NH}_4^+$ (white precipitate or opacity if lower concentrations of Cd^{2+} are used) $\text{Cd}(\text{OH})_2 + 6\text{NH}_3 = [\text{Cd}(\text{NH}_3)_6]^{2+} + 2\text{OH}^-$ (dissolution in the excess of ammonia)
CH-3	Ca(HCOO) ₂	$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4\downarrow$ (white precipitate, slow)

* If these chemicals are unavailable, other soluble salts of Cs^+ (or any other alkali metal), Cd^{2+} , and Ca^{2+} can be used, for example, acetates, nitrates, and chlorides.

* If Cs salt (but not formate) is available, you can demonstrate to the students the reaction of CsMnO_4 precipitation upon its reaction with KMnO_4 . Purple crystals are formed.

2.7.

Chosen anions	S^{2-}	WO_4^{2-} or PO_4^{3-}
---------------	-----------------	--

Vial	Ionic equation(s) with observations
CH-1	–
CH-2	$\text{Cd}^{2+} + \text{S}^{2-} = \text{CdS}\downarrow$ (yellow precipitate) and $\text{Cd}^{2+} + \text{WO}_4^{2-} = \text{CdWO}_4\downarrow$ (white precipitate) or $3\text{Cd}^{2+} + 2\text{PO}_4^{3-} = \text{Cd}_3(\text{PO}_4)_2\downarrow$ (or hydroxyphosphate, white precipitate)
CH-3	$\text{Ca}^{2+} + \text{S}^{2-} = \text{CaS}\downarrow$ (small amount of precipitate as it is slightly soluble, may not be spotted instantly) and $\text{Ca}^{2+} + \text{WO}_4^{2-} = \text{CaWO}_4\downarrow$ (white precipitate) or $3\text{Ca}^{2+} + 2\text{PO}_4^{3-} = \text{Ca}_3(\text{PO}_4)_2\downarrow$ (or hydroxyphosphate, e.g., $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, white precipitate)

Part C

2.8.

Vial	Cation	Associated code(s)
A	Cu^{2+}	CH
B	VO^{2+}	VD VS

Combination	Ionic equation(s)
A +NH ₃	$\text{Cu}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} = \text{Cu}(\text{OH})_2\downarrow + 2\text{NH}_4^+$ (blue precipitate) $\text{Cu}(\text{OH})_2 + 4\text{NH}_3 + 2\text{H}_2\text{O} = [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 2\text{OH}^-$ (dark blue solution)
A +Zn(H ⁺)	$\text{Cu}^{2+} + \text{Zn} = \text{Cu}\downarrow + \text{Zn}^{2+}$ (solution turns from blue to colourless)
B +NH ₃	$\text{VO}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} = \text{VO}(\text{OH})_2\downarrow + 2\text{NH}_4^+$ (brown precipitate) No dissolution in excess of NH ₃
B +Zn(H ⁺)	$2\text{VO}^{2+} + \text{Zn} + 4\text{H}^+ = 2\text{V}^{3+} + \text{Zn}^{2+} + 2\text{H}_2\text{O}$ (green solution) $2\text{V}^{3+} + \text{Zn}(\text{H}^+) = 2\text{V}^{2+} + \text{Zn}^{2+}$ (violet solution)

2.9. **A (CH)** – Cu(HCOO)₂, test with KMnO₄ (without or with H₂SO₄). **B (VS)** – VOSO₄, test with Ca(HCOO)₂ (**CH-3**).

Vial	Anion	Reaction equation(s) with observations
A	HCOO ⁻	$6\text{Cu}(\text{HCOO})_2 + 8\text{KMnO}_4 + \text{H}_2\text{O} = 8\text{MnO}_2\downarrow + 3(\text{CuOH})_2\text{CO}_3\downarrow + 8\text{KHCO}_3 + \text{CO}_2\uparrow$ (disappearance of purple colour, green to brown precipitate, gas evolution not observable) or $5\text{Cu}(\text{HCOO})_2 + 4\text{KMnO}_4 + 11\text{H}_2\text{SO}_4 = 5\text{CuSO}_4 + 2\text{K}_2\text{SO}_4 + 4\text{MnSO}_4 + 10\text{CO}_2\uparrow + 16\text{H}_2\text{O}$ (disappearance of purple colour, slow)
B	SO ₄ ²⁻	$\text{VOSO}_4 + \text{Ca}(\text{HCOO})_2 = \text{VO}(\text{HCOO})_2 + \text{CaSO}_4\downarrow$ (white precipitate, slow)

*If Cu(HCOO)₂ is not available, either use a mixture of Cu(CH₃COO)₂ or Cu(NO₃)₂ and Na(HCOO) solutions, or dissolve Cu(OH)₂ in a solution of HCOOH.

