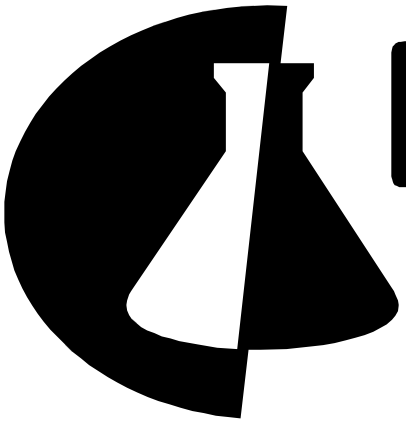

IChO

46. International Chemistry Olympiad Vietnam 2014

National German Competition

Volume 20

Preface

To become a member of the German IChO-team you have to be successful in four rounds of a national competition which is led by PD Dr. Sabine Nick.

The problems to be solved in the 1st round are sent to all high schools. To solve the problems the students may use all resources available, e.g. text-books etc.

All those students who solve about 70% of the tasks correctly will receive the problems of the 2nd round, which are to be solved in the same way as mentioned above. These problems are the most difficult ones in the whole competition.

The top 60 of the participants of the 2nd round are invited to the 3rd round, a one-week chemistry camp. Besides lectures and excursions to chemical plants or universities there are two written theoretical tests of 5 hours each.

The top 15 of the 3rd round are the participants of the 4th round, a one-week practical training. There are two written five-hour tests - one theoretical and one practical - under the same conditions as at the IChO. Here the team is selected.

In this booklet all problems of the selection procedure and their solutions are collected. Future participants should use this booklet to become acquainted with the problems of the competition. Therefore the solutions to the problems given in this booklet are more detailed than the answers we expect from the students in the competition.

In the appendix you find tables of historical interest.

Wolfgang Hampe

This booklet including the problems of the 46th IchO and the latest statistics is available as of September 2014 from

http://www.icho.de (”Aufgaben”)

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Part 1: The problems of the four rounds

Part 2: The solutions to the problems of the four rounds

Part 3: The problems of the IChO

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(Association of former participants and friends of the IChO)
Internet address: www.fcho.de

Part 1

The problem set of the four rounds

First Round

Problem 1-1 Chemistry and Horses

There is a typical smell in stables caused by a compound **A** formed by bacterial decomposition of urea contained in the urine of horses.

*a) What is compound **A**? Write down the equation for the decomposition of urea.*

A horse produces 10 to 50 mL of urine per kg body mass per day. The content of urea depends on the protein content of the fodder and amounts to an average of 5 mmol/L (3.3 – 6.7 mmol/L).

b) Which mass of compound A can be theoretically formed in a stable with 23 horses having a body mass of 550 kg each?
(Use 35 mL/kg body weight as amount of urine and ρ = 1000 kg/m^3 as the approximate density of the urine of horses.)

In the 19th century many scientists were engaged in the analysis of natural materials and compounds including the excretions of people and animals.
Justus v. Liebig, a famous German chemist, published in 1829 in a journal called Poggendorfs Annalen: "*Mixing urine of horses with an excess of hydrochloric acid leads after some time to a yellow-brownish crystalline precipitate. By washing with water the unpleasant smell of the precipitate does not vanish.*"
He had prepared a new compound **B**, the composition of which he published as follows

Nitrogen	7.337 parts in 100 parts	Carbon	63.032 parts in 100 parts
Hydrogen	5.000 parts in 100 parts	Oxygen	24.631 parts in 100 parts.

*c) Determine the empirical formula of **B**.*

Liebig's discovery was path breaking as the former assumption that compound **B** could be benzoic acid was refuted because the compound contained nitrogen. Five years later Liebig revised his results and published new results of an analysis (compound **B'**):

Nitrogen	7.816 /100	Carbon	60.742 /100
Hydrogen	4.959 /100	Oxygen	26.483 /100.

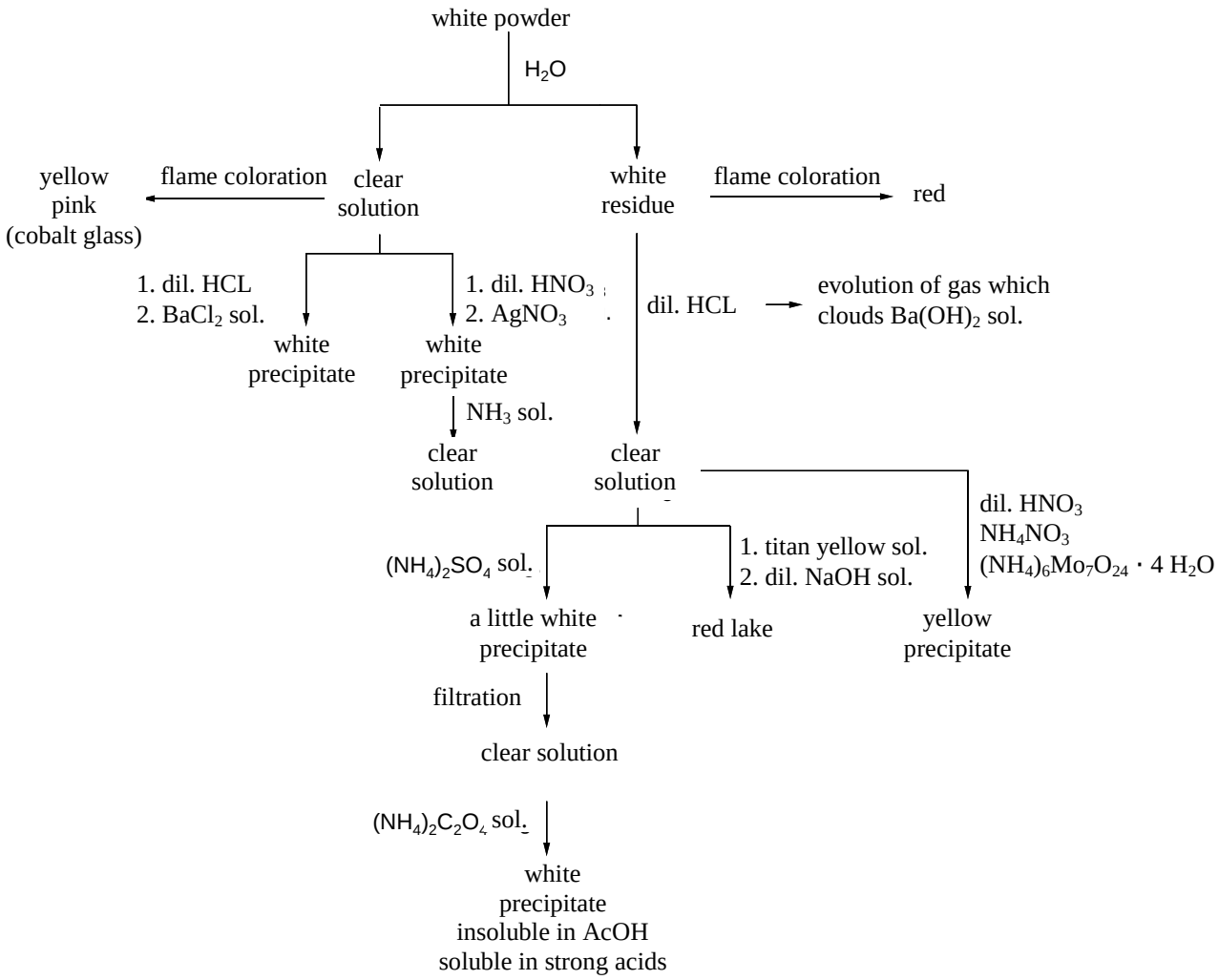
Compound **B'** dissolves well in hot water. **B'** reacts with zinc forming hydrogen amongst other compounds and forms a lot of metallic salts. When heated with mineral acids or with bases **B'** decomposes to benzoic acid and an amino acid.

*d) Determine compound **B'**. What is the name of **B'**? Draw its line-bond structure.*

If compound **B'** is heated to decomposition a resin like residue and benzoic acid form besides a compound **C** with the molecular formula C_7H_5N. Liebig describes **C** as a "... liquid, yellowish, pleasant smelling, ammonia containing oil which shows great similarity to fatty oils."

*e) What is compound **C**? How can ammonia be generated from **C**? Draw a reaction scheme which illustrates the forming of ammonia.*

A young girl, Mareike, finds a plastic bag near to the box of her horse. It contains white powder. Part of the powder has already fallen out of the bag and lies directly in front of the box. Nobody knows which kind of powder this is. So Mareike takes a part of it and gives it to her older sister who just finished her PhD in chemistry. She remembers from her first years of university how to analyze an inorganic powder and delivers the following result:



Mareike is relieved because her sister did not find anything dangerous.

f) Which ions are in the powder if only the reactions and observations mentioned in the scheme are taken into account? Which salts could be theoretically existent in the powder?

Problem 1-2 Redox Reactions

The redox reaction is an important type of chemical reactions.

a) Explain the concept of "redox reactions" shortly. In doing so use the reaction of sodium with water as an example. Write down the relevant reaction equation(s) and apply oxidation numbers.

b) Which of the following equations represent a redox reaction?

i) $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

ii) $Cl_2 + 2\ HI \rightleftharpoons I_2 + 2\ HCl$

iii) $2\ Al + AlCl_3 \rightleftharpoons 3\ AlCl$

iv) $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ HCrO_4^-$

v) $[Fe(H_2O)_6]^{3+} + 3\ SCN^- \rightleftharpoons [Fe(H_2O)_3(SCN)_3] + 3\ H_2O$

vi) $Cr_2O_7^{2-} + 4\ H_2O_2 + 2\ H^+ \rightleftharpoons 2\ CrO(O_2)_2 + 5\ H_2O$

vii) $[Ti(OH)_2(H_2O)_4]^{2+} + H_2O_2 \rightleftharpoons [Ti(O_2) \cdot aq]^{2+} + 6\ H_2O$

viii) $2\ AsH_3 \rightleftharpoons 2\ As + 3\ H_2$

Batteries are galvanic elements, electrochemical cells in which redox reactions take place.

c) Write down the main difference between primary and secondary galvanic elements.

To harness the energy of a chemical reaction so as to produce an electric current has a long tradition. Small vessels made of clay were excavated from a settlement near to Bagdad (dated 250 BC to 225 AD). They contained a copper cylinder and an iron rod.
Until today it's not clear whether these vessels point to the use of galvanic elements in those times.

d) Which metal could have served as anode, which as cathode if these vessels had been used to provide electrical power?
Write down the chemical half equations (anode and cathode).
(E^0 (Cu/Cu^{2+}) = +0.34 V, E^0 (Fe/Fe^{2+}) = –0.41 V)

e) Name two more preconditions for the construction of an electrical power providing battery.

f) What is the cell potential of the Bagdad battery under standard conditions?

The table on the next page presents some standard half-cell potentials in aqueous solutions at 298 K.

Reduced form	Oxidized Form	E° [V]
$Zn^{2+} + 2\ e^-$	Zn	-0.76
$Fe^{3+} + 3\ e^-$	Fe	-0.04
$2\ H^+ + 2\ e^-$	H_2	± 0.00
$Cu^{2+} + 2\ e^-$	Cu	+0.34
$I_2 + 2\ e^-$	2 I-	+0.54
$Fe^{3+} + e^-$	Fe^{2+}	+0.77
$Cl_2 + 2\ e^-$	2 Cl-	+1.36

g) Which statements concerning the respective experiments are correct? Use the data from the table to find your answer.

i) Granulates of zinc are given into diluted hydrochloric acid:
1. Chlorine evolves.
2. Hydrogen evolves.
3. Nothing happens.
4. Zinc dissolves.

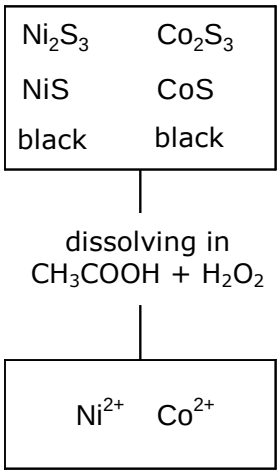
ii) Splinters of copper are given into diluted hydrochloric acid:
1. Chlorine evolves.
2. Hydrogen evolves.
3. Nothing happens.
4. Copper dissolves.

iii) A solution of iron(III) ions is mixed with a solution of potassium iodide:
1. Iodine forms.
2. Iron precipitates.
3. Nothing happens.
4. The solution turns blue.

In the separation scheme of cations cobalt and nickel are precipitated as sulfides. For further identification the sulfides are dissolved in H_3CCOOH/H_2O_2 or conc. HNO_3.

h) Is the dissolving of NiS and CoS a redox reaction? Account for your answer!

i) Why is it better to use H_3CCOOH/H_2O_2 instead of conc. HNO_3?



Problem 1-3 Thermal Degradation of a Compound

In order to synthesize a coordination compound a mixture of 1 mmol of copper(I) bromide and 1 mmol of 2,5-dimethyl pyrazine was stirred in acetonitrile. A solid **X** precipitated. **X** was separated, dried and subjected to an elementary analysis with the following results:

C: 28.65%, N: 11.12%, H: 3.21%.

Additionally the content of copper and bromine were detected by atomic absorption spectroscopy (AAS): Cu: 25.25%, Br: 31.75%.

*a) Find the empirical formula, the molecular formula and the molar mass of **X**!*

For further characterization of **X** the thermal properties were detected by using differential thermal analysis (DTA) and thermogravimetric analysis (TG) simultaneously coupled with mass spectrometry (MS). The results are shown in the following image.

In the MS measurement only the fragment with the highest m/Z rate is shown.

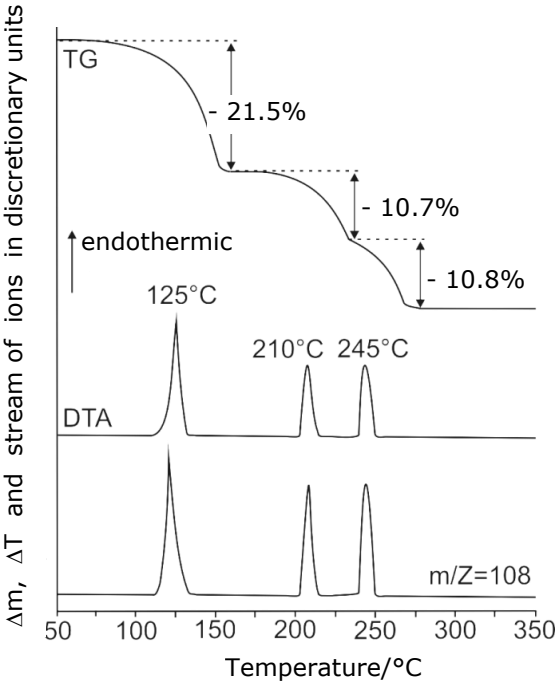


*Image of the DTA, TG and MS-trend-scan curve of compound **X** (each loss of mass in the TG curve refers to the original existing mass)*

*b) Which information about the thermal reactivity (behavior at heating) of **X** provides*

i) the TG curve concerning the loss of mass,
ii) the DTA curve concerning the heat of reaction of the events,
iii) the MS-trend-scan-curve concerning the leaving components?

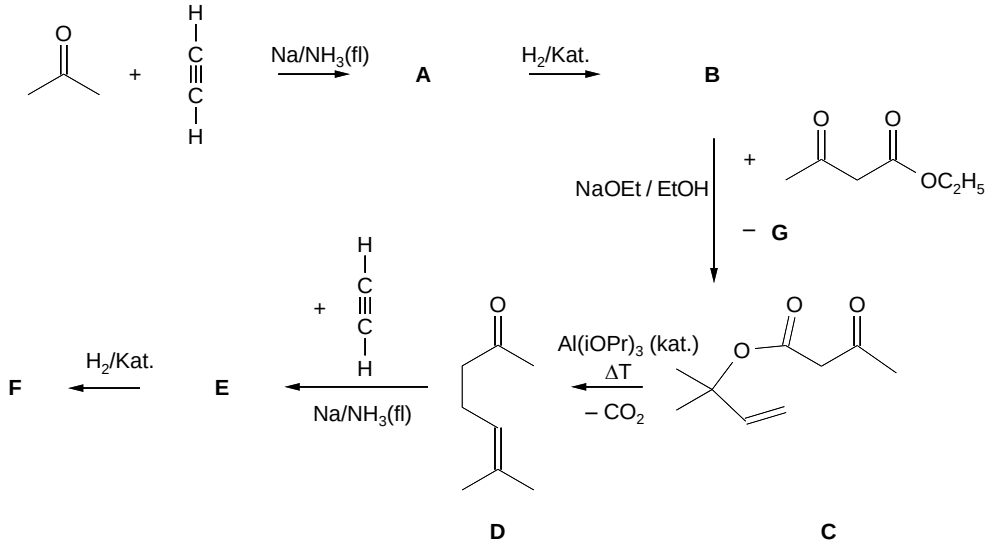
c) Determine the composition (molecular formula) of the compounds which form after the first, second and third step of the splitting-off.
(Hint: Compare the experimental with the theoretically possible loss of weight.)

Problem 1-4 An Organic Riddle

Below you find the scheme of the synthesis of compound **F. F** is an intermediate in the production of compound **H**. **H** is a natural product which can be synthesized as well as obtained from natural resources.

a) *Draw the line-bond structures of **A**, **B**, **E**, **F** and **G**!*
*(Hint: In step **A** to **B** as well as in step **E to F** 1 mol of hydrogen reacts with 1 mol of **A** and **E**, respectively.)*

b) *Propose a mechanism for the reaction of **C** to **D**.*

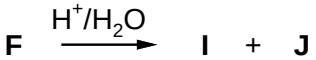


F reacts with t-butyl acetate under cleavage of t-butanol to form **H**.

c) *Draw the line-bond structure of **H** and write down its name.*

d) *Which is the natural source of **H**?*

If **F** is treated with an aqueous solution of acid two compounds **I** and **J** are formed which have the same molecular formula as **F**:



e) *Draw the line-bond structures of **I** and **J** and write down their names. Explain why both compounds form.*

Second Round (homework)

Problem 2–1 An Inorganic Riddle

A compound **X** has to be found which contains a metal **M** in the oxidation state +IV.
X crystallizes from an aqueous solution as a monohydrate. The percentage by weight of **M** in the monohydrate of **X** is about 18 %.
X is insoluble in water and decomposes when heated. **X** shines metallically black-violet. In solid **X** the metal **M** has an octahedral surrounding of oxygen. The simplest oxide of **M** crystallizes in a sodium chloride structure.
The compounds **A**, **B** and **C** are necessary to synthesize **X**.

Compound **A** forms white, non-hygroskopic crystals. **A** can be obtained by oxidation of sodium iodate or sodium iodide with chlorine or bromine in alkaline aqueous solution. **A** exists as an ortho form ("water rich"). The molar mass of **A** is higher than 250 g/mol and the stoichiometric ratio of sodium and oxygen in **A** is n(Na):n(O) = 1:2.

B is an ionic compound. Its anion is a strong oxidation agent and can be obtained by oxidizing sulfates or hydrogen sulfates by very strong oxidation agents (fluorine or in an electrochemical way). The cation shows yellow flame coloration.

An aqueous solution of compound **C** shows the following reactions:

- With an aqueous solution of NaOH a precipitate forms, which does not dissolve in an excess of NaOH but is soluble in acids.
- With barium chloride a white precipitate forms, which does not dissolve in acids.
- With sulfur hydrogen a black solid precipitates from an ammoniac solution of **C**.
- There is no coloring with an aqueous solution of potassium cyanate.

a) *Determine the molecular formulae of the compounds **A**, **B** and **C**.*

b) *What is the oxidation state of sulfur in the anion of **B**? Account for your answer.*

c) *Write down the molecular formula of **X** and the reaction equation of the formation of **X** · H_2O. Assign oxidation numbers to all atoms and ions of the reaction equations.*

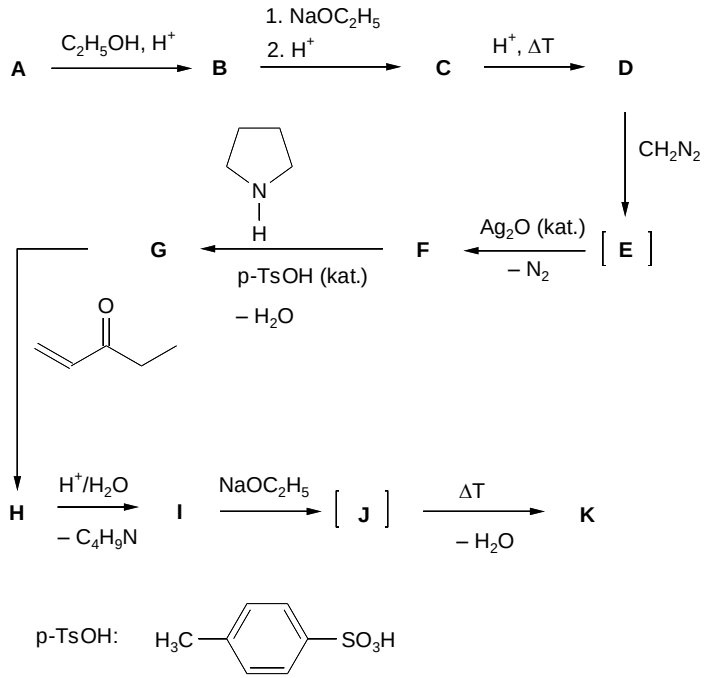
d) *What do you expect compound **X** to be, diamagnetic or paramagnetic? Account for your answer using an orbital diagram. Which factors have an impact on the occupation of the orbitals?*

Metal **M** and titanium are the main components of one representative of a modern class of alloys.

e) *Under which name is this alloy known? Which extraordinary property does this kind of alloys have?*

Problem 2-2 An Organic Synthesis

The following scheme shows the synthesis of the compound **K**:



- **K** contains at least one carbon ring.
- **K** forms a precipitate with dinitrophenylhydrazine.
- The test of **K** with Fehling's solution is negative.
- 1 mol of **K** adds bit by bit 1 mol of bromine (Br_2).
- The elementary analysis of **K** gives the following result:
  80.44 % of C, 9.82 % of H, 9.74 % of O.

Further information:

- **A** is an unbranched dicarboxylic acid.
- **A** consists of nearly 50 % of carbon.
- **A** reacts with ethanol in the molar ratio n(A):n(ethanol) = 1 : 2.
- **D** has the molecular formula C_5H_8O.
- In the reaction **C** $\longrightarrow$ **D** a gaseous compound forms as side product (not shown in the scheme).
- **F** is a cyclic compound.
- The ^{1}H-NMR of **F** shows three groups of protons (1.74 ppm, 1.88 ppm, 2.22 ppm), the ^{13}C-NMR shows carbon in four different chemical surroundings (23.8 pppm, 26.5 ppm, 40.4 ppm, 208.5 ppm)
- The reaction **F** $\longrightarrow$ **G** is performed in toluene using a water separator.
- **I** has the molecular formula $C_{11}H_{18}O_2$.
- The compounds **E** and **J** are intermediates which cannot be separated.

a) *Determine the structural formulae of **A** through **K**!*

b) *Mark all stereogenic centers in **J** with a star. Draw 3D images of all stereoisomers and identify at each stereogenic center whether it has an S- or an R-confirmation. Which kind of stereoisomerism do you find between the stereoisomers?*

(Hint: ◀ in front of the paper plane ||||||| behind the paper plane)

c) *Sketch the mechanism of the following reactions shortly. Under which name are the reactions (i, iii und iv) and the combination of iii and iv well-known?*

*i) **B** ⟶ **C** ii) **C** ⟶ **D** iii) **G** ⟶ **H** iv) **I** ⟶ **J***

d) *Give the reason why compound **F** is not made to react directly with ethyl vinyl ketone but in a "detour reaction" via compound **G**.*

e) *In the reaction of **I** with sodium ethanolate to form **J** several constitutional isomers may form as products. Draw images of these constitutional isomers. Account for the fact that in the end exclusively **J** is formed.*

Problem 2 -3 Spectroscopy

Modern chemists have available to them a powerful array of instrumental techniques for determine molecular structures. Interactions between electromagnetic radiation and molecules can be probed by two techniques: IR and Raman spectroscopy.

a) *Describe the fundamental difference between these two techniques with regard to the origin of measured frequencies.*

An important difference between these two methods is that different selection rules apply. IR spectroscopy requires that there is a change in dipole moment during the vibration while the requirement of Raman spectroscopy is that the polarizibility of the molecule must change during the vibrations.

The number of vibrational normal modes (z) of a molecule containing N atoms is easy to be calculated:

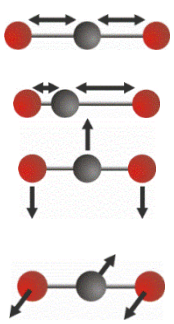
Linear molecules	z = 3 N – 5
Non-linear molecules	z = 3 N – 6

b) *Sketch all possible vibrations of the molecules i) and ii) and 4 possible vibrations of the molecule iii)*

i) H_2O ii) N_2 iii) BF_3

and indicate whether they are IR and/or Raman active. Give a plot for each vibration.

Example CO_2



symmetric stretch

antisymmetric stretch

bending mode

bending mode
(upward and downward movement with respect to the paper plane)

c) *How many peaks do you expect in the IR spectrum of carbon dioxide? Account for your decision!*

d) *In the calculation of the number of normal modes in a linear molecule 5 is subtracted from 3N, at non-linear molecules 6. Explain why.*

We expect the spectrum to provide information about vibrations in a molecule. The resolution of such spectra is often bad, i.e. the absorption bands are very broad. The reason is that vibrational transition is accompanied by different transitions in the rotational energy.
It is possible to avoid rotation by cooling the sample down. This can be done by expansion in a carrier gas into vacuum. In this case the pressure in a system of reservoir and chamber has to obey the following equation:

$$\frac{p_{chamber}}{p_{reservoir}} \leq \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma+1}}$$

with γ = isentropic expansion factor of the gas which can be related to the degrees of freedom.

e) *Calculate the maximal pressure in the chamber for such an expansion with a reservoir pressure of 650 mbar and helium as gas.*

S-(−)-Limonene was studied in a series of measurement. It was expanded in a chamber with helium as carrier gas. The mixture into the chamber was detected by Raman spectroscopy. Vibrations of different conformers were observed.

f) *How many and which kind of vibrations do you expect in S-(−)-limonene?*

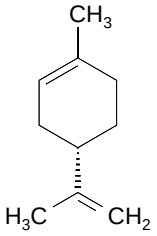
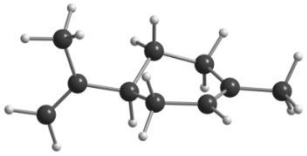


Fig. 1: S-(−)-Limonene

The assignment of the vibrations to the different conformers is conducted by quantum chemical calculations. It is possible to determine the temperature of expansion using the ratio of intensities of the conformers.

Conformer A



Conformer B

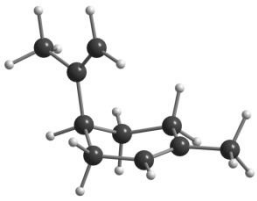


Fig. 2: Conformers of S-(−)-limonene: equatorial conformer A and axial conformer B.

The energetically more favorable is the (pseudo) equatorial conformer A. There are two more conformers which are energetically nearly equal to each other. They differ only in the rotation of the isopropylene group ("rotamers"). The energy of the axial conformer B lies considerably below these two conformers.
The calculated difference in energy between A and B is $6{,}475 \cdot 10^{-5}$ Hartree.

g) Calculate the energy difference in kJ/mol and eV! Is the transition A $\longrightarrow$ B at room temperature (25°C) possible? Explain by using the probability of the existence of B at this temperature (Boltzmann distribution).

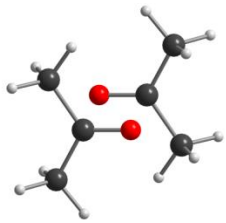
h) If the ratio of intensities (i(A):i(B)) is 7:1, what is the expansion temperature?

i) Why is the equatorial arrangement in ring systems mostly more favorable than the axial?

j) Which reason could account for the fact that in the case of limonene conformer B is more favorable than the two rotamers?

Acetone and its dimer were inspected in the same way. The dimer of acetone may have one of the two arrangements shown below:

Dimer 1:



Dimer 2:

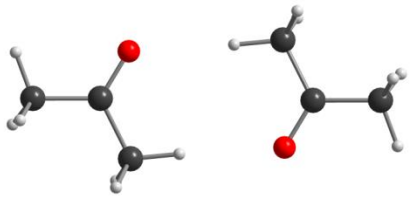


Fig. 3: Possible dimers of acetone

It was predicted in comparison with quantum mechanical calculations which kind of dimer should be present. At high temperature and low concentration only the monomer was detected while at low temperature and high concentration the dimer was detected, too.

The symmetry of a molecule is important for spectroscopy because it gives information which vibrations can be observed. The symmetry elements are merged in so called point groups. Generally the Schoenflies notation is used for molecules.

k) Determine the point group (in Schoenflies notation) of acetone and the two considered dimers. Use a drawing to sketch the respective symmetry elements.

The C=O bond tends to form dimers. It can be detected by its stretching vibration. Fig.4 shows this region at different temperatures and concentrations. Fig 5 is the result of theoretical calculations of C=O stretching modes of acetone and its two considerable dimers.

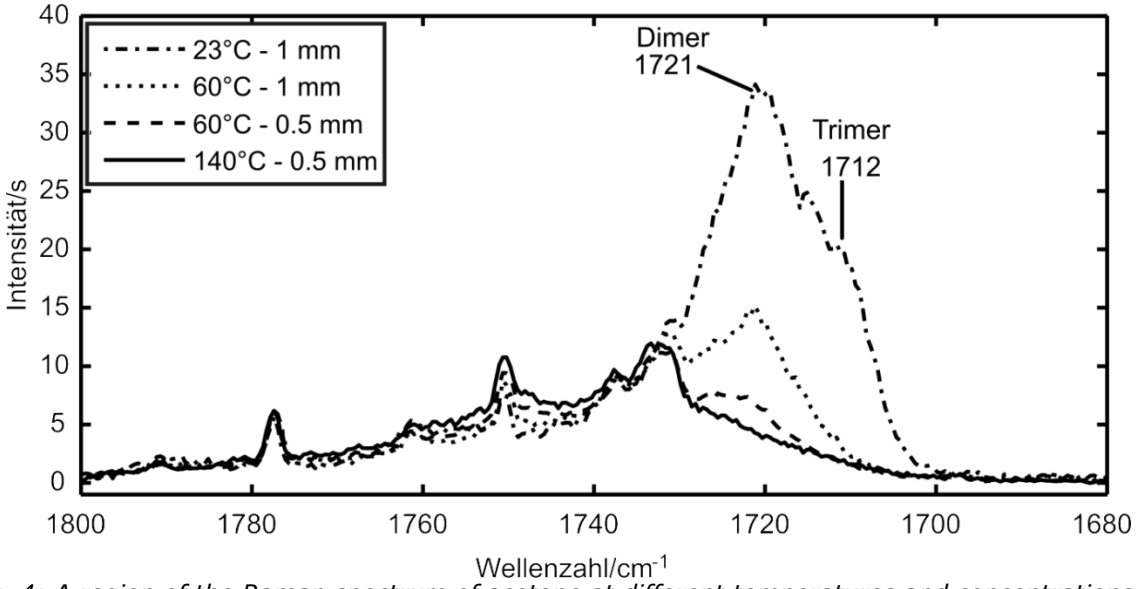


Fig. 4: A region of the Raman spectrum of acetone at different temperatures and concentrations.

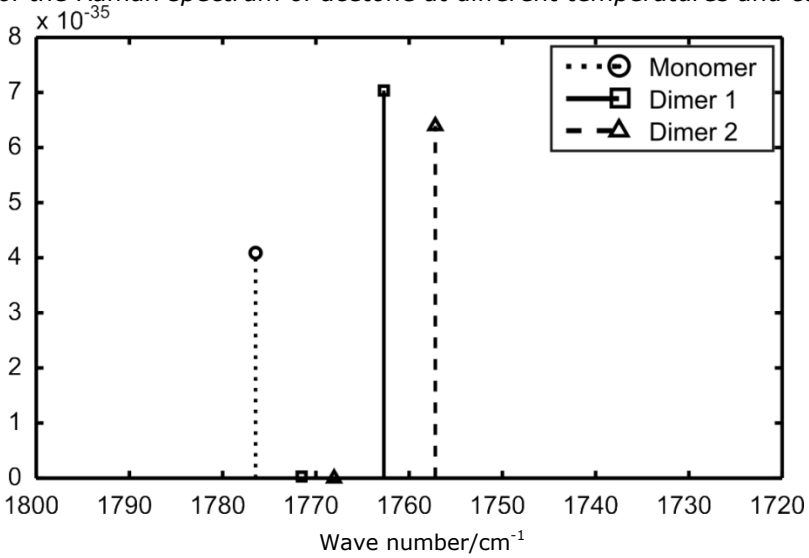
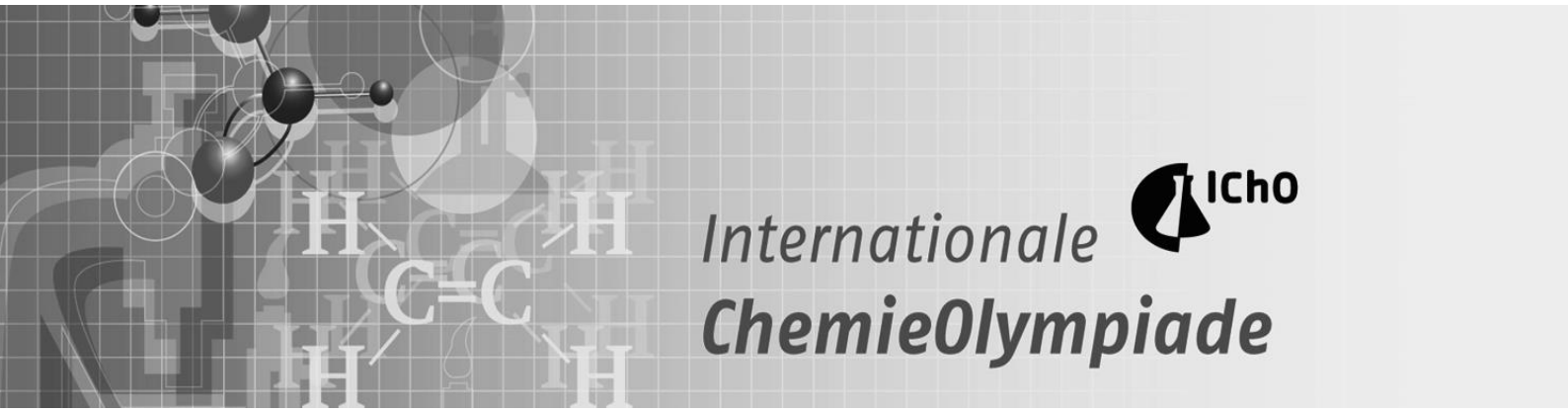


Fig. 5: Calculated wave numbers of acetone and acetone dimers

l) Which of the two considered dimers is presumably the real dimer of acetone?



Problems Round 3

Test 1 Göttingen 2014: Problems 3-01 to 3-10

Test 2 Göttingen 2014: Problems 3-11 to 3-20

time	5 hours.
your name	write it on every answer sheet.
relevant calculations	write them down into the appropriate boxes. otherwise you will get no points
atomic masses	use only the periodic table given.
constants	use only the values given in the table.
answers	only in the appropriate boxes of the answer sheets, nothing else will be marked.
draft paper	use the back of the pages of the problem booklet**,** but everything written there will not be marked.
problem booklet	you may keep it.

Good Luck

Useful formulas and data

$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$ $\Delta G^0 = - \Delta E \cdot z \cdot F$ $\Delta G^0 = - R \cdot T \cdot \ln K$

$\Delta G = \Delta G^0 + R \cdot T \cdot \ln Q$ $\ln (Kp_1/Kp_2) = \frac{-H^0}{R} \cdot (T_1^{-1} - T_2^{-1})$

$p \cdot V = n \cdot R \cdot T$ for ideal gases and osmotic pressure

Nernst equation : $E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_{Ox}/c_{Red})$

for metals $E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c(Me^{z+}/c^0)$

for non-metals $E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_0/c(NiMe^{z-})$

for hydrogen $E = E^0 + \frac{R \cdot T}{F} \cdot \ln \frac{c(H^+)/c^0}{(p(H_2)/p_0)^{1/2}}$

with $c^0 = 1$ mol/L, $p^0 = 1.000 \cdot 10^5$ Pa

Rate laws

0. order	$c = c_o - k \cdot t$	
1. order	$c = c_o \cdot e^{-k_1 \cdot t}$	
2. order	$c^{-1} = k_2 \cdot t + c_o^{-1}$	

Arrhenius equation: $k = A \cdot e^{-Ea/(R \cdot T)}$

A	pre-exponential factor
E_a	activation energy

Law of Lambert and Beer: $A = \varepsilon \cdot c \cdot d$

A	absorbance
ε	molar absorption coefficient
d	length of the cuvette
c	concentration

Transmission $T = \frac{I}{I_0}$ Absorbance $A = \lg \frac{I_0}{I}$ with I Intensity

Speed of light $c = 3.000 \cdot 10^8$ ms^{-1}

Gas constant $R = 8.314$ JK^{-1}mol^{-1}

Faraday constant $F = 96485$ Cmol^{-1}

Avogadro constant $N_A = 6.022 \cdot 10^{23}$ mol^{-1}

Planck constant $h = 6.6261 \cdot 10^{-34}$ Js

$p^o = 1.000 \cdot 10^5$ Pa 1 atm $= 1.013 \cdot 10^5$ Pa 1 bar $= 1 \cdot 10^5$ Pa

1 Å $= 10^{-10}$ m

A periodic table was provided.

Third Round Test 1

Problem 3-01 Multiple Choice

With one or more correct answers even if the question is written in singular.

a) In an experiment magnesium reacts with a diluted solution of hydrogen chloride: $Mg_{(s)} + 2\ HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$.
By which measurement during the process of the reaction could the rate reaction determined best?

A	the mass of Mg	**B**	the pH value of the solution	**C**	the concentration of $MgCl_2$	**D**	the volume of H_2

b) Which of the center atoms in the following species obeys the octet rule?

A	NO	**B**	BH_4^-	**C**	PCl_5	**D**	BF_3	**E**	XeF_4

c) Which of the following statements about oxygen containing compounds is correct?

A	KNO_3 is a salt without oxidizing ability.
B	Oxygen in PbO_2 has the oxidation number -1, thus it is a peroxide.
C	C and Si are in the same group so that both, CO_2 and SiO_2, are gaseous at 298 K.
D	The oxidation number of oxygen in OF_2 is +2
E	H_2O_2 has oxidizing ability but no reducing ability.

d) Ozone can be prepared from oxygen by silent discharge (dielectric-barrier discharge) in an ozonizer. 10 mL of oxygen give a mixture of 9.3 mL (at standard conditions). Which volume of ozone is formed?

A	0.35 mL	**B**	0.7 mL	**C**	1.05 mL	**D**	1.4 mL	**E**	2.8 mL

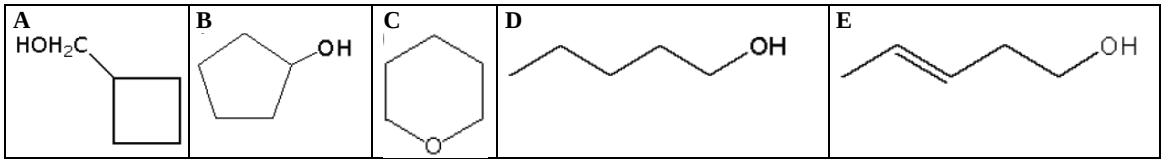
e) A colorless sample of a gas may contain CO_2, SO_2, HCl and HI. The sample was passed through a proper amount of chlorine water and reacted completely without any gas left. Then the colorless solution was acidified and seperated into two test tubes. Solutions of $AgNO_3$ and $BaCl_2$, respectively, were added. In both test tubes a white precipitate was found. Which of the following statements is correct?

A	The sample contains CO_2.
B	The sample contains SO_2.
C	The sample may contain HCl.
D	The sample may contain HI.
E	The precipitates in the test tubes may be AgCl and $BaSO_4$, respectively.

f) Which of the following statements about halides and their hydrogen acids are correct?

A	The order of electron affinity is F > Cl > Br > I.
B	The order of electronegativity is F > Cl > Br > I.
C	The order of polarity of the molecules is HF > HCl > HBr > HI.
D	The order of acid strength is HF > HCl > HBr > HI.
E	The order of amount of bond enthalpy is HF > HCl > HBr > HI.

g) Each of the following five compounds contains 5 carbon atoms. Which of them has the lowest boiling temperature?



Problem 3-02 Stoichiometric Calculations I

1.000 g of a mixture of potassium chromate and potassium dichromate is dissolved in water. The solution is filled up to 100.0 mL. Approximately 0.5 g of potassium iodide and 20 mL of diluted sulfuric acid are added to 10.0 mL of this solution.
Ions of iodide reduce both chromate as well as dichromate to form chromium(III) ions (Cr^{3+}) and elementary iodine (I_2).

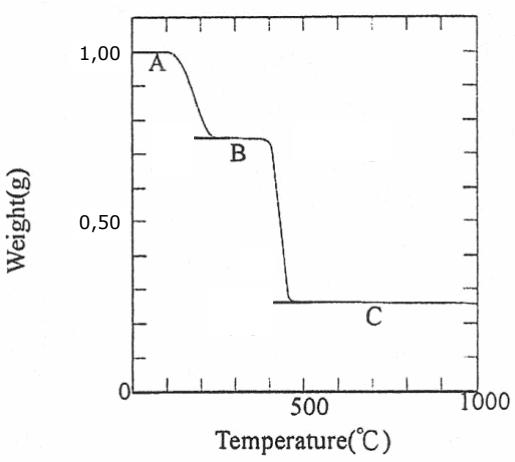
a) Write down balanced equations for both reactions.

The elementary iodine is titrated with thiosulfate solution (c = 0.100 mol/L)
Consumption: 18.40 mL.

b) Determine the mass of potassium chromate in the original mixture.

c) Account for the fact that the mass of the added potassium iodide is given only roughly without concern for the accuracy of the result.

1.00 g of magnesium oxalate ($MgC_2O_4 \cdot x\ H_2O$, denoted A) is heated in a slow stream of nitrogen. In doing so the mass of A is reduced as shown in the figure below. Compound B and C are formed. It is known that between 100°C and 250°C only water splits off.



d) Write down the equation for the reaction B ⟶ C.

e) Determine x as an integer!

Problem 3-03

a) Use the "Valence Shell Electron Pair Repulsion Theory" (VSEPR theory) to predict the structure of the following molecules and draw 3-D structures:

PCl_5 BrF_3 BrF_5 BF_4^- SF_4 XeF_2

Name the type of each structure.

(Example: The type of the $SnCl_3^-$ structure is AX_3E with A = central atom, X = ligand, E = electron pair)

The trigonal bipyramidal $OsO_2F_3^+$ cation exists under certain conditions.

b) Draw all possible geometrical isomers of this cation.

Problem 3-04 Complex Compounds

The three compounds A, B and C form at room temperature white crystalline solids. In all of these three compounds you find n(Pt):n(Cl):n(NH_3) = 1:2:2.
A is soluble in polar solvents such as ethanol, while B is soluble in petroleum ether (a mixture of hydrocarbons) and carbon tetrachloride.
A and B are non-electrolytes while C is a strong electrolyte.
One of these compounds is used in cancer therapy.

a) Draw the structural formulae of A, B and C.

b) Account for the fact that A dissolves in polar solvents, B in non-polar solvents.

c) Write down the electron configuration of the Pt^{2+} ion.

Problem 3-05 Alkali Metals

The metals of the first group of the periodic table are very reactive.

a) Account for this fact. Which redox ability do they show?

Alkali metals (except for lithium) evaporate already at moderate temperatures. Atoms and diatomic molecules exist in the gas phase.

b) Show using an MO diagram that dimers of sodium may exist (take only the outer occupied orbitals into consideration). Determine the bond order.

All alkali metals form oxides Me_2O, peroxides Me_2O_2 and hyperoxides MeO_2 (Me = alkali metal). The stability differs from one alkali metal to the other.

c) Draw Lewis structures of the anions. Give an example for a system which is isoelectronic to the peroxide anion.

There are double oxides Me_4O of potassium, rubidium and cesium in which peroxides are found as well as hyperoxides.

d) How is it possible to describe Me_4O_6, as a combination of these to oxides? (Example: Fe_3O_4 can be written as $FeO \cdot Fe_2O_3$.)

Oxides and hydroxides of alkali metals are used as carbon dioxide absorbers by fire departments, at diving and even in astronautics. Lithium hydroxide saved the life of the crew of Apollo 13 when there was too much carbon dioxide in their cabin.

e) Write down the equations for the reaction of the following compounds with carbon dioxide.

i) LiOH ii) Na_2O_2 iii) KO_2

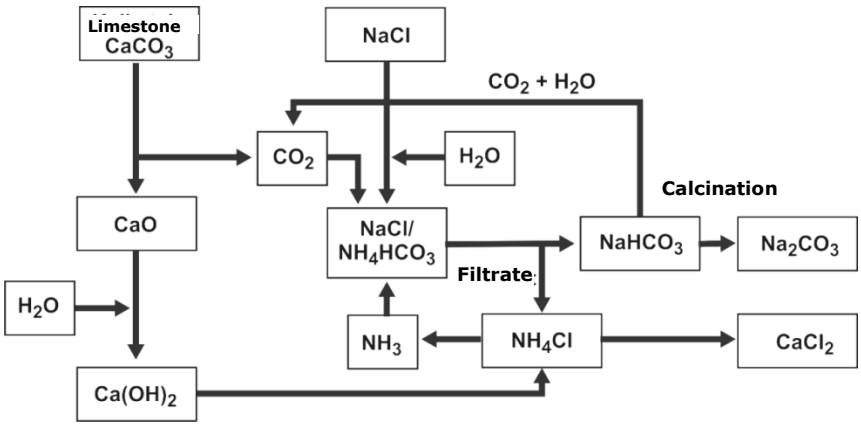
Lithium cations show a very small ionic mobility in water compared to the other ions (see table below). In cation exchangers the adsorption of alkali cations occurs in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Cesium is added fastest, lithium quite slowly.

Mobility of selected ions in water at 25 °C in 10^{-8} m^2 s^{-1} V^{-1}

Ag^+	Ca^{2+}	H^+	K^+	Na^+	Li^+	NH_4^+	$[N(CH_3)_4]^+$	Rb^+	Cs^+
6.42	6.17	36.23	7.62	5.19	4.01	7.63	4.65	7.92	8.00

f) Which property seems to be responsible for the different mobility of the ions mentioned in the table? Give a reasonable explanation for the small mobility of lithium cations in aqueous solution.

The following image shows the flow chart of the Solvay process. In this process all reaction steps are attuned so many reagents are in a circular flow.



g) For which product is the Solvay process set up? Write an equation of the total reaction.

The Solvay process is based on the pair of salts $NaCl/NH_4HCO_3$, the position of tis equilibrium is used for a salt converting reaction. While NaCl is added to the process NH_4HCO_3 is gained in the flow of the reactions.

h) Write down an equation of the equilibrium reaction of this pair of salts. Which position of the equilibrium is favored? Write an equation for the formation of NH_4HCO_3 using the information given in the flow chart.

i) Write down the equation of the calcination reaction.

j) What is calcium hydroxide used for? Write a reaction equation.

Problem 3-06 Acids

A weak acid is dissolved in a buffer solution of pH = 8.8. The total concentration of the acid is $2.0 \cdot 10^{-2}$ mol/L. The anion A^- is coloured and has an absorbance coefficient of ε = 21 $L \cdot mol^{-1} \cdot cm^{-1}$ at the relevant wave length.
In a cuvette with d = 1.0 cm 60 % of the incoming light of the relevant wave length is absorbed.

a) Calculate the pK_a value of the acid HA.

20 mL of 3-chlorbutanoic acid (c = 1.00 mol/L) is titrated with a solution of sodium hydroxide (c = 1.00 mol/L) until the equivalence point is reached.

b) Determine the pH value at the equivalence point.

c) Write down the appropriate indicator.

The indicator methyl orange changes its colour at pH $\approx$ 3.7.

d) Determine how much solution of sodium hydroxide in the titration (in b) of 3-chlorobutanoic acid is necessary to change the colour of this indicator.

pK_a(3-chlorobutanoic acid) = 4.05

Problem 3-07 Qualitative Analysis

Seven test tubes contain diluted solutions of the following compounds: Ammonia, barium nitrate, lead acetate, potassium iodide, copper sulfate, sodium hydroxide (10 %), silver nitrate.
Reactions were carried out between these solutions. The observations are listed in the table below.

