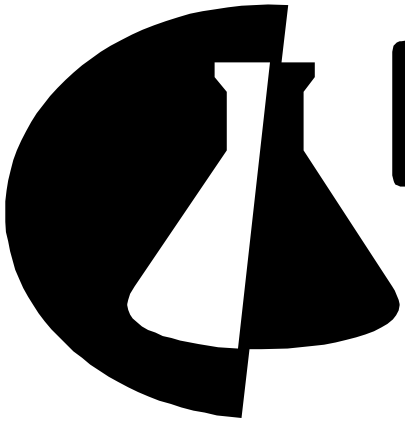

39. International Chemistry Olympiad Russia 2007

National German Competition

Volume 13

The 39th International Chemistry Olympiad

Chemistry: art, science and fun

National German Competition

Volume 13

Preface

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

The problems to be solved in the 1st round are sent to all highschools. To solve the problems the students may use all resources available, e.g. textbooks 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, excursions to chemical plants or universities and cultural events 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 the solutions are collected

In the appendix you find tables of historical interest.

Acknowledgements

It is a great pleasure to thank the many people whose help and suggestions were so valuable in preparing and reviewing all the problems and in helping us to perform the third and the fourth round.
I thank Dr. Angela Koch who reviewed my English translations.

Wolfgang Hampe

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Part 1

The problem set of the four rounds

First Round (homework)

Problem 1-1 Aspects of a Salt

A great amount of the chemical elements are found in nature as compounds in the form of salts. As you may expect most of these natural salts are only moderately or not at all soluble in water.

Many salts e.g. sodium hydroxide lead to a heating of the solution when dissolved in water, while others e.g. ammonium chloride let a solution cool down when dissolved.

Solubility and heat tonality during dissolution depend on two quantities, solvation energy and lattice energy.

In case of water as solvent solvation energy is called hydration energy. It is the energy which is set free by electrostatic interaction between water molecules and charged ions.

Lattice energy is the energy which is released when different charged ions approach each other from infinity to form a crystal. It tells you something about die bond strength between the ions in the solid:

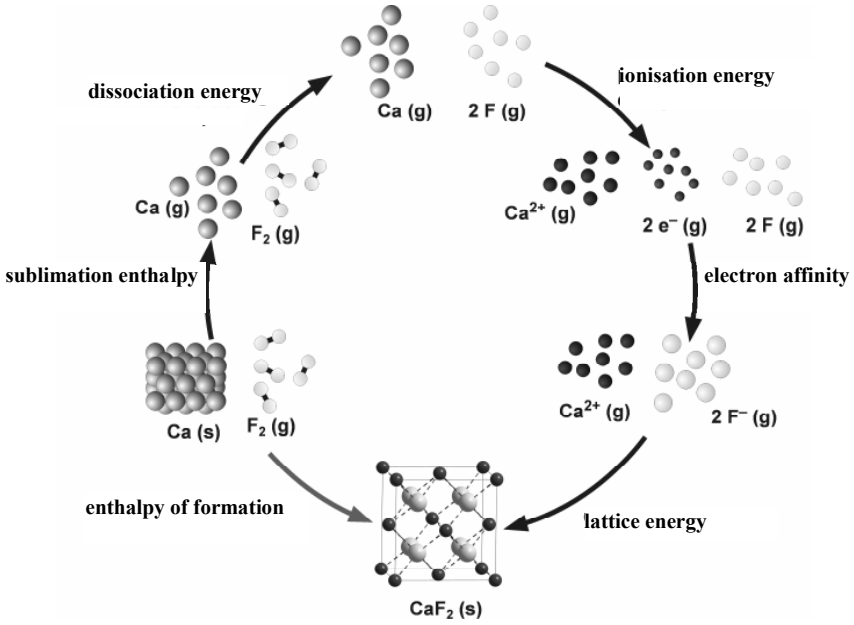
$$b\ M^{a+}\ (g) + a\ X^{b-}\ (g) \longrightarrow M_bX_a\ (f)$$

Both energies play an important role during the dissolution of a salt.

The lattice energy can only in exceptional cases be determinated directly. Nevertheless for many salts it can be found approximately by using other experimentally determinated data with the help of a Born-Haber-cycle. For this purpose the energies of all partial steps as well as of the enthalpy of formation of the ionic compound must be considered.

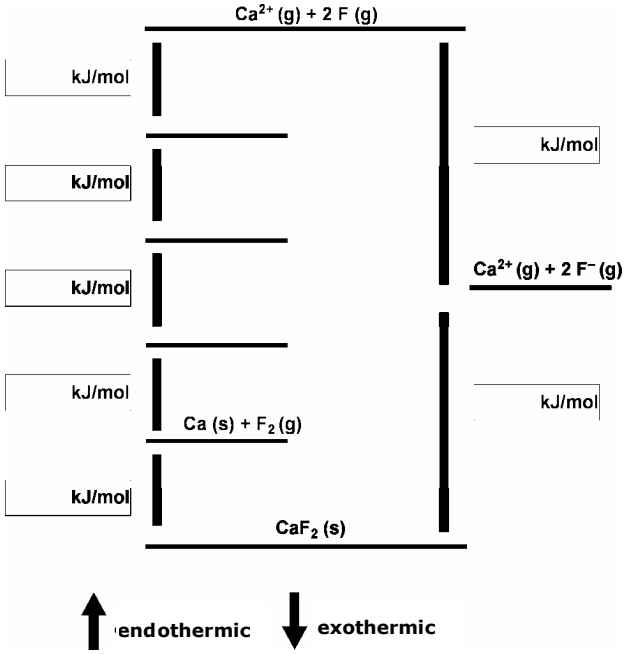
For calcium fluoride the following energies of the partial steps as shown in the diagram on the next page can be assumed:

Ca (s)	$\longrightarrow$	Ca (g)	$\Delta H = +\ 178.2$ kJ/mol
Ca (g)	$\longrightarrow$	Ca^+ (g)	$\Delta H = +\ 589.7$ kJ/mol
Ca^+ (g)	$\longrightarrow$	Ca^{2+} (g)	$\Delta H = +1145.0$ kJ/mol
½ F_2 (g)	$\longrightarrow$	F (g)	$\Delta H = +\ 79.0$ kJ/mol
F (g)	$\longrightarrow$	F^- (g)	$\Delta H = -\ 322.0$ kJ/mol
Ca (s) + F_2 (g)	$\longrightarrow$	CaF_2 (s)	$\Delta H = -1219.6$ kJ/mol



a) *Copy the diagram below and fill in the respective reactions of the partial steps of the cycle as well as the appropriate energy values (the lengths of the lines do not correspond to the values of the corresponding energy). Mark endo- and exothermic processes by changing the lines into arrows.*

Calculate the lattice energy of calcium fluoride.



In nature calcium fluoride is found as the mineral fluorite which is hardly soluble in water. Generally the solubility of an ionic compound can be quantified by the solubility product. The solubility product of calcium fluoride at 25°C is given by $pK_L = 10.52$.

b) Write the mathematical equation for the solubility product of calcium fluoride. Calculate die solubility of calcium fluoride in pure water at 25°C in g/L. Show your calculation.

Calcium fluoride is the starting material to produce hydrogen fluoride. It reacts with concentrated sulfuric acid at 200 – 250°C in a rotary kiln, 20 m long and 3 m wide, made from steel.

c) Write the equation of the reaction of sulfuric acid with calcium fluoride.

d) Calculate the volume (in mL) of sulfuric acid (96 % m/m, d = 1.84 g /cm^3) which is necessary to produce 1000 L of hydrogen flurorid. Assume complete reaction at 1.013 bar isobar and 200°C.

To produce the element fluorine hydrogen fluoride is needed. You get fluorine by electrolysis of a mixture of moisture-free hydrogen fluoride and potasium fluoride.

e) Chlorine can be produced by elctrolysis of an aquous solution of a chloride. Explain the reason why this process is not possible for fluorine. Argue on the base of standard potentials.
Write down the reactions at the cathode and the anode of an electrolysis of an aquous solution of sodium fluoride.

Problem 1-2 Pigments

Within living memory men use pigments to memorize and pass on important information by scriptures and images. Because of their extraordinary light and weather resistence inorganic pigments are especially suitable for durable drafts and paintings. At first naturally occuring pigments, often of limited availability, made of finely ground minerals and earths were applied. Later on synthesis of products indentical to natural pigments or of totally new pigments opened undreamed-of possibilities. First syntheses were performed in the ancient world and even nowadays new pigments are produced.
In the following text the syntheses of four inorganic pigments are described:

1) 5.0 g of sodium dichromate are finely ground with 0.62 g of sulfur, heated up to 800°C. The product is leached out with water.
2) 3.0 g of lead(II) oxide are finely ground with 1.0 g tin(IV) oxide amd heated up to 650°C.
3) Lead(II) oxide is annealed while exposed to air.
4) 2.0 g of silica, 0.66 g of copper(II) oxide, 0.83 g of calcium carbonate and 0.75 g of borax are finely ground and annealed at 900°C for several days.

a) Write the names of the produced pigments, their compositions and the reaction equations of the syntheses.

b) What is the benefit of borax in synthesis 4)? How can you purify the raw product easily?

c) Cite one more blue (iron containing), yellow (lead containing), green (copper but no other metal containing) and red (mercury containing and used in painting) inorganic pigment and record a possible synthesis by writing reaction equations.

In a painter's shop an old unlabeled can with a green pigment in it was found. The painter would like to use it but has to find out first the exact composition of the green pigment. Therefore 1.818 g of the green powder are opened up. The solution is filled up with diluted sulfuric acid. 20mL of this solution are treated with excess of potassium iodide and afterwards titrated with sodium thiosulfate (c = 0.100 mol/L) until the brown colour disappears. Consumption: 16.45 mL

d) Specify which metal is detected by this way.
Write all reaction equations of this determination method.
Calculate the content of Me in this sample.

e) Could the green powder be a mixture of pigments of part a)? Justify your answer.

Another analysis shall reveal the exact composition of the green powder. Therefore 2.000 g are heated under airtight conditions. Besides 1.439 g of a black, not volatile compound water vapor and a gas, which clouds barium-hydroxide solution, form.

f) Determine the compostion of the green pigment.

Problem 1-3 Reactions of Benzene

The reaction of benzene with n-butylchloride (1-chloromethane) leads in the presence of Lewis acids (MeX_3) to a mixture of mono- and polysubstituted derivates of benzene.

a) Give a definiton of Lewis and examples of the type Typs MeX_3.

b) Enunciate the reaction mechanism of the reaction mentioned above, the formation of a monosubstituted benzene compound (active reagent, intermediate, formation of the product).

c) There is also a high yield of polysubstituted compounds. Explain why! How can you lower this yield?

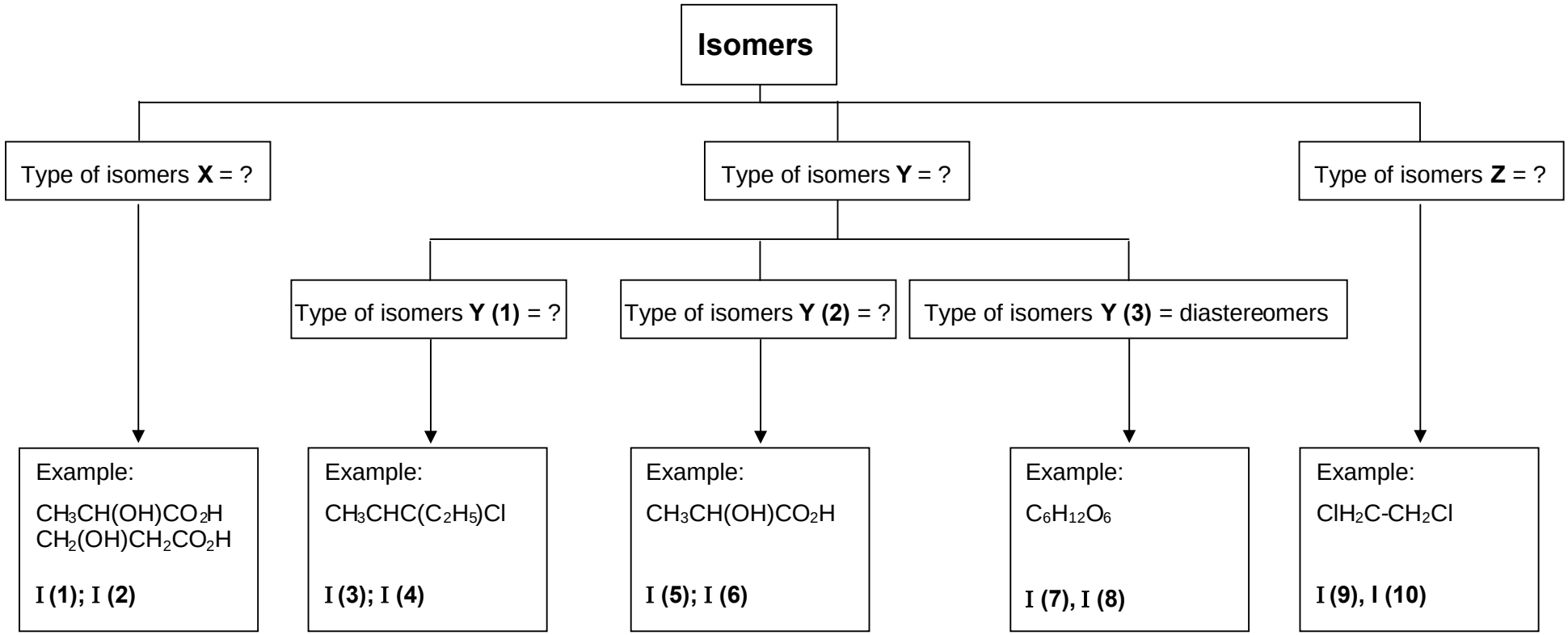
d) In the mixture of products of the reaction above mentioned you also find tert.-butylbenzene compounds. Give the reason of their formation.

Problem 1-4 Types of Isomers

The diagram on the next page shows a survey of diffrerent types of isomers.

a) Draw the structures and give the exact names of the compounds **I(1)** to **I(6)**, draw the structures of **I(7)** and **I(8)** and the Newman projections of **I(9)** and **I(10)** .

b) Which kind of isomers are characterised by **X, Y, Y(1), Y(2)** and **Z** ?
Give the respective names of the types of isomers.


Isomers
Type of isomers **X** = ?
Type of isomers **Y** = ?
Type of isomers **Z** = ?
Type of isomers **Y (1)** = ?
Type of isomers **Y (2)** = ?
Type of isomers **Y (3)** = diastereomers
Example:
$CH_3CH(OH)CO_2H$
$CH_2(OH)CH_2CO_2H$
I (1); I (2)
Example:
$CH_3CHC(C_2H_5)Cl$
I (3); I (4)
Example:
$CH_3CH(OH)CO_2H$
I (5); I (6)
Example:
$C_6H_{12}O_6$
I (7), I (8)
Example:
$ClH_2C\text{-}CH_2Cl$
I (9), I (10)

Second Round (homework)

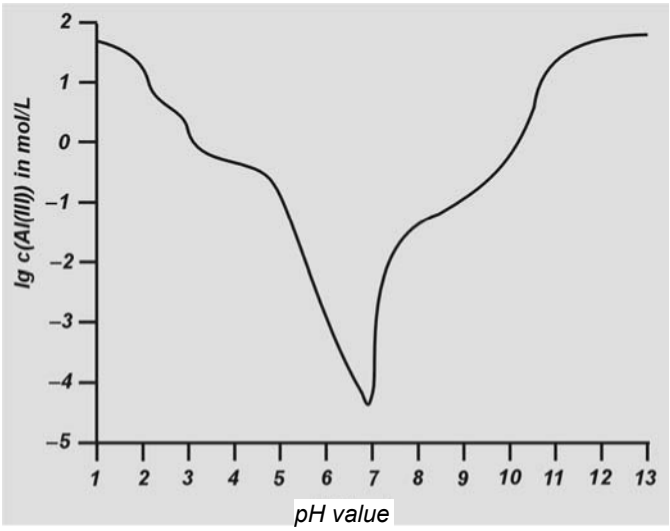
Problem 2-1: Aluminium and Some of its Compounds

Aluminium is after steel the most important metal used. Raw material for the production of aluminium is bauxite with the main components aluminium oxid and iron oxide.
The composition of bauxite is to be analysed: 0.3437 g of bauxite are opened up. Al(III) and Fe(III) are precipitated with ammonia as water containing hydroxides. Annealing to constant weight results in 0.2544 g of iron and aluminium oxide.
To determinate the content of iron another sample of 0.6444 g of bauxite is opened up and treated with sodium hydroxide. Annealing of the precipitate of the residue leads to 0.1588 g of Fe(III)-oxide.

a) Calculate the mass content (percentage) of iron and aluminium in the examined bauxite.

To seperate both oxides in large scale mostly the „Bayer“-process is used which takes advantage of the different solubilities of the hydroxides of both metals.

The sparingly soluble iron hydroxide is filtered off. Diluting the remaining solution with water leads to precipitation of aluminium hydroxide.



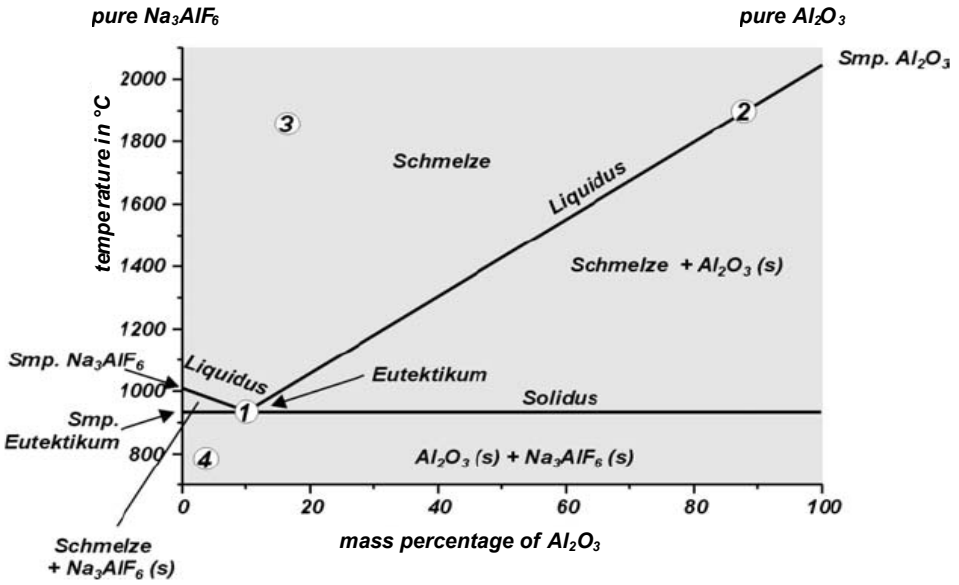
Aluminium(III) concentration in a saturated aqueous solution depending on pH value at 25°C

b) Account for the strong pH dependance of the concentration of Al(III) in an aqueous solution.

Aluminium is technically produced by fused-salt electrolysis of aluminium oxide and cryolite (Na_3AlF_6). Therefore an eutectical mixture is used where the melting-point depression is

greatest (Aluminium oxide has a melting point of 2045°C, cryolite of 1009°C, the eutectical mixture with a fraction of 10 % of Al_2O_3 melts already at 935°C).

The depencance of the melting temperatures on the concentration of the constituents of a binary mixture at constant pressure can be depicted in a melting diagram. With the help of Gibbs phase law (number of phases + number of degrees of freedom = number of ingridients + 2) you may determine how many parameters can be varied without a change in the system.



(Translation: Smp. = melting point, Schmelze = melt, Eutektikum = eutectic mixture)

Melting diagram of the system aluminium oxide/cryoliter

c) Determine the degrees of freedom of the designated points 1, 2, 3 and 4 using Gibbs phase law.

Aluminium(III) chloride has a melting point of only 192.4°C. Nevertheless it is widely abstained from using $AlCl_3$ for electrochemical production of aluminium.

d) Give the reasons.

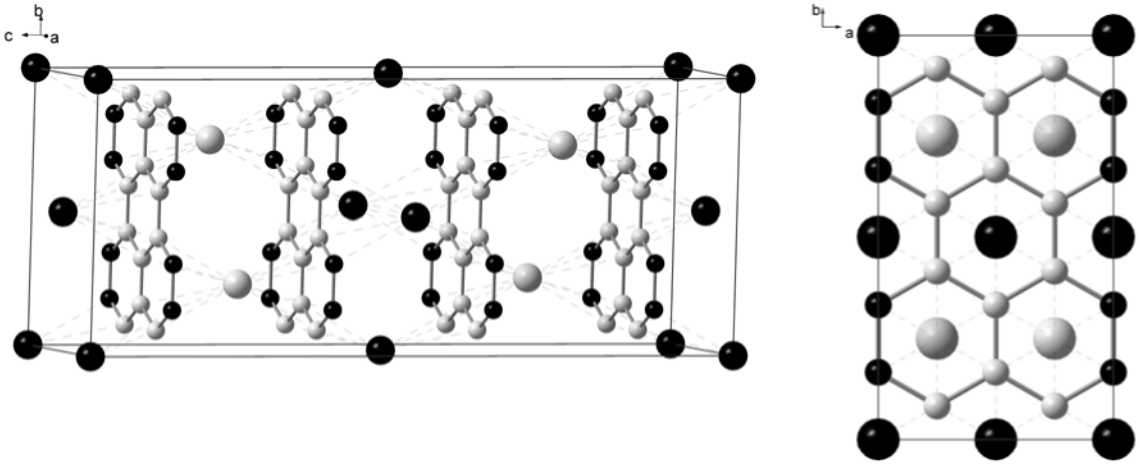
Aluminium oxide reacts at high temperatures with carbon to form aluminium carbide. Aluminium carbide reacts with water to from a gas X among other compounds.

	ΔH_f^0 in kJ/mol	S_0 inJ/(mol·K)
Al_4C_3 (s)	- 129.2	105
H_2O (l)	- 285.83	69.91
gas X	- 74.8	186.26
$Al(OH)_3$(s)	- 2567.0	140.2

e) Write the reaction equations of the formation of aluminium carbide and of the reaction of aluminium carbide with water including the formula of gas X.
Calculate the equilibrium constant of the hydolysis of aluminium carbide at 25 °C. Which side of the reaction is favored ?

f) Which amount of aluminium carbide (in g) is needed to produce 100 L of gas X (p = 1013 hPa, T = 298 K)?

Intercalation compounds may also be formally counted as carbides. Many electron donors as alkali, alkaline earth and lanthanoide metals intercalade in a graphite matrix with different compositions. The illustration shows the unit cell of a carbon/potassium intercalation compound.



Unit cell of an intercalation compound of potassium in graphite from two different points of view (the black atoms are partially situated in adjacent unit cells; big atoms: potassium, small atoms: carbon).

g) Calculate the empirical formula of the displayed compound.

The oxide of aluminium is found as corundum in several natural deposits. The colourless corundum is the number five in hardness of all known substance. Due to this fact it is used as polishing and grinding agent In its crystal structure the O^{2-}- ions form hexagonal close-packing, the Al^{3+}-ions occupy 2/3 of the octahedral gaps. The exchange of a small percentage of aluminium cations by other metal ions leads to intensely coloured gem stones. The red ruby contains chromium(III) cations, the blue sapphire iron(II)- and titanium(IV)-cations.

h) Explain why corundum is colourless and elucidate the colour of ruby with the help of crystal-field splitting. Where does the colour of sapphire come from?

Green chromium(III) oxide shows the structure of corundum. Here too the chromium(III) ions are responsible for the colour.

i) Why do chromium(III) oxide and ruby differ in colour? Give an explanation using the crystal-field theory.

Problem 2-2 Synthesis of a Copper Complex

A is a five membered cyclic compound composed from 71.61 % C, 7.51 % H, 20.88 % N (mass percent) with a molar mass of 67 g/mol.
B is an aromatic compound with the empirical formula $C_{11}H_{14}O$, which reacts with Tollens' reagent. It is substituted in p position, its ^{1}H- and ^{13}C-NMR spectra are given below. In the IR spektrum you find an intensive band at approx. 1700 cm^{-1}.
A and B are mixed and dissolved in propionic acid and filled in a flask with reflux condensor. They react in the molar ratio of 1:1 at boiling temperature to form the intensive violet coloured macrocyclic compound C (85.88 % C, 7.45 % H, 6.67 % N) with a molar mass of 839 g/mol. In the ^{1}H-NMR spectrum of C you find 5 signals at -2.74, 1.61, 7.75, 8.15 and 8.87 ppm with the intensity ratio of 1 : 18 : 4 : 4 : 4.

a) Determine the empirical formala and the structure of A.

b) Is A aromatic or antiaromatic? Account for your decision.

c) Give the structure and the name of B..

d) Determine the empirical formula of C. How many molecules of A and B form a molecule C?

e) Describe the first steps of the reaction mechanism (total reaction of one molecule of B). Which kind of reaction mechanism is concerned?

f) Draw one resonance structure of C.

During the reaction of A and B to form C you find an oxidation (dehydrogenation).

g) Specify which oxidizing agents could be possible in this process.

Compound C reacts with copper(II) acetate in dimethyl formamide as solvent to form complex D ($CuC_{60}H_{60}N_4$).

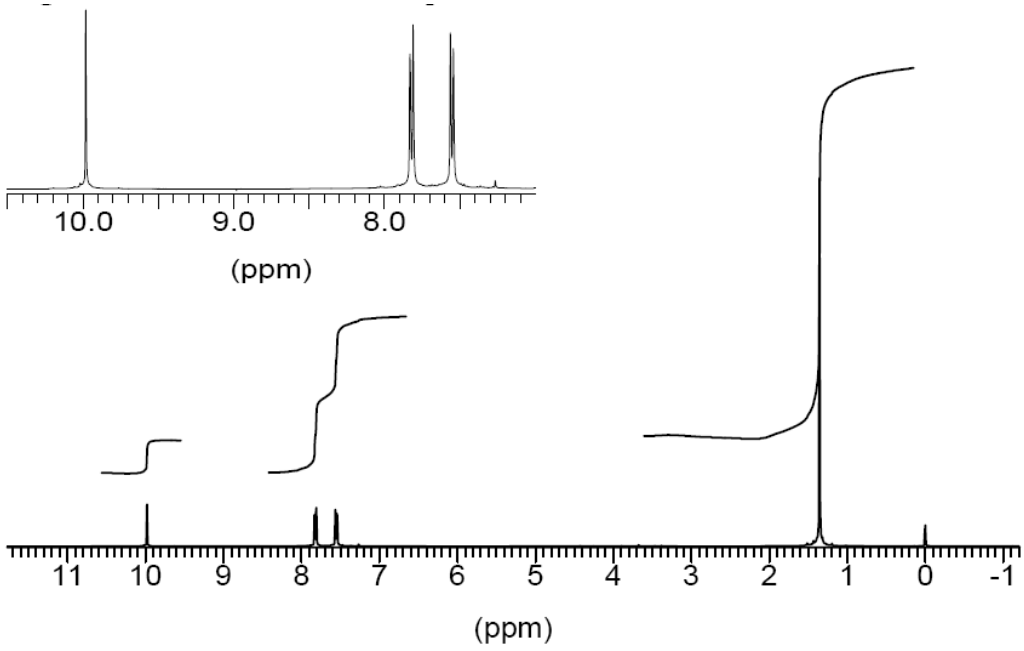
h) Draw one resonance structure of the macrocyclic complex D.

i) Give the number of π electrons in the largest aromatic system of D and show it in an example of your own choice.

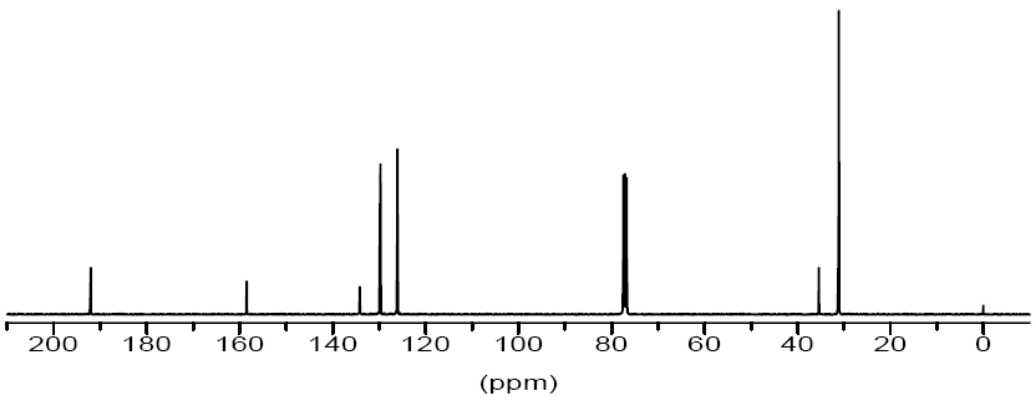
j) Plot a diagram of the energy levels of the 3d orrbitals of the Cu^{2+} ions in the ligand field of the ligand C^{2-} in correct energetic order.

k) The paramagnetic d^9 valence-electron system of Cu^{2+} ions may principally lead to diamagnetic compounds. Explain how this can happen.

^{1}H-NMR spectrum of compound B (with a enlarged cutout)



^{13}C-NMR spectrum of compound B**:**

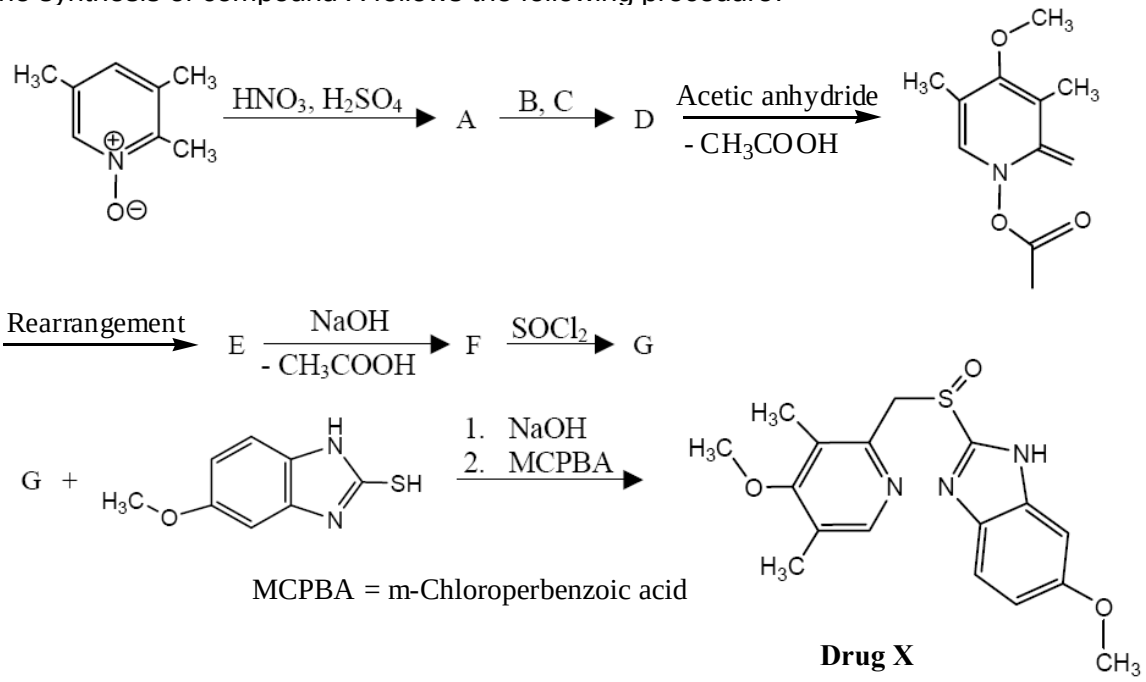


The signal at approx. 77 ppm is due to the solvent.

Problem 2-3 Study of a Drug

A drug X is looked at. It inhibits the pumping of protons and suppresses the secretion of chloric acid in the stomach. Amongst others it is used to treat gastric ulcer.

The synthesis of compound X follows the following procedure:



a) Write the name of the starting compound and plot the structures of A, D, E, F, G.

b) Give the mechanism of the reaction of D with acetic anhydride.
Hint: Be aware of tautomerism.

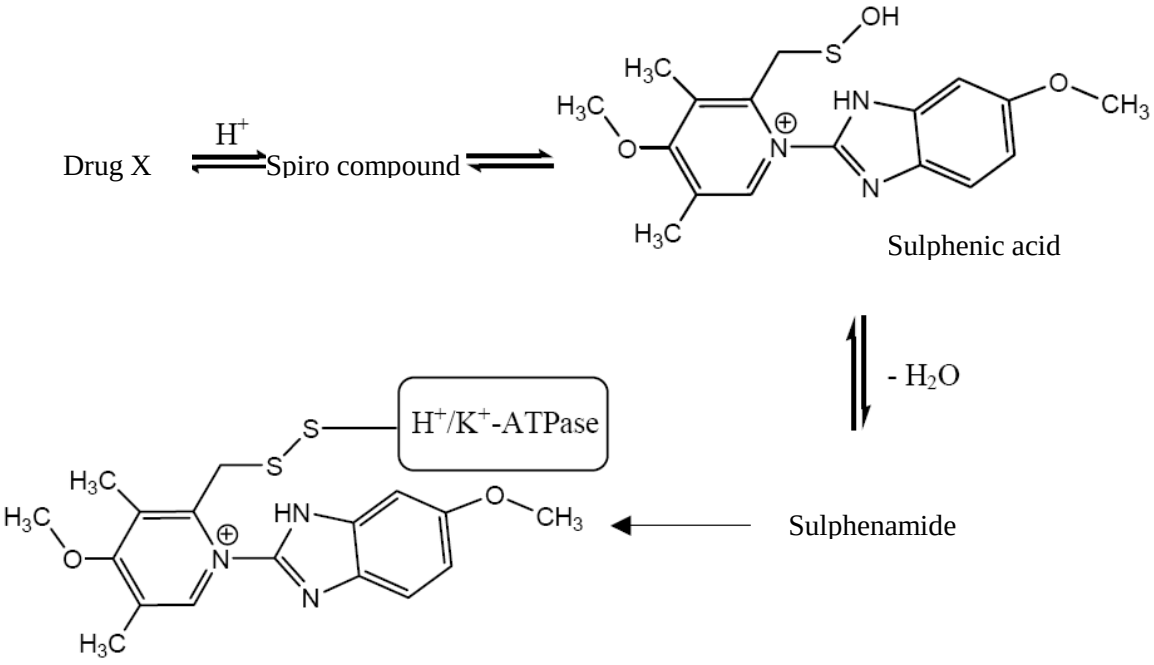
c) Give the reaction mechanism of the rearrangement. Which is the driving force of this reaction?

d) For what was MCPBA (m-chloroperbenzoic acid) used in the last step of the synthesis?

e) Is the product of the sythesis chiral? Account for your answer.

Compound X is a "prodrug". Prodrugs are materials which come pharmacological into operation after metabolism in the body. The drug X reacts only in acidic surrounding to form the active inhibitor of proton pumps (H^+/K^+-ATPase).
This happens via a spiro compound as intermediate followed by rearrangement to form a sulphenic acid. Sulphenic acid reacts by cleavage of water to form the active metabolite, a cyclic sulphenamide. The sulfenamide reacts with H^+/K^+-ATPase by forming a disulphide bridge and thus the enzyme is blocked irreversible

f) Plot the structures of the spiro compound and of the sulphenamide.



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Problems Round 3

Test 1 Berlin and Köln 2007: Problems 3-01 to 3-10

Test 2 Berlin and Köln 2007: Problems 3-11 to 3-20

time	5 hours,
your name	write it on **every** answer sheet,
relevant calculations	write them down in 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

$\Delta G = \Delta H - T \cdot \Delta S$ $\Delta G = - \Delta E \cdot z \cdot F$ $\Delta G = - R \cdot T \cdot \ln K_{th}$

$S^o(T) = S^o(298) + Cp \cdot \ln(T/298)$

$\Delta U_{reaction} = \Delta H_{reaction} + W$ (p,V-work only at constant pressure: $W = - p \cdot \Delta V$)

$K_{th} = K_p \cdot p_o^{-\Delta n}$; $K_{th} = K_c \, (mol/l)^{-\Delta n}$ $\ln (Kp_1/Kp_2) = -\Delta H/R \cdot (T_1^{-1} - T_2^{-1})$

$p \cdot V = n \cdot R \cdot T$

Nernst equation: $E = E_0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_{Ox}/c_{Red})$

for metals $c_{Red} = 1$ mol/L
for non-metals $c_{Ox} = 1$ mol/L

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

Bragg's equation: $n \cdot \lambda = 2a \cdot \sin\vartheta$

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

ε molar absorption coefficient
d length of the cuvette
c concentration

Henry's law for dissolving gases in water (A(g) $\rightleftharpoons$ A(aq))

$K_H = \frac{c(A(aq))}{p(A(g))}$ K_H Henry constant

$R = 8{,}314$ JK^{-1}mol^{-1} $F = 96485$ Cmol^{-1} $N_A = 6{,}022 \cdot 10^{23}$mol^{-1}

$p_o = 1{,}000 \cdot 10^5$ 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 3-1 Multiple Choice (with one or more correct answers)

a) Which relationships between the radii of these species are correct?