2.10. Bonus question:

☐ polyethylene ☐ proteins ☐ fats ☐ starch ☒ cellulose

Solution: A Simple Aldol Condensation

3.1. Answer depends on the student's TLC and should be consistent with their observations.

3.2. Answer depends on the student's TLC and should be consistent with their observations.

3.3. The used 1.3 mL of cinnamaldehyde correspond to

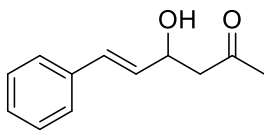
$$1.3 \text{ mL} \cdot 1.05 \frac{\text{g}}{\text{mL}} = 1.37 \text{ g, i. e. } \frac{1.37 \text{ g}}{132.16 \frac{\text{g}}{\text{mol}}} = 0.0103 \text{ mol of the compound.}$$

Theoretically, they yield an equimolar amount of product, i. e.

$$0.0103 \text{ mol} \cdot 172.23 \frac{\text{g}}{\text{mol}} = 1.8 \text{ g of product.}$$

3.4. NaOH is not consumed in the reaction, which works also with 3 equivalents of NaOH.

3.5. Structure of the aldol intermediate:



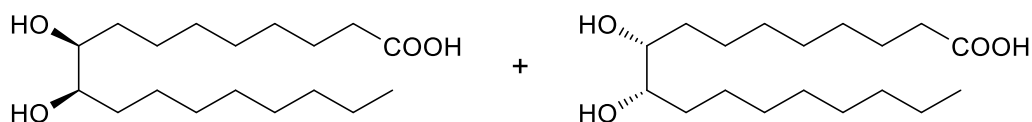
Solution: Dihydroxylation of Oleic Acid

4.1. Answer depends on the student's TLC and should be consistent with their observations.

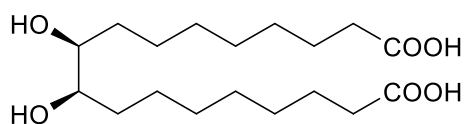
4.2. The product of the above reaction does not contain any UV-active functional group (functional group absorbing UV light in the wavelength range of a typical UV lamp). Therefore, it does not show under the UV lamp. On the other hand, KMnO_4 (purple) from the staining solution oxidizes the product (and other oxidizable compounds) and its consumption leaves whitish spots on a purple background.

4.3. In the above reaction, 1.6 equivalents of KMnO_4 are used in relation to oleic acid. After dihydroxylation of the latter, the excess of permanganate is reduced by sodium sulfite, first to manganese dioxide (basic solution), then to Mn(II) (acidic solution). The elimination of excess KMnO_4 prevents the product from being further oxidized (cleavage of the CC-bond of the diol unit under formation of carboxy termini).

4.4. The permanganate ion can approach the double bond from either side of the plane defined by the double bond unit of oleic acid to effectuate the *cis*-transfer of two O-atoms. This results in the formation of two product enantiomers.



4.5. The *cis*-dihydroxylation product of the shown dicarboxylic acid is achiral and it is formed as a single stereoisomer.



Solution: Synthesis of Lidocaine

5.1. Answer depends on the student's TLC and should be consistent with their observations.

5.2. Answer depends on the student's TLC (if applicable) and should be consistent with their observations.

5.3. Answer depends on the student's TLC (if applicable) and should be consistent with their observations.

5.4. After completion of the reaction, the reaction mixture is washed multiple times with water in order to remove the side product diethylammonium chloride and excess diethylamine.