	A	**B**	**C**	**D**	**E**	**F**	**G**
A		–	–	–	white turbidity	white turbidity	white pr.
B			yellow pr. dis.	light yellow pr.	–	–	light brown pr. ΔT: violet vapors
C				–	white pr. dis.	white pr.	white pr.
D					brown pr.	brown pr. dis.	–
E						–	blue pr. ΔT: black
F							blue pr. dis.

pr. A precipitate was formed.

dis. The precipitate dissolved in an excess of one of the components.

ΔT Attitude when heated. – No visible reaction

March the substances listed above to the letters.

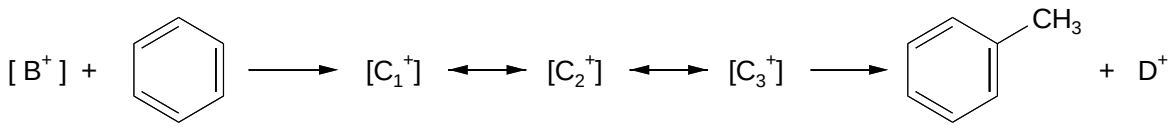
Write equations of each of the reactions B and C, B and G, C and E, C and F, D and F, E and G, F and G*. Identify the aggregation state and the hydration using (s), (l), (g), (aq).*

Problem 3-08 Electrophilic Substitution

Methyl chloride reacts with benzene in the presence of aluminum trichloride to form methyl benzene (toluene).

a) Complete the species A to D in the following reaction schemes:

$CH_3X + AlCl_3 \longrightarrow A^- + [\ B^+\ ]$



Toluene reacts with a mixture of conc. nitric acid and sulfuric acid (nitrating acid) to form a mixture of different nitrotoluenes with the following composition:

2-nitrotoluene 63 %, 3-nitrotoluene 3%, 4-nitrotoluene 34 %.

b) Account for the different yields using the resonance structures during the different possible ways of substitution and the influence of the methyl group.

4-Nitrotoluene reacts with nitrating acid.

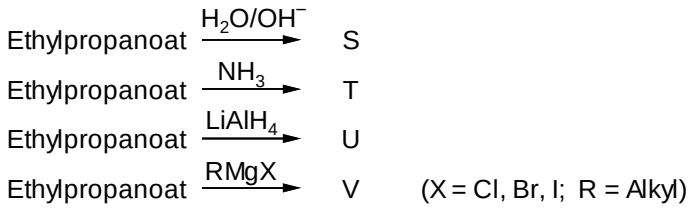
c) Which compound is predominantly formed? Give the name of the compound and the structural formula. Account for the increased yield by using the directing effect of the already present substituent.

4-Methylphenol reacts with bromine in the presence of iron(III) bromide. A mixture of products is formed, in which one compound preponderates.

d) Plot the structural formula and give the name of this compound. Account for the higher yield (compared to the other products) of the favored product.

Problem 3-09 Reactions of Esters

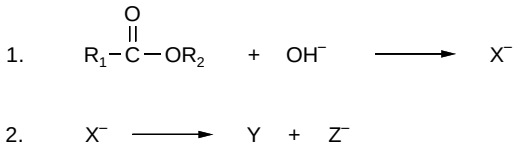
Ethyl propanoate ($C_5H_{10}O_2$) can react in many different ways:



S, T, U and V represent the products generated from the propane unit.

a) Complete the compounds S to V. Write down the family of each of these compounds.

The hydrolysis of esters is a nucleophilic substitution reaction. Two typical intermediate steps are



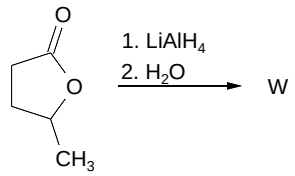
b) Complete the formulae of the compounds X^-, Y and Z^- of the hydrolysis!

The reaction mechanism of the ester hydrolysis can be investigated by an isotopically labelled oxygen (^{18}O) in the ester group ($R_1CO^{18}OR_2$).

c) Which result of the investigation would back the formation of your intermediates in b)?

The ester ethyl-2-pentenoate ($C_7H_{12}O_2$) reacts with lithium aluminum hydride dissolved in ether followed by a reaction with water. Two products Q and R form. Compound Q decolors a solution of bromine.

d) Write down the reaction equation of the hydration of ethyl-2-pentenoate! Give the names of the compounds Q and R.



The following lactone reacts with lithium aluminum hydride, too.

e) Give the structural formula and the name of W.

Problem 3-10 Isomeric Compounds

There are several kinds of isomers which can be classified into constitutional isomers and stereoisomers. Furthermore stereoisomers can be subdivided into configurational isomers (enantiomers and diastereomers) and conformational isomers (conformers).

a) Give an example of a pair of

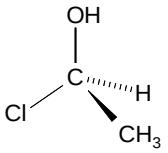
i) constitutional isomers, *ii)* conformers,

iii) enantiomers, *iv)* diastereomers.

b) To which category do cis-trans isomers (E/Z isomers) belong?

c) On the answer sheet there are the structural formulae of several compounds. Mark all stereogenic centers with an asterisk (*).

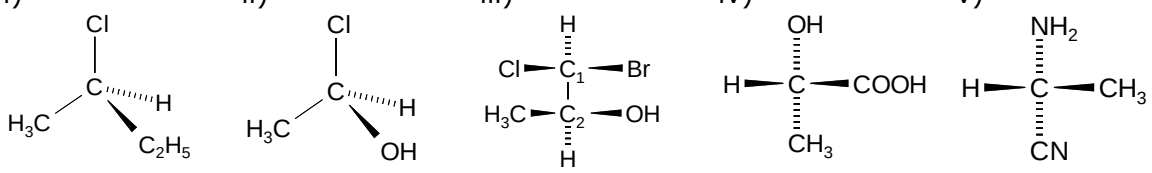
To indicate the three-dimensional arrangement (configuration) of an enantiomer the R/S nomenclature is used in most cases. The compound shown on the right has an R configuration.



d) Write down the R/S rules which determine the R configuration of this compound.

e) Determine the configuration of the following compounds:

i) ii) iii) iv) v)



Third Round Test 2

Problem 3-11 Multiple Choice

With one or more correct answers even if the question is written in singular.

a) In which example does the (formal) oxidation state +VI occur?

A $Fe_4[Fe(CN)_6]_3$	**B** $K_2Cr_2O_7$	**C** $CoAl_2O_4$	**D** Na_2FeO_4	**E** $Cr(C_6H_6)_2$

b) Which element does show flame coloration in the visible range?

A Cu	**B** Ba	**C** Mg	**D** Zn	**E** As

c) In which compound in solid state do you find ions?

A $FeCl_3$	**B** BCl_3	**C** $HgCl_2$	**D** $ZnCl_2$	**E** AgCl

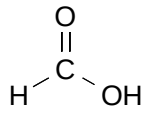
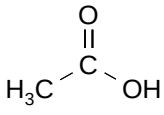
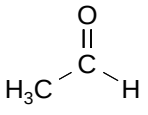
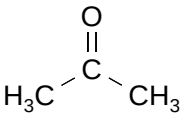
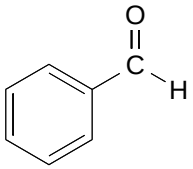
d) All compounds below show an acidic reaction in aqueous solution. Which of them does not react as a Brönsted acid?

A H_2SO_4	**B** H_3PO_4	**C** H_3BO_3	**D** H_4SiO_4	**E** H_2CrO_4

e) Which compound does react amphoteric?

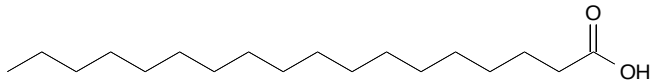
A $Be(OH)_2$	**B** $Cu(OH)_2$	**C** $Zn(OH)_2$	**D** $Ca(OH)_2$	**E** $Ba(OH)_2$

f) In the Fehling probe a diluted solution of copper(II) sulfate (Fehling 1) and a basic solution of potassium sodium tartrate (Fehling II) are used. Testing the following compounds which of them leads to a positive reaction?

A 	**B** 	**C** 	**D** 	**E** 

g) Which compounds can be gained from natural fats by saponification followed treatment with acid?

A



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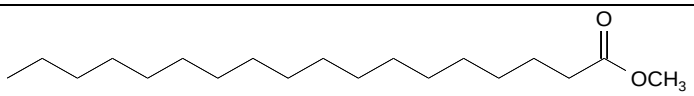

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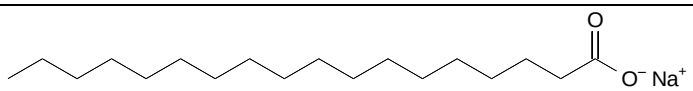
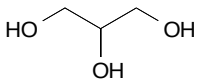
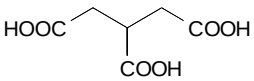


D



E



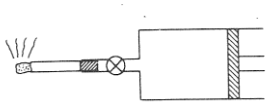
Problem 3-12 Smoking

In order to determine the amount of carbon monoxide in the smoke of cigarettes it is oxidized by iodine(V) oxide. In doing so iodine is formed among others. The reaction takes place in methanol. Iodine(V) oxide forms a colourless, iodine a brownish solution.
The iodine formed in the reaction can be detected quantitatively by photometry.
Standard solutions are used to find the absorption coefficient.
Stand solution I contains $1.00 \cdot 10^{-3}$ mol/L of I_2. The standard solutions II, III and IV were prepared in the following way: 50.0 mL, 25.0 mL and 15.0 mL, respectively, of standard solution I were given into a 100 mL volumetric flasks and filled with methanol up to the calibration mark. The following results of the measurement in a photometer and a 1 cm cuvette were reported:

Standard solution	I	II	III	IV
Absorbance	0.89	0.44	0.23	0.13

a) Determine the absorption coefficient.

As shown in the figure 500 mL of smoke are taken from a cigarette (p = 102.4 kPa, ϑ = 30 °C) and passed sufficiently slowly through an absorption bottle with 100 mL of a solution of iodine(V) oxide in methanol. In the beginning the solution was colourless, in the end it showed a brownish colour.



The absorbance of this solution was 0.69 (under the same conditions as above).

b) Calculate the content (vol.%) of CO in the smoke of cigarettes.

Problem 3-13 Stoichiometric Calculations II

The following equation is usually given to describe the decomposition of manganese(II) nitrate:
$Mn(NO_3)_2 \longrightarrow MnO_2 + 2\ NO_2$.
Actually the manganese oxide formed is not stoichiometric with an oxygen/manganese ratio n(O):n(Mn) < 2.
In an experiment 52.04 % loss of mass was observed after heating manganese(II) nitrate at 200 ° C.[1]

a) Give the empirical formula of oxide formed i.e. determine x in MnO_x. Which other nitrogen containing gas besides NO_2 was formed in this reaction? Calculate the ratio of volume of the gases formed.

[1] From Hungary National Competition 2012

Cyanide can be determined indirectly by titration with EDTA. (EDTA = ethylenediamine tetraacetic acid binds 1 mol of metal ion per 1 mol of EDTA.)

An exactly known amount of Ni^{2+} ions is added in excess to a cyanide ions containing solution to react in the following way: $Ni^{2+} + 4\ CN^- \longrightarrow Ni(CN)_4^{2-}$. $Ni(CN)_4^{2-}$ does not react with EDTA while Ni^{2+} does.

In an analysis 20.0 mL of a solution of Ni^{2+} were added to 20.0 ml of a cyanide solution. To titrate this mixture 21.3 mL of a solution of EDTA (c = 0.0100 mol/L) were needed. In another experiment 17.1 mL of a solution of EDTA were needed to titrate 10.0 mL of the Ni^{2+} solution used in the analysis.

b) Determine the concentration of CN^- in the original cyanide solution.

Problem 3-14 Ring Flip of Chair Conformations

The chair conformation of a six membered ring is an important structural element of organic chemistry. The ring flip of a chair, which is a change in conformation, takes place via different intermediate steps. The following potential diagram describes such a flip.

a) Apply the respective terms and conformations (drawing and respective letter) to the empty boxes of the image on the next page.

b) Give a value of the activation energy E_A for the chair flip. Which conformers can be isolated?

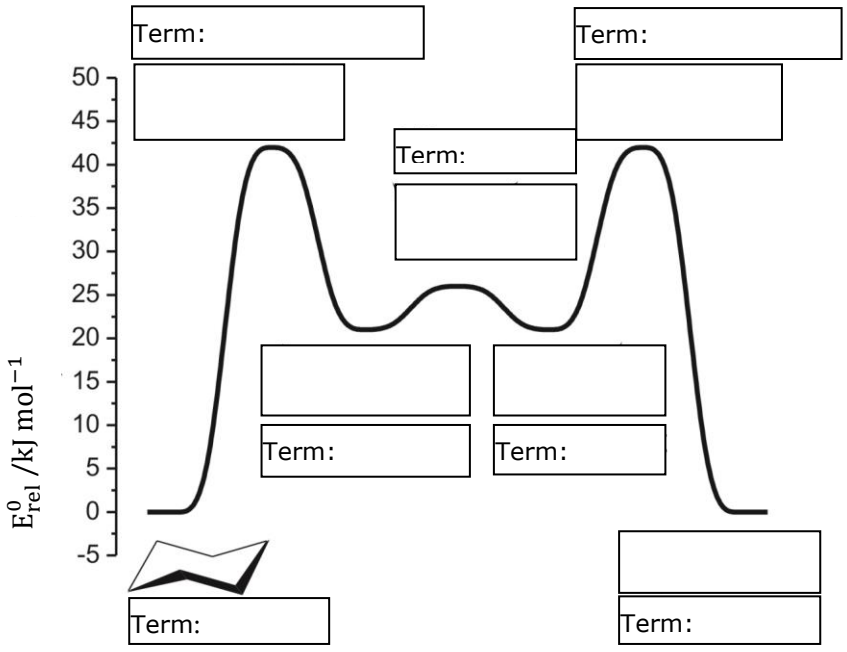
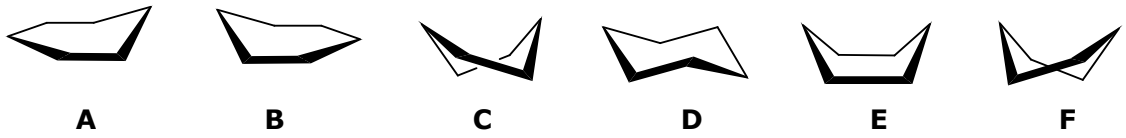


Fig: Potential diagram of the chair flip of cyclohexane

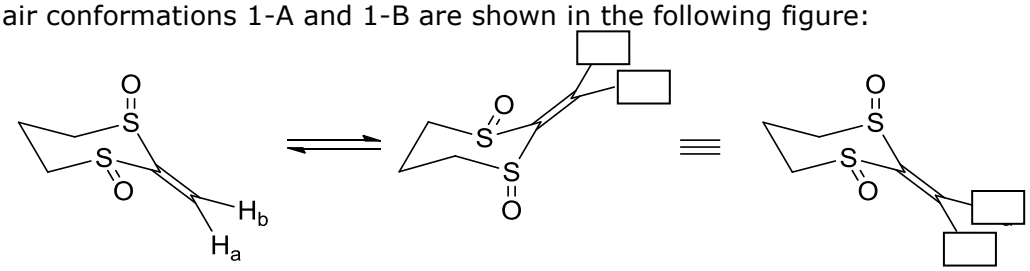
Conformations:



A **B** **C** **D** **E** **F**

Terms: Chair, half-chair, boat, twist boat.

In an investigation to determine the activation energy of the chair flip of compound **1** the ^{1}H-NMR signals of the two protons H_a and H_b were detected at different temperatures.
The chair conformations 1-A and 1-B are shown in the following figure:



1-A **1-B** **1-B**

c) *Fill in H_a and H_b, respectively, in the empty boxes of both presentations of **1-B** (the presentation on the right hand side is a rotated presentation of **1-B** in the middle). What happens to H_a and H_b in the process of chair flip?*

In the ^{1}H-NMR spectrum at 25 °C as well as at – 55 °C the two diastereotopic protons H_a and H_b of compound **1** offer one singlet at δ = 6.54 ppm. When the sample is cooled down to –84 °C two signals with a distance of 182 Hz are observed.
An excerpt of the spectra of the signals of the protons H_a and H_b at different temperatures is given in following chart:

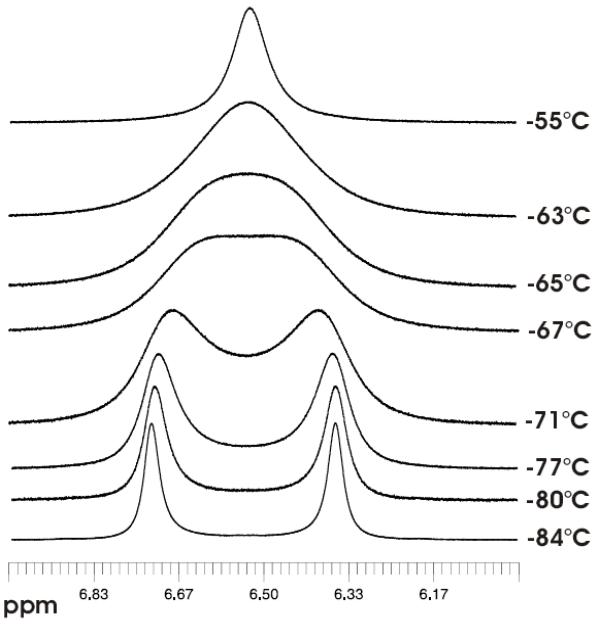


Fig: ^{1}H-NMR spectrum (500 MHz in CD_3OD) of **1** at different temperatures

d) Account for this behavior at -84 °C and – 55 °C.

The rate constant k(T) of the chair flip at different temperatures can be found by simulation processes using the shape of the NMR graph and the distance of the two signals.

Table: Rate constants k(T) achieved from simulation processes

ϑ/°C	–55	–63	–65	–67	–71	–77	–80
k/s^{-1}	2000	540	400	356	200	70	40

The rate constant k(T) is the mean frequency of transition for the equilibrium

1-A $\rightleftharpoons$ **1-B**.

e) Draw a diagram ln[(k/s^{-1})/(T/K)] against 1/(T/K) and determine the equation of the graph.

The Eyring equation explains the reaction rate k of a chemical reaction depending on the free standard Gibbs energy of activation $\Delta G^{\ddagger}$.

Eyring equation $k = k_B/h \cdot T \cdot e^{-\Delta G^{\ddagger}/RT}$

with k_B = Boltzmann constant, h = Planck constant

$k = 2.084 \cdot 10^{10}\ s^{-1} \cdot (T/K) \cdot e^{-\Delta G^{\ddagger}/RT}$ respectively

$\ln k/s^{-1} = 23.76 + \ln T/K - \Delta G^{\ddagger}/RT$ (1)

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \cdot \Delta S^{\ddagger}$ (2)

f) Determine $\Delta G^{\ddagger}$ for the chair flip at -63 °C.
Take $\ln \frac{k/s^{-1}}{T/K} = -6200 \cdot \frac{1}{T/K} + 30.00$ as the equation of the graph in e).

Problem 3-15

Given the following data for the dehydrogenation of ethane:

$\Delta G°_{900\ K}$ = 22.39 kJ/mol $S°_{900\ K}(H_2)$ = 163.0 J·mol^{-1}·K^{-1}

$S°_{900\ K}$(ethane) = 319.7 J·mol^{-1}·K^{-1} $S°_{900\ K}$(ethene) = 291.7 J·mol^{-1}·K^{-1}

a) Write down the reaction equation for the dehydrogenation.

b) Calculate K_{p900} for the dehydrogenation reaction at 900 K.

c) Determine the enthalpy of hydrogenation ΔH_{Hyd} of ethene at 900 K.

d) What is the composition (in % of vol.) of the reaction mixture if you let ethane pass over a catalyst for dehydrogenation? The total pressure in equilibrium is 1013 hPa. (If you could not solve b) take $K_{p900} = 6.00 \cdot 10^{-2}$.)

e) Calculate K_p at 600 K. Assume that the enthalpy of dehydrogenation in the interval 600 K ≤ T ≤ 900 K is independent of temperature.

(If you could not solve b) take K_{p900} = 6.00·10^{-2}, if you could not solve c) take a ΔH_{Hyd} with $|\Delta H_{Hyd}|$ = 140 kJ/mol.)

f) Compare the values of K_p at 900 K and 600 K and give a short comment.

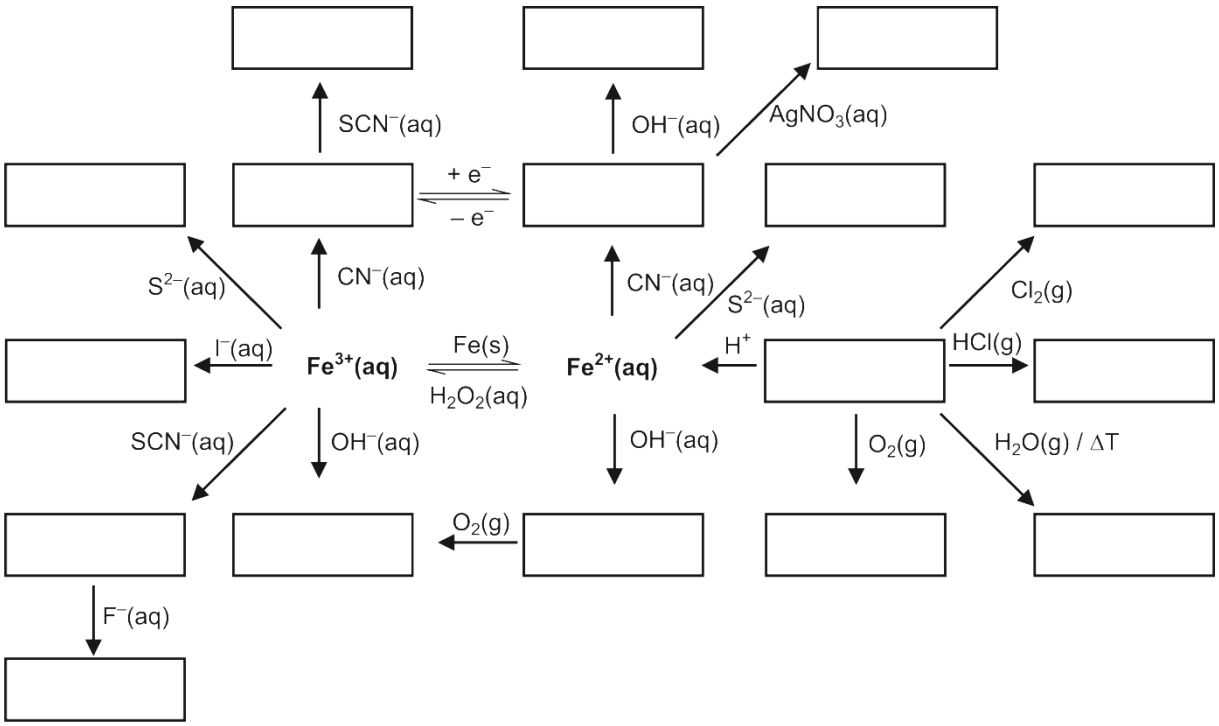
Problem 3-16 Iron

Given the reaction scheme on the next page.

a) Complete the reaction scheme (only the iron species have to be filled in).
If necessary use the excerpt from the electrochemical series:

			E° in V
Fe	⇌	$Fe^{2+} + 2\ e^-$	-0,44
S^{2-}	⇌	$^1/_8\ S_8 + 2\ e^-$	-0,14
Fe	⇌	$Fe^{3+} + 3\ e^-$	-0,04
H_2	⇌	$2\ H^+ + 2\ e^-$	0,00
$2\ I^-$	⇌	$I_2 + 2\ e^-$	+0,54
Fe^{2+}	⇌	$Fe^{3+} + e^-$	+0,77
$2\ Cl^-$	⇌	$Cl_2 + 2\ e^-$	+1,36

Reaction scheme:



Scheme taken from "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), published in Spektrum Akademischer Verlag, Heidelberg, 2004 Elsevier GmbH München.

Potassium hexacyanoferrates(II, III) are well known compounds of iron, in which iron is octahedral coordinated. Often the common names yellow respectively red potassium prussiate are used. One of them is thermodynamically and kinetically more stable.

b) Which prussiate should be more stable according to its electron configuration? Which of them is a better oxidant? Account for your answers!

The photo shows two track layers using the thermit welding process to bond railway lines.

c) Which mixture is used in this process? What are the reaction products of this process? Write down a balanced reaction equation.

Source of the image: http://www.vol.at/gleisbaustelle-feldkirch-schaan-am-samstag-fertig/3620704

If iron(III) chloride is dissolved in water the solution reacts acidic.

d) Give reaction equations which explain this fact.

There are three different modifications of iron, which can be converted into each other by changing the temperature. α-Iron crystallizes with abody-centered cubic pattern, γ-iron has a cubic close packed structure.

e) Draw the images of unit cells of these two structures and determine the number Z of iron atoms in each cell.

The different packing should cause different densities of α- and γ-iron.

f) Calculate the density of iron in both structures using r(Fe) = 126 pm as average radius of iron.

Problem 3-17 Electrochemistry

1.40 g of pure lead(II) sulfate was added to 150 cm^3 of water and stirred until the equilibrium is installed above the deposit of lead(II) sulfate at the bottom.
Then a lead electrode and a reference electrode (E^o_{Ref} = 0.238 V) were inserted. The voltage measured amounted to ΔE = 0.478 V (T = 298 K).

a) Calculate the solubility product of lead sulfate.

The same sample of lead sulfate was not given into water but instead into 150 cm^3 of sulfuric acid with pH= 3. Assume for simplification that sulfuric acid protolyses totally.

(Use in this part of the problem K_{sp} = $2.00 \cdot 10^{-8}$ as solubility product of lead sulfate.)

b) Which voltage between the lead electrode and the reference do you expect?

$E^{o}(Pb/Pb^{2+})$ = -0.126 V

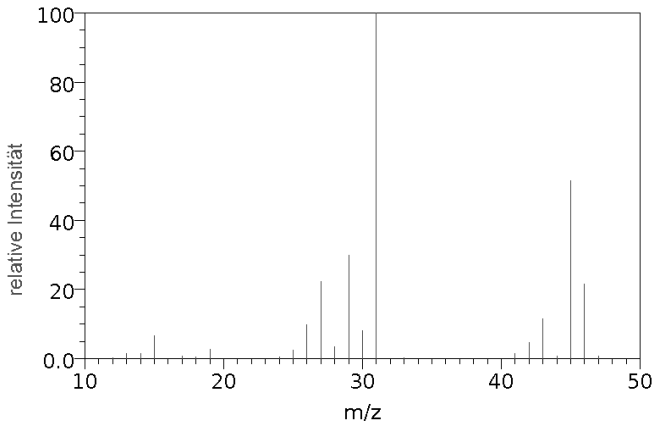
Problem 3-18 Analysis of an Organic Compound

The following plots on the next page show the mass spectrum and the ^{1}H NMR spectrum of an unknown compound X.

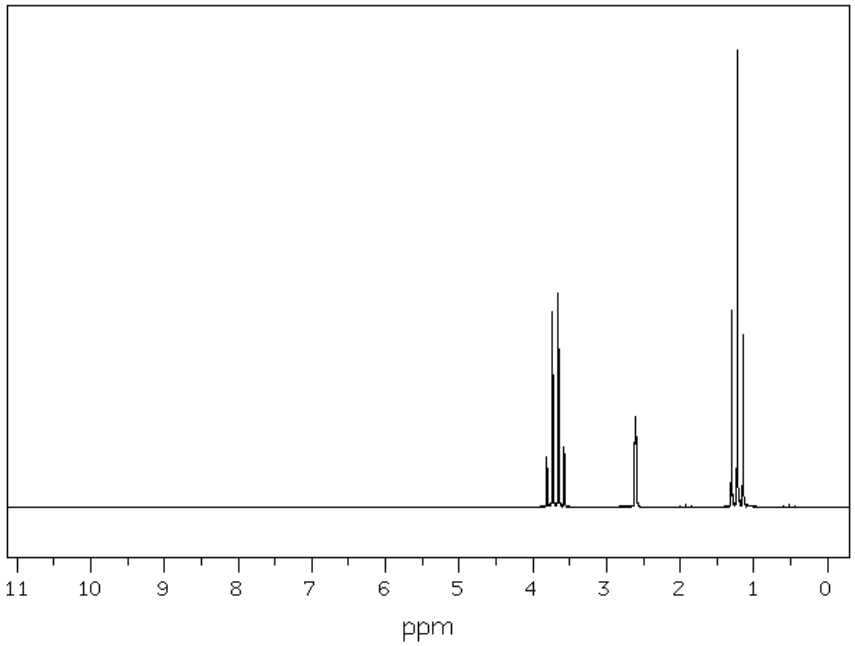
a) Determine the formula of X.

b) Which fragments of X are represented by m/e = 45; m/e = 31 and m/e = 29?

c) Assign the signals in the ^{1}H NMR spectrum to the respective H atoms of substance X.



Mass spectrum of X (m/e = 46 is the molecular peak)
Source: NIST Chemistry WebBook (http://webbook.nist.gov/chemistry



^{1}H NMR spectrum of X in $CDCl_3$. Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 27.01.14)

There is a structural isomer Y of compound X .

d) What is compound Y? How many signals with their multiplicity do you expect in a ^{1}H-NMR-Spektrum of Y? (Do not state the chemical shift!)

e) How many signals of the following 8 compounds in a ^{1}H NMR spectrum do you expect? (Do not state multiplets!)

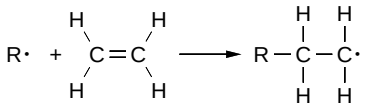
i) CH_3-CH_2Cl *ii)* $CH_3-CHCl-CH_3$ *iii)* $CH_3-CHCl-CH_2Cl$ *iv)* $CH_3-CH_2-CH_2Cl$

v) *vi)* *vii)* *viii)*

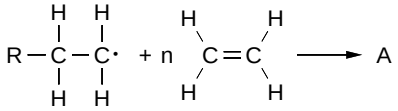
Problem 3-19 Radical Addition to Alkenes: Polymers

In the radical addition to alkenes to form polymers you may distinguish three steps:

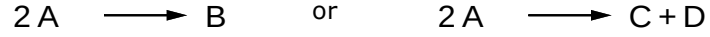
Initiation:



Propagation:

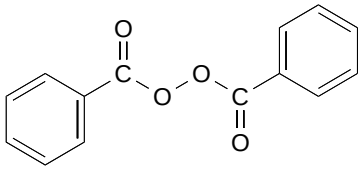


Termination:



a) Write down the structural formulae of A to D.

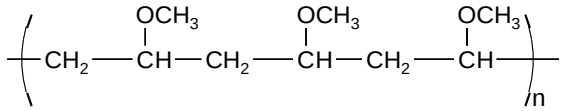
Dibenzoyl peroxide is used to initiate the polymerization of ethene

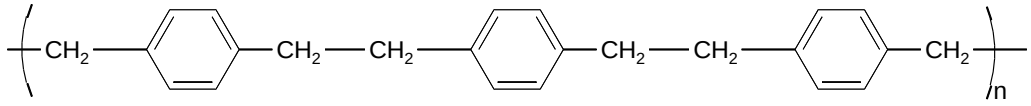


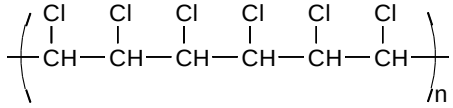
Benzoyl peroxide

b) Write the equation for the initiation reaction and the first step of the propagation.

c) Show the monomer units you would use to prepare the following polymers:

i) 

ii) 

iii) 

The polymerization of a substituted vinyl monomer can lead to a polymer with numerous chirality centers. The polymer having all substituents on the same side of the zigzag backbone is called isotactic, the one in which the substituents alternate regularly on opposite sides of the backbone is called syndiotactic, and the one having the substituents randomly orientated is called atactic.

The monomer propene forms polypropylenes the properties of which differ depending on the tacticity: Atactic polypropylene dissolves in heptane but isotactic polypropylene does not.

d) Draw 3-D structures of isotactic, syndiotactic and atactic polypropylene.

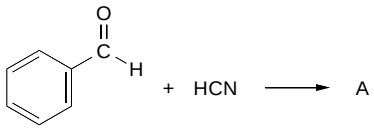
(Hint: ◄ in front of the paper plane, ||||||| behind the paper plane).

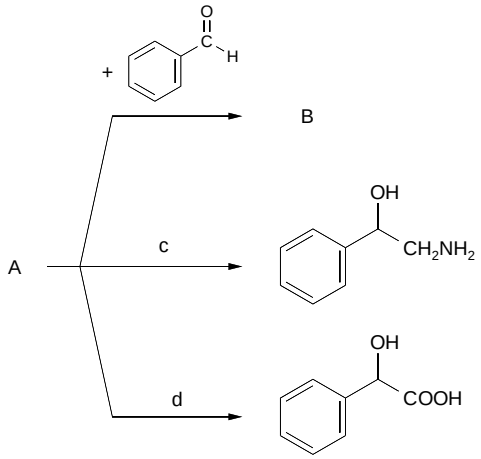
1,3-Butadiene polymerizes in two different structures with a regular sequence of the structural units.

e) Draw the structural formulae of both polymers.

Problem 3-20 Reactions of Aldehydes and Ketones

Given the following reaction schemes.





a)

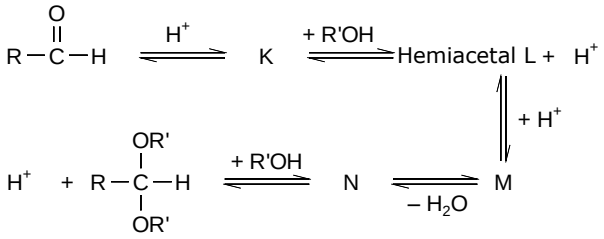
Draw the structural formulae of the compounds A and B and of the reagents c and d.

b) Name the kind of reaction for the formation of A starting with benzaldehyde. Show the reaction mechanism using structural formulae and arrows which show the movements of the electrons.

Alcohols, too, react with aldehydes and ketones. At first hemiacetals are formed and then acetals:

Aldehyde/ketone + alcohol $\xrightarrow{H^+}$ hemiacetal $\xrightarrow{H^+}$ acetal

The formation of an acetal is performed in several steps:



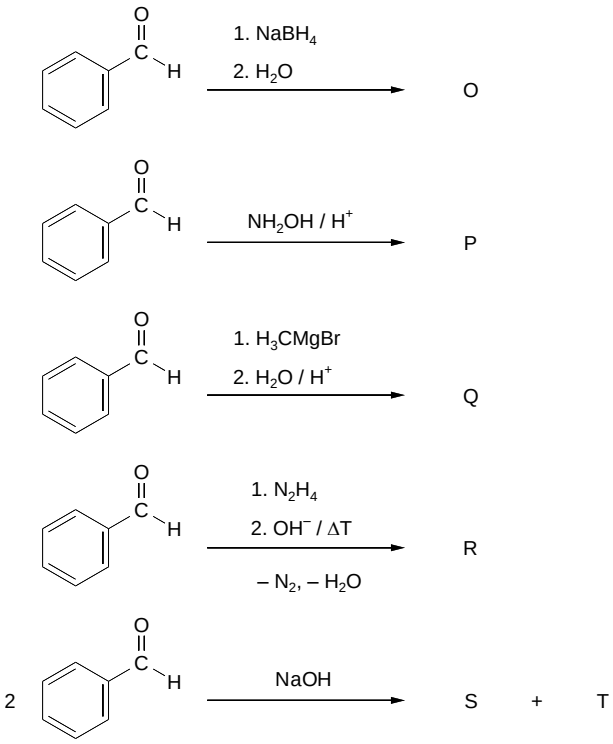
c) Complete the structural formulae K to N.

d) How can the equilibrium of the synthesis be shifted to the formation of the acetal?

Alcohols with more than one -OH group like glycerol (propane-1,2,3-triol) react with ketones to form acetals, too.

e) Write down the equation for the reaction of acetone and glycerol.

Consider the following reactions of benzaldehyde:



f) Draw the structural formulae of O to T.

The last reaction of e) when benzaldehyde reacts to S and T is an example for a Cannizzaro reaction. In this reaction carbon disproportionates. Aldehydes without a hydrogen atom in α position react in this way.
The first step of the Cannizzaro reaction gives a tetrahedral intermediate.

g) Show the mechanism of the Cannizzaro reaction taking the given example of benzaldehyde. Use structural formulae and arrows which show the movement of the electrons.

h) Account for the reason why carbonyl compounds with hydrogen in α position do not undergo a Cannizzaro reaction.

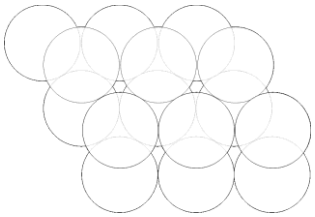
Fourth Round (theoretical problems)

(A periodic table and the same list of formulae and data as in the third round were provided)

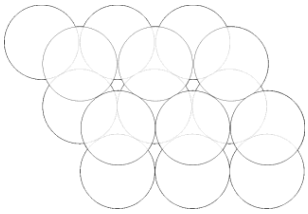
4–1 Structure of Solids

There are two close-packed structures, cubic and hexagonal. Two layers of these structures are shown below:

close-packed cubic

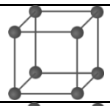
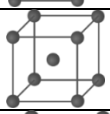
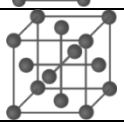


close-packed hexagonal



a) Complete the plots on the answer sheet by adding three adjacent spheres (●) of the next layer.

Besides the close-packed structures there are two more packings of spheres in which metals crystallize. The elementary cells of the three cubic packings are plotted in the table below.

Elementary cell	Denotation	Coordination number	Metal atoms per cell
			
			
			

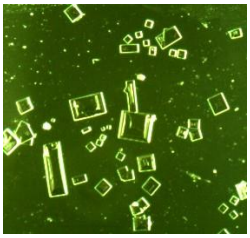
b) Complete the missing data!

Close-packed structures do not only play a prominent role in the structures of solid metals, they also can be used to derive the structures of many salts. For example, one kind of ions forms a close-packed structure while the counterions are arranged in the octahedral and tetrahedral interstices.

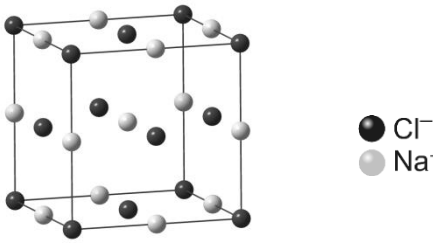
c) Draw a tetrahedral and an octahedral interstice into the given structures on the answer sheet.

d) How many tetrahedral and octahedral interstices do you find in a close-packed cubic structure with n spheres?

In the crystal of sodium chloride, both Na^+ and Cl^- ions form a close-packed cubic lattice. The symmetry of the crystals can be seen well under a microscope. The coordination numbers are (6,6).



Below you find an elementary cell of sodium chloride, where the cations are generally arranged in the interstices. The length of the edge is 562 pm.



e) Determine the empirical formula of this elementary cell.

f) Calculate the radii of the chloride and the sodium ions. Assume for simplification, that the smaller kind of ions is inserted in a way that the bigger ones are in contact with the nearest of each other.

4-2 Complexes, Ligands and trans-Effect

A

a) What is the meaning of the term "complex" in chemistry? Complete the missing terms on the answer sheet.

Complexes differ very much in their stability. Especially stable coordination compounds form if polydentate ligands coordinate with a metal ion.

b) Plot images of metal complexes (Me: metal) which show the spatial arrangement of the ligands given below.
(If there is the possibility to coordinate more than one ligand plot only one. If there are isomers the plot of one is sufficient.

i) Ethylenediamine (1,2-Diaminoethane), $C_2H_8N_2$
ii) Oxalato, $C_2O_4^{2-}$
iii) Ethylenediamminetetraceto, $C_{10}H_{12}N_2O_8^{4-}$
iv) 18-Crown-6, $C_{12}H_{24}O_6$

In aqueous solutions ligands can displace each other. The following reactions of nickel complexes are given:

$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6\ H_2O$

$[Ni(H_2O)_6]^{2+} + en + 4\ NH_3 \rightleftharpoons [Ni(en)(NH_3)_4]^{2+} + 6\ H_2O$

$[Ni(H_2O)_6]^{2+} + 2\ en + 2\ NH_3 \rightleftharpoons [Ni(en)_2(NH_3)_2]^{2+} + 6\ H_2O$

$[Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6\ H_2O$

(en = Ethylenediamine)

c) *Which complex on the right hand side of the equations should have the least, which one the highest complex stability?*
Account for your answer using the (thermodynamic) chelate effect!

Existing ligands have an essential influence on the products of nucleophilic substitutions of square-planar complexes.
When in a square-planar complex $[MeLX_3]$ ligand X is substituted by ligand Y two products may occur.

d) *Plot the structures of these products.*

Ligands show a different ability to direct into trans position (<: smaller ability of trans directions as):

$$F^-,\ H_2O,\ OH^- < NH_3 < py < Cl^- < Br^- < I^-,\ SCN^-,\ NO_2^- < PR_3 > H^-,\ NO,\ CO,\ CN^-,\ C_2H_4$$

This so-called trans effect is due to kinetic reasons and describes the influence of a ligand on the displace rate in its trans position.
A well-known example is cis-platinum (cis-$[PtCl_2(NH_3)_2]$, which is used as a drug against certain tumors.
$[Pt(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$, NH_3 and HCl are to your disposal.

e) *Create a way to synthesize the cis and the trans isomer considering the trans effect.*

B

Many poorly soluble salts can be dissolved by formation of their ammine complexes. Nickel hydroxide e.g. is not soluble in an excess of a solution of sodium hydroxide but in a concentrated solution of Ammonia it dissolves as $[Ni(NH_3)_6]^{+2}$.

f) *Calculate the minimum concentration of free NH_3 in mol/L, which is necessary to produce a solution of c($[Ni(NH_3)_6]^{+2}$) = 0.1 mol/L.*

$K_L(Ni(OH)_2) = 3.2 \cdot 10^{-17}$, $K_D([Ni(NH_3)_6]^{+2}) = 10^{-8.7}$ (K_D: Instability constant)

C Salt X contains a hexaquocomplex and a metal with the oxidation state +III. In an aqueous solution it reacts acidic. The water-free salt can sublimate while the water containing salt decays into one solid and two gaseous products when heated.

If you lead the gaseous products through two U-tubes, one filled with calcium chloride the other one filled with granulated sodium hydroxide the total amount of gas is absorbed.
830 mg of the water containing salt is decayed by heating. The gain in mass of the calcium chloride containing U-tube is 281 mg, that of the sodium hydroxide containing U-tube 376 mg.

g) Determine X!

Problem 4-3 Kinetics[2]

A

Sulfuryl dichloride (SO_2Cl_2) is a compound widely used as chlorinating/sulfonating component. At room temperature, SO_2Cl_2 is a colorless liquid with a pungent ordour and a boiling point of 70 °C. It decomposes to SO_2 and Cl_2 when heated to or above 100 °C.
An empty container was filled with SO_2Cl_2. Its decomposition was followed by monitoring the change in total pressure at 375 K. The following data were obtained:

time in s	0	2500	5000	7500	10000
total pressure in atm	0.500	0.527	0.553	0.576	0.599

a) By graphical approach show that the decomposition is a first order reaction and calculate the rate constant.

When the decomposition reaction is carried out at 112 °C (starting again with p_0 = 0.5 atm), the total pressure is found to be 0.78 atm after 1 h.

b) Calculate the activation energy of the decomposition reaction.

B

In many calculations using ΔH° and S° it is assumed that these values do not change for temperatures which are not too far away from 298 K.
Standard values for substances of part **A**:

	Cl_2	SO_2	SO_2Cl_2
Δ_fH° in kJ/mol	0	-296.8	-354.8
S° in J/(K·mol)	223.1	248.2	311.1

c) Using the Gibbs equation calculate ΔG for the decomposition reaction at 400 K assuming that ΔH and ΔS have the same values as at 298 K. Determine K_p from the calculated value of ΔG.

[2] Some ideas and data from "Preparatory Problems 2011, Turkey"

Actually these properties of state change with temperature according to the following (simplified) equations:

	Cl_2	SO_2	SO_2Cl_2
$\Delta_f H°(T)$ in kJ/mol	$-10.2 + 34.2\cdot10^{-3}\cdot T/K$	$-309.1 + 41.4\cdot10^{-3}\cdot T/K$	$-369.2 + 48.2\cdot10^{-3}\cdot T/K$
$S°(T)$ in J/(K·mol)	$28.3 + 34.2\cdot\ln T/K$	$12.34 + 41.4\cdot\ln T/K$	$36.5 + 48.2\cdot\ln T/K$

d) Calculate ΔG for the decomposition reaction at 400 K using the relevant equations. Determine K_p from the calculated value of ΔG, too. Judge whether the assumption of c) is justified in this case.

C

The reaction $S_2O_8^{2-}(aq) + 3\ I^-(aq) \longrightarrow 2\ SO_4^{2-}(aq) + I_3^-(aq)$
follows the rate law $v = \frac{d[I_3^-]}{dt} = k \cdot c(S_2O_8^{2-}) \cdot c(I^-)$.

The following mechanism is proposed:

$I^- + S_2O_8^{2-} \xrightarrow{k_1} IS_2O_8^{3-}$

$IS_2O_8^{3-} \xrightarrow{k_2} 2\ SO_4^{2-} + I^+$

$I^+ + I^- \xrightarrow{k_3} I_2$

$I_2 + I^- \xrightarrow{k_4} I_3^-$

e) Check whether the mechanism is consistent with the given rate law. Assume that the steady state approximation can be applied to all intermediates.

Problem 4-4 Distributions

The distribution of a weak monoprotic acid between water (w) and ether (e) follows the equation:

$$\frac{c(HA_e)}{c(HA_w)} = K_D \qquad (1).$$

HA_e: Molecules of the acid in ether
HA_w: Molecules of the acid in water
In this case $K_D = 5.4$ is given.

1 L of a diluted weak acid HA is strongly acidified with hydrochloric acid. Then the acid HA is extracted with 500 mL of ether. Hydrochloric acid does not dissolve in ether.

a) Which molar fraction of the acid HA can be extracted in this way? Account for the acidification with hydrochloric acid.

The extraction is more effective if the sample of ether is divided in n smaller portions with equal size followed by an extraction one after another.

b) Determine in how many parts 500 mL of ether have to be divided to extract at least 89 % of the acid HA.

The distribution coefficient K_D for two immiscible solvents S_1 and S_2 (see equation (1)) for a compound A refers to compound A. If there are dissociation, dimerisation and complexation the calculation is more complicated.

In 100 mL of a buffer solution of pH = 3.0 a monoprotic acid HA (pK_S = 2.89) is dissolved. A part of the acid is extracted with 50 mL of ether. Let K_D be 4.3.
After the extraction there are 0.0432 mol of the acid in the sample of ether.

c) *Determine the initial total concentration of the acid HA in the buffer solution.*
Assume that the pH value of the buffer solution is the same before and after the extraction and that there is no protolysis of HA in ether.

In case of c) the distributions coefficient D is often used:

$$D = \frac{\text{Total concentration of all species of A in } S_1}{\text{Total concentration of all species of A in } S_2}$$

d) *Calculate D for the acid HA under the conditions of c).*

e) *Derive a formula for D containing only K_a, K_D and $c(H^+)$.*

$\rightleftharpoons$ $[Ni(en)(NH_3)_4]^{2+}$ + 6 H_2O
$[Ni(H_2O)_6]^{2+}$ + 2 en + 2 NH_3 $\rightleftharpoons$ $[Ni(en)_2(NH_3)_2]^{2+}$ + 6 H_2O
$[Ni(H_2O)_6]^{2+}$ + 3 en $\rightleftharpoons$ $[Ni(en)_3]^{2+}$ + 6 H_2O
(en = Ethylenediamine)

c) *Which complex on the right hand side of the equations should have the least, which one the highest complex stability?*
Account for your answer using the (thermodynamic) chelate effect!

Existing ligands have an essential influence on the products of nucleophilic substitutions of square-planar complexes.
When in a square-planar complex $[MeLX_3]$ ligand X is substituted by ligand Y two products may occur.

d) *Plot the structures of these products.*

Ligands show a different ability to direct into trans position (<: smaller ability of trans directions as):

$$F^-, H_2O, OH^- < NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^- < PR_3 > H^-, NO, CO, CN^-, C_2H_4$$

This so-called trans effect is due to kinetic reasons and describes the influence of a ligand on the displace rate in its trans position.
A well-known example is cis-platinum (cis-$[PtCl_2(NH_3)_2]$, which is used as a drug against certain tumors.

$[Pt(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$, NH_3 and HCl are to your disposal.

e) Create a way to synthesize the cis and the trans isomer considering the trans effect.

B

Many poorly soluble salts can be dissolved by formation of their ammine complexes. Nickel hydroxide e.g. is not soluble in an excess of a solution of sodium hydroxide but in a concentrated solution of Ammonia it dissolves as $[Ni(NH_3)_6]^{+2}$.

f) Calculate the minimum concentration of free NH_3 in mol/L, which is necessary to produce a solution of $c([Ni(NH_3)_6]^{+2}) = 0.1$ mol/L.