A) $r(Na) < r(Na^+)$; $r(F) < r(F^-)$	**B)** $r(Na) > r(Na^+)$; $r(F) > r(F^-)$	**C)** $r(Na) < r(Na^+)$; $r(F) > r(F^-)$	**D)** $r(Na) > r(Na^+)$; $r(F) < r(F^-)$

b) In which reaction do you expect an increase of entropy?

A) $H_2O(l) \longrightarrow H_2O(s)$	**B)** $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$	**C)** $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	**D)** $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

c) M is a trivalent metal which reacts with acids to form hydrogen and a salt. 2 mol of M react completely with a certain acid H_nA (n = 1, 2 or 3) to produce 3 mol of hydrogen. Which of the following formula(s) match this question?

A) MA	**B)** M_2A	**C)** M_3A_2	**D)** M_2A_3	**E)** MA_3

d) A metal from period 4 is added to water and a vigorous reaction takes place with the evolution of a gas. Which of the statements are correct?

1. Oxygen is evolved.
2. Hydrogen is evolved.
3. The resulting solution is acidic.
4. The resulting solution is basic.

A) 1 and 3 only	**B)** 2 and 3 only	**C)** 2 and 4 only	**D)** 1 and 4 only

e) Which of the following pairs are corresponding acid-base pairs?

A) HCO_3^-/CO_3^{2-}	**B)** NH_4^+/NH_2^-	**C)** HCl/Cl^-	**D)** $HSO_3^-/S_2O_3^{2-}$	**E)** H_3O^+/OH^-

f) The ^1H NMR spectrum of an unknown compound having the molecular formular $C_3H_5Cl_3$ shows only two sets of ^1H NMR signals at δ 2.20 ppm (3 H singlet) and δ 4.02 ppm (2 H singlet) respectively. What is a likely structure for this unknown sample ?

A) $Cl_3C\text{-}CH_2\text{-}CH_3$	**B)** $ClH_2C\text{-}CCl_2\text{-}CH_3$	**C)** $ClH_2C\text{-}CHCl\text{-}CH_2Cl$	**D)** $ClH_2C\text{-}CH_2\text{-}CHCl_2$

g) How many aromatic isomers exist of C_7H_7Cl ?

A) 2	**B)** 3	**C)** 4	**D)** 5	**E)** 6

h) ^8_3Li is a radioactive isotope that emits β^- particles to form an unstable nuclid, that emits α particles. Which is the stable isotope Y that results from the following chain reaction

$$^8_3Li \longrightarrow X + \beta^- \qquad X \longrightarrow Y + \alpha$$

A) ^3_2He	**B)** ^4_2He	**C)** ^6_4Be	**D)** $^{12}_6C$

Problem 3-2 Acids

There are two acids, monochloroacetic acid (c = 0.01 mol/L , $K_1 = 1.4 \cdot 10^{-3}$) and trichloro-acetic acid (c = 0.01 mol/L , $K_2 = 0.2$).

a) Calculate the pH-values of these acids.

b) 100 mL of monochloroacetic acid have to be diluted to form a solution with pH = 2.9. *Calculate the voume to which the dilution has to be performed.*

c) The given acids shall be mixed to form a solution with pH = 2.3. What is the required ratio of their volumens? (Hint: Start your calculation with 1 L of monochloroacetic acid.)

Problem 3-3 VSEPR

The geometric structure of various chemical species can be determined by means of Valence Shell Electron Pair Repulsion (VSEPR) theory.

a) Consider 2, 3, 4, 5 and 6 valence electron pairs distributed around the central atom A in the molecule AX_2 or in the ion AX_2^{-n} .
Which numbers of electron pairs, containing both bonding and lone pairs, could result in a linear spatial arrangement? Explain why each arrangement may or may not lead to a linear species X-A-X.

b) Some of the electron pair arrangements could give more than one molecular shape (which then are no longer linear).
Show these additional possibilities.

c) For which of the cases of linear arrangements in a) exist species at this time?
Give the formula of one chemical species.

d) Valence Bond Theory can also be used to account for the geometries of chemical species.
Give the hybridization that corresponds to each of the geometries in question a).

Problem 3-4 Lattice and Bond Energies

Titanium(II)-oxide exists in a crystal structure similar to sodium chloride.

a) Plot a unit cell of titanium(II)-oxide

The length of the edge of the unit cell is given by a = 0.420 nm.

b) Calculate the density in g/cm^3.

Given the following data :

Sublimation enthalpie of titanium	425	kJ/mol
1. ionization enthalpie of titanium	658	kJ/mol
2. ionization enthalpie of titanium	1310	kJ/mol
Bond energy of oxygen	498	kJ/mol
Electron affinity of O	- 141,5	kJ/mol
Electron affinity of O^-	797,5	kJ/mol
Standard enthalpie of formation of TiO	- 523	kJ/mol

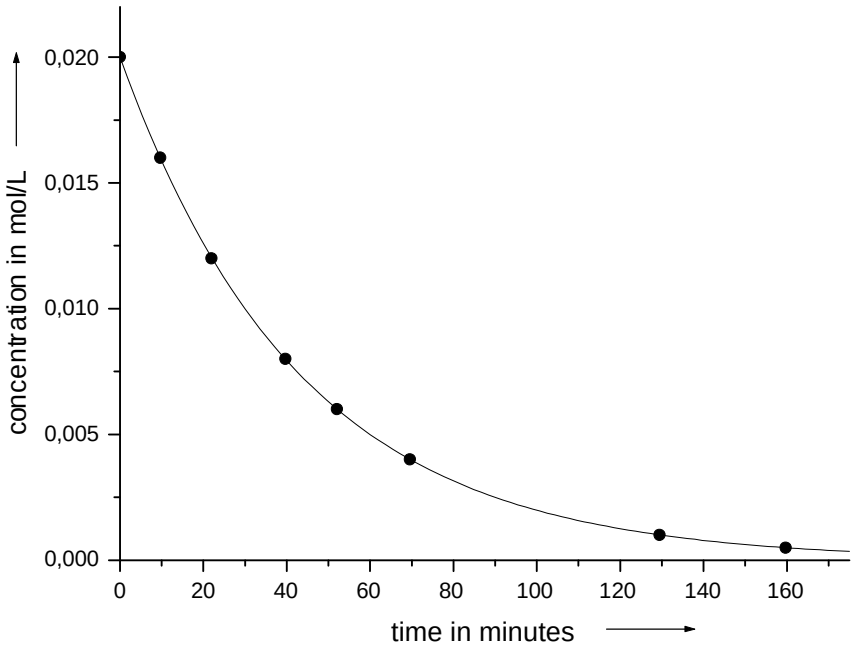
c) Calculate the lattice energy of titanium(II)oxide.

The bond energy of a N-N single bond is 163 kJ/mol, for a N≡N triple bond it is 945 kJ/mol. Four nitrogen atoms may form a tetrahedral molecule of N_4 or two N_2 molecules.

d) Which is the favorite? Account for your opinion.

Problem 3-5 Kinetics

The kinetic study of the thermal decomposition of a compouns A with the initial concentration of 0.020 mol/L lead to the plot below. It shows the concentration of A as a function of time.



a) Determine approximately the initial reaction rate by using the plot.

b) Check whether the reaction is of first order.

c) Calculate the rate constant.

Problem 3-6 Heat and Pressure

A common lecture demonstration involves electrically ignition of methanol and air in a plastic bottle. Liquid methanol is poured into a 500 mL bottle and shaken until the air is saturated with methanol vapor. The excess of methanol is poured out, the bottle is sealed and the mixture is then ignited.

a) Write a balanced equation of the reaction.

b) Determine the value of ΔH for the reaction in a).

Assume a temperature of 25°C and a pressure of $1{,}100 \cdot 10^5$ Pa. The vapor pressure of methanol at 25°C is $0.165 \cdot 10^5$ Pa. Assume that air contains 20% of oxygen and 80% of nitrogen.

c) Identify the limiting reagent in the 500 mL bottle.

d) Determine the amount of heat released by the reaction in the 500 mL bottle.

e) Show that after the reaction there is a total amount of $n_{total} = 23.44 \cdot 10^{-3}$ mol of substances in the bottle.

f) Assume that 500 J of the heat produced in the combustion is at disposal for heating the gas. Find the temperature of the gas in the bottle. Calculate the pressure at this temperature.

Substance	$CH_3OH(g)$	$CO_2(g)$	$H_2O(g)$
ΔH_F in $kJ \cdot mol^{-1}$	- 201.5	- 393.5	- 241.5

The density of the mixture after copmbustion is 1.30 $g \cdot L^{-1}$, the heat capacity of this mixture is 1.01 $J \cdot g^{-1} \cdot K^{-1}$.

Problem 3-7

Chlorosulfonic acid is a strong sulfonating agent and used in organic chemistry to introduce the sulfo group $-SO_3H$. In water it reacts to form sulfuric acid and hydrochloric acid. During the production of chlorosulfuric acid a mixture forms containing HSO_3Cl, H_2SO_4 and SO_3. The content of these compounds in technical chlorosulfonic acid has to be determined.

For this purpose 2.9426 g of the product are dissoluted 50 mL of sodium hydroxide solution (c = 1.9820 mol/L). The solution is then filled up to 100 mL.

20 mL of this solution are acidified with nitric acid and then titrated with silver nitrate solution (c = 0.1120 mol/L), consumption 35.70 mL.

Another 20 mL of the solution are titrated with hydrochlorid acid (c = 0.1554 mol/L), consumption 33.60 mL.

a) Write all equations of the reactions involved in the procedures mentioned above.

b) Calculate the composition (in mass percent) of the tested sample of chlorosulfonic acid.

Problem 3-8 Reactions of Alkenes

2-Methyl-1-butene dissolved in carbon tetrachloride reacts with hydrogen bromide to form 2-bromo-2-methylbutane.

a) Write the reaction equation.

b) Give the mechanism of this reaction.

2-Pentyl-1,3-butadiene dissolved in carbon tetrachloride reacts with an excess of hydrogen bromide.

c) Write the reaction equation. Provide the name of the product.

The reaction of 2-methyl-1-butene with hydrogen bromide is performed in water instead of carbon tetrabromide as solvent.

d) Write the reaction equation of the formation of the main product of this reaction.

e) Give the reaction mechanism of the formation of the main product.

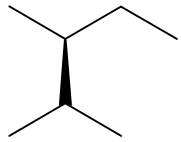
The reaction of 2-methyl-1-butene with hydrogen bromide is performed in methanol as solvent.

f) Write the reaction equation of the formation of the main product of this reaction. Give the name of the main product.

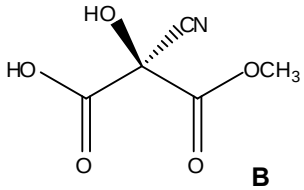
Problem 3-9 Stereochemistry

a) *Assign an asterix * to those of the molecules A to H which have a stereogenic center. Characterise the absolute configuration of the relevant molecules with the R/S nomenclature rules.*

b) *Which pairs of molecules show enantiomeric, which diastereomeric and which identical compounds?*



A



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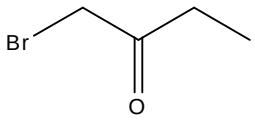

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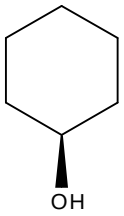

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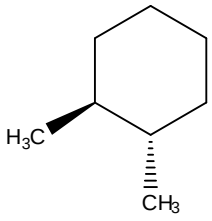

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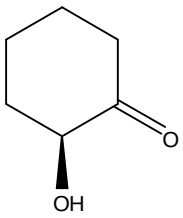

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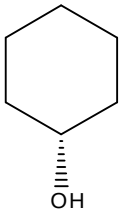

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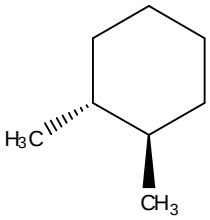


H

Problem 3-10 Reactions of Enolate Ions

Part A:

1-Bromobutane (RBr) dissolved in ethanol reacts in the presence of sodium ethoxide with diethyl malonate (malonic acid: $H_2C(COOH)_2$) to form compound **A**: $RHC(CO_2C_2H_5)_2$.

a) Write the equation of this reaction.

During this reaction malonic ester forms an enolate ion which reacts with alkyl bromide.

b) Propose the mechanism of this reaction. What kind of reaction is it?

When compound **A** is heated in a aqueous solution of an acid it undergoes hydrolysis and cleaves off carbon dioxide.

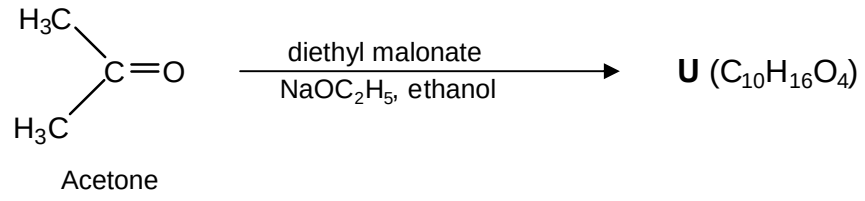
*c) Which compound **B** is formed in this reaction?*

If compound **A** dissolved in ethanol reacts in the presence of sodium ethoxide with methyl iodide compund **C** is formed.

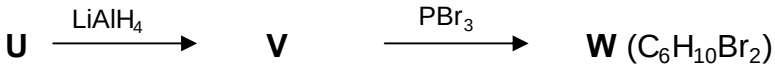
d) Write the equation of this reaction.

Part B:

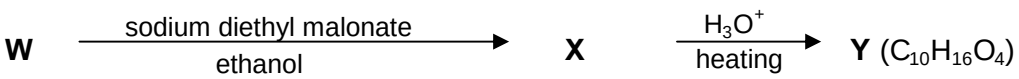
The following reaction is performed:



Acetone



Compound **W** reacts with sodium diethyl malonate to form compound **X**.
Heating **X** in acid you get compound **Y** by splitting off carbon dioxide.



*e) Draw the line-bond structures of the compounds **U** through **Y**.*

Third round, test 2

Problem 3-11 Multiple Choice (with one or more correct answers)

a) How many electrons are gained by one mole of permanganate ions, when they react totally with reducing agents in acidic solution?

A) 5	**B)** $6.02 \cdot 10^{23}$	**C)** 5 mol	**D)** $\frac{1}{5} \cdot 6.02 \cdot 10^{23}$	**E)** $5 \cdot 6.02 \cdot 10^{23}$

b) Which of the following processes is not a redox reaction?

A) Reactions in a catalyzer of a car	**B)** Darkening of a peeled apple	**C)** Precipitation of lime-stone in a dish washer	**D)** Wine becoming acidic

c) Which of the following salts shows an acidic reaction if solved in water?

A) $FeSO_4 \cdot 7H_2O$	**B)** $BaCO_3$	**C)** $NaHCO_3$	**D)** KCN	**E)** $AlCl_3$

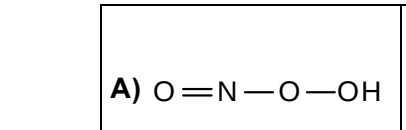
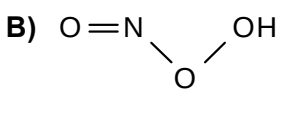
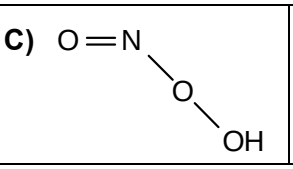
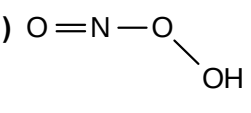
d) 0.1 molar solutions of the follwing pair of reagents are mixed at room temperature. Which mixture does not show a precipitation?

A) HCl + $AgNO_3$	**B)** NaOH + $CuSO_4$	**C)** $CaCl_2$ + Na_2CO_3	**D)** H_2SO_4 + $Ba(OH)_2$	**E)** NH_4NO_3 + K_2CrO_4

e) Which substance is expected to have the greatest absolute value of lattice enthalpy?

A) LiF	**B)** LiI	**C)** CsF	**D)** CsI

f) ONOOH is the empirical formula of peroxonitrous acid. Which is the correct structural formula considering the bond angles? (none of the bonds shown sticks out of the plain)

A) 	**B)** 	**C)** 	**D)** 

g) Which of the following organic compounds with the molar mass M has the highest boiling point?

A) Propanal (M = 58)	**B)** Acetone (M = 60)	**C)** 2-Propanol (M = 60)	**D)** Acetic acid (M = 60)	**E)** n-Butane (M = 58)

h) Which of these species are paramagnetic? 1. Ti^{4+} 2. Fe^{2+} 3. Zn^0

A) 1 only	**B)** 2 only	**C)** 3 only	**D)** 1 and 2 only	**E)** 1 and 3 only

Problem 3-12 To Fat?

A human being of 80 kg is assumend to have a content of 0.35 mass percent of potassium with a rate of 0.012 % of ^{40}K related to the total amount of potassium.

a) Calculate the average rate of disintegration (disintegrations/s) of ^{40}K (half life $4.5 \cdot 10^{10}$ y) in this person.

It was suggested to determine the content of fat in a man by measuring the radiation caused by ^{40}K.

b) Do you expect a higher or a lower amount of disintegrations per kg of mass of a stout person? Give reasons.

Problem 3-13 pH, pK, Equilibria

A solution was prepared by mixing 25.00 mL of a solution of aniline (c = 0.08 mol/L), 25.00 mL of a solution of 4-chlorobenzenesulfonic acid (c = 0.060 mol/L) and 1 mL of an indicator (HIn, c = $1.23 \cdot 10^{-4}$ mol/L). This solution then was diluted to 100.00 mL.
The absorbance of this solution was measured at 550 nm in a 5 cm - cell: A = 0.110.

a) Calculate the pH of the diluted solution.

b) Determine the pK_a - value of the indicator

(In this context do not use your calculated pH value of a). Assume pH = 5.)

Data:

pK_b(aniline) = 9.37 pK_a(4-chlorobenzenesulfonic acid) = 3.98

Molar absorbtivities at 550 nm $\varepsilon_{550}(HIn) = 2.26 \cdot 10^4$ L·mol^{-1}·cm^{-1}

$\varepsilon_{550}(In^-) = 1.53 \cdot 10^4$ L·mol^{-1}·cm^{-1}

Problem 3-14 Relations within the Periodic Table

The chemical properties of the main group elements of the periodic table vary in a characteristic way, both within in the group and within the period. The properties of hydrogen compounds of different main group elements have to be determined.

		$(BH_3)_x$		NH_3		HF
NaH	MgH_2	$(AlH_3)_y$	SiH_4	PH_3	H_2S	HCl
				AsH_3		HBr
				SbH_3		HI
				BiH_3		

a) *How is hydrogen bound in NaH and in MgH_2? Account for your answer and propose an experiment to give evidence.*

b) *Report how x and y of the hydrogen compounds of the 3rd main group differ. Explain the bond type, commonness and differences.*

c) *How does the base strength (in aqueous solution)) of the hydrogen compounds of the 5th maingroup alter with increasing molar mass (without reasons)?*

d) *How does the acid strength (in aqueous solution) of the hydrogen halides change with increasing molar mass? Give the reasons.*

e) *How does the acid strength and the vbond type change within the 3rd period. Characterise the circumstances using SiH_4 and H_2S as examples.*

Problem 3-15 Electrochemistry

Solution A with pH = 4 contains Mn^{2+} (c = 0.01 mol/L) and MnO_4^- ions (c = 0.004 mol/L). Immersing a platinum electrode in it produces the half cell A.

Solution B with pH = 9 contains potasium chromate (c = $8 \cdot 10^{-3}$ mol/L) in the presence of solid Ag_2CrO_4. Immersing a silver electrode in it produces the half cell B.

These half cells are connected with a salt bridge. The voltage of the cell is measured at 25°C: 0.573 V.

a) *Calculate the solubility product of silver chromate.*

$E°(MnO_4^-/Mn^{2+}) = 1.491$ V $\qquad$ $E°(Ag^+/Ag) = 0.800$ V

b) *Explain, why the given pH values are important for this problem.*

Manganese forms ions with different oxidation states. In tables you find

$E°(Mn^{2+}/Mn) = -1.181$ V $\qquad$ ($Mn^{2+} + 2\ e^- \rightleftharpoons Mn$)

$E°(MnO_4^-/MnO_2) = 1.679$ V $\qquad$ ($MnO_4^- + 4\ H_3O^+ + 3\ e^- \rightleftharpoons MnO_2 + 6\ H_2O$)

$E°(MnO_4^-/MnO_4^{2-}) = 0.564$ V

$E°(MnO_4^-/Mn^{2+}) = 1.491$ V

c) *Determine $E°(MnO_2/Mn^{2+})$ and $E°(MnO_4^{2-}/MnO_2)$.*

Problem 3-16 Inorganic Reactions

Material A shows the following properties or reactions:

(1) A reacts with diluted hydrochloric acid to give solution B.

(2) A certain amount of zinc powder, which is insufficient for a total reaction, is added and reacts with solution B. The mixture is stirred and filtered. Precipitate C is obtained.

(3) C reacts with oxygen to become A.

Possible materials to be A: Cu, CuO, ZnO, MgO, Mg.

a) What material is A? Account accurately for your decision.

There are four unlabeled test tubes with diluted aqueous solutions of sodium sulfide, sodium carbonate, hydrochlorid acid and sulfuric acid.
An aqueous solution of barium hydroxide and magnesium powder are provided as additional reagents.

b) Propose a scheme of analysis to identify the solutions in each test tube. To identify all solutions not more than 6 tests should be necessary. A test is defined as the interaction of one solution of the unlabeled test tubes with one of the additional reagents or with the solution of another test tube.

c) Write down the respective reaction equations.

Problem 3-17 Thermodynamics

At high temperatures carbon dioxide decomposes in small amounts into carbon monoxide and oxygen. The fraction of CO_2 that decomposes at equivalence pressure of 1013 hPa varies with the temperarture: at 1000 K $2.0 \cdot 10^{-7}$ and at 1400 K $1.3 \cdot 10^{-4}$.

Assume $p_{standard} = 1{,}013 \cdot 10^5$ Pa as standard pressure.

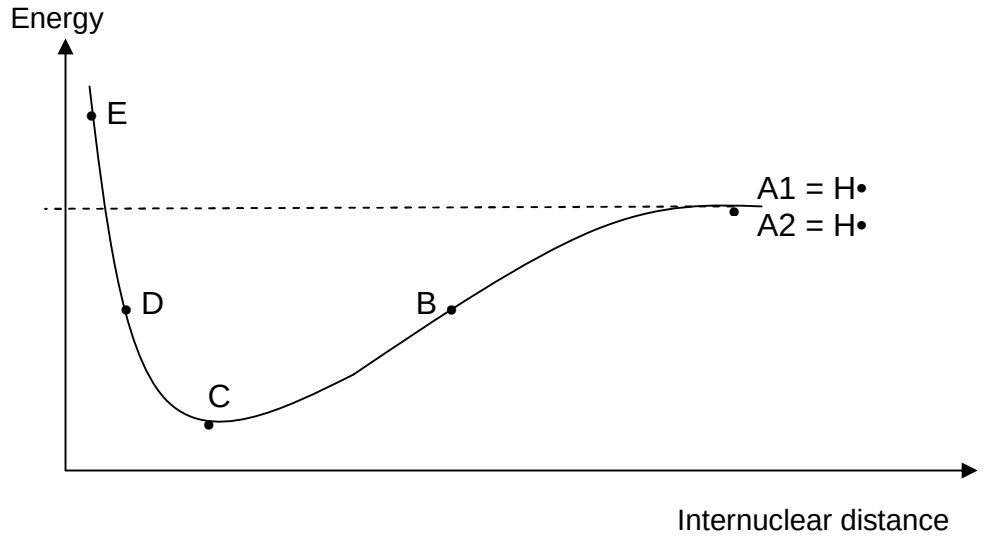
a) Write the reaction equation of this termal decomposition.

b) Calculate $K_p(1000)$, $K_p(1400)$, $\Delta G°(1000)$, $\Delta H°(1000)$ and $\Delta S°(1000)$ assuming that the reaction enthalpies in the relevant temperature interval are constant.

c) How will the fraction of decomposed carbon monoxide change if the total pressure is decreased to 101.3 hPa. First give a qualitative answer, which you then verify by a calculation of the reaction at 1000 K.

Problem 3-18 Bonds and Structures

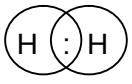
The following diagram is a plot of energy versus internuclear distance for two hydrogen atoms



a) *Account for the energy changes in B, C, D and E compared with the energy of two isolated hydrogen atoms by using the theory of overlapping of the s orbitals.*
How stable is the system in B, C, D and E?

b) *Which point corresponds to the stable H_2 molecule?*
Mark the bond length and the bond energy on the axes of the diagram.

The Lewis formula of H_2 can be written as H : H
The Valence-Bond-Theory describes bonds as overlapping of orbitals of atoms. For instance H_2 may be described as



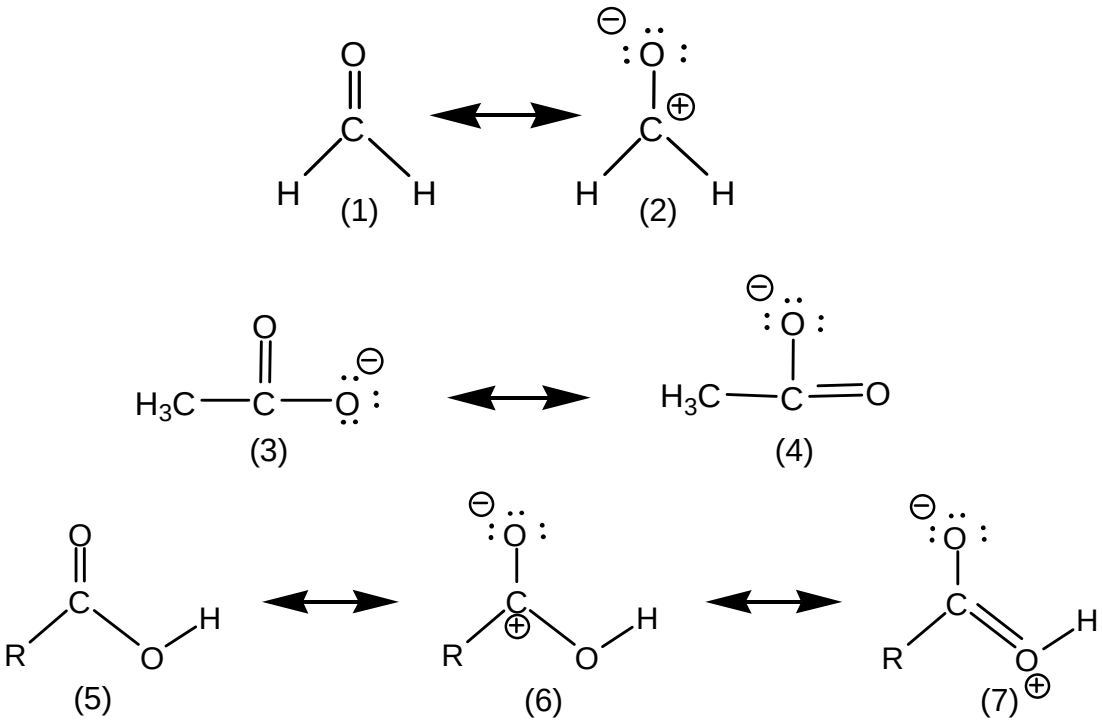
c) *Draw the Lewis structure and the line-bond structure following the Valence Bond Theory of N_2.*

d) *Depict the MO diagram of O_2. Start from the 2p orbitals of two oxygen atoms.*

e) *Estimate the angle (∡ HNH) of ammonia and (∡ HOH) of water compared with the tetrahedral bond angle (∡ HCH) of methane.*
Draw the structures of ammonia and water und account for the reason that the angles are different from the tetrahedral bond angle.

The structure of a lot of molecules is described by two or more resonance structures.

f) Which of the resonance forms contribute more to the overall resonance hybrid?



g) What does an individual resonance structure represent?

There are often several different structures with the same empirical formula (constitutional isomerism).

h) Draw all possible constitutional isomers of C_4H_6 (9 examples are to be overbidden).

Problem 3-19 Reactions and Analysis

A cyclic compound **A** (C_7H_{12}) has to be analyzed.
Therefore an ozonolysis of compound **A** is performed. The obtained product is treated with a reducing agent such as zink metal in hydrochloric acid. This leads to only one compound **B**: 2,2-dimethylpentane-1,5-dial ($C_7H_{12}O_2$).

If compound **A** reacts with permanganate in alkaline solution under mild conditions at 0°C, compound **C** ($C_7H_{14}O_2$) is formed. Compound **C** doesn't show any optical activity.

In a hot aqueous solution of potassium permanganate, however, **A** reacts opening the ring to form **D** ($C_7H_{12}O_4$)**,** a compound with the properties of an acid.

Finally compound **A** is treated with a per-acid. Two compounds **E** and **F** ($C_7H_{14}O_2$ each) occur, both are optically active.

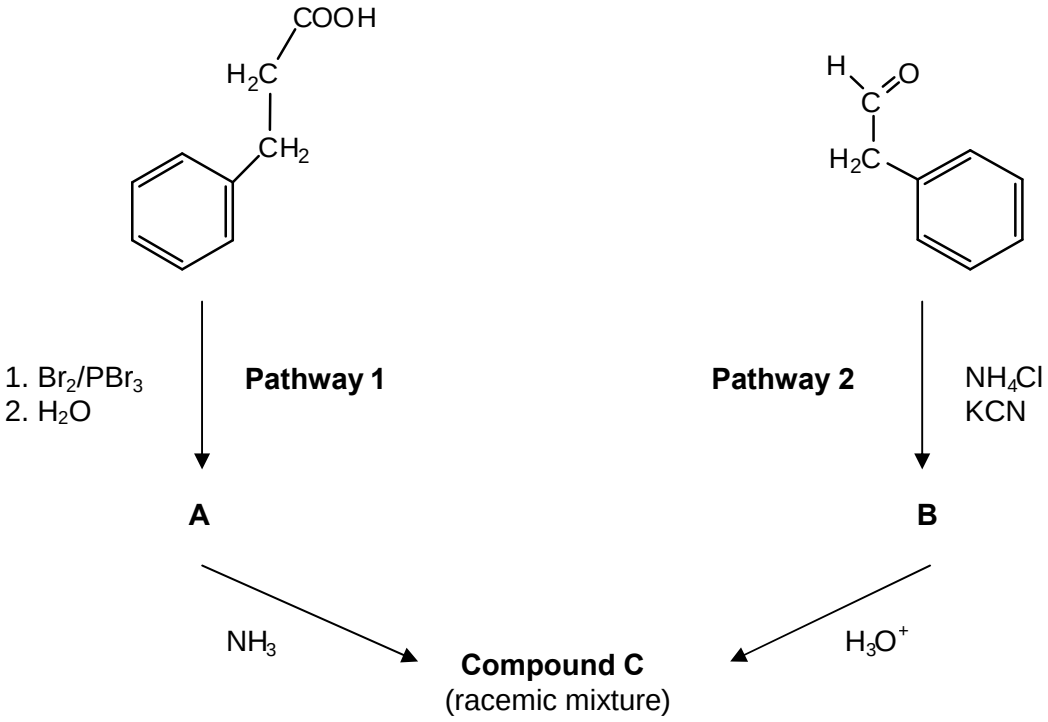
a) *Determine the compounds **A** through **F**.*
*Write the equations of the reactions that lead to all of the compounds **B** to **F**.*

b) *Provide the mechanism of the reaction that leads to compound **C**.*

c) *Draw 3D-structures of the compounds **C**, **E** and **F**.*
*Which of the pairs **C/E**, **C/F** and **E/F** are enantiomers or diastereomers respectively.*

Aufgabe 3-20 Organic Synthesis

Compound **C** may be obtained on two different pathways. Using them compound **C** is generated as a recemic mixture.

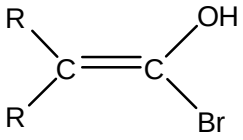


a) *Draw the structural formulas of **A**, **B** and **C**. Provide the name of compound **C**.*

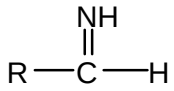
b) *Draw both enantiomers in Fischer projection (carbon atom with the highest oxidation number on top). Assign R- and S-configuration respectively to each drawing.*

c) *Show the mechanism of the formation of **A** and **B**.*

Hint pathway 1: An enol occurs as intermediate:



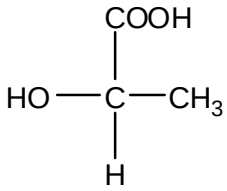
Hint pathway 2: In a reaction NH_3 with an imine occurs as intermediate:



The racemate of compound **C** is treated with R-lactic acid ($CH_3CH(OH)COOH$).

d) Draw a Fischer projection of R-lactic acid.

e) Does the Fischer projection below show R- or S-lactic acid?



f) What kind of salts do form after addition of R-lactic acid? Draw the structural formulas of anions and cations of the salts. Assign R and S according to the configuration.

*g) Explain how it is possible to get pure enantiomers of compound **C** after additon of R-lactic acid.*

Fourth round (theoretical problems)

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

Problem 4-1 Atoms - Structure and Decay

Element no. 117 (Ununseptium, Uus) has not been created until now but you may speculate.

a) Show its supposible electronic configuration (like $1s^2 2s^2 p^6 3\ldots$ without abbreviations). To which group may it belong to?

The element carbon consists of the stable isotopes ^{12}C (98,90 % of mass) and ^{13}C (1,10 % of mass). Furthermore there is a very small fraction of the radioactive isotope ^{14}C (halve-live $t_{1/2}$ = 5730 a). It emerges from nitrogen by neutron bombardment (cosmic radiation) in the atmosphere. ^{14}C shows β-particle emission.

b) Give equations of the formation and decay of ^{14}C.

$^{14}CO_2$ mingles with all the other CO_2 and thus enters the CO_2 cycle of nature. The rate of decay of carbon which is incorporated in the natural CO_2 cycle is 13.6 decays/min per g of carbon. When herbal material dies off, the rate of carbon decreases respectively.
^{14}C decays at a rate equal to (N = number of atoms, t = Zeit, λ = rate constant):

$$\text{rate} = -\frac{dN}{dt} = \lambda \cdot N.$$

Integration of this equation leads to the well-known law of radioactive decay.

A piece of wood from a ship of the Vicings which was found in 1983 showed a rate of decay of 12.0 decays/min per g of carbon.

c) In which year was the tree cut down?

d) What is the value of the abundance ratio (number of atoms of ^{12}C/number of atoms of atoms of ^{14}C) of carbon involved in the natural CO_2 cycle?

When the elements generated, a lot of radionuclides were formed among others. Some of them - special isotopes of uranium and thorium - still exist on earth because of their longevity. Natural uranium consists of several isotopes, the longest-living of which are ^{238}U (99.275 % , $t_{½} = 4.468 \cdot 10^9$ a) and ^{235}U (0.720 %, $t_{½} = 7.038 \cdot 10^8$ a). The other isotopes of uranium possess considerably shorter half-lives.

Thorium consists only of the long-living isotope ^{232}Th ($t_{½}$ = 1.405·10^{10} a). Another relatively long-living isotope was ^{237}Np ($t_{½}$ = 2.14·10^{6} a), which is already totally decayed. All these isotopes undergo α-decay.

e) At which time in the past was the fraction of both uranium isotopes equal?

In natural uranium there is another isotope, ^{234}U with a fraction of about 0.005%. It is not a remnant of the origin of earth but it is formed constantly by one of the four isotopes mentioned above. A radioactive equilibrium is reached, at which the concentration of ^{234}U is constant, e.g. the rates of formation and decay are equal.

f) From which of the isotopes mentioned above does ^{234}U originate by a series of α- and β^--decays? Show the way of formation.

g) Calculate the half-live of ^{234}U.

Problem 4-2 How does it happen?

There are two proposals of reactions sulfuric acid forms in the atmosphere

proposal A $H_2O_{(g)} + SO_{3\,(g)} \longrightarrow H_2SO_{4\,(g)}$

proposal B $2\,H_2O_{(g)} + SO_{3\,(g)} \longrightarrow H_2SO_{4\,(g)} + H_2O_{(g)}$

a) Considering the possibility of collisions only which order of reaction would you expect for proposal A and for proposal B?

Proposal B could procede in a mechanism of two steps:

$$SO_3 + 2\,H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3{\cdot}2H_2O \quad \text{(rapidly)}$$

$$SO_3{\cdot}2H_2O \xrightarrow{k_2} H_2SO_4 + H_2O \quad \text{(slowly)}$$

$SO_3{\cdot}2H_2O$ is a complex stabilised by hydrogen bridges. It is $k_2 << k_1$ und k_{-1} .

b) Derive the respective rate law of the formation of sulfuric acid and give the reaction order of this two-step mechanism. Use the steady-state approximation.