5.5.a) Amount of *N*-(2,6-dimethylphenyl)chloroacetamide used in the reaction:

$$\frac{1 \text{ g}}{197.66 \frac{\text{g}}{\text{mol}}} = 5.06 \cdot 10^{-3} \text{ mol}$$

Amount of diethylamine used in the reaction:

$$\frac{2.1 \text{ mL} \cdot 0.706 \frac{\text{g}}{\text{mL}}}{73.14 \frac{\text{g}}{\text{mol}}} = 20.27 \cdot 10^{-3} \text{ mol}$$

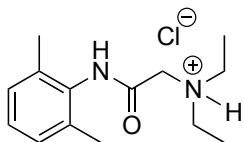
Consequently, the molar ratio *N*-(2,6-dimethylphenyl)chloroacetamide to diethylamine is:

$$\frac{20.27 \cdot 10^{-3}}{5.06 \cdot 10^{-3}} = 4.01$$

In other words, ca. 4 equivalents of diethylamine have been used in relation to *N*-(2,6-dimethylphenyl)chloroacetamide.

b) In the course of the reaction, a part of diethylamine, which acts as a nucleophile and a base at the same time, is protonated (the reaction formally generates one equivalent of HCl). The protonated part (= diethylammonium ion) is no longer available for the nucleophilic substitution with *N*-(2,6-dimethylphenyl)chloroacetamide. It needs to be compensated for by using an excess of diethylamine in the reaction.

5.6.



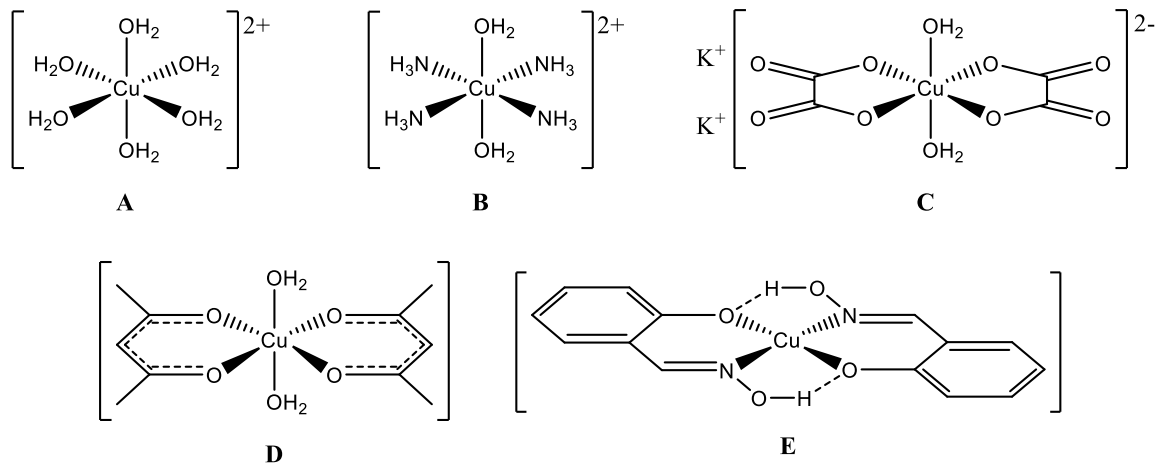
Solution: Transformation of Vanillin to Vanillyl Alcohol

- 6.1.** Answer depends on the student's TLC and should be consistent with their observations.
- 6.2.** In the above procedure, vanillin is reduced to vanillyl alcohol.
- 6.3.** The gas evolving after the addition of HCl (aq) is hydrogen (H_2).
- 6.4.** Yes, the reaction could still come to completion, because each equivalent of $NaBH_4$ can transfer more than one hydride to the carbonyl group of vanillin.

Solution: Colourful Copper

Complex	A	B	C	D	E
Colour	Light blue	Dark Blue	Light blue	Violet	Green
Molecular formula	$[\text{CuH}_{12}\text{O}_6]^{2+}$	$[\text{CuH}_{16}\text{N}_4\text{O}_2]^{2+}$	$\text{K}_2[\text{CuC}_4\text{H}_4\text{O}_{10}]$	$[\text{CuC}_{10}\text{H}_{18}\text{O}_6]$	$[\text{CuC}_{14}\text{H}_{12}\text{N}_2\text{O}_4]$

7.1.