$K_L(Ni(OH)_2) = 3.2 \cdot 10^{-17}$, $K_D([Ni(NH_3)_6]^{+2}) = 10^{-8.7}$ (K_D: Instability constant)

C

Salt X contains a hexaquocomplex and a metal with the oxidation state +III. In an aqueous solution it reacts acidic. The water-free salt can sublimate while the water containing salt decays into one solid and two gaseous products when heated.
If you lead the gaseous products through two U-tubes, one filled with calcium chloride the other one filled with granulated sodium hydroxide the total amount of gas is absorbed.
830 mg of the water containing salt is decayed by heating. The gain in mass of the calcium chloride containing U-tube is 281 mg, that of the sodium hydroxide containing U-tube 376 mg.

g) Determine X!

4-5 Ligand Field Theory and Magnetism

Following the ligand field theory there is a splitting of the d orbitals when a complex is formed. The strength of the field splitting caused by the ligand as well as the central atom is essential concerning the question whether a high- spin or a low-spin complex is formed.

a) Which d electron configurations can form high-spin and low-spin complexes in an octahedral ligand field? Give a short explanation.

b) Add the d electrons to the given orbital scheme on the answer sheet. Which magnetic property (para- or diamagnetic) do you expect?

For paramagnetic first-row transition metal complexes the magnetic moment μ in units of Bohr magneton (BM) is reasonably well approximated by the spin-only formula

$\mu_{theo} = \sqrt{n \cdot (n+2)}$ BM n: Number of unpaired electrons.

c) Calculate the spin only magnetic moments for metal centers with 1, 2, 3, 4 and 5 unpaired electrons.

By comparing the theoretical magnetic moment (μ_{theo}) with the experimentally gained data (μ_{exp}) you can find out whether a compound is a high-spin or a low-spin complex. μ_{exp} can be calculated by a complex formula which can be simplified for the case below:

$\mu_{exp} = 2.83 \cdot \sqrt{C/(cm^3 \cdot K \cdot mol^{-1})}$ BM C: Curie constant

The Curie constant can be determined by detecting the susceptibility χ at different temperatures with a magnetic balance (Gouy balance):

$\chi = \frac{C}{T}$ T: Temperature χ: Susceptibility

The susceptibility of an octahedral manganese(II) complex was detected as follows:

T in K	2	10	20	30	60	90	120	220	270	300
χ in $cm^3 \cdot mol^{-1}$	1.804	0.442	0.226	0.152	0.076	0.051	0.038	0.021	0.017	0.015

d) Determine the Curie constant (with two decimals) by plotting $1/\chi$ vs. T

e) Calculate μ_{exp}.

f) Is this manganese (II) complex a high-spin or a low-spin complex? Account for your answer.

Problem 4-6 Uranium

A

Radioactive decay reactions can be systemized by general equations. In case of electron capture the number of nucleons does not change but the atomic number is reduced by 1:

$$ {}^{A}_{Z}El_1 + {}^{0}_{-1}\beta \longrightarrow {}^{A}_{Z-1}El_2 $$

a) Write such general equations of the change in the number of nucleons and the atomic number for the α- and β^--decay.

Today natural uranium consists of several isotopes. The most long-life ones are ^{238}U (99.275 % of mass, $t_{½}$ = $4.468 \cdot 10^9$ a) and ^{235}U (0.720 % of mass, $t_{½}$ = $7.038 \cdot 10^8$ a). The other isotopes have a considerably shorter half-life.

b) At what point of time in the past (t_x) was the mass of ^{235}U half of the mass of ^{238}U?

When ^{238}U und ^{235}U came into being more radionuclides such as ^{232}Th ($t_{½}$=$1.405 \cdot 10^{10}$ a) and ^{237}Np ($t_{½}$=$2.14 \cdot 10^6$ a) were formed. All these isotopes undergo α-decay.

A further radioactive isotope, ^{234}U, with a fraction of about 0,005 % can be found in natural uranium. It does not originate from the time of formation of the earth, but is formed continuously by the decay of one of the four isotopes mentioned above. A radioactive equilibrium has established itself in which the concentration of ^{234}U is constant, that means that the formation- and decay rates are the same.

c) From which of the isotopes mentioned above is ^{234}U formed by a series of α- und β^--decays? Write down the path of formation.

d) Calculate the half-life of ^{234}U.

B

Uranium is interesting, too, as partner in chemical reactions. There are a lot of oxidation states in uranium ions.

Standard potentials of half reactions:

$U^{3+} + 3\ e^- \longrightarrow U$	$E^o = -1.798$ V
$UO_2^{2+} + 4\ H^+ + 6\ e^- \longrightarrow U + 2\ H_2O$	$E^o = -1.444$ V
$U^{4+} + e^- \longrightarrow U^{3+}$	$E^o = -0.607$ V
$UO_2^{2+} + e^- \longrightarrow UO_2^+$	$E^o = +0.062$ V
$UO_2^{2+} + 4\ H^+ + 2\ e^- \longrightarrow U^{4+} + 2\ H_2O$	$E^o = +0.327$ V
$UO_2^+ + 4\ H^+ + e^- \longrightarrow U^{4+} + 2\ H_2O$	$E^o = +0.620$ V

e) Attach the oxidation state of uranium to each species.

A small amount of uranium is given into a strong monoprotic acid HX (c = 1 mol/l) in the presence of hydrogen with p = 1 bar and T = 298 K. You may assume that the conjugated base X^- does not react with uranium or one of its ions. To answer the following question you may consider the reactions in a respective galvanic cell with the concentration of the specific uranium species of 1 mol/L.

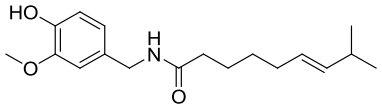
f) Determine the destiny of the small amount of uranium. Write down equations of all proceeding reactions. Account for the reactions by comparing the potentials of the relevant half-cells. Give the potential of the correspondent cell.

Problem 4–7 Total Synthesis of Capsaicin

Fruit of the species Carolina Reaper – the hottest chili of the world

Paprika and especially chili were grown as early as 7000 B.C. in middle and south America. After the discovery of America by Columbus first plants were brought to Europe. Today chili is ingredient of the traditional cuisine of many countries all over the world. Active ingredients obtained from chili can be used as medicine, for plant protection and for non-fatal weapons like tear gas and pepper spray.

The ingredient which is responsible for the pungency of chili is the alkaloid Capsaicin (8-methyl-N-vanillyl-6-nonenamide):



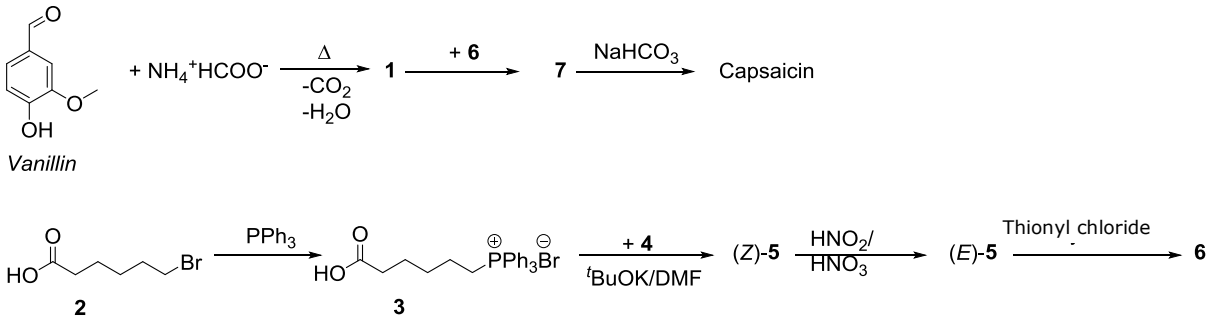
a) Mark and enumerate the functional groups of capsaicin.

b) Determine the configuration of the double bond using the E,Z designation.

The pungency of chili is indicated by the so called Scoville scale. A measured amount of alcohol extract of the capsaicin oil of the dried pepper is produced, after which a solution of sugar and water is added incrementally until the "heat" is just barely detectable by a panel of tasters; the degree of dilution gives its measure on the Scoville scale called Scoville Heat unit (SHU). Today the pungency is detected by HPLC. 1ppm of capsaicin (referred to mass) corresponds to 16 SHU.

c) Calculate the content (in ppm und µg/g) of capsaicin for the hottest known chili (species Carolina Reaper) which has 2 200 000 SHU (for comparison: pure capsaicin has 16 000 000 SHU).

Often natural compounds are produced in a larger scale by total synthesis – i.e. a synthesis starting with simple composed organic compounds which can be received easily.
Such a total synthesis of capsaicin which was developed 1989 by Kaga et al. uses vanillin, the main ingredient of vanilla flavor, as starting material:



Total synthesis of capsaicin from vanillin (Kaga, 1989)

The first step is the reaction of the carbonyl group with ammonia and methanoic acid which is produced in situ by heating ammonium formate. The carbonyl group is nucleophilicly attacked; the generated hydroxyl group is protonated and then cleaved as water. The produced carbocation is reduced by methanoic acid, carbon dioxide escapes as side product. Thus in the first step a nitrogen containing product with the empirical formula $C_8H_{11}NO_2$ is formed.

*d) Draw the structural formula of **1**.*

e) Using structural formulae give the mechanism of the formation of the carbocation in the reactive above. Show with the help of resonance structures (including nitrogen) how the cation is stabilized.

The second component of the total synthesis is formed from 6-bromohexanoic acid **2** which can be bought. Compound **2** reacts with triphenylphosphine to the corresponding triphosphonium salt **3**. **3** reacts with isobutyl aldehyde **4** and ^{t}BuOK in DMF. The product (*Z*)-**5** isomerizes when treated with a mixture of nitrous acid and nitric acid to form (*E*)-**5**.

*f) Plot the structural formulae of (Z)-**5** and (E)-**5** an. Which kind of isomers are these compounds?*

Subsequently (*E*)-**5** is brought to reaction with thionyl chloride to form the acid chloride **6** ($C_{10}H_{17}ClO$).

g) Write down the reaction equation.

In the last step the compounds **1** and **6** react in a condensation reaction. The desired product capsaicin is gained as a salt. Free capsaicin can be obtained by treating this salt with a solution of sodium hydrogen carbonate.

*h) Plot the structural formula of **7**.*

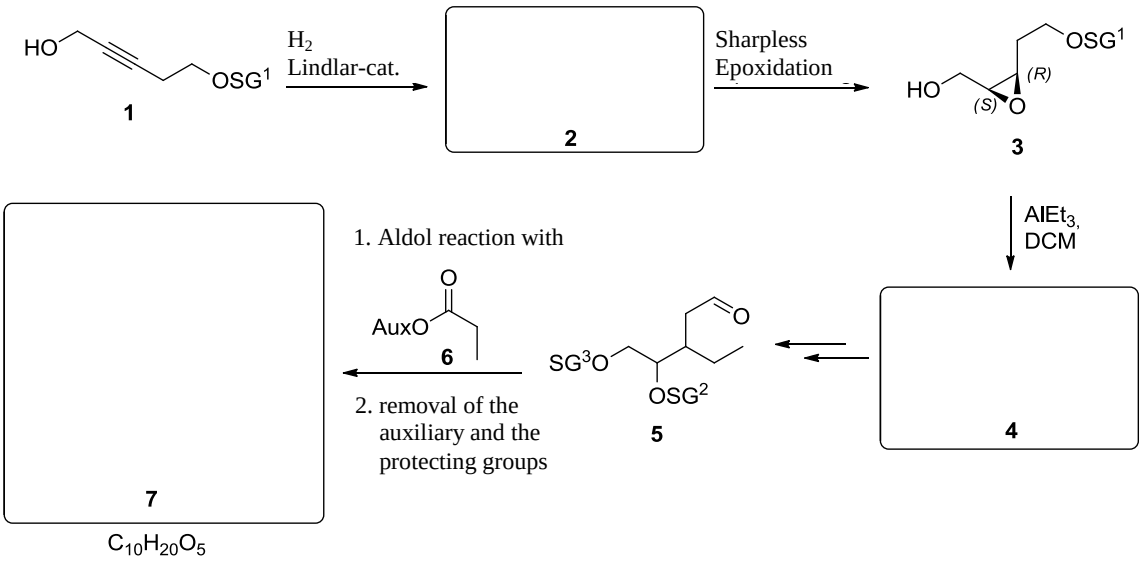
*i) Give the mechanism of the reaction of **1** and **6**.*

*j) Why is it not possible to synthesize capsaicin directly from **1** and (E)-**5**?*

*k) What is the name of the bond which is formed in the reaction between **1** and **6**? Can you expect a free rotation (analog to the rotation of a C-C bond in ethane) in this kind of bond? Account for your answer.*

Problem 4-8 Stereoselective Reactions

There are a lot of stereoselective reactions for a chemist to synthesize molecules with several stereogenic centers. Thereby it is possible to insert new stereogenic centers or to use stereogenic centers already existing in the molecule to form new ones.
The synthesis shown below is a part of a total synthesis of a natural compound with a lot of stereogenic centers:



In the first step the alkyne**1** which is supplied with the protecting group SG^1 is reduced to the cis-alkene **2**.

In the second step a Sharpless epoxidation on alkene **2** follows. By using specific reagents it can be processed in a way that both epoxides are available (showing to the front or to the back). In this case the (2S,3R)-enantiomer **3** was produced (numbers starting from the carbon with the free OH group).

*a) Draw the structural formula of the alkyne **2**.*

In the next reaction step the epoxide is stereo- and regioselectively opened in position 3 by introducing an ethylene group with the help of triethylene aluminum ($AlEt_3$) in dichloromethane (DCM) as solvent.
This reaction is a nucleophilic attack from the back side.

*b) Draw the structural formula of compound **4**.*
(Hint: ◄ in front of the paper plane, ||||||| behind the paper plane, —— in the paper plane)

*c) Give the configuration of the stereogenic centers in **4** using CIP sequence rules.*

The enantiomer **4`** of compound **4** shall be synthesized.

*d) Which of the reactions up to this point have to be changed? Draw the synthesis scheme upto this new compound **4'** starting from **1**.*

Subsequently the protecting groups SG^2 and SG^3 are introduced, SG^1 removed and the alcohol oxidized to an aldehyde.

Then a stereoselective aldol reaction with the carboxylic acid ester **6** is performed which is supplied with a so called auxiliary group (Aux). This is a group which can be attached

to a molecule for a stereoselective reaction so that only a specific stereoisomer is formed.

During the aldol reaction the ester **6** is at first deprotonated to form an enolate and then the aldehyde **5** is added. This procedure leads to a **(5R,6R)-**configuration independent of the configuration of the other stereogenic centers in the molecule.

The empirical formula of the molecule after removing the auxiliary and the protecting groups SG^2 [a]nd SG^3 is $C_{10}H_{20}O_5$. Compound **7** contains three OH groups and a free carboxylic acid.

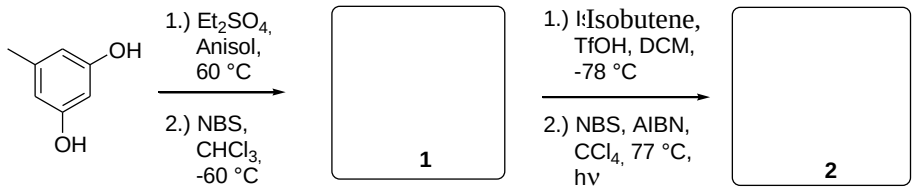
*e) Draw the structural formula of compound **7**.*

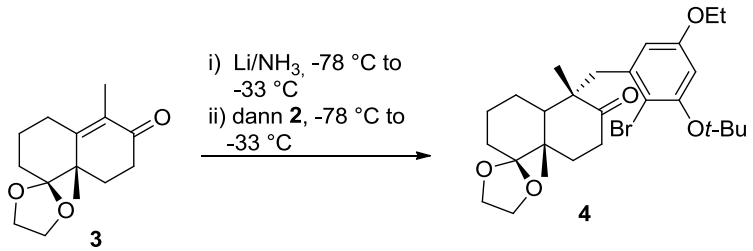
*f) What do you get if the sequence of reactions is performed with the enantiomer **4'**, the enantiomer or a diastereomer of product **7**? Account for your answer!*

Problem 4-9 Natural Material from the Ocean

Dysidavaron A is a compound which was extracted from *Dysidea avara,* a sponge living in the Mediterranean. The total synthesis was performed only recently.

The synthesis starts with 3,5-dihydroxytoluene which is modified in four steps to form compound **2**. Compound **2** reacts with ketone **3** in a reductive, stereoselective alkylation to form compound **4**. Thereby ketone **3** performs a nucleophilic substitution reaction at compound **2**. (See clue concerning the reagents at the end of the problem.)



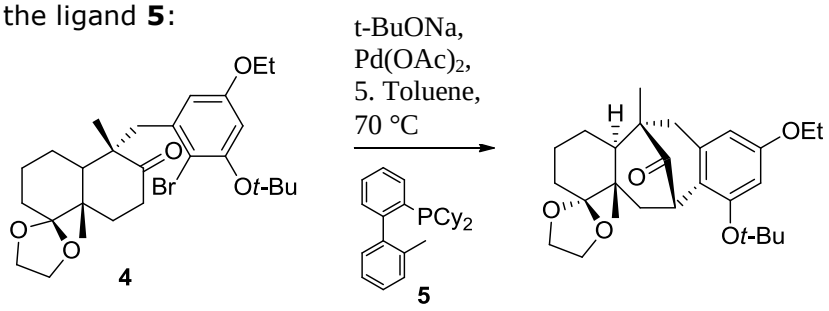


*a) Draw the structural formulae of the compounds **1** and **2**! (Hint: Look at compound **4** accurately).*

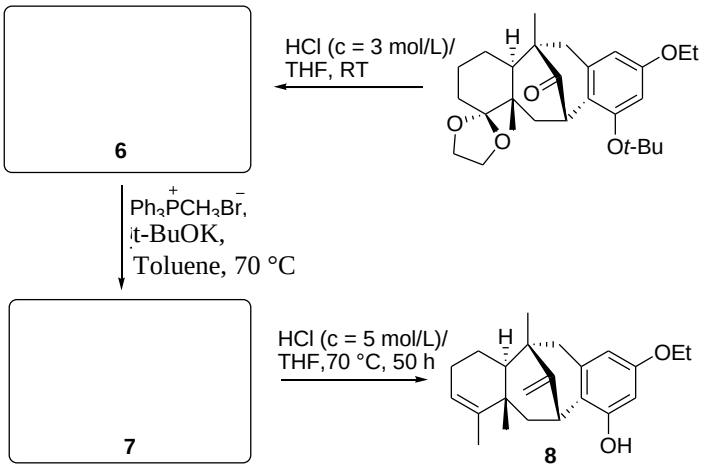
One of the reactions with NBS is a radical substitution, the other one an electrophilic substitution.

b) Give the conditions of the different substitutions. In which position of the molecule (aromatic nucleus or side chain) does the particular reaction occur?

In the further course of reaction a ring closure takes place with the help of the catalyst $Pd(OAc)_2$ and the ligand **5**:



In the following the resulting ketal is transformed into compound **6**. Then **6** reacts in a Wittig reaction to compound **7**. **7** does not contain any carbonyl group.



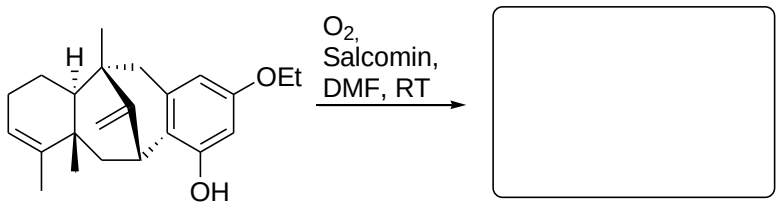
*c) Draw the structural formula of **6**! (Hint: The t-Bu- and the Et-groups are stable under the given reaction conditions.)*

*d) Draw the structural formula of compound **7**!*

There are two reactions in the last step of the reaction sequence to synthesize **8** shown above: a t-Bu group is cleaving off and a rearrangement to form a more stable product takes place.

e) Is it a kineticcally or a thermodynamically more stable product? Account for your answer using the given reaction conditions.

In the last step to form the natural compound Dysidavaron A the aromate in compound **8** is oxidized to a quinone ring.



$C_{23}H_{28}O_3$

f) Draw the structural formula of Dysidavaron A.

Clue to the abbreviations and reagent:

NBS: *N*-Bromosuccinimide is a reagent for mild bromation. It works without catalyst.

TfOH: Trifluoromethane sulfonic acid, pK_s=-20

DCM: Dichloromethane

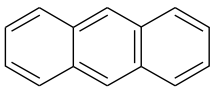
AIBN: Azo-bis-(isobutyronitrile). It decomposes at temperatures above 25 °C and is a radical initiator.

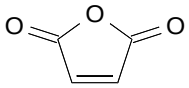
THF: Tetrahydrofuran

Fourth Round (practical problems)

4-10 Synthesis of an Organic Compound

In this experiment a polycyclic aromatic compound is brought to reaction with maleic acid anhydride:





Equipment:

Stand with boss and clamps (2x), 2 round bottom flasks (100 mL), 2 cork rings, reflux condenser, magnetic stirrer plate with stirring bar, crystallization dish for an oil bath, spatula, Büchner funnel with 3 filter papers, balanced beaker (100 mL) with number to deliver the product, TLC chamber, 1 TLC plate, filter paper for saturation of the chamber, 2 small vessels to prepare the solutions, 2 capillary tubes for TLC spotters, measuring cylinder (25 mL), zipper bag to place the TLC plate, tweezers, pencil.

Chemicals:

Anthracene (1 g)	
Maleic acid anhydride (0,4 g)	
Xylene	
Silicone oil for oil bath	
Acetic ester	
Cyclohexane	
Anthracene for TLC	

Safety precautions:

Wear eye protection and protective clothing.

Procedure:

Synthesis

Anthracene and maleic acid anhydride are given into 15 to 20 mL of xylene and then stirred for 30 minutes by heating using the reflux condenser. The yellow solution in the beginning should become nearly colourless. Then the solution should cool down. Thereby a solid precipitates. The solid is filtered off by using the Büchner funnel and then recrystallized in acetic ester. The recrystallized product is filtered off with the Büchner funnel and then dried for 10 to 15 minutes in the drier at 70 °C.

TLC investigation

Dissolve a small amount of anthracene and of the product in acetic ester using the two small vessels (it is not necessary to get a clear solution). Mark two start points on the TLC plate using the pencil and spot one of them with a bit of the solution of anthracene, the other one with a bit of the solution of the product using the capillary tubes provided.

Run a TLC in the TLC chamber which is saturated with the solvent (cyclohexane:acetic ester 1:1). Mark the solvent front with the pencil as well as the spots using UV light at 366 nm. Determine the R_f values.
Place the TLC plate in the zipper bag.

Disposal:
Put all chemicals and the filter papers into the provided waste boxes.

Problems:

a) *Which kind of reaction is performed in this experiment?*

b) *Plot the structural formula of the product.*

c) *Determine your yield in % of the theoretical yield.*

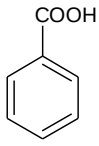
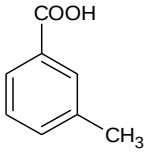
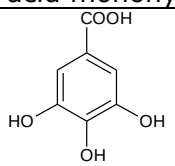
d) *Deliver your product in the provided balanced beaker to the instructor. Insert the number of your beaker into the answer sheet.*

e) *Sketch the TLC plate on the answer sheet and deliver the plate in the zipper bag to the instructor.*

f) *How do the two compounds differ in the UV light at 366 nm and why?*

4-11 Alkalimetric Identification of an Organic Acid

In this problem you get a sample of a solution of an organic acid. You have to titrate the acid and find out which acid you got.
Your volumetric flask contains one of the three acids shown below. All of them have nearly the same pK_a value and the endpoint of the titration can be determined with the given indicator. The mass of the solid dissolved in your flask will be given to you by the instructor.

Benzoic acid	3-Methylbenzoic acid	Gallic acid monohydrate
		
$C_7H_6O_2$	$C_8H_8O_2$	$C_7H_6O_5 \cdot H_2O$
M = 122.12 g/mol	M = 136.15 g/mol	M = 188.13 g/mol

Equipment:

Volumetric flask (100 mL) with the sample of the solution, volumetric pipette (20 mL), 2 Erlenmeyer flasks, small beaker, pipette control, burette (25 mL), stand with boss and clamps, spatula, micro spatula.

Chemicals:

Solution of a given amount of an organic acid	
Standard solution of sodium hydroxide, c(NaOH) = 0.01 mol/L	
Tashiro indicator	
Demineralized water	

Procedure:

If there is solid in your sample dissolve it by addition of demineralized water. Then fill the volumetric flask up to the calibration mark. The solution has to be mixed well.

Determination of the content of the acid

Exactly 20 mL of the solution are transferred to an Erlenmeyer flask and then filled up to appr. 100 mL. Add 5 to 10 drops of the Tashiro indicator solution and titrate the violet solution until it is purely green.

Disposal:

Give all solutions into the provided waste boxes.

Problems:

a) Insert the number of your sample into the answer sheet.

b) Record the consumption of the standard solution of sodium hydroxide and calculate the concentration of the acid in mol/L.

c) Compare your result with the weight of the acid dissolved in your solution and determine which of the three solutions you had got.

4-12 Complexometric Determination of Calcium and Magnesium

At first calcium is titrated using calcon-carboxylic acid as indicator. Then the indicator is destroyed by cooking with a solution of hydrogen peroxide. Afterwards magnesium is determined using indicator buffer pellets (indicator Eriochrome Black T + ammonium acetate).

Equipment:

Volumetric flask (250 mL) with solution of the sample, volumetric pipette (25 mL), 2 Erlenmeyer flasks, small beaker, pipette control, stand with boss and clamps, spatula, micro spatula.

Chemicals:

Solution of calcium and magnesium compounds	
Standard solution of $Na_2EDTA \cdot 2\ H_2O$, c(Na_2EDTA) = 0.05 mol/L	

Indicator buffer pellets	
Solution of ammonia, w(NH_3) = 25 %	
Calcon-carboxylic acid (s), trituration with sodium chloride, w($C_{21}H_{14}N_2O_7S$) = 0.2 %	
Solution of sodium hydroxide, w(NaOH) = 15 %	
Solution of hydrogen peroxide, w(H_2O_2) = 35 %	
Hydrochloric acid, c(HCl) = 2 mol/L	
Demineralized water	

Safety precautions:

Use conc. solution of ammonia under the hood. Be cautious when using conc. solution of hydrogen peroxide.

Procedure:

Fill the volumetric flask up to the calibration mark. The solution has to be mixed well.

<u>Determination of calcium</u>

Exactly 25 mL of the sample are transferred to an Erlenmeyer flask und and then filled up to appr. 100 mL. 2 mL of the solution of sodium hydroxide are added. After adding a tip of a spatula of the Calcon-carboxylic acid trituration the solution is titrated with standard solution of $Na_2EDTA{\cdot}2\ H_2O$ until the change of colours from pink to sky-blue. This colour has to persist for at least 1 minute.

<u>Determination of magnesium</u>

Appr. 1 mL of the solution of hydrogen peroxide is added to the solution after the determination of calcium. The solution is heated on a magnetic stirrer until the solution und the turbidity are discoloured (the solution should not cook too long). Precipitated magnesium hydroxide is dissolved with a small amount of hydrochloric acid. It does not matter if the clear solution has a light colouring. After adding a buffer pellet and 1 to 2 mL of ammonia the solution is titrated with the standard solution of $Na_2EDTA{\cdot}2\ H_2O$, until the change of colours from red to green.

Disposal:

The titrated solution has to be neutralized and can be given into the sink together with the rest of the solution of Na_2EDTA.

Problems

a) Insert the number of your volumetric flask into the answer sheet.

b) Record the consumption of the standard solution of Na_2EDTA for both determinations.

c) Calculate the mass concentration (mg/L) of calcium ions in your sample.

d) Calculate the mass concentration (mg/L) of magnesium calcium ions in your sample.

Part 2

The answers to the problems of the four rounds

The solutions are more detailed than expected from the pupils. That may facilitate their comprehension in case of mistakes.

Answers Round 1

Solution to problem 1-1:

a) A = Ammonia $(NH_2)_2CO + H_2O \rightleftharpoons CO_2 + 2\ NH_3$

b) $M(CH_4N_2O) = 60.06$ g/mol. $M(NH_3) = 17.031$ g/mol

1 L of urine ≙ 1 kg of urine ≙ 0.005 kg of urea.

$m(urea) = 550\ kg/horse \cdot 35 \cdot 10^{-3}\ L/kg \cdot 23\ horses \cdot 0.005\ mol/L \cdot 60.06\ g/mol$

m(urea) = 132.96 g

1 mol of CH_4N_2O ≙ 2 mol of NH_3, 132.96 g of CH_4N_2O ≙ 132.96/60.06 mol = 2.214 mol

2.214 mol CH_4N_2O give 4.428 mol of NH_3 ≙ 75.4 g of NH_3.

c) $n(C) : n(H) : n(O) : n(N) = \frac{63.032}{12.01} : \frac{5.000}{1.008} : \frac{24.631}{16.00} : \frac{7.337}{14.01} = 5.428 : 4.960 : 1.539 : 0.524$

$= 10.35 : 9.47 : 2.94 : 1.00 \Rightarrow$ Empirical formula: $C_{20}H_{19}O_6N_2$

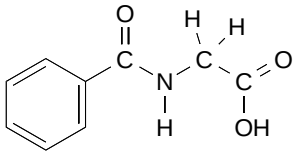
(or $C_{21}H_{19}O_6N_2$)

d) $n(C) : n(H) : n(O) : n(N) = \frac{60.742}{12.01} : \frac{4.959}{1.008} : \frac{26.483}{16.00} : \frac{7.816}{14.01} = 5.058 : 4.920 : 1.655 : 0.558$

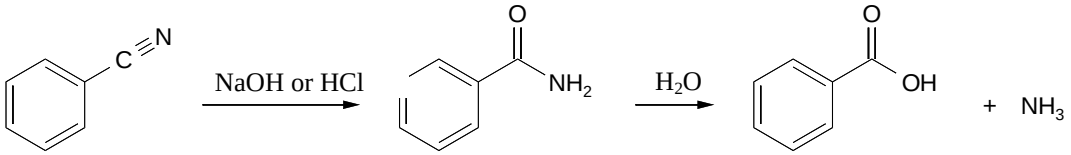
$= 9.07 : 8.82 : 2.97 : 1.00 \Rightarrow$ Empirical formula: $C_9H_9O_3N$

B' is an acid which hydrolyses to benzoic acid and an amino acid. 7 C atoms belong to benzoic acid; the remaining 2 C atoms form the amino acid which thus can only be the simplest amino acid, glycine, $C_2H_5NO_2$.

B' is an acid amide of benzoic acid, hippuric acid (benzamidoacetic acid, N-benzoylglycine):



e) C is benzonitrile. Basic or acidic hydrolysis of C yields an amide, which is subsequently hydrolyzed to benzoic acid and ammonia:



f) The white powder contains the following ions:

Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, Cl^-, SO_4^{2-}, PO_4^{3-} ($H_2PO_4^-$, HPO_4^{2-}).

According to the solubility the following salts are possible components of the powder:

Na_2SO_4, K_2SO_4, NaCl, KCl, $CaCO_3$, $MgCO_3$, $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(H_2PO_4)_2$, $Mg_3(PO_4)_2$, $MgHPO_4$, $Mg(H_2PO_4)_2$, MgO, CaO.

Remark: The white powder is a typical dietary supplement for horses. Composition: $CaCO_3$, $CaHPO_4$, NaCl, KCl, MgO, Na_2SO_4. In this problem supplements like vitamins and trace elements are not considered.

Solution to problem 1-2

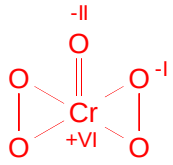
a) In a redox reaction electrons are (formally) transferred. In the process the respective oxidation numbers are increased/decreased. In the reaction of sodium with water the sodium atoms release an electron each and are oxidized, the hydrogen atoms of water are reduced by these electrons and form elementary hydrogen.

0 +I -II +I –II +I 0

$2\ Na + 2\ H_2O \rightleftharpoons 2\ NaOH + H_2$

b) Only the equations ii) and iii) represent redox reactions.

In vi) (and analogous in vii) there is no change of the oxidation number. Hydrogen peroxide becomes attached to the chromium center as a peroxide dianion.



+VI -II +I -I +I +VI –II -I +I,-II

$Cr_2O_7^{2-} + 4\ H_2O_2 + 2\ H^+ \rightarrow 2\ CrO_5 + 5\ H_2O$

onegativity of arsenic and hydrogen are equal. Thus the oxidation numbers in the compound as well as in the elements are 0

c) Primary elements cannot be recharged, secondary elements can.

d) Copper as cathode: $Cu^{2+} + 2\ e^- \rightarrow Cu$, iron as anode: $Fe \rightarrow Fe^{2+} + 2\ e^-$

e) Separation of the anode chamber from the cathode chamber by a porous barrier, electrolyte/salt solution.

f) 0.34 V – (-0.41 V) = 0.75 V

g) Correct answers: i) 2, 4; ii) 3; iii) 1.

h) Yes, in this case dissolving is a redox reaction:

$CoS + 4\ H_2O_2 \rightleftharpoons CoSO_4 + 4\ H_2O$

$NiS + 4\ H_2O_2 \rightleftharpoons NiSO_4 + 4\ H_2O$

$3\ CoS + 2\ HNO_3 + 6\ H^+ \rightleftharpoons 3\ Co^{2+} + 2\ NO + 3\ S + 4\ H_2O$

$3\ NiS + 2\ HNO_3 + 6\ H^+ \rightleftharpoons 3\ Ni^{2+} + 2\ NO + 3\ S + 4\ H_2O$

Oxygen and nitrogen, respectively, are reduced, sulfur is oxidized. The metal ions do not change their oxidation state.

i) In the reaction with conc. HNO_3 elementary sulfur forms which does not dissolve and may disturb the following analytic steps (or has to be separated). Nitrogen oxides may occur. Hydrogen peroxide oxidizes sulfur up to sulfate.

Solution to problem 1-3:

a) n(C) : n(N) : n(H) : n(Cu) : n(Br) =

$$\frac{28.65}{12.01} : \frac{11.12}{14.01} : \frac{3.21}{1.008} : \frac{25.25}{63.55} : \frac{31.75}{79.90} = 2.386 : 0.794 : 3.185 : 0.397 : 0.397$$

Empirical formula: $C_6N_2H_8CuBr$

Molecular formula: $(CuBr)(C_6H_8N_2)$

Molar mass: $M(C_6N_2H_8CuBr) = 251.59$ g/mol

b) i) TG curve: The compound decomposes in three steps loosing mass in each of them. In each step a solid compound should form.

ii) DTA curve: Each step is an endothermic reaction.

iii) MS-trend-scan curve: In each step a fragment with m/Z = 108 splits off.
m/Z = 108 ≙ M(2,5-dimethyl pyrazine). ⇒ In each of the three steps 2,5-dimethyl pyrazine is split off..

c) $M(C_6H_8N_2)$ = 108.14 g/mol

Theoretically possible loss of weight:

Splitting-off of 1 mol of dimethyl pyrazine: $\Delta m = \frac{108.14}{251.59} \cdot 100\%$ = 42.98%

Splitting-off of ½ mol of dimethyl pyrazine: Δm = ½ · 42.98% = 21.49 %

Splitting-off of ¼ mol of dimethyl pyrazine Δm = ¼ · 42.98% = 10.74 %

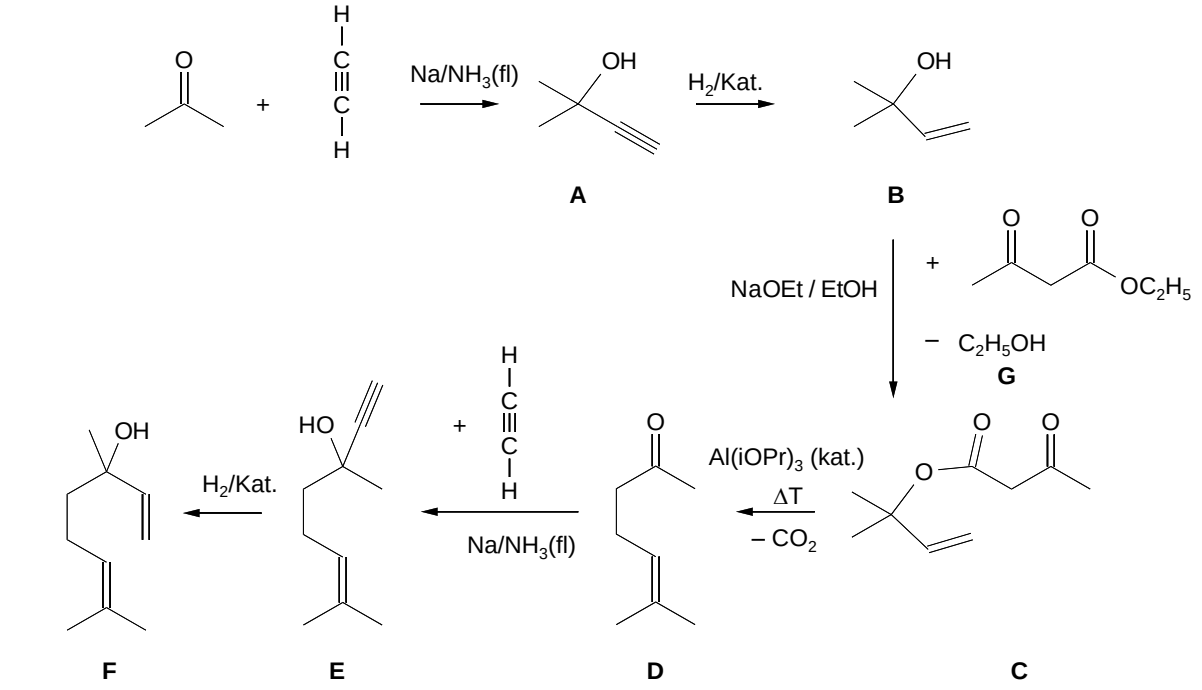
⇒ 1. Step: splitting-off of ½ dimethyl pyrazine product: $(CuBr)_2(C_6H_8N_2)$

2. Step: splitting-off of ¼ dimethyl pyrazine product: $(CuBr)_4(C_6H_8N_2)$

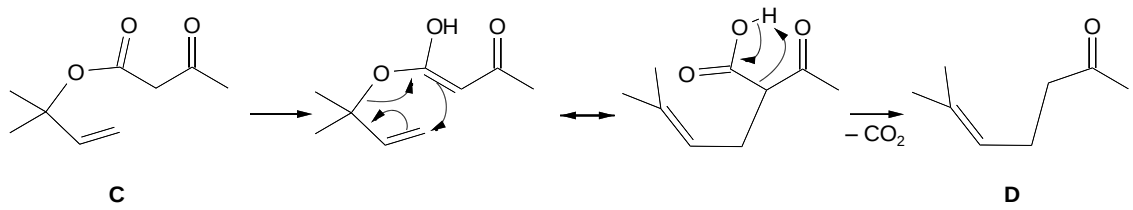
3. Step: splitting-off of ¼ dimethyl pyrazine product: (CuBr)

Solution to problem 1-4

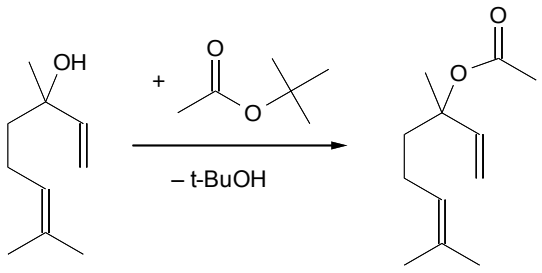
a)



b) Reaction of C to D (in the middle: Claisen rearrangement):



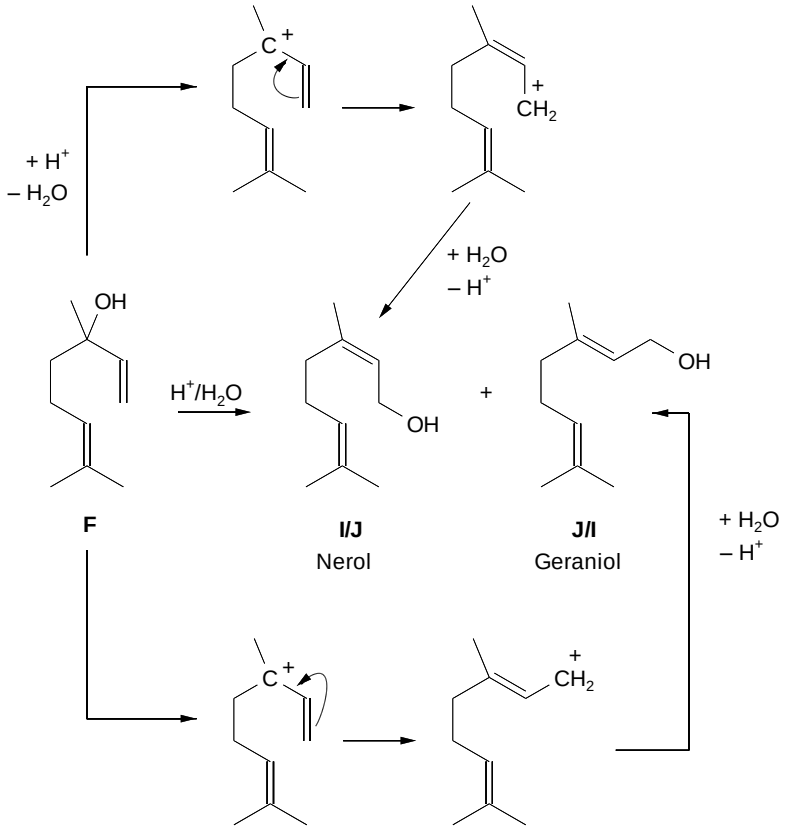
c) Linalyl acetate



F **H**

d) Linalyl acetate is a component of lavender oil, clary sage oil, bergamot oil.

e) Linalool (**F**) may undergo an allyl rearrangement to form the isomers nerol and geraniol:



Answers Round 2

Solution of problem 2-1

a) A: $Na_3H_2IO_6$

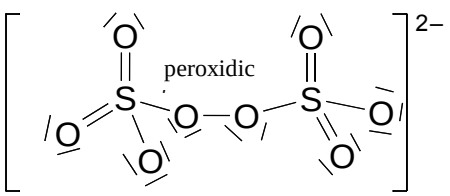
B: $Na_2S_2O_8$

C: $NiSO_4$

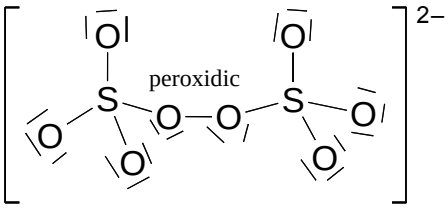
Remark: Nickel sulfate crystallizes from an aqueous solution with 6 or 7 molecules of crystal water and is sold as such a compound.

b) Oxidation state of sulfur: +VI.

Two of the oxygen atoms are peroxidic and thus possess the formal oxidation state –I.



or



c) Compound X: $NaNiIO_6$

$\overset{+II,+VI,-II}{NiSO_4} + \overset{+I,+I,+VII,-II}{Na_3H_2IO_6} + \overset{+I,\ +VI,\ -II}{Na_2S_2O_8} + \overset{+I,-II}{H_2O} \rightleftharpoons \overset{+I,+IV,+VII-II,\ +I,-II}{NaNiIO_6 \cdot H_2O} + 2\ \overset{+I,\ +I,+VI,-II}{NaHSO_4} + \overset{+I,+VI,-II}{Na_2SO_4}$

or

$\overset{+II}{Ni^{2+}} + \overset{+I,+VII,-II}{H_2IO_6^{3-}} + \overset{+VI,-II}{S_2O_8^{2-}} + \overset{+I}{Na^+} + \overset{+I,-II}{H_2O} \rightleftharpoons \overset{+I,+IV,+VII\ -II,\ +I,-II}{NaNiIO_6 \cdot H_2O} + 2\ \overset{+I,+VI,-II}{HSO_4^-}$

Percentage of nickel

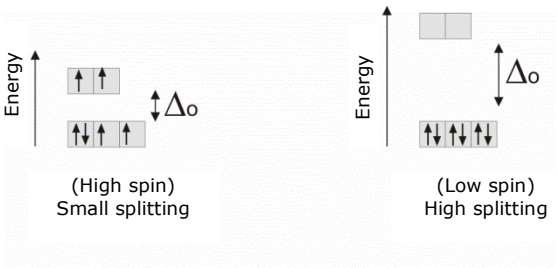
$M(NaNiIO_6 \cdot H_2O) = 322.5993$ g/mol $w(Ni) = (58{,}69/322{,}60) \cdot 100\%$ $w(Ni) = 18.19\ \%$

d) You may expect diamagnetism for a Ni(IV) compound (no unpaired electron).

Nickel has the oxidation state +IV and thus a d^6 system.

Whether there is a low spin or a high spin configuration depends on the splitting of the ligand field.

The splitting is influenced by the ligands (in this case oxygen – situated in the middle of the spectrochemical series), by the metallic center (in this case nickel - rather small splitting (3d system), the higher the quantum number, the higher the splitting) and by the charge of the central atom (in this case high charge – great splitting). In this case the charge should be crucial:



Remark: There are actually Ni(III) centers in this compound (especially after aging) thus you can observe a small amount of paramagnetism.

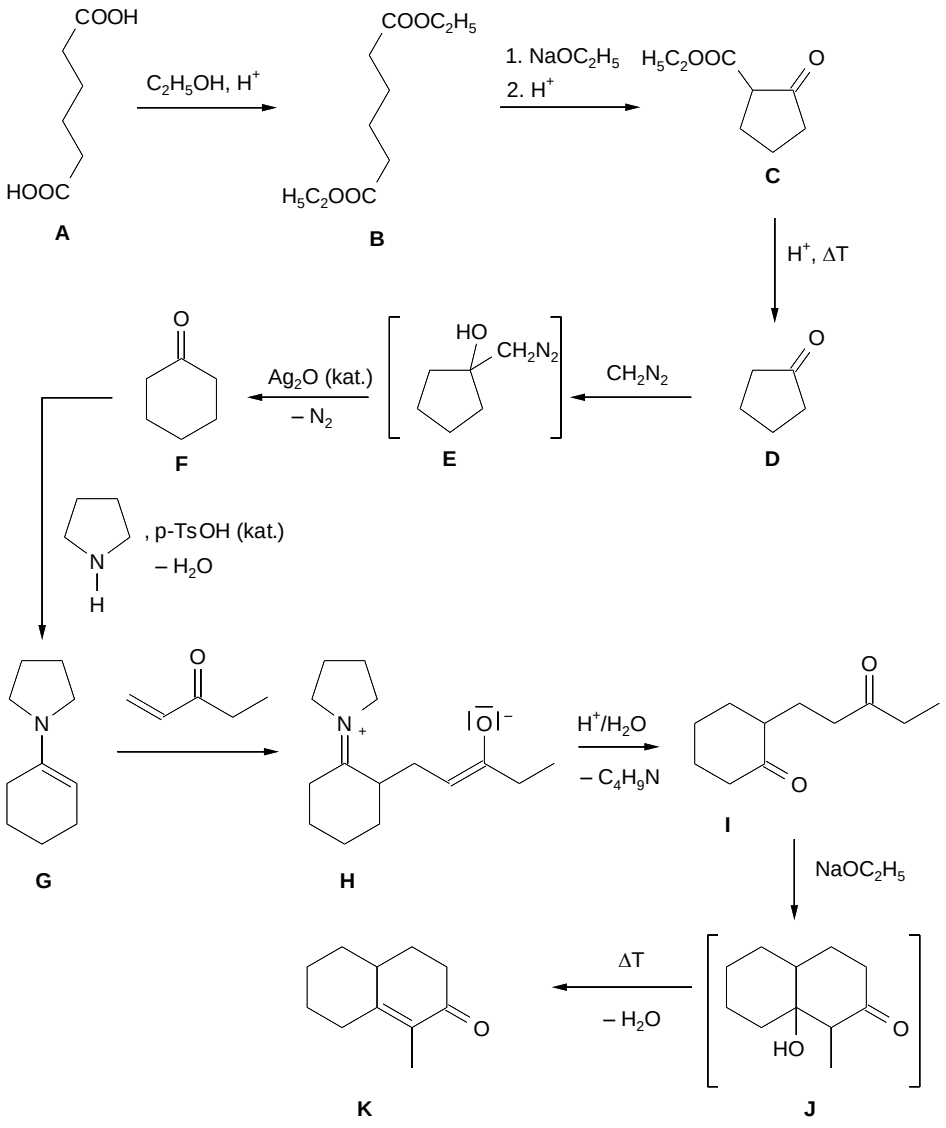
e) The alloy is known as nitinol, a shape memory alloy. If it is deformed it will recover to the original shape when heated.