Quantum-mechanical examinations show that the „activation energies“ of the total processes A and B are

Ea(A) = + 80 kJ mol^{-1} for proposal A Ea(B) = - 20 kJ mol^{-1} for proposal B

c) Show the relation between rate constant and temperature (Arrhenius equation) of each of the two proposals and predict the temperature dependance of the rate constants.

The formation of H_2SO_4 in the upper atmosphere (T = 175 K) is faster then on the surface of the earth (T = 300 K).

d) Which of the proposed reactions prevails in the upper atmosphere?

Problem 4-3 Miscellaneous of Inorganics

If you want to determine the iron content of a solution which contains Fe^{3+} as well as Fe^{2+}, you have to transfer all iron ions to Fe^{3+} or to Fe^{2+}.
Given some redox couples with their redox potentials:

		E° in V
Fe^{3+}	Fe^{2+}	+ 0.77
Fe^{2+}	Fe	- 0.41
I_2	$2\ I^-$	+ 0.54
SO_4^{2-} (H^+)	H_2SO_3	+ 0.20
Sn^{4+}	Sn^{2+}	+ 0.15
Zn^{2+}	Zn	- 0.76

a) Which of them are able to transfer Fe^{3+} to Fe^{2+} at standard conditions? Write balanced reaction equations.

*b) Calculate the equilibrium constant of **one** of the possible reactions.*

The cation Fe^{3+} or better $Fe(H_2O)_6^{3+}$ may act as an acid with $K_a = 6{,}3 \cdot 10^{-3}$ mol/L.

c) Give the equation of this protolysis reaction.

A solution contains a total concentration of $c_{total}(Fe^{3+}) = 8.5 \cdot 10^{-3}$ mol/L.

d) Determine the pH value and α, the degree of protolysis ($\alpha = c_{ions\ that\ underwent\ protolysis}/c_{total}$).

Whether the solution reaches the calculated pH value depends amongst other things on whether $Fe(OH)_3$ (solubility product $K_{sp} = 6.3 \cdot 10^{-38}$) precipitates or not.
With $c_{gesamt}(Fe^{3+}) = 3 \cdot 10^{-3}$ mol/L the degree of protolysis is $\alpha = 0{,}74$.

e) Assay whether in such a solution $Fe(OH)_3$ precipitates.

B

The silicate ion (SiO_4^{4-}) derives from silicic acid H_4SiO_4. This acid tends to intramolecular condensation.

The silicon-oxygen compounds consist of tetrahedral components which exist in their crystal structures as singles, in groups, chains or layers or they form a three dimensional framework.
A general way to write the empirical formula of such silicon-oxygen compounds is $[Si_xO_y]^n$.

f) Derive a formula for the charge n in dependung on x and y!

g) How many corners does one tetrahedron of the anion $(SiO_3^{2-})_m$ have in common with its neighbours?

h) What is the empirical formula of a silicon-oxygen compound in which 4 tetrahedrons are connected with their corners to form a chain and with silver as cation?

Lapis lazuli (lazurite) is a deep blue mineral used for jewellery. It consists of an three dimensional framework, in which three out of six silicon atoms are substituted by aluminium atoms. The blue colour is caused by S_3^- ions. The ration of number of tetrahedrons to number of S_3^- ions amounts to 6:1. The cations of the mineral are sodium ions.

i) What is the empirical formula of lapis lazuli?

j) Write a balanced (ionic) equation of the formation of sulphur and hydrogen sulphide if you treat lapis lazuli with hydrochloric acid.

k) Draw the Lewis formula of an S_3^- ion. *Pay attention to the geometrical situation!*

Problem 4-4 Equilibria

(Assume $p_{standard} = 1{,}013 \cdot 10^5$ Pa for the total problem.)

In a system in which the equilibrium $3\ H_2 + N_2 \rightleftharpoons 2\ NH_3$ is established at 400 K the following partial pressures are found:
$p(H_2) = 0.376$ bar $\quad p(N_2) = 0.125$ bar $\quad p(NH_3) = 0.499$ bar.

a) Calculate the equilibrium constant K_p and $\Delta G°$.

If the equlibrium in a system is disturbed, it may establish again. You may calculate the "driving force" ΔG with the formula

$\Delta G = \Delta G° + RT \cdot \ln Q \quad$ with $Q = \dfrac{p(NH_3)^2}{p(H_2)^3 \cdot p(N_2)} \cdot p_{standard}^{-\Delta n}$.

Looking at the sign of ΔG you may realize in which direction the reaction will move.
There are $n(H_2) = 500$ mol of hydrogen (H_2) in a system with the partial pressures given above.

b) Calculate the amount of N_2 and NH_3 in this system.

The amount of 10 mol of hydrogen is added to this system. There is no change in temperature and total pressure. Thus the equilibrium is distrubed.

c) *Calculate ΔG of the proceeding reaction and determine in which direction the system will proceed by using the sign of ΔG.*

In a $H_2/N_2/NH_3$ system in equilibrium at 410 K and a total pressure of 1 bar you find K_p = 36.79 bar^{-2}. In this system there are 100 mol of H_2, 500 mol of N_2 and 175 mol of NH_3. Then 10 mol of N_2 are added, temperature and pressure are maintained.

d) *State at first without calculation in which direction the system will proceed. Show by calculation whether your statement was correct or not.*

Problem 4-5 Copper Sulfate

In complex compounds of Copper(II) the coordination numbers four and six are favoured, the last ones are often Jahn-Teller distorted.

a) *Draw diagrams for a tetrahedral and an octahedral ligand field showing the energy levels of all 3d-orbitals. Calculate the Crystal Field Stabilization Energy (CFSE) of both cases. Furthermore determine the CFSE of the tetrahedral complex in units of the octahedral coordination (Δ_o, with $\Delta_t = 4/9\ \Delta_o$). Which coordination will be prefered?*

One of the most important detection methods of copper(II) in aquous solutions is the reaction with ammonia, which can be descibed with the following equilibrium:

$$[Cu(H_2O)_6]^{2+} + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\ H_2O$$

The equilibrium shifts nearly completely to the right side.

b) *Explain this reaction using the principle of Hard and Soft Acids and Bases (HSAB)!*

The hexaqua complex of copper(II) shows a light blue, the tetraammin-diaqua complex an intensively blue colour. Measuring the uv/vis spektra of an aquous solution of the complexes maxima of absorbtion are observed at 15000 cm^{-1} and 12000 cm^{-1} respectively.

c) *Account for the different colours of these two complexes using the Ligand Field Theorie and assign the maxima of absorbtion to the appropriate complex compounds.*

Diluted ammonia solution is added slowly to an aquous solution of copper sulfate until there is a excess of ammonia.

d) *What will you observe? Write reaction equations.*

If you produce blue crystals of $CuSO_4 \cdot 5\ H_2O$ from a solution of copper sulfate and safe them in open containers in heated rooms they will get white rims, they “wheather“ slowly. There exist different copper-sulfate hydrates $CuSO_4 \cdot n\ H_2O$ (n = 1, 3, 5), which change into each other depending on air humidity. If you want to keep blue crystals you have to cover them all over with a clear lacquer.

e) Determine the pressure of water vapor at 25°C in air with relative air humidity = 100 %.

f) Using the thermodynamic data below, determine the threshold of relative air humidity (in % at 25°C) at which copper-sulfate hydrates with mit n = 5 and n = 3 change into each other.

Verbindung	$\Delta_f H°(298\ K)$ in $kJ \cdot mol^{-1}$	$S°(298\ K)$ in $J \cdot mol^{-1} \cdot K^{-1}$
$CuSO_4 \cdot 5\ H_2O_{(s)}$	- 2278.0	305.4
$CuSO_4 \cdot 3\ H_2O_{(s)}$	- 1683.1	225.1
$H_2O_{(l)}$	- 285.8	70.1
$H_2O_{(g)}$	- 241.8	188.7

Assume $p = p_{standard} = 1.013 \cdot 10^5$ Pa.

Problem 4-6 Minerals

Mr. Busybody goes in for sports and often consumes healthy products containing minerals. Some time ago he bought a new magnesium-calcium preparation though he had an old one at home. He was sorry about having lost the package inserts of both products, so he does not know how many tablets he has to take for an optimal supply. On the packaging the ingridients are only partially visible:

Product A	**Product B**
Magnesium	Magnesium
Calcium	Calcium
Filling material (7.8 %)	Filling material (86.4 %)
Mass per tablet: 1.2 g	Mass per tablet: 1.25 g

Mr. Busybody feels betrayed. Product B contains a huge amount of filling material while the price was the same as that of product A.

He asks his brother, a chemist, for help. The brother knows that such products often contain magnesium and calcium as citrates ($Mg_3C_{12}H_{10}O_{14} \cdot 14\ H_2O$ and $Ca_3C_{12}H_{10}O_{14} \cdot 4\ H_2O$) or as carbonates. He dissolves two tablets in diluted hydrochloric acid and boils away carbon dioxide. Then he adds an excess of ammonium chloride, neutralizes both solutions with am-

monia (indicator methyl red) and precipitates calcium as calcium oxalate (CaC_2O_4). It is filtered off, washed, dissolved in half-concentrated sulphuric acid and titrated with permanganate solution at 70°C.

a) What is the reason of adding ammonium chloride before precipitating?

b) Why should the solution be nearly neutral during precipitation?

c) Write reaction equations of the formation of calcium oxalate as well as of the reaction of oxalate anions with permanganate anions.

As solutions of permanganate slowly decompose while time goes by, their exact concentration is determined just before titration by means of a pure substance (As_2O_3) as standard.
He weighed a certain amount of As_2O_3 exactly and needed 12,80 mL of a permanganate solution to oxidate it in an acid solution. From this result he calculated c($KMnO_4^-$) = 0,0200 mol/L.

d) Write the equation of the reaction of arsenic(III) oxide (As_2O_3) with permanganate ions . Calculate the mass of arsenic(III) oxide which he used.

The determination of calcium gave the following data:

	Tablets of A:	Tablets of B:
consumption of mL $KMnO_4$ (c = 0.02 mol/L)	34.90 35.00 34.90	31.90 31.90 32.00

e) Calculate the content of calcium of one tablet of each product (in mg).

To determine magnesium the filtrate of the precipitation of oxalate is concentrated to small volume and then slightly acidified with diluted hydrochloric acid. Ammonium chloride and ammonium hydrogenphosphate are added and the solution heated to boiling. After adding phenolphthalein ammonia solution is added until the solution shows clouding and the indicator changes. After adding more ammonia the precipitate of $MgNH_4PO_4$ is filtered off, washed and annealed at not more than 1100°C until the mass is constant.

f) Write the reaction equation of the formation of $MgNH_4PO_4$!

g) Write the equation of the reaction that happens during the annealing.

The precipitation of $MgNH_4PO_4$ is in great extend influenced by the concentrations of ammonium cations and hydroxide anions.

h) Which influence may NH_4^+ and OH^- have upon the precipitation of $MgNH_4PO_4$ and thus on the determination of magnesium?

To answer this question you should take into consideration which reactions the ions in the solution may undergo with NH_4^+ and OH^- respectively and which other precipitates could occur. Account also for compounds which do not contain magnesium but do not account ions, which could be in the solution because of the determination of calcium.

The product X of the annealing contains 21.84 % of mass of magnesium.
The determination of magnesium gave the following values:

	Tablets of A:	Tablets of B:
Mass of X (mg)	192.5 191.4 193.1	236.5 239.1 238.8

i) Calculate the mass of magnesium in one tablet of each product.

j) Which product contains citrates as ingredients, which carbonates? Which of the products contains a higher percentage of minerals per tablet?

Problem 4-7 Polymerization

There are different methods to polymerize monomeric olefines, e.g. radical, anionic, cationic. To start radical polymerization you may use peroxides or azo compounds, because they decompose on heating to form radicals which initiate a chain reaction.

a) Show the way vinyl chloride (H_2C=CHCl) polymerizes. Use a peroxide to initiate the reaction (do not take stereochemical aspects into account; let at least to monomers react).

b) Show chain-termination reactions which may occur during the polymerization of vinyl chloride.

Cationic polymerization may be initiated by proton acids, Lewis acids and salts with carbenium ions. Olefines with electron providing substituents are especially suited for cationic, those with electron withdrawing substituents for anionic polymerization, which is catalyzed by strong bases such as sodium amide.

c) Show the way of the cationic polymerization of isobutene ($(H_3C)_2C=CH_2$), initated by sulphuric acid (do not take stereochemical aspects into account; let at least two monomers react).

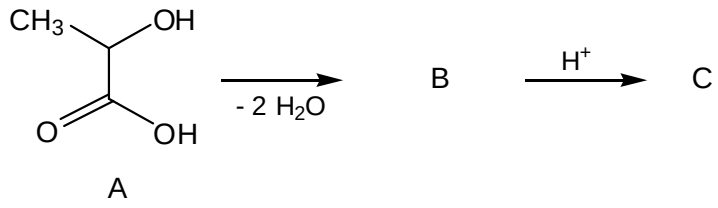
d) Show the way of the anionic polymerization of methylacrylate (acrylic-acid methylester, H_2C=CH-$COOCH_3$) initated by amide anions(NH_2^-)(do not take stereochemical aspects into account; let at least to monomers react).

The material that starts a polymerization reaction is often called catalyzer.

e) Why is this designation misleading and should be used with caution?

There are more polymeres besides polyolefines. An important group of polymers are polyester. Biodegradable plastics as Biopol (Poly-β-hydroxy buryric acid) and polylactic acid belong to this group.

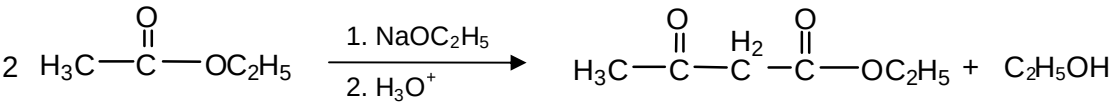
f) Complete the reaction equation of the production of polylactic acid C!



A

Problem 4-8 Reactions of Carboxylic Acid Esters and Phenols

Esters with at least one H-atom at the α-C-atom react in the presence of strong bases as follows:



acetic acid methylester

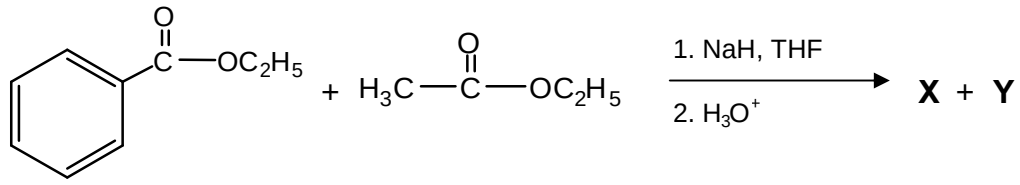
a) Which reaction takes place with 1. $NaOC_2H_5$*?*

b) What are the nucleophilic and the electrophilic reactants in the reaction above? Show them by drawing their Lewis formula.

c) A compound with a tetrahedral C atom instead of the original carbonyl C atom occurs. Draw its structural formula.

The reaction described above may also proceed between two different esters and a strong base

d) Which products do you expect in the reaction shown on the next page? Draw the structural formulas of ***X*** *and* ***Y****.*



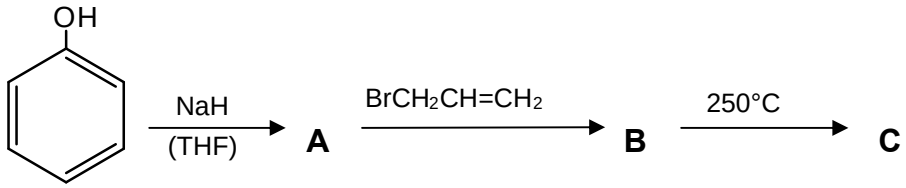
Sodium phenolate reacts under pressure with carbon dioxide to form salicylic acid ($C_7H_6O_3$).

e) Write the reaction equation. As intermediate the anion of a keto carboxlic acid forms.Show its structural formula.

f) Show the resonance structures of the phenolate anion.

g) Which analogy exists between this reaction and the self-condensation of acetic acid methylesters described in the beginning of this problem?

Given the following reaction:

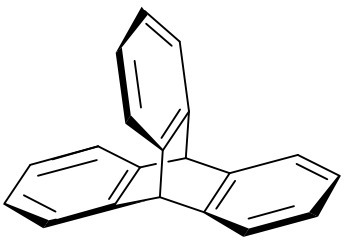


C shows an IR band at approximately 3000 cm^{-1} as phenol does too. This band is missing for compound **B**.

h) Show the structures of the compounds A to C.

Problem 4-9 Diels-Alder Synthesis

Triptycene has athe following structure:



a) What are the names of the reactants which form triptycene in a Diels-Alder reaction? Write a reaction equation.

b) How many monosubstituted isomers of triptycene exist? Show their structural formulas (use "R" as substituent).

1,3-cyclopentadiene and maleic anhydride (maleic acid: $C_4H_4O_4$) react depending on the reaction conditions to two different isomeric compounds, an endo product and an exo product respectively.

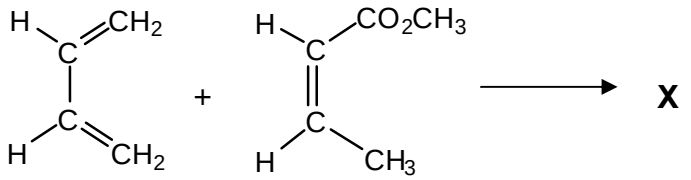
c) Draw the structures of these two isomers.

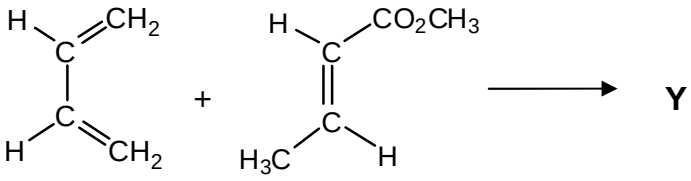
One condition of the reaction of a diene with a dienophilic substance is the optimal arrangement of the reactants involved.

d) Sketch the transition state that leads to the endo product.

Diels-Alder reactions proceeds with high stereospecifity.

*e) Which product will form in the following reactions? Draw the structural formulas of **X** and **Y** and indicate whether there is an E- or a Z-product.*





Fourth round (practical problems)

Problem 4-10: Synthesis of an Organic Compound

Equipment:

Round bottom flask (250 mL)		reflux condenser	balance	Büchner funnel
stirrer bar	funnel	filter paper	suction flask	ice water bath
drying oven (65 °C)	pH paper	spatula	TCL chamber	TCL plate
capillary tube	pen	UV lamp	test tube	
magnetic stirrer with heating plate		melting point apparatus		

Chemicals (R- and S-sets were provided)**:**

Name, formula	**R phrases**	**S phrases**
unknown alkyl aromatic substance, phase-transfer catalyst		
Na_2CO_3 (s),	Xi; 36	22-26,
$H_3C(C_8H_{17})NCl$ (l)	Xn; N; 22-38-41-50/53	26-39-51,
$KMnO_4$ (s),	Xn; N; 8-22-50/53,	60-61,
$NaHSO_3$ solution, w($NaHSO_3$) = 39%	Xn; 22-31,	25-46,
H_2SO_4, w(H_2SO_4) = 48 %,	C; 35,	26-30-36/37/39-45
solvent cyclohexane/ethyl acetate	F; Xi; N; Xn;	9-16-25-26-33-60-61-62
C_6H_{12} / $H_3C\text{-}COOC_2H_5$ (l)	11-36-38-50/53-65-66-67	
toluol, C_7H_8 (l)	F; Xn; 11-38-48/20-63-65-67	36/37-46-62
demineralized water		

Procedure:

Place 70 mL of water, 1.41 g of alkyl aromatic substance, 2.12 g (0.02 mol) of sodium carbonate and 0.5 mL of phase-transfer catalyst in a 250 mL round bottom flask.

Add 15.8 g (0.10 mol) of potassium permanganate and mix thoroughly by swinging.

Put in the stirring bar, connect the reflux condenser, stir and heat the solution for 1 h.

Remove the heating plate. When the solution is no longer boiling but still hot, suck off the brown solid which has formed (**Do not inhale the vapors!**), wash twice with a small amount of hot water. If necessary remove the colour of the filtrate using sodium hydrogencarbonate.

Then use half concentrated sulphuric acid to acidify the filtrate with caution until crystallisation is to be observed. Adding more acid leads to further precipitation. To complete the crystrallisation you have to cool in the ice bath.

The crystallized crude product is sucked off and recrystallzed. Before recrystallization you have to clean the used apparatus with sodium hydrogencarbonate. Then recrystallize from water. In order to crystallize the product again, cool down the flask until it is handhot, then cool down in an ice bath.

The recrystallized product is sucked off and dried in a drying oven for 15 minutes at 65°C.

a) *Fig. 1 shows the ^{13}C-NMR spectrum of the reactant. Which of the compounds **A**, **B** or **C** is it? Assing the signals to the C atoms.*

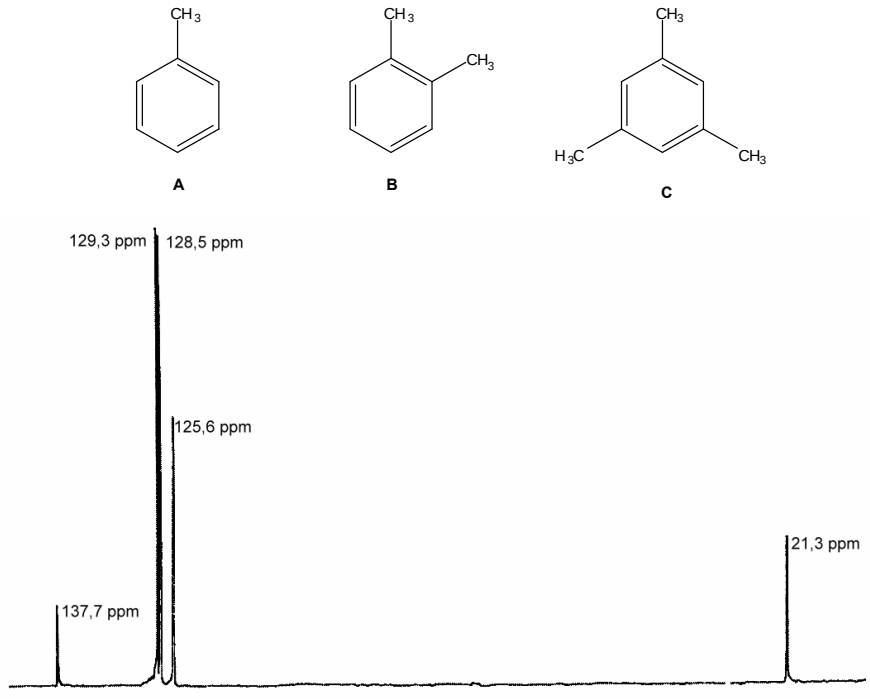


Fig. 1: ^{13}C-NMR Spectrum of the reactant

b) *Draw the structural formula of the product. Which properties do you expect the product to have?*

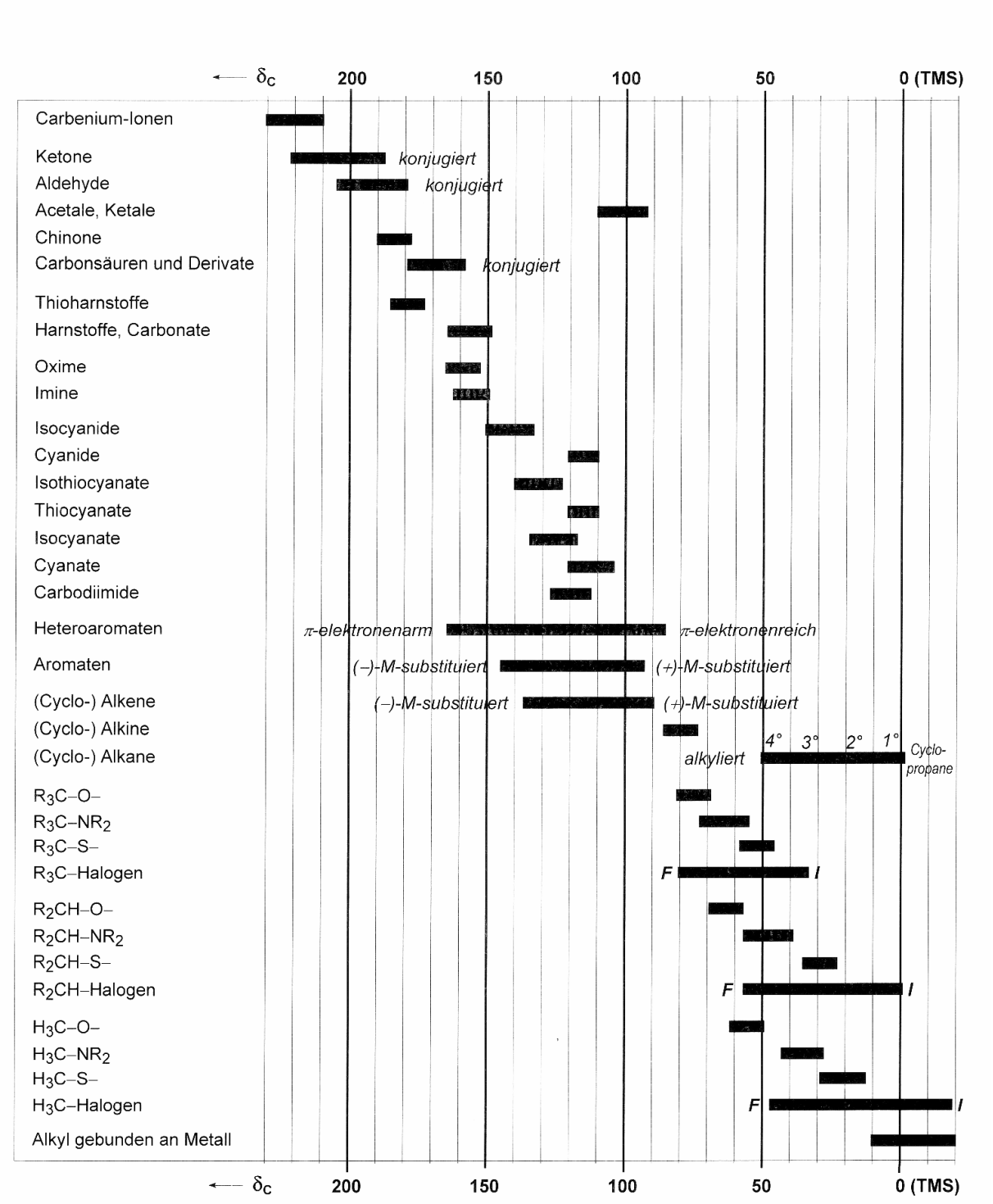
c) *Potassium permanganate oxidizes the alkyl aromatic substance to the highest possible oxidation state. Give the balanced reaction equation and assign oxidation numbers to the relevant atoms.*

d) *Determine the melting point of the product and the yield.*

e) *Prepare a thin-layer chromatography (TLC), solvent cyclohexane / Ethyl acetate 1:1.*
To applicate the substance to the TLC plate solve a small amount of it in toluol and use a capillary tube. Look at the dried TLC plate unter an UV lamp and mark the spots of the product with a pen. Give the R_f value of the product.

Mark your plate with your name and give it to the inspector.

Fig. 2: ^{13}C- ranges of chemical shifts of some organic compounds (from *Eberhard Breitmaier: Vom NMR-Spektrum zur Strukturformel organischer Verbindungen, 3. Auflage, Wiley-VCH, Weinheim 2005)*



Problem 4-11 Water Hardness

The amount of magnesium and calcium salts dissolved in water is called water hardness (calcium and magnesium hardness). You have to distinguish between temporary (carbonate) hardness caused by dissolved hydrogencarbonates, $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$, - and permanent hardness caused by dissolved other magnesium and calcium salts such as chlorides, sulphates and nitrates. The sum of temporary and permanent hardness is called total hardness.

Determination of carbonate hardness in tap water (temporary hardness)

Equipment:

beaker (500 mL)	Erlenmeyer flask (300 mL)	pipette (100 mL) with pipette control
burette (25 mL)	stand with funnel and clamp	thermometer (0 - 100°C)
glas rod	Bunsen burner with stand and plate	

Chemicals:

tap water (l), standard solution of hydrochloric acid, c(HCl) = 0.1 mol/L,
bromocresol green indicator solution, $w(C_{21}H_{14}Br_4O_5S)$ = 0.1 % in ethanol, $w(C_2H_5OH)$ = 20 %,
demineralized water (l)

Procedure:

Use the pipette to transfer 100 mL of tap water from a beaker to an Erlenmeyer flask.
Add 5 to 7 drops of the indicator solution and titrate with standard hydrochloric acid (c(HCl) = 0,1 mol/L) until the colour of the indicator changes from blue to yellow. Then the solution is heated to boiling in order to remove carbon dioxide, cooled down to 30 -35°C. 3 more drops of the indicator solution are added, then titrated until the colour changes again.

Disposal:

The titrated solution contains sodium chloride and a very small amount of bromocresol green only. It can be given into the sink directly.

a) Calculate the concentration (in mmol/L) of hydrogencarbonate in water!

b) Why was it necessary to romove carbon dioxide from the solution?

Determination of the total hardness of tap water

Equipment:

beaker (500 mL)	Erlenmeyer flask (300 mL)	pipette (50 mL) with pipette control
pipette (2 mL)	burette (25 mL)	stand with funnel and clamp

Chemicals:

tap water(l),
standard solution of $Na_2EDTA \cdot 2\ H_2O$, c(Na_2EDTA) = 0.01 mol/L,
indicator buffer pills (Merck) (Xn), R 22-36-42/43, S 22-24-37-45
ammoniak solution, w(NH_3) = 25 %, (C; N), R 34-50, S 26-36/37/39-45-61,
demineralized water (l)

Safety precautions:

Use concentrated ammmonia solution under the hood only.

Procedure:

Use the pipette to transfer 50 mL of tap water from a beaker to an Erlenmeyer flask, add one indicator buffer pill and let it dissolve. Add 1 mL of ammonia solution (w(NH_3) = 25 %) and tritrate instantly and speedy with standard solution of Na_2EDTA (c(Na_2EDTA) = 0.01 mol/L).

Disposal:

The titrated solution and the remnants of the Na_2EDTA solution have to be neutralized and may then been put into the sink.

c) Calculate the concentration (in mmol/L) of calcium and magnesium ions in tap water!

Determination of the calcium hardness of tap water

Equipment

beaker (500 mL)	Erlenmeyer flask (300 mL)	pipette (50 mL) with pipette control
burette (25 mL)	measuriang cylinder (10 mL)	stand with funnel and clamp
microspatula	universal indicator paper	

Chemicals:

tap water (l)
standard solution of $Na_2EDTA \cdot 2\ H_2O$, c(Na_2EDTA) = 0.01 mol/L,
calcon carboxylic acid (s), trituration with sodium chloride w($C_{21}H_{14}N_2O_7S$) = 0.2 %,
potassium hydroxide solution, w(KOH) = 25 %, (C), R 22-35, S 26-36/37/39-45
demineralized water (l),

Procedure:

Use the pipette to transfer 50 mL of tap water from a beaker to an Erlenmeyer flask and add 5 mL of potassium hydroxide solution (w(KOH) = 25 %, after addition the pH should be at 12) and a microspatula tip of calconcarboxylic-acid trituration.
Titrate with standard solution of Na_2EDTA (c(Na_2EDTA) = 0.01 mol/L) until the colour changes from pink to sky blue.

Disposal:

The titrated solution and the remnants of the Na_2EDTA solution have to be neutralized and may then put into the sink.

d) Calculate the concentration (in mmol) of calcium ions in tap water.

e) Calculate the concentration (in mmol) of magnesium ions in tap water?

It may occur that the carbonate hardness is higher than the total hardness.

f) What does this mean for the hardness caused by calcium and magnesium ions and the determination of the total hardness?

Instead of concentrations you often find the specification of hardness in German hardness degrees °dH. This is an old fashioned but practically still used unit.
1°dH responds to 10 mg/L of calcium oxide (CaO) or 7.18 mg/L of magnesium oxide (MgO) respectively. 5.6°d corresponds to a concentration of 1 mmol/L of calcium ions.

g) Give your results of carbonate hardness and of total hardness in °dH (referred to CaO)!

Part 2

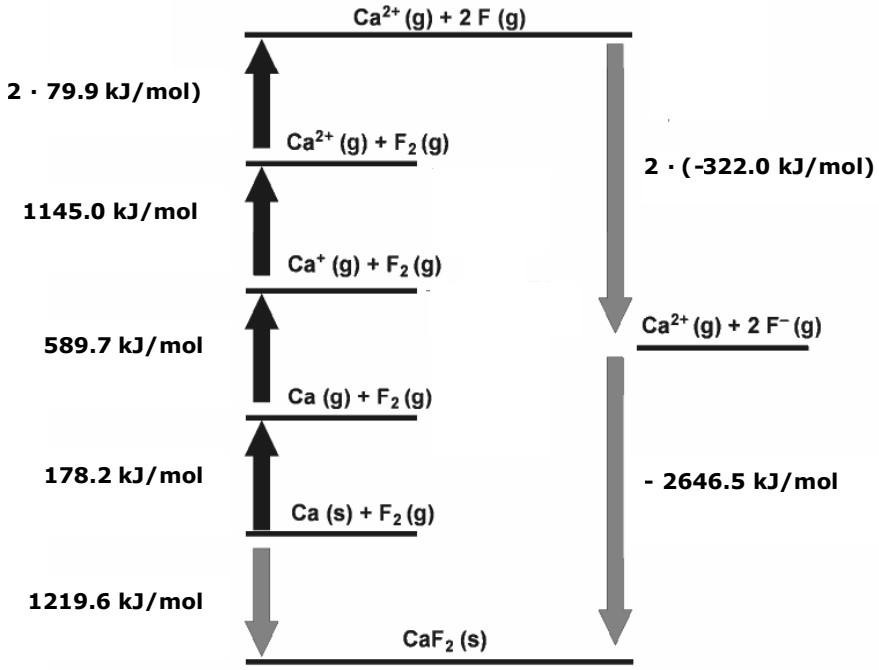
The answers to the problems of the four rounds

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)



Lattice energy of calcium fluoride = – 2646.5 kJ/mol

b) $c(Ca^{2+}) \cdot c(F^-)^2 = K_L$

$c(Ca^{2+}) = ½\ c(F^-) \quad \Rightarrow \quad ½\ c(F^-) \cdot c(F^-)^2 = 3 \cdot 10^{-11}\ mol^3/L^3 \Rightarrow \quad c(F^-) = 3.92 \cdot 10^{-4}\ mol/L$

solubility of $(CaF_2) \quad = ½\ c(F^-) \cdot M(CaF_2)$

solubility of $(CaF_2) \quad = ½\ 3.92 \cdot 10^{-4}\ mol/L \cdot\ 78.08\ g/mol$ **= 15.3 mg/L**

c) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF$

d) Amount of 1000 L hydrogen fluoride at 1.013 bar and 473.15 K using $p \cdot V = n \cdot R \cdot T$

$$n(HF) = \frac{1.013 \cdot 10^5\ Pa \cdot 1 m^3}{8.314\ JK^{-1}\ mol^{-1} \cdot 473.15\ K} \qquad n(HF) = 25.75\ mol$$

$n(H_2SO_4) = ½ \cdot n(HF) \qquad n(H_2SO_4) = 12.88\ mol$

1 mL (1.84 g) sulfuric acid (96%) contains $n_1 = 1.84\ g \cdot 0.96 / M(H_2SO_4)\ mol\ H_2SO_4$

$n_1 = 1.84\ \cdot 0.96/98.086\ mol = 18.0 \cdot 10^{-3}\ mol$

$V(H_2SO_4) = n(H_2SO_4)/n_1\ mL \quad V(H_2SO_4) = 12.88/18.0 \cdot 10^{-3}\ mL$ **$V(H_2SO_4)$ = 715.6 mL**

e) $2\ H_2O \rightleftharpoons O_2 + 4\ H^+ + 4\ e^-$ $\quad E^0 = 0.82$ V

2 HF (aq) $\rightleftharpoons F_2 + 2\ H^+ + 2\ e^-$ $\quad E^0 = 2.64$ V

The standard potenial of the system hydrogen fluoride/fluorine at pH = 7 is +2.64 V (3.05 V at pH = 0), that of the system water/oygen at pH = 7 is +0.817 V (1.23 V at pH = 0). Thus it is impossible to produce fluorine by electolysis of a floride solution, as water reacts before fluoride anions are discharged.