7.2. Correct answer: "Precipitation of $\text{Cu}(\text{OH})_2$ "

7.3. Calculation based on $m_{\text{prep}} = 225.0 \text{ mg}$ **X** (CuCl_2) being used:

$$m_{\text{isol}} = 562.0 \text{ mg expected}$$

$$\begin{aligned}
 MW_{\text{Cu}(\text{C}_7\text{H}_6\text{NO}_2)_2} &= MW_{\text{Cu}} + 14 * MW_{\text{C}} + 12 * MW_{\text{H}} + 2 * MW_{\text{N}} + 4 * MW_{\text{O}} \\
 &= 63.55 \frac{\text{g}}{\text{mol}} + 14 * 12.01 \frac{\text{g}}{\text{mol}} + 14 * 1.008 \frac{\text{g}}{\text{mol}} + 2 * 14.07 \frac{\text{g}}{\text{mol}} + 4 \\
 &\quad * 16.00 \frac{\text{g}}{\text{mol}} \\
 &= 335.9 \frac{\text{g}}{\text{mol}}
 \end{aligned}$$

$$n_{\text{Cu,isol}} = \frac{m_{\text{solid}}}{MW_{\text{Cu}(\text{C}_7\text{H}_6\text{NO}_2)_2}} = 1.67 \text{ mmol}$$

The initial mass of copper is therefore calculated as:

$$m_{\text{Cu,isol}} = n_{\text{Cu,isol}} * MW_{\text{Cu}} = 1.67 \text{ mmol} * 63.55 \frac{\text{g}}{\text{mol}} = 106.1 \text{ mg}$$

The copper content is therefore calculated as:

$$wt\%_{\text{Cu,isol}} = \frac{m_{\text{Cu,isol}}}{m_{\text{prep}}} = 47.2\%$$

7.4. Calculation based on $m_{\text{titr}} = 100.0 \text{ mg}$ **X** (CuCl_2) being used:

$$n_{\text{Cu},\text{titr}} = V_{\text{sample}} * \frac{V_{\text{titr}}}{V_{\text{aliquot}}} * [\text{EDTA}]_{\text{standard}} = 0.500 \text{ L} * \frac{7.44 \text{ mL}}{50.00 \text{ mL}} * 10.0 \text{ mM} = 0.74 \text{ mmol}$$

$$m_{\text{Cu},\text{titr}} = n_{\text{Cu},\text{titr}} * MW_{\text{Cu}} = 0.74 \text{ mmol} * 63.55 \frac{\text{g}}{\text{mol}} = 47.0 \text{ mg}$$

$$wt\%_{\text{Cu},\text{titr}} = \frac{m_{\text{Cu},\text{titr}}}{m_{\text{titr}}} = 47.0\%$$

7.5. Based on the provided information, the anion of an anhydrous Cu(II) salt needs to be identified:

$$wt\%_{\text{Cu}} = \frac{MW_{\text{Cu}}}{MW_{\text{anion}} + MW_{\text{Cu}}}$$

$$MW_{\text{anion}} = MW_{\text{Cu}} * \frac{1 - wt\%_{\text{Cu}}}{wt\%_{\text{Cu}}} = 63.55 \frac{\text{g}}{\text{mol}} * \frac{1 - 0.473}{0.473} = 70.81 \frac{\text{g}}{\text{mol}}$$

This corresponds to twice the molecular weight of chlorine ($MW = 35.45 \text{ g/mol}$). Therefore, it can be concluded that the sample was anhydrous Cu(II) chloride, CuCl_2 . Near misses such as carbonate ($MW = 60.01 \text{ g/mol}$) or azide ($MW = 42.03 \text{ g/mol}$) can be excluded by their Cu(II) salts being insoluble in water.