Solution to problem 2-2

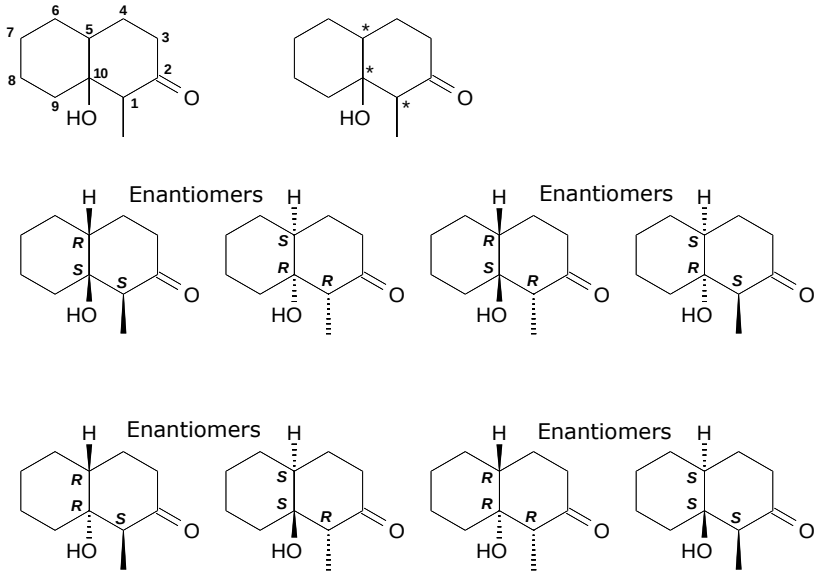
a) At first **A** has to be found.

Dioic acid	Molecular formula	% C
HOOC-COOH	$C_2H_4O_4$	26.68
HOOC-CH_2-COOH	$C_3H_4O_4$	34.63
HOOC-CH_2-CH_2-COOH	$C_4H_6O_4$	40.68
HOOC-CH_2-CH_2-CH_2-COOH	$C_5H_8O_4$	45.46
HOOC-CH_2-CH_2-CH_2-CH_2-COOH	$C_6H_{10}O_4$	49.31
HOOC-CH_2-CH_2-CH_2-CH_2-CH_2-COOH	$C_7H_{12}O_4$	52.50

A is probably adipic acid $C_6H_{10}O_4$.

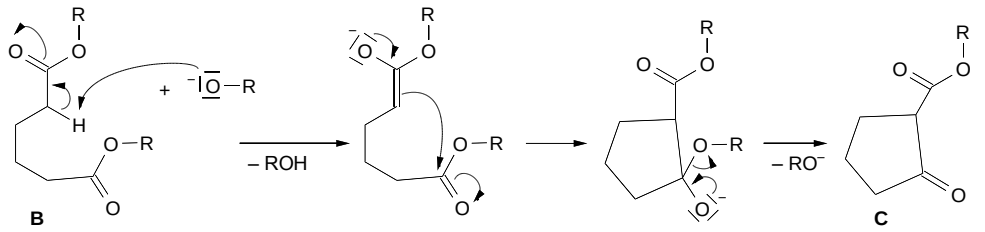


b) **J** is a bicyclic compound with 3 stereogenic centers, thus it has 8 stereoisomers.

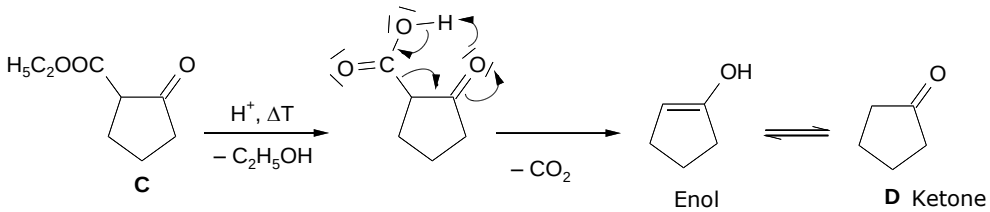


All stereomers which are not enantiomers are diastereomers.

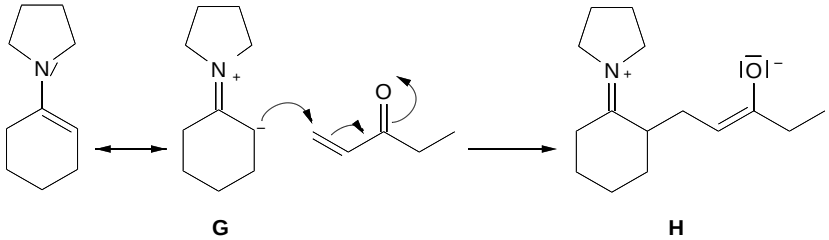
c) i) Well-known as Dieckmann condensation (intramolecular Claisen condensation, R = C_2H_5):



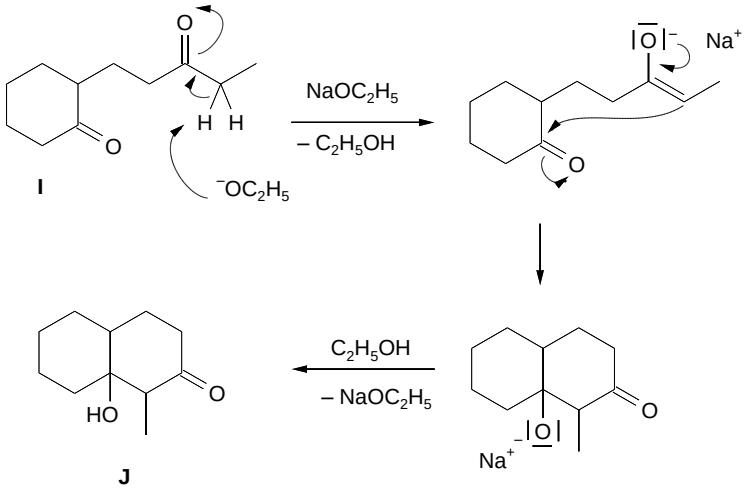
ii)



iii) Well-known as Michael addition of a nucleophile (enamine) to an a,ß unsaturated carbonyl compound:



iv) Intramolecular aldol reaction:



A combination of iii and iv (Michael addition followed by an intramolecular aldol reaction) is denoted as Robinson annulation.

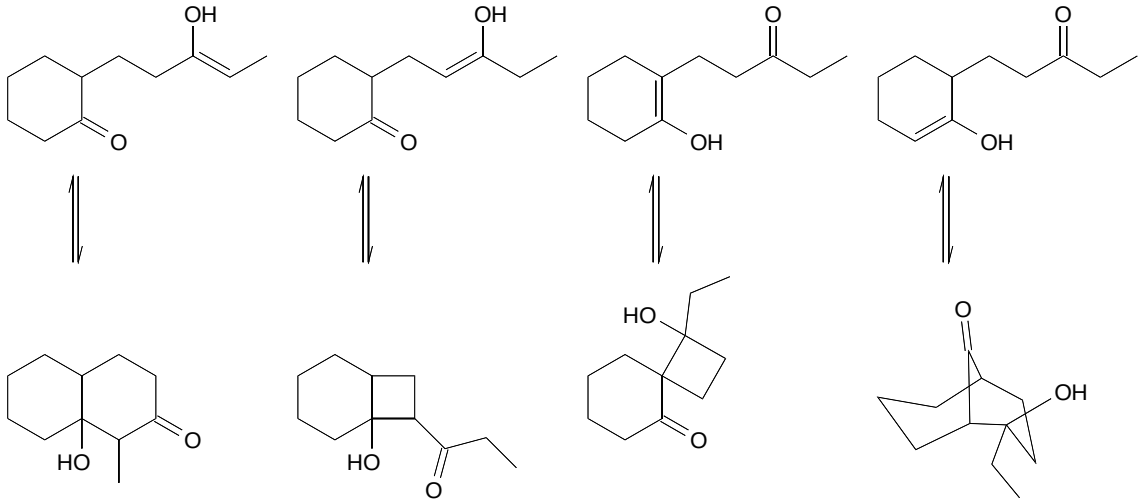
d) If cyclohexanone reacts directly with ethyl vinyl ketone in the presence of a base there is the risk of a multiple alkylation i.e. the alkylation product may react with more ethyl vinyl ketone to form the respective α,α'-di-alkylation products.

First of all ethyl vinyl ketone is in not stable in a basic solution, it tends to polymerize. Thus the yield of the wanted product is normally very small.

The synthesis via the enamine has the advantage that basic conditions are not necessary. The polymerization of the ethyl vinyl ketone is suppressed and the product of the alkylation (an iminium ion) cannot react again with ethyl vinyl ketone so that there is no multiple alkylation.

e) Compound **I** contains two carbonyl groups, both of them can be deprotonated to form an enolate. Thus there may be four different products in an intramolecular aldol addition. All these reactions are reversible so that at the end the thermodynamic most stable product is formed. Two of the four aldol adducts contain strained four membered rings and thus are instable. Another product has a bicyclic structure from which water cannot be eliminated. The only stable product the aldol adduct **J** with two six membered rings free of strain and the possibility of splitting off of water.

Possible enolates from I:



Product J

four membered rings

Bicyclic structure, no elimination of water possible

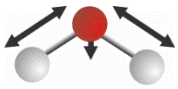
Solution to problem 2-3

a) IR spectroscopy: IR radiation is shone through a sample and certain frequencies are absorbed. The molecules gain vibrational energies. The transmitted frequencies are determined in a plot.

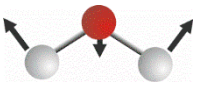
Raman spectroscopy: The sample is irradiated with an intense beam of monochromatic light, most conveniently running in the visible spectrum. Most of the scattered photons have the same frequency as the original from the laser but a small amount of the photons (Raman photons) are absorbed by the molecules and afterwards emitted with different frequencies. The shift in energy between the Raman photons and the original laser photons is equal to the difference in energy of two vibrational energy levels.

Thus IR spectroscopy is a direct method to detect molecule vibrations whereas Raman spectroscopy is an indirect method.

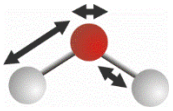
b) i) $z = 3 \cdot 3 - 6 = 3$



Raman aktive
IR aktive

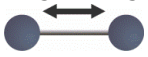


Raman aktiv
IR *aktiv*



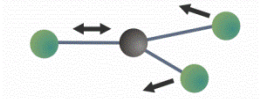
Raman aktive
IR *aktive*

ii) $z = 3 \cdot 2 - 5 = 1$

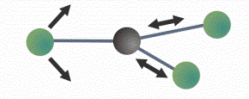


Raman aktive *IR inaktive*

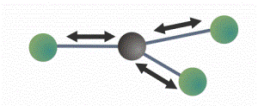
iii) $z = 4 \cdot 3 - 6 = 6$



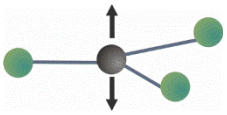
Raman active
IR active



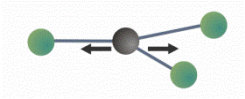
Raman active
IR active



Raman active
IR inactive



Raman inactive
IR active



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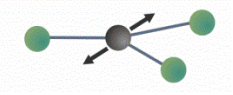


Raman active
IR active

c) Only three signals are expected because you find a change in the dipole moment only at the asymmetric stretching mode and in the bending modes.
Remark: The two binding modes are degenerated. Thus there are only two signals observed. (2350,1 cm^{-1} und 667,5 cm^{-1}, Phys. Rev., Vol. 41, S. 291–303, 1932).

d) To describe the vibrational movements of the atoms you have to consider their original position in the coordinate system as well as their new positions caused by the vibration.
The positions of N atoms are defined by 3N coordinates (x, y, z). Here the position of the total molecule in space is determined (translation) as well as its orientation with respect to the coordinate system (rotation).
The orientation of a linear molecule is given in one direction ⇒ two coordinates are sufficient to describe the position of the molecular axis. That means that you have to subtract three modes of translation and two modes of rotation to get the vibrational modes (-5).
In non-linear molecules one more rotation mode is possible, that means that you have to subtract three modes of translation and three modes of rotation to get the vibrational modes (-6).

e) $\gamma = \frac{f+2}{f}$ Number of degrees of freedom of helium: 3 ⇒ γ_{He} = 5/3 = 1.67

$p_{chamber} \leq p_{reservoir} \cdot \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma+1}} = 650\ mbar \cdot \left(\frac{2}{5/3+1}\right)^{\frac{5/3}{5/3+1}} = 543\ mbar$

f) Limonene has the molecular formula $C_{10}H_{16}$ ⇒ N = 26.
z = 3 N – 6 ⇒ number of vibrations z = 3 · 26 – 6 = 72
Kind of vibrations: C-H stretching (2700-3100 cm^{-1}), C=C stretching (1700-1800 cm^{-1}) and skeleton vibrations (below von 1500 cm^{-1})

g) 1 Hartree = $4.360 \cdot 10^{-18}$ J ⇒ E(B) – E(A) = ΔE = $6.475 \cdot 10^{-5}$ Hartree = $2.823 \cdot 10^{-22}$ J
For 1 mol: $2.8231 \cdot 10^{-22}$ J · $6.022 \cdot 10^{-23}$ mol^{-1} = 170.00 J = 0.17 kJ/mol
1 eV = 96.485 kJ/mol ⇒ ΔE = $1.762 \cdot 10^{-3}$ eV
The transition *A* ⟶ *B* is possible at room temperature.
That can be justified by the Boltzmann distribution at 25°C:

$\frac{N_1}{N_2} = e^{-\Delta E/k_B T}$ N_1 = number of molecules of B, N_2 = number of molecules of A,

k_B = Boltzmann's constant = 8.314 $JK^{-1}mol^{1}$

⇒ $\frac{N_1}{N_2} = e^{-\frac{170\ J \cdot mol^{-1}}{8.314\ J \cdot K^{-1} \cdot 298\ K}} = 0.934$

Both states are nearly equally occupied. 100 molecules of the ground state (A) correspond to 93 molecules of the excited state (B), e.g. the energetically unfavorable conformer B occurs nearly as often as the favored A.

h) Using the Boltzmann distribution again:

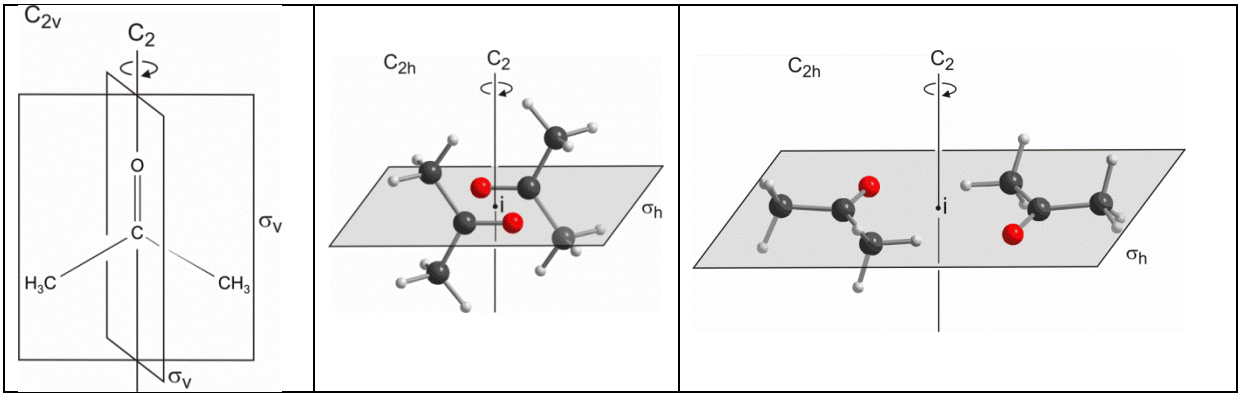
$$\frac{N_1}{N_2} = e^{-\Delta E/k_B T} \quad \Rightarrow \quad \ln\left(\frac{N_1}{N_2}\right) = -\frac{\Delta E}{k_B T} \quad \Rightarrow \quad T = -\frac{\Delta E}{k_B ln\left(\frac{N_1}{N_2}\right)}$$

$$T = \frac{170\ J \cdot mol^{-1}}{8.314\ J \cdot K^{-1} \cdot ln\left(\frac{1}{7}\right)} = 10.5\ K$$

i) Axial substituents in a ring system are relatively close to each other. Thus they show repulsion due to steric effects. The larger the substituent the stronger is this repulsion. There is much more space in equatorial positions thus larger substituents prefer this position.

j) The stability of B with regard to the two rotamers is due to the intramolecular interaction of the isopropylene group with the double bond of the ring. If the methylene unit of the isopropylene group points in the direchtion of the double bond a weak hydrogen bridge bond occurs (methylene group = donator, double bond = acceptor).

k)



l) The center of the band of the monomer can be estimated from fig. 4: 1740 cm^{-1}.
From the calculation you can see that dimer 1 differs by ~ 20 cm^{-1} from the monomer, dimer 2 by ~ 20 cm^{-1}. Thus you can assign the dimer peak at 1721 cm^{-1} to dimer 1.

Answers Round 3 Test 1

Solution to problem 3-01

a) D b) B c) D d) D e) B,C E f) B,C,E g) C

Solution to problem 3-02

a) $6\ I^- + 2\ CrO_4^{2-} + 16\ H_3O^+ \longrightarrow 3\ I_2 + 2\ Cr^{3+} + 24\ H_2O$

$6\ I^- + Cr_2O_7^{2-} + 14\ H_3O^+ \longrightarrow 3\ I_2 + 2\ Cr^{3+} + 21\ H_2O$

b) In the mixture: m_1 = mass of chromate with M_1 = 194.2 g/mol

m_2 = mass of dichromate with M_2 = 294.2 g/mol

$n_1 \cdot 194.2$ g/mol + $n_2 \cdot 294.2$ g/mol = 1.000 g (n_i = amounts)

$n_2 = \frac{1.000\ g}{294.2\ g/mol} - \frac{194.2}{294.2} \cdot n_1$ $n_2 = 3.399 \cdot 10^{-3}$ mol - $0.660 \cdot n_1$ (1)

$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$

$n(S_2O_3^{2-}) = 18.40$ mL $\cdot$ 0.100 mol/L = $1.840 \cdot 10^{-3}$ mol

$\Rightarrow$ $n(I_2) = 0.920 \cdot 10^{-3}$ mol

$n(I_2) = 1.5 \cdot n_1/10 + 3 \cdot n_2/10$ (2)

(1) in (2): $0.920 \cdot 10^{-3}$ mol = $0.15 \cdot n_1 + 0.3 \cdot (3.399 \cdot 10^{-3}$ mol - $0.660 \cdot n_1)$

$\Rightarrow n_1 = 2.077 \cdot 10^{-3}$ mol $m_1 = 2.077 \cdot 10^{-3}$ mol $\cdot$ 194.2 g/mol = 0.403 g

c) In the solution for the reactions mentioned in a) there is an excess of potassium iodide. Only the mass of iodide which has reacted to iodine is necessary for the exact calculation. This mass is determined accurately by the titration with thiosulfate.

d) $MgC_2O_4 \longrightarrow MgO + CO_2 + CO$

e) $B = MgC_2O_4$ with $M(MgC_2O_4)$ = 112.3 g/mol

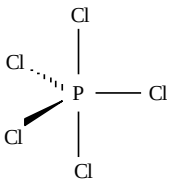
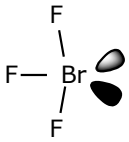
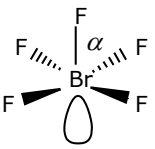
From the figure: m(B) = 0.75 g $\Rightarrow n(MgC_2O_4) = \frac{0.75\ g}{112.3\ g/mol} = 6.68 \cdot 10^{-3}$ mol

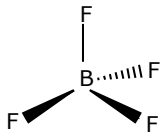
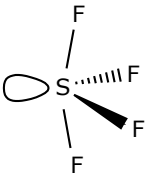
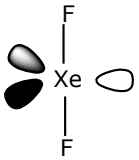
$n(H_2O) = \frac{0.25\ g}{18.02\ g/mol} = 0.0139$ mol

$n(MgC_2O_4) : n(H_2O) = 6.68 \cdot 10^{-3} : 0.0139 = 1.00 : 2.08$ $\Rightarrow x = 2$

Solution to problem 3-03

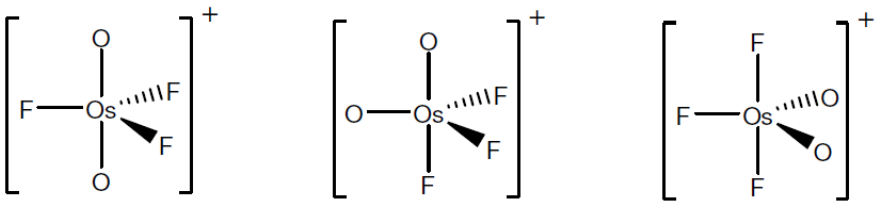
a)

Formula, type	PCl_5 AX_5	BrF_3 AX_3E_2	BrF_5 AX_5E
Structure	(Trigonal dipyramid) 	(Distorted T-form)  Angle FBrF = 86.2°	(Distorted tetragonal pyramid)  α = 81.9°, Br lies below the plain of the 4 equatorial F

Formula, type	BF_4^- AX_4	SF_4 AX_4E	XeF_2 AX_2E_3
Structure	(Tetrahedron) 	(Distorted tetrahedron)  Angle FSF(equ.) = 101° Angle FSF (axial) = 173°	(linear) 

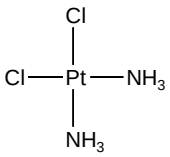
The angles and the statements in brackets are not expected.

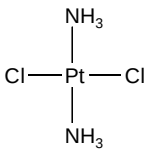
b)

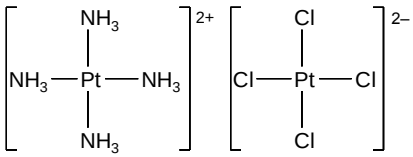


Solution to problem 3-04

a)

A 

B 

C 

b) A is a polar compound which can be dissolved in polar solvents.
B is a non-polar compound thus it can be dissolved in non-polar solvents.

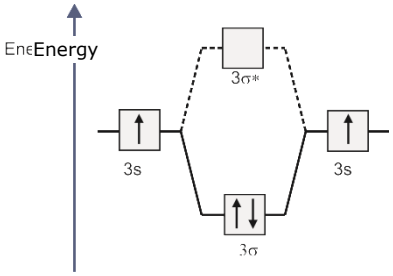
c) $[Xe]4f^{14}5d^8$

d) It has to be a low-spin complex because of the diamagnetic behavior (no unpaired electrons) of the compounds.

Solution to problem 3-05

a) Alkali metals own only one valence electron and have small first ionization energies.
Thus they tend to reach noble gas configuration by releasing an electron.
They react as strong reducing agents.

b)



Bond order = $\frac{Number\ of\ bonding\ electron\ s - number\ of\ antibonding\ electrons}{2} = \frac{2-0}{2} = 1$

Explanation (not expected in this detailedness): Starting with two 3s atomic orbitals with a single electron in each of them two σ molecular orbitals arise. One is bonding, the other one antibonding. There are two electrons in the bonding MO, the antibonding MO is empty. This leads to a single bond of both atoms.

c) $\left[\overline{\underline{O}}\right]^{2-}$ $\left[\overline{\underline{O}}-\overline{\underline{O}}\right]^{-}$ $\left[\overline{\underline{O}}-\overline{\underline{O}}\right]^{2-}$ is isoelectronic to O_2^{2-}.

d) $Me_2O_2 \cdot 2\ MeO_2$

e) i) $2\ LiOH + CO_2 \rightleftharpoons Li_2CO_3 + H_2O$

ii) $2\ Na_2O_2 + 2\ CO_2 \rightleftharpoons 2\ Na_2CO_3 + O_2$

iii) $4\ KO_2 + 2\ CO_2 \rightleftharpoons 2\ K_2CO_3 + 3\ O_2$

bzw. $4\ KO_2 + 2\ H_2O + 4\ CO_2 \rightleftharpoons 4\ KHCO_3 + 3\ O_2$

f) The ion mobility depends on the size of the ions: Big cations show a smaller mobility than smaller ones. Lithium cations show a small mobility because of their large hydration sheet.

g) Formation of sodium carbonate:
$CaCO_3 + 2\ NaCl \rightleftharpoons Na_2CO_3 + CaCl_2$

h) $NH_4HCO_3 + NaCl \rightleftharpoons NH_4Cl + NaHCO_3$ the right hand side is favored
$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4HCO_3$

i) $2\ NaHCO_3 \rightleftharpoons Na_2CO_3 + CO2 + H_2O$

j) Calcium hydroxide is used for the recovery of ammonia:
$Ca(OH)_2 + 2\ NH_4Cl \rightleftharpoons CaCl_2 + 2\ NH_3 + 2\ H_2O$

Solution to problem 3-06

a) $A = \varepsilon \cdot c \cdot d$ with absorbance $A = \lg \frac{I_0}{I}$ and $I = 0.4 \cdot I_0$

$\Rightarrow$ $c(A^-) = -\lg 0.4 / (21\ L\ mol^{-1}\ cm^{-1} \cdot 1\ cm)$ $c(A^-) = 1.9 \cdot 10^{-2}$ mol/L

pH = 8.8 $\Rightarrow c(H^+) = 10^{-8.8}$ mol/L

$K_a = \frac{c(H^+)/c_0 \cdot c(A^-)/c_0}{c(HA)/c_0}$ with c_0 = 1 mol/L $K_a = \frac{10^{-8.8} \cdot 1.9 \cdot 10^{-2}}{(2.0-1.9) \cdot 10^{-2}}$

$K_a = 3.0 \cdot 10^{-8}$ $pK_a = -\lg K_a$ $pK_a = 7.5$

b) Using 20 mL of NaOH solution 40 mL of a solution of the sodium salt of 3-chlorobutanoic acid (c = 0.5 mol/L) are formed (3-chlorobutanoic acid will be denoted as HR).

R^- is a weak base with $K_b = 10^{-14} / 10^{-4.05}$ $K_b = 10^{-9.95}$

$10^{-9.95} = \frac{c(HR)/c_0 \cdot c(OH^-)/c_0}{c(R^-)/c_0}$ x mol/L = $c(HR) = c(OH^-) \ll c(R^-) = 0.50$ mol/L

$10^{-9.95} = x^2 / 0.5$ $x = 7.49 \cdot 10^{-6}$ $c(OH^-) = 7.49 \cdot 10^{-6}$ mol/L

$\Rightarrow$ pOH = 5.13 pH = 14 – 5.13 pH ≈ 8.9

c) Phenolphthalein

d) $pH = pK_a + \lg \frac{c(R^-)}{c(HR)}$ $\Rightarrow$ $pH = pK_a + \lg \frac{n(R^-)}{n(HR)}$

$n(R^-) = V(NaOH) \cdot c(NaOH) = V(NaOH) \cdot 1$ mol/L

$n(HR) = V_0(HR) \cdot c_0(HR) - n(R^-) = 20$ mmol - $V(NaOH) \cdot 1$ mol/L

$\Rightarrow 3.7 = 4.05 + \lg \frac{V(NaOH) \cdot 1 \text{ mol/L}}{20 \text{ mmol} - V(NaOH) \cdot 1 \text{ mol/L}}$

$\Rightarrow V(NaOH) = \frac{20 \cdot 10^{-0.35}}{1 + 10^{-0.35}}$ mL V(NaOH) = 6.2 mL

Solution to problem 3-07

A: Barium nitrate B: Potassium iodide C: Lead acetate D: Silver nitrate

E: Sodium hydroxide F: Ammonia G: Copper sulfate

B and C: $2\ KI\ (aq) + Pb(OAc)_2\ (aq) \rightleftharpoons PbI_2\ (s) + 2\ KOAc\ (aq)$

$PbI_2\ (aq) + 2\ KI\ (aq) \rightleftharpoons K_2[PbI_4]\ (aq)$

B and G: $4\ KI\ (aq) + 2\ CuSO_4\ (aq) \rightleftharpoons 2\ CuI\ (s) + I_2\ (aq/g) + 2\ K_2SO_4\ (aq)$

C and E: $Pb(OAc)_2\ (aq) + 2\ NaOH\ (aq) \rightleftharpoons Pb(OH)_2\ (s) + 2\ NaOAc\ (aq)$

$Pb(OH)_2\ (s) + NaOH\ (aq) \rightleftharpoons Na[Pb(OH)_3]\ (aq)$

C and F: $Pb(OAc)_2\ (aq) + 2\ NH_3\ (aq) + 2\ H_2O\ (l) \rightleftharpoons Pb(OH)_2\ (s) + 2\ NH_4OAc\ (aq)$

D and F: $2\ AgNO_3\ (aq) + 2\ NH_3\ (aq) + H_2O\ (l) \rightleftharpoons Ag_2O\ (s) + 2\ NH_4NO_3\ (aq)$

$Ag_2O\ (s) + 2\ NH_3\ (aq) + H_2O\ (l) \rightleftharpoons 2\ [Ag(NH_3)_2]OH\ (aq)$

E and G: $2\ NaOH\ (aq) + CuSO_4\ (aq) \rightleftharpoons Cu(OH)_2\ (s) + Na_2SO_4\ (aq)$

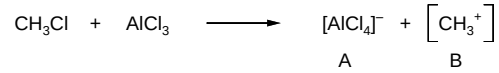
$Cu(OH)_2\ (s) \xrightarrow{\Delta T} CuO\ (s) + H_2O$

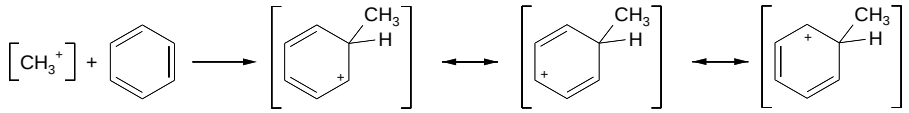
F and G: $2\ NH_3\ (aq) + CuSO_4\ (aq) + 2\ H_2O\ (l) \rightleftharpoons Cu(OH)_2\ (s) + (NH_4)_2SO_4\ (aq)$

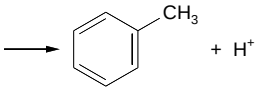
$Cu(OH)_2\ (s) + 4\ NH_3\ (aq) \rightleftharpoons [Cu(NH_3)_4](OH)_2\ (aq)$

Solution to problem 3-08

a)

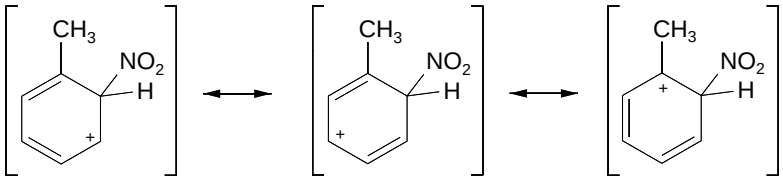




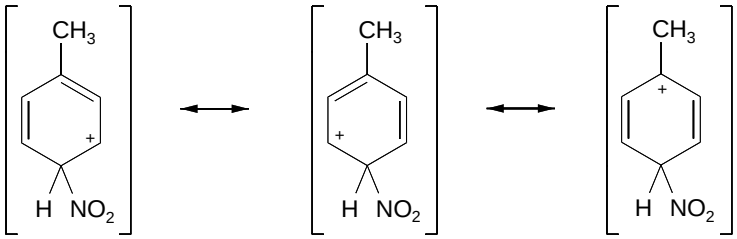


b) The so called σ complex is an intermediate in the reactions.

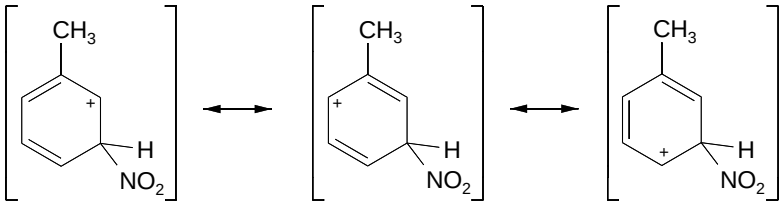
ortho-substitution



para-substitution



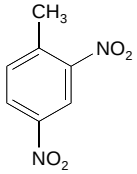
meta-substitution



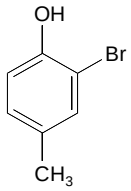
In the ortho- and para-substitution there are resonance structures with a positive partial charge at the carbon atom with the methyl substituent. These structures are stabilized by the +I effect of the methyl group. Thus the production of the ortho and the para product are favored.
Remark: In text books you can find explanation using hyperconjugation. This is not expected in this problem.

c) Main product: 2,4-Dinitrotoluene (1-Methyl-2,4-dinitrobenzene)

The methyl group directs the bromine substituent into 2 and 6 position (ortho-position to methyl), the nitro group into the 2 and 6 position, too, (meta position to the nitro group). So both substituents direct in the same position.

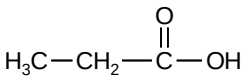
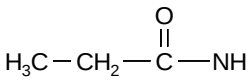


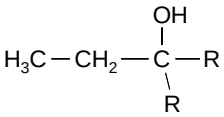
d) Main product: 2-Bromine-4-methylphenol (2-Brom-p-kresol)



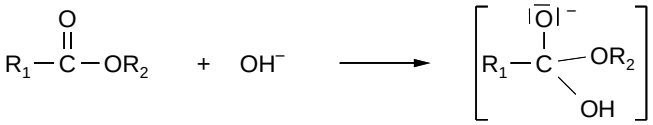
The hydroxyl group directs the bromine substituent into 2 and 6 position (ortho-position to the hydroxyl group). Against this the methyl group directs into 3 and 5 position (ortho-position to the methyl group). As the hydroxyl group has a stronger reactivity 2-bromine-4-methylphenol is formed with a higher yield.

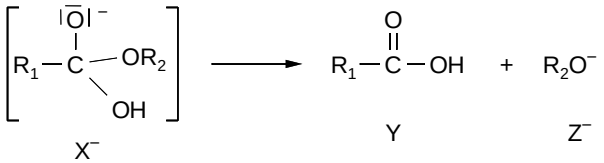
Solution to problem 3-09

a) S =  Acid  Amide

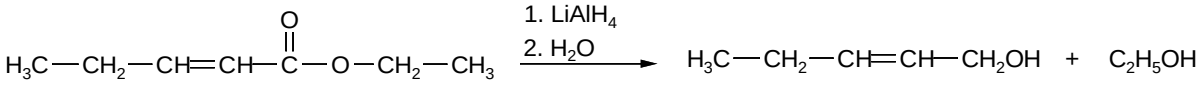
U = Alcohol  Alcohol

b)

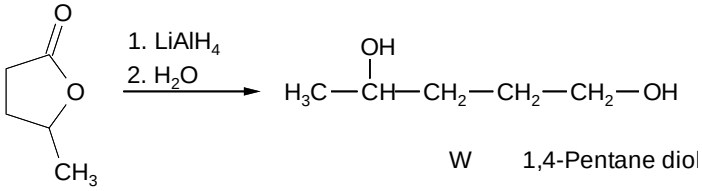
1. 

2. 

c) The isotopically labelled oxygen atom should only be found in the alcohol not in the acidic part.

d) 

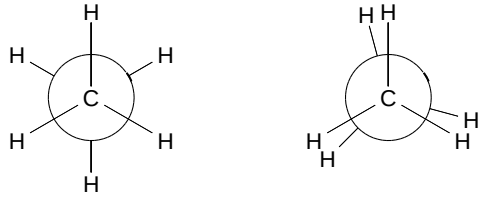
Remark: Lithium aluminum hydride does not react with the C=C double bond.

e) 

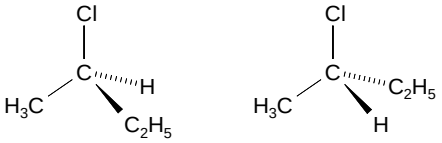
Solution to problem 3-10

a) i) C_2H_6O: $H_3C - CH_2 - OH$ and $CH_3 - O - CH_3$

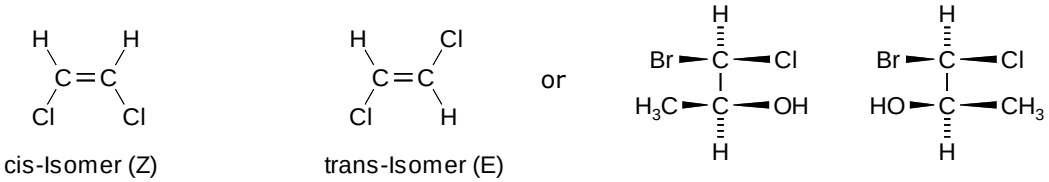
ii) H_3C-CH_3:



iii)

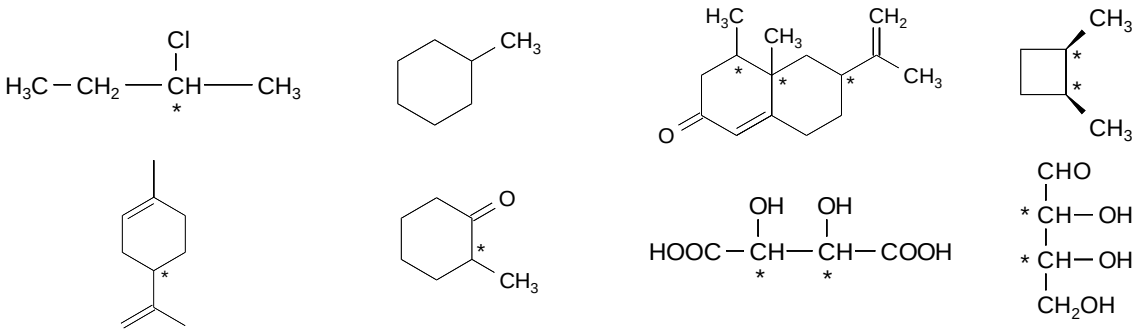


iv)



b) Cis-trans-isomers are diastereomers.

c)



d) Rule 1: Look at the four atoms directly attached to the chirality center and rank them according to atomic number. The atom with the highest atomic number is ranked first, the atom with the lowest atomic number is ranked fourth: Cl > O > C > H.

Rule 2: Orientate the molecule so that the group with the lowest priority (H) points directly back, away from us. The three remaining substitutes radiate towards us like the spokes of a steering wheel.

Rule 3: If a curved arrow drawn from the highest to the second highest to the third highest (1→2→3) is clockwise the chirality center has an R configuration. If the arrow is counter-clockwise it has an S configuration..

e) i) R ii) R iii) 1S, 2S iv) S v) R

Answers of Round 3 Test 2

Solution to problem 3-11

a) B,D b) A,B.E c) A,D,E d) C e)A,B,C f) A,C g) A,D

Solution to problem 3-12

a) $\varepsilon = \frac{A}{c \cdot d}$

Solution No.	I	II	III	IV
c in mol/L	$1.00 \cdot 10^{-3}$	$0.50 \cdot 10^{-3}$	$0.25 \cdot 10^{-3}$	$0.15 \cdot 10^{-3}$
ε in $L \cdot mol^{-1} \cdot cm^{-1}$	890	880	920	867

Mean value $\varepsilon = 889\ L \cdot mol^{-1} \cdot cm^{-1}$

b) Oxidation of CO: $5\ CO + I_2O_5 \longrightarrow I_2 + 5\ CO_2$

$c(I_2) = \frac{A}{\varepsilon \cdot d}$ $c(I_2) = 0.69/889$ mol/L $c(I_2) = 7.76 \cdot 10^{-4}$ mol/L

$\Rightarrow n(I_2)$ in 100 mL solution $= 7.76 \cdot 10^{-5}$ mol

$\Rightarrow n(CO) = 3.88 \cdot 10^{-4}$ mol

$V(CO) = \frac{n \cdot R \cdot T}{p}$ $V(CO) = \frac{3.88 \cdot 10^{-4} \cdot 8.314 \cdot 303}{102400}\ m^3$

$V(CO) = 9.55 \cdot 10^{-6}\ m^3 = 9.55$ mL $\triangleq 1.9$ %

Solution to problem 3-13

a) Let m = 178.96 g ($\triangleq$ 1 mol of $Mn(NO_3)_2$) react

178.96 g · 52.04 % = 93.13 g

$\Rightarrow$ $m(MnO_x) = 85.83$ g with 54.94 g of manganese and 30.89 g of oxygen

$n(O) = \frac{30.89\ g}{16.00\ g/mol} = 1.93$ mol x = 1.93

It has to be a gas richer in oxygen than NO_2: N_2O_5

Balance for the reaction of 1 mol of $Mn(NO_3)_2$)

amount of nitrogen: $n(NO_2) + 2 \cdot n(N_2O_5) = 2$ mol

amount of oxygen: x mol $+ 2 \cdot n(NO_2) + 5 \cdot n(N_2O_5) = 6.00$ mol with x = 1.93

$2 \cdot n(NO_2) + 5 \cdot n(N_2O_5) = 4.07$ mol

$-2 \cdot n(NO_2) - 4 \cdot n(N_2O_5) = -4.00$ mol

$n(N_2O_5) = 0.07$ mol and $n(NO_2) = 1.86$ mol

$V(NO_2) : V(N_2O_5) = n(NO_2) : n(N_2O_5) = 1.86 : 0.07 \approx 25.6 : 1$

b) Concentration of Ni^{2+}:

10.0 mL · $c(Ni^{2+})$ = 17.1 mL · 0.0100 mol/L $\Rightarrow c(Ni^{2+}) = 0.0171$ mol/L

$n(Ni^{2+})$ in 20.0 mL : $20.0 \cdot 10^{-3}$ L · 0.0171 mol/L $= 3.42 \cdot 10^{-4}$ mol

excess of Ni^{2+}: 21.3 mL · 0.0100 mol/L $= 2.13 \cdot 10^{-4}$ mol

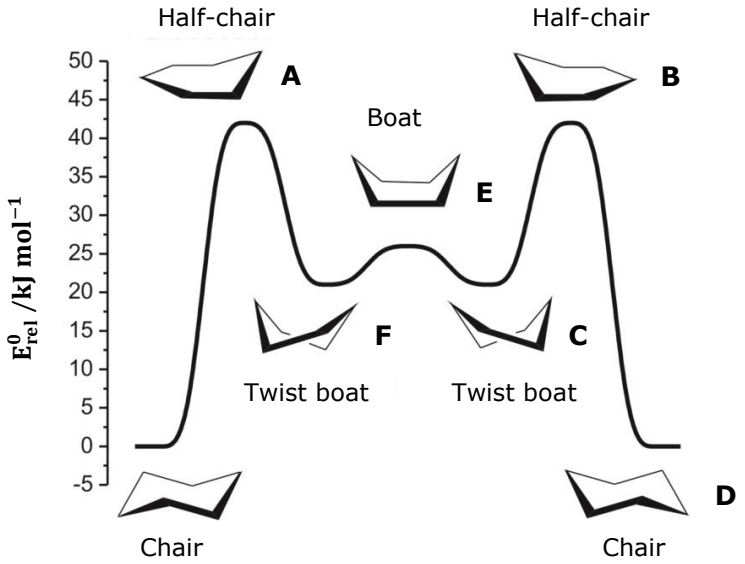
Ni^{2+} bound by CN^- = $3.42 \cdot 10^{-4}$ mol - $2.13 \cdot 10^{-4}$ mol $= 1.29 \cdot 10^{-4}$ mol

$n(CN^-)$ in 20 mL = 4 · $n(Ni^{2+})$ bound by CN^- $= 5.16 \cdot 10^{-4}$ mol

$c(CN^-) = 5.16 \cdot 10^{-4}$ mol/($20.0 \cdot 10^{-3}$ L) = 0.0258 mol/L

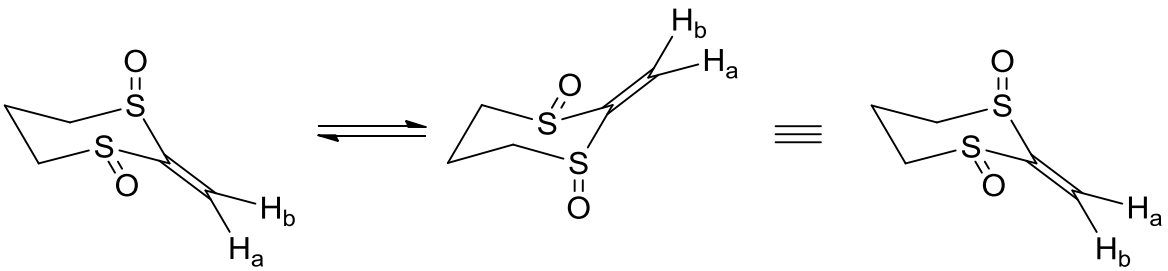
Solution to problem 3-14

a)



b) Read from the diagram: $E_A \approx$ 42-43 kJ/mol,
boat and twist-boat conformers can be isolated.

c) In the process **1-A** ⟶ **1-B** the protons H_a and H_b change their positions.



1-A **1-B** **1-B**

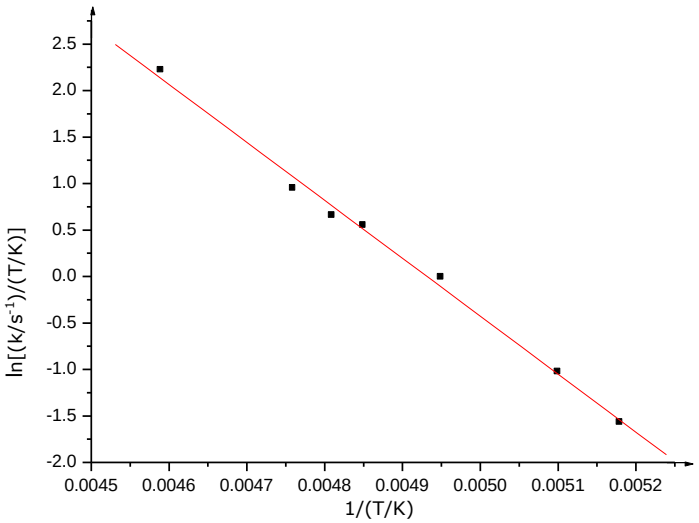
d)

For each of the two protons H_a und H_b a singlet is observed at deep temperatures (-84 °C). The chair flip is slower than the time necessary for one NMR measurement (lifetime of the NMR signal). Thus for these two protons different signals can be detected.

At a higher temperature (-55 °C) only one singlet is observed. The chair flip now is much quicker than the NMR measurement. A singlet can be detected if t(chair flip) ≪ t(NMR measurement).

e) (In e) and f) the units are omitted in order to arrange the calculations more clearly.)