During an electrolysis only water is decomposed, fluorine anions and sodium cation stay unchanged in solution:

cathode: $2\ H^+ + 2\ e^- \longrightarrow H_2$ $\quad$ anode: $2\ OH^- \longrightarrow O_2 + 2\ H^+ + 4\ e^-$

Solution to problem 1-2

a) Chrome green, chromium(III) oxide (Cr_2O_3): $Na_2Cr_2O_7 + S \longrightarrow Cr_2O_3 + Na_2SO_4$

lead-tin yellow, lead(II) stannate (Pb_2SnO_4): $2\ PbO + SnO_2 \longrightarrow Pb_2SnO_4$

minium, lead(II,IV) oxide (Pb_3O_4): $6\ PbO + O_2 \longrightarrow 2\ Pb_3O_4$

Egyptian blue, calcium-copper(II) silicate ($CaCuSi_4O_{10}$):

$CaCO_3 + CuO + 4\ SiO_2 \longrightarrow CaCuSi_4O_{10} + CO_2$

b) Disodiumtetraborate decahydrate does not take part in the reaction. It serves as a fluxing agent, which lowers the melting point of the mixture of reactants and provides for good contact between them. This guarantees a steady-going and quick reaction.

Purification of the raw product which contains boric acid and residues of the reactants: The finely ground raw product is treated with water and diluted hydrochloric acid. During this procedure disodiumtetraborate, calcium carbonate and copper oxide are dissolved. An excess of silica is not removed and stays as inpurity as it is colourless and does not interfere.

c) blue: iron(III) salt + yellow potassium prussiate $\longrightarrow$ **Prussian blue**

$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow K[Fe^{III}Fe^{II}(CN)_6] + 3\ KCl$

or $4\ FeCl_3 + 3\ K_4[Fe(CN)_6] \longrightarrow Fe^{III}[Fe^{III}Fe^{II}(CN)_6]_3 + 12\ KCl$

auch als $Fe_4[Fe(CN)_6]_3$

yellow: lead nitrate + potassium chromate $\longrightarrow$ **chrome yellow**

$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2\ KNO_3$

green: copper(II) oxide + acetic acid $\longrightarrow$ **verdigris**

$CuO + 2\ CH_3COOH + 4\ H_2O \longrightarrow Cu(CH_3COO)_2 \cdot 3Cu(OH)_2 \cdot 2H_2O$

red: mercury(II) salt + hydrogen sulfide $\longrightarrow$ **cinnabar**

$Hg(NO_3)_2 + H_2S \longrightarrow$ HgS (black modification) $+ 2\ HNO_3$

you get the more stable red modification by sublimation and recristrallization

d) Me = copper

Identification: $2\ Cu^{2+} + 4\ I^- \longrightarrow 2\ CuI\downarrow + I_2$

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

16.45 mL of $S_2O_3^{2-}$ solution lead to $16.45 \cdot 10^{-3}$ L· 0.1 mol/L = $16.45 \cdot 10^{-4}$ mol of Cu^{2+} in 20 mL or $16.45 \cdot 10^{-3}$ mol Cu^{2+} in 200 mL.

Thus the sample (1.818 g) contains $16.45 \cdot 10^{-3} \cdot$ 63.55 g = 1.045 g or 57.48% of copper.

e) Egyptian blue is the only relevant pigment containing copper. A mixture of Egyptian blue and lead-tin yellow would be green but the content of copper in the unknown green pigment is higher then in pure Egyptian blue.

(Content of copper in Egyptian blue = $\frac{63.55 g/mol}{M(CaCuSi_4O_{10})} \cdot 100\% = \frac{6355}{375.99}\%$ = 16.90 %)

Answer: **No**

f) Black compound = copper(II) oxide, unknown gas = carbon dioxide

n(CuO) = 1.439 / (63.55 + 16) mol = $1.809 \cdot 10^{-2}$ mol

m(H_2O und CO_2) = 2.000 g – 1.439 g = 0.561 g

By trying out you get n(H_2O) = n(CO_2)

M(H_2O + CO_2) = 62.026 g/mol

n(H_2O + CO_2) = 0.561 / 62.026 mol = $9.045 \cdot 10^{-3}$ mol (= ½ ·n(CuO))

$\Rightarrow$ empirical formula of the green pigment: $Cu_2H_2CO_5$

The green powder is malachite $CuCO_3 \cdot Cu(OH)_2$

Solution to problem 1-3

a) Following Lewis (1923) acids are acceptors of electron pairs, e.g. a molecule ore ion with an uncomplete noble gas configuration (electron gap).

Lewis acids accept an elctron pair which a Lewis base provides

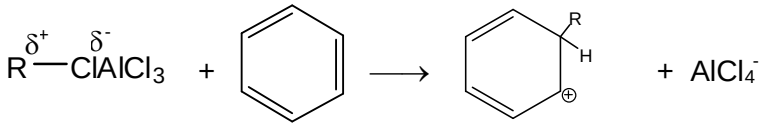
Examples (Typ MeX_3): BF_3, $AlCl_3$, $FeCl_3$, ...

b) Reaction mechanism: Electrophilic alkylation (Friedel-Crafts-reaction)

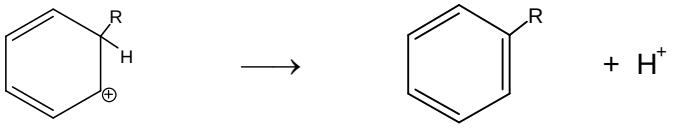
1. step: the active reagent forms

$RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$ (R = $CH_3(CH_2)_2CH_2$—; Lewis acid $AlCl_3$)

2. step: the intermediate forms (electrophilic attack)



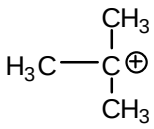
3. step: the product forms



protogenic reaction and aromatizing

c) The formation of the alkylbenzene compound activates the ring (+I-effect) to form a polysubstituted alkyl compounds. That monoalkyl benzene is more reactive than benzene.
A great excess of benzene cuts back the formation of plysubstituted compounds.

d) The electrophilic reagent of the alkylation is a complex bound carbocation (carbernium ion). Since hydrogen attached to a positively charged carbon atom cannot stabilize the cation but adjacent C-H or C-C bonds can, the most stable carbocation is the one in which the positive carbon has the greatest number of stabilizing alkyl groups attached to it.
By rearrangement the primary alkyl residue forms the more stable tert. butyl residue:



Solution to problem 1-4

Isomers

X = structural isomers

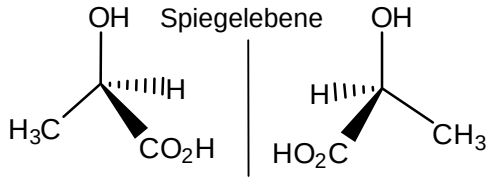
Y = stereoisomers

Z = conformational isomers

Y(1) = Cis-trans isomers(Z-E-isomers)

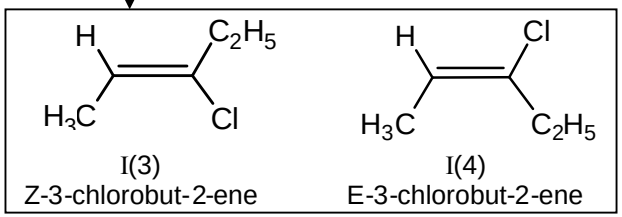
Y(2) = enantiomers

Y(3) = diastereomers



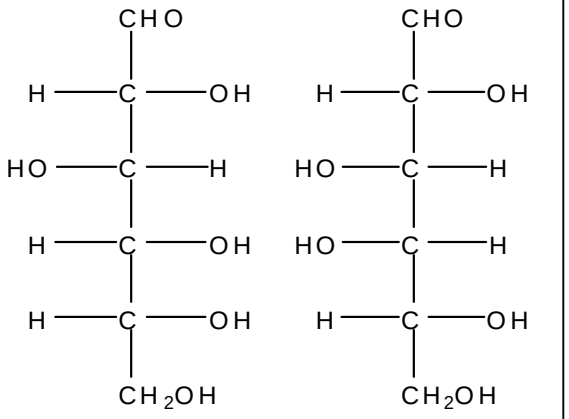
I(5) 2R-2-hydroxypropionic acid

I(6) 2S-2-hydroxypropionic acid



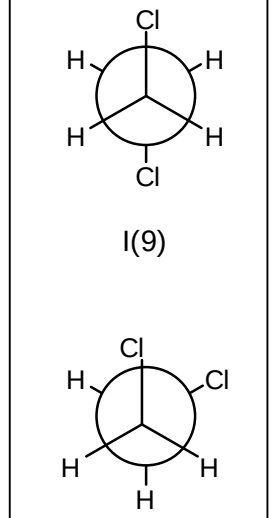
I(3) Z-3-chlorobut-2-ene

I(4) E-3-chlorobut-2-ene



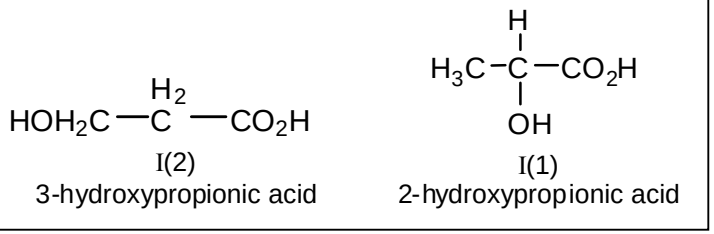
I(7) D-

I(8) D-galactose



I(9)

I(10)



I(2) 3-hydroxypropionic acid

I(1) 2-hydroxypropionic acid

Answers Round 2

Solution to problem 2-1

a) 0.3437 g Bauxit lead to 0.2544 g mixture of oxides ⇒

0.6444 g Bauxit lead to m_1 = 0.4770 g mixture of oxides

$m(Al_2O_3) = m_1 - m(Fe_2O_3)$ = 0.4770 g - 0.1588 g = 0.3182 g

mass content of aluminium = $\frac{2 \cdot M(Al) \cdot 0.3182}{M(Al_2O_3) \cdot 0.6444} \cdot 100\%$ = **26.1 %**

mass content of iron = $\frac{2 \cdot M(Fe) \cdot 0.3182}{M(Fe_2O_3) \cdot 0.6444} \cdot 100\%$ **= 17.2 %**

b) In aqueous acidic solution Aluminium(III) is existent as an aquo complex $[Al(H_2O)_6]^{3+}$. In case of rising the pH water molecules can act as proton donors:

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+ \rightleftharpoons [Al(H_2O)_4(OH)_2]^+ + 2\ H^+$$

Besides deprotonation the mononuclear complexes aggregate so that finally the oxide hydrate $Al(OH)_3 \cdot H_2O$ precipitates (~ pH = 7). It dissolves in an excess of hydroxide anions as $[Al(OH)_4]^-$, the concentration of Al(III)-Konzentration in the soluion rises again.

c)

Point	Phase	Ingridients	F
①	4 (solid Al_2O_3, solid Na_3AlF_3, solution, vapor)	2	0
②	3 (solid Na_3AlF_3, solution, vapor)	2	1
③	2 (solution, vapor)	2	2
④	2 (solid Na_3AlF_6, solid eutectic mixture),	2	2

d) The melt of aluminmium chloride does not contain ions but dimer molecules. No electric conduct is possible.

e) **$2\ Al_2O_3 + 9\ C \rightleftharpoons Al_4C_3 + 6\ CO$**

$Al_4C_3 + 12\ H_2O \rightleftharpoons 3\ CH_4 + 4\ Al(OH)_3$

$\Delta H = [3 \cdot (-74.8) + 4 \cdot (-2567.0)] - [(-129.2) + 12 \cdot (-285.83)]$ kJ/mol = - 6933.24 kJ/mol

$\Delta S = [(3 \cdot 186.26 + 4 \cdot 140.2) - (105 + 12 \cdot 69.91)]$ kJ·K^{-1}·mol^{-1} = 0.17566 kJ·K^{-1}·mol^{-1}

ΔG = -6933.24 kJ/mol – 298.15 K · 0.17566 kJ·K^{-1}·mol^{-1} = - 6985.61 kJ/mol

$\Delta G = -RT \cdot \ln K$ $K = e^{-(-6985610/((8.314 \cdot 298.15)}$

K = $e^{2818.12} = 10^{1223.89}$ = **$7.8 \cdot 10^{1223}$** the side of the products is favored.

f) $p \cdot V = n \cdot R \cdot T$ $n = (1.013 \cdot 10^5\ Pa \cdot 0.100\ m^3) / (8.314\ J \cdot K^{-1} \cdot mol^{-1} \cdot 298\ K)$ = 4.089 mol

143.959 g (1 mol) Al_4C_3 lead to 3 mol CH_4

to form 4.089 mol $143.959 \cdot 10^{-3}$ kg · 4.089/3 = **0.1962 kg carbide are needed**.

g) Potassium: $8\ ^1/_8 + 6 \cdot ½ + 4 = 8$

carbon: $4 \cdot 8 \cdot ½ + 4 \cdot 12 = 64$

n(C) : n(K) = 64 : 8 **empirical formula C_8K**

h) Aluminium(III) has no d-electrons so there is no d → d transiation to generate colour. Chromium(III) has a d^3-electron configuration. In an octahedral field the t_{2g} level is half filled with 3 unpaired electrons, the e_g level, however, is unoccupied so d → d transitions to generate colour are possible.

In sapphire a charge transfer transition (Fe(II) →Ti(IV)) is responsible for the colour.

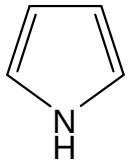
i) Aluminium(III) ions have a smaller ion radius than chromium(III) ions ($r(Al^{3+})$ = 67.5 pm, $r(Cr^{3+})$ = 75.3 pm). Thus the size of the octahedral gaps differs in the different structures and therefore the crystal fields induced by a the oxygen dianions too.

By means of the shorter distance O^{2-} - metal in ruby, the octahedral crystal field of ruby is stronger than that of chromium oxide. This leads to a larger splitting of the $t_{2g} – e_g$-levels in ruby. The d → d transitions happen at higher energies and smaller wavelength (absobence of light of blue colour).

Solution to problem 2-1

a) A = C_4H_5N Pyrrole

.

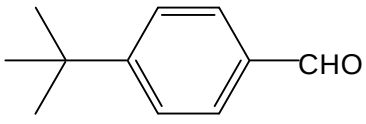


Note:

Due to the true formula C_4H_5N only C and N can be present in the ring, otherwise there could not arise a five membered ring.

b) A is aromatic because there is a conjugated planar cyclic 6 π-electron system (2 C=C bonds +1 free electron pair of the N atom in a p orbital), which fulfills the Hückel 4n + 2 rule.

c) 4-tert-Butyl benzaldehyde



Notes:

B has to be an aldehyde.

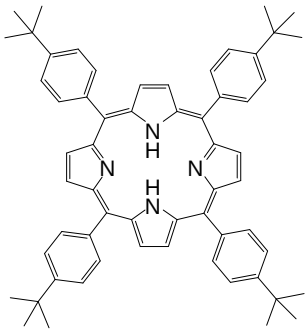
In the ^{13}C-NMR spectrum you find 4 signals in the aromatic range. Their pattern (roughly X:X:Y:Y; X » Y) points to a p-substituted aromatic compound. The coupling pattern of

the “aromatic“ H atoms (2 doublets) approves this fact. The ^{13}C-NMR signal at 192 ppm, the ^{1}H-NMR signal at 10 ppm and the IR band argue for the aldehyde group. In the ^{1}H-NMR spectrum remains a singlet with the intensity of 9 H atoms, while in the ^{13}C-NMR spectrum there are 2 signals in the range of alkyl-C atoms. This is the pattern of a tert-butyl group.

d) n(C) : n(H) : n(N) = 30 : 31 : 2, empirical formula: $C_{30}H_{31}N_2$.
due to M = 839 g/mol C has the true formula $C_{60}H_{62}N_4$.
4 molecules of A react with 4 molecules of B to form C.

e) Electrophilic aromatic substitution
Description:
Pyrrole with π electrons in a cyclic conjugated system is a site of electron density. It reacts in a condensation reaction with aldehydes whereabout the positions 2 and 5 of the pyrrole ring are especially activated.
At first the O atom of the aldehyde is protonated whereby the C atom of the aldehyde is activated as electrophile. This C atom is attacked by the π-electron system of the nucleophilic pyrrole ring to form a σ complex with the C atom in position 2 of the pyrrole ring. After the poroton is abstracted from position 2 of the pyrrole we find an alcohol. The OH group of this alcohol can be protonated and after abstraction of a water molecule the alcohol is transformed into an electrohilic carbocation which may react with pyrrole again.

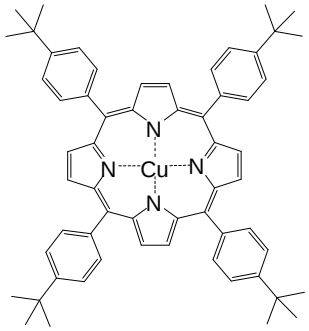
f)



g) Possible oxidizing agents:
- Oxygen of the air (the reflux condensor is open)
- 4-tert-butyl benzaldehyde (could be reduced to 4-tert-butyl benzylalkohol)

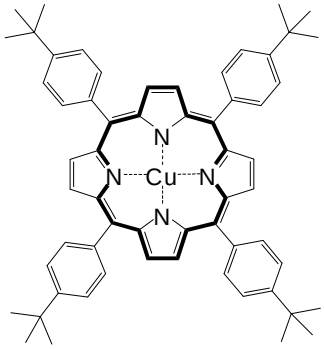
Note:
After condensation of 4 A and 4 B more H atoms have to be abstracted in order to yield C. This can be accomplished by the oxidizing agents mentioned above.

h)



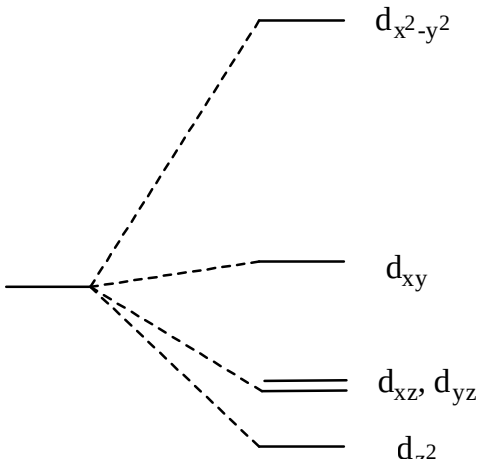
Note:
The incorporation of the Cu^{2+} ion goes along with the abstraction of 2 protons.

i) The largest aromatic system in D has18 π electrons.



Note:
The answer "20 π electrons" is wrong. The largest cyclic conjugated π-electron system in D has indeed 20 electrons but it were antiaromatic because it does not fulfill Hückel's rule (20 = 4·4 +4).

j) Note:
As the ligand system of C is a π-electron system which aims at being planar, the Cu^{2+} ion in D is surrounded by 4 N atoms which form a planar square.
This leads to the shown ligand field splitting of the d orbitals.

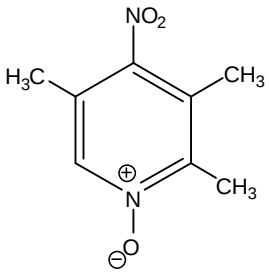


k) As Cu^{2+} has an uneven number of electrons a single Cu^{2+} ion may form a diamgnetic compound if it binds to a radical with an uneven number of electrons too
or
two Cu^{2+} ions may form a binuclear complex, in which antiparallel spin coupling of the unpaired electrons exists.

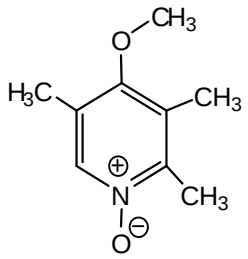
Solution to problem 2-3

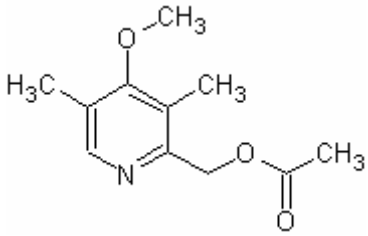
a) Starting material**:** 2,3,5-trimethylpyridine**-**N-oxide or 2,3,5-trimethyl-pyridin**-**1-oxide

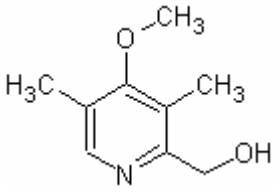
Compound A:

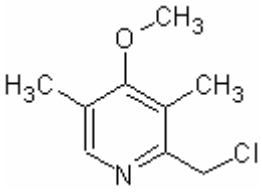


Compounds B and C:
NaOH and MeOH (not asked for)

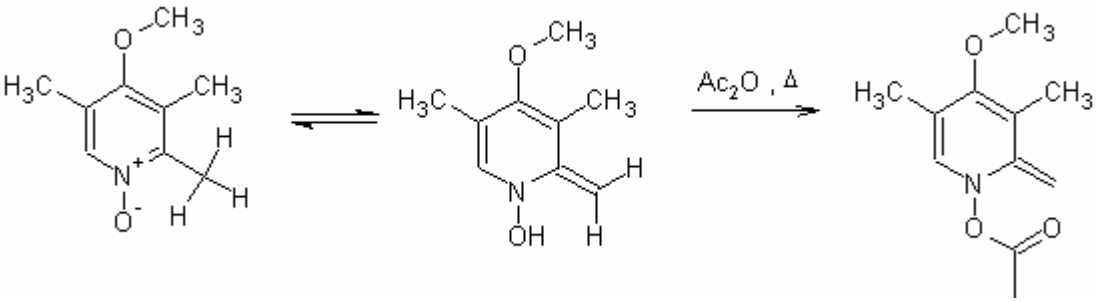
Compound D: 

Compound E: 

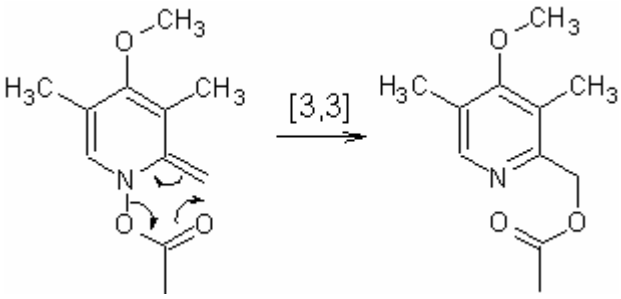
Compound F 

Compound G: 

b) 1. Step: Tautomerism



c) It is the matter of a [3,3] sigmatrope rearrangement (not asked for)

Mechanism: 

The driving force is the regeneration of an aromatic system.

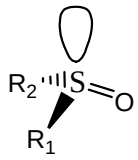
<u>Note to the solutions b) and c):</u>

It is thinkable that acetic anhydride is at first attacked by the O^- atom and only then an H atom is stripped off the CH_3 group then followed by the rearrangement.

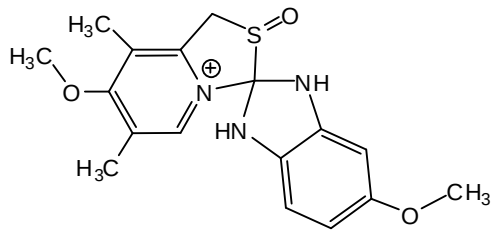
This should be graded as correct too.

d) MCPBA was used to oxidize the thioether in the last step of the reaction.

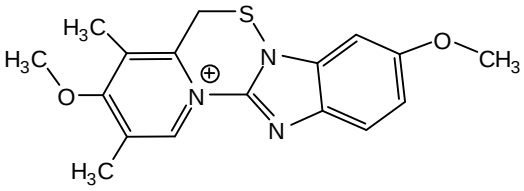
e) The product of the synthesis is chiral. The stereogenic center is the sulphur atom. It has a free electron pair and exists in a tetrahedral configuration.



f)



Spiro compound (intermediate)



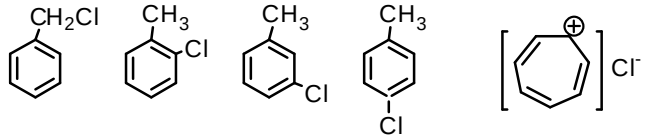
Sulfenamide (mixture of isomers)

Answers Round 3 Test 1

Solution to problem 3-1

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

specifying g)



Solution to problem 3-2

a) $R\text{-}H + H_2O \rightleftarrows R^- + H_3O^+$

$$K = \frac{c(R^-)\cdot c(H_3O^+)}{c(HR)} = \frac{c(R^-)\cdot c(H_3O^+)}{[0.01\ mol/L - c(R^-)]\cdot 1\ mol/L}$$

and $c(R^-) = c(H_3O^+) = x$

$$K = \frac{x^2}{[0.01\ mol - x]\cdot 1\ mol/L}$$

Monochloroacetic acid $K_1 = 1.4\cdot10^{-3}$ $x = 3.11\cdot10^{-3}$ mol/L **pH = 2.51**

Trichloroacetic acid $K_2 = 0.2$ $x = 9.54\cdot10^{-3}$ mol/L **pH = 2.02**

b) $c(R^-) = c(H_3O^+) = 10^{-2.9}$ mol/L $\quad 1.4\cdot10^{-3} = \frac{(10^{-2.9}\,mol/L)^2}{[c(HR) - 10^{-2.9}\,mol/L]\cdot 1\ mol/L}$

$c(HR) = 2.39\cdot10^{-3}$ mol/L

$c_1\cdot V_1 = c_2\cdot V_2$ $\quad 0.01mol/L\cdot100mL = 2.39\cdot10^{-3}\ mol/L\cdot V_2$ **V_2 = 418 mL**

c) V_1 = 1 L HR_1 (Monochloroacetic acid)

V_2 = x L HR_2 (Trichloroacetic acid) total volume = (1 + x) L

initial concentration of HR_1 in the mixture $c_0(HR_1) = \frac{0.01}{x+1}$ mol/L

initial concentration of HR_2 in the mixture $c_0(HR_2) = \frac{0.01\cdot x}{x+1}$ mol/L

$c(H_3O^+) = 10^{-2.3}$ mol/L

$$1.4\cdot10^{-3} = \frac{c(R_1^-)\cdot10^{-2.3}}{\frac{0.01}{x+1}\ mol/L - c(R_1^-)} \qquad c(R_1^-) = \frac{2.183\cdot10^{-3}}{x+1}\,mol/L$$

$$0.2 = \frac{c(R_2^-)\cdot10^{-2.3}}{\frac{0.01\cdot x}{x+1}\ mol/L - c(R_2^-)} \qquad c(R_2^-) = 9.756\cdot10^{-3}\cdot\frac{x}{x+1}\ mol$$

$$\frac{2.183\cdot10^{-3}}{x+1} + 9.756\cdot10^{-3}\cdot\frac{x}{x+1} = 10^{-2.3} \qquad x = \frac{2.183\cdot10^{-3} - 10^{-2.3}}{10^{-2.3} - 9.756\cdot10^{-3}} \qquad x = 0.596$$

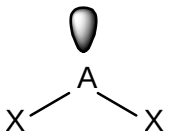
$V_1 : V_2$ = 1 : 0.596 = 1.68 : 1

Solution to problem 3-3

a) n = 2 X - A - X

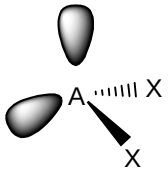
The electron pairs repel each other and move apart from each other as far as possible (180°).

n = 3



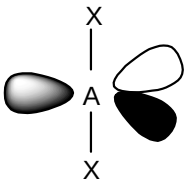
Not linear because the free electron pair repels the binding pairs.

n = 4



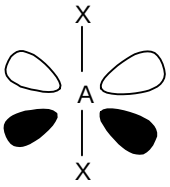
Not linear because the free electron pairs repel the binding pairs.

n = 5



The free electron pairs occupy the largest space and move as far apart as possible. They are situated in a plane and therefore the molecule or the ion is linear.

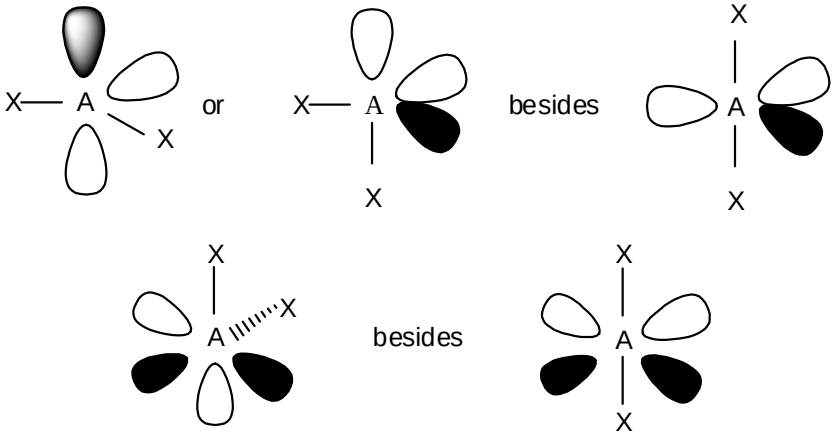
n = 6



Here, too, the not binding electron pairs repel each other and are situated as far apart as possible. They lie in a plane and thus the molecule or the ion is linear.

Linearity occurs with 2, 5 or 6 electron pairs.

b) There is more than one possibility when 5 or 6 pairs are present:



c) n = 2: $BeCl_2$ n = 5: I_3^- (ICl_2^- , XeF_2)

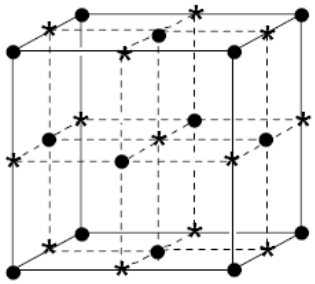
d)

Number of electron pairs	2	3	4	5	6
Hybridization	sp	sp^2	sp^3	dsp^3	d^2sp^3

Solution to problem 3-4

a) •Oxygen ions

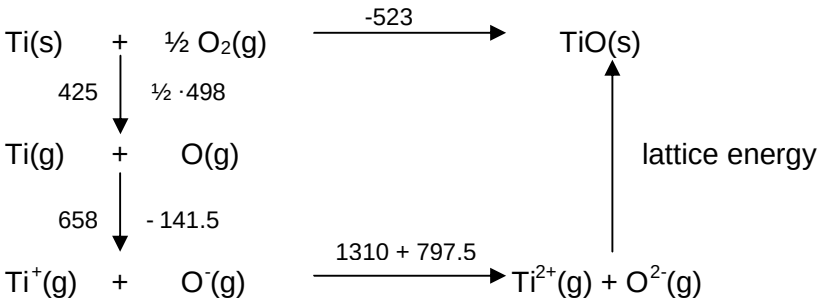
* Titanium ions



b) The unit cell contains 4 oxygen- and 4 titanium ions.

$\rho = \frac{m}{V}$ $\qquad \rho = \frac{4\cdot(16.00+47.87)\text{gmol}^{-1}}{6,.22\cdot10^{23}\text{mol}^{-1}\cdot(0.42\cdot10^{-7}\text{cm})^3}$ $\qquad$ **ρ = 5.73 g/cm^3**

c)



lattice energy = (- 1310 - 797.5 - 658 + 141.5 - 425 - ½·498 - 523) kJ/mol

lattice energy = - 3821 kJ/mol

d) The following reactions have to be compared

1) 4 N $\longrightarrow$ N_4 und 2) 4 N $\longrightarrow$ 2 N_2

$\Delta H_{1)}$ = - 6·163 kJ/mol = - 978 kJ/mol $\qquad \Delta S_{1)} < 0$

$\Delta H_{2)}$ = - 2·945 kJ/mol = - 1890 kJ/mol $\qquad \Delta S_{2)} < 0$

You may assume $\Delta S_{1)} < \Delta S_2$ ($\Leftrightarrow \Delta S_2 - \Delta S_1 > 0$) as the entropy of the reaction of 4 particles to 1 particle decreases in a greater amount than in the reaction of 4 particles to 2.

$\Delta G_{1)}$ = - 978 kJ/mol - T·$\Delta S_{1)}$ $\qquad \Delta G_{2)}$ = - 1890 kJ/mol - T·$\Delta S_{2)}$

$\Delta G_{2)} - \Delta G_{1)}$ = - 912 kJ/mol - T·($\Delta S_{2)} - \Delta S_{1)}$) < 0 $\quad \Rightarrow \quad \Delta G_{2)} < \Delta G_{1)}$

Reaction 2) is favoured.

Solution to problem 3-5

a) $v_{initial} = \Delta c/\Delta t$.

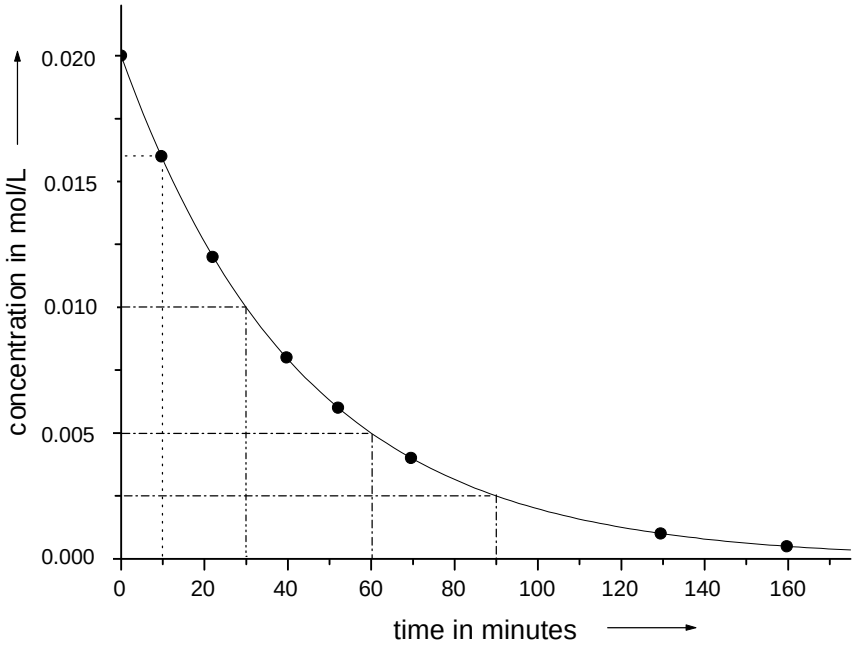
By measuring you get for the first point (10 minutes)

$\frac{0.020\ \text{mol/L}}{6.65\ \text{cm}} = \frac{x}{5.3\ \text{cm}} \quad \Rightarrow \quad x = 0.016\ \text{mol/L} \quad \Rightarrow \quad \Delta c \approx 0.004\ \text{mol/L}$

$v_{initial} = \frac{0.004\text{mol/L}}{10\text{min}}$ $\qquad$ **$v_{initial} = 4\cdot10^{-4}$ mol·L^{-1}·min^{-1}**

b) Dividing the concentrations in half 0.020 → 0.010 → 0.005 → 0.0025 quite exactly, always the same time is needed (see below) i.e. the half life is constant in the measured range. This is only the case in reactions of **1. order**.

c) The half life is $t_{1/2}$ = 30 minutes. The rate constant follows the equation
$k = \ln 2 / t_{1/2}$ $k = \ln 2 / (30\ \text{min})$ **$k = 0.023\ \text{min}^{-1}$** .



Solution to problem 3-6

a) $2\ CH_3OH + 3\ O_2 \longrightarrow 2\ CO_2 + 4\ H_2O$

b) $\Delta H = -½ \cdot (2 \cdot 393.5 + 4 \cdot 241.5 - 2 \cdot 201.5)$ kJ/mol **$\Delta H = -675$ kJmol^{-1}**
(per 1 mol of CH_3OH)

c) $n(CH_3OH) = p \cdot V/(R \cdot T)$ $n(CH_3OH) = \frac{0.165 \cdot 10^5 \cdot 0.5 \cdot 10^{-3}}{8.314 \cdot 298}$ mol = 0.00333 mol

$n(O_2) = \frac{(1.100 - 0.165) \cdot 10^5 \cdot 0.2 \cdot 0.5 \cdot 10^{-3}}{8.314 \cdot 298}$ = 0.00377 mol

Oxygen is the limiting reagent.

d) $\Delta H_r = -2 \cdot 675$ kJ kJnol^{-1} $\cdot$ 0.00377/3 **$\Delta H_r = -1.70$ kJ**

e) before the reaction took place:
$n_0(CH_3OH) = 3.33 \cdot 10^{-3}$ mol (see c)
$n_0(O_2) = 3.77 \cdot 10^{-3}$ mol (see c)
$n_0(N_2) = 4 \cdot 3.77 \cdot 10^{-3}$ mol $= 15.08 \cdot 10^{-3}$ mol

after the reaction took place:

$n_1(N_2)$ = $15.08 \cdot 10^{-3}$ mol

$n_2(CO_2)$ = $2/3 \cdot n_0(O_2)$ = $2.51 \cdot 10^{-3}$ mol

$n_3(H_2O)$ = $4/3 \cdot n_0(O_2)$ = $5.03 \cdot 10^{-3}$ mol

$n_4(CH_3OH)$ = $n_0(CH_3OH) - n_2(CO_2)$ = $0.82 \cdot 10^{-3}$ mol

$\sum_1^4 n_i = n_{ges}$ = **$23.44 \cdot 10^{-3}$ mol** q.e.d.

f) m(gases) = 0.5·1.30 g = 0.65 g $\Delta T = \frac{500}{0.65 \cdot 1.01}$ K = 762 K

T = 1060 K. which corresponds to **787°C**

$p \cdot V = n \cdot R \cdot T$ $p_{1060\,K} = 23.44 \cdot 10^{-3} \cdot 8.314 \cdot 1060 / (0.5 \cdot 10^{-3})$ Pa **$p_{1060\,K} = 4.13 \cdot 10^5$ Pa**

Solution to problem 3-7

a) $HSO_3Cl + 3\ OH^- \longrightarrow SO_4^{2-} + Cl^- + 2\ H_2O$

$H_2SO_4 + 2\ OH^- \longrightarrow SO_4^{2-} + 2\ H_2O$

$SO_3 + 2\ OH^- \longrightarrow SO_4^{2-} + H_2O$

$Ag^+ + Cl^- \longrightarrow AgCl$

b) $n(Cl^-) = n(HSO_3Cl)$

$n(HSO_3Cl) = 5 \cdot 0.0357\ L \cdot 0.112\ mol/L = 0.0200$ mol

$m(0.02\ mol\ HSO_3Cl) = 0.02\ mol \cdot 116.53\ g/mol = 2.3306\ g$ ⇒ **79.2 % HSO_3Cl**

To neutralize 0.02 mol HSO_3Cl you need 0.02·3 mol = 0.06 mol NaOH.