7.6. Answer depends on student's performance and should be consistent with their observations.

Hard Water – Easy Titrations

Chemicals:

Chemical	State	Comment	GHS Hazard Statements
Water Sample W	Liquid	Prepared from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (10035-04-8), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (7791-18-6), and NaHCO_3 (144-55-8)	H319; P264, P280, P305+P351+P338, P337+P313
0.010 M HCl standard solution (7647-01-0)	Liquid		Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.
1.0 M HCl solution (7647-01-0)	Liquid	Corrosive	H290; P234, P390
Methyl orange solution (10 g/L in EtOH)	Liquid	Prepared from methyl orange (547-58-0) and EtOH (64-17-5) Flammable	H225, H301, H319; P210, P233, P240, P241, P242, P264, P270, P301+P310, P305+P351+P338, P405, P501
0.010 M EDTA standard solution	Liquid	Prepared from EDTA disodium salt dehydrate (6381-92-6)	H332, H373, H412; P260, P271, P273, P304+P340+P312, P314, P501
1.0 M NaOH (1310-73-2)	Liquid	Corrosive	H290; P234, P390
Buffer solution (pH = 10, $\text{C}_{\text{HB}^+} + \text{C}_{\text{B}} = 8.8 \text{ M}$)	Liquid	Prepared from NH_4Cl (12125-02-9) and NH_3 (25%, w/w, in H_2O) (1336-21-6)	H302, H314, H319, H335, H410; P261, P264, P270, P271, P273, P280, P303+P361+P353, P305+P351+P338, P310+P312, P337+P313

Eriochrome® Black T (1 wt% in NaCl)	Solid	Prepared from Eriochrome® Black T (1787-61-7) and NaCl (7647-14-5)	H319, H441; P264, P273, P280, P305+P351+P338, P337+P313, P391
Murexide (1 wt% in NaCl)	Solid	Prepared from Murexide (3051-09-0) and NaCl (7647-14-5)	Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.

Glassware and Equipment:

Item	Count	Intended Use
Volumetric flask, 500 mL	1	Distribution of W to students
Bottle, 200 mL	1	Distribution of EDTA standard solution to students
Bottle, 100 mL	1	Distribution of HCl standard solution to students
Bottle, 50 mL	3	Distribution of 1.0 M HCl (1), 1.0 M NaOH (1), buffer solution (1) to students
Vial, 10 mL	3	Distribution of methyl orange solution (1), Eriochrome® Black T mixture (1), and murexide mixture (1) to students
Beaker, 50 mL	1	To check the pH value of W and to fill burette
pH indicator strips	10	To check the pH value of W , of neutralized sample in part II, and of alkalified sample in part III
Burette, 25 mL	1	For titrations

Laboratory stand with burette holder	1	For titrations
Funnel, fitting the burette	1	To fill the burette
Erlenmeyer flask, 250 mL	3	For titrations
Volumetric pipette, 25.00 mL	1	To aliquot samples
Pipette bulb	1	To aliquot samples
Plastic pipette	3	For addition of methyl orange (1), 1.0 M HCl (1), and 1.0 M NaOH (1)
Hot plate	1	For sample preparation in part II
Water bath	1	For sample preparation in part II
Thermometer	1	To monitor water bath temperature
Spatula	1	For addition of Eriochrome® Black T and Murexide
H ₂ O wash bottle	1	To clean glassware

Preparations:

Preparations are outlined to suffice for ~20 students.

Students' samples **W**:

1. Prepare individual stocks for CaCl₂·2H₂O, MgCl₂·6H₂O, and NaHCO₃ in 500 mL volumetric flasks:
 - 1800 mg CaCl₂·2H₂O to 500 mL H₂O
 - 550 mg MgCl₂·6H₂O to 500 mL H₂O
 - 1150 mg NaHCO₃ to 500 mL H₂O
2. Aliquot 25 mL of each stock solution to a student's 500 mL volumetric flask and dilute to the mark with H₂O. The corresponding solution contains [Ca²⁺] = 1.22 mM, [Mg²⁺] = 0.27 mM, and [HCO₃⁻] = 1.37 mM.

Methyl orange:

1. In a 100 mL volumetric flask, dissolve 1.00 g methyl orange in EtOH.
2. Distribute the solution to students' vials.

EDTA standard solution:

1. In a 1000 mL volumetric flask, dissolve 3.72 g in H₂O.
2. Distribute to the standard solution to students' bottles.

pH buffer (pH = 10, C_{HB+} + C_B = 8.8 M):

1. In a 1000 mL volumetric flask, add
 - 70 g NH₄Cl
 - 570 mL concentrated NH₃ (25% in H₂O)
2. Fill to the mark with H₂O.
3. Distribute to the buffer to students' bottles.