ϑ/°C	T/K	k/s^{-1}	1/(T/K) · 10^3	$\ln \frac{k/s^{-1}}{T/K}$
- 55	218	2000	4.59	2.216
- 63	210	540	4.76	0.944
- 65	208	400	4.81	0.654
- 67	206	356	4.85	0.547
- 71	202	200	4.95	- 0.010
- 77	196	70	5.10	- 1.030
- 80	193	40	5.18	- 1.574



$$\ln \frac{k/s^{-1}}{T/K} = -6233 \cdot \frac{1}{T/K} + 30.74$$

Fig.: Graph ln[(k/s^{-1})/(T/K)] against 1/(T/K) with linear fit

f) (2) $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \cdot \Delta S^{\ddagger}$ inserted in (1) $\ln k/s^{-1} = \ln T/K + 23.76 - \Delta G^{\ddagger}/(RT)$:

$$\ln \frac{k/s^{-1}}{T/K} = -(\Delta H^{\ddagger}/R) \cdot \frac{1}{T} + 23.76 + \Delta S^{\ddagger}/R$$

By comparison with the given equation $\ln \frac{k/s^{-1}}{T/K} = -6200 \cdot \frac{1}{T/K} + 30.00$ you get:

i) $\Delta H^{\ddagger}/(R/T^{-1}) = 6200$ $\Rightarrow \Delta H^{\ddagger} = 51.55$ kJ/mol

ii) $30 = 23.76 + \Delta S^{\ddagger}/R$ $\Rightarrow \Delta S^{\ddagger} = 51.88$ J K^{-1} mol^{-1}

$\Delta G^{\ddagger} = 51.55$ kJ/mol – (273 – 63) K · 51.88/1000 kJ K^{-1} mol^{-1} $\Delta G^{\ddagger} = 40.66$ kJ/mol

Solution to problem 3-15

a) $C_2H_6 \rightleftharpoons C_2H_4 + H_2$

b) $K_{p900} = e^{-\frac{\Delta G^0}{R \cdot T}}$ $K_{p900} = e^{-\frac{22390}{8.314 \cdot 900}}$ $K_{p900} = 5.02 \cdot 10^{-2}$

c) $C_2H_4 + H_2 \rightleftharpoons C_2H_6$

$\Delta S°_{hyd} = S°_{900\ K}(\text{ethane}) - S°_{900\ K}(\text{ethene}) - S°_{900\ K}(H_2)$

$\Delta S°_{hyd} = 319.7\ J \cdot mol^{-1} \cdot K^{-1} - 291.7\ J \cdot mol^{-1} \cdot K^{-1} - 163.0\ J \cdot mol^{-1} \cdot K^{-1} = -135\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta H° = \Delta G° + T \cdot \Delta S°$ $\Delta H°_{hyd} = -22.39$ kJ/mol + 900 K · (-135 J·mol^{-1}·K^{-1})

$\Delta H°_{hyd} = -143.9$ kJ/mol

d)

	C_2H_6	$\rightleftharpoons$	C_2H_4	+	H_2	
n_i before the reaction in mol	1		0		0	
n_i in equilibrium in mol	1-x		x		x	$\Sigma = 1 + x$
p_i in equilibrium	$\frac{1-x}{1+x} \cdot p_{total}$		$\frac{x}{1+x} \cdot p_{total}$		$\frac{x}{1+x} \cdot p_{total}$	

$$\Rightarrow K_{p900} = \frac{\frac{x^2}{(1+x)^2} \cdot (\frac{p_{total}}{p_0})^2}{\frac{1-x}{1+x} \cdot \frac{p_{total}}{p_0}}$$ with $p_{total} = 1.013 \cdot 10^5$ Pa and $p_0 = 1.000 \cdot 10^5$ Pa

$$5.02 \cdot 10^{-2} = \frac{x^2}{1-x^2} \cdot 1.013 \qquad x = 0.22$$

$\Rightarrow$ $p(H_2) = p(\text{ethene}) = \frac{0.22}{1.22} \cdot p_{total} = 0.18 \cdot p_{total}$ $\quad p(\text{ethane}) = \frac{0.78}{1.22} \cdot p_{total} = 0.64 \cdot p_{total}$

$\Rightarrow$ $V(H_2) = V(\text{ethene}) \triangleq 18\ \%$ each $\quad V(\text{ethane}) \triangleq 64\ \%$

e) $\ln(K_{p600}/K_{p900}) = \frac{-\Delta H}{R} \cdot (T_1^{-1} - T_2^{-1})$ $\quad \ln(K_{p600}) = \frac{-143900}{8.314} \cdot (600^{-1} - 900^{-1}) + \ln 5.02 \cdot 10^{-2}$

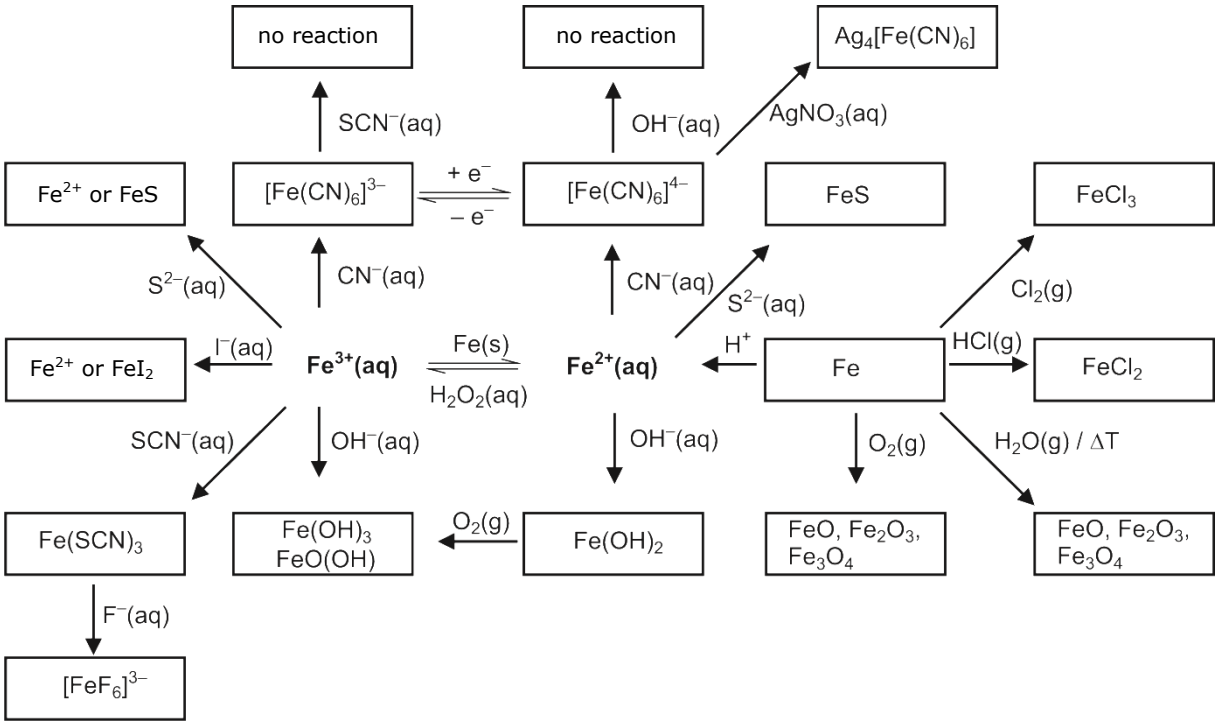
$\ln(K_{p600}) = -12.6$ $\quad K_{p600} = 3.4 \cdot 10^{-6}$

f) $K_{p600} < K_{p900}$

The dehydrogenation is endothermic. For an endothermic reaction increasing the temperature increases the value of the equilibrium constant and thus the equilibrium moves towards the products (Le Chatelier's principle).

Solution to problem 3-16

a)



Remark: Only one species is asked in each box. In some cases the species are built more complicated than written down.

b) In yellow prussiate $K_4[Fe(CN)_6]$ iron exists in the oxidation state II. This corresponds to 24 electrons or 6 valence electrons respectively. The cyanide ligands add 6 x 2 = 12 electrons and in doing so a noble gas configuration is formed (36/18 electrons). In red prussiate one electron is missing to form the stable noble gas configuration. Thus it is more unstable and a better oxidant.

c) The mixture contains iron(II) oxide and elementary aluminum. The products are iron and aluminum oxide: $Fe_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Fe$

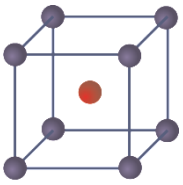
Remark: In this process a temperature of about 2400°C is reached at which iron is liquid.

d) $FeCl_3 + 6\ H_2O \rightleftharpoons [Fe(H_2O)_6]^{3+} + 3\ Cl^-$

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$

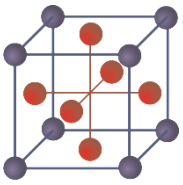
e)

cubic body-centered



Z = 2

cubic close packed



Z = 4

f) Density: $\rho = \frac{Z \cdot M(Fe)}{V_{cell} \cdot N_A}$

α-Iron:

Space diagonal: $d_s = a \cdot \sqrt{3}$ (a = edge length of the cube)

$d_s = 4 \cdot r(Fe) \Rightarrow 4 \cdot r(Fe) = a \cdot \sqrt{3}$

$\Rightarrow a = \frac{4 \cdot r(Fe)}{\sqrt{3}}$ with $r(Fe) = 126\ pm = 126 \cdot 10^{-10}\ cm$

$\Rightarrow$ edge length of the cube: $a = 2.91 \cdot 10^{-8}\ cm$

volume of the cell : $V_{cell} = a^3$ $V_{cell} = 2{,}46 \cdot 10^{-23}\ cm^3$

with Z = 2: $d = \frac{2 \cdot 55.85\ g \cdot mol^{-1}}{2.46 \cdot 10^{-23}\ cm^3 \cdot 6.022 \cdot 10^{23}\ mol^{-1}} = 7.54\ g \cdot cm^{-1}$

γ-Iron:

Face diagonal: $d_f = a \cdot \sqrt{2}$ (a = edge length of the cube)

$d_f = 4 \cdot r(Fe) \Rightarrow 4\ r(Fe) = a \cdot \sqrt{2}$

$\Rightarrow a = \frac{4 \cdot r(Fe)}{\sqrt{2}}$ with $r(Fe) = 126\ pm = 126 \cdot 10^{-10}\ cm$

$\Rightarrow$ edge length of the unit cell: $a = 3.56 \cdot 10^{-8}\ cm$

volume of the cell : $V_{cell} = a^3$ $V_{cell} = 4.53 \cdot 10^{-23}\ cm^3$

with Z = 4: $\rho = \frac{4 \cdot 55.85\ g \cdot mol^{-1}}{4.53 \cdot 10^{-23}\ cm^3 \cdot 6.022 \cdot 10^{23}\ mol^{-1}} = 8.19\ g \cdot cm^{-1}$

Solution to problem 3-17

a) There are two possibilities for the potential of the lead electrode:

$E(Pb^{2+}/Pb) = (0.238 - 0.478)\ V = -0.240\ V$ or $E(Pb^{2+}/Pb) = (0.478 + 0.238)\ V = +0.716\ V$.

As the value of the lead concentration is very small only the first value has to be considered.

$-0.240\ V = -0.126\ V + \frac{R \cdot T}{2 \cdot F} \cdot \ln [c(Pb^{2+})/(1\ molL^{-1})]$

$\ln [c(Pb^{2+})/(1\ molL^{-1})] = -0.114\ V \cdot \frac{2 \cdot 96485}{8.314 \cdot 298}$ $\ln c(Pb^{2+}) = -8.879$

$c(Pb^{2+}) = c(SO_4^{2-}) = 1.393 \cdot 10^{-4}\ mol/L$ $K_{sp}(PbSO_4) = 1.94 \cdot 10^{-8}$

b) pH = 3,00 $\Rightarrow$ $c(H_3O^+) = 1.0 \cdot 10^{-3}\ mol/L$ $\Rightarrow$ $c(SO_4^{2-}) = ½ \cdot 1.0 \cdot 10^{-3}\ mol/L$

*

$K_{sp} = c(SO_4^{2-}) \cdot c(Pb^{2+})/(1\ mol/L)^2$ $2.00 \cdot 10^{-8} = ½ \cdot 1.0 \cdot 10^{-3} \cdot c(Pb^{2+})/(1\ mol/L)$

$c(Pb^{2+}) = 4.0 \cdot 10^{-5}\ mol/L$

$E_{Pb\text{-}electrode} = -0.126\ V + \frac{R \cdot T}{2 \cdot F} \cdot \ln 4.00 \cdot 10^{-5}$ $E_{Pb\text{-}electrode} = -0.256\ V$

$\Delta E = E^{o}_{Ref} - E_{Pb\text{-}electrode}$ $\Delta E = 0.494\ V$

* In the strict sense you have to consider the amount of SO_4^{2-} resulting from the dissolution of lead sulfate, yet the difference is very small:

$c(Pb^{2+}) \cdot [c(Pb^{2+}) + ½ \cdot 1.0 \cdot 10^{-3}\ mol/L] = 2.00 \cdot 10^{-8}\ (mol/L)^2 \quad \Rightarrow c(Pb^{2+}) = 3.72 \cdot 10^{-5}\ mol/L$

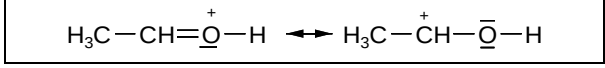
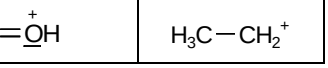
$E^{*}_{Pb\text{-}electrode} = -0.126\ V + \frac{R \cdot T}{2 \cdot F} \cdot \ln 3.72 \cdot 10^{-5}$ $E^{*}_{Pb\text{-}electrode} = -0.257\ V$

$\Delta E^{*} = 0.495\ V$

Solution to problem 3-18

a) $X = CH_3CH_2OH$

b) Fragments in the mass spectrum

m/e = 45	m/e = 31	m/e = 29
		

c) Peaks in the ^1H NMR spectrum:

Quartet at ~3.7 (3.687) ppm: signal of the CH_2 group

Triplet at ~1.2 (1.226) ppm: signal of the CH_3 group

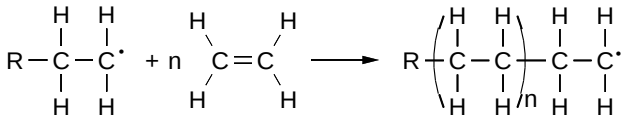
Singlet at ~2.6 (2.61) ppm: Signal of the OH group

d) Y = Dimethyl ether. In the ^1H-NMR a singlet is expected.

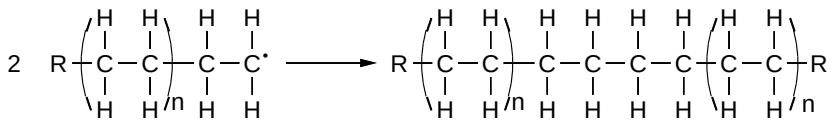
e) i) 2 ii) 2 iii) 4 (the two H atoms of the CH_2Cl group are diastereotopic because of the adjacent stereogenic center) iv) 3 v) 2 vi) 3 vii) 3 viii) 2

Solution to problem 3-19

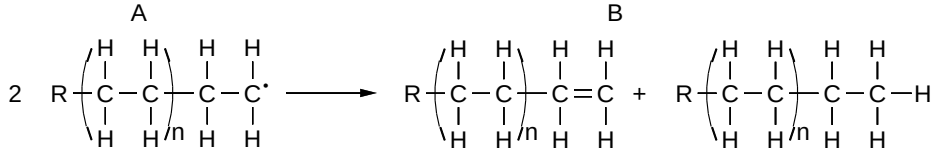
a)



A

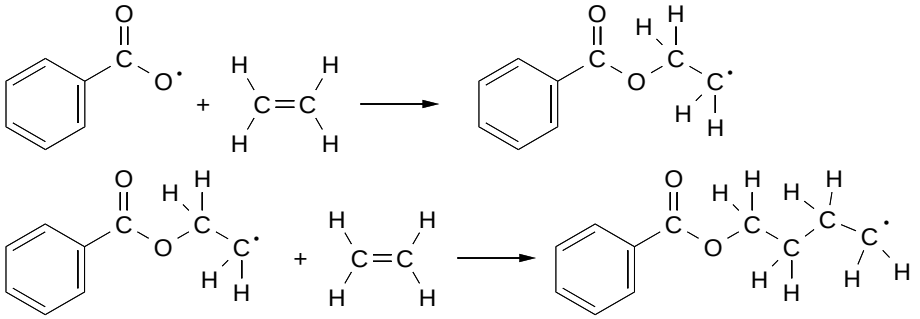


A B



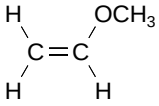
A C/D C/D

b)

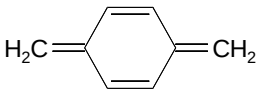


c)

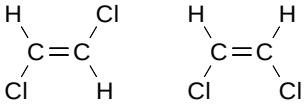
i)



ii)

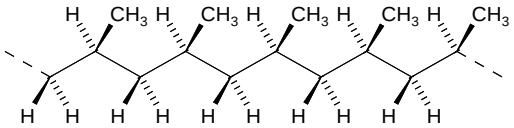


iii)

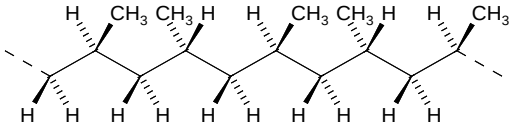


d)

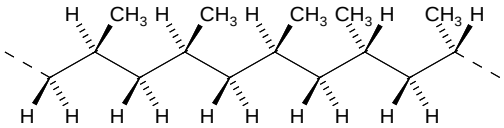
isotactic:



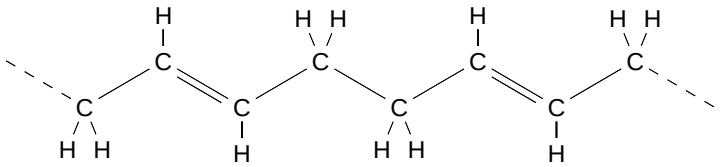
syndiotactic:

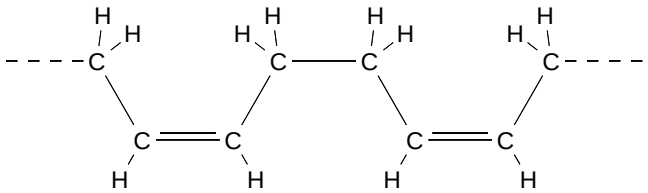


atactic:



e)

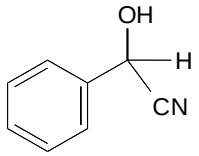




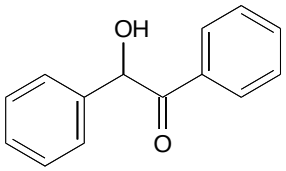
Solution to problem 3-20

a)

A



B



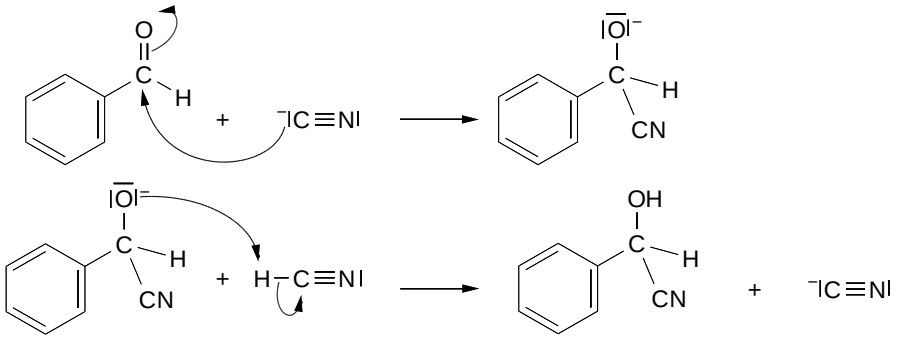
c

$LiAlH_4$

d

H^+ / H_2O

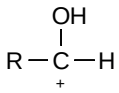
b) Nucleophilic addition.



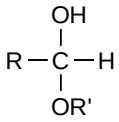
(Remark: The reaction of HCN with aldehydes and ketones is known as cyanohydrin reaction.)

c)

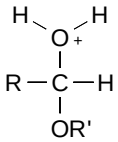
K



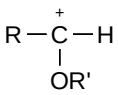
L



M

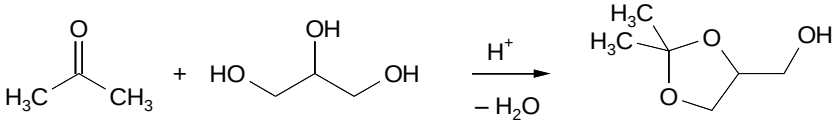


N



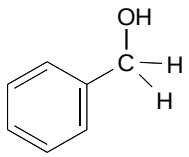
d) The equilibrium can be shifted towards the product by withdrawal of water using a water separator.

e)

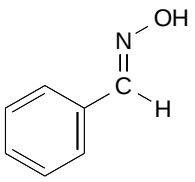


f)

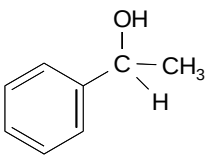
O



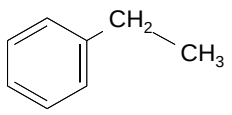
P



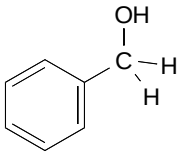
Q



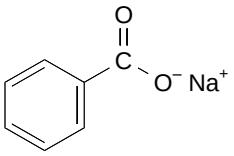
R



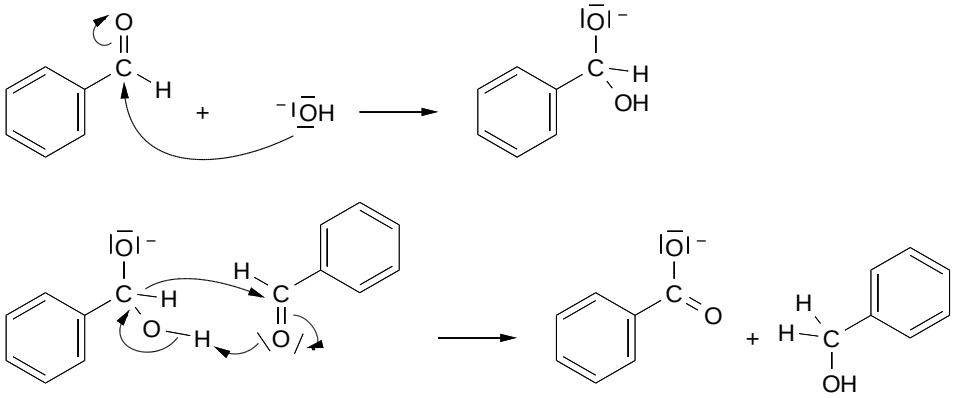
S/T



T/S



g)



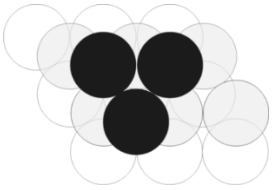
h) Aldehydes with a hydrogen in α position form enols when they are treated with a base. Thus a Cannizzaro reaction cannot occur.

Answers Round 4 (theoretical)

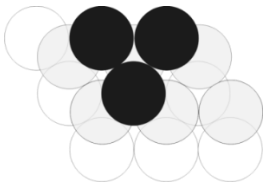
Solution to problem 4-1

a)

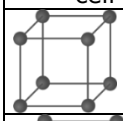
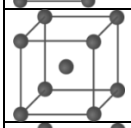
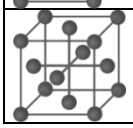
close-packed cubic



close-packed hexagonal

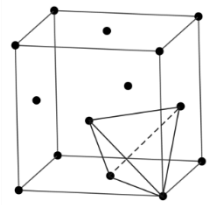


b)

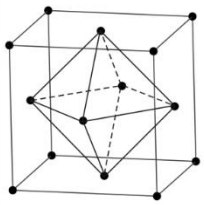
Elementary cell	Denotation	Coordination number	Metal atoms per cell
	primitive cubic	6	1
	body centered cubic	8	2
	face-centered cubic	12	4

c)

Tetrahedral interstice



Octahedral interstice



d) In each el. cell: 4 octahedral interstices and 4 atoms ⇒ n octahedral interstices

In each el. cell: 8 tetrahedral interstices and 4 atoms ⇒ 2n tetrahedral interstices

e) Chloride anions: $8 \times {}^{1}/_{8} + 3 \times ½ = 4$

Sodium cations: $12 \times ¼ + 1 = 4$

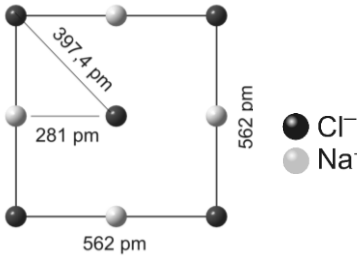
Thus the formula of the elementary cell is Na_4Cl_4

f) $2 \cdot r_{Cl} = \sqrt{\left(\frac{562}{2}\,\text{pm}\right)^2 + \left(\frac{562}{2}\,\text{pm}\right)^2} = 397{,}4\,\text{pm}$

⇒ r_{Cl} = 198.7 pm

562,0 pm = $2 \cdot r_{Cl} + 2 \cdot r_{Na}$

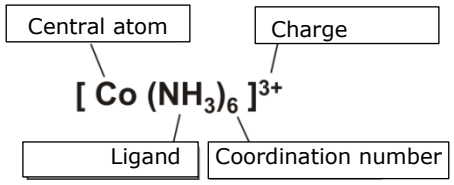
⇒ r_{Na} = 82,3 pm



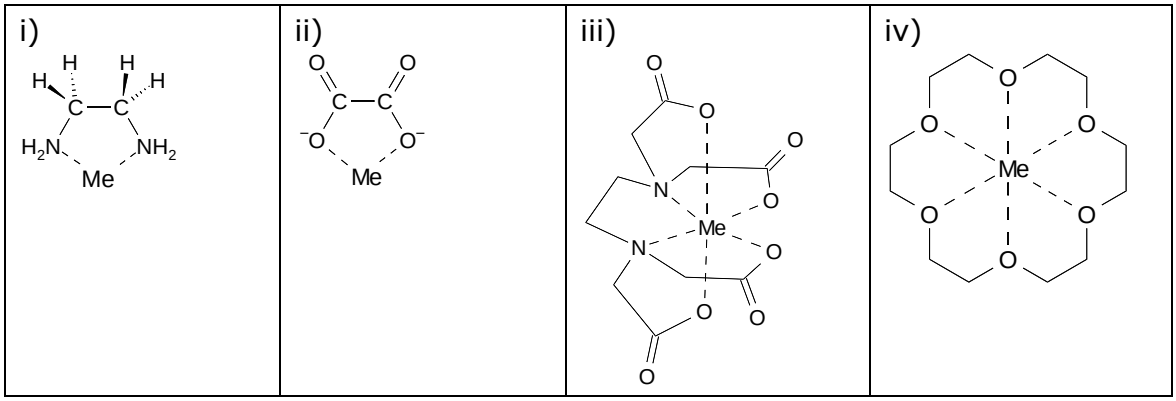
Remark: The assumption that the chloride anions are in contact to each other leads to a size too large for them and to a too small size of the sodium cations.

Solution to problem 4-2

a)



b)

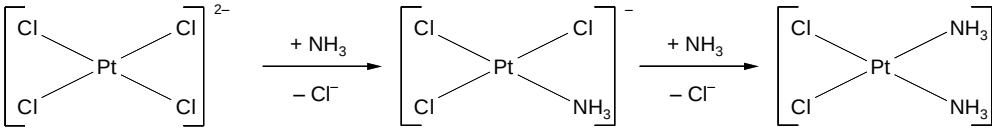


c) The gain in entropy arising from the fact that the number of molecules increases from left to right is highest for the formation of the trien complex, lowest (not changing) for the formation of the hexammine complex. Thus $[Ni(en)_3]^{2+}$ should be most stable, $[Ni(NH_3)_6]^{2+}$ least stable.

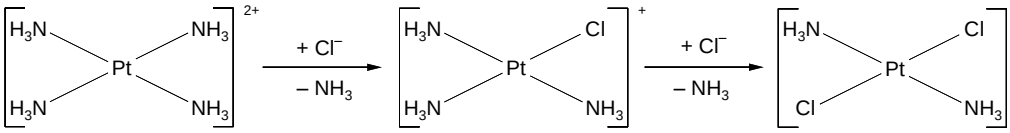
d)

e) Chlorine is strongly trans directing ⇒

Synthesis of the cis product:



Synthesis of the trans product:



f) The following equilibria have to be taken into account:

$Ni(OH)_2 \rightleftharpoons Ni^+ + 2\ OH^-$ $\quad K_L = 3.2 \cdot 10^{-17}$

$Ni^+ + 6\ NH_3 \rightleftharpoons [Ni(NH_3)_6]^{+2}$ $\quad K_B = 1/K_D = 5.01 \cdot 10^8$

In total:

$Ni(OH)_2 + 6\ NH_3 \rightleftharpoons [Ni(NH_3)_6]^+ + 2\ OH^-$ $\quad K = K_L \cdot K_B = 1.6 \cdot 10^{-8}$

To form $c([Ni(NH_3)_6]^{+2}) = 0.1$ mol/L you need 0.1 mol $Ni(OH)_2$ to dissolve

$\Rightarrow c(OH^-) = 0.2$ mol/L

$$\frac{c([Ni(NH_3)_6]^{2+}) \cdot c^2(OH^-)}{c^6(NH_3)} = 1.6 \cdot 10^{-8} \quad \Rightarrow \quad \frac{0{,}1 \cdot 0{,}2^2}{c^6(NH_3)} = 1.6 \cdot 10^{-8} \quad \Rightarrow c(NH_3) = 7.9 \text{ mol/L}$$

g) The acidic reaction and the possibility of sublimation point to a salt of a hydrated metal ion as iron(III) chloride or aluminum(III) chloride. Both of them sublimate as water-free compounds as dimers and cannot be dehydrated undecomposed.

$[Me(H_2O)_6]A_3 \xrightarrow{\Delta T} Me(OH)_3 + 3\ HA + 3\ H_2O$

$2\ Me(OH)_3 \xrightarrow{\Delta T} Me_2O_3 + 3\ H_2O$

Total:

$2\ [Me(H_2O)_6]A_3 \xrightarrow{\Delta T} Me_2O_3 + 6\ HA + 9\ H_2O$

0.830 g 0.376 g 0.280 g

0.280 g H_2O ≙ 0.0155 mol

0.0155 mol · 6/9 = 0.0103 mol ≙ 0.376 g HA

$\Rightarrow M(HA) = \frac{0.376\ g}{0.0103\ mol} = 36.50\ g \cdot mol^{-1}$ ⇒ M(A) = 35.5 ⇒ A = Cl

0.830 g ≙ 0.0155 mol · 2/9 = 0.00344 mol

$M([Me(H_2O)_6]Cl_3 = \frac{0.830\ g}{0.00344\ mol} = 241.28\ g \cdot mol^{-1}$

⇒ M(Me) = 26.93 g/mol ⇒ Me = Al Formula of the salt: $[Al(H_2O)_6]Cl_3$

Solution to problem 4-3

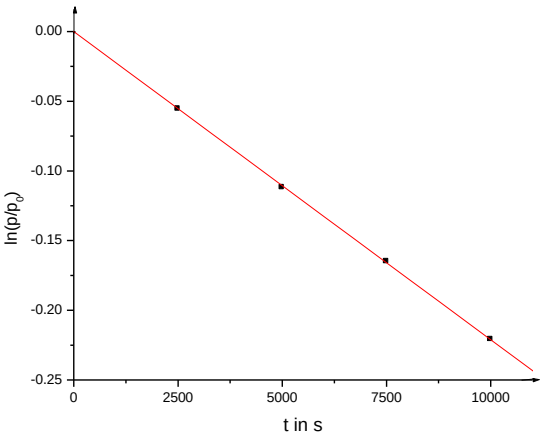
a) For a reaction of first order $\ln(p(SO_2Cl_2)/p_0) = f(t)$ is a linear function.

At first $p(SO_2Cl_2)$ (x) has to be determined:

$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

$p_0 - x$ x x $p_{total} = p_0 + x$ with $p_0 = 0.5$ atm

Timet in s	0	2500	5000	7500	10000
x in atm	0	0.027	0.053	0.076	0.099
$p(SO_2Cl_2)$ in atm	0.500	0.473	0.447	0.424	0.401
$\ln(p(SO_2Cl_2)/p_0)$	0	-0.555	-0.112	-0.165	-0.221



The plot is linear:

$\ln(p(SO_2Cl_2)/p_0) = -k \cdot t$

$\Rightarrow k = -\frac{\ln(p(SO_2Cl_2))/p_0)}{t}$

$k = \frac{0.221}{10000\ s} = 2.21 \cdot 10^{-5}\ s^{-1}$

b) 112 °C = 385 K p_{total} = 0.78 atm ⇒ x = 0.28 atm $p(SO_2Cl_2)$ = 0.22 atm

$k = -\frac{\ln(p/p_0)}{t} = -\frac{\ln(0.22/0.50)}{3600}$ $k = 2.28 \cdot 10^{-4}\ s^{-1}$

$k = A \cdot e^{-Ea/(R \cdot T)} \quad \Rightarrow \quad \ln \frac{2.28 \cdot 10^{-4}}{2.21 \cdot 10^{-5}} = \frac{Ea}{R} \cdot \frac{10\ K}{375\ K \cdot 385\ K} \qquad Ea = 280\ kJ/mol$

c) $\Delta G = \Delta H - T \cdot \Delta S$

$\Delta G = (-296.8 + 354.8)\ kJ - 400\ K \cdot (248.2 + 223.1 - 311.1)\ J/(K \cdot mol)$

$\Delta G = [58.0 - 0.4 \cdot 160.2]\ kJ/mol = -6.08\ kJ/mol$

$\ln K_p = -\Delta G/(R \cdot T) \qquad \ln K_p = 6080/(8.314 \cdot 400) = 1.83 \qquad K_p = 6.23$

d) $\Delta H = [-10.2 - 309.1 + 369.2 + 400\ K \cdot 10^{-3} \cdot (34.2 + 41.4 - 48.2)]\ kJ/mol = 60.86\ kJ/mol$

$\Delta S = [28.3 + 12.34 - 36.5 + \ln 400 \cdot (34.2 + 41.4 - 48.2)]\ J/(K \cdot mol)$

$\Delta S = 168.3\ J/(K \cdot mol)$

$\Delta G = [\ 60.86 - 0.4 \cdot 168.3]\ kJ/mol = -6.46\ kJ/mol$

$\ln K_p = 6460/(8.314 \cdot 400) = 1.943 \qquad K_p = 6.98$ The assumption is justified.

e) $v = \frac{d[I_3^-]}{dt} = k_4 \cdot [I_2] \cdot [I^-]$

$\frac{d[I_2]}{dt} = k_3 \cdot [I^+] \cdot [I^-] - k_4 \cdot [I_2] \cdot [I^-] = 0 \quad \Rightarrow \quad k_4 \cdot [I_2] \cdot [I^-] = k_3 \cdot [I^+] \cdot [I^-]$

$\frac{d[I^+]}{dt} = k_2 \cdot [IS_2O_8^{3-}] - k_3 \cdot [I^+] \cdot [I^-] = 0 \quad \Rightarrow \quad k_4 \cdot [I_2] \cdot [I^-] = k_2 \cdot [IS_2O_8^{3-}]$

$\frac{d[IS_2O_8^{3-}]}{dt} = k_1 \cdot [I^-]\,[S_2O_8^{2-}] - k_2 \cdot [IS_2O_8^{3-}] \quad \Rightarrow \quad k_4 \cdot [I_2] \cdot [I^-] = k_1 \cdot [I^-]\,[S_2O_8^{2-}]$

Thus the mechanism is consistent with the rate law.

Solution to problem 4-4

a) Let c_o be the initial concentration of the acid HA in water.

$\frac{c(HA_e)}{c(HA_w)} = 5.4 \qquad 5.4 \cdot c(HA_w) = c(HA_e) \qquad (1)$

and because the total amount of acid is constant

$V_e \cdot c(HA_e) + V_w \cdot c(HA_w) = V_w \cdot c_0\ , \quad \Rightarrow \quad 0.5\ L \cdot c(HA_e) + 1\ L \cdot c(HA_w) = 1\ L \cdot c_0\ ,$

$\Rightarrow \quad c(HA)_e = 2 \cdot c_0 - 2 \cdot c(HA)_w \qquad (2)$

(1) and (2) $\Rightarrow \qquad c(HA_w) = \frac{2 \cdot c_0}{5.4+2} = 0.27 \cdot c_0\ ,$

27 % of the acid stay in the aqueous phase, 73 % are extracted.

The given law is only valid for the species HA, not for particles like A^- and others. The condition for a correct result in part a) is that the acid in the aqueous phase (and in ether, too) exists completely as HA molecules. This can be achieved be decreasing the pH value in the aqueous phase with hydrochloric acid.

b) The volume of one portion of ether is 0.5 L/n.

1. Extraction: $0.5/n \cdot c_1(HA_e) + c_1(HA_w) = c_0$

$c_1(HA_e) = 2n \cdot c_0 - 2n \cdot c_1(HA_w)$

inserted in (1): $c_1(HA_w) \cdot 5{,}4 = 2n \cdot c_0 - 2n \cdot c_1(HA_w)$

$\Rightarrow \quad c_1(HA_w) = \frac{2n}{5.4+2n} \cdot c_0 \qquad (3)$

In the second extraction the initial concentration of the aqueous phase is $c_1(HA_w)$

$\Rightarrow \quad c_2(HA_w) = \frac{2n \cdot}{5.4+2n} \cdot \frac{2n \cdot}{5.4+2n} \cdot c_0 = \left(\frac{2n \cdot}{5.4+2n}\right)^2 \cdot c_0$

After n extractions the concentration in the aqueous phase is $c_n(HA_w) = \left(\frac{2n\cdot}{5.4+2n}\right)^n \cdot c_0$

After the last extraction $c_n(HA_w)$ has to be smaller than 0.110: $c_n(HA_w) \leq 0.110 \cdot c_0$

n	1	2	3	4	5	6
$c_n(HA_w)/c_0$	0.27	0.18	0.146	0.127	0.115	0.108

$\Rightarrow$ n = 6

c) $c(HA_e)$ = 0.0432 mol/50 mL $\quad c(HA_e)$ = 0.864 mol/L

$4.3 \cdot c(HA_w) = c(HA_e) \quad \Rightarrow \quad c(HA_w)$ = 0.201 mol/L

$K_S = \frac{c(A^-)\cdot c(H^+)}{c(HA_w)} \quad \Rightarrow \quad 10^{-2.89} = \frac{c(A^-)\cdot 10^{-3.0}}{0.201\ \text{mol/L}} \quad \Rightarrow c(A^-)$ = 0.259 mol/L

$c_0(HA) = 10 \cdot [n(HA)_{\text{ in 50 mL of ether}} + n(HA)_{\text{ in 100 mL of water}} + n(A^-)_{\text{ in 100 mL of water}})]/L$

$c_0(HA) = 10 \cdot [0.0432 + 0.0201 + 0.0259]$ mol/L = 0.892 mol/L

d) With the results of c) you get $D = \frac{0.864}{0.201+0.259}$ D = 1.88

e) Equation (1) $\Rightarrow \quad D = \frac{c(HA_e)}{c(HA_w)+c(A^-)}$ with $c(HA_e) = K_D \cdot c(HA_w)$

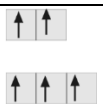
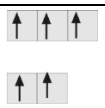
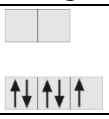
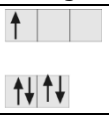
and $\quad K_S = \frac{c(A^-)\cdot c(H^+)}{c(HA_w)} \quad \Rightarrow \quad c(A^-) = \frac{c(HA_w)\cdot K_S}{c(H^+)}$

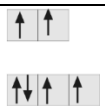
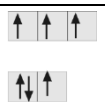
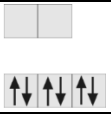
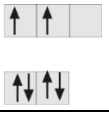
$\Rightarrow \quad D = \frac{c(HA_w)\cdot K_D}{c(HA_w)\cdot[1 + K_S/c(H^+)]}$ or $\quad D = K_D \cdot \frac{c(H^+)}{K_S + c(H^+)}$

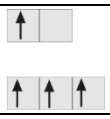
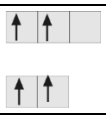
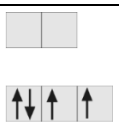
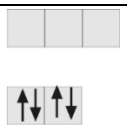
Solution to problem 4-5

a) High- and low-spin complexes are possible between four and seven electrons in the d orbital. Only in these cases different fillings of the molecular orbitals are possible.

b)

***Fe*$^{3+}$**	*Octahedral field*	*Tetrahedral field*
high-spin		
magnetic property	paramagnetic	paramagnetic
low-spin		
magnetic property	paramagnetic	paramagnetic

Co^{3+}	Octahedral field	Tetrahedral field
high-spin		
magnetic property	paramagnetic	paramagnetic
low-spin		
magnetic property	diamagnetic	paramagnetic

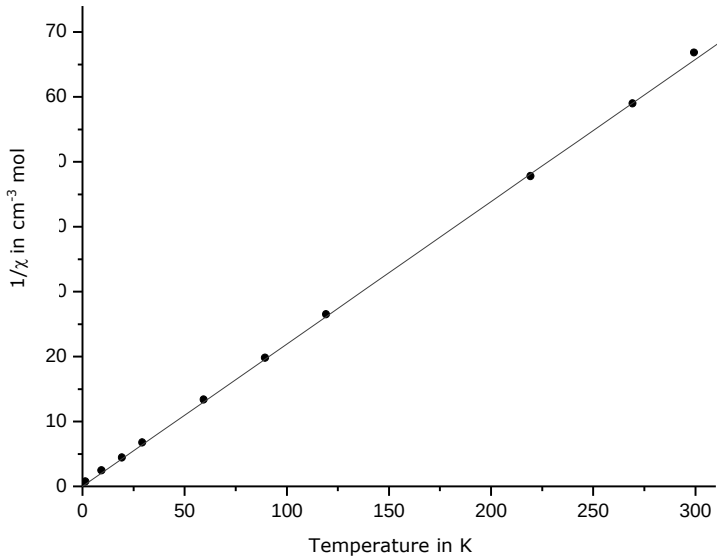
Mn^{3+}	Octahedral field	Tetrahedral field
high-spin		
magnetic property	paramagnetic	paramagnetic
low-spin		
magnetic property	paramagnetic	diamagnetic

c)

Number of unpaired electrons n	1	2	3	4	5
Magnetic moment μ_{theo} (in BM)	1,73	2,83	3,87	4,90	5,92

d) Plot of $\frac{1}{\chi_{para}} = \frac{1}{C} \cdot T$

T in K	2	10	20	30	60	90	120	220	270	300
$1/\chi$ in cm^{-3}·mol	0,55	2,26	4,24	6,58	13,16	19,61	26,32	47,62	58,82	66,67



Slope 1/C = 0.22 cm^{-3}·mol ⇒ C = 4.55 cm^3·K·mol^{-1}

e) $\mu_{exp} = 2.83 \cdot \sqrt{4.55}$ BM μ_{exp} = 6.04 BM

f) It has to be a high-spin complex with five unpaired electrons because μ_{exp} and μ_{theo} are in good agreement.

Remark:
The spin-only formula is not expected to give precise agreement with experimental data.

Solution to problem 4-6

a) α-decay: ${}^{A}_{Z}El_1 \longrightarrow {}^{4}_{2}\alpha + {}^{A-4}_{Z-2}El_2$ β⁻-decay: ${}^{A}_{Z}El_1 \longrightarrow {}^{0}_{-1}\beta + {}^{A}_{Z+1}El_2$

b) m_0 = mass t_x years ago

$99.275 = m_0(^{238}U) \cdot e^{-k_{238} \cdot t_x}$ $\quad$ $0.720 = m_0(^{235}U) \cdot e^{-k_{235} \cdot t_x}$

$m_0(^{238}U) = 99.275 \cdot e^{k_{238} \cdot t_x}$ $\quad$ $m_0(^{235}U) = 0.720 \cdot e^{k_{235} \cdot t_x}$

$\Rightarrow$ ½ · $99.275 \cdot e^{k_{238} \cdot t_x} = 0.720 \cdot e^{k_{235} \cdot t_x}$ with $k = \ln 2 / t_{1/2}$

$\Rightarrow t_x = \ln \frac{99.275}{2 \cdot 0.720} / (\frac{\ln 2}{7.038 \cdot 10^8\ a} - \frac{\ln 2}{4.468 \cdot 10^9\ a})$ $\quad$ $t_x = 5.102 \cdot 10^9$ a

c) The mass numbers only change by α-decay, namely by 4 units.

$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta^-} {}^{234}Pa \xrightarrow{\beta^-} {}^{234}U$

d) The formation rate of ^{234}U from ^{238}U is the same as the decay rate of ^{234}U. The rate law is that of a reaction of first order: $-\frac{dn}{dt} = k \cdot n$.

$\Rightarrow$ $n_{234} \cdot k_{234} = n_{238} \cdot k_{238}$

$n_{234} \cdot \frac{ln2}{t_{1/2}(^{234}U)} = n_{238} \cdot \frac{ln2}{t_{1/2}(^{238}U)}$

$t_{1/2}(^{234}U) = t_{1/2}(^{238}U) \cdot \frac{n_{234}}{n_{238}}$

$t_{1/2}(^{234}U) = 4.468 \cdot 10^9\ a \cdot \frac{0.005}{99.275}$ $\quad$ $t_{1/2}(^{234}U) = 2.25 \cdot 10^5$ a

e) U (0) $\quad U^{3+}$ (+III) $\quad U^{4+}$ (+IV) $\quad UO_2^+$ (+V) $\quad UO_2^{2+}$ (+VI)

f) The given conditions are standard conditions thus the standard potentials can be used to determine the spontaneous reaction. The standard reduction potentials are the potentials in comparison to a standard hydrogen half cell ($2\ H^+ + 2\ e \longrightarrow H_2$ $\quad E^o = 0{,}000$ V).
The half cell with the positive potential represents the cathode where a spontaneous reduction takes place.

$E°_{cell} = E^o(\text{cathode}) - E^o(\text{anode})$, $\quad \Delta G = - n \cdot F \cdot E°$

Thus the following reactions proceed:

1. Two reactions of uranium with the acid have to be taken into account:

$2\ U + 6\ H^+ \longrightarrow 2\ U^{3+} + 3\ H_2$ $\quad E^0_{cell} = +1.798$ V $\quad \Delta G < 0$

$U + 2\ H^+ + 2\ H_2O \longrightarrow UO_2^{2+} + 3\ H_2$ $\quad E^0_{cell} = +1.444$ V $\quad \Delta G < 0$

Irrespective which process is preferred neither U^{3+} nor UO^{2+} are final products.

2. U^{3+} oxidizes spontaneously to form U^{4+}:

$2\ U^{3+} + 2\ H^+ \longrightarrow 2\ U^{4+} + H_2$ $\quad E^0_{cell} = +0.607$ V $\quad \Delta G < 0$

and UO_2^{2+} is reduced spontaneously to form UO_2^+ or U^{4+}:

$2\ UO_2^{2+} + H_2 \longrightarrow 2\ UO_2^+ + 2\ H^+$ $\quad E^0_{cell\ I} = +0.062$ V $\quad \Delta G < 0$ $\quad$ or

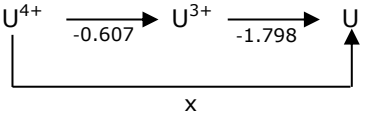
$UO_2^{2+} + 2\ H^+ + H_2 \longrightarrow U^{4+} + 2\ H_2O$ $\quad E^0_{cell} = +0.327$ V $\quad \Delta G < 0$

3. UO_2^+ in turn is reduced to U^{4+}:

$2\ UO_2^+ + 6\ H^+ + H_2 \longrightarrow 2\ U^{4+} + 4\ H_2O$ $\quad E^0_{cell} = +0.620$ V $\quad \Delta G < 0$

U^{4+} is the only species which cannot react spontaneously with H^+ or H_2, thus it will be the predominant specie under these conditions.

$\Delta E°_{cell} = E°(2\ H^+/H_2) - E°(U^{4+}/U) = 0\ V - x\ V$

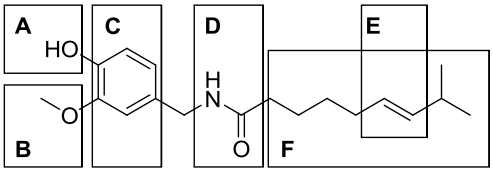


$4x = -0.607 + 3 \cdot (-1.798)$

$x = -1.500$ $\quad \Rightarrow \quad \Delta E°_{cell} = 1.500$ V

Solution to problem 4-7

a) Functional groups



A - Phenolic hydroxyl group	D – Amide group
B – Methoxy group	E – Double bond
C –Polysubstituted benzene	F – Hydrocarbon chain

Remark: The hydrocarbon chain is often neglected as a functional group though it is of great importance for the hydrophobic properties of natural compounds.

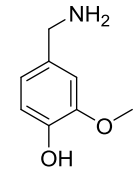
b) (*E)*-Isomer

c) $\frac{16\ \text{SHU}}{1\ \text{ppm}} = \frac{2.2\cdot10^6\ \text{SHU}}{\text{x}}$ $\Rightarrow$ x ≈ $1.38\cdot10^5$ ppm

1 ppm corresponds to 1μg/g = 10^{-6} g / g

The species Carolina Reaper contains $1{,}38\cdot10^5$ µg Capsaicin /g.