The following amount of NaOH reacted with H_2SO_4 and SO_3:

$n(NaOH) = [0.05 \cdot 1.9820 - 5 \cdot 0.0336 \cdot 0.1554 - 0.06]\ mol/L = 0.0130$ mol

$m(H_2SO_4) + m(SO_3) = 2.9426\ g - 2.3306\ g = 0.612\ g$

let $x = n(SO_3)$ and $y = n(H_2SO_4)$

$2 \cdot x + 2 \cdot y = 0.0130$ mol

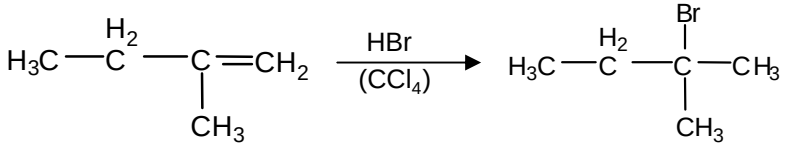
$80.07\ g/mol \cdot x + 98.09\ g/mol \cdot y = 0.612\ g$ ⇒ $x = 1.42 \cdot 10^{-3}$ mol $y = 5.08 \cdot 10^{-3}$

$1.42 \cdot 10^{-3}$ mol SO_3 have the mass of 0.114 g ⇒ **3.9 % SO_3**

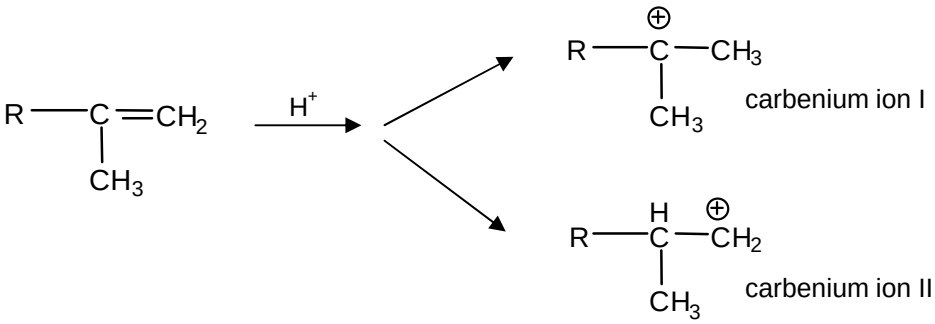
$5.08 \cdot 10^{-3}$ mol H_2SO_4 have the mass of 0.498 g ⇒ **16.9 % H_2SO_4**

Solution to problem 3-8

a)

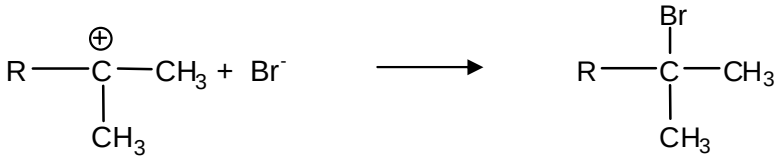


b) **1.step**



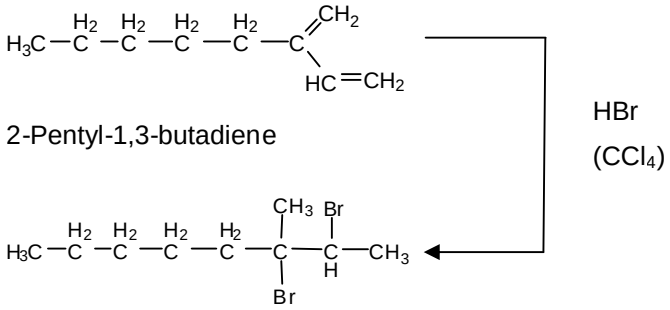
Carbenium ion I is favoured as intermediate

2. step:

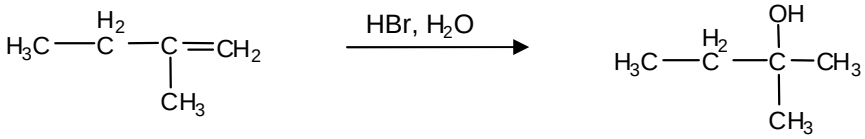


The addition of Br^- is possible from different sides, thus a mixture of enantiomers form.

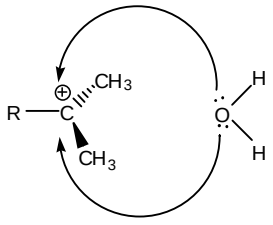
c)



d)

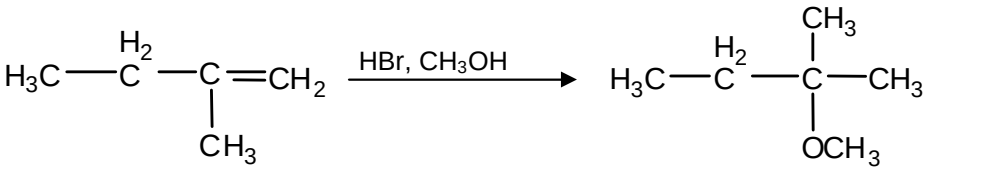


e) The solvent water is not inert but reacts in a competitive reaction with the carbenium ion::



Attack of an nucleophile. An alcohol is formed by release of a proton.

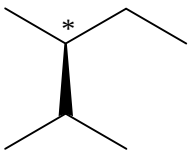
f)



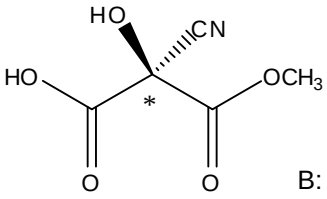
2-Methoxy-2-methylbutane

Solution to problem 3-9

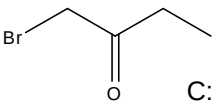
a)



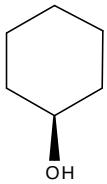
A: 3S



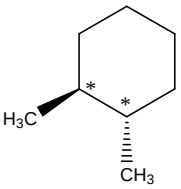
B: 2R



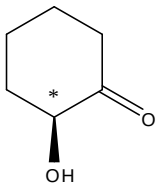
C: no stereogenic center



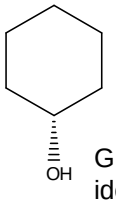
D: no stereogenic center



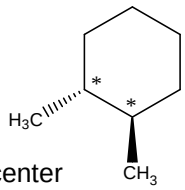
E: 2 stereogenic centers (1S and 2S)



F: 1S



G: no strereogenic center identical with D



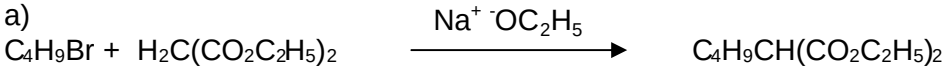
H: 2 stereogenic centers (1R and 2R)

b) no diasteromic compounds, E and H are enantiomers, G and D are identical

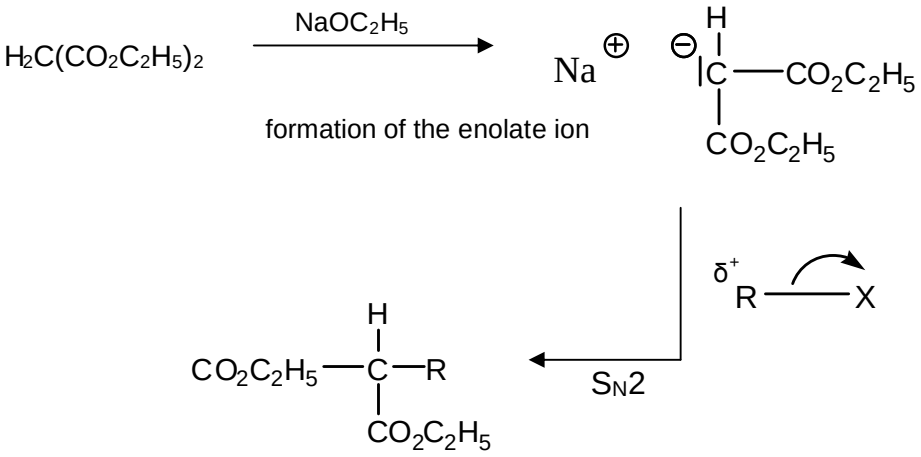
Solution to problem 3-10

Part A:

a)



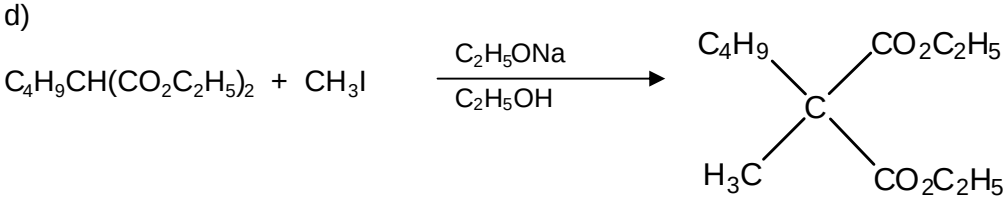
b)



S_N2 reaction

c) $C_5H_{11}COOH$ **(B)**

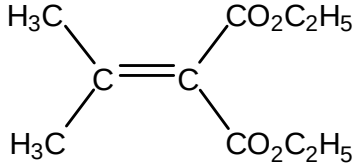
d)



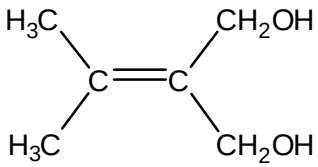
(C)

Part B:

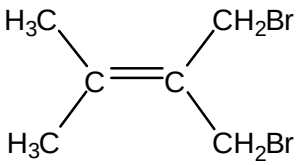
e)



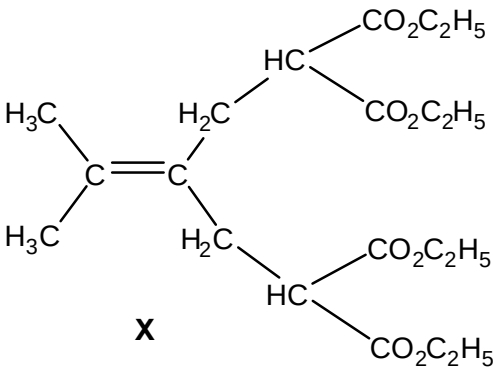
U ($C_{10}H_{16}O_4$)



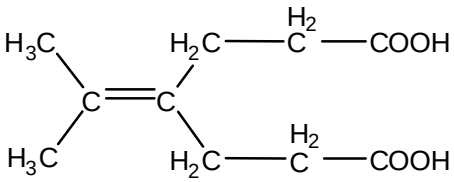
V



W ($C_6H_{10}Br_2$)



X



Y ($C_{10}H_{16}O_4$)

Answers Round 3 Test 2

Solution to problem 3-11

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

Solution to problem 3-12

a) The rat law of a radioactive decay can be described as being first order:

$n = n_0 \cdot e^{-k \cdot t}$ or $dn/dt = k \cdot n$, whereas dn/dt is the rate of disintegration looked for.

$k \cdot t_{½} = \ln 2$ $k = \ln 2 / (4.5 \cdot 10^{10} \cdot 365 \cdot 24 \cdot 3600\ s)$ $k = 4.884 \cdot 10^{-19}\ s^{-1}$

Amount of ^{40}K in the body $n = (80 \cdot 10^3 \cdot 0.35 \cdot 10^{-2} \cdot 0.012 \cdot 10^{-2}\ g) / (40\ g/mol)$

$n = 8.4 \cdot 10^{-4}$ mol

rate of disintegration $= 4.884 \cdot 10^{-19}\ s^{-1} \cdot 8.4 \cdot 10^{-4}\ mol \cdot 6.022 \cdot 10^{23}\ mol^{-1}$

= **247 disintegrations/s**

b) Fat does not contain potassium, thus you can expect a lower rate of disintegration.

Solution to problem 3-13

a) Aniline reacts as base B, 4-chlorobenzenesulfonic acid as acid HA.

The pH value is set by the ratio of $c(B)/c(BH^+)$ or alternatively $c(HA)/c(A^-)$.

Besides the acid/base equilibrium the following equilibrium rules

	B	+	HA	⇌	BH^+	+	A^-
initial concentration in mol/L	0,02		0,015		0		0
concentr. in equilibrium in mol/L	0,02-x		0,015 - x		x		x

$$K = \frac{c(BH^+) \cdot c(A^-)}{c(B) \cdot c(HA)}$$

You may determine K with the help of the given acid and the base constants:

$$K_a = \frac{c(H^+) \cdot c(A^-)}{c(HA)} \quad \Rightarrow \quad \frac{c(A^-)}{c(HA)} = \frac{K_a}{c(H^+)}$$

$$K_b = \frac{c(BH^+) \cdot c(OH)}{c(B)} \quad \Rightarrow \quad \frac{c(BH^+)}{c(B)} = \frac{K_b \cdot c(H^+)}{K_W}$$

$$\frac{c(BH^+) \cdot c(A^-)}{c(B) \cdot c(HA)} = \frac{K_a \cdot K_b}{K_W} \qquad K = 10^{-3.98 - 9.37 + 14} \qquad K = 4.47$$

$$\Rightarrow \qquad 4.47 = \frac{x^2}{(0.02 - x) \cdot (0.015 - x)}$$

$$x^2 - 0.04509 \cdot x + 3.865 \cdot 10^{-4} = 0$$

($x_1 = 0.03358$ not possible) $x_2 = 0.01151$

$\Rightarrow$ $pH = pK_a(HA) + \log \frac{c(A^-)}{c(HA)}$ $pH = 3.98 + \log \frac{0.01151}{0.015 - 0.01151}$ $pH = 4.50$

or $pH = pK_a(BH^+) + \log \frac{c(B)}{c(BH^+)}$ $pH = (14 - 9.37) + \log \frac{8.49 \cdot 10^{-3}}{0.01151}$ $pH = 4.50$

pH = 4.5

b) $A = 0.110 = 1.53 \cdot 10^4\ L \cdot mol^{-1} \cdot cm^{-1} \cdot 5\ cm \cdot c(In^-) + 2.26 \cdot 10^4\ L \cdot mol^{-1} \cdot cm^{-1} \cdot 5\ cm \cdot c(HIn)$

$c(HIn) + c(In^-) = 1.23 \cdot 10^{-6}$ mol/L

$\Rightarrow$ $c(HIn) = 4.358 \cdot 10^{-7}$ mol/L $c(In^-) = 7.942 \cdot 10^{-7}$ mol/L

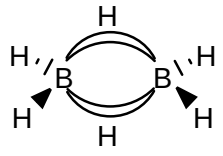
$K_a(HIn) = \frac{1.0 \cdot 10^{-5} \cdot c(In^-)}{c(HIn)}$ $-\log K = -\log \frac{1.0 \cdot 10^{-5} \cdot 7.942}{4.358}$ **pK(HIn) ≈ 4.74**

Solution to problem 3-14

a) Hydrogen exists in bonds essentially as hydride ion. The reason is the considerably lower electronegativity of sodium and magnesium in comparison to hydrogen.

Experiments:
- fused-salt electrolysis of NaH and MgH_2 respectively: hydrogen forms at the anode
- reaction with water:
  $Na + H_2O \longrightarrow NaOH + H_2 \uparrow$ (Formation of hydrogen)

b) x = 2, $(BH_3)_2$ Diborane
y very large, $(AlH_3)_n$ polymeric aluminium hydride
Commonness: in both cases three-centre bonds exist.



Borane (BH_3) is present as dimer, as BH_3 is an electron-deficient compound with only 6 electrons in the valence shell of B. By forming diborane with a B-H-B 2-electon-3-center bond both B atoms satisfy the octet rule.

Difference: As each B atom is surrounded by 4 H atoms an almost ideal tetrahedral-coordinate surrounding of the B atoms in diborane results.
Because aluminium has more possibilities of coordination (KZ 6) it foms six such banana-shaped bonds instead of two of a boron atom. Therefore aluminium has a octahedral surrounding of 6 hydrogen atoms and thus forms a polymeric solid compound in contrast to gaseous diborane.

c) The base strength decreases.

d) The acid stgrength increases.
$HX + H_2O \rightleftharpoons X^- + H_3O^+$

The proton affinity of X^- determines the amount of products formed. As the proton affinity decreases from fluorine to iodine (increasing ionic radius) the acid strength increases.

e) The acid strength increases from the left to the right. On the left hand side of a period you find ionic bonds which change slowly to covalent bonds if you step to the right.

SiH_4: Neither acid nor base, covalent bond
H_2S: Weak acid

Solution of problem 3-15

a) Potential of half cell A:

$MnO_4^- + 8\ H_3O^+ \rightleftharpoons Mn^{2+} + 12\ H_2O$ $\qquad E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_{Ox}/c_{Red})$

$E_A = 1.491\ V + \frac{8.314 \cdot 298}{5 \cdot 96485} V \cdot \ln \frac{0.004 \cdot (10^{-4})^8}{0.01}$ $\qquad E_A = 1.108\ V$

Potential of half cel B:

$E_A - E_B = 0.573\ V$ $\qquad E_B = 0.535\ V$ ($E_B = 1.679$ V is not possible because the silver-ion concentration would be higher than 1 mol/L)

$E_B = 0.800\ V + \frac{8.314 \cdot 298}{96485} V \cdot \ln [c(Ag^+)/1\ mol/L]$

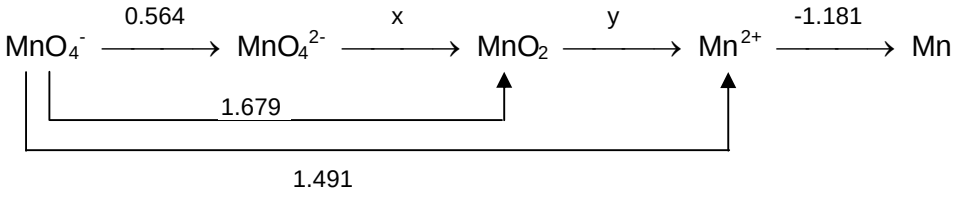
$\ln [c(Ag^+)/1\ mol/L] = (0.535\ V - 0.800\ V) \cdot 96485/(8.314 \cdot 298)$

$c(Ag^+) = 3.296 \cdot 10^{-5}$ mol/L $\qquad c(CrO_4^{2-}) = 8 \cdot 10^{-3}$

$K_L(Ag_2CrO_4) = c(Ag^+)^2 \cdot c(CrO_4^{2-})$ $\qquad K_L(Ag_2CrO_4) = 8.68 \cdot 10^{-12}$

b) The pH value of half cell A is necessary to calculate ist potential.
The pH value of half cell B is important because only in a basic surrounding there is a marginal amount of $C_2O_7^{2-}$ ions. Otherwise the indication of the concentration of CrO_4^{2-} is irrevalent.

c)



$1 \cdot 0.564 + 2 \cdot x = 3 \cdot 1.679$ $\qquad x = 2.2365$ $\qquad E°(MnO_4^{2-}/MnO_2) = 2.2365$ V

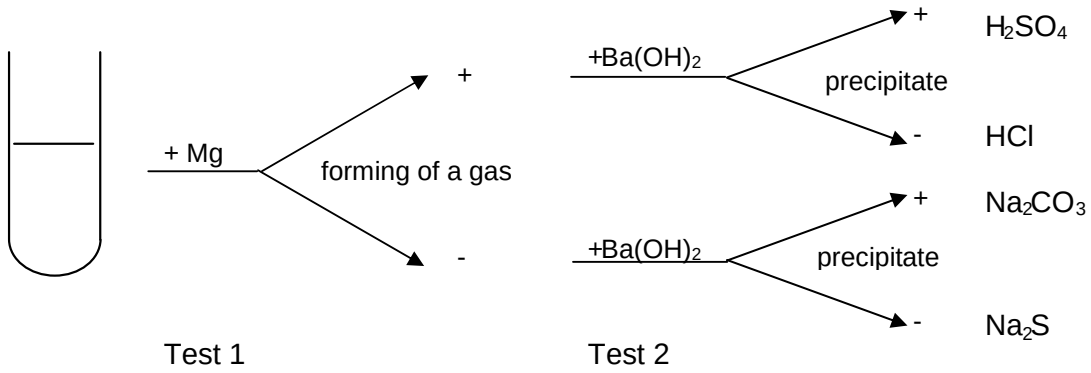
$3 \cdot 1.679 + 2 \cdot y = 5 \cdot 1.491$ $\qquad y = 1.209$ $\qquad E°(MnO_2/Mn^{2+}) = 1.209$ V

(same result from $0.564 + 2 \cdot 2.2365 + 2 \cdot y = 5 \cdot 1.491$)

Solution to problem 3-16

a) Because of (1) copper is eliminated.
Solution B could be a solution of the chloride of copper, zinc or magnesium.
Powder of zinc does not react with zinc or magnesium ions thus the new solid can only be copper.
Copper reacts with oxygen of the air thus **A = CuO**

b)



To determine the content of a test tube you need 2 tests. As soon as you know the content of 3 test tubes (= 6 tests) you know automatically the content of the last one. If you have special results you may need less tests.

c) Test 1 $Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2\uparrow$
$Mg + 2\,HCl \longrightarrow MgCl_2 + H_2\uparrow$

Test 2 $MgSO_4 + Ba(OH)_2 \longrightarrow BaSO_4\downarrow + Mg(OH)_2$
$Na_2CO_3 + Ba(OH)_2 \longrightarrow BaCO_3\downarrow + 2\,NaOH$
(or equations of ionic reactions)

Solution to problem 3-17

a) $2\,CO_2 \longrightarrow 2\,CO + O_2$

b) E.g. initial amount of CO_2 before decomposition = 1 mol

in mol →	$n(CO_2)$	$n(CO)$	$n(O_2)$	$\Sigma(n)$	$x(CO_2)$	$x(CO)$	$x(O_2)$
1000 K	$1 - 2\cdot10^{-7}$	$2\cdot10^{-7}$	$1\cdot10^{-7}$	$1 + 1\cdot10^{-7}$	$\frac{1-2\cdot10^{-7}}{1+1\cdot10^{-7}}$	$\frac{2\cdot10^{-7}}{1+1\cdot10^{-7}}$	$\frac{1\cdot10^{-7}}{1+1\cdot10^{-7}}$
1400 K	$1 - 1.3\cdot10^{-4}$	$1.3\cdot10^{-4}$	$0.65\cdot10^{-4}$	$1+0.65\cdot10^{-4}$	$\frac{1-1.3\cdot10^{-4}}{1+0.65\cdot10^{-4}}$	$\frac{1.3\cdot10^{-4}}{1+0.65\cdot10^{-4}}$	$\frac{0.65\cdot10^{-4}}{1+0.65\cdot10^{-4}}$

$p = x\cdot p_{gesamt}$ $\quad p_{gesamt} = 1.013\cdot10^5$ Pa

in Pa →	$p(CO_2)$	$p(CO)$	$p(O_2)$
1000 K	$\frac{1-2\cdot10^{-7}}{1+1\cdot10^{-7}}\cdot1.013\cdot10^5$	$\frac{2\cdot10^{-7}}{1+1\cdot10^{-7}}\cdot1.013\cdot10^5$	$\frac{1\cdot10^{-7}}{1+1\cdot10^{-7}}\cdot1.013\cdot10^5$
1400 K	$\frac{1-1.3\cdot10^{-4}}{1+0.65\cdot10^{-4}}\cdot1.013\cdot10^5$	$\frac{1.3\cdot10^{-4}}{1+0.65\cdot10^{-4}}$	$\frac{0.65\cdot10^{-4}}{1+0.65\cdot10^{-4}}\cdot1.013\cdot10^5$

$K_p = \frac{p^2(CO)\cdot p(O_2)}{p^2(CO_2)}$ $\quad K_p = \frac{n^2(CO)\cdot n(O_2)}{n^2(CO_2)}\cdot\frac{1.013\cdot10^5}{\Sigma(n)}\,Pa$

$K_{th} = K_p \cdot p_{standard}^{-\Delta n}$ $\quad$ hier $\Delta n = 1$ $\quad K_{th} = \frac{n^2(CO)\cdot n(O_2)}{n^2(CO_2)}\cdot\frac{1.013\cdot10^5}{\Sigma(n)}\cdot\frac{1}{1.013\cdot10^5}$

$K_p(1000) = \frac{(2\cdot10^{-7})^2\cdot1\cdot10^{-7}}{(1-2\cdot10^{-7})^2}\cdot\frac{1.013\cdot10^5}{1+1\cdot10^{-7}}\,Pa$ $\quad$ **$K_p(1000) = 4.05\cdot10^{-16}$ Pa**

$K_{th} = K_p \cdot p_o^{-\Delta n}$ $\quad$ hier mit $\Delta n = 1$ $\quad K_{th}(1000) = 4.00\cdot10^{-21}$

$K_p(1400) = \frac{(1.3\cdot10^{-4})^2\cdot0.65\cdot10^{-4}}{(1-1.3\cdot10^{-4})^2}\cdot\frac{1.013\cdot10^5}{1+0.65\cdot10^{-4}}\,Pa$ **$K_p(1400) = 1.11\cdot10^{-7}$ Pa**

$\Delta G° = - R\cdot T\cdot \ln K_{th}$ $\quad$ **$\Delta G°(1000) = 390.5$ kJ/conversion a)**

$\ln (K_{p1}/K_{p2}) = - \Delta H/R\cdot(T_1^{-1} - T_2^{-1})$ $\quad \Delta H°(1000) = - R\cdot \ln (K_{p1}/K_{p2}) / (T_1^{-1} - T_2^{-1})$

$\Delta H° = - 8.314 \cdot \ln\frac{4.05\cdot10^{-16}}{1.11\cdot10^{-7}} / (\frac{1}{1000} - \frac{1}{1400})\,J$ $\quad$ **$\Delta H°(1000) = 565.4$ kJ/conversion a)**

$\Delta G° = \Delta H° - T\cdot\Delta S°$ $\quad \Delta S° = -(\Delta G° - \Delta H°)/T$

$\Delta S°(1000) = (565400 - 390500)/1000$ J/K $\quad$ **$\Delta S°(1000) = 175$ J/K**

c) As the number of particles increases during the reaction you may reckon that the products are favoured and thus the amount of decomposed carbon dioxide will increase. If the fraction $(2\cdot10^{-7})$ stays constant you would get $Q = \frac{(2\cdot10^{-7})^2\cdot1\cdot10^{-7}}{(1-2\cdot10^{-7})^2}\cdot\frac{1.013\cdot10^4}{1+1\cdot10^{-7}}$ Pa.

This value is ten times smaller than $K_p(1000)$. To reach the equilibrium the numerator has to increase and the denominator has to decrease. This is only possible by increasing the fraction.

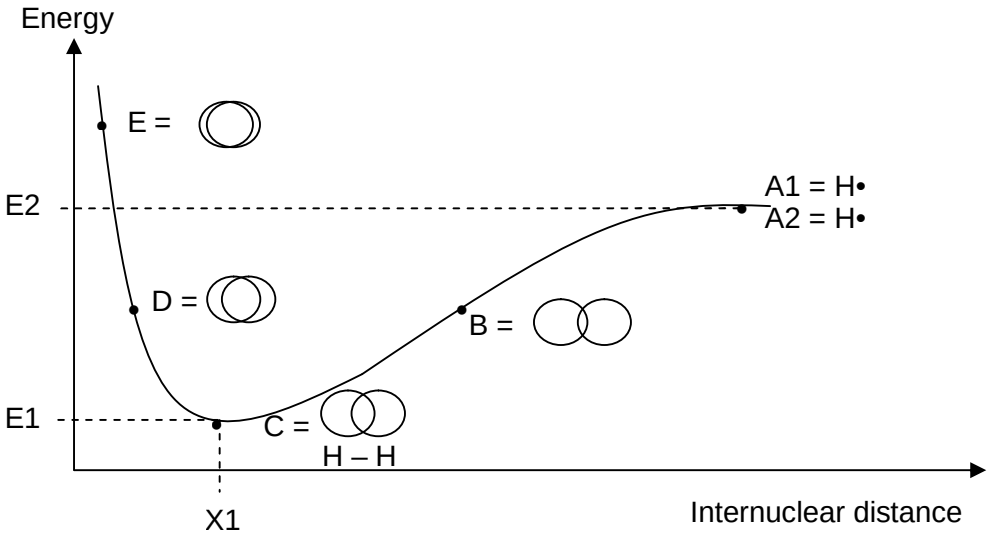
$4{,}05\cdot10^{-16} = \frac{(x)^2\cdot x/2}{(1-x)^2}\cdot\frac{1.013\cdot10^4}{1+x/2}$ $\quad$ by trying $\quad 4.3081\cdot10^{-7} < x < 4.3082\cdot10^{-7}$

or as $x<<1$ by simplification $1-x \approx 1$ and $1 + x/2 \approx 1$:

$x^3 = 7.996\cdot10^{-20}$ $\quad x \approx 4.308_{15}\cdot10^{-7}$ $\quad$ **$x > 2.0\cdot10^{-7}$** q.e.d.

Solution to problem 3-18

a)



B: the 1s orbitals overlap a bit but not in an optimal way. The energy of the H_2 molecule is lower than that of the isolated atoms.

C: Attraction and repulsion by the positive nucleus und the negative electron shell are in equilibrium. The energy of the H_2 molecule is lower than that of the isolated atoms.

D: The positive nuclei of the H_2 molecule are closer together, they repel each other, there is no equilibrum between attraction and repulsion. The energy of the system is higher than in C but still lower than that of the two single atoms.

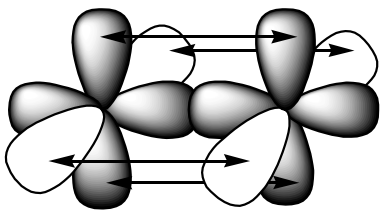
E: Though there is a great overlapping the repulsion is very strong and leads to a high energy, higher than that of both single atoms.

b) Point C,
bond length corresponds to X1 and bond energy to E2 – E1.

c) Lewis formula of N_2:

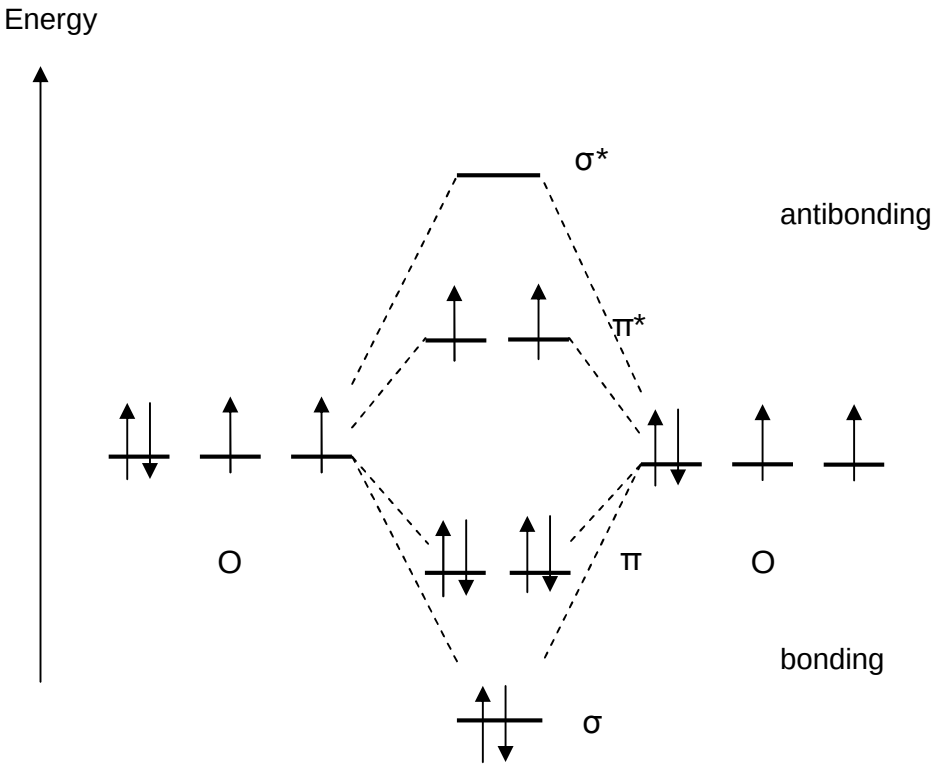
: N ⋮⋮ N **:** or |N ≡ N|

Bond following Valence Bond Theory:

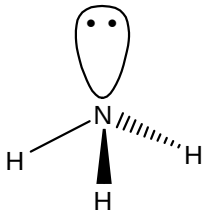


p_x and p_x form a σ bond (or overlap of sp hybrid orbitals)
p_y and p_y form a π bond
p_z and p_z form a π bond

d) Simplified MO diagram of O_2:

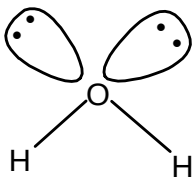


e) Structure of NH_3:



∢HNH is smaller than ∢HCH.
Reason: a non binding orbital with a free electron pair needs more space than a binding one.
The tetraedron is pressed.

Structure of H_2O:

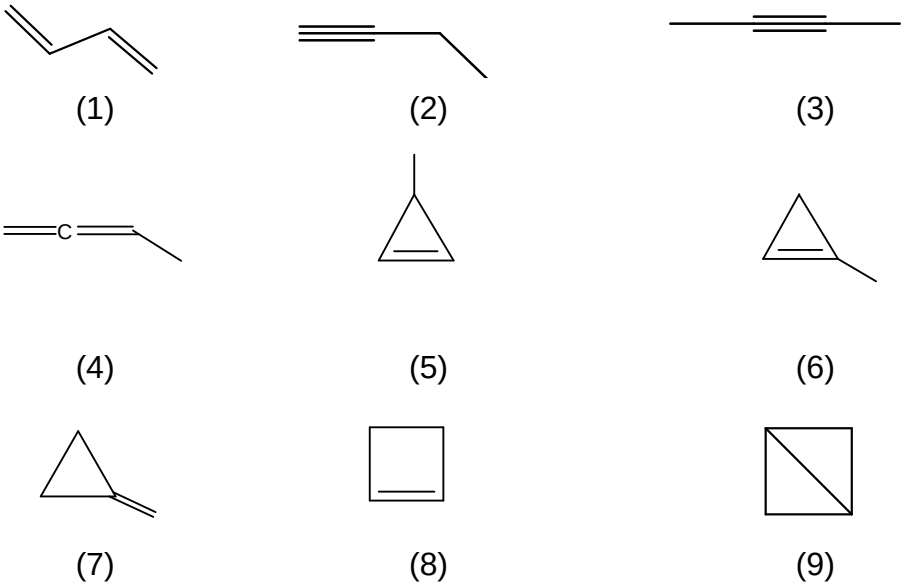


Again a smaller angle ∢HOH than the tetrahedral bond angle ∢HCH and even smaller than angle ∢HNH in ammonia.
Reason: large required space for two orbitals filled with non binding electrons.

f) 1. pair: (1)
2. pair: no difference between (3) and (4)
3. pair: (5)

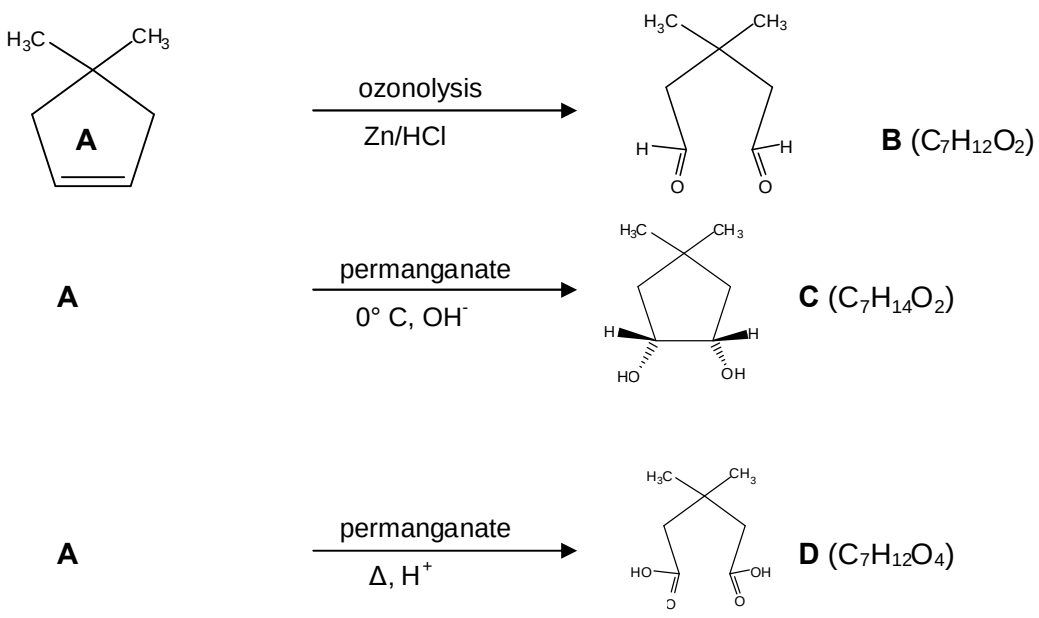
g) Resonance structures are the attempt to draw the structure of a molecule by line-bond structures. Non of them is correct by itself. The true structure is somewhere in between.