Eriochrome® Black T:

1. Grind 25 mg Eriochrome® Black T and 10 g NaCl to a fine powder.
2. Distribute to students' vials.

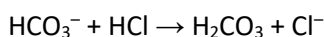
Murexide:

1. Grind 100 mg murexide and 10 g NaCl to a fine powder.
2. Distribute to students' vials.

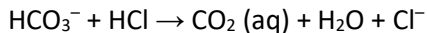
0.010 M HCl solution, 1.0 M HCl solution, 1.0 M NaOH solutions are commercially available or can be prepared from simple dilution or dissolution.

Solutions (calculations based on preparations outlined above):

1. The pH value of **W** is about 8 depending on the used amount of NaHCO₃. Being 2 pH units below $pK_{a,2}$, it can be calculated that $[HCO_3^-]/[CO_3^{2-}] > 100$ and, therefore, the presence of CO₃²⁻ can be neglected:



or



2. Carbonate hardness (CH) includes all Ca^{2+} and Mg^{2+} balanced by HCO_3^- and CO_3^{2-} in solution. As established in task 1, the presence of CO_3^{2-} can be neglected:

$$([\text{Ca}^{2+}] + [\text{Mg}^{2+}])_{\text{CH}} = \frac{1}{2} * [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \cong \frac{1}{2} * [\text{HCO}_3^-]$$

$$[\text{HCO}_3^-] = \frac{V_1}{V_{\text{sample},1}} * [\text{HCl}]_{\text{standard}} = \frac{6.85 \text{ mL}}{50.00 \text{ mL}} * 10.0 \text{ mM} = 1.37 \text{ mM}$$

$$([\text{Ca}^{2+}] + [\text{Mg}^{2+}])_{\text{CH}} = \frac{1}{2} * 1.37 \text{ mM} = 0.69 \text{ mM}$$

3. Total hardness (TH) can be calculated directly from the co-titration of both alkaline earth metals:

$$([\text{Ca}^{2+}] + [\text{Mg}^{2+}])_{\text{TH}} = \frac{V_2}{V_{\text{sample},2}} * [\text{EDTA}]_{\text{standard}} = \frac{7.47 \text{ mL}}{50.00 \text{ mL}} * 10.0 \text{ mM} = 1.49 \text{ mM}$$

4. The ratio can be calculated from the titration of Ca^{2+} and the previous result:

$$[\text{Ca}^{2+}] = \frac{V_3}{V_{\text{sample},3}} * [\text{EDTA}]_{\text{standard}} = \frac{6.12 \text{ mL}}{50.00 \text{ mL}} * 10.0 \text{ mM} = 1.22 \text{ mM}$$

$$\frac{[\text{Ca}^{2+}]}{[\text{Mg}^{2+}]} = \frac{[\text{Ca}^{2+}]}{([\text{Ca}^{2+}] + [\text{Mg}^{2+}])_{\text{TH}} - [\text{Ca}^{2+}]} = \frac{1.22 \text{ mM}}{1.49 \text{ mM} - 1.22 \text{ mM}} = 4.51$$

5. The correct answers are:

- Addition of $\text{Ca}(\text{OH})_2$: Lime softening, i.e. Ca^{2+} removal by $\text{Ca}^{2+} + 2 \text{HCO}_3^- + \text{Ca}(\text{OH})_2 \rightarrow 2 \text{CaCO}_3 \downarrow + 2 \text{H}_2\text{O}$
- Pass through ion exchange resin (NaCl-regenerated): Ca^{2+} and Mg^{2+} removal by $2 (\text{R-SO}_3)\text{Na} + \text{M}^{2+} \rightarrow 2 (\text{R-SO}_3)_2\text{M} + 2 \text{Na}^+$ using R-SO_3^{2-} to abbreviate the resin
- Boiling: Removal of carbonate hardness by HCO_3^- auto-protonation by $\text{M}^{2+} + 2 \text{HCO}_3^- \rightarrow \text{MCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}$