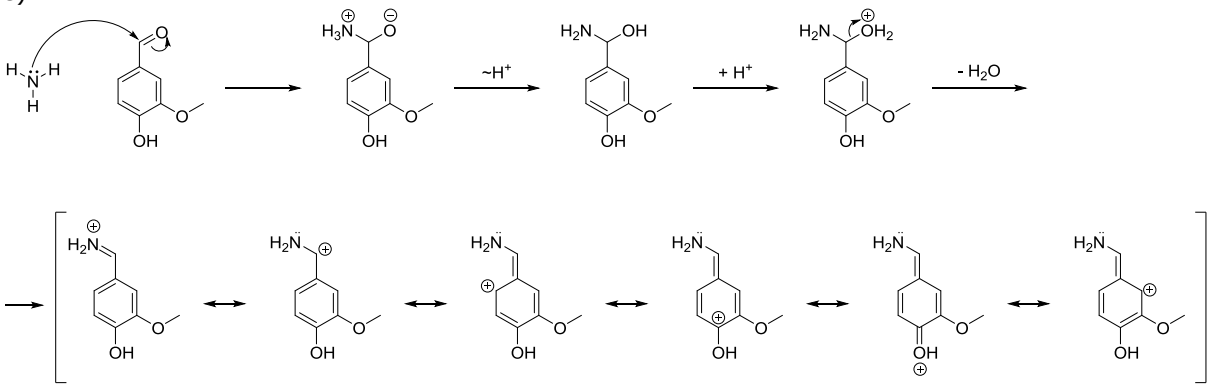
d)



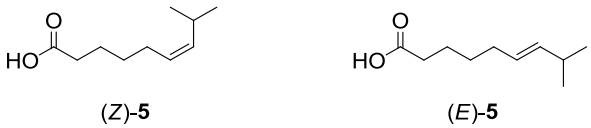
1

Vanillylamine
4-(Aminomethyl)-2-methoxyphenol
(Names not requested)

e)



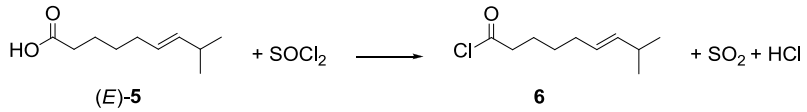
f)



(*Z*)-**5** (*E*)-**5**

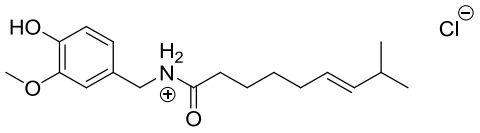
Cis-trans isomers

g)



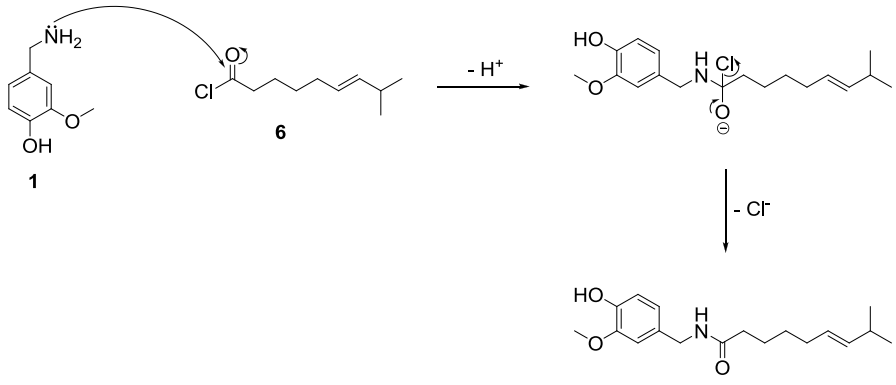
(*E*)-**5** **6**

h)



7

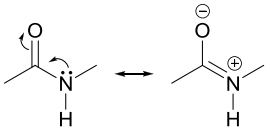
i)



j) Reasons why the reaction of **1** and **5** does not lead directly to capsaicin:

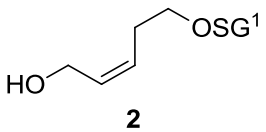
- **5** reacts as an acid and protonates the amino group and in so doing decreases its nucleophilic character.
- The hydroxyl group is a poor leaving group and has to be converted in a better one (e.g. chloride).

k) In the reaction of **1** and **6** an amide bond is formed. The rotation is hindered by the resonance stabilization which leads to a partial double bond:



Solution to problem 4-8

a)



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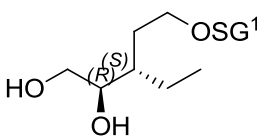
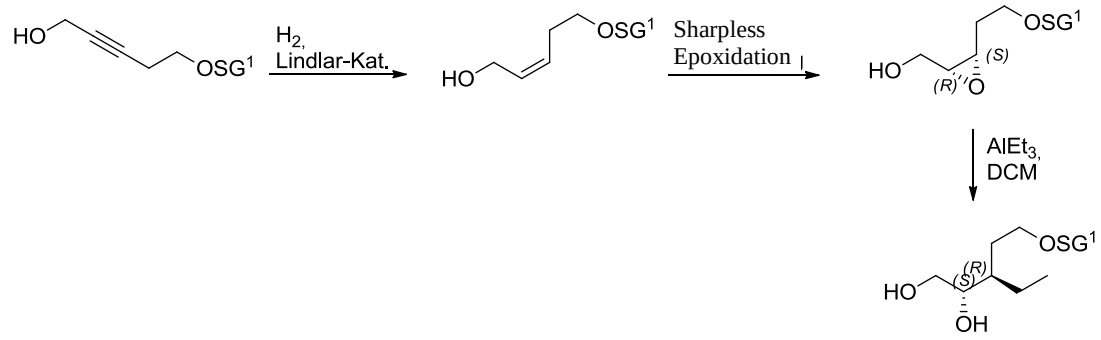
b)



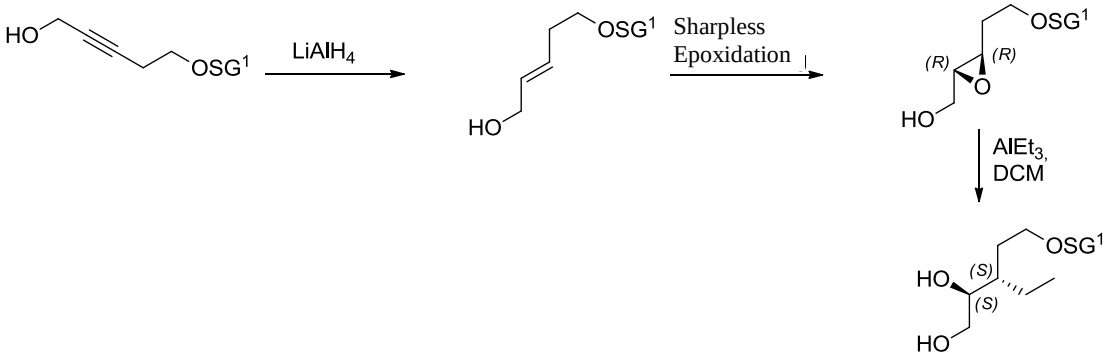
4

c) 2R, 3S

d) Only the Sharpless epoxidation has to be changed:

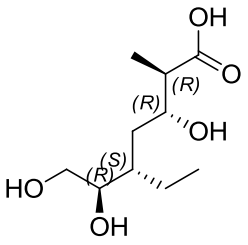


Remark: If the reduction of the alkyne is changed a diastereomer to **4** is synthesized:



The opening at position 3 uses the existing stereogenic centers and has no influence on the desired change.

e)

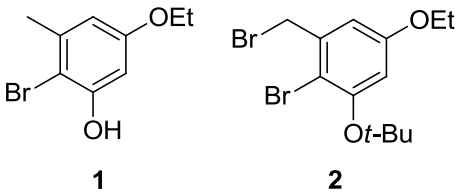


7

f) The aldol reaction introduces the two new stereogenic centers independent of the other stereogenic centers in the molecule. Thus a diastereomer to product **7** is formed.

Solution to problem 4-9:

a)

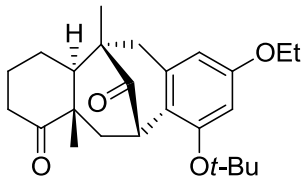


1 **2**

b) The first reaction (with NBS in CH_3Cl at -60 °C) favors the electrophilic substitution at the aromatic ring. Often these electrophilic substitutions are carried out with Br_2 and $FeBr_3$ as catalyst. In this case a catalyst was not necessary.

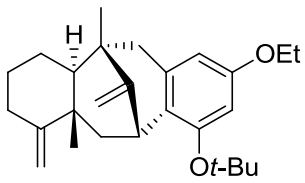
The second reaction (with NBS, the radical initiator AIBN in CCl_4 at 77 °C = boiling temperature of CCl_4) favors the radical substitution at the side chain.

c)



6

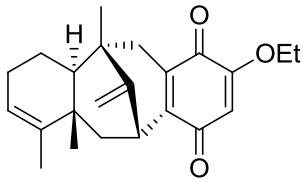
d)



7

e) It is the thermodynamically more stable product (higher substituted double bond) which is favored by the long reaction time und the raised temperature. The rearrangement takes place only at the $H_2C=$ group at the left 6-membered ring. A comparable rearrangement at the $H_2C=$ group at the bridge above the 8-membered ring would lead to an extreme ring tension.

f)



46th International Chemistry Olympiad

July 25, 2014

Hanoi, Vietnam

EXAMINATIONS

Good luck !

Chemistry: The flavor of life

Theoretical Test

Physical Constants, Units, Formulas and Equations

Avogadro's constant	N_A = 6.0221 × 10^{23} mol^{-1}
Universal gas constant	R = 8.3145 $J \cdot K^{-1} \cdot mol^{-1}$
Speed of light	c = 2.9979 × 10^8 $m \cdot s^{-1}$
Planck's constant	h= 6.6261 × 10^{-34} J·s
Standard pressure	p° = 1 bar = 10^5 Pa
Atmospheric pressure	1 atm = 1.01325 × 10^5 Pa = 760 mmHg
Zero of the Celsius scale	273.15 K
Mass of electron	m_e = 9.1094 × 10^{-31} kg

1 nanometer (nm) = 10^{-9} m ; 1 angstrom (Å) = 10^{-10} m

1 electron volt (eV) = 1.6022 × 10^{-19} J = 96485 $J \cdot mol^{-1}$

Energy of a light quantum with wavelength λ	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$
van't Hoff equation in integral form	$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Relationship between internal energy, heat and work	$\Delta U = q + w$
Molar heat capacity at constant volume	$C_{v,m} = \left(\frac{dU}{dT}\right)_v$
Change in internal energy from T_1 to T_2 assuming constant $C_{v,m}$	$U(T_2)=U(T_1)+nC_{v,m}(T_2-T_1)$,
Spin only formula relating number of unpaired electrons to effective magnetic moment	$\mu_{eff} = \sqrt{n(n+2)}$ B.M.

A periodical table was provided

Problem 1 Particles in a box: polyenes

In quantum mechanics, the movement of π electrons along a neutral chain of conjugated carbon atoms may be modeled using the 'particle in a box' method. The energy of the π electrons is given by the following equation:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where n is the quantum number (n = 1, 2, 3, …), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2)\times 1.40$ Å (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ, to the number of double bonds k and constant B is as follows:

$$\lambda\ (\text{nm}) = B \times \frac{(k+2)^2}{(2k+1)} \qquad \text{Equation 1}$$

1. *Using this semi-empirical formula with B = 65.01 nm calculate the value of the wavelength λ (nm) for octatetraene (CH_2 = CH – CH = CH – CH = CH – CH = CH_2).*

2. *Derive Equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants and hence calculate theoretical value of the constant $B_{calc.}$.*

3. *We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, determine the number of conjugated double bonds (k) in this polyene and give its structure. [If you did not solve Part 2, use the semi-empirical Equation 1 with B = 65.01 nm to complete Part 3.]*

4. *For the polyene molecule found in Part 3, calculate the difference in energy between the HOMO and the LUMO, ΔE, ($kJ\cdot mol^{-1}$).*
In case Part 3 was not solved, take k = 5 to solve this problem.

The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x, L_y, and L_z, yielding the following expression for the allowed energy levels:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

The three quantum numbers n_x, n_y, and n_z must be integer values and are independent of each other.

5a. *Give the expressions for the three different lowest energies, assuming that the box is cubic with a length of L.*

5b. *Levels with the same energy are said to be degenerate. Draw a sketch showing all the energy levels, including any degenerate levels that correspond to quantum numbers having values of 1 or 2 for a cubic box.*

Problem 2 Dissociating Gas Cycle

Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

1.00 mole of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

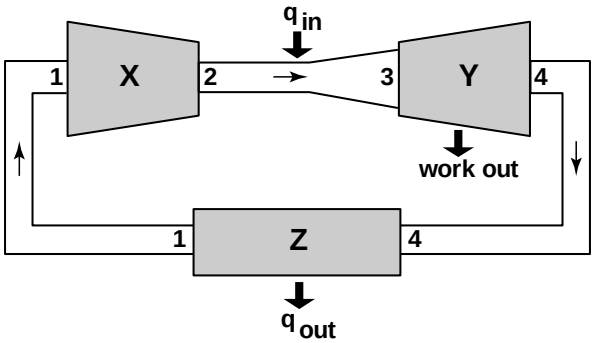
1a. *Calculate ΔG^0 of the reaction at 298K, assuming the gases are ideal.*

1b. *Calculate ΔH^0 and ΔS^0 of the reaction, assuming that they do not change significantly with temperature.*

If you cannot calculate ΔH^0, use ΔH^0 = 30.0 kJ·mol^{-1} for further calculations.

The tendency of N_2O_4 to dissociate reversibly into NO_2 enables its potential use in advanced power generation systems. A simplified scheme for one such system is shown below in Figure (a). Initially, "cool" N_2O_4 is compressed (1→2) in a compressor (X), and heated (2→3). Some N_2O_4 dissociates into NO_2. The hot mixture is expanded (3→4) through a turbine (Y), resulting in a decrease in both temperature and pressure. The mixture is then cooled further (4→1) in a heat sink (Z), to promote the reformation of N_2O_4. This recombination reduces the pressure, thus facilitates the compression of N_2O_4 to start a new cycle. All these processes are assumed to take place reversibly.

(a)



To understand the benefits of using reversible dissociating gases such as N_2O_4, we will focus on step 3 → 4 and consider an ideal gas turbine working with 1 mol of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, no heat is exchanged.

2. *Give the equation to calculate the work done by the system w(air) during the reversible adiabatic expansion for 1 mol of air during stage 3 → 4. Assume that $C_{v,m}$(air)*

(the isochoric molar heat capacity of air) is constant, and the temperature changes from T_3 to T_4.

***3**. Estimate the ratio $w_{(N2O4)}/w_{(air)}$, in which $w_{(N2O4)}$ is the work done by the gas during the reversible adiabatic expansion process 3 → 4 with the cycle working with 1 mol of N_2O_4. T_3 and T_4 are the same as in Part 2. Take the conditions at stage 3 to be T_3 = 440 K and P_3 = 12.156 bar and assume that:*

(i) The gas is at its equilibrium composition at stage 3;

(ii) $C_{v,m}$ for the gas is the same as for air;

(iii) The adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture (N_2O_4 + NO_2) is unchanged until the expansion is completed.

Problem 3 High-valent Silver Compounds

Silver chemistry is dominated by Ag (I) compounds. Compounds of silver in higher oxidation state (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electro-chemical oxidations or in chemical oxidations using powerful oxidizing agents.

In some peroxodisulphate ($S_2O_8^{2-}$) oxidations catalyzed by Ag^+, black solid (A) with the composition AgO can be isolated.

***1a.** Choose the appropriate magnetic behavior of A if it exists as $Ag^{II}O$.*

Single crystal X - ray studies reveal that the lattice of A contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, A should be assigned as $Ag^{I}Ag^{III}O_2$ rather than $Ag^{II}O$.

***1b**. Assign the oxidation number of Ag1 and Ag2.*

***1c.** What is the coordination number of O atoms in the lattice of A?*

***1d.** How many Ag^I and Ag^{III} bond to one O atom in the lattice of A?*

***1e.** Predict the magnetic behavior of A. Check the appropriate box below.*

***1f.** The compound A can also be formed on warming a solution of Ag^+ with peroxodisulphate. Write down the equation for the formation of A.*

Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound A is not a $Ag^{II}O$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

Atom	Standard enthalpy of formation ($kJ \cdot mol^{-1}$)	1st ionization ($kJ \cdot mol^{-1}$)	2nd ionization ($kJ \cdot mol^{-1}$)	3rd ionization ($kJ \cdot mol^{-1}$)	1st electron affinity ($kJ \cdot mol^{-1}$)	2nd electron affinity ($kJ \cdot mol^{-1}$)
Cu(g)	337.4	751.7	1964.1	3560.2		
Ag(g)	284.9	737.2	2080.2	3367.2		
O(g)	249.0				-141.0	844.0

Compounds	ΔH^{o}_{f} ($kJ \cdot mol^{-1}$)
$Ag^{I}Ag^{III}O_{2\,(s)}$	–24.3
$Cu^{II}O_{\,(s)}$	–157.3

The relationship between the lattice dissociation energy (U_{lat}) and the lattice dissociation enthalpy (ΔH_{lat}) for monoatomic ion lattices is $\Delta H_{lat} = U_{lat} + nRT$, where n is the number of ions in the formula unit.

2a. *Calculate U_{lat} at 298 K of $Ag^{I}Ag^{III}O_2$ and $Cu^{II}O$. Assume that they are ionic compounds.*

If you cannot calculate the U_{lat} of $Ag^{I}Ag^{III}O_2$ and $Cu^{II}O$, use following values for further calculations: U_{lat} of $Ag^{I}Ag^{III}O_2$ = 8310.0 $kJ \cdot mol^{-1}$; U_{lat} of $Cu^{II}O$ = 3600.0 $kJ \cdot mol^{-1}$.

The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

$$U_{lat} = \mathrm{C} \times \left(\frac{1}{V_m} \right)^{\frac{1}{3}}$$

Where: V_m (nm^3) is the volume of the formula unit and C ($kJ \cdot nm \cdot mol^{-1}$) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

Oxides	V_m (nm^3)
$Cu^{II}O$	0.02030
$Ag^{III}{}_2O_3$	0.06182
$Ag^{II}Ag^{III}{}_2O_4$	0.08985

2b. *Calculate U_{lat} for the hypothetical compound $Ag^{II}O$. Assume that $Ag^{II}O$ and $Cu^{II}O$ have the same type of lattice, and that $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}{}_2O_4) - V_m(Ag^{III}{}_2O_3)$.*

2c. *By constructing an appropriate thermodynamic cycle or otherwise, estimate the enthalpy change for the solid-state transformation from $Ag^{II}O$ to 1 mole of $Ag^{I}Ag^{III}O_2$.*

(Use U_{lat} $Ag^{II}O$ = 3180.0 kJ·mol^{-1} and U_{lat} $Ag^{I}Ag^{III}O_2$ = 8310.0 kJ·mol^{-1} if you cannot calculate U_{lat} $Ag^{II}O$ in Part 2b).

2d. *Indicate which compound is thermodynamically more stable by checking the appropriate box on the answer sheet.*

When $Ag^{I}Ag^{III}O_2$ is dissolved in aqueous $HClO_4$ solution, a paramagnetic compound (B) is first formed then slowly decomposes to form a diamagnetic compound (C).

3. *Given that B and C are the only compounds containing silver formed in these reactions, write down the equations for the formation of B and C.*

Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex Z is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of $AgNO_3$ and 2 mL of pyridine (d = 0.982 g/mL) is added to a stirred, ice-cold aqueous solution of 5.000 g of $K_2S_2O_8$. The reaction mixture becomes yellow, then an orange solid (Z) is formed which has a mass of 1.719 g when dried.

Elemental analysis of Z shows the mass percentages of C, H, N elements are 38.96%, 3.28%, 9.09%, respectively.

A 0.6164 g Z is added to aqueous NH_3. The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (D). The filtrate is collected and treated with excess $BaCl_2$ solution to obtain 0.4668 g (when dry) of white precipitate (E).

4a. *Determine the empirical formula of Z and calculate the percentage yield in the preparation.*

4b. *Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in Z, the effective magnetic moment (μ_{eff}) of Z was determined and found to be 1.78 BM. Use the spin only formula to determine the number of unpaired electrons in Z and the molecular formula of Z. (Z contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)*

4c. *Write down all chemical equations for the preparation of Z, and its analysis. (Formation of Z, Destruction of Z with NH_3, Formation of D, Formation of E)*

Problem 4. Zeise's Salt

Zeise's salt, $K[PtCl_3C_2H_4]$, was one of the first organometallic compounds to be reported. W. C. Zeise, a professor at the University of Copenhagen, prepared this compound in

1827 by reacting $PtCl_4$ with boiling ethanol and then adding potassium chloride (Method 1). This compound may also be prepared by refluxing a mixture of $K_2[PtCl_6]$ and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from $K_2[PtCl_4]$ and ethylene (Method 3).

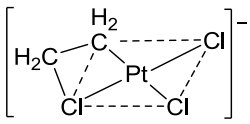
1a. *Write balanced equations for each of the above mentioned preparations of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise's salt consumes 2 moles of ethanol.*

Mass spectrometry of the anion $[PtCl_3C_2H_4]^-$ shows one set of peaks with mass numbers 325-337 and various intensities.

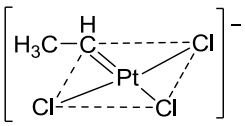
1b*. Calculate the mass number of the anion which consists of the largest natural abundance isotopes (using given below data).*

Isotope	$^{192}_{78}Pt$	$^{194}_{78}Pt$	$^{195}_{78}Pt$	$^{196}_{78}Pt$	$^{198}_{78}Pt$	$^{35}_{17}Cl$	$^{37}_{17}Cl$	$^{12}_{6}C$	$^{13}_{6}C$	$^{1}_{1}H$
Natural abundance in %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

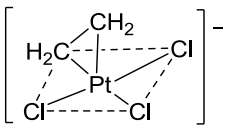
Some early structures proposed for Zeise's salt anion were:



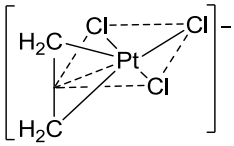
(**Z1**)



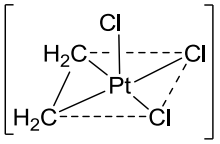
(**Z2**)



(**Z3**)



(**Z4**)



(**Z5**)

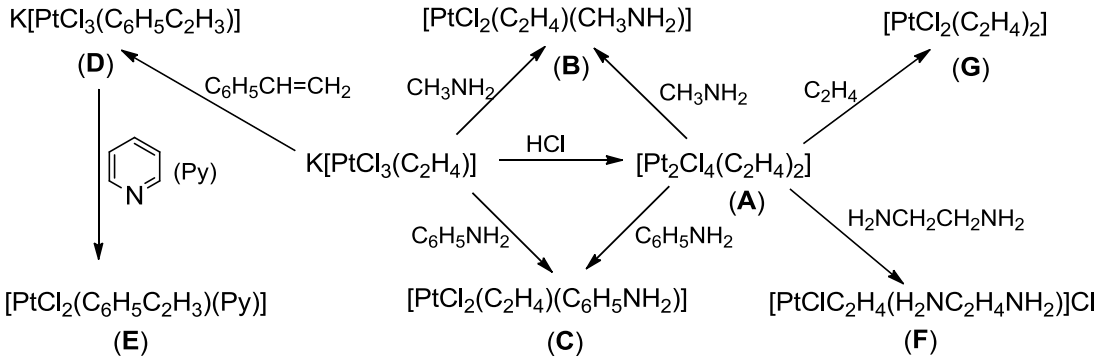
In structure Z1, Z2, and Z5 both carbons are in the same plane as dashed square. (You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.)

2. *NMR spectroscopy allowed the structure for Zeise's salt to be determined as structure Z4. For each structure Z1-Z5, indicate in the table below how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are.*

For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position trans to themselves (the trans effect). The ordering of ligands is:

$CO, CN^-, C_2H_4 > PR_3, H^- > CH_3^-, C_6H_5^-, I^-, SCN^- > Br^- > Cl^- > Py > NH_3 > OH^-, H_2O$

In the series above a left ligand has stronger *trans effect* than a right ligand.
Some reactions of Zeise's salt and the complex $[Pt_2Cl_4(C_2H_4)_2]$ are given below.



3a. *Draw the structure of A, given that the molecule of this complex has a center of symmetry, no Pt-Pt bond, and no bridging alkene.*

3b. *Draw the structures of B, C, D, E, F and G.*

3c. *Suggest the driving force(s) for the formation of D and F by choosing one or more of the following statements (for example, i and ii):*

i) Formation of gas *ii) Formation of liquid*

iii) Trans effect *iv) Chelate effect*

Problem 5. Acid-base Equilibria in Water

A solution (X) contains two weak monoprotic acids (those having *one* acidic proton); HA with the acid dissociation constant of K_{HA} = 1.74 × 10^{-7}, and HB with the acid dissociation constant of K_{HB} = 1.34 × 10^{-7}. The solution X has a pH of 3.75.

Titration of 100 mL solution X requires 100 mL of NaOH solution (0.220 mol/L) for completion.

1. *Calculate the initial (total) concentration (mol·L^{-1}) of each acid in the solution X. Use reasonable approximations where appropriate. [K_W = 1.00 × 10^{-14} at 298 K.]*

2. *Calculate the pH of the solution Y which initially contains 6.00×10^{-2} mol/L of NaA and 4.00×10^{-2} mol/L of NaB.*

Adding large amounts of distilled water to solution X gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero.

3. *Calculate the percentage of dissociation of each acid in this dilute solution.*

A buffer solution is added to solution Y to maintain a pH of 10.0. Assume no change in volume of the resulting solution Z.

4. *Calculate the solubility (in mol·L^{-1}) of a substance $M(OH)_2$ in Z, given that the anions A^- and B^- can form complexes with M^{2+}:*

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $\quad K_{sp} = 3.10 \times 10^{-12}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $\quad K_1 = 2.1 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $\quad K_2 = 5.0 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $\quad K'_1 = 6.2 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $\quad K'_2 = 3.3 \times 10^2$

Problem 6. Chemical Kinetics

The transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to synthesize arylamines. The overall reaction for the nickel-catalyzed amination of aryl chloride in basic conditions is:

$$\mathbf{ArCl} + \mathbf{RNH_2} \xrightarrow[\mathrm{NaO^tBu},\ \mathit{Solvent}]{\mathrm{NiLL'}} \mathbf{Ar\text{-}NHR} + \mathbf{HCl}$$

in which NiLL' is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

To determine the reaction order with respect to each reactant, the dependence of the initial rate of the reaction on the concentrations of each reagent was carried out with all other reagents present in large excess. Some kinetic data at 298 K are shown in the tables below. (Use the given grids on the answer sheet if you like)

[ArCl] (mol·L^{-1})	0.1	0.2	0.4	0.6
Initial rate (mol·$^{L-}$1·s^{-1})	1.88×10^{-5}	4.13×10^{-5}	9.42×10^{-5}	1.50×10^{-4}

[NiLL'] (mol·L^{-1})	6×10^{-3}	9×10^{-3}	1.2×10^{-2}	1.5×10^{-2}
Initial rate (mol·L^{-1}·s^{-1})	4.12×10^{-5}	6.01×10^{-5}	7.80×10^{-5}	1.10×10^{-4}

[L'] (mol·L^{-1})	0.06	0.09	0.12	0.15
Initial rate (mol·L^{-1}·s^{-1})	5.8×10^{-5}	4.3×10^{-5}	3.4×10^{-5}	2.8×10^{-5}

6a. *Determine the order with respect to the reagents assuming they are integers.*

To study the mechanism for this reaction, ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, NiL(Ar)Cl, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL' (step 1) at 50 °C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

$$\mathbf{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{NiL} + \mathbf{L'} \qquad \mathbf{(1)}$$

$$\mathbf{NiL} + \mathbf{ArCl} \xrightarrow{k_2} \mathbf{NiL(Ar)Cl} \qquad \mathbf{(2)}$$

6b. *Using the steady state approximation, derive an expression for the rate equation for the formation of [NiL(Ar)Cl].*

The next steps in the overall reaction involve the amine (RNH_2) and ^{t}BuONa. To determine the order with respect to RNH_2 and ^{t}BuONa, the dependence of the initial rates of

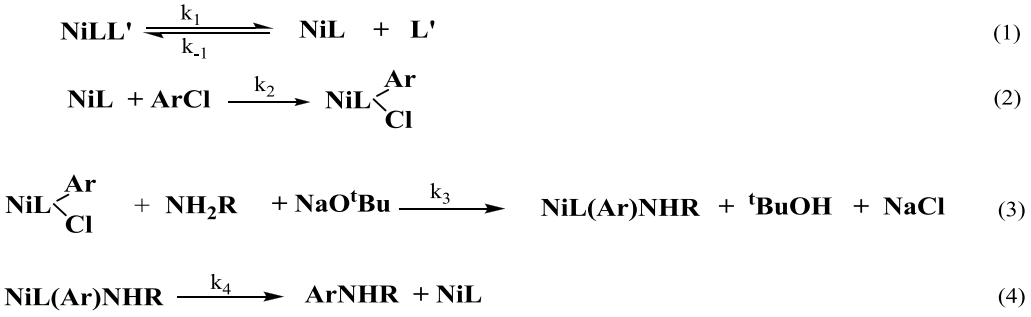
the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

$[NaO^tBu]$ ($mol \cdot L^{-1}$)	0.2	0.6	0.9	1.2
Initial rate ($mol \cdot L^{-1} \cdot s^{-1}$)	4.16×10^{-5}	4.12×10^{-5}	4.24×10^{-5}	4.2×10^{-5}

$[RNH_2]$ ($mol \cdot L^{-1}$)	0.3	0.6	0.9	1.2
Initial rate ($mol \cdot L^{-1} \cdot s^{-1}$)	4.12×10^{-5}	4.26×10^{-5}	4.21×10^{-5}	4.23×10^{-5}

6c. *Determine the order with respect to each of these reagents, assuming each is an integer. (Use the grids if you like.)*

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining.
A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:

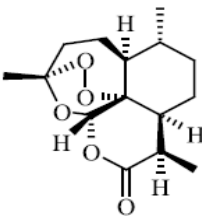


6d. *Use the steady-state approximation and material balance equation to derive the rate law for d[ArNHR]/dt for the above mechanism in terms of the initial concentration of the catalyst $[NiLL']_0$ and concentrations of [ArCl], $[NH_2R]$, $[NaO^tBu]$, and [L'].*

6e. *Give the simplified form of the rate equation in 6d assuming that k_1 is very small. d[ArNHR]/dt = - d[ArCl]/dt = ...*

Problem 7. Synthesis of Artemisinin

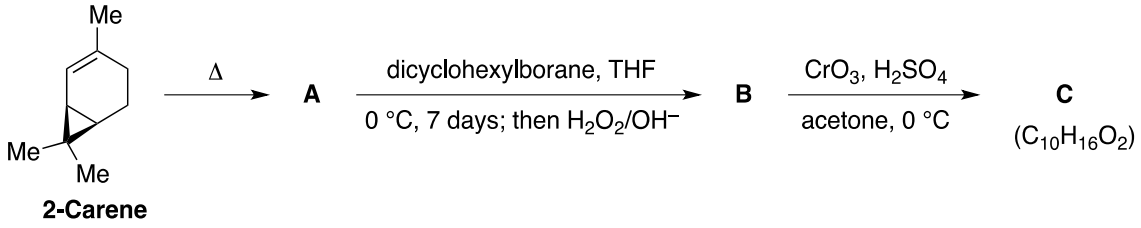
(+)-Artemisinin, isolated from *Artemisia annua* L. (Qinghao, *Compositae*) is a potent antimalarial effective against resistant strains of *Plasmodium*. A simple route for the synthesis of Artemisinin is outlined below.



(+)-Artemisinin

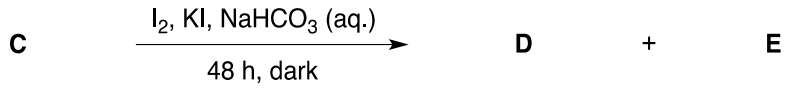
First, pyrolysis of (+)-2-Carene broke the cyclopropane ring forming, among other products, (1*R*)-(+)-*trans*-isolimonene **A** ($C_{10}H_{16}$), which then was subjected to regioselective hydroboration using dicyclohexylborane to give the required alcohol **B** in 82% yield as a

mixture of diastereomers. In the next step, **B** was converted to the corresponding γ,δ-unsaturated acid **C** in 80% yield by Jones' oxidation.



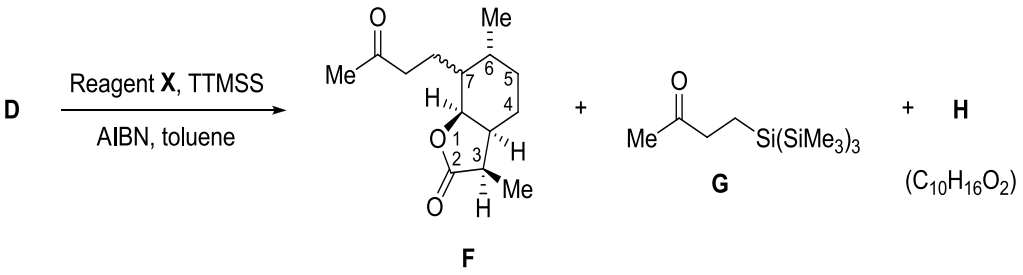
7a. *Draw the structures (with stereochemistry) of the compounds A-C.*

The acid C was subjected to iodolactonization using KI, I_2 in aqueous. $NaHCO_3$ solution to afford diastereomeric iodolactones D and E (which differ in stereochemistry only at C_3) in 70% yield.



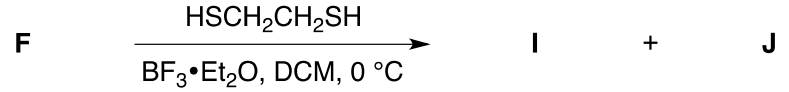
7b. *Draw the structures (with stereochemistry) of the compounds D and E.*

The iodolactone D was subjected to an intermolecular radical reaction with ketone X using tris(trimethylsilyl)silane (TTMSS) and AIBN (azobisisobutyronitrile) in a catalytic amount, refluxing in toluene to yield the corresponding alkylated lactone F in 72% yield as a mixture of diastereomers which differ only in stereochemistry at C_7 along with compound G (~10%) and the reduced product H, $C_{10}H_{16}O_2$ (<5%).



7c. *Draw the structures (with stereochemistry) of compound H and the reagent X.*

The keto group of **F** reacted with ethanedithiol and BF_3•Et_2O in dichloromethane (DCM) at 0 °C to afford two diastereomers: thioketal lactones **I** and **J** in nearly quantitative yield (98%). The thioketalization facilitated the separation of the major isomer **J** in which the thioketal group is on the opposite face of the ring to the adjacent methyl group.



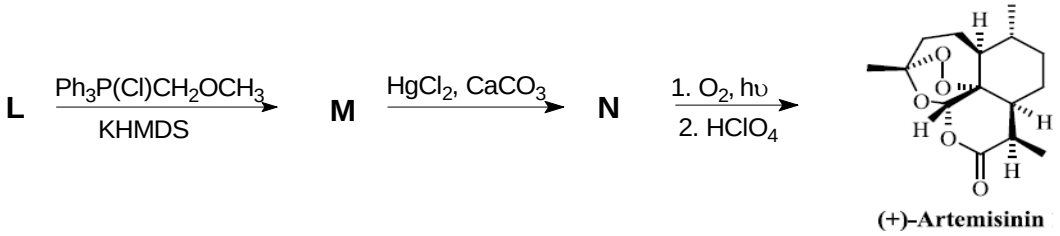
7d. *Draw the structures (with stereochemistry) of the compounds I and J.*

The isomer J was further subjected to alkaline hydrolysis followed by esterification with diazomethane providing hydroxy methyl ester K in 50% yield. The hydroxy methyl ester K was transformed into the keto ester L using PCC (Pyridium Chloro Chromate) as the oxidizing agent in dichloromethane (DCM).

A two-dimensional NMR study of the compound L revealed that the two protons adjacent to the newly-formed carbonyl group are *cis* to each other and confirmed the structure of L.

7e. *Draw the structures (with stereochemistry) of the compounds K and L.*

The ketone L was subjected to a Wittig reaction with methoxymethyl triphenylphosphonium chloride and KHMDS (Potassium HexaMethylDiSilazid - a strong, non-nucleophilic base) to furnish the required methyl vinyl ether M in 45% yield. Deprotection of thioketal using $HgCl_2$, $CaCO_3$ resulted in the key intermediate N (80%). Finally, the compound N was transformed into the target molecule Artemisinin by photo-oxidation followed by acid hydrolysis with 70% $HClO_4$.

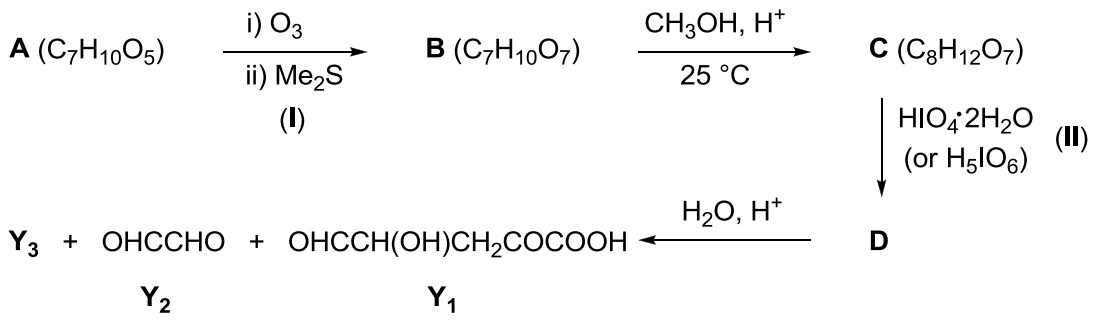


7f. *Draw the structures (with stereochemistry) of the compounds M and N.*

Problem 8. Star Anise

Illicium verum, commonly called *Star anise*, is a small native evergreen tree grown in northeast Vietnam. *Star anise* fruit is used in traditional Vietnamese medicine. It is also a major ingredient in the making the flavor of '*phở*', a Vietnamese favorite soup.

Acid A is isolated from the *star anise* fruit. The constitutional formula of A has been deduced from the following sequence of reactions:

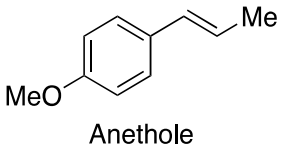


(**I**): this overall process results in alkene cleavage at the C=C bond, with each carbon of this becoming doubly bonded to an oxygen atom.

(**II**): this oxidative cleavage process of 1,2-diols breaks C(OH)–C(OH) bond and produces corresponding carbonyl compounds.

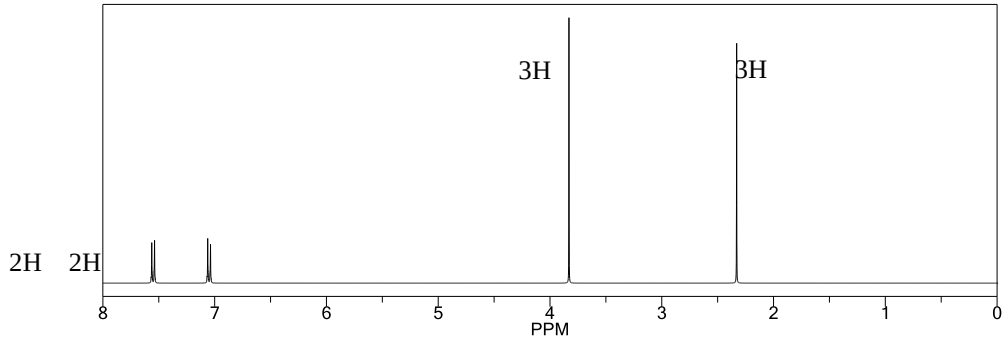
8a. *Draw the structures for the compounds Y_1 and Y_2 and hence deduce the structure of Y_3 and A, B, C, D, given that in A there is only one ethylenic hydrogen atom.*

Anethole, a main component of star anise oil, is an inexpensive chemical precursor for the production of many pharmaceutical drugs.



Anethole

Treating anethole with sodium nitrite in acetic acid gives a crystalline solid **E** ($C_{10}H_{10}N_2O_3$). The IR spectrum of **E** shows there is no non-aromatic C=C double bond. The ^{1}H NMR spectrum of **E** is given below.



8b. *What differences in the structure between E and anethole can be obtained from the ^{1}H NMR data? Pick one ore more of the statements below*

i) E contains a *cis*-C=C ethylenic bond while that of anethole is *trans*.

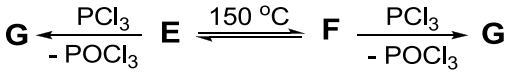
ii) E cannot contain a non-aromatic C=C bond.

iii) E is the adduct of anethole and N_2O_2.

iv) E is the adduct of anethole and N_2O_3.

v) E does not contain two *trans* ethylenic protons as anethole.

On heating at 150 °C for several hours, **E** is partially isomerized into **F**. Under the same conditions, **F** gives the identical equilibrium mixture to that obtained from **E**. On heating with phosphorus trichloride, both **E** and **F** lose one oxygen atom giving compound **G**. Compounds **E** and **F** have the same functional groups.

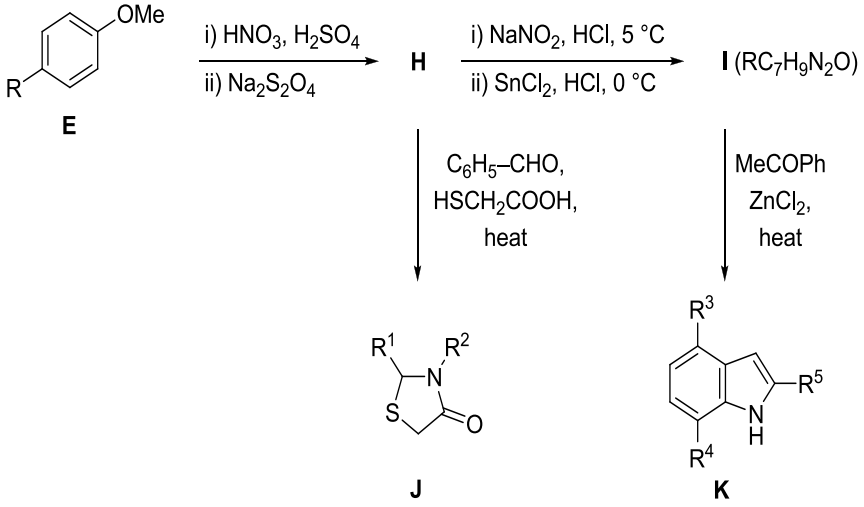


The chemical shifts of methyl protons in **E**, **F** and **G** are given below.

	E	**F**	**G**
CH_3-O	3.8 ppm	3.8 ppm	3.8 ppm
CH_3-C	2.3 ppm	2.6 ppm	2.6 ppm

8c. *Suggest structures for **E**, **F** and **G**, assuming that they do NOT contain three-membered rings.*

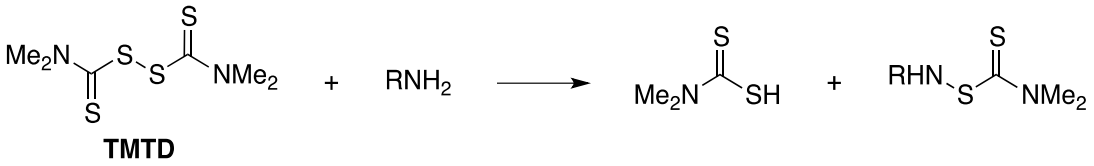
A simplified structure for compound **E** is shown below; the R group does not change throughout the rest of this question. Compound **E** is nitrated and subsequently reduced with sodium dithionite to **H**. Treatment of **H** with sodium nitrite and hydrochloric acid at 0–5 °C and subsequently reduced with stannous chloride to provide **I** ($R–C_7H_9N_2O$). One-pot reaction (three component reaction) of **H**, benzaldehyde and thioglycolic acid ($HSCH_2CO_2H$) leads to the formation of **J**. Reaction of **I** and methyl phenyl ketone in the presence of $ZnCl_2$ affords **K**.



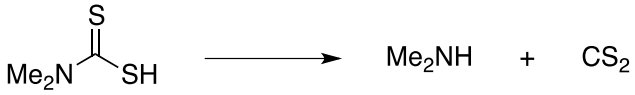
8d. *Give the structures for H, I, J and K.*

Problem 9. Heterocycle Preparation

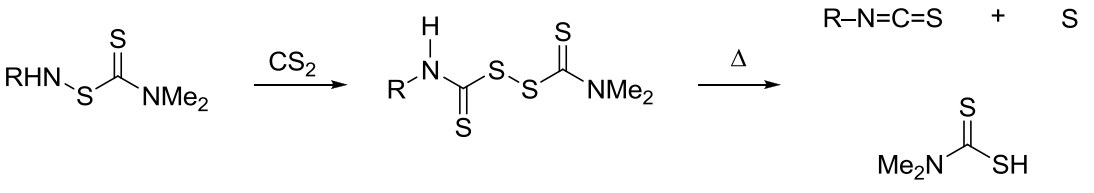
Tetramethylthiurame disulfide (TMTD) is emerging as a useful reagent to prepare many sulfur-nitrogen functional groups and heterocycles in organic chemistry. The reactions of TMTD with primary amines, as well some corresponding post-transformations of the resulting product(s) are presented in the following schemes:



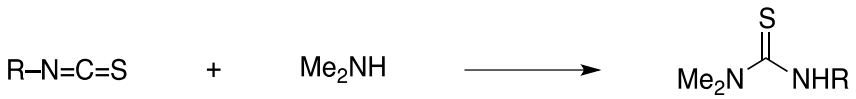
(1)



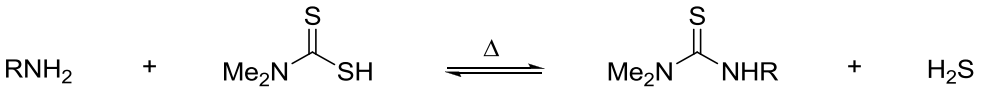
(2)



(3)



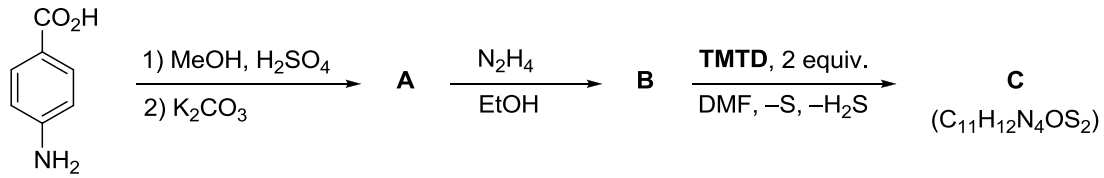
(4)



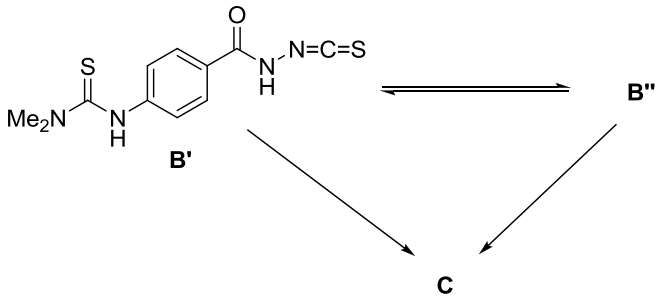
(5)

Similar transformations of benzohydrazides (containing nucleophilic NH_2 group) and TMTD have been observed.

In the synthetic scheme below, the thiocarbamoylation reaction of an aryl hydrazine with TMTD produces compound **C** containing a heterocyclic moiety from *p*-aminobenzoic acid.



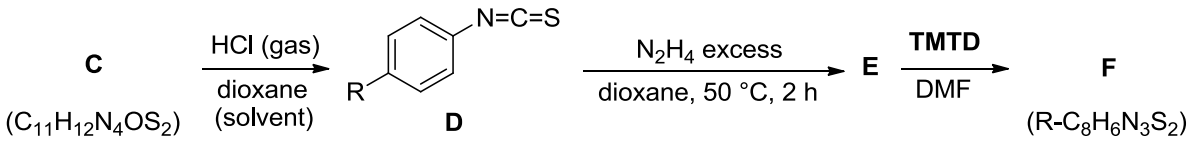
During the formation of **C** from **B**, an intermediate **B'** was observed. This intermediate tautomerizes to **B''**. **C** can be formed from **B'** or **B''**.



9a. *Give the structures of A, B, and C.*

9b. *Suggest a structure for the tautomer B'' and give a curly-arrow mechanism for the formation of C.*

Compound C was then converted to F by the following pathway:



[The group R remains exactly the same throughout the rest of the question.]

9c. *Draw the structures of E, and F. (You do not need to draw the structure for the R group from this point.)*

E was only obtained when D was slowly added to the solution of excess N_2H_4 in dioxane. If N_2H_4 was added to the solution of D in dioxane instead, a major side product D' ($R_2C_{14}H_{12}N_4S_2$) was formed.

9d. *Give the structure of D'.*

Slightly heating D with ethanolamine ($HOCH_2CH_2NH_2$) in dioxane for 2 hours yielded G ($R–C_9H_{11}N_2OS$).

9e. *Draw the structural formula of G.*

9f. *Heating G in the presence of p-toluenesulfonic acid as the catalyst could form a number of different five-membered heterocyclic products.*

i) Draw 2 structures that have different molecular formulae.

ii) Draw 2 structures that are constitutional isomers.

iii) Draw 2 structures that are stereoisomers.

Practical Test

23. July 2014

List of chemicals

The concentration indicated on the label is approximate. The exact values are indicated in the table.