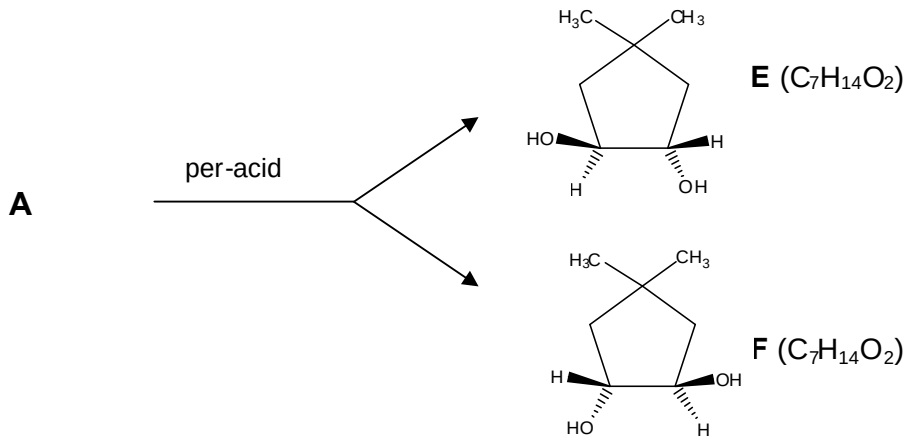
h) Structures of C_4H_6



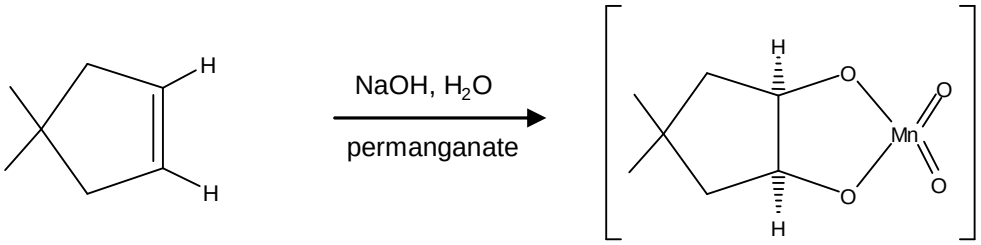
Solution to problem 3-19

a)

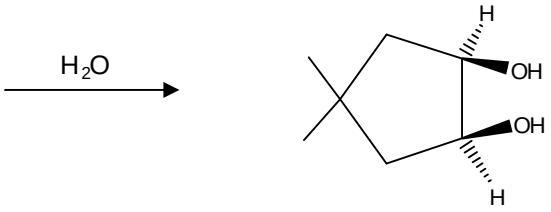




b) Mechanism of the reaction of alkenes with permanganate



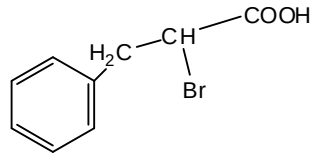
cyclic intermediate leads by performing hydrolysis to cis diol



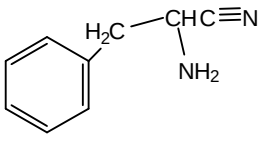
c) 3D structures of **C**, **E** and **F** see a)
C/**E** and **C**/**F** diastereomers **E**/**F** enantiomers

Solution to problem 3-20

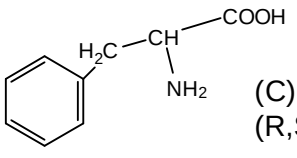
a)



(A)

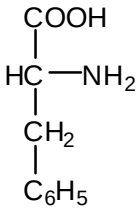


(B)

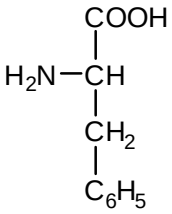


(C)
(R,S)-Phenylalanine

b)



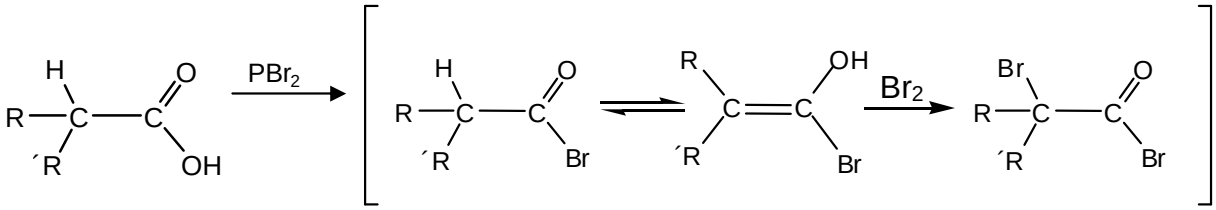
R-Phenylalanine

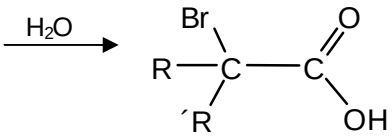


S-Phenylalanine

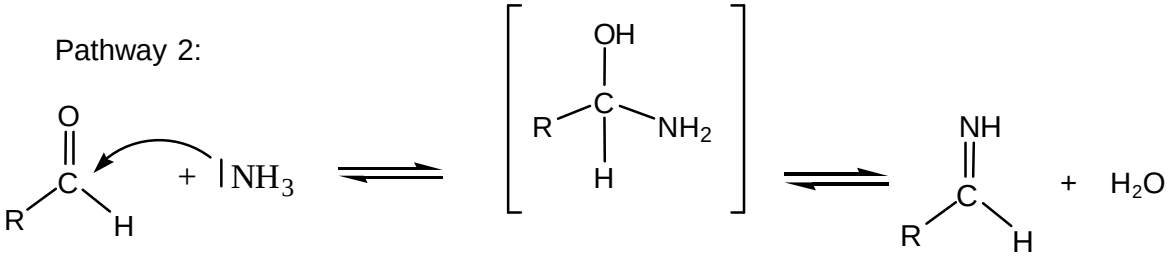
c) Pathway 1:

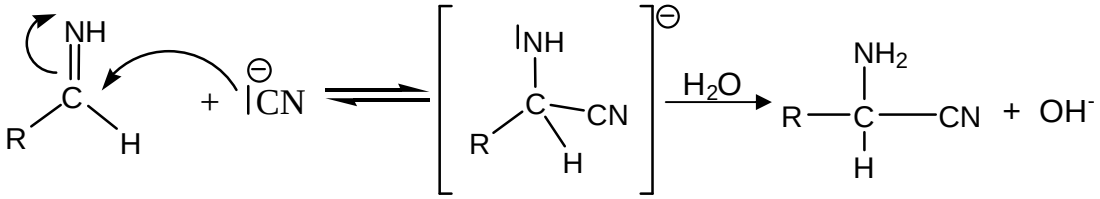
(Hell-Volhard-Zelinsky-reaction) An acid bromide forms, which tautomerizes to an enol. The enol adds bromine. Then in a halogen/OH exchange acid takes place.





Pathway 2:



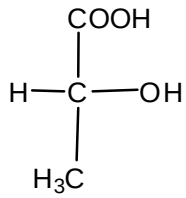


Reaction with lNH_3.

Cleavage of water and formation of an imine.

Addition of CN^- to the double bond of the imine.

d)

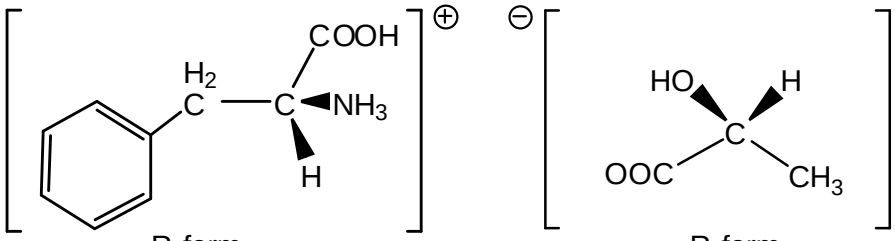


R-Lactic acid

e) R-form.

f) Two salts:

e.g.:



R-form R,R-salt R-form

accordingly: S,R-salt

g) Both salts are diastereomers.

1. step: They can be seperated by fractional cristallization.
2. step: By adding acid (HCl) both salts form R-lactic acid and one of them R-amino acid, the other one S-amino acid.

Answers Round 4 (theoretical)

Solution to problem 4-1

a) $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}f^{14}\ 5s^2p^6d^{10}f^{14}\ 6s^2p^6d^{10}\ 7s^2p^5$ group of halogens

b) ${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$ ${}^{14}_{6}C \longrightarrow {}^{14}_{7}N + e^-$

c) rate law $N = N_0 \cdot e^{-\lambda \cdot t}$ with $\lambda = \frac{\ln 2}{t_{1/2}}$

$t = \lambda^{-1} \cdot \ln \frac{N_0}{N}$ (The number of decays is proportional to N)

$t = \frac{5730}{\ln 2}\,a \cdot \ln \frac{13.6}{12}$ $t = 1035$ a The tree was cut in the year of **948**.

d) Rate $= \lambda \cdot N \Rightarrow$ $N = \frac{13.6}{\ln 2} \cdot 5730 \cdot 365 \cdot 24 \cdot 60 =$ $5.91 \cdot 10^{10}$ atoms of ^{14}C/g C

1 g of carbon contains 0.989 g of ^{12}C. that are $\frac{0{,}989}{12} \cdot 6.022 \cdot 10^{23}$ atoms of ^{12}C/g C

$$\frac{N(^{12}C)}{N(^{14}C)} = \frac{0.989 \cdot 6.022 \cdot 10^{23}}{12} \cdot \frac{\ln 2}{13.6 \cdot 5730 \cdot 365 \cdot 24 \cdot 60} = \frac{8.40 \cdot 10^{11}}{1}$$

e) $N_{0(238)} \cdot e^{-\lambda(238) \cdot t} = N_{0(235)} \cdot e^{-\lambda(235) \cdot t}$

$\frac{N_{0(238)}}{N_{0(235)}} = e^{-\lambda(235) \cdot t + \lambda(238) \cdot t}$ $\lambda = \frac{\ln 2}{t_{1/2}}$

$$t = -\ln \frac{N_{0(238)}}{N_{0(235)}} / \left(\ln 2 \cdot \left(\frac{1}{t_{1/2(235)}} - \frac{1}{t_{1/2(238)}}\right)\right)$$

$$t = -\ln \frac{99.275}{0.720} / \left(\ln 2 \cdot \left(\frac{1}{4.468 \cdot 10^9} - \frac{1}{7.038 \cdot 10^8}\right)\right)$$ **$t = -5.9 \cdot 10^9$ a**

(The age of the earth amounts between $4.6 \cdot 10^9$ and $5 \cdot 10^9$ a)

f) ${}^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta} {}^{234}Pa \xrightarrow{\beta} {}^{234}U$

g) $N_{238} \cdot \lambda_{238} = N_{234} \cdot \lambda_{234}$

$t_{1/2(234)} = t_{1/2(238)} \cdot \frac{N_{234}}{N_{238}}$

$t_{1/2(234)} = 4.468 \cdot 10^9\ a \cdot \frac{0.005}{99.275}$ **$t_{1/2(234)} = 2.3 \cdot 10^5$ Jahre**

Solution to problem 4-2

a) Proposal A: **2. order** proposal B: **3. order**

b) $\frac{d[H_2SO_4]}{dt} = k_2 \cdot [SO_3 \cdot 2H_2O]$. With the steady-state approximation you have to substitute $[SO_3 \cdot 2H_2O]$ by $[SO_3]$ and $[H_2O]$.

$$\frac{d[SO_3 \cdot 2H_2O]}{dt} = k_1 \cdot [SO_3] \cdot [H_2O]^2 - k_{-1}[SO_3 \cdot 2H_2O] - k_2 \cdot [SO_3 \cdot 2H_2O] = 0$$

$$\Rightarrow \quad (k_{-1} + k_2) \cdot [SO_3 \cdot 2H_2O] = k_1 \cdot [SO_3] \cdot [H_2O]^2$$

$$[SO_3 \cdot 2H_2O] = \frac{k_1 \cdot [SO_3] \cdot [H_2O]^2}{k_{-1} + k_2}.$$

$$\frac{d[H_2SO_4]}{dt} = k_2 \cdot [SO_3 \cdot 2H_2O] = \frac{k_1 \cdot k_2 [SO_3] \cdot [H_2O]^2}{k_{-1} + k_2} \quad .$$

Thus the rate law of the formation of H_2SO_4 is of **3.order.**

c) Proposal A: Arrhenius equation: $k = A \cdot e^{-Ea/(R \cdot T)} = A \cdot e^{-80000/RT}$

$\Rightarrow$ The rate constant increases with increasing temperature

Proposal B: Arrhenius equation: : $k = A \cdot e^{-Ea/(R \cdot T)} = A \cdot e^{+20000/RT}$

$\Rightarrow$ The rate constant decreases with increasing temperature

d) Proposal B

Solution to problem 4-3

A

a) Only redox couples with -0.41 V < E° < 0.77 V are relevant:

$2\ Fe^{3+} + 2\ I^- \longrightarrow 2\ Fe^{2+} + I_2$ (i)

$2\ Fe^{3+} + H_2SO_3 + H_2O \longrightarrow 2\ Fe^{2+} + SO_4^{2-} + 4\ H^+$ (ii)

$2\ Fe^{3+} + Sn^{2+} \longrightarrow 2\ Fe^{2+} + Sn^{4+}$ (iii)

b) At equilibrium $E(Fe^{3+}/Fe^{2+}) = E(Ox/Red)$:

$$0.77\ V + \frac{8.314 \cdot 298}{96485} V \cdot \ln \frac{c(Fe^{3+})}{c(Fe^{2+})} = E°(Ox/Red) + \frac{8.314 \cdot 298}{z \cdot 96485} V \cdot \ln \frac{c(Ox)}{c(Red)}$$

(i) $\frac{(0.77 - 0.54) \cdot 2 \cdot 96485}{8.314 \cdot 298} = \ln \frac{c^2(Fe^{2+})}{c^2(Fe^{3+}) \cdot c^2(I^-)}$ $\ln K = 17.9$ **$K = 60.2 \cdot 10^6$**

(ii) $\ln \frac{c^2(Fe^{2+}) \cdot c(SO_4^{2-}) \cdot c^4(H^+)}{c^2(Fe^{3+}) \cdot c(H_2SO_3)} = 44.4$ **$K = 1.91 \cdot 10^{19}$**

(iii) $\ln \frac{c^2(Fe^{2+}) \cdot c(Sn^{4+})}{c^2(Fe^{3+}) \cdot c(Sn^{2+})} = 48.3$ **$K = 9.38 \cdot 10^{20}$**

c). d)

		$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$		
	initial	c_{total}	0	≈ 0
	at equilibrium	$c_{total} - x$	x	x

$K_a = \frac{x^2}{c_{total} - x}$ $\quad x^2 + 6.3\cdot10^{-3}\cdot x - 6.3\cdot10^{-3}\cdot8.5\cdot10^{-3} = 0$

$x_1 = 4.82\cdot10^{-3}$ $\quad pH = -\log x_1$ $\quad$ **pH = 2.32**

$\alpha = x_1/c_{total}$ $\quad \alpha = 4.82\cdot10^{-3}/8.5\cdot10^{-3}$ $\quad$ **α = 0.567**

e) $c(Fe^{3+}) = c_{total} - \alpha\cdot c_{total}$ $\quad c(Fe^{3+}) = 3\cdot10^{-3}$ mol/L · (1 - 0.740)

$c(Fe^{3+}) = 7.80\cdot10^{-4}$ mol/L

$c(H_3O^+) = \alpha\cdot c_{total}$ $\quad c(H_3O^+) = 2.22\cdot10^{-3}$ mol/L $\quad c(OH^-) = 10^{-14}/2.22\cdot10^{-3}$ mol/L

$c(OH^-) = 4.50\cdot10^{-12}$ mol/L

$c(Fe^{3+})\cdot c(OH^-)^3 = 7.11\cdot10^{-38}$ (mol/L)^4 > $6.3\cdot10^{-38}$ (mol/L)^4

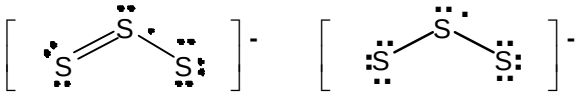
A precipitate of $Fe(OH)_3$ will form!

B

f) n = 4x-2y $\quad$ g) 2 $\quad$ h) $Ag_{10}[Si_4O_{13}]$

i) $Na_4[Al_3Si_3O_{12}]S_3$ $\quad$ j) $2\ S_3^- + 2\ H_3O^+ \longrightarrow 5\ S + H_2S + 2\ H_2O$

k)



Solution to problem 4-4

a) $K_p = \frac{p(NH_3)^2}{p(H_2)^3\cdot p(N_2)}$ $\quad K_p = \frac{0.499^2}{0.376^3\cdot0.125}$ $\quad$ **K_p = 37.47 bar $^{-2}$**

$K = K_p\cdot p_{standard}^{-\Delta n}$ $\quad \Delta n = -2$ $\quad K = 37.47\cdot1.013^2 = 38.45$

$\Delta G° = -RT\cdot\ln K$ $\quad \Delta G° = -8.314\cdot400\cdot\ln 38.45$ Jmol^{-1}

$\Delta G°$ = -12136 Jmol^{-1} **≈ -12.140 kJmol^{-1}**

b) $n(N_2) = \frac{n(H_2)}{p(H_2)}\cdot p(N_2)$ $\quad n(N_2) = \frac{500mol}{0.376}\cdot0{,}125$ $\quad$ **$n(N_2)$ = 166 mol**

$n(NH_3) = \frac{n(H_2)}{p(H_2)}\cdot p(NH_3)$ $\quad n(NH_3) = \frac{500mol}{0.376}\cdot0.499$ $\quad$ **$n(NH_3)$ = 664 mol**

$p_{gesamt} = p(H_2) + p(N_2) + p(NH_3)$ $\quad p_{gesamt}$ = 1 bar $\quad n_{gesamt}$ = 1330 mol

c) Due to the addition of hydrogen all partial pressures change: $n_{gesamt.\ neu}$= 1340 mol.

$p_{neu}(H_2) = \frac{510}{1340}\cdot 1bar$ $\quad p_{neu}(H_2)$ = 0.381 bar

$p_{neu}(N_2) = \frac{166}{1340}\cdot 1bar$ $\quad p_{neu}(N_2)$ = 0.124 bar

$p_{neu}(NH_3) = \frac{664}{1340}\cdot 1bar$ $\quad p_{neu}(NH_3)$ = 0.496 bar

$\Delta G = [-12140 + 8.314\cdot400\cdot\ln(\frac{0.496^2}{0.381^3\cdot0.124}\cdot1.013^2)]$ Jmol^{-1} $\quad$ **$\Delta G \approx$ - 149 Jmol^{-1}**

The mixture reacts towards the right hand side to form more NH_3.

d) You may argue with Le Chatelier's principle that by adding N_2 the system will react to form more product NH_3. But in this case Le Chatelier's principle (a system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize its effect) does not allow an intuitive statement about the direction of the reaction, because all of the three partial pressures change in different ways.

Calculation:

$n_{equi}(H_2) + n_{gl}(N_2) + n_{gl}(NH_3) = 775$ mol

$n_{new}(H_2) + n_{new}(N_2) + n_{new}(NH_3) = 785$ mol

$p_{new}(H_2) = \frac{100}{785} \cdot 1\text{bar}$ $\quad p_{new}(N_2) = \frac{510}{785} \cdot 1\text{bar}$ $\quad p_{new}(NH_3) = \frac{175}{785} \cdot 1\text{bar}$

$$\frac{175^2}{100^3 \cdot 510} \cdot 785^2 \text{ bar}^{-2} = 37.00 \text{ bar}^{-2} > K_p = 36.79 \text{ bar}^{-2}$$

Thus the numerator is too high, the system reacts to form N_2 and H_2, reacts to the left.

You get the same result if you calculate ΔG:

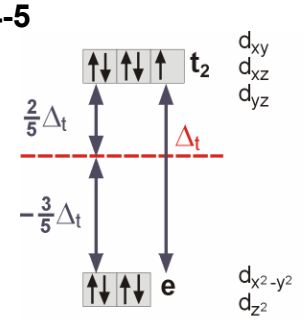
$K = K_p \cdot 1.013 \text{ bar}^2$ $\quad \Delta G° = -8.314 \cdot 410 \cdot \ln(36.79 \cdot 1.013^2)$ J·mol^{-1}

$$\Delta G = 8.314 \cdot 410 \cdot [-\ln(36.79 \cdot 1.013^2) + \ln(\frac{175^2}{100^3 \cdot 510} \cdot 785^2 \cdot 1.013^2)] \text{ J·mol}^{-1}$$

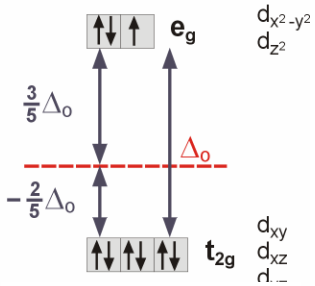
$\Delta G = +19.74$ J·mol$^{-1} > 0$ $\quad \Rightarrow$ the systems reacts towards the left.

Solution to problem 4-5

a)



Splitting of the d-orbitals in a tetrahedral crystal field



Splitting of the d-orbitals in an octahedral crystal field

Kristallfeld **Kristallfeld**

Tetrahedron: $CFSE = \left(-\frac{3}{5}\Delta_t\right) \cdot 4 + \left(\frac{2}{5}\Delta_t\right) \cdot 5 = -0.4\Delta_t \equiv -0.178\Delta_o$ ($\Delta_t = 4/9\ \Delta_o$)

Octahedron: $CFSE = \left(-\frac{2}{5}\Delta_o\right) \cdot 6 + \left(\frac{3}{5}\Delta_o\right) \cdot 3 = -0.6\Delta_o$

CSFE(octahedron) < CSFE(tetrahedron) $\Rightarrow$ octahedral coordination is preferred.

b) Following the principle of HSAB the combinations hard/hard and soft/soft are more stable than mixed ones. Copper (II) (d^9 system) is a weak acid and thus forms with the weak base NH_3 a more stable adduct as with the hard base OH_2.

c) The splitting of the d-orbitals in the ammin complex is larger as ammonia leads to stronger ligand fields than water, following the spectrochemical series. Therefore the energetically higher maximum of absorbtion of 15000 cm^{-1} belongs to the tetraammin complex. The hexaqua complex absorbs at 12000 cm^{-1} in the range of infrared, thus it is only faintly coloured. By changing ligands (water-ammonia) a transition to blue occurs: absorbtion of the the tetraammin complex in the range of orange-red leads to an intensively blue colour.

d) at first formation of an light blue precipitate:

$Cu^{2+} + 2\ OH^- \rightleftharpoons Cu(OH)_2$

followed by dissoluiton and formation of the intensively blue ammin:

$Cu(OH)_2 + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 2\ OH^-$

e) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ $\quad \Delta G° = \Delta H° - T\cdot\Delta S°$

$\Delta H° = 44.0\ kJ\cdot mol^{-1}$ $\quad \Delta S° = 118.6\ J\cdot mol^{-1}\cdot K^{-1}$ $\quad \Delta G° = 8.657\ kJ\cdot mol^{-1}$

$K_p = p°(H_2O_{(g)})$ $\quad K = \dfrac{p^0(H_2O)}{p_{standard}}$

$\Delta G° = -RT\cdot\ln K$ $\quad K = e^{-8657/(8.314\cdot 298)}$ $\quad K = 3.04\cdot 10^{-2}$

$p°(H_2O_{(g)}) = 3.04\cdot 10^{-2}\cdot p_{standard}$ $\quad$ **$p°(H_2O_{(g)}) = 3080$ Pa**

f) $CuSO_4\cdot 5\ H_2O_{(s)} \rightleftharpoons CuSO_4\cdot 3\ H_2O_{(s)} + 2\ H_2O_{(g)}$

$\Delta G° = [-1683.1 - 2\cdot 241.8 + 2278 - 0.298\cdot(225.1 + 2\cdot 188.7 - 305.4)]\ kJ\cdot mol^{-1}$

$\Delta G° = [111.3 - 88.5]\ kJ\cdot mol^{-1} = 22.8\ kJ\cdot mol^{-1}$

$K = e^{-22800/(8.314\cdot 298)}$ $\quad K = 1.008\cdot 10^{-4}$

$K_p = p^2(H_2O)$ $\quad K = \left(\dfrac{p(H_2O)}{p_{standard}}\right)^2$ $\quad \left(\dfrac{p(H_2O)}{p_{standard}}\right)^2 = 1.008\cdot 10^{-4}$

$p(H_2O) = 1.04\cdot 10^{-2}\cdot p_{standard}$ $\quad p(H_2O) = 1017$ Pa

„threshold“ $= \dfrac{p(H_2O)}{p^0(H_2O)}\cdot 100\% = \dfrac{1017}{3080}\cdot 100\%$ **$= 33$ % air humidity**

Solution to problem 4-6

a) Ammonium chloride is added in order to keep magnesium in solution and to inhibit the precipitation of magnesium as $Mg(OH)_2$. Ammonium chloride decreases the hydroxide concentration.

b) Calcium oxalate is soluble in acids, a pH value which is too high leads to the formation of the hydroxide.

c) $Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$

$2\ MnO_4^{2-} + 5\ C_2O_4^{2-} + 16\ H_3O^+ \rightleftharpoons 2\ Mn^{2+} + 10\ CO_2 + 24\ H_2O$

d) $5\ As_2O_3 + 4\ MnO_4^- + 12\ H_3O^+ \rightleftharpoons 10\ H_3AsO_4 + 4\ Mn^{2+} + 3\ H_2O$

$n(MnO_4^-) = 4/5 \cdot n(As_2O_3)$ $n(As_2O_3) = (0.02\ mol/L \cdot 0.0128\ L)/0.8$

$n(As_2O_3) = 3.2 \cdot 10^{-4}\ mol$ $m(As_2O_3) = n(As_2O_3) \cdot M(As_2O_3)$

$m(As_2O_3) = 3.2 \cdot 10^{-4}\ mol \cdot 197.84\ gmol^{-1}$ **$m(As_2O_3) = 0.0633\ g$**

e) $\frac{consumpt. \cdot 0.02 mmol/mL \cdot 5 \cdot M(Ca)}{2}$ = mass of Ca

tablets of A: mean consumption = 34.93 mL

mass of calcium cations = 70.00 mg / 2 tablets **35.00 mg of Ca/tablet A**

tabets of B: mean consumption = 31.93 mL

mass of calcium cations = 64.00 mg / 2 tablets **32.00 mg of Ca/tablet B**

f) $Mg^{2+} + (NH_4)_2HPO_4 + NH_3 \rightleftharpoons Mg(NH_4)PO_4 + 2\ NH_4^+$

g) $2\ Mg(NH_4)PO_4 \rightleftharpoons Mg_2P_2O_7 + 2\ NH_3 + H_2O$

h) An excess of NH_4^+ leads to the formation of HPO_4^- and may induce the precipitation of $MgHPO_4$. An excess of OH^- leads to the formation of magnesium phosphate and besides that to the precipitation of magnesium hydroxide. Ammonium chloride and diammonium hydrogensphosphate if in too high concentrations may also precipitate.

i)

	Tablets of A	Tablets of B
mean mass m	192.33 mg	238.13 mg
mass of Mg in 2 tablets = m · 0.2184	42 mg	52 mg
mass of Mg in 1 tablet	21 mg	26 mg

j) $M(CaCO_3) = 100.09$ g/mol. $M(MgCO_3) = 84.31$ g/mol

$M(C_{12}H_{10}Ca_3O_{14} \cdot 4\ H_2O) = 570.50$ g/mol. $M(C_{12}H_{10}Mg_3O_{14} \cdot 14\ H_2O) = 703.35$ g/mol

	Tablets of A	Tablets of B
masse of one tablet	1.2 g	1.25 g
filling material	0.094 g (7.8%)	1.080 g (86.4%)
mass of minerals	1.105 g	0.170 g
mass of $CaCO_3$ with a content of 32 mg Ca^{2+}		0.080 g
mass of $MgCO_3$ with a content of 26 mg Mg^{2+}		0.090 g
mass of Ca citrate with a content of 35 mg Ca^{2+}	0.498 g	
mass of Mg citrate with a content of 21 mg Mg^{2+}	0.608 g	
filling material (m(Ca^{2+}) + m((Mg^{2+}) /tablet	56 mg	58 mg
filling material (m(Ca^{2+}) + m((Mg^{2+}) /tablet	4.66 %	4.64 %

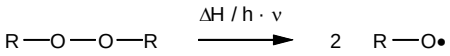
Only the combinations shown above fulfill the given conditions of the masses of the tablets.

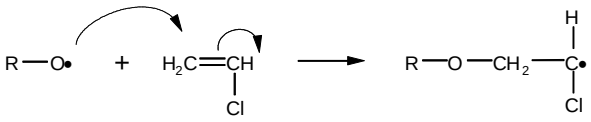
⇒ **Product A: citrates, product B: carbonates**

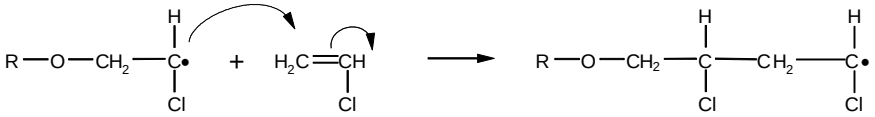
The content of minerals is approximately identical.

Solution to problem 4-7

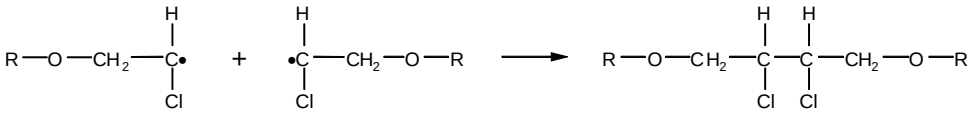
a)

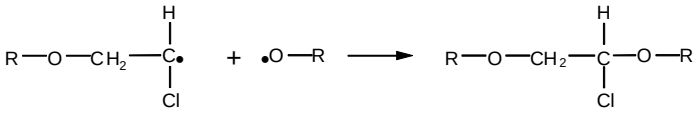




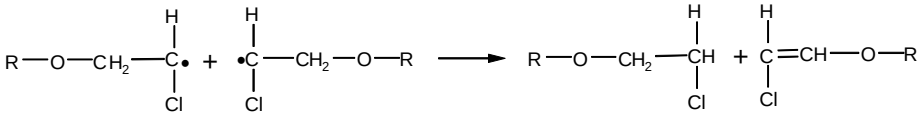


b) recombination of two radicals

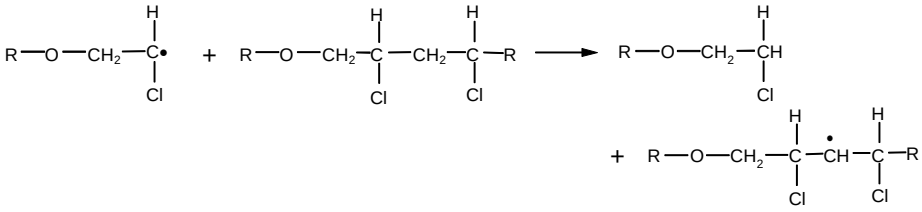




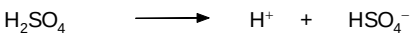
disproportionation

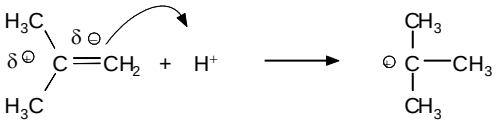


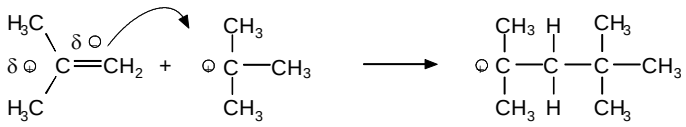
transfer of the radical function onto another molecule



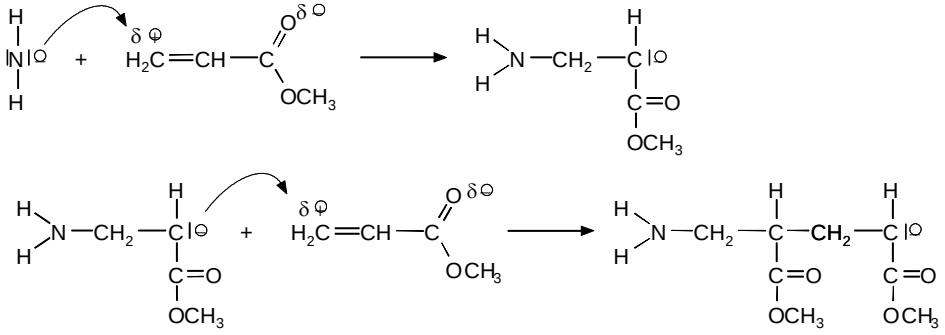
c)





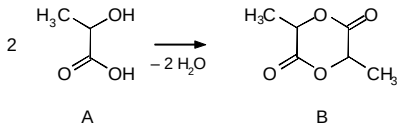


d)

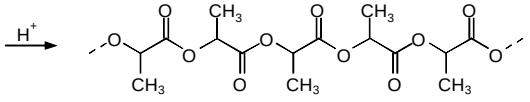


e) The initializing compound is incorporated in the polymer and thus consumed. A real catalyzer is set free after the reaction

f)

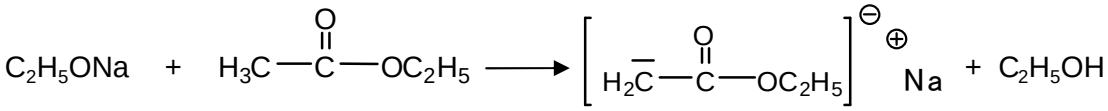


A B

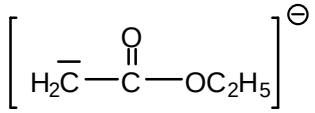


C

Solution to problem 4-8

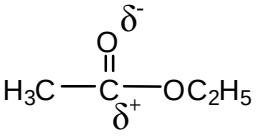
a) 

b) Nucleophilic part of reaction:

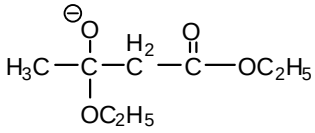


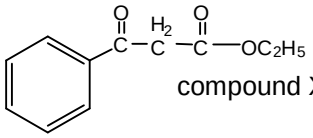
(donator)

Electrophilic part of reaction:



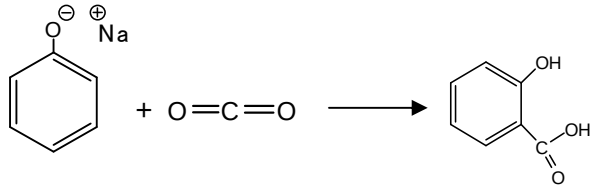
(acceptor)

c) Intermediate:  (instable)