Chemical/Reagent	Quantity	Placed in	Labeled	Safety
Practical Problem 1				
0.100 M KI solution	120 mL	Glass bottle	0.1 M KI	H320
Solution #A1 contains KI, $Na_2S_2O_3$, and starch indicator in distilled water	40 mL	Glass bottle	Solution #**A1**	H314, H302, H315, H319
Solution #B1 contains $Fe(NO_3)_3$, HNO_3 in distilled water	40 mL	Glass bottle	Solution #**B1**	H314, H315, H319, H335
Solution #A2-1 contains 5.883×10^{-4} M $Na_2S_2O_3$, KNO_3, and starch indicator in distilled water	360 mL	Glass bottle	Solution #**A2-1**	H314 H272
Solution #B2 contains 0.1020 M $Fe(NO_3)_3$ and HNO_3 in distilled water.	100 mL	Glass bottle	Solution #**B2**	H314, H272, H315, H319
Distilled water	1 L	Glass bottle	H_2O (Practical Problem 1)	
Practical Problem 2				
Artemisinin	1.000 g	Small bottle	Artemisinin	
Sodium borohydride, $NaBH_4$	0.53 g	Small bottle	$NaBH_4$	H301-H311
CH_3OH	20 mL	Glass bottle	Methanol	H225, H301
n-Hexane	30 mL	Bottle	*n*-Hexane	H225
cerium staining reagent for TLC	3-5 mL	Bottle	Ceri reagent	
CH_3COOH	1 mL	1.5 mL vial	Acetic Acid	H226, H314
Ethyl acetate	5 mL	Glass bottle	Ethyl acetate	
Bag of NaCl for salt bath	0.5 kg	Ice bath	NaCl bag	
$CaCl_2$ in drying tube	5-10 g	Tube	$CaCl_2$	H319
Practical Problem 3				
~ 30 wt.% H_2SO_4, solution in water	40 mL	Bottle	~30 wt.% H_2SO_4	H314
1.00×10^{-2}M $KMnO_4$, aqueous solution	50 mL	Bottle	~0.01 M $KMnO_4$,	H272, H302,
2.00×10^{-3}M EDTA, aqueous solution	40 mL	Bottle	2.00×10^{-3} M EDTA	H319
pH = 9-10 Buffer aqueous Solution, NH_4Cl + NH_3	40 mL	Bottle	*pH* = 9-10 Buffer Solution	H302 , H319
~20 wt.% NaOH, aqueous solution	20 mL	Plastic bottle	~20 wt.% NaOH,	H314
~3 M H_3PO_4, solution in water	15 mL	Bottle	~3 M H_3PO_4	H314
Indicator: ETOO, solid in KCl	*ca.* 0.5 g	Plastic bottle	ETOO	H301

List of Glassware and Equipment

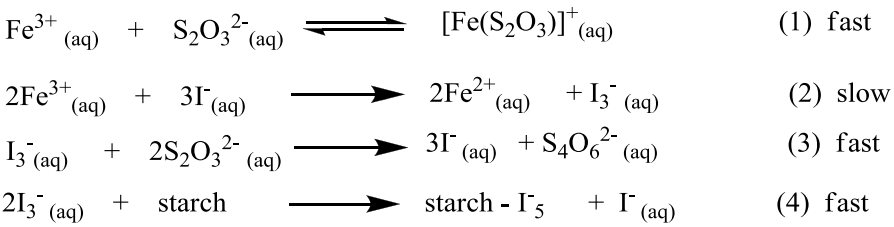
Problem	Item on every working place	Quantity
Practical Problems 1-3	Hotplate stirrer	1
	Magnetic stirring bar (seek in Kit #1)	1
	Plastic wash bottle filled with distilled water (refill if necessary from the 1 L glass bottle of distilled water provided)	1
	1-L glass beaker for inorganic waste liquid	1
	250-mL conical flask for organic waste liquid	1
	Pipette rack with: 1-mL graduated pipette 5-mL graduated pipette (One for Problem 1; another labeled 'MeOH' for Problem 2) 10-mL graduated pipette 10-mL volumetric pipette 25-mL graduated pipette Pasteur pipette and bulb Glass spatula spoon Cleaning brush Large glass stirring rod Glass funnel	1 1 2 1 1 1 2 2 1 1 1
	Bag of paper towels	1
	Goggles	1
	Digital thermometer	1
	Three-way pipette bulb with a little rubber adapter for bigger pipettes	1
	Ceramic Büchner funnel with fitted rubber bung	1
	Büchner flask	1
	Pair of rubber gloves	1
	One cotton glove	1
KIT # 1	**Practical Problem 1 (KIT # 1)**	
	Digital stop watch	1
	Insulating plate for the hotplate stirrer labeled **I.P.**	1
	100-mL glass beaker	6
KIT # 2	**Practical Problem 2 (KIT # 2)**	
	5-mL graduated measuring cylinder	1
	50-mL graduated measuring cylinder	2
	100-mL two-neck round bottom flask with plastic stopper (in ice bath)	1
	100-mL conical (Erlenmeyer) flask	1
	Hair dryer	1
	Petri dish with cover containing 1 TLC plate, 2 capillaries in paper holder	1
	Plastic pot for ice bath	1
	Stand & clamp	1
	TLC developing chamber with glass lid	1
	Tweezers	2
	Metal spatula	1
	Very small test tubes for TLC in container	2
	Zipper store bag (containing cotton wool, round filter paper, watch glass for Problem 2 labeled with WHITE student code)	1
	Empty Petri dish with cover	1

KIT # 3	**Practical Problem 3 (KIT # 3)**	
	50-mL glass beaker (for transferring EDTA and $KMnO_4$ solutions to burettes)	2
	25-mL burette with BLUE graduation marks	1
	25-mL burette with BROWN graduation marks	1
	250 mL glass beaker	2
	250 mL conical flask (Erlenmeyer flask)	2
	100 mL volumetric flask with stopper	2
	10 mL glass graduated measuring cylinder	1
	100 mL glass graduated measuring cylinder	1
	Burette stand & clamp	1
	Reel of pH paper	1
	Zipper store bag (containing a large round filter paper for the glass funnel)	1
	Items on the tables for the common use:	
	Electronic balance with 0.1-mg resolution (6-8 students/each)	

Attention: You MUST do the experiments in the order Problem 1, 2 and then 3 (this is in order to control the temperature of the magnetic stirrer properly).

<u>Practical Problem 1</u>. The oxidation of iodide by iron(III) ions – a kinetic study based on the thiosulfate clock reaction

Clock reactions are commonly used as demonstrations by chemical educators owing to their visual appeal. Oxidation of iodide by iron(III) ions in a weakly acidic medium is a reaction that can be transformed into a clock reaction. In the presence of thiosulfate and starch, chemical changes in this clock reaction can be presented by the following equations:



Reaction (1) is a fast reversible equilibrium which occurs in the reaction mixture giving a reservoir of iron(III) and thiosulfate ions. After being produced in reaction (2), iodine in the form of triiodide ion (I_3^-), is immediately consumed by thiosulfate in reaction (3). Therefore, no iodine accumulates in the presence of thiosulfate. When thiosulfate is totally depleted, the triiodide ion accumulates and it may be detected by use of starch indicator according to reaction (4).

The kinetics of reaction (2) is easily investigated using the initial rates method. One has to measure the time elapsed between mixing the two solutions and the sudden color change.

For the oxidation of iodide by iron(III) ions (reaction 2), the reaction rate can be defined as:

$$v = -\frac{d\left[\mathrm{Fe^{3+}}\right]}{dt} \qquad (5)$$

The initial reaction rate can then be approximated by:

$$v_0 \approx -\frac{\Delta\left[\mathrm{Fe^{3+}}\right]}{\Delta t} \qquad (6)$$

with $\Delta[Fe^{3+}]$ being the change in the concentration of iron(III) ions in the initial period of the reaction. If Δt is the time measured, then $\Delta[Fe^{3+}]$ is the change in iron(III) ion concentration from the moment of mixing to the moment of complete thiosulfate consumption (assume that the reaction rate does not depend on thiosulfate concentration). Therefore, from the reactions' stoichiometry it follows:

$$-\Delta\left[\mathrm{Fe^{3+}}\right] = \left[\mathrm{S_2O_3^{2-}}\right]_0 \qquad (7)$$

and consequently:

$$v_0 \approx \frac{\left[\mathrm{S_2O_3^{2-}}\right]_0}{\Delta t} \qquad (8)$$

The initial thiosulfate concentration is constant and significantly lower than that of iron(III) and iodide ions. The above expression enables us to determine the initial reaction rate by measuring the time required for the sudden color change to take place, Δt.
The rate of reaction is first order with respect to $[Fe^{3+}]$, and you will determine the order with respect to $[I^-]$. This means the initial reaction rate of reaction can be expressed as:

$$v_0 = k[Fe^{3+}]_0[I^-]_0^y \qquad (9)$$

where k is the rate constant and y is the order with respect to $[I^-]$.
We assume that the reaction rate does not depend on the thiosulfate concentration, and that the reaction between Fe^{3+} and $S_2O_3^{2-}$ is negligible. You have to observe carefully the color changes during the clock reaction and to determine the reaction order with respect to $[I^-]$, and the rate constant of clock reaction.

Experimental Set-up

Instructions for using the digital timer (stopwatch)

1. Press the [MODE] button until the 00:00:00 icon is displayed.
2. To begin timing, press the [START/STOP] button.
3. To stop timing, press the [START/STOP] button again.
4. To clear the display, press the [SPLIT/RESET] button.

PRECAUTIONS

- To minimize fluctuations in temperature only use the distilled water on your bench (in the wash bottle and in the glass 1 L bottle).
- The heating function of the heating magnetic stirrer must be TURNED OFF (as shown in Figure 1 below) and be sure that the stirrer plate is not hot before starting your experiment. Put the insulating plate (labeled I.P.) on top of the stirrer plate for added insulation.
- Start the stopwatch as soon as the solutions #A and #B are mixed. Stop the stopwatch as soon as the solution suddenly turns dark blue.
- Magnetic stirrer bar (take it with the provided tweezers) and beakers should be washed and rinsed with distilled water and wiped dry with paper towel to reuse.

General Procedure

Solution # A (containing $Na_2S_2O_3$, KI, KNO_3 and starch) is first placed in the beaker and is stirred using the magnetic bar. The rate of stirring is set at level 8 as indicated in Figure 1. Solution #B (containing $Fe(NO_3)_3$ and HNO_3) is quickly added into solution #A and *the stopwatch is simultaneously started. The time is recorded at the moment the solution suddenly turns dark blue*. The temperature of the solution is recorded using the digital thermometer.

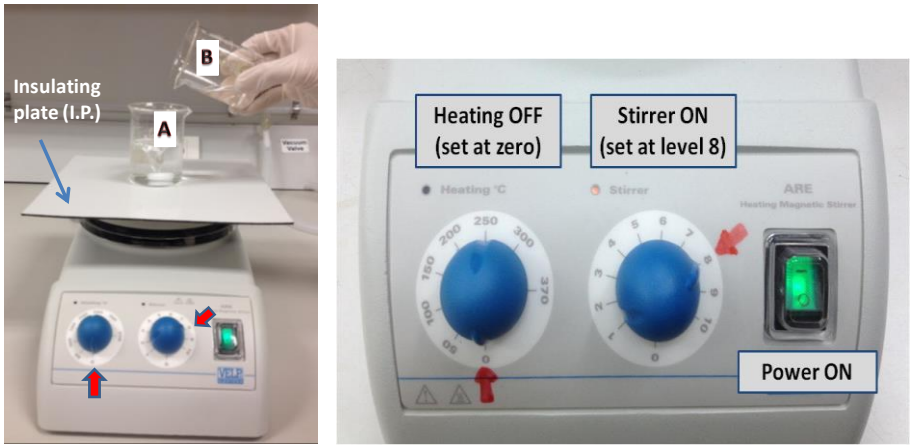


Figure 1. The apparatus employed for kinetic study of the clock reaction.

1. *Practice run to observe the color changes*

- There is no need to accurately measure the volumes used in this part – just use the marks on the beaker as a guide.
- Pour *ca.* 20 mL of solution # A1 (*containing KI, $Na_2S_2O_3$, and starch in water*) to a 100-mL graduated beaker containing a magnetic stirrer bar. Place the beaker on top of the insulating plate on the magnetic stirrer.
- Pour *ca.* 20 mL of solution # B1 (*containing $Fe(NO_3)_3$ and HNO_3 in water*) in another 100 mL graduated beaker.
- Quickly pour the solution # B1 into solution # A1 and start stopwatch simultaneously. Stop stopwatch when the color of the mixture changes. There is no need to record this time. Answer the following questions.

Task 1.1: *Write down the molecular formula of the limiting reactant for the given clock reaction.*

Task 1.2: *What are the ions or compounds responsible for the colors observed in this experiment? Tick the appropriate box.*

Color	Compound
Purple	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-
Dark blue	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-

2. *Determination of the order with respect to [I^-] (y), and the rate constant (k)*

In this section, Δ*t* is determined for different initial concentrations of KI according to the table below. The experiment is repeated as necessary for each concentration of KI.

Hint: Use 25 mL graduated pipette for solution #A2-1, 10 mL graduated pipette for KI, 5 mL graduated pipette for solution #B2, and one of the burettes for water (you will need to refill the burette from the wash bottle for each measurement).

- Prepare 55 mL of solution # A2 in a 100 mL beaker containing a magnetic stirrer bar and place it on top of the insulating plate on the stirrer. Solution #A2 contains solution #A2-1, KI, and distilled water (see the table below for the volume of each component).
- Add 5 mL of solution # B2 in another 100 mL beaker.

Quickly pour prepared solution #B2 into solution #A2. Determine the time (Δ*t*) necessary for the color change by a stopwatch. The temperature of the solution is recorded.

Task 1.3: *Record the time (Δt) for each run in the table below. (You DO NOT need to fill all three columns for the runs.) For each concentration of KI, record your accepted reaction time ($\Delta t_{accepted}$) and temperature. You will be only graded on your values of $\Delta t_{accepted}$ and $T_{accepted}$.*

No	55 mL of solution #A2									$\Delta t_{accepted}$ (s)	$T_{accepted}$ (ºC)
	#A2-1 (mL)	H_2O (mL)	KI (mL)	Run 1		Run 2		Run 3			
				Δ*t* (s)	*T* (ºC)	Δ*t* (s)	*T* (ºC)	Δ*t* (s)	*T* (ºC)		
1	20.4	31.6	3.0								
2	20.4	30.1	4.5								
3	20.4	28.6	6.0								
4	20.4	27.4	7.2								
5	20.4	25.6	9.0								

When you are satisfied you have all the necessary data for Problem 1, before continuing further with the analysis, it is strongly recommended that you start the practical procedure for Problem 2 since there is a reaction time of one hour in that Problem.

Task 1.4: *Fill in the table below and plot the results in the graph.*

Hint: *Make sure your data is graphed as large as possible in the provided space.*

No.	1	2	3	4	5
$\ln([I^-]_0/M)$	- 5.30	- 4.89	- 4.61	- 4.42	- 4.20
$\Delta t_{accepted}$ (s)					
$\ln(\Delta t_{accepted\ /\ s})$					

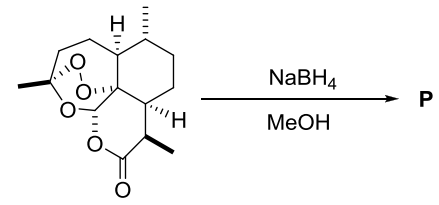
***Task 1.5*:** *Draw the best fit line on your graph and use this to determine the order with respect to [I^-] (y).*

Task 1.6: *Complete the table below and calculate k for each of the concentrations of iodide. Report your accepted value for the rate constant, giving the appropriate unit. Remember that the order with respect to [Fe^{3+}] is equal to one.*

No	$\Delta t_{accepted}$ (s)	$[Fe^{3+}]_0$ ($\times 10^{-3}$ M)	$[I^-]_0$ ($\times 10^{-3}$ M)	$[S_2O_3^{2-}]_0$ ($\times 10^{-3}$ M)	***k***
1			5.0		
2			7.5		
3			10.0		
4			12.0		
5			15.0		
$k_{accepted}$ = …….					

Practical Problem 2. Synthesis of a derivative of Artemisinin

Artemisinin (also known as Quinghaosu) is an antimalarial drug isolated from the yellow flower herb *Artemisia annua* L., in Vietnam. This drug is highly efficacious against the chloroquine-resistant *Plasmodium falciparum*. However, artemisinin has a poor solubility in both oil and water so that one needs to prepare its new derivatives to improve the applicability of this drug. The reduction of artemisinin is an attractive method to synthesize new derivatives of artemisinin as shown in Scheme 1.



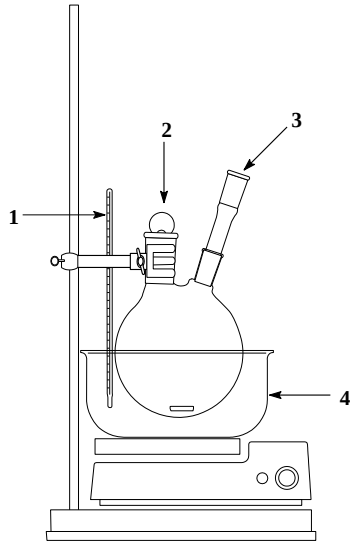
artemisinin
Molecular Weight: 282.3

Scheme 1

In this practical exam you are going to reduce artemisinin to product **P** and check its purity using Thin-Layer Chromatography (TLC).

Experimental Set-up

- The experimental set-up is shown in Figure 2.1.
- By moving the finger clamp, you can adjust the position of the two-neck round-bottom flask.



1: Digital thermometer; 2: Plastic Stopper; 3: $CaCl_2$ drying tube; 4: Ice Bath

Figure 2.1. Reaction system for Problem 2

Procedure

Step 1. Synthesis of a Derivative of Artemisinin

1. Prepare an ice bath with a temperature between –20 and –15 ^{o}C by mixing ice and sodium chloride in the plastic pot (approximate ratio of NaCl : crushed ice = 1 scoop : 3 scoops). Use the digital thermometer to monitor the temperature. Place the bath on the magnetic stirrer. Put a layer of three tissues between the bath and the stirrer.
2. Connect the $CaCl_2$ drying tube to the small neck of the round-bottom flask and close the other neck with the plastic stopper.
3. Place a magnetic stirring bar into the dry round-bottom flask and set up the reaction system onto the clamp-stand so that the system is immersed in the ice bath. Monitor the temperature using the digital thermometer.
4. *Setting aside a tiny amount (ca. 2 mg) of artemisinin for TLC analysis*, open the stopper and add the 1 gram of artemisinin through the bigger neck.
5. Use the glass funnel to add 15 mL of methanol (measured using the 50-mL graduated cylinder). Close the stopper and turn on the magnetic stirrer. (*Set the magnetic stirrer to level 4*). Start the stopwatch to keep track of the time.
6. After *ca.* 5 min stirring, open the stopper and add carefully 0.53 g of $NaBH_4$ in small portions over 15 min using a spatula. Close the stopper in between addition. *(Caution: Adding $NaBH_4$ rapidly causes side-reactions and overflowing).* Keep stirring for 50 min. Maintain the temperature of the ice bath below –5 ^{o}C; remove some of the liquid and add more NaCl-crushed ice mixture if necessary. Cool the vial containing the 1 mL of acetic acid in the ice bath.

During this waiting time, you are advised to finish calculations from Problem 1, answer the questions below, and prepare further experimental steps.

7. *Prepare 50 mL of ice-cold distilled water (cooled in the ice bath) in the 100 mL-* conical flask. Measure *ca.* 20-22 mL *n*-hexane in the 50 mL measuring cylinder and cool it in the ice bath. After the reaction is complete, keep the reaction flask in the ice bath below 0 ^{o}C. Remove the $CaCl_2$ tube, open the stopper, and add gradually *ca.* 0.5 mL of the cold acetic acid from the vial into the reaction flask until the pH is between 6 and 7. (Use the glass rod to spot the reaction mixture on to the pH paper.) With stirring, slowly add the 50 mL of ice cold water over 2 min. A white solid precipitates in the reaction flask.
8. Assemble the vacuum filtration apparatus. Put a filter paper onto the Büchner funnel, wet the filter paper with distilled water and open the vacuum valve. Transfer the reaction mixture on to the filter, and remove the stirring bar from the reaction flask using the spatula. Wash the product three times with portions of 10 mL ice-cold water *(cooled in the ice bath).* Wash the product two times with portions of 10 mL ice-cold *n*-hexane *(cooled in the ice bath).* Continue to use the pump to dry the solid on the filter. After *ca.* 5 min, carefully transfer the dried powder on to the watch glass labeled with your code and put into the labeled Petri dish. Turn off the vacuum valve when you do not use it! *Note: Your sample will be collected, dried and weighed later by the lab assistant.*

Task 2.1 *The recording of your yield –will be performed after the exam by the lab assistants.*

Step 2. TLC Analysis of the product

1. Check your TLC plate before use. Unused damaged plates will be replaced upon request without penalty. Use the pencil to draw the start front line, and the line where the solvent front will be run to **exactly as shown in Figure 2.2**. Write your student code on the top of the TLC plate in pencil.

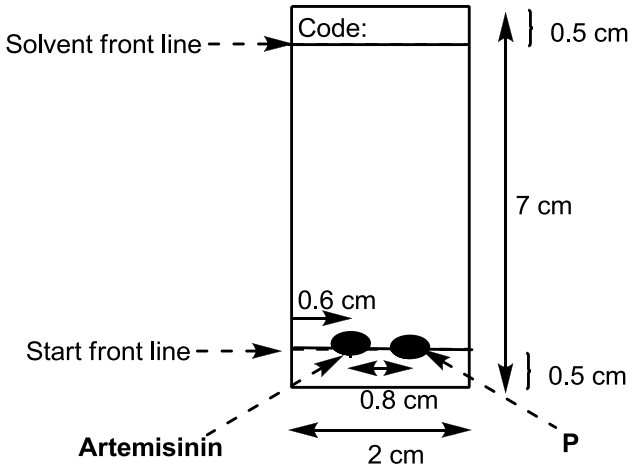


Figure 2.2. Instruction of TLC plate preparation

2. Dissolve *ca.* 1 mg of artemisinin *(a spatula tip)* in *ca.* 0.5 mL of methanol in the labeled very small test tube (use the labeled 5 mL graduated pipette). Dissolve *ca.* 1 mg of the product in *ca.* 1 mL of methanol in the labeled test tube.
3. Spot the artemisinin solution and the product solution on the TLC plate using two different glass capillary spotters so the finished plate is as shown in Figure 2.2.
4. Prepare the TLC developing chamber. Use the 5 mL graduated cylinder to make 5 mL of a mixture of *n*-hexane/ethyl acetate (7/3, v/v) as the solvent system. Pour the mixture of *n*-hexane/ethyl acetate into the chamber *(Note: The solvent level should not reach the spots on the plate if prepared as shown).* Cover and swirl the chamber and allow it to stand for 2 min.

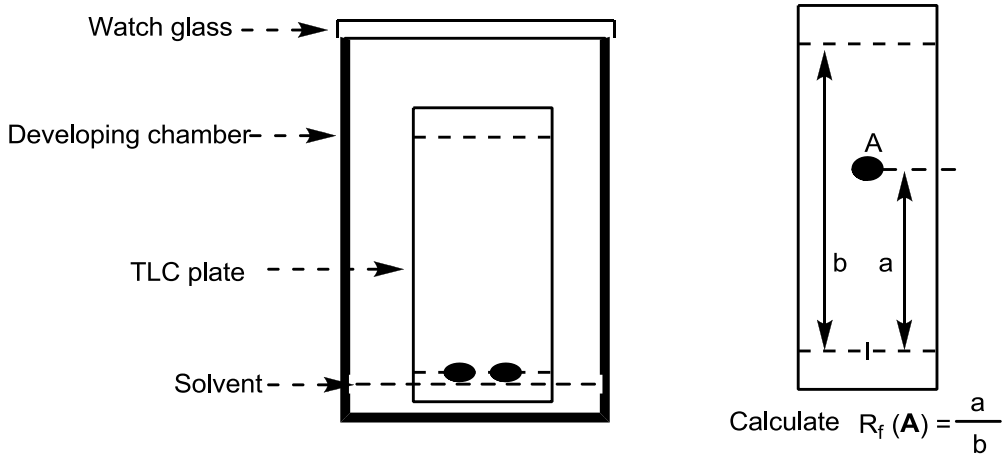


Figure 2.3. A TLC plate placed in the TLC developing chamber and instruction for R_f calculation of compound A

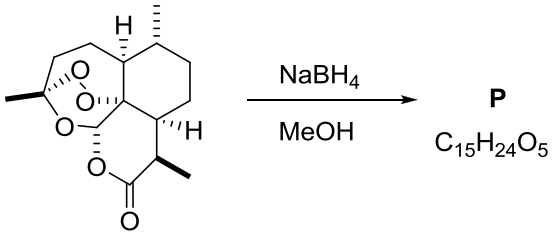
5. Insert the TLC plate upright into the TLC developing chamber. Wait until the solvent system reaches the pre-drawn solvent front line. (*Note: You are advised to work on some question below while you wait for the TLC to run.*)
6. When the solvent front reaches the line, remove the TLC plate using the tweezers and then dry the solvent using the hair dryer set at level 1.
7. Dip the piece of cotton wool into the cerium staining reagent, *taking care not to let the tweezers come into contact with the solution since the metal stains the plate*. Carefully apply the stain to the whole TLC plate.
8. Heat the TLC plate using the hair dryer set at level 2 (*Attention: Do NOT set the hair dryer to COLD*) until the blue spots of artemisinin and the product appear on the TLC plate.
9. Ask the lab assistant to take a photo of your final TLC plate together with your student code.
10. Circle all the visualized spots and calculate the R_f values of both artemisinin and the product (*See instruction in Fig. 2.3*). Store your TLC plate in the Petri dish.

Task 2.2: *Fill the values of R_f in Table and determine the ration.*

Task 2.3: *Check the total number of developed spots on the TLC plate.*

Step 3. Identifying the reaction product P

The reduction of artemisinin leads to the formation of two stereoisomers (P). Comparing the ^{1}H-NMR spectrum (in $CDCl_3$) of one of these isomers with the spectrum of artemisinin shows an extra signal at δ_H = 5.29 ppm as a doublet, and also an extra signal as a broad singlet at δ_H = 2.82 ppm.



artemisinin
$C_{15}H_{22}O_5$

Task 2.4: *Suggest structure for P.* (*You do not need to draw the stereochemistry of the compounds*).

Task 2.5: *P is mixture of two stereoisomers. What is their stereochemical relationship? Check the appropriate box below.*

Practical Problem 3.
Analysis of a hydrated zinc iron(II) oxalate double salt

Zinc iron(II) oxalate double salt is a common precursor in the synthesis of zinc ferrite which is widely used in many types of electronic devices due to its interesting magnetic properties. However, such double salts may exist with different compositions and different amount of water depending on how the sample was synthesized.

You will analyze a pure sample of hydrated zinc iron(II) oxalate double salt (**Z**) in order to determine its empirical formula.

Procedure

The concentration of the standard $KMnO_4$ is posted on the lab walls.

Bring a clean 250 mL beaker to the lab assistant who will be waiting by the balance. You will receive a pure sample of Z for analysis. Accurately weigh between 0.7-0.8 g of the pure sample Z onto the weighing paper (*m in g*). This should then be immediately quantitatively transferred into your 250 mL beaker for analysis, and its mass recorded in table below.

Task 3.1: *Record the mass of the sample of pure Z taken.*

Analysis of Z

- Using the 100 mL graduated measuring cylinder, measure *ca.* 30 mL of 30 wt.% H_2SO_4 solution and add it into the 250-mL beaker containing your accurately weighed pure sample of Z. To speed up the dissolving of your sample you may use the hotplate stirrer to warm up the mixture, but be careful not to boil it. *You should not use the digital thermometer as the acid may damage it*. After the solid has dissolved, remove the beaker from the hotplate stirrer and cool it to close to room temperature. After the solution has cooled, quantitatively transfer it into the 100 mL volumetric flask. Add distilled water up to the 100 mL–mark. We will now call this solution C.
- Use an appropriately labeled beaker to transfer the standardized $KMnO_4$ solution into the burette graduated with brown marks.
- Use another appropriately labeled beaker to transfer the standardize EDTA solution into the burette graduated with blue marks.

Titration with $KMnO_4$

a) Using the 5 mL graduated pipette add 5.00 mL of the solution **C** into a 250 mL conical flask.

b) To this conical flask add about 2 mL of 30 wt.% H_2SO_4 solution, about 3 mL of 3.0 M H_3PO_4 solution, and about 10 mL of distilled water. Heat the mixture on the hot plate stirrer until hot, but be careful not to boil it.

c) Titrate the hot solution with the standardized $KMnO_4$ solution, recording your burette readings in the table below. At the end point of the titration, the pink color of the solution appears. Repeat the titration as desired and report your accepted volume of $KMnO_4$ solution consumed (V_1 mL) in the table.

Task 3.2: *Record volumes of standardized $KMnO_4$ solution consumed.*

Task 3.3: *Can aqueous HCl or HNO_3 be used instead of H_2SO_4 for the dissolving of sample Z and the subsequent analyses?*

Titration with EDTA

- Clean both the 250 mL beakers ready for the next part of the experiment. Pipette 10.00 mL of solution **C** into a 250 mL beaker. Heat and stir the solution on the hotplate stirrer, but be careful not to boil it. Add *ca.* 15 mL of 20 wt.% NaOH solution to the beaker and keep it on the hotplate for *ca*. *3-5* min in order to complete the precipitation of iron hydroxide, and to convert all Zn^{2+} ions into the ionic complex $[Zn(OH)_4]^{2-}$.
- Using a glass funnel and the large quantitative filter paper, filter the hot suspension directly into the 250 mL conical flask. From this point take care with the volumes as you will be preparing a standard solution of exactly 100 mL from the filtrate. As it is filtering, prepare some warm distilled water in a 250 mL beaker (*ca*. 50 mL). Wash

the precipitate on the filter paper (at least 5 times) with small portions (*ca.* 5 mL) of the warm distilled water. Cool the filtrate down and then quantitatively transfer it into the 100 mL volumetric flask via a glass funnel. Add distilled water to make up to the 100 mL mark. This will now be referred to as solution D.

- Pipette 10.00 mL of solution D into a 250 mL conical flask. Add *ca.*10 mL ammonia buffer solution (*pH* = 9 – 10) and a small quantity of the ETOO indicator using the glass spatula spoon. Mix well to obtain a purple solution. Titrate the solution with the standardized 2.00 × 10^{-3} M EDTA solution and record your burette readings in the table below. At the end point, the color of the solution turns blue. Repeat the titration as desired and report your accepted volume of EDTA solution consumed (V_2 mL) in the table.

Task 3.4: *Record the volumes of EDTA solution consumed.*

Determination of the empirical formula of Z

Task 3.5: *Calculate the number of moles of Zn^{2+}, $n_{Zn^{2+}}$, present in 100 mL of solution C.*

Task 3.6: *Give the ionic equations for the reduction-oxidation reactions taking place in the titration with $KMnO_4$.*

Task 3.7: *Calculate the number of moles of Fe^{2+}, $n_{Fe^{2+}}$, present in 100 mL of solution C.*

[YOU WILL NEED THE PRECISE CONCENTRATION OF $KMnO_4$ POSTED ON THE WALLS IN YOUR LAB]

Task 3.8: *Calculate the number of moles of $C_2O_4^{2-}$ anion, $n_{C_2O_4^{2-}}$, in 100 mL of solution C.*

Task 3.9: *Calculate the number of moles of water, n_{H_2O}, in the original sample of Z taken for analysis.*

Task 3.10: *Give the empirical formula of Z.*

Solutions to the theoretical Problems

Solution to problem 1.

1. $\lambda = 65.01 \cdot \frac{(k+2)^2}{2k+1}$ mit k = 4; λ = 260.0 nm

2. $E = \frac{n^2h^2}{8mL^2}$ $\Delta E = E_{LUMO} - E_{HOMO} = h\cdot\nu = \frac{h\cdot c}{\lambda}$ $\Rightarrow$

$\Delta E = \frac{h^2}{8mL^2}[(k+1)^2 - k^2] = \frac{h^2}{8mL^2}[2k+1]$ mit L = (k+2) · 1,40 Å:

$\Delta E = \frac{h\cdot c}{\lambda} = \frac{h^2(2k+1)}{8m[(k+2)\cdot 1.40\cdot 10^{-10}]^2}$ $\Rightarrow$ $\lambda = \frac{8m[(k+2)\cdot 1.40\cdot 10^{-10}]^2}{h(2k+1)}$

$\lambda = \frac{8\cdot 9.1094\cdot 10^{-31}\cdot 2.9979\cdot 10^{8}\cdot (1.40\cdot 10^{-10}]^2}{6.6261\cdot 10^{-34}} \cdot \frac{(k+2)^2}{2k+1}$ m

$\lambda = 6.462\cdot 10^{-8}\cdot\frac{(k+2)^2}{2k+1}$ m = $64.62 \cdot \frac{(k+2)^2}{2k+1}$ nm $\Rightarrow$ B_{calc} = 64,6 nm

3. With λ = 600 nm we have $\frac{600}{64.62} = 9{,}825 = \frac{(k+2)^2}{2k+1}$

$k^2 - 14{,}57\,k - 5{,}285 = 0$ $k_1 = 14{,}92$ ($k_2 = -0.355$)

k = 15 $\Rightarrow$ the formula of polyene is $CH_2 = CH - (CH = CH)_{13} - CH = CH_2$

4. $\Delta E = E_{LUMO} - E_{HOMO} = \frac{h^2}{8mL^2}[2k+1]$

$\Delta E = \frac{(6.6261\cdot 10^{-34})^2\cdot 10^{-3}\cdot 6.022\cdot 10^{23}}{8\cdot 9.1094\cdot 10^{-31}\cdot (1.40\cdot 10^{-10}]^2}\cdot\frac{2k+1}{(k+2)^2}$ kJ·mol^{-1}

$\Delta E = 1851\cdot\frac{2k+1}{(k+2)^2}$ kJ·mol^{-1}

For polyene with *k* = 15 ; ΔE = 199 kJ·mol^{-1}.

5a. $L_x = L_y = L_z$; $E_{xyz} = \frac{h^2(n_x^2+n_y^2+n_z^2)}{8mL^2}$

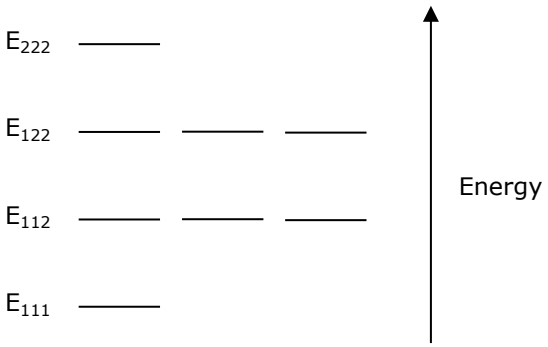
$E_{111} = \frac{h^2(1^2+1^2+1^2)}{8mL^2} = \frac{3h^2}{8mL^2}$

$E_{112} = \frac{h^2(1^2+1^2+2^2)}{8mL^2} = \frac{6h^2}{8mL^2} = E_{121} = E_{211}$

$E_{122} = \frac{h^2(1^2+2^2+2^2)}{8mL^2} = \frac{9h^2}{8mL^2} = E_{212} = E_{221}$

5b. E_{111}: only a single state.
E_{112}: triple degenerate, either n_x, n_y or n_z can equal to 2.
E_{122}: triple degenerate, either n_x, n_y or n_z can equal to 1.
E_{222}: single state.

Energy diagram (cubic box):



Solution to problem 2.

1a.

	N_2O_4	$\rightleftharpoons$	2 NO_2
Initial molar number	1		0
At equilibrium	1 - x		2·x

$n_{total,equi.}$ = 1 - x + 2x = 1 + x $P_{total,equi} = P_{ini}(1 + x)$

$$n_{total,equi.} = \frac{p \cdot V}{R \cdot T} = \frac{1.190 \cdot 10^5 \text{ Pa} \cdot 24.44 \cdot\cdot 10^{-3} \text{ m}^3}{8.3145 \text{ JK}^{-1}\text{mol}^{-1} \cdot 298 \text{ K}} = 1.174 \text{ mol}$$

1.174 = 1 + x x = 0.174

<u>At equilibrium:</u>

$$p(N_2O_4) = \frac{1-x}{1+x} \cdot p_{total} = \frac{1-0.174}{1+0.174} \cdot 1.190 \text{ bar} = 0.837 \text{ bar}$$

$$p(NO_2 = \frac{2 \cdot x}{1+x} \cdot p_{total} = \frac{2 \cdot 0.174}{1+0.174} \cdot 1.190 \text{ bar} = 0.353 \text{ bar}$$

$$K_{298} = \frac{(p(NO_2)/p^0)^2}{(p(N_2O_4)/p^0} = \frac{(0.353/1)^2}{0.837/1} = 0.1489$$

<u>At 298 K:</u>

$\Delta G° = -R \cdot T \cdot \ln K_{298} = (-8.3145 \cdot 298 \cdot \ln 0.1489)$ J·mol^{-1} = 4719 J·mol^{-1} = 4.72 kJ·mol^{-1}

1b. <u>ΔG^0 at 348 K:</u>

$$n_{total,equi.} = \frac{p \cdot V}{R \cdot T} = \frac{1.886 \cdot 10^5 \text{ Pa} \cdot 24.44 \cdot\cdot 10^{-3} \text{ m}^3}{8.3145 \text{ JK}^{-1}\text{mol}^{-1} \cdot 348 \text{ K}} = 1.593 \text{ mol}$$

1.593 = 1 + x x = 0.593

<u>At equilibrium:</u>

$$p(N_2O_4) = \frac{1-x}{1+x} \cdot p_{total} = \frac{1-0.593}{1+0.593} \cdot 1.886 \text{ bar} = 0.482 \text{ bar}$$

$$p(NO_2 = \frac{2 \cdot x}{1+x} \cdot p_{total} = \frac{2 \cdot 0.593}{1+0.593} \cdot 1.886 \text{ bar} = 1.404 \text{ bar}$$

$$K_{348} = \frac{(p(NO_2)/p^0)^2}{(p(N_2O_4)/p^0} = \frac{(1.404/1)^2}{0.482/1} = 4.0897$$

<u>At 348 K:</u>

$\Delta G° = -R \cdot T \cdot \ln K_{348} = (-8.3145 \cdot 348 \cdot \ln 4.0897)$ J·mol^{-1} = -4075 J·mol^{-1} = -4.07 kJ·mol^{-1}

ΔG^0_{348} = -4.07 kJ·mol^{-1} = $\Delta H° - 348 \text{ K} \cdot \Delta S°$ (1)

ΔG^0_{298} = 4.72 kJ·mol^{-1} = $\Delta H° - 298 \text{ K} \cdot \Delta S°$ (2)

(2) - (1) ⇒ $\Delta S° = 0.176$ kJ·mol^{-1}·K^{-1}

$\Delta H^0 = 4.720 + 298 \times 0.176$ $\Delta H^0 = 57.2$ kJ·mol^{-1}

2. $\Delta U = q + w$; work done by turbine w(air)=-w

q = 0, thus w(air) = $\Delta U = C_{v,m}$(air)$[T_3-T_4]$

3. $$\ln\frac{K_{440}}{K_{348}} = \frac{\Delta H^0}{R} \cdot \left[\frac{1}{348} - \frac{1}{440}\right] = \frac{57200}{8.3145} \cdot \left[\frac{1}{348} - \frac{1}{440}\right]$$

⇒ ln K_{440} = 5.542 K_{440} = 255.2

	N_2O_4	$\rightleftharpoons$	2 NO_2
Initial molar number	1		0
At equilibrium	1 - x		2·x

$n_{total,equi.}$ = 1 - x + 2x = 1 + x $P_{total,equi}$ = 12.156 bar

<u>At equilibrium:</u>

$$p(N_2O_4) = \frac{1-x}{1+x} \cdot 12.156 \text{ bar} \qquad p(NO_2 = \frac{2 \cdot x}{1+x} \cdot 12.156 \text{ bar}$$

$$K_{440} = \frac{(p(NO_2)/p^0)^2}{(p(N_2O_4)/p^0} = \frac{(\frac{2x}{1+x} \cdot 12.156/1)^2}{\frac{1-x}{1+x} \cdot 12.156/1} = 255.2 \quad \Rightarrow \quad \frac{(\frac{2x}{1+x})^2}{\frac{1-x}{1+x}} = \frac{255.2}{12.156}$$

$\frac{(\frac{2x}{1+x})^2}{\frac{1-x}{1+x}} = 20.99 \quad \Rightarrow \quad \frac{4x^2}{1-x^2} = 20.99 \quad 4\,x^2 = 20.99 - 20.99\,x^2$

$\Rightarrow \quad x = 0.92 \quad n_{total} = 1 + x = 1.92$

$w_{N_2O_4} = 1.92 \cdot C_{v,air} \cdot (T_3 - T_4) \quad \Rightarrow \quad \frac{w_{N_2O_4}}{w_{air}} = 1.92$

Solution to problem 3.

1a. Paramagnetic

1b. Oxidation number of Ag1 : +1 Oxidation number of Ag2 : +3

1c. The coordination number of O atoms: 3

1d. Number of Ag^{I} = 1
Number of Ag^{III} = 2

1e. Diamagnetic
The Ag^{I} is d^{10} hence diamagnetic; the Ag^{III} is square planar d^8 also diamagnetic

1f. $S_2O_8^{2-}{}_{(aq)} + 2\,Ag^{+}{}_{(aq)} + 2\,H_2O_{(l)} \longrightarrow 2\,SO_4^{2-}{}_{(aq)} + Ag^{I}Ag^{III}O_{2\,(s)} + 4\,H^{+}{}_{(aq)}$

2a. U_{lat} of $Ag^{I}Ag^{III}O_2$:

$\Delta H_{lat}(Ag^{I}Ag^{III}O_2) = 2\,\Delta H^{o}_{f}(O^{2-}) + \Delta H^{o}_{f}(Ag^{+}) + \Delta H^{o}_{f}(Ag^{3+}) - \Delta H^{o}_{f}(Ag^{I}Ag^{III}O_2)$
$= [(2\times249 - 2\times141 + 2\times844) + (284.9 + 737.2) + (284.9 + 737.2 + 2080.2 + 3367.2) - (-24.3)]\ kJ\cdot mol^{-1}$
$= 9419.9\ kJ\cdot mol^{-1}$

$U_{lat}(Ag^{I}Ag^{III}O_2) = \Delta H_{lat}(Ag^{I}Ag^{III}O_2) - 4\cdot R\cdot T$
$= (9419.9 - 10.0)\ kJ\cdot mol^{-1} = 9409.9\ kJ\cdot mol^{-1}$

U_{lat} of $Cu^{II}O$:

$\Delta H_{lat}(Cu^{II}O) = \Delta H^{o}_{f}(O^{2-}) + \Delta H^{o}_{f}(Cu^{2+}) - \Delta H^{o}_{f}(Cu^{II}O)$
$= [(249 - 141 + 844) + (337.4 + 751.7 + 1964.1) - (-157.3)]\ kJ\cdot mol^{-1}$
$= 4162.5\ kJ\cdot mol^{-1}$

$U_{lat}(Cu^{II}O) = \Delta H_{lat}(Cu^{II}O) - 2\cdot R\cdot T = (4162.5 - 5.0)\ kJ\cdot mol^{-1} = 4157.5$

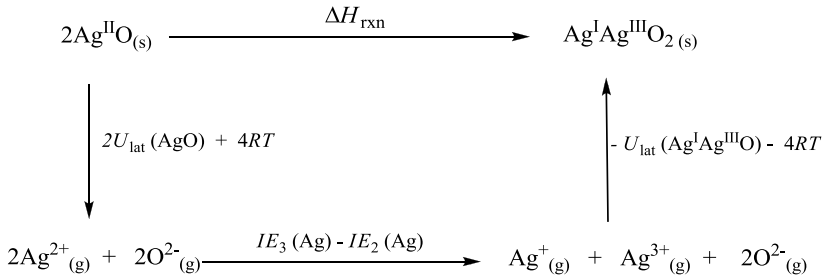
2b. $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}{}_2O_4) - V_m(Ag^{III}{}_2O_3) = (0.08985 - 0.06182)\ nm^3 = 0.02803\ nm^3$

From the relationship $U_{lat} = C\times(V_m)^{-1/3}$ we have

$\frac{U_{lat}(Ag\ oxide)}{U_{lat}(Cu\ oxide)} \approx \left[\frac{V_m(Cu\ oxide)}{V_m(Ag\ oxide)}\right]^{1/3}$

$U_{lat}(Ag^{II}O) = 4157.5 \cdot \sqrt[3]{\frac{0.02030}{0.02803}}\ kJ\cdot mol^{-1} = 3733.6\ kJ\cdot mol^{-1}$

2c.



$\Delta H_{rxn} = 2\cdot U_{lat}(Ag^{II}O) + 4\cdot R\cdot T + IE_3 - IE_2 - U_{lat}(Ag^{I}Ag^{III}O_2) - 4\cdot R\cdot T$
$= (2\times3733.6 + 3367.2 - 2080.2 - 9409.9)$
$= -655.7\ kJ\cdot mol^{-1}$

2d. $Ag^{I}Ag^{III}O_2$

3. For **B**: $Ag^{I}Ag^{III}O_{2\,(s)} + 4\ HClO_{4\,(aq)} \longrightarrow 2Ag(ClO_4)_{2\,(aq)} + 2\ H_2O_{\,(l)}$

For **C**: $4Ag(ClO_4)_{2\,(aq)} + 2\ H_2O_{\,(l)} \longrightarrow 4\ AgClO_{4\,(aq)} + 4\ HClO_{4\,(aq)} + O_{2\,(g)}$

4a.

- n(Ag) in 0.6164 g of **Z** = n(AgCl) = 0.001 mol
- $n(SO_4^{2-})$ from 0.6160 g of **Z** = $n(BaSO_4)$ = 0.002 mol
- Mass percentage of Ag = $0.001 \cdot 107.87/0.6164 \cdot 100$ % = 17.50 %
- Mass percentage of SO_4^{2-} = $0.002 \cdot 96.06/0.6164 \cdot 100$ % = 31.17 %
- From EA:

$n(Ag^{2+}) : n(SO_4^{2-}) : n(C) : n(H) : n(N) = \frac{17.50}{107.85} : \frac{31,17}{192,12} : \frac{38.96}{12.01} : \frac{3.28}{1.01} : \frac{9.09}{14.01} = 1 : 2 : 20 : 20 : 4$

The empirical formula of **Z** is: $C_{20}H_{20}AgN_4O_8S_2$

Yield = $\frac{1.719}{\frac{0.500}{169.87} \cdot 616.4} \cdot 100$ % = 94.7 %

4b.

- $\sqrt{n \cdot (n+2)}$ = 1.78 (*n* is number of unpaired electron of Ag)
- *n* = 1, corresponds to Ag^{II} (d^9)
- Most rational molecular formula of Z is $[Ag^{II}(Py)_4](S_2O_8)$

4c. Formation of Z:

$2\ Ag^{+}_{\ (aq)} + 8\ Py_{\ (l)} + 3\ S_2O_8^{2-}{}_{(aq)} \longrightarrow 2\ [Ag^{II}(Py)_4](S_2O_8)_{\ (s)} + 2\ SO_4^{2-}{}_{(aq)}$

Destruction of **Z** with NH_3:

$[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 6\ NH_{3(l)} \longrightarrow [Ag(NH_3)_2]^{+}_{(aq)} + ½\ N_{2(g)} + 2\ SO_4^{2-}{}_{(aq)} + 3\ NH_4^{+}{}_{(aq)} + 4\ Py_{(l)}$

(All reasonable N –containing products and O_2 are acceptable)

Formation of **D**:

$[Ag(NH_3)_2]^{+}_{\ (aq)} + 2\ H^{+}_{\ (aq)} + Cl^{-}_{\ (aq)} \longrightarrow AgCl_{\ (s)} + 2\ NH_4^{+}{}_{(aq)}$

Formation of **E**:

$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4\ (s)}$

Solution to problem 4.

1a. $PtCl_4 + 2\ C_2H_5OH \longrightarrow H[PtCl_3C_2H_4] + CH_3CH{=}O + HCl + H_2O$

$H[PtCl_3C_2H_4] + KCl \longrightarrow K[PtCl_3C_2H_4] + HCl$

$K_2[PtCl_6] + 2\ C_2H_5OH \longrightarrow K[PtCl_3C_2H_4] + CH_3CH{=}O + KCl + 2\ HCl + H_2O$

$K_2[PtCl_4] + C_2H_4 \longrightarrow K[PtCl_3C_2H_4] + KCl$

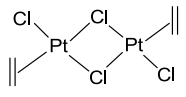
1b. 195 + 3×35 + 2×12 + 4×1 = 328

2.

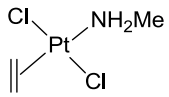
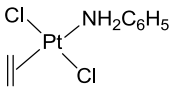
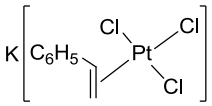
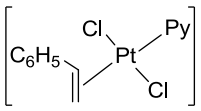
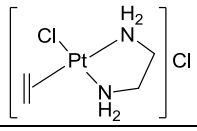
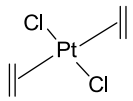
Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1	2	2
Z2	2	2
Z3	2	2
Z4	1	1
Z5	2	1

3a.

A



3b.

B 	**C** 	**D** 
E 	**F** 	**G** 

3c.

Structure	**D**	**F**
Driving force(s)	i	iii and iv

Solution to problem 5.

1. HA $\rightleftharpoons$ $H^+ + A^-$ and HB $\rightleftharpoons$ $H^+ + B^-$ and H_2O $\rightleftharpoons$ $H^+ + OH^-$

Amount of H^+: $[H^+] = [OH^-] + [A^-] + [B^-]$

In the acidic solution (pH = 3.75), $[OH^-]$ can be neglected, so:

$[H^+] = [A^-] + [B^-]$ (1)

$K_{HA} = \frac{[H^+]\cdot[A^-]}{[HA]}$ and $[HA] = [HA]_i - [A^-]$ (*where $[HA]_i$ is the initial concentration*)

$\Rightarrow$ $[H^+] \cdot [A^-] = K_{HA} \cdot [HA] = K_{HA} \cdot ([HA]_i - [A^-])$

$\Rightarrow$ $[A^-] = \frac{K_{HA}\cdot[HA]_i}{K_{HA}+[H^+]}$ and, similarly, $[B^-] = \frac{K_{HB}\cdot[HB]_i}{K_{HB}+[H^+]}$

Substitution into Eq.(1): $[H^+] = \frac{K_{HA}\cdot[HA]_i}{K_{HA}+[H^+]} + \frac{K_{HB}\cdot[HB]_i}{K_{HB}+[H^+]}$

Since K_{HA}, K_{HB} are much smaller than $[H^+]$, thus: $[H^+] = \frac{K_{HA}\cdot[HA]_i}{[H^+]} + \frac{K_{HB}\cdot[HB]_i}{[H^+]}$

$1.74 \times 10^{-7} \cdot [HA]_i + 1.34 \cdot 10^{-7} \cdot [HB]_i = [H^+]^2 = (10^{-3.75})^2$

$1.74 \times [HA]_i + 1.34 \times [HB]_i = 0.316$ (2)

Neutralization reactions:

HA + NaOH $\longrightarrow$ NaA + H_2O and HB + NaOH $\longrightarrow$ NaB + H_2O

$n_{HA} + n_{HB} = n_{NaOH}$

$\Rightarrow$ $([HA]_i + [HB]_i) \cdot 0.1$ L $= 0.220$ mol/L $\cdot 0.1$ L

$[HA]_i + [HB]_i = 0.220$ mol/L (3)

Solving Eq.(2) and Eq.(3) gives: $[HA]_i = 0.053$ mol/L and $[HB]_i = 0.167$ mol/L

Concentration of HA = 0.053 mol/L Concentration of HB = 0.167 mol/L

2. Solution Y contains 0.06 mol/L of NaA and 0.04 mol/L of NaB. The solution is basic, OH^- was produced from the reactions:

$NaA + H_2O \rightleftharpoons HA + OH^-$ $K_{b,A} = K_w/K_{HA} = 5.75 \cdot 10^{-8}$

$NaB + H_2O \rightleftharpoons HB + OH^-$ $K_{b,B} = K_w/K_{HB} = 7.46 \cdot 10^{-8}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00\ 10^{-14}$

and we have $[H^+] + [HA] + [HB] = [OH^-]$

In the basic solution, $[H^+]$ can be neglected, so:

$[HA] + [HB] = [OH^-]$ (4)

$K_{b,A} = \frac{[OH^-]\cdot[HA]}{[A^-]}$ and $[A^-] = 0.06 - [HA]$

$\Rightarrow$ [HA] = $\frac{K_{b,A}\cdot 0.06\ mol/L}{K_{b,A}+[OH^-]}$ and, similarly, [HB] = $\frac{K_{b,B}\cdot 0.04\ mol/L}{K_{b,B}+[OH^-]}$

Substitution into Eq. (4): $\frac{K_{b,A}\cdot 0.06\ mol/L}{K_{b,A}+[OH^-]} + \frac{K_{b,B}\cdot 0.04\ mol/L}{K_{b,B}+[OH^-]} = [OH-]$

Assume that $K_{b,A}$ and $K_{b,B}$ are much smaller than $[OH^-]$ (*), thus:
$[OH^-]^2 = (5.75 \cdot 10^{-8} \times 0.06 + 7.46 \cdot 10^{-8} \times 0.04)\ (mol/L)^2$
$[OH^-] = 8.02 \cdot 10^{-5}$ mol/L (the assumption (*) is justified)
So pOH = 4.10 and pH = 9.90

3. HA in the dilute solution: $[A^-] = \alpha \times [HA]_i$ $[HA] = (1 - \alpha) \times [HA]_i$
$[H^+] = 10^{-7}$ mol/L
Substitution of these equilibrium concentrations into K_{HA} expression:

$K_{HA} = \frac{10^{-7}\cdot\alpha\cdot[HA]}{(1-\alpha)\cdot[HA]}$ $\Rightarrow$ $\frac{10^{-7}\cdot\alpha}{(1-\alpha)} = 1.74 \cdot 10^{-7}$ $\Rightarrow \alpha = 0.635$

Similarly, for HB: $\frac{10^{-7}\cdot\alpha}{(1-\alpha)} = 1.34 \cdot 10^{-7}$ $\Rightarrow \alpha = 0.573$

$\Rightarrow$ percentage of dissociation of HA = 65.5 %
percentage of dissociation of HB = 57.3 %

4. Equilibria in the solution:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$
$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00 \times 10^{-14}$
$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.10 \times 10^3$
$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.00 \times 10^2$
$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.20 \times 10^3$
$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.30 \times 10^2$

Solubility of $M(OH)_2$ = s = $[M^{2+}] + [MA^+] + [MA_2] + [MB^+] + [MB_2]$
pH of **Z** = 10.0
$[M]^{2+} = \frac{K_{sp}}{[OH^-]^2} = \frac{3.10\cdot10^{-12}}{(10^{-4})^2} = 3.10 \cdot 10^{-4}$ mol/L

At pH = 10.0:
$[A^-]_{total} = \frac{K_{HA}\cdot 0.06\ mol/L}{K_{HA}+10^{-10}} = 0.06$ mol/L
$[MA^+] = K_1 \cdot [M^{2+}] \cdot [A^-] = 2.1 \cdot 10^3 \cdot 3.10 \cdot 10^{-4} \cdot [A^-] = 0.651 \cdot [A^-]$ (5)
$[MA_2] = K_1 \cdot K_2 \cdot [M^{2+}] \cdot [A^-]^2 = 325.5 \cdot [A^-]^2$ (6)
$[A^-]_{total} = [A^-] + [MA^+] + 2 \cdot [MA_2] = 0.06$ mol(L (7)

Substitute Eq. (5) and Eq. (6) into Eq. (7):
$[A^-] + 0.651 \cdot [A^-] + 2 \cdot 325.5 \times [A^-]^2 = 0.06$
$\Rightarrow$ $[A^-] = 8.42 \times 10^{-3}$ mol/L
Substitute this value into Eq. (5) and Eq. (6):
$[MA^+] = 0.651 \cdot [A^-] = 5.48 \times 10^{-3}$ mol/L
$[MA_2] = 325.5 \cdot [A^-]^2 = 2.31 \times 10^{-2}$ mol/L
Similarly,
$[B^-]_{total} = 0.04$ mol/L
$[MB^+] = K_1 \cdot [M^{2+}] \cdot [B^-] = 6.2 \cdot 10^3 \cdot 3.10 \cdot 10^{-4} \cdot [B^-] = 1.92 \cdot [B^-]$ (8)

$MB_2]$ $= K_1 \cdot K_2 \cdot [M^{2+}] \cdot [B^-]^2$ $= 634.3 \cdot [B^-]^2$ (9)

$[B^-]_{total}$ $= [B^-] + [MB^+] + 2 \times [MB_2] = 0.04$ M (10)

Substitute Eq. (8) and Eq. (9) into Eq. (10):

$[B^-] + 1.92 \cdot [B^-] + 2 \cdot 634.3 \cdot [B^-]^2 = 0.04$

$\Rightarrow \quad [B^-] = 4.58 \times 10^{-3}$ mol/L

Substitute this value into Eq. (8) and Eq. (9):

$[MB^+] = 1.92 \cdot [B^-] \quad = 8.79 \cdot 10^{-3}$ mol/L

$[MB_2] = 634.3 \cdot [B^-]^2 \quad = 1.33 \cdot 10^{-2}$ mol/L

Thus, solubility of $M(OH)_2$ in Z is s'

$s' = 3.10 \cdot 10^{-4} + 5.48 \cdot 10^{-3} + 2.31 \cdot 10^{-2} + 8.79 \cdot 10^{-3} + 1.33 \cdot 10^{-2} = 5.10 \cdot 10^{-2}$ mol/L

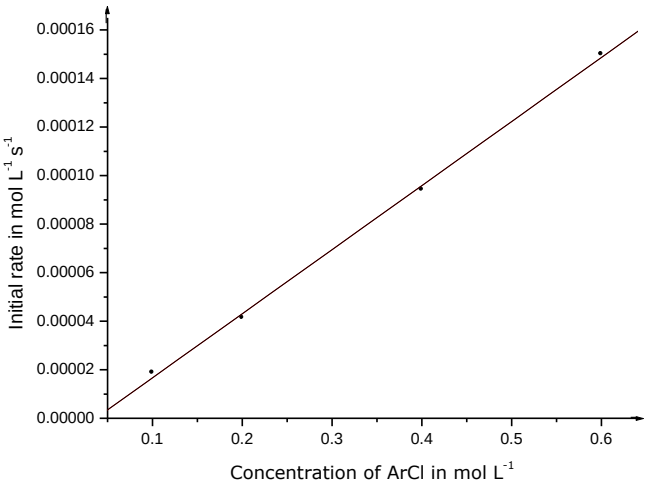
Solubility of $M(OH)_2$ in Z = $5.10 \cdot 10^{-2}$ mol/L.

Solution to problem 6.

6a.

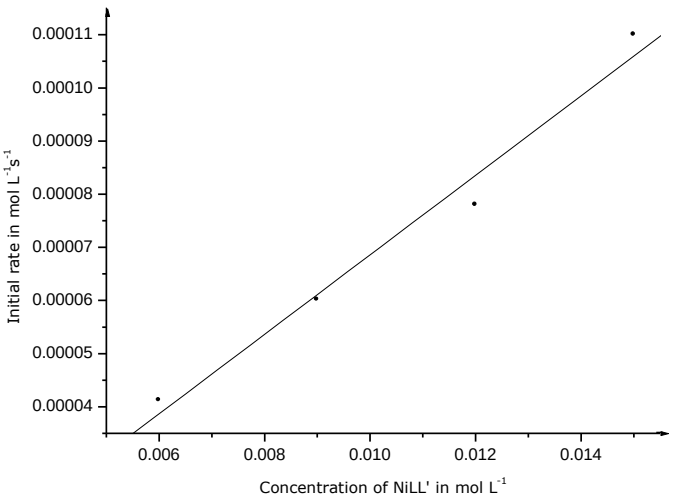
[ArCl] in $mol \cdot L^{-1}$	Initial rate in $mol \cdot L^{-1} \cdot s^{-1}$
0.1	$1.88 \cdot 10^{-5}$
0.2	$4.13 \cdot 10^{-5}$
0.4	$9.42 \cdot 10^{-5}$
0.6	$1.50 \cdot 10^{-4}$

Order with respect to [ArCl] = 1

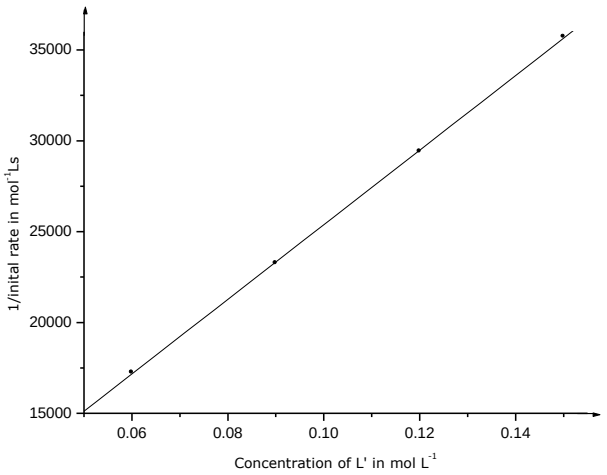


[NiLL'] in $mol \cdot L^{-1}$	Initial rate in $mol \cdot L^{-1} \cdot s^{-1}$
6×10^{-3}	$4.12 \cdot 10^{-5}$
9×10^{-3}	$6.01 \cdot 10^{-5}$
1.2×10^{-2}	$7.80 \cdot 10^{-5}$
1.5×10^{-2}	$1.10 \cdot 10^{-4}$

Order with respect to [NiLL'] = 1



[L′] in $mol \cdot L^{-1}$	Initial rate in $mol \cdot L^{-1} \cdot s^{-1}$	1/(Initial rate) in $mol^{-1} \cdot L \cdot s$
0.06	$5.8 \cdot 10^{-5}$	17240
0.09	$4.3 \cdot 10^{-5}$	23260
0.12	$3.4 \cdot 10^{-5}$	29412
0.15	$2.8 \cdot 10^{-5}$	35710

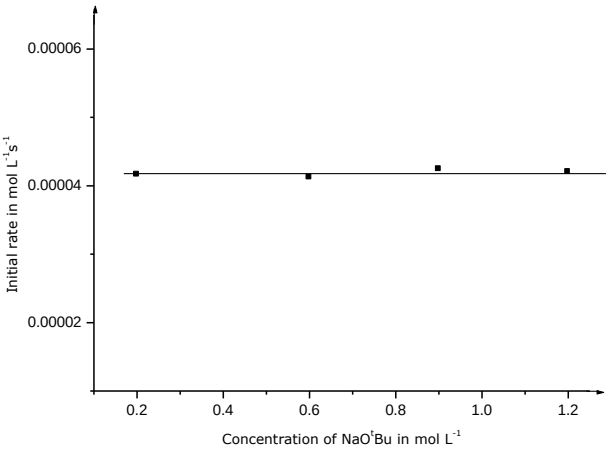


Order with respect to [L′] = -1

6b. rate = $\frac{k_1 k_2 [\text{Nill}'][\text{ArCl}]}{k_{-1}[\text{L}'] + k_2[\text{ArCl}]} = \frac{k_1 (k_2 / k_{-1} [\text{Nill}'][\text{ArCl}]}{[\text{L}'] + (k_2 / k_{-1}[\text{ArCl}]}$

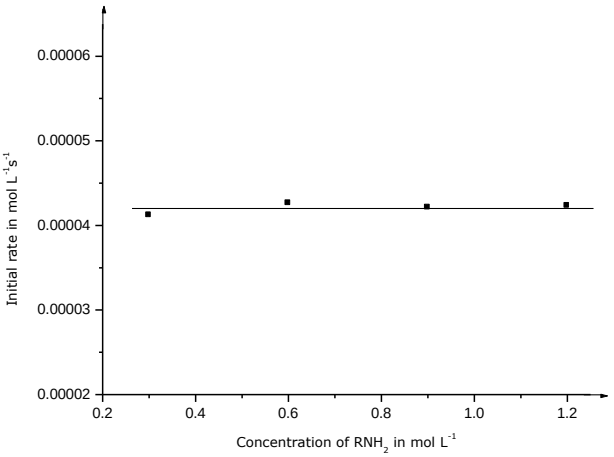
6c.

[NaO^tBu] in $mol \cdot L^{-1}$	Initial rate in $mol \cdot L^{-1} \cdot s^{-1}$
0.2	$4.16 \cdot 10^{-5}$
0.6	$4.12 \cdot 10^{-5}$
0.9	$4.24 \cdot 10^{-5}$
1.2	$4.20 \cdot 10^{-5}$



Order with respect to [NaO^tBu] = 0

[RNH_2] in $mol \cdot L^{-1}$	Initial rate in $mol \cdot L^{-1} \cdot s^{-1}$
0.3	$4.12 \cdot 10^{-5}$
0.6	$4.26 \cdot 10^{-5}$
0.9	$4.21 \cdot 10^{-5}$
1.2	$4.23 \cdot 10^{-5}$



Order with respect to [RNH_2] = 0

6d. Using the mechanism depicted by Reaction (1) through (4), the rate equation:

$\frac{d[NiLL']}{dt} = -k_1 \cdot [NiLL'] + k_{-1} \cdot [NiL] \cdot [L']$

$\frac{d[NiL]}{dt} = k_1 \cdot [NiLL'] - k_{-1} \cdot [NiL] \cdot [L'] - k_2 \cdot [NiL] \cdot [ArCl] + k_4 \cdot [NiL(Ar)NHR]$

Apply the steady-state approximation to the concentrations for the intermediates:

$\frac{d[NiL]}{dt} = 0$

$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)HNR]$ (1)

$\frac{d[NiL(Ar)Cl]}{dt} = k_2[NiL][ArCl] - k_3[RNH_2][NaO^tBu]\,[NiL(Ar)Cl] = 0$

$[NiL(Ar)Cl] = \frac{k_2}{k_3} \cdot \frac{[ArCl]\,[NiL]}{[NH_2R]\,[NaO^tBu]}$ (2)

$\frac{d[NiL(Ar)NHR]}{dt} = k_3[NiL(Ar)Cl]\,[NH_2R]\,[NaO^tBu] - k_4[NiL(Ar)NHR] = 0$

$[NiL(Ar)NHR] = \frac{k_3}{k_4} \cdot [NiL(Ar)Cl]\,[NH_2R]\,[NaO^tBu]$ (3)

Substitute Equation (2) into Equation (3):

$[NiL(Ar)NHR] = \frac{k_3}{k_4} \cdot [NH_2R]\,[NaO^tBu] \cdot \frac{k_2}{k_3} \cdot \frac{[ArCl]\,[NiL]}{[NH_2R]\,[NaO^tBu]} = \frac{k_2}{k_4} \cdot [ArCl]\,[NiL]$ (4)

Substitute Equation (4) into Equation (1):

$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4 \cdot \frac{k_2}{k_4} \cdot [ArCl]\,[NiL] = k_{-1}[NiL][L']$ (5)

The material balance equation with respect to the catalyst is

$[NiLL']_0 = [NiLL'] + [NiL] + [NiLAr(Cl)] + [NiLAr(Cl)NHR]$

$[NiLL']_0 = \frac{k_{-1}}{k_1}\,[NiL][L'] + [NiL] + \frac{k_2}{k_3} \cdot \frac{[ArCl]\,[NiL]}{[NH_2R]\,[NaO^tBu]} + \frac{k_2}{k_4} \cdot [ArCl]\,[NiL]$

$[NiLL']_0 = [NiL]\left(\frac{k_{-1}}{k_1}[L'] + 1 + \frac{k_2}{k_3} \cdot \frac{[ArCl]}{[NH_2R]\,[NaO^tBu]} + \frac{k_2}{k_4} \cdot [ArCl]\right)$

$[NiL] = [NiLL']_0 \cdot \frac{k_1k_3k_4[NH_2R][NaO^tBu]}{k_{-1}k_3k_4[L'][NH_2R][NaO^tBu] + k_1k_3k_4[NH_2R][NaO^tBu] + k_1k_2k_4[ArCl] + k_1k_2k_3[ArCl][NH_2R][NaO^tBu]}$ (6)

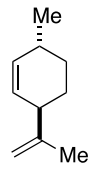
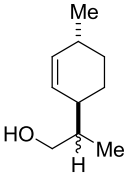
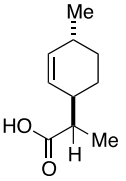
Substituting Equation (6) into the differential rate for [ArCl], $-\frac{d[ArCl]}{dt} = k_2[ArCl][NiL]$, results in the following predicted rate law expression for the reaction mechanism:

$\frac{d[ArNHR]}{dt} = \frac{d[ArCl]}{dt} = k_2[ArCl][NiL] = \frac{k_1k_2k_3k_4[ArCl][NiLL']_0[NH_2R][NaO^tBu]}{k_{-1}k_3k_4[L'][NH_2R][NaO^tBu] + k_1k_3k_4[NH_2R][NaO^tBu] + k_1k_2k_4[ArCl] + k_1k_2k_3[ArCl][NH_2R][NaO^tBu]}$

6e. $\frac{d[ArNHR]}{dt} = \frac{d[ArCl]}{dt} = k_2[ArCl]\,[NiL] = \frac{k_1k_2[ArCl][NiLL']_0}{k_{-1}[L']}$

Solution to problem 7.

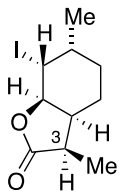
7a.

A	**B**	**C**
		

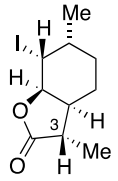
7b.

The acid **C** was converted to diastereomeric iodolactones **D** and **E** (epimeric at the chiral center C_3). Look at the number-indicated in the structure **F** in the next step.

D



E



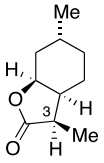
7c.

Because alkylated lactone **F** is known, we can deduce the reagent **X** as methyl vinyl ketone. **H** is the reduced product of **D**.

X

methyl vinyl ketone

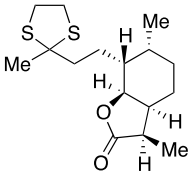
H



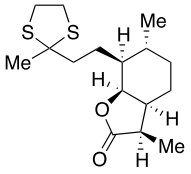
7d.

The keto group of lactone **F** reacted with ethanedithiol and $BF_3{\cdot}Et_2O$ in dichloromethane to afford thioketal lactones, **I** and the major isomer **J**.

I



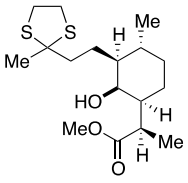
J



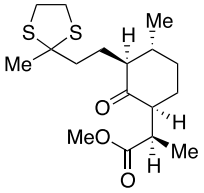
7e.

Hydrolysis followed by esterification of **J** provided hydroxy ester **K**.
Oxidation of the hydroxy group in **K** by PCC resulted in the keto ester **L** in which two protons adjacent to the carbonyl group are cis-oriented.

K



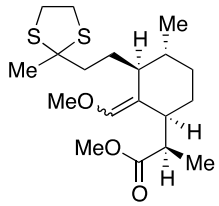
L



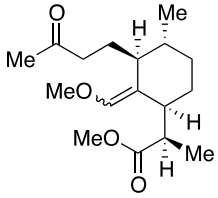
7f.

The Wittig reaction of the ketone **L** resulted in the formation of methyl vinyl ether **M**.
Deprotection of the thioketal group forms the intermediate **N**.

M

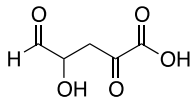
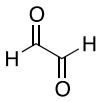
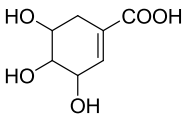
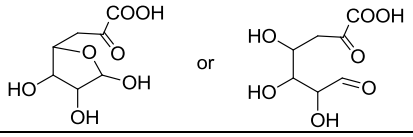
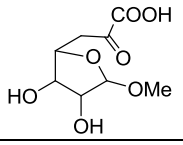
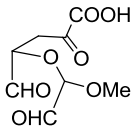


N



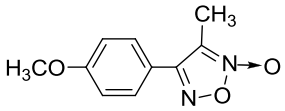
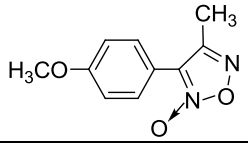
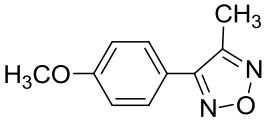
Solution to problem 8.

8a.

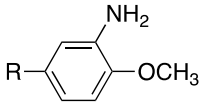
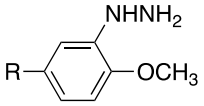
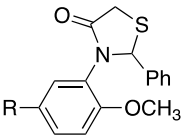
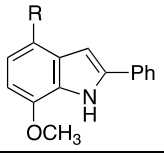
Y_1 	**Y_2** 	**Y_3** CH_3OH
A 	**B** 	
C 	**D** 	

8b. **E** does not contain two *trans* ethylenic protons as anethole.

8c.

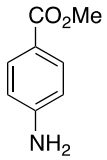
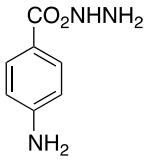
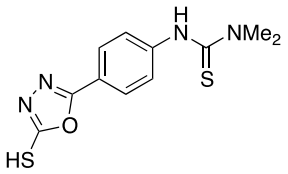
E 	**F** 	**G** 

8d.

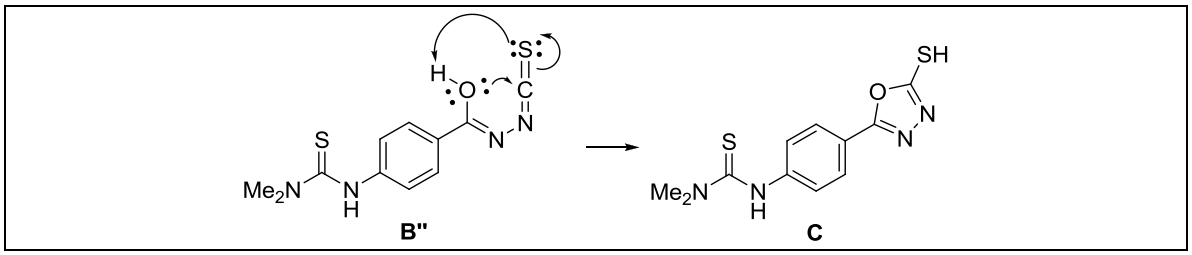
H 	**I** 
J 	**K** 

Solution to problem 9.

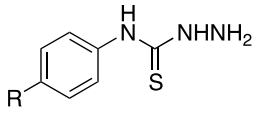
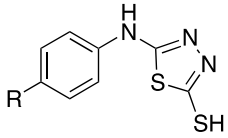
9a.

A 	**B** 	**C**  **C**: $C_{11}H_{12}N_4OS_2$

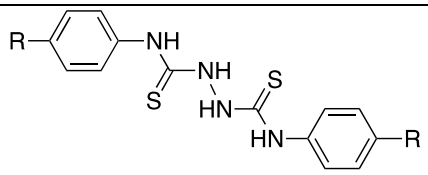
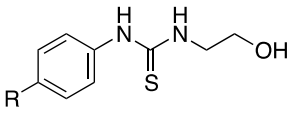
9b.



9c.

E	**F**
	

9d. **9e.**

	G
 **D'**: $R_2C_{14}H_{12}N_4S_2$	

9f.

i)

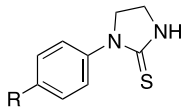
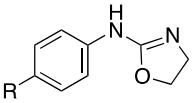
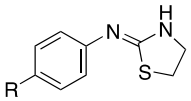
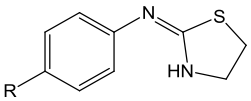
E.g.	**H_1**	**H_2**

ii)

E.g.	**H_1**	**H_3**

iii)

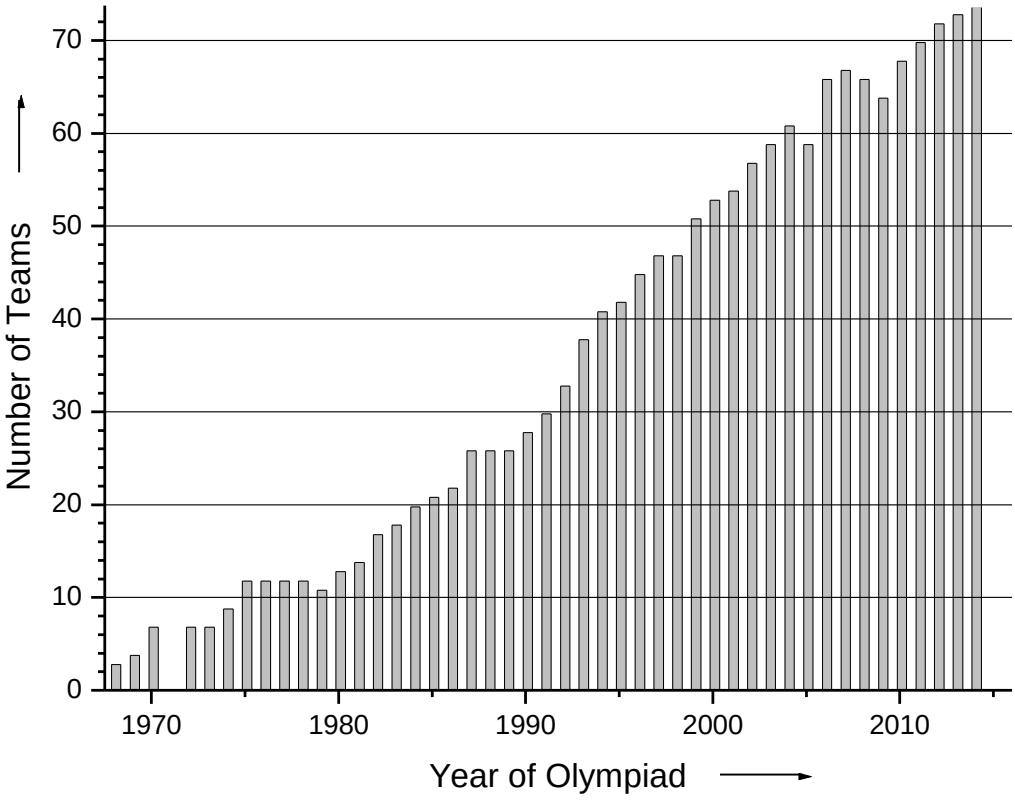
E.g.	**H_3**	**H_4**

H_1	**H_2**	**H_3**	**H_4**
			

About the history of the International Chemistry-Olympiads

The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The number of teams attending the IChO in the following years are shown in the plot below.

Number of teams attending the IChO



The participating countries are shown in the following table.

Participating Delegations

●= host. + = participant. o = observer

Country ↓ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
Argentina																											+	+	+	+	+
Armenia																															
Australia																			o	+	+	+	+	+	+	+	+	+	+	●	+
Austria							+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																													o	o	
Belarus																												+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brazil																													o	o	+
Bulgaria			+	+	+		+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	●	+	+
China																			+	+	+	+	+	+	+	+	●	+	+	+	+
Chinese Taipei																								+	+	+	+	+	+	+	+
Costa Rica																															
Croatia																														o	o
Cuba																	+	o	+	+	+	+	+		+	+	+	+	+		+
Cyprus																						o	+	+	+	+	+	+	+	+	+
Czech Rep.																									+	+	+	+	+	+	+
Czechoslovakia	●	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+							
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR		o	+	+	+	+	+	●	+	+	+	+	+	+	+		+	+	+	+	●	+									
Egypt																															
El Salvador																															
Estonia																										+	+	+	+	+	+
Finland									o	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+
France												o	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+
fYROM (Macedonia)																															
Georgia																															
Germany						o	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	●	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+
Iceland																															
India																													o	o	+
Indonesia																												o	+	+	+
Iran																									+	+	+	+	+	+	+
Ireland																												o	o	+	+
Israel																															
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99

Participating Delegations

•= host. + = participant. o = observer

Year → / Country ↓	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14
Argentina	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Armenia					o	o	+	+	+	+	+	+	+	+	+
Australia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Austria	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belarus	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belgium	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brazil	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Bulgaria	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China	+	+	+	+	+		+	+	+	+	+	+	+	+	+
Chinese Taipei	+	+	+	+	+	•	+	+	+	+	+	+	+	+	+
Costa Rica									o	o	+	+	+	+	+
Croatia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Cuba		+	+	+	+	+	+	+	+	+	+	+			+
Cyprus	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czech Rep.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czechoslovakia															
Denmark	•	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR															
Egypt	o	o	+	+	+	+	+					+	+		
El Salvador												o	o	+	+
Estonia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Finland	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
France	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
fYROM (Macedonia)												o	o	+	+
Georgia													o	o	+
Germany	+	+	+	+	•	+	+	+	+	+	+	+	+	+	+
Greece	+	+	+	•	+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	+	+	+	+	+	+	•	+	+	+	+	+	+
Iceland	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+
India	+	•	+	+	+	+	+	+	+	+	+	+	+	+	+
Indonesia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iran	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ireland	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Israel					o	o	+	+	+	+	+	+	+	+	+
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14

Participating Delegations

●= host. + = participant. o = observer

Country ↓ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
Italy												+	+	+	+	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+
Japan																															
Yugoslavia						+	+	+	+					+	+	+	+	+	+												
Kazakhstan																												o	o	+	+
Kenya																													o		
Korea																								+	+	+	+	+	+	+	+
Kuwait															o	o			+	+	+	+	+		+	+	+	+	+		+
Kyrgyzstan																												o	o	+	
Liechtenstein																															
Latvia																							+	+	+	+	+	+	+	+	+
Lithuania																							+	+	+	+	+	+	+	+	+
Malaysia																															
Mexico																								+	+	+	+	+	+	+	+
Moldova																															
Mongolia																															
Montenegro																															
Netherlands												+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+
New Zealand																								+	+	+	+	+	+	+	+
Nigeria																															
Norway												o	+	+	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+
Pakistan																															
Oman																															
Peru																															
Philippines																														o	
Poland	+	●	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+
Portugal																															
Romania		+	+	+	●	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GUS/Russ.Fed																								+	+	+	+	●	+	+	+
Saudi Arabia																															
Serbia																															
Singapore																			o	+		+	+	+	+	+	+	+	+	+	+
Slovakia																								+	+	+	+	+	+	+	+
Slovenia																							+	+	+	+	+	+	+	+	+
South Africa																															
Spain										o																		+	+	+	+
↑ Country \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99

Participating Delegations

●= host. + = participant. o = observer

Country ↓ \ Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14
Italy	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Japan			o	+	+	+	+	+	+	+	●	+	+	+	+
Yugoslavia			o												
Kazakhstan	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Kenya		o													
Korea	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+
Kuwait	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Kyrgyzstan	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Latvia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Liechtenstein										o	o	o	o	o	+
Lithuania	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Malaysia					o	+	+	+	+		+	+	+	+	+
Mexico	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Moldova					o		o	+	+	+	+	+	+	+	+
Mongolia		o			o	o	+	+	+	+	+	+	+	+	+
Montenegro													o	o	+
Netherlands	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+
New Zealand	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Nigeria								o			o	o	+	+	+
Norway	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
0man														o	o
Pakistan					o	o	+	+	+	+	+	+	+	+	+
Peru			o	o	+	+		+	+	+	+	+	+	+	+
Philippines															
Poland	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Portugal		o	o	+	+	+	+	+	+	+	+	+	+	+	+
Romania	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GUS/Russ.Fed	+	+	+	+	+	+	+	●	+	+	+	+	+	●	+
Saudi Arabia					o	o	+	+		o	o	+	+	+	+
Serbia											o	o	+	+	+
Singapore	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Slovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Slovenia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
South Africa															o
Spain	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14

Participating Delegations

●= host. + = participant. o = observer

Year → / Country ↓	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
Sweden						+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Switzerland																		o	+	+	+	+	+	+	+	+	+	+	+	+	+
Syria																															
Tajikistan																															
Thailand																					o	+	+	+	+	+	+	+	+	+	+
Turkey									o	+															o	+	+	+	+	+	+
Turkmenistan																															o
UdSSR			+	●	+	+	+	+	+	+	●		+	+	+	+	+	+	+	+	+		+								
Ukraine																										+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+
Uruguay																													o	o	+
Uzbekistan																															
Venezuela														o		o									+	+	+	+	+	+	+
Vietnam																												+	+	+	+
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99

Participating Delegations

•= host. + = participant. o = observer

Year → / Country ↓	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14
Sweden	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Switzerland	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Syria									o	o	+	+	+	+	+
Tajikistan			o	o	+	+	+	+	+		+	+	+	+	+
Thailand	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Turkey	+	+	+	+	+	+	+	+	+	+	+	•	+	+	+
Turkmenistan	o	o	+	+	+		+	+	+	+	+	+	+	+	+
UdSSR															
Ukraine	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United Kingdom	+	+	+	+	+	+	+	+	+	•	+	+	+	+	+
United States	+	+	+	+	+	+	+	+	+	+	+	+	•	+	+
Uruguay	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uzbekistan												o	o	+	+
Venezuela	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Vietnam	+	+	+	+	+	+	+	+	+	+	+	+	+	+	•
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14

Inofficial ranking since 1974

(set up by adding the points of the teams. up to position 50)

	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988
IChO held in	**RO**	**H**	**DDR**	**CS**	**PL**	**SU**	**A**	**BG**	**S**	**RO**	**D**	**CS**	**NL**	**H**	**FIN**
1	SU	SU	DDR	CS	SU	PL	PL	H	CS	RO	D	SU	NL	SU	RC
.	RO	H	SU	SU	PL	SU	D	CS	D	SU	CS	CS	PL	RC	D
.	CS	PL	H	H	D	RO	DDR	PL	PL	D	SU	D	D	RO	USA
.	H	BG	PL	PL	DDR	CS	H	BG	NL	CS	H	A	SU	CS	PL
5	PL	RO	A	S	CS	A	A	A	A	H	A	NL	A	D	GB
.	DDR	DDR	RO	A	H	S	RO	D	SU	A	GB	H	USA	F	DDR
.	BG	S	BG	D	A	H	BG	DDR	H	F	PL	DDR	H	GB	N
.	YU	CS	CS	DDR	RO	D	CS	RO	BG	DDR	USA	PL	BG	PL	RO
.	S	A	S	RO	S	BG	S	SU	DDR	PL	RO	USA	F	H	H
10	D*	D	D	BG	BG	FIN	FIN	NL	S	NL	DK	F	RO	DDR	SU
.		YU	YU	YU	TR	DDR	NL	FIN	F	BG	S	GB	CS	NL	I
.		B	B	B	FIN		I	S	FIN	GB	NL	RO	GB	USA	NL
.							B	F	N	N	FIN	BG	S	BG	BG
.								I	RO	DK	F	N	DDR	A	CS
15			* hors concourse						DK	FIN	BG	S	CDN	S	AUS
.									YU	S	N	FIN	N	FIN	SGP
.									I	I	I	YU	DK	N	F
.										YU	GR	B	B	DK	A
.											YU	GR	FIN	I	FIN
20											B	DK	GR	GR	CDN
.												C	KWT	C	DK
.													YU	B	C
.														YU	S
.														CDN	B
25														CH	CH
.														KWT	KWT

(List of abbreviations see 152)

	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
IChO held in	**DDR**	**F**	**PL**	**USA**	**I**	**N**	**RC**	**RUS**	**CDN**	**AUS**	**T**	**DK**
1	DDR	RC	RC	RC	RC	RC	RC	IR	H	SGP	USA	RC
.	D	PL	RO	H	TPE	GB	IR	RC	D	USA	ROK	RUS
.	RC	D	H	PL	USA	USA	RO	RUS	TR	ROK	RC	USA
.	BG	USA	PL	USA	I	A	A	A	TPE	RC	IR	H
5	SU	CS	NL	A	GUS	SGP	D	D	IR	H	RO	TPE
.	H	RO	USA	GUS	H	ROK	GB	USA	RUS	RA	H	A
.	PL	F	I	D	D	TPE	SK	UA	ROK	RUS	TPE	SK
.	RO	A	D	RO	CDN	CZ	TPE	CZ	RC	AUS	UA	BY
.	CS	DDR	N	F	SGP	GUS	I	H	SGP	D	PL	VN
10	I	H	GB	I	CZ	IR	CZ	RO	PL	GB	AUS	TR
.	NL	GB	CS	SGP	A	D	RUS	GB	USA	PL	VN	SGP
.	GB	I	SU	CS	RO	H	H	TPE	UA	A	D	D
.	A	AUS	A	AUS	P	RO	AUS	BY	AUS	RO	RA	ROK
.	USA	SGP	AUS	NL	NZ	DK	SGP	SGP	CDN	TPE	BY	IR
15	S	NL	DK	DK	ROK	I	F	RA	RO	SK	T	CZ
.	F	N	SGP	ROK	LV	T	TR	TR	A	NL	F	FIN
.	N	DK	CDN	GB	IR	NZ	PL	F	T	IR	TR	T
.	AUS	T	BG	CH	DK	UA	USA	I	EST	UA	SGP	MEX
.	CDN	FIN	F	T	AUS	AUS	DK	AUS	CZ	VN	IND	GB
20	DK	CDN	S	LV	NL	F	RA	ROK	VN	LT	GB	AUS
.	FIN	BG	T	NZ	LT	PL	ROK	EST	F	TR	RUS	IND
.	B	C	CH	S	SK	NL	UA	CDN	S	BY	MEX	CDN
.	C	S	LV	LT	F	SK	LT	T	BY	F	A	RA
.	GR	CH	LT	N	C	CDN	T	VN	NZ	I	IRL	UA
25	CH	B	FIN	CDN	GB	LT	NL	SK	LV	T	NZ	PL
.	KWT	GR	C	SLO	T	S	CH	CH	RA	FIN	I	NZ
.		KWT	GR	BG	BG	N	BG	NL	SLO	CZ	CDN	BG
.		CY	B	TPE	B	BG	S	NZ	GB	CDN	LT	F
.			CY	B	S	FIN	NZ	DK	SK	S	NL	DK
30			SLO	FIN	FIN	EST	EST	PL	LT	BG	SK	NL
.				GR	SLO	LV	CDN	SLO	I	N	BG	B
.				CY	GR	CH	MEX	MEX	DK	MEX	KZ	RO
.				MEX	MEX	MEX	N	LV	NL	CH	DK	KZ
.					N	SLO	SLO	N	IRL	SLO	CH	LT
35					CH	B	LV	CY	N	EST	CZ	CH
.					YV	CY	CY	BG	MEX	CY	FIN	SLO
.					CY	GR	B	S	CH	LV	B	EST
.					KWT	TR	GR	LT	CY	DK	S	S
.						YV	FIN	E	E	NZ	CY	YV
40						C	YV	B	FIN	GR	EST	CY
.						KWT	KWT	GR	BG	KZ	LV	HR
.							C	FIN	YV	E	SLO	I
.								YV	GR	IRL	YV	RI
.								C	B	B	BR	N
45								KWT	RI	KS	E	AZ
.									KWT	YV	N	IRL
.									C	RI	RI	E
.											GR	LV
.											ROU	GR
50											C	BR

(List of abbreviations see 152)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**	**H**	**GB**	**J**	**TR**	**USA**
1	RC	RC	RC	RC	ROK	RC	RC	RC	TPE	RC	RC	TPE
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS	RC	T	ROK	ROK
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA	ROK	ROK	RUS	RUS
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK	RUS	J	RI	IND
5	IR	A	BY	D	AZ	VN	ROK	T	SGP	TPE	USA	RC
.	TR	UA	RUS	PL	TPE	T	D	BY	J	H	T	SGP
.	IND	USA	IND	TPE	T	J	T	VN	USA	CZ	SGP	J
.	AUS	PL	SGP	H	RA	Pl	IND	TPE	H	SGP	CDN	D
.	TPE	IND	D	TR	D	IND	H	H	IR	USA	H	H
10	T	D	TPE	VN	IND	D	SK	SGP	GB	IR	IR	UA
.	SGP	IR	UA	IND	A	SK	LT	KZ	RO	RUS	TR	RI
.	PL	H	PL	IR	CZ	DK	USA	A	T	TR	IND	USA
.	RO	RUS	CDN	RO	UA	SGP	VN	PL	D	LT	CZ	BY
.	F	CDN	CZ	LT	PL	BR	GB	IR	IND	D	F	VN
15	SK	TR	RO	CZ	AUS	CDN	BY	IND	PL	PL	J	RO
.	H	AUS	KZ	USA	TR	AZ	EST	RO	AUS	GB	TPE	LIT
.	VN	GB	VN	SGP	H	UA	UA	AUS	A	IND	D	CZ
.	CZ	SGP	EST	CDN	SK	USA	RI	D	BY	RI	SK	KZ
.	RA	E	GB	AZ	USA	H	IR	SK	VN	RO	KZ	RA
20	BY	SK	AUS	AUS	GB	CZ	RO	TR	F	A	AUS	PL
.	C	BY	H	KZ	RO	AUS	AUS	LT	RI	VN	VN	SK
.	D	VN	SK	GB	BY	IRL	A	EST	TR	SK	RO	IR
.	GB	FIN	USA	J	SGP	F	KZ	I	LT	CDN	GB	A
.	UA	F	YV	A	J	IR	SGP	GB	UA	EST	BY	GB
25	A	LT	IND	BY	RI	A	NZ	CDN	EST	AUS	PL	AUS
.	MEX	CZ	F	SK	LV	TR	CZ	NZ	CZ	UA	A	IL
.	DK	KZ	A	T	BG	RI	F	BR	SK	F	LT	HR
.	CDN	LV	I	RA	HR	GB	TR	USA	CDN	RA	EST	BR
.	EST	NL	TR	EST	MEX	RO	J	LV	I	NZ	RA	CDN
30	RI	RO	AZ	F	KZ	NL	ARM	RI	RA	BY	UA	NZ
.	HR	RA	MEX	NZ	LT	HR	SLO	F	NZ	KZ	FIN	TR
.	I	EST	LT	SLO	F	LT	RA	CZ	TM	BR	SLO	EST
.	N	HR	NL	HR	EST	KZ	BR	J	MEX	IL	I	LV
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK	KZ	HR	BR	F
35	CY	NZ	HR	NL	I	EST	I	RA	IL	SLO	HR	ARM
.	KZ	I	J	I	DK	RA	MAL	MEX	BR	FIN	NZ	I
.	B	DK	DK	CH	SLO	BR	IL	SLO	HR	DK	TM	NL
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL	AZ	NL	LV	TM
.	NZ	N	GR	RI	NL	LV	NL	AZ	DK	E	S	DK
40	CH	YV	LT	S	IRL	MAL	CH	HR	S	I	NL	TJ
.	E	MEX	E	BG	GR	S	S	TM	LV	LV	PE	YVA
.	FIN	BR	TM	KS	NZ	IRL	LV	BG	IRL	BG	PK	BG
.	SLO	S	BR	E	KS	IL	DK	MGL	FIN	CR	TJ	SLO
.	NL	RI	BG	GR	S	FIN	MD	IRL	N	CH	E	CH
45	LV	TM	CH	BR	B	IS	E	MAL	E	IRL	MEX	FIN
.	BR	B	NZ	TM	BR	I	BG	E	NL	MEX	CH	MEX
.	S	IRL	IS	CY	CH	CY	TM	S	MGL	MGL	MGL	MGL
.	YV	CH	IRL	YVA	P	N	HR	NL	PE	MAL	IL	T
.	IRL	C	CY	IRL	IS	TM	PK	CH	PK	N	CY	PK
50	GR	CY	KS	IS	N	CH	N	ROU	SLO	S	BG	AZ

(List of abbreviations see 152)

	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
IChO held in	**RUS**	**VN**										
1	RC	SGP										
.	ROK	UA										
.	TPE	RUS										
.	USA	VN										
5	H	TPE										
.	SGP	RC										
.	RUS	USA										
.	PL	TR										
.	UA	RO										
10	IND	T										
.	VN	IR										
.	T	PL										
.	BY	ROK										
.	J	RI										
15	KZ	J										
.	IR	BY										
.	SK	GB										
.	CZ	D										
.	RI	LT										
20	D	IND										
.	RO	SK										
.	A	CZ										
.	LIT	H										
.	AUS	AUS										
25	GB	UZ										
.	TR	CDN										
.	NZ	SRB										
.	HR	RA										
.	F	MEX										
30	DK	A										
.	MD	NZ										
.	CDN	EST										
.	LV	KZ										
.	SLO	MAL										
35	RA	KSA										
.	SRB	HR										
.	BR	DK										
.	EST	BR										
.	UZ	NL										
40	AZ	PK										
.	I	F										
.	E	I										
.	IL	BG										
.	CY	E										
45	N	SLO										
.	ARM	TM										
.	PK	LV										
.	CH	CH										
.	BG	PE										
50	TJ	N										

(List of abbreviations see 152)

List of abbreviations

A	Austria
ARM	Armenia
AUS	Australia
AZ	Azerbaijan
B	Belgium
BG	Bulgaria
BR	Brazil
BY	Belarus
C	Cuba
CDN	Canada
CH	Switzerland
CS	Czechoslovakia
CY	Cyprus Republic
CZ	Czech Republic
D	Germany
DDR	German Democratic Republic
DK	Denmark
E	Spain
EAK	Kenya
EST	Estonia
ET	Egypt
F	France
FIN	Finland
GB	United Kingdom
GR	Greece
GUS	Commonwealth of Independent States
H	Hungary
HR	Croatia
I	Italy
IL	Israel
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgyzstan
KSA	Saudi Arabia
KWT	Kuwait
KZ	Kazakhstan
LV	Latvia
LT	Lithuania
MAL	Malaysia
MD	Moldova
MEX	Mexico
MGL	Mongolia
N	Norway
NL	Netherlands
NZ	New Zealand
P	Portugal
PE	Peru
PK	Pakistan
PL	Poland
RA	Argentina
RI	Indonesia
RC	China
RO	Romania
ROK	South Korea
ROU	Uruguay
RUS	Russian Federation
S	Sweden
SGP	Singapore
SK	Slovakia
SLO	Slovenia
SRB	Serbia
SU	Soviet Union
T	Thailand
TJ	Tadzhikistan
TM	Turkmenistan
TPE	Chinese Taipei
TR	Turkey
UA	Ukraine
USA	United States of America
UZ	Uzbekistan
VN	Vietnam
WAN	Nigeria
YU	Yugoslavia
YV	Venezuela