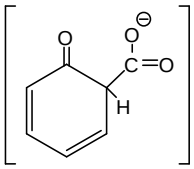
d) 
compound X

C_2H_5OH
compound Y

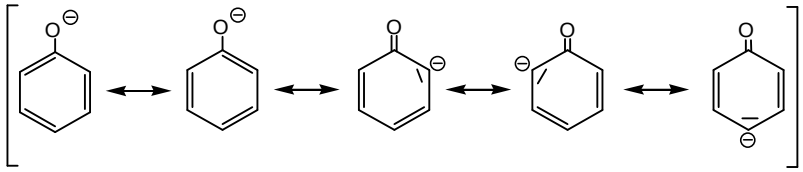
e) Reaction to form slicylic acid



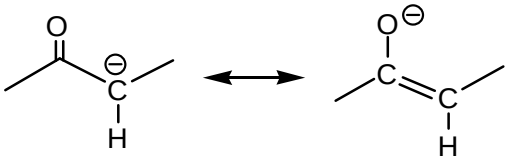
intermediate:
anion of a keto carboxylic acid



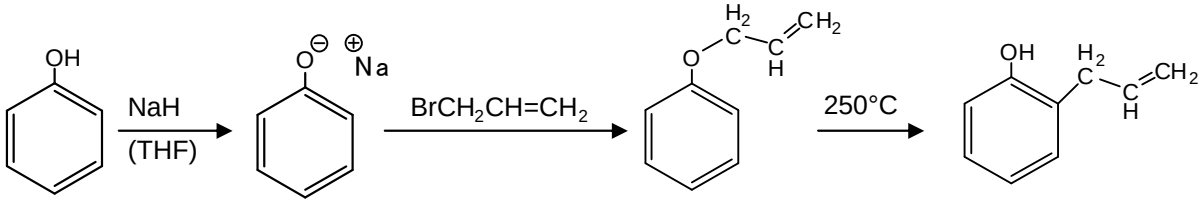
f)



g) A phenolate anion possesses an α-C-atom with negative charge as an enolate ion does

enolate ion: 

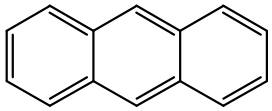
h)



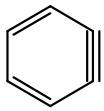
compound A | compound B | compound C

Solution to problem 4-9

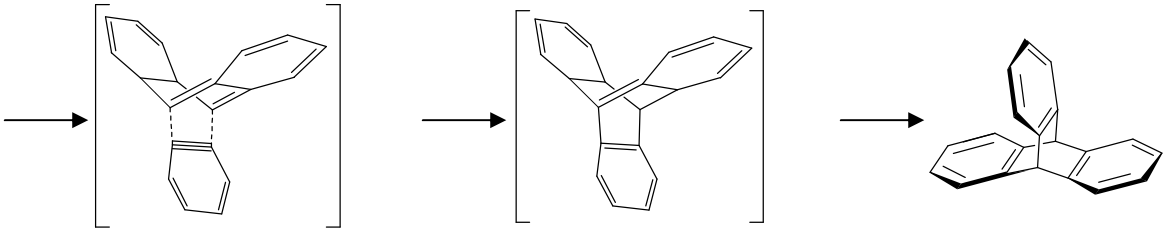
a)



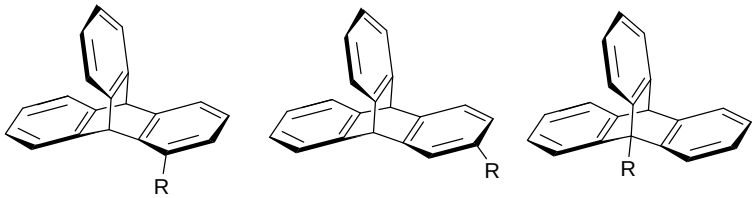
Anthracene



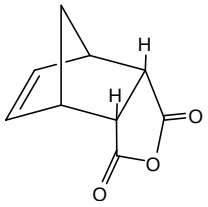
Dehydrobenzene



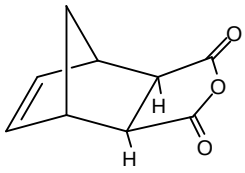
b) 3 Isomers:



c)

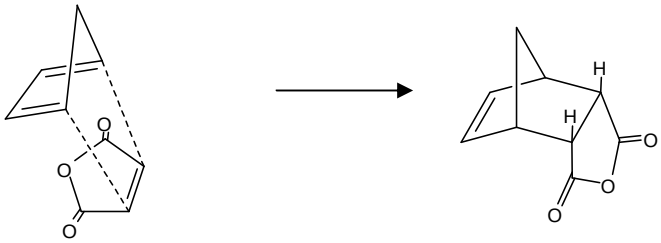


endo



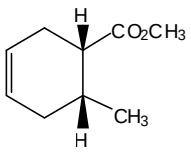
exo

d)

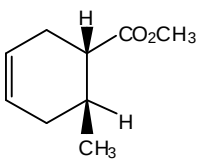


endo-product

e)



compound X, Z-product

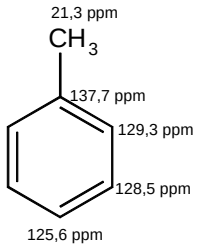


compound Y, E-product

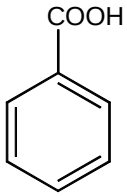
Answers Round 4 (practical)

Solution to problem 4-10

a) A: Toluol



b)



The aquous solution should be slightly acidic.

c)

$$2\ \overset{+VII}{MnO_4^-} + R\text{-}\overset{-III}{CH_3} \longrightarrow 2\ \overset{+IV}{MnO_2} + \overset{+III}{RCOO^-} + H_2O + OH^-$$

$$MnO_4^- + 3\ e^- + 2\ H_2O \longrightarrow MnO_2 + 4\ OH^-$$

$$R\text{-}CH_3 + 7\ OH^- \longrightarrow RCOO^- + 6\ e^- + 5\ H_2O$$

d) melting point 122°C

e) $R_f = 0.70$

Solution to problem 4-11

a) The concentration of the hydrogencarbonate ions may be calulated by the formula
10/L · consumption (in mL) · 0.1 mmol/mL = c(HCO_3^-) (in mmol/L).

b) Dissolved carbon dioxide causes a slightly acidic reaction of the solution. Thus the colour of the indicator changes before the equivalent point is reached.

c) 1 mL of Na_2EDTA solution with c(Na_2EDTA = 0.01 mol/L $\triangleq$ 0.01 mmol/L of (Ca^{2+} + Mg^{2+})
The total hardness may then be calculated by
20/L · consumption (in mL) · 0.01 mmol/mL = c(Ca^{2+} + Mg^{2+}) (in mmol/L)

d) The concentraton of calcium ions may be calculated by
20/L · consumption (in mL) · 0.01 mmol/mL = c(Ca^{2+}) (in mmol/L)

e) The magnesium hardness ist the difference between the total hardness and the calcium hardness. Usually the magnesium hardness is considerably smaller than the calcium hardness.

f) If the carbonate hardness is higher than the permanent hardness, no permanent hardness caused by $Ca^{2+}$and Mg^{2+} ions exist. The reason is that hydrogencarbonates of other metals are dissolved in water, which are not detected in the determination of the total hardness.

g) Carbonte hardness according to a):
1 mL of HCl with c(HCl) = 0.1 mol/L $\triangleq$ 0.1 mmol/L of HCO_3^-
$\triangleq$ 0.05 mmol/L of CaO.

The carbonate hardness in °dH may then be calculated by:

$$\frac{\text{consumpt. of HCl (in mL)} \cdot 0.1\,\text{mol/L} \cdot 10\,\text{/L} \cdot 0.5 \cdot \text{M(CaO) (in g/mol)}}{10\,\text{mg/L}} = \text{carb. hardness in °dH}$$

Total hardness according to c):

$$\frac{\text{consumpt. of EDTA (in mL)} \cdot 0.01\,\text{mol/L} \cdot 20\,\text{/L} \cdot \text{M(CaO) (in g/mol)}}{10\,\text{mg/L}} = \text{total hardness in °dH}$$

Part 3

CHEMISTRY: ART, SCIENCE, FUN

THEORETICAL EXAMINATION
PROBLEMS

JULY 20, 2007
MOSCOW, RUSSIA

General Directions

- Write your name and code number on each page of the answer sheet.
- You have 5 hours to fulfil the task. Failure to stop after the STOP command may result in zero points for the task.
- Write answers and calculations within the designated box.
- Use only the pen and the calculator provided.
- There are 18 pages of Problems (incl. Cover Sheet and Periodic Table) and **23** pages of Answer Sheet.
- An English-language version is available.
- You may go to the restroom with permission.
- After finishing the examination, place all sheets including Problems and Answer Sheet in the envelope and seal.
- Remain seated until instructed to leave the room.

Constants and useful formulas

Gas constant $R = 8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Avogadro constant $N_A = 6.022\cdot10^{23}\ \text{mol}^{-1}$

Planck constants $h = 6.626\cdot10^{-34}\ \text{J}\cdot\text{s}$

$\hbar = 1.055\cdot10^{-34}\ \text{J}\cdot\text{s}$

Speed of light $c = 3.00\cdot10^{8}\ \text{m}\cdot\text{s}^{-1}$

Uncertainty relation	$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$
Gibbs energy of a condensed phase at pressure p	$G = pV + \text{const}$
Excess pressure caused by surface tension	$\Delta P_{\text{in}} = 2\sigma / r$
Relation between equilibrium constant and Gibbs energy	$RT \ln K = -\Delta_r G^\circ$
Gibbs energy at constant temperature	$\Delta G = \Delta H - T\Delta S$
Isotherm of a chemical reaction	$\Delta G = \Delta G^\circ + RT\cdot\ln Q$ with $Q = \frac{\text{product of } c(\text{products})}{\text{product of } c(\text{reactants})}$
Arrhenius equation	$k = A\exp\left(-\frac{E_A}{RT}\right)$
Osmotic pressure of a solution	$p = cRT$
Beer- Lambert law	$A = \log\frac{P_0}{P} = \varepsilon\cdot l c$

V(cylinder) = $\pi r^2 h$

S(sphere) = $4\pi r^2$

V(sphere) = $\frac{4}{3}\pi r^3$

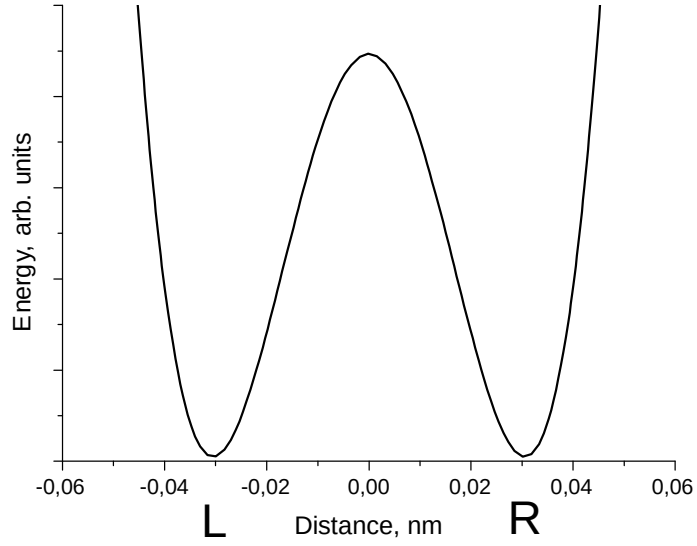
Problem 1. Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

1.1.1 *Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.*

1.1.2 *In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).*

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

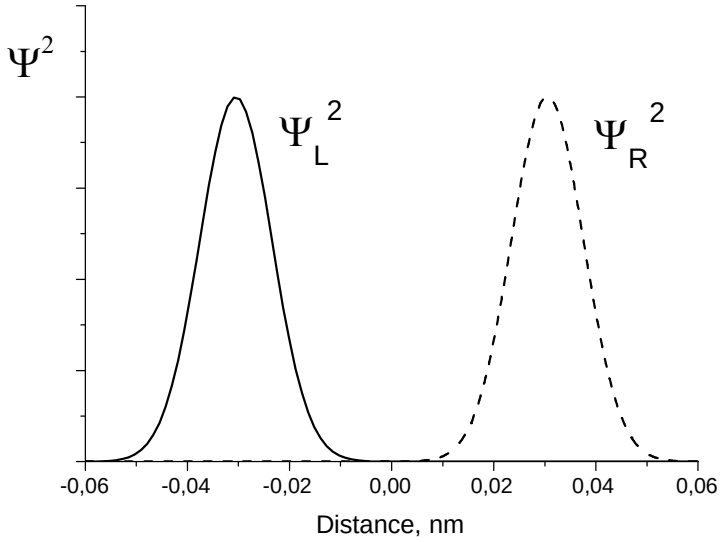


1.2.1 *Draw the structures corresponding to two minima on this curve.*

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency ω = 6.48·10^{11} s^{-1}. Probability density for a proton depends on time as follows:

$$\Psi^2(x,t) = \frac{1}{2}\left[\Psi_{\mathrm{L}}^2(x) + \Psi_{\mathrm{R}}^2(x) + \left(\Psi_{\mathrm{L}}^2(x) - \Psi_{\mathrm{R}}^2(x)\right)\cos\left(\omega t\right)\right],$$

wavefunctions $\Psi_{\mathrm{L}}(x)$ and $\Psi_{\mathrm{R}}(x)$ describe a proton localized in the left and right wells, respectively:



1.3.1 *Write down the expressions for the probability density at three moments: (a) t = 0, (b) t = $\pi/(2\omega)$, (c) t = π/ω. Sketch the graphs of these three functions.*

1.3.2 *Without calculations, determine the probability of finding the proton in the left well at t = $\pi/(2\omega)$*

1.3.3 *How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?*

1.3.4 *From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in* ***1.3.3*** *and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).*

Problem 2. Nanochemistry

Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)

$$CO + 3H_2 \xrightarrow{Fe,\ Co} CH_4 + H_2O$$

Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:

$$Co(s) + H_2O\ (gas) \rightleftharpoons CoO(s) + H_2\ (gas) \qquad (1)$$

Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

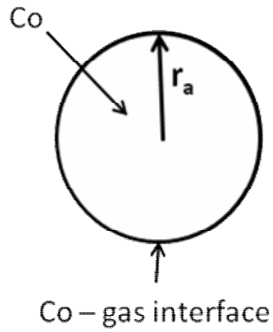


Fig. 1

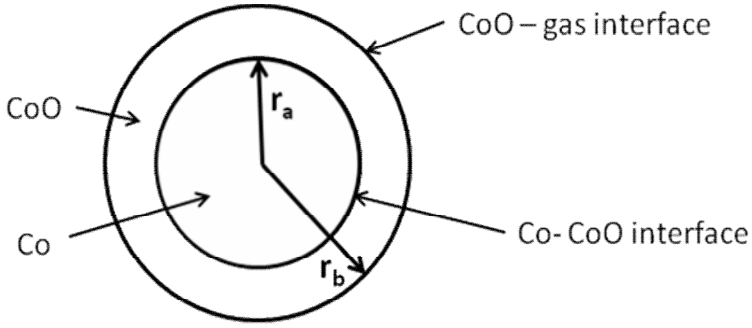


Fig. 2

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^0(r) = G^0(\text{bulk}) + \frac{2\sigma}{r}V$$

2.1.1 *Calculate the standard Gibbs energy* $\Delta_r G^0(1)$ *and the equilibrium constant for the reaction (1) at T = 500 K.*

2.1.2 *Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig.1) of radius*

(a) 10^{-8} *m,·*

(b) 10^{-9} *m.*

The surface tension at the Co-gas interface is 0.16 J/m^2. CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO, CH_4, H_2, H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is *p* = 1 bar, temperature is *T* = 500 K. The mole fraction of hydrogen (%) in the mixture is 0.15%.

2.2.1 *At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of*

(a) a bulk phase

(b) spherical nanoparticles with r_a *= 1 nm (Fig. 1).*

2.2.2 *What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio* $p(\mathrm{H_2O})/p(\mathrm{H_2})$ *and a constant temperature:*

(a) to increase r_a*;*

(b) to decrease r_a*;*

(c) change of r_a *has no effect.*

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (fig. 2).
In the following problems denote surface tensions as $\sigma_{\mathrm{CoO\text{-}gas}}$, $\sigma_{\mathrm{CoO\text{-}Co}}$, radii as r_a, r_b, molar volumes as *V*(Co); *V*(CoO).

2.3.1 *Write down the expression for the standard molar Gibbs function of CoO.*

2.3.2 *Write down the expression for the standard molar Gibbs function of Co.*

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{\mathrm{in}} - P_{\mathrm{ex}} = \Delta P = \Delta P_1 + \Delta P_2 = 2\frac{\sigma_1}{r_1} + 2\frac{\sigma_2}{r_2}$$

r_i, σ_i are radius and surface tension at the spherical interface *i,* respectively.

2.3.3 *Express the standard Gibbs energy of the reaction (1)* $\Delta_r G^0(1, r_a, r_b)$ *in terms of* $\sigma_{\mathrm{CoO\text{-}gas}}$, $\sigma_{\mathrm{CoO\text{-}Co}}$, r_a, r_b, *V(Co); V(CoO) and* $\Delta_r G^0(1)$.

2.3.4 *When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal,* $r_a = r_b = r_0$, *and* $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. *Assume that* $\sigma_{\mathrm{CoO\text{-}gas}} = 2\sigma_{\mathrm{CoO\text{-}Co}}$. *Which plot in the Answer Sheet describes correctly the dependence of* $\Delta_r G^0(1, r_0)$ *on* r_0 *?*

2.3.5 *What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio* $p(\mathrm{H_2O})/p(\mathrm{H_2})$ *and a constant temperature:*

a) increase r_0

b) decrease r_0

c) change of r_0 *has no effect.*

Reference data:

Substance	ρ, g/cm^3	$\Delta_f G^\circ_{500}$, kJ/mol
Co (s)	8.90	
CoO (s)	5.68	–198.4
H_2O (gas)		–219.1

Problem 3. Unstable chemical reactions

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.
Consider a simple reaction mechanism involving autocatalytic step:

$$\mathrm{B} + 2\mathrm{X} \xrightarrow{k_1} 3\mathrm{X}$$

$$\mathrm{X} + \mathrm{D} \xrightarrow{k_2} \mathrm{P}$$

(B and D are reagents, X is an intermediate and P is a product).

3.1.1 *Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.*

3.1.2 *Deduce a rate equation using steady-state approximation. Find the orders:*
(i) a partial reaction order with respect to B;
(ii) a partial reaction order with respect to D;
(iii) the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: [B] = [D] = const.

3.2.1 *Without solving the kinetic equation draw the kinetic curve [X](t) for the cases: 1) $[X]_0 > k_2/k_1$; 2) $[X]_0 < k_2/k_1$.*

3.2.2 *Without solving the kinetic equation draw the kinetic curve [X](t) for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[B]_0 = [D]_0$, $[X]_0 > k_2/k_1$.*

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:

$$\mathrm{C_2H_6} + \mathrm{X} + \ldots \xrightarrow{k_1} 2\mathrm{X}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} 2\mathrm{Y} + \ldots$$

$$\mathrm{C_2H_6} + \mathrm{Y} + \ldots \xrightarrow{k_3} 2\mathrm{P}$$

Under specific conditions this reaction displays oscillatory behavior.
Intermediates are peroxide $C_2H_6O_2$ and aldehyde C_2H_4O, P is a stable product.

3.3.1 *Identify X, Y, and P. Fill the blanks in the reaction mechanism.*

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, $cm^3 \cdot mol^{-1} \cdot s^{-1}$	E_A, $kJ \cdot mol^{-1}$
1	$1.0 \cdot 10^{11}$	90
2	$3.0 \cdot 10^{12}$	100

3.4.1 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

Problem 4. Determination of water by Fischer titraton

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO_2 and pyridine (C_5H_5N, Py) – Fischer reagent. The following reactions occur during the titration:

$SO_2 + CH_3OH + H_2O + I_2 = 2HI + CH_3OSO_3H$

$Py + HI = PyH^+I^-$

$Py + CH_3OSO_3H = PyH^+CH_3OSO_3^-$

Iodine content is usually expressed in mg of water reacting with 1 mL of the titrant solution (hereunder *T,* mg/mL), which equals the mass of water (mg) reacting with 1.00 mL of the iodine solution. *T* is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1. *Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I_2 with SO_2 and H_2O occur in this case? Write down balanced reaction equation.*

Calculate the T values of iodine solution in each of the following cases:

4.2.1. 12.20 mL of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2H_2O$.

4.2.2. A known amount of water (21.537 g) was placed into a 1.000 L volumetric flask which was filled by methanol up to the mark. For titration of 10.00 mL of the obtained solution, 22.70 mL of Fischer reagent solution were needed, whereas 2.20 mL of iodine were used for titration of 25.00 mL of methanol.

4.2.3. 5.624 g of water were diluted by methanol up to a total volume of 1.000 L (solution **A**); 22.45 mL of this solution were used for titration of 15.00 mL of a Fischer reagent (solut. **B**).

Then 25.00 mL of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 mL of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 mL of the latter solution were spent.

4.3. *An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.*

For the titration of 0.6387 g of a hydrated compound $Fe_2(SO_4)_3 \cdot xH_2O$, 10.59 mL of iodine solution (T = 15.46 mg/mL) were consumed.

4.4.1*. What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.*

4.4.2. *Write down an equation of the overall reaction of $Fe_2(SO_4)_3 \cdot xH_2O$ with the Fischer reagent.*

4.4.3. *Calculate the composition of the hydrate $Fe_2(SO_4)_3 \cdot xH_2O$ (x = integer).*

Problem 5. A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three colorless organic liquids **A**, **B**, **C** was treated by water with a drop of hydrochloric acid at heating to give, after separation from water, a 1:2 (molar ratio) mixture of acetic acid and ethanol without any other components. To the mixture after hydrolysis a catalytic amount (one-two drops) of concentrated sulfuric acid was added, and after long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical to any of **A**, **B**, **C**.

5.1.1 *Draw the structure of compound **D**?*

5.1.2 *Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.*

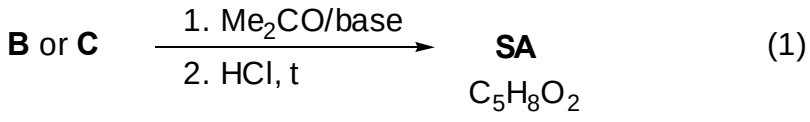
5.1.3 *Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1:1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85%); b) higher than 85%; c) lower than 85%.*

^{1}H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1:3:2.
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. The remaining solution after acidification and short boiling gave 2:3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.
The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 L (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds except diethyl ether could be identified after hydrogenation.

5.2.1 *Determine and draw the structures of **A**, **B**, and **C**.*

5.2.2 *Which intermediate compounds are formed during the acidic hydrolysis of **C**, and basic hydrolysis of **B**.*

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).



5.3.1 *Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.*

5.3.2 *Give structure of **E**.*

Problem 6. Silicates as the base of the Earth crust

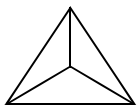
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of "liquid glass" (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1.1 *The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.*

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.1.2. *Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the "Yes" box if it leads to changes of pH. Otherwise check the "No" box.*

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-}, **1**):



(**1**)

For $[Si_3O_9]^{n-}$ ion found in aqueous solution of silicates.

6.2.1 *Determine the charge (n).*

6.2.2 *Determine the number of oxygen atoms bridging adjacent tetrahedra.*

6.2.3 *Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.*

Charged monolayers with the composition $[Si_4O_{10}]^{m-}$ are found in kaolinite (clay).

6.2.4 *Using the same strategy as in **6.2.1-6.2.3**, depict a fragment of the layered structure joining 16 tetrahedra **(1)**. Note that 10 tetrahedra have shared vertices with 2 neighbors each, and the rest 6 have shared vertices with 3 neighbors each.*

Being placed into the LGL solution, salts of transition metals give rise to fancy "trees" tinted relevant to the color of the salt of the corresponding transition metal. Crystals of $CuSO_4 \cdot 5H_2O$ produce "trees" of blue color, whereas those of $NiSO_4 \cdot 7H_2O$ form green "trees".

6.3.1 *Determine the pH of 0.1 M aqueous solution of copper sulfate at 25°C, assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[Cu(H_2O)_4]^{2+}$ $K_a^I = 1 \cdot 10^{-7}$ M.*

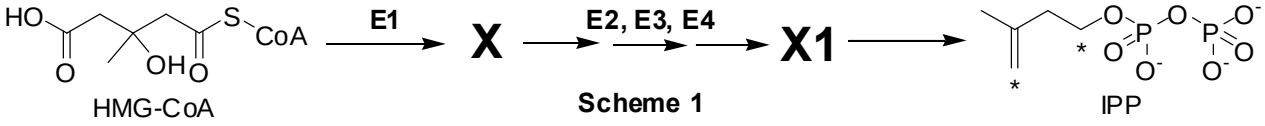
6.3.2 *Write down equation of a reaction between aqueous solutions of $CuSO_4$ and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.*

Problem 7. Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

X is an optically active monocarbonic acid composed of atoms of only three elements. It is formed in organisms from (*S*)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:

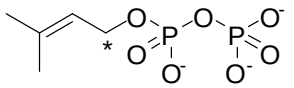


Scheme 1

7.1.1 *In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.*

7.1.2 *Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.*

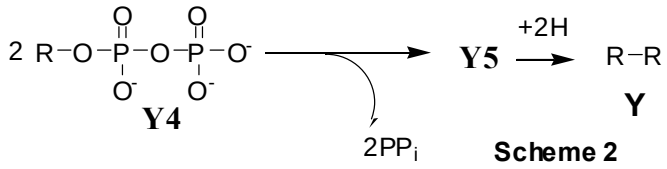
Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



DAP

7.2.1 *Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.*

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



Scheme 2

At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1:1 to the coupling product.

7.2.2 *Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.*

7.2.3 *Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.*

7.2.4 *Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.*

The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in *trans* configuration.

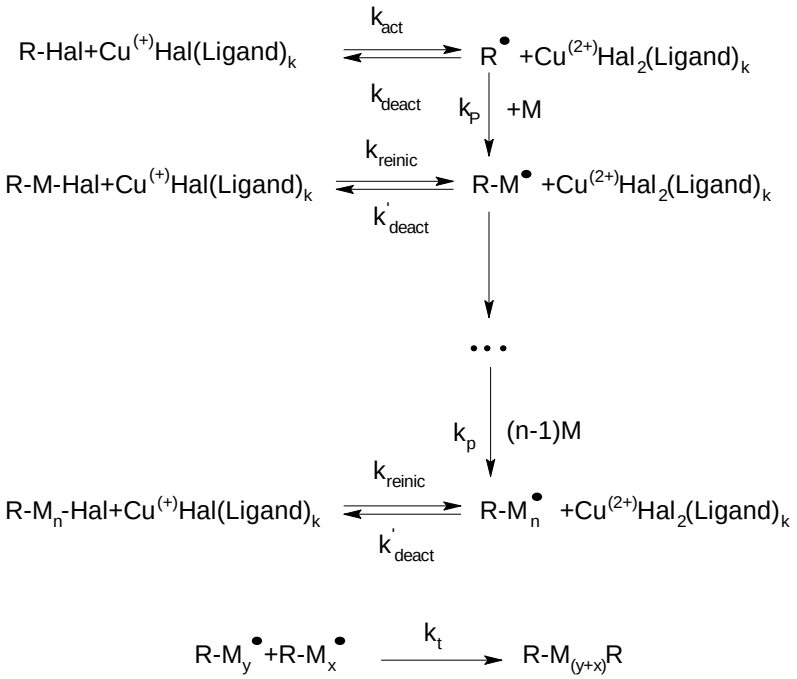
7.2.5 *Draw structures of **Y** and **Y4** with stereochemical details.*

Problem 8. ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen).

The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.



8.1.1 *Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.*

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

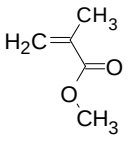
8.1.2 *Compare the rate of deactivation to the rates of ATRP elementary stages.*

Dependence of monomer concentration ([*M*]) on reaction time (*t*) for ATRP is:

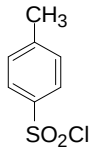
$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p \cdot [R^{\cdot}] \cdot t \,,$$

$[M]_0$ - initial monomer concentration, k_p – rate constant of propagation, $[R^{\cdot}]$ – concentration of active radicals.

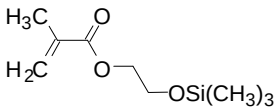
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is 1616 $L \cdot mol^{-1}s^{-1}$, and the steady state concentration of radicals is $1.76 \cdot 10^{-7}$ mol $\cdot L^{-1}$.



MMA



TsCl



HEMA-TMS

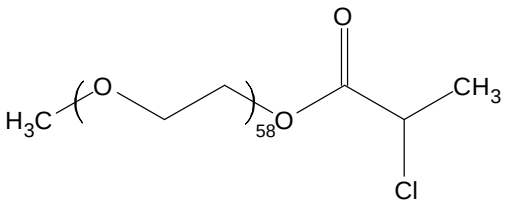
8.2.1 *Calculate mass (m) of the polymer obtained.*

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.2.2 *Calculate degree of polymerization (DP) of the obtained polymer.*

8.2.3 *Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, $(A_{65}$-graft-$C_{100})$-stat-B_{34} means that chains of polymer C are grafted on units A in the statistic copolymer of A and B.*

ATRP was applied to synthesize two block copolymers, P1 and P2. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P1 consisted of styrene (C), and in P2 of p-chloromethylstyrene (D) units.

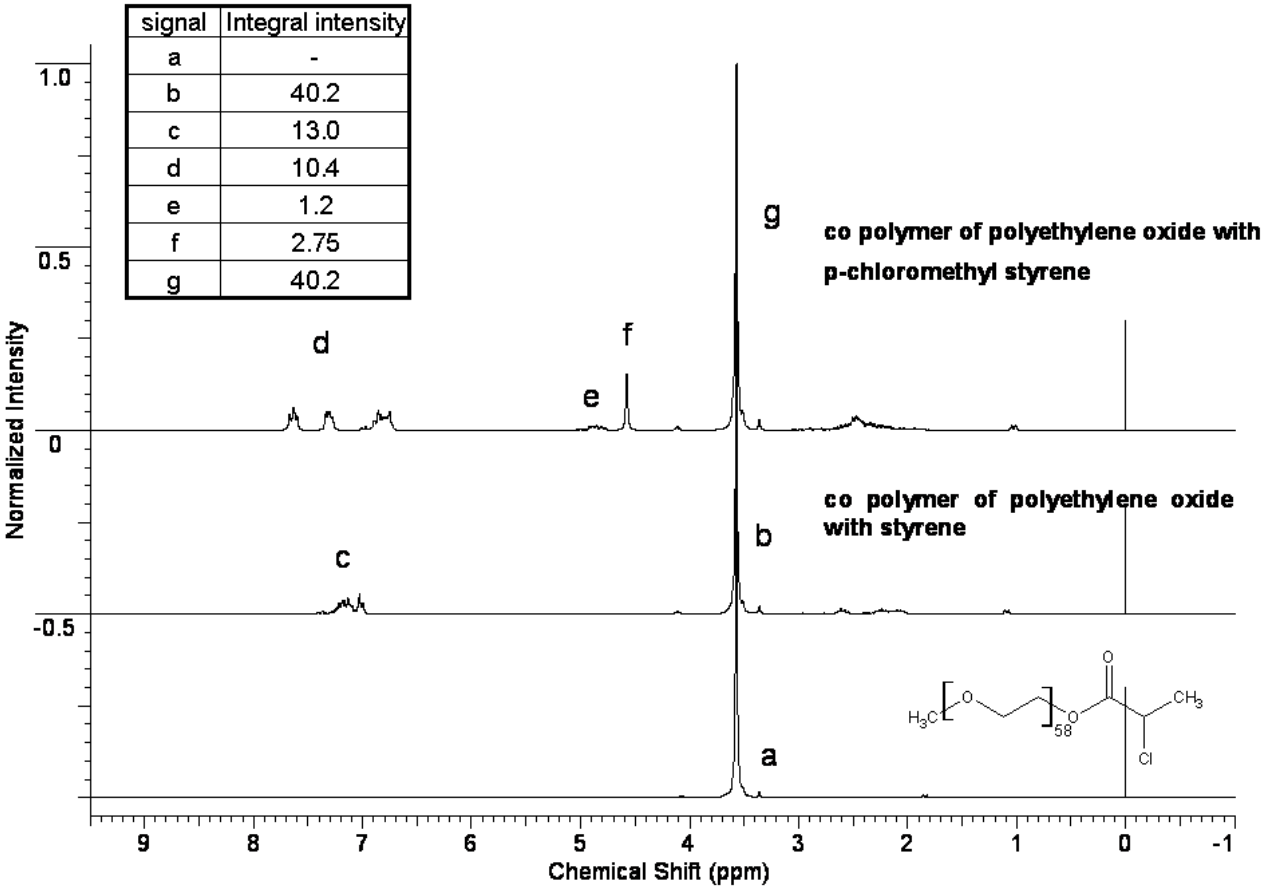
^{1}H NMR spectra of the macroinitiator, P1 and P2 are given below. Integral intensities of characteristic signals can be found in the table.

8.3.1 *Assign ^{1}H NMR signals to substructures given in the Answer Sheet.*

8.3.2 *Determine molar fractions of units C and D and molecular weights of P1 and P2.*

8.3.3 *Write down all possible reactions of activation occurring during the synthesis of P1 and P2. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.*

8.3.4 *Draw the structure of P1 and one of possible structures of P2 representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.*



CHEMISTRY: ART, SCIENCE, FUN

PRACTICAL EXAMINATION
PROBLEMS

JULY 18, 2007
MOSCOW, RUSSIA

General Directions

- **safety rules** follow them as in the Preparatory problems described, no eating or drinking is allowed in the lab.
- **violating safety rules** you get one warning, offend again: you are out.
- **problem booklet** 12 pages (incl. cover sheet and Periodic table of elements) with 2 problems. Start with problem 1.
- **time** 5 hours; 30 minutes warning before the end.
- **answer sheets: 5** pages (incl. cover sheet).
- **your name and student code** write it on **every** answer sheet.
- **answers** only in the appropriate places of the answer sheets, nothing else will be marked. Relevant calculations have to be shown.
- **use only the pen and calculator provided.**
- **results** the number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- **burette** read it as accurately as possible.
- **more chemicals** needed? Ask your lab assistant. No penalty for this.
- **Extra sample to be analyzed or broken column** a penalty of 10 marks.
- **questions** concerning safety, apparatus, chemicals, organization, toilet break: **ask your lab assistant.**
- **chemical waste** put it only in the designated containers.
- **official English-language version available** on request **for clarification only.** Ask your lab assistant.
- **after the stop signal** put your answer sheets and spectra in the envelope (don’t seal), deliver them to your lab assistant. Keep the problem booklet together with the pen and calculator.
- **You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.**
- **During the Practical examination some of your glassware and plastics may have to be used more than once. Clean it carefully.**

List of Chemicals

Reagent	Quantity	Placed in	Labeled
Task 1			
Eluent 1	100 mL	Amber glass bottle*	Eluent 1
Eluent 1	1 mL	Plastic microtube	Eluent 1
Eluent 2	50 mL	Amber glass bottle*	Eluent 2
Eluent 2	1 mL	Plastic microtube	Eluent 2
Eluent 3	50 mL	Amber glass bottle*	Eluent 3
Eluent 3	1 mL	Plastic microtube	Eluent 3
0.5 M Carbonate buffer solution, pH 9.5	10 mL	Glass vial	$NaHCO_3$
0.5 M Tris-HCl buffer solution, pH 8.5	10 mL	Glass vial	Tris-HCl
Mixture of amino acids to be analyzed**	1.2 mL	Plastic microtube	A number between 301 and 600
Ellmann reagent: 0.2 M Phosphate buffer solution containing 10 mM EDTA and 3 mM 5,5'-Dithiobis(2-nitrobenzoic acid), pH 7.0	10 mL	Glass vial	DTNB
Pauli's reagent: solution of sodium 4-diazonium-benzenesulfonate in 0.1 M aqueous HCl	1 ml	Plastic microtube	Pauli
Sodium hydroxide, 10% aqueous solution	10 mL	Glass vial	NaOH 10%
8-Hydroxyquinoline, 5.2 mM solution in ethanol/n-butanol (9:1) mixture	5 ml	Glass vial	8-HQ
Sodium hypobromite, 0.24 M solution in 10% aqueous NaOH	1.2 ml	Plastic microtube	NaBrO
2,4,6–Trinitrobenzenesulfonic acid, 3.4 mM aqueous solution	1 mL	Plastic microtube	TNBS
8 M Aqueous urea solution	1 mL	Plastic microtube	Urea
Task 2			
HCl, standard solution, ~1 M (see exact value on the label)	40 mL	Amber glass vial	HCl <and exact concentration>
NaOH (to be standardized)	200 mL	Amber glass vial	NaOH
Powdery sample to be analyzed**	0.5 – 1 g	150 mL beaker covered with watch glass	<number of workplace>
H_2O distilled	400 mL	Plastic wash bottle	H_2O
H_2O distilled (shared between 2 students)	30 mL	Glass drop bottle	H_2O
H_2O distilled (for common use)	5 L	Bottle with tubing and clamp on top of the bench	H_2O
NaH_2PO_4, 15% solution (shared between 2 students)	20 mL	Glass drop bottle	NaH_2PO_4 15%
Bromocresol Green, 0.5% solution in 20% ethanol (shared among 3-4 students in a raw)	30 mL	Glass drop bottle	Bromcresol green
Thymolphthalein, 0.5% solution in ethanol (shared among 3-4 students in a raw)	30 mL	Glass drop bottle	Thymolphtalein
$K_2C_2O_4$, 15% solution (shared between 2 students)	50 mL	Amber glass vial	$K_2C_2O_4$ 15%

*Fixed on the top shelf (do not try to remove), with connected tubing and clamp

**10 marks penalty for an extra portion of the sample

Components of Eluents 1 to 3

Eluent 1: 0.1 M aqueous sodium citrate, 50 mM sodium chloride, 40 mM thiodiglycol, 1 mM caprylic acid, 0.1% Brij-35; pH 4.9.

Eluent 2: 0.2 M aqueous sodium phosphate, 0.1% Brij-35; pH 7.0.

Eluent 3: 0.2 M aqueous sodium hydroxide.

Apparatus and Suppliers

Item	Quantity
Test tube rack	1
Laboratory stand	1
Chromatography column with ion-exchange resin	1
Laboratory stand with white covering	1
Double clamp for burette	1
Ring for funnel	1
25 mL Burette	1
100 mL flask labeled “Waste”	1
100 mL Volumetric flask	2
100 mL Erlenmeyer flask	2
Syringe with needle	1
Graduated test tubes for collecting fractions and preparing mixtures	50
96-well plate	1
Pipettor (micropipette) with fixed volume of 0.1 mL	1
Disposable tips (in blue plastic cup)	20
Spectrophotometric cuvettes labeled “A1”, “B1”, “A2”, “B2”, “A3”, “B3” in cuvette holder	6
10 mL Graduated plastic pipettes	3
10 mL Glass pipette	1
Pipette filler	1
3-Way Bulb	1
Glass rod	1
Filter funnel	1
Small funnel	1
60 mL Amber glass vials for combined fractions (peaks)	3
10 mL Measuring cylinder labeled “$K_2C_2O_4$ 15%” (shared between 2 students)	1
10 mL Measuring cylinder (shared between 2 students)	1
50 mL Measuring cylinder	1
100 mL Measuring cylinder labeled “H_2O” (shared among 3-4 students in a row)	1
Plastic plate with filters*** (shared among 3-4 students in a row)	3 filters per student
Heating plate (for common use in a fume hood)	6 plates per hood
Rubber protection tips (for common use a fume hood)	6 pairs per hood
Spectrophotometer (shared by a group of students; see the number of the spectrophotometer to be used at your bench “SP____”)	
Marker	1
Ruler	1
White sheet of paper	1

***If needed, ask your lab assistant for extra filters.

Safety regulations, S-phrases, R-phrases

Disodium hydrogen phosphate	R:36/37/38 S:26-36
Ethylenediaminetetraacetic acid, disodium salt	R:36/37/38 S:26-36/37/39
Tris-HCl	R:36/37/38 S:26-36
Arginine	R:36 S:26
Cysteine	R:22
Histidine	S:22-24/25
Hydrochloric acid	R:34-37 S:26-36-45
Sodium 4-diazoniumbenzenesulfonate	R:1-37/37 S:26-36
Sodium hydroxide	R:34-35 S:26-36-37/39-45
8-Hydroxyquinoline	R:22-36/37/38 S:26-36/37
Ethanol	R:11 S:7-16
Butanol-1	R:10-22-37/38-41-67 S:7/9-13-26-37/39-46
Sodium hypobromite	R31-34 S:26-36-45
5,5'-Dithiobis(2-nitrobenzoic acid)	R:36/37/38 S:26-36
2,4,6-Trinitrobenzene sulfonic acid	R: 1-22-36/38-43 S: 26-36/37
Sodium chloride	R:36 S:26
Thiodiglycol	R:36 S:26
Caprylic acid	R:34 S:26-27-45-36/37/39
Brij-35	R:36/37/38 S:26-36
Sodium dihydrogen phosphate	S:22-24/25
Sodium carbonate	R:36 S:22-26
Calcium carbonate	R:41-37/38 S:26-39
Bromocresol Green	S:22-24/25
Thymolphthalein	S:22-24/25
Potassium oxalate	R:34 S:26-27-36/37/39

Risk Phrases

Indication of Particular Risks

R1: **Explosive when dry**
10: **Flammable**
22: **Harmful if swallowed**
31: **Contact with acids liberates toxic gas**
34: **Causes burns**
35: **Causes severe burns**
36: **Irritating to the eyes**
37: **Irritating to the respiratory system**
41: Risk of serious damage to eyes
43: **May cause sensitization by skin contact**
67: Vapors may cause drowsiness and dizziness

Combination of Particular Risks

R24/25: **Toxic in contact with skin and if swallowed**
36/37/38: **Irritating to eyes, respiratory system and skin**
36/38: **Irritating to eyes and skin**
37/38: **Irritating to respiratory system and skin**

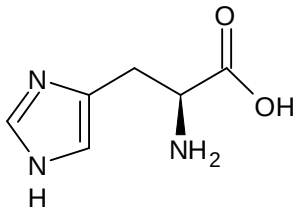
Safety Phrases

Indication of Safety Precautions

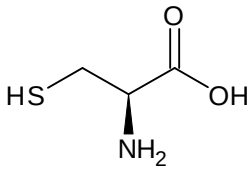
S13: Keep away from food, drink and animal feeding stuffs
22: **Do not breathe dust**
26: **In case of contact with eyes, rinse immediately with plenty of water and seek medical advice**
27: **Take off immediately all contaminated clothing**
36: **Wear suitable protective clothing**
39: **Wear eye/face protection**
45: **In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)**
46: **If swallowed, seek medical advice immediately and show this container or label**

Problem 1. Ion-exchange chromatography of amino acids

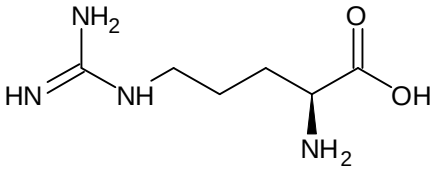
Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we **strongly suggest you starting the exam with Problem 1**.



His



Cys



Arg

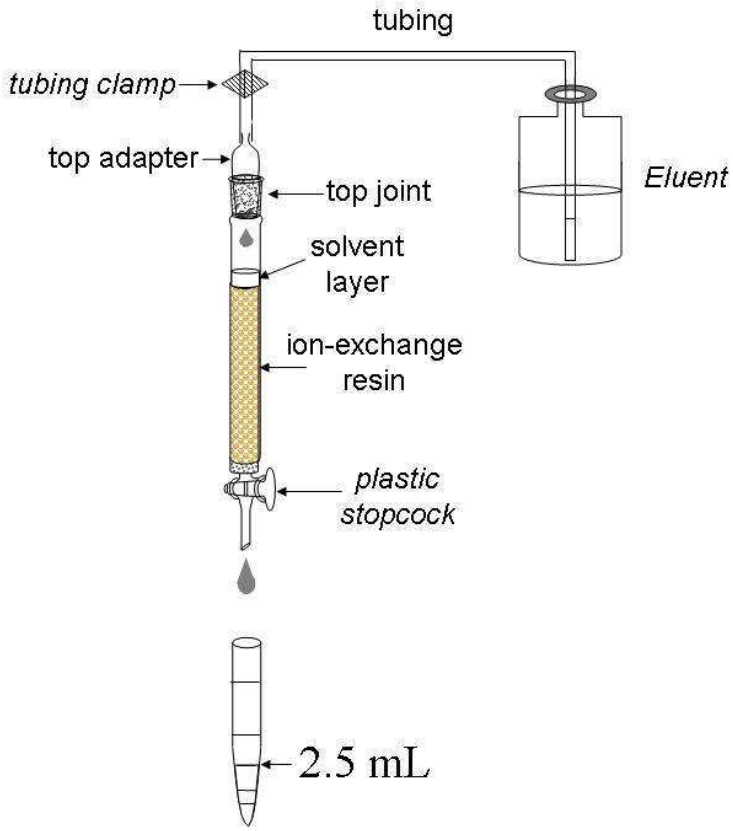
Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (pH 4.9).

Procedure

Chromatography. Step 1

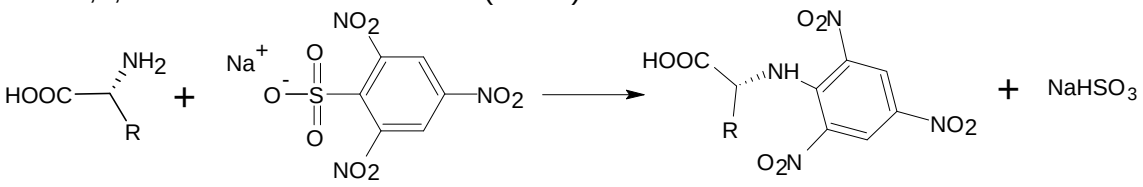
Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labeled “Waste” so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the “Waste” flask). Close the stopcock and add about 1 mL of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the “Waste” flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always open the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 mL (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α-amino groups with sodium 2,4,6–trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 mL of TNBS solution with 10 mL of carbonate buffer solution and place 0.1 mL of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 mL of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within

3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.
Note: all aliquots of 0.1 mL should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1a *Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.*

Continue collecting fractions and analyzing them until you get **at least two wells with coloration as in A1 well**, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (**Important!**), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1b *Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.*

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.
Stop chromatography by closing the stopcock and fixing the clamp.
Based on the results of qualitative analysis, choose the fractions which contain the amino acids.
1.1c *Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.*
1.2 *Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.*

Pour combined fractions in the amber glass vials labeled “Peak 1”, “Peak 2”, “Peak 3”. Prepare samples for quantitative spectrophotometric analysis as described below.

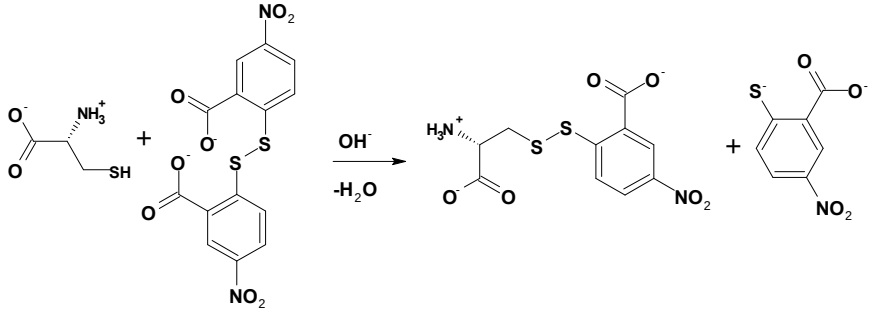
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cuvettes to the operator. Prepare the probes as follows.

Important! When storing, always put cuvettes in the cuvette holder! All cuvettes have 2 ribbed and 2 working vertical surfaces. While operating with cuvettes, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A1 (Reference). Place 0.1 mL of Eluent 1 from plastic microtube into a test tube and add 2.9 mL of Ellmann reagent (DTNB).

Test tube B1 (Sample). Place 0.1 mL of the analyzed solution into a test tube and add 2.9 mL of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cuvettes labeled A1 (for reference) and B1 (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A2 (Reference). Place 2.8 mL of Tris-HCl buffer solution into a test tube, add 0.1 mL of Eluent 2 from plastic microtube and 0.1 mL of Pauli reagent.

Test tube B2 (Sample). Place 2.8 mL of Tris-HCl buffer solution into a test tube, add 0.1 mL of the analyzed solution and 0.1 mL of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cuvettes labeled A2 (for reference) and B2 (for sample).

Assay 3 (peak 3). Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions (Sakaguchi reaction).

Test tube A3 (Reference). Place 0.1 mL of Eluent 3 into a test tube and add 1.5 mL of 10% NaOH solution, 1 mL of 8-hydroxyquinoline solution and 0.5 mL of sodium hypobromite solution.

Test tube B3 (Sample). Place 0.1 mL of the analyzed solution into a test tube and add 1.5 mL of 10% NaOH solution, 1 mL 8-hydroxyquinoline solution and 0.5 mL of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange color. Add 0.2 mL of 8 M urea solution to each test tube, mix the contents and transfer about 3 mL of each mixture to the corresponding cuvettes labeled A3 (for reference) and B3 (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cuvettes to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 *Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.*

Reference data:

The values of extinction coefficients: Product of Ellmann reaction: 13600 $M^{-1}cm^{-1}$ at 410 nm Product of Pauli reaction: 6400 $M^{-1}cm^{-1}$ at 470 nm Product of Sakaguchi reaction: 7700 $M^{-1}cm^{-1}$ at 500 nm	Molar masses of the amino acids. Cysteine 121 g/mol Histidine 155 g/mol Arginine 174 g/mol

1.4. *Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.*

Problem 2. Determination of carbonate and hydrogen phosphate in an abrasive sample

Na_2CO_3, $CaCO_3$ and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4, whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to $H_2PO_4^-$ ion, the endpoint lying in slightly acidic medium (pH of ~4.5). It corresponds to the color change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colorless to blue (moderately alkaline medium, pH of ~10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

a) the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
b) the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. <u>Dissolution of the sample and removal of CO_2</u>

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 mL (**exactly, with a pipette! *Carefully*, not removing the glass and avoiding losses because of splashing!**) of ca. 1 mol/L HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat ***carefully*** the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2-3 min.

Step 2. <u>Precipitation of calcium</u>

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1-2 mL of 15% $K_2C_2O_4$ solution with measuring

cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 mL of HCl solution into a 100 mL volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 mL of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1-2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5-10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 mL. Report all the final volume values with 0.01 mL accuracy.

2.1a *Complete the table in the Answer Sheet.*

2.1b *Calculate the concentration of NaOH solution (in mol/L).*

Step 4. Filtering off calcium oxalate

After the most part of CaC_2O_4 precipitates filter the precipitate off collecting the filtrate into a 100 mL volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 mL aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15-20 mL of distilled water. Titrate the sample solution with NaOH solution until the color coincides with that of the reference solution.

2.2 *Complete the table in the Answer Sheet.*

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 mL aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5-10 s appears.

2.3 *Complete the table in the Answer Sheet.*

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

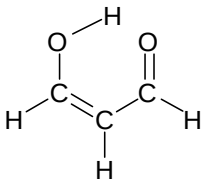
2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+}.

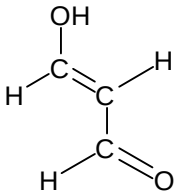
2.6b A list of mistakes possible at different steps is given in the table in the answer sheet. Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+”or “–“ if the result is higher (positive error) or lower (negative error) than the true one.

Solution to problem 1

1.1.1

O=CH–CH_2–CH=O





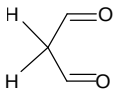
1.1.2

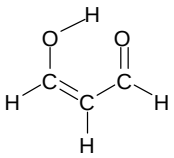
Acidic hydrogen atom is in CH_2 (in enol forms acidic hydrogen is in OH)

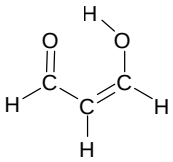
Acidity of CH_2 group is caused by the stability of carbanion due to conjugation with two carbonyl groups. The first answer is correct

1.2.1

The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form such distance between two possible positions of proton is impossible. Tunneling takes place only in enol *Z*-form:



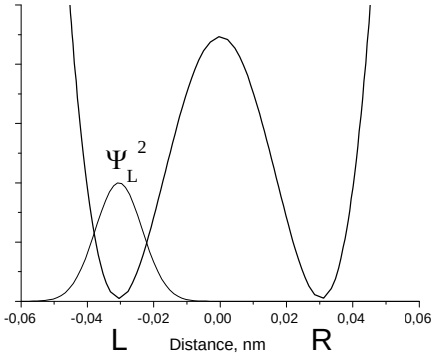




1.3.1 *Expressions and plots of probability density*

(a) $\Psi^2(x,0) = \frac{1}{2}\left[\Psi_{\mathrm{L}}^2(x) + \Psi_{\mathrm{R}}^2(x) + \Psi_{\mathrm{L}}^2(x) - \Psi_{\mathrm{R}}^2(x)\right] = \Psi_{\mathrm{L}}^2(x)$

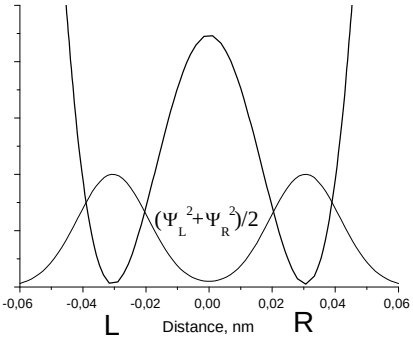
The probability density is concentrated in the left well:



(b) In the middle of the time interval

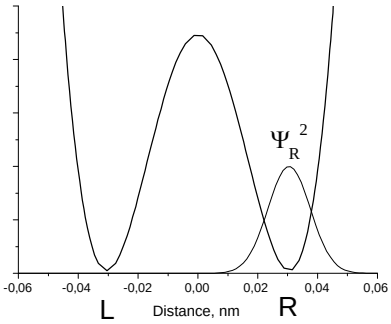
$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2}\left[\Psi_{\mathrm{L}}^2(x) + \Psi_{\mathrm{R}}^2(x)\right]$

The probability density has a symmetric form, a proton is delocalized between two wells:



(c) $\Psi^2\left(x, \frac{\pi}{\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x) - \Psi_L^2(x) + \Psi_R^2(x)\right] = \Psi_R^2(x)$

The probability density is concentrated in the right well:



1.3.2

The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.3.3 The time of transfer from one well to another is $t = \pi / \omega$.

$$t = \frac{3.14}{6.48 \cdot 10^{11}} = 4.85 \cdot 10^{-12}\ \text{s}$$

The proton velocity $V = \frac{0.06 \cdot 10^{-9}}{4.85 \cdot 10^{-12}} = 12$ m/s.

1.3.4

The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (0.06 nm will be also accepted).

The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta V = \frac{\hbar}{2m\Delta x} = \frac{1.055 \cdot 10^{-34}}{2 \cdot \frac{0.001}{6.02 \cdot 10^{23}} \cdot 0.03 \cdot 10^{-9}} \approx 1000\ \text{m/s}$$

Comparing this uncertainty with the velocity 12 m/s we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct

Solution to problem 2

2.1.1

The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G^0_{500}(1) = \Delta G^0_{f,500}(\text{CoO,s}) - \Delta G^0_{f,500}(\text{H}_2\text{O,g}) = -198.4 + 219.1 = 20.7\ \text{kJ/mol}$$

$$K = e^{-\frac{\Delta_r G^0_{500}(1)}{RT}} = e^{-\frac{20700}{8.314 \cdot 500}} = 6.88 \cdot 10^{-3}$$

2.1.2

The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\Delta_r G^\circ_{500}(1, r_a) = G^0_{bulk,500}(\mathrm{CoO,s}) + G^0_{500}(\mathrm{H_2,g}) - G^0_{500}(\mathrm{H_2O,g}) - G^0_{sph}(\mathrm{Co}) =$$

$$= G^0_{500}(\mathrm{CoO,s}) + G^0_{500}(\mathrm{H_2,g}) - G^0_{500}(\mathrm{H_2O,gas}) - \left(G^0_{500}(\mathrm{Co,s}) + \frac{2\sigma_{\text{Co-gas}} V(\mathrm{Co})}{r_a} \right) =$$

$$= \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}} V(\mathrm{Co})}{r_a};$$

$$V(\mathrm{Co}) = \frac{M_{\mathrm{Co}}}{\rho(\mathrm{Co})} = \frac{10^{-6} \cdot 59.0}{8.90} = 6.6 \cdot 10^{-6} \ \frac{\mathrm{m}^3}{\mathrm{mol}};$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$\frac{2\sigma_{\text{Co-gas}} V(\mathrm{Co})}{r_a}$ = 210 and 2100 J/mol.

$\Delta_r G^\circ_{500}(1, r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ/mol, respectively.

The equilibrium constant is calculated from the equation

$$K(1, r_a) = \exp\left(-\frac{\Delta_r G^\circ_{500}(1, r_a)}{RT} \right);$$

$K(1, r_a) = 7.22 \times 10^{-3}$; $r_a = 10^{-8}$ m $\qquad$ $K(1, r_a) = 11.4 \times 10^{-3}$; $r_a = 10^{-9}$ m

2.2.1

The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G^\circ_{500}(1, r_a) = \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\mathrm{Co})$$

$\Delta_r G^\circ_{500}(1)$ is 20.7 kJ/mol. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^\circ_{500}(1, r_a)$ is 18.6 kJ/mol.

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is

$$\Delta_r G(1) = \Delta_r G^\circ_{500}(1) + RT \ln\left(\frac{p(\mathrm{H_2})}{p(\mathrm{H_2O})} \right) = \Delta_r G^\circ_{500}(1) - RT \ln\left(\frac{p(\mathrm{H_2O})}{p(\mathrm{H_2})} \right) \le 0$$

and for spherical cobalt nanoparticles with r_a = 1 nm:

$$\Delta_r G(1, r_a) = \Delta_r G^\circ_{500}(1, r_a) + RT \ln\left(\frac{p(\mathrm{H_2})}{p(\mathrm{H_2O})} \right) = \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\mathrm{Co}) - RT \ln\left(\frac{p(\mathrm{H_2O})}{p(\mathrm{H_2})} \right) \le 0$$

$\Delta_r G^\circ_{500}(1)$ is 20.7 kJ/mol. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^\circ_{500}(1, r_a)$ is 18.6 kJ/mol.

The minimum ratios $\frac{p(\mathrm{H_2O})}{p(\mathrm{H_2})}$ are 145.6 (a) and 87.7 (b), respectively.

The hydrogen pressure is 1bar·0.0015 = $1.5 \cdot 10^{-3}$ bar

The minimum pressures of water are
$1.5 \cdot 10^{-3} \cdot 145.6 = 0.218$ bar (a) and $1.5 \cdot 10^{-3} \cdot 87.7 = 0.132$ bar (b), for the bulk cobalt and for nanoparticles, respectively.

H_2O%(bulk Co) = 21.8% H_2O%(nanoparticles with $r_a = 1*10^{-9}$ m)= 13.2%.
We assume that bulk cobalt oxide is formed.

2.2.2

For the spontaneous oxidation

$$\Delta_r G(1, r_a) = \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and

$$\Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \le RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right)$$

The left hand side of the last inequality becomes more positive with the increase of r_a. At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a. The answer (a) is correct.

2.3.1

The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G^0_{sph}(\text{CoO}, r_b) = G_{bulk}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^\circ(\text{CoO,s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

2.3.2

The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$G^0_{\text{sph}}(\text{Co}, r_a, r_b) = G_{\text{bulk}}(\text{Co}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= G^\circ(\text{Co,s}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right)$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint)

2.3.3

The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\Delta_r G^0(1, r_a, r_b) = G^0_{sph}(\mathrm{CoO}, r_b) + G^\circ(\mathrm{H_2}, gas) - G^\circ(\mathrm{H_2O,gas}) - G^0_{sph}(Co, r_a, r_b) =$$

$$= G^\circ(\mathrm{CoO,s}) + G^\circ(\mathrm{H_2}, gas) - G^\circ(\mathrm{H_2O,gas}) - G^\circ(\mathrm{Co,s}) +$$

$$+ \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\mathrm{CoO}) - 2V(\mathrm{Co})\left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a} \right) =$$

$$= \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\mathrm{CoO}) - V(\mathrm{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\mathrm{Co})$$

2.3.4.

Under the assumptions made

$$\Delta_r G^\circ(1, r_a, r_b) = \Delta_r G^0(1, r_0) = \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\mathrm{CoO}) - V(\mathrm{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\mathrm{Co}) =$$

$$= \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\mathrm{CoO}) - \frac{3}{2} V(\mathrm{Co}) \right)$$

The term in brackets in the right-hand side is positive

$$\left(V(\mathrm{CoO}) - \frac{3}{2} V(\mathrm{Co}) \right) = 6.56 \cdot 10^{-6}\ \mathrm{m^3}$$

$\Delta_r G^0(1, r_0)$ is directly proportional to $\left(\frac{1}{r_0} \right)$. The plot (a) is correct.

2.3.5.

The spontaneous forward reaction (1) is possible, when $\Delta_r G(1, r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\mathrm{CoO}) - \frac{3}{2} V(\mathrm{Co}) \right) \leq RT \ln \frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0. At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0.

The answer (b) is correct.

Solution to problem 3

3.1.1

The overall reaction equation $\mathrm{B + D \longrightarrow P}$

The kinetic equation for X $\dfrac{d[\mathrm{X}]}{dt} = k_1[\mathrm{B}][\mathrm{X}]^2 - k_2[\mathrm{D}][\mathrm{X}]$

3.1.2

Under the steady-state conditions $\dfrac{d[\mathrm{P}]}{dt} = k_2[\mathrm{D}][\mathrm{X}] = k_1[\mathrm{B}][\mathrm{X}]^2$,

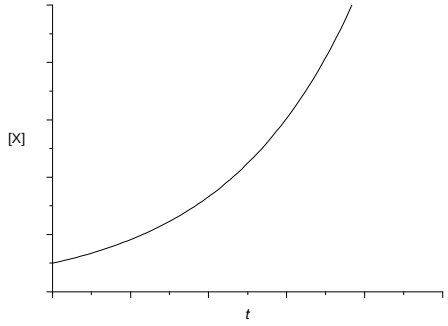
whence $[\mathrm{X}] = \dfrac{k_2[\mathrm{D}]}{k_1[\mathrm{B}]}$ $\qquad\qquad$ $\dfrac{d[\mathrm{P}]}{dt} = \dfrac{k_2{}^2[\mathrm{D}]^2}{k_1[\mathrm{B}]}$

Reaction order with respect to D: 2, with respect to B: -1; the overall order is 1.

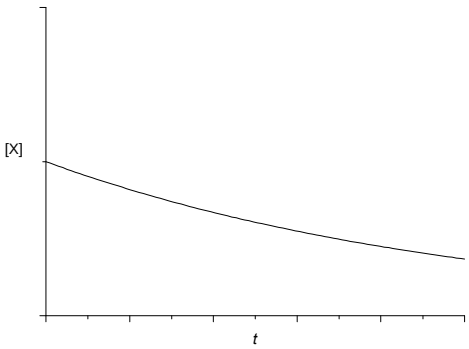
3.2.1

In an open system the initial reaction rate is: $\dfrac{d[\mathrm{X}]}{dt} = [\mathrm{B}][\mathrm{X}]\left(k_1[\mathrm{X}] - k_2\right)$

1) If $[\mathrm{X}]_0 > k_2/k_1$, then $d[\mathrm{X}]/dt > 0$ at any time, and the concentration of X monotonically increases:



2) If $[\mathrm{X}]_0 < k_2/k_1$, then $d[\mathrm{X}]/dt < 0$ at any time, and the concentration of X monotonically decreases:

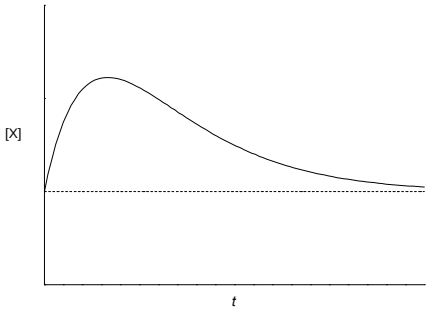


3.2.2

In a closed system the initial reaction rate is:

$$\left.\frac{d[\mathrm{X}]}{dt}\right|_{t=0} = k_1[\mathrm{B}]_0[\mathrm{X}]_0^2 - k_2[\mathrm{D}]_0[\mathrm{X}]_0 = [\mathrm{B}]_0[\mathrm{X}]_0\left(k_1[\mathrm{X}]_0 - k_2\right) > 0$$

Hence, at the beginning of the reaction [X] increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.3.1

X – $C_2H_6O_2$, Y – C_2H_4O, P – C_2H_6O. Dots denote O_2 and H_2O.

$C_2H_6 + C_2H_6O_2 + \mathbf{O_2} \longrightarrow 2\ C_2H_6O_2$

$C_2H_6O_2 + C_2H_4O \longrightarrow 2\ C_2H_4O + \mathbf{H_2O}$

$C_2H_6 + C_2H_4O + \mathbf{H_2O} \longrightarrow 2\ C_2H_6O$

3.4.1

At the highest possible temperature the rate constants are equal:

$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \frac{A_2}{A_1}} = 354\ \text{K}$$

Solution to problem 4

4.1.

Equation: $I_2 + SO_2 + 2\ H_2O + 4\ Py \longrightarrow 2\ PyHI + (PyH)_2SO_4$

4.2.1.

M($Na_2C_4H_4O_6{\cdot}2H_2O$) = 230.05 2M($H_2O$) = 36.04

m(H_2O) = 1.3520 · 36.04 / 230.05 = 0.2118 g = 211.8 mg

T = 211.8 / 12.20 = 17.36 mg/mL

4.2.2.

Volume of iodine spent for 10 mL of pure CH_3OH = 2.20·10.00/25.00 = 0.88 mL

T = 21.537·0.01·10^3 / (22.70 – 0.88) = 9.87 mg/mL

More exactly

10.00 mL of the solution contain (1000-21.5)·10.00 / 1000 = 9.785 mL of methanol

Volume of iodine spent for 9,785 mL of pure CH_3OH = 2.20·9,785 / 25.00 = 0.86 mL
T = 21.537·0.01·10^3 / (22.70 – 0.86) = 9.86 mg/mL

4.2.3.

Approach 1.

Let 1 mL of CH_3OH contain *x* mg H_2O, then 1 mL of A contains ((1.000 – 0.006)·*x* + 5.624) mg H_2O.

15.00·*T* = 22.45·(0.994·*x* + 5.624) – 1st titration,

10.00·*T* = 25.00·*x* + 10.79·(0.994·*x* + 5.624) – 2nd titration.

Hence, *x* = 1.13 mg/mL, *T* = 10.09 *mg/mL* (10.10 without taking into account 0.994 factor)

Approach 2.

Let *y* mL of B be spent for the titration of water, contained in 1 mL of CH_3OH. Then $T = \frac{22.45 \cdot 5.624}{15.00 - 22.45 \cdot 0.994 \cdot y}$ (1st titration) = $\frac{10.79 \cdot 5.624}{10.00 - 25.00y - 10.79y}$ (2nd titration).

Hence, *y* = 0.1116 and *T* = 10.10 mg/mL

T = 10.09 *mg/mL* (10.10 without taking into account 0.994 factor)

4.3.

$CaO + SO_2 \longrightarrow CaSO_3$

$2CaO + 2I_2 \longrightarrow CaI_2 + Ca(OI)_2$

$6CaO + 6I_2 \longrightarrow 5CaI_2 + Ca(IO_3)_2$ (Instead of CaO, $Ca(OH)_2$ may be written.)

4.4.1

$Fe_2(SO_4)_3 + 2HI \longrightarrow 2FeSO_4 + \mathbf{I_2} + H_2SO_4$

$Fe_2(SO_4)_3 + \mathbf{H_2O} + SO_2 + CH_3OH \longrightarrow 2FeSO_4 + CH_3OHSO_3 + H_2SO_4$

(or in ionic form)

4.4.2. *Equation:*

$Fe_2(SO_4)_3 \cdot xH_2O + \mathbf{(x-1)}I_2 + xSO_2 + xCH_3OH \longrightarrow$

$2FeSO_4 + xCH_3OHSO_3 + H_2SO_4 + 2(x-1)HI$

4.4.3.

$M(Fe_2(SO_4)_3 \cdot xH_2O) = 399.9 + 18.02x$

$m_{H2O}\,(g) = \frac{0.6387 \cdot 18.02x}{(399.9 + 18.02x)}$;

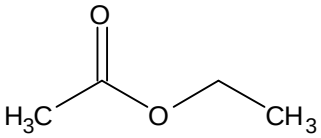
$m_{H2O}\,(g) = 10.59(mL) \times 15.46(mg/mL) \times 0.001(g/mg) \cdot \frac{x}{x-1}$

$\Rightarrow$ 0.1637·(399.9 + 18.02*x*) = 11.51*x* – 11.51; *x* = 8.994

Formula: $Fe_2(SO_4)_3 \cdot 9\,H_2O$ *x* = 9

Solution to problem 5

5.1.1



Ethyl acetate, ethyl ethanoate

5.1.2

☑ esters

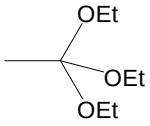
5.1.3

Qualitative estimation of yield can be done assuming that the reaction is at equilibrium, and that the equilibrium constant is supposed to not vary with temperature and composition of the reaction mixtures.

$$K = \frac{[\mathrm{AcOEt}][\mathrm{H_2O}]}{[\mathrm{AcOH}][\mathrm{EtOH}]} = \frac{(0.85)^2}{0.15 \cdot 1.15} = 4.2$$

Calculation of yield using this constant in 1:1 mixture gives 67%

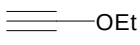
5.2.1



$CH_3C(OEt)_3$

triethyl orthoacetate, 1,1,1-triethoxyethane

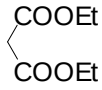
A



$HC{\equiv}COEt$

ethoxyacetylene, ethynylethyl ether

B



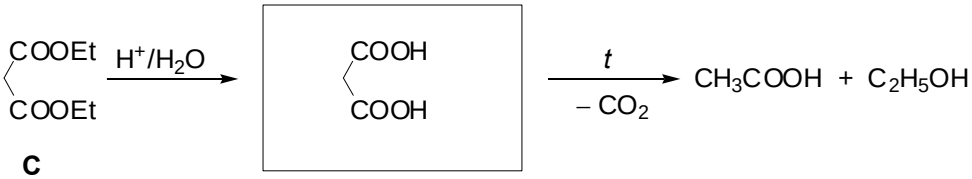
$CH_2(COOEt)_2$

diethyl malonate

C

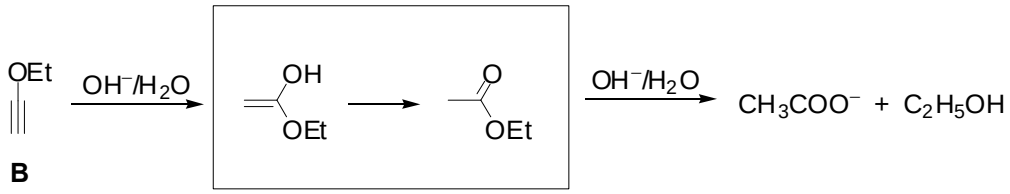
5.2.2

a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate



C

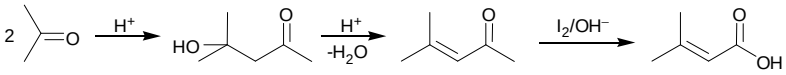
b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed



Indication of any of keto- or enol forms of ethylacetate
Hydrolysis of strong ether bond to give hydroxyacetylene, or any forms coming along this path (ketene, diketene) is impossible and is not allowed

5.3.1

From acetone alone the synthesis includes aldol condensation, dehydration, with subsequent iodoform reaction
3 marks



5.3.2

Iodoform, triiodomethane, CHI_3

Solution to problem 6

6.1.1

$SiO_3^{2-} + 2CO_2 + 2H_2O \longrightarrow$ "H_2SiO_3"↓ (Silica acid gel) $+2HCO_3^-$ or
$SiO_2(OH)_2^{2-} + 2CO_2 + H_2O \longrightarrow$ "H_2SiO_3"↓ $+2HCO_3^-$ or
$SiO_3^{2-} + CO_2 + H_2O \longrightarrow$ "H_2SiO_3"↓ $+ CO_3^{2-}$

6.1.2

a) protonation of ortho-silicate ions leading to the formation of Si-OH groups
$SiO_4^{4-} + H_2O \longrightarrow [SiO_3(OH)]^{3-} + OH^-$ or
$SiO_4^{4-} + H^+ \longrightarrow [SiO_3(OH)]^{3-}$ or
$[SiO_2(OH)_2]^{2-} + H^+ \longrightarrow [SiO(OH)_3]^-$ Yes ☒

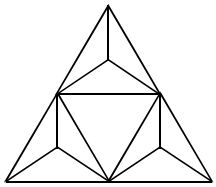
b) formation of hydrated $[SiO_4(H_2O)_2]^{4-}$ anions
$SiO_4^{4-} + 2H_2O \longrightarrow [SiO_4(H_2O)_2]^{4-}$ No ☒

c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds
$2\ SiO_4^{4-} + H_2O \longrightarrow [O_3Si\text{-}O\text{-}SiO_3]^{6-} + 2\ OH^-$ or
$2\ SiO_4^{4-} + 2H^+ \longrightarrow [O_3Si\text{-}O\text{-}SiO_3]^{6-} + H_2O$ or
$2SiO_2(OH)_2^{2-} + H_2O \longrightarrow [O\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}O]^{2-} + 2\ OH^-$ Yes ☒

6.2.1 n= 6 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

6.2.2 $Si_3O_9 \equiv 3\ [SiO_4] - 3\ O$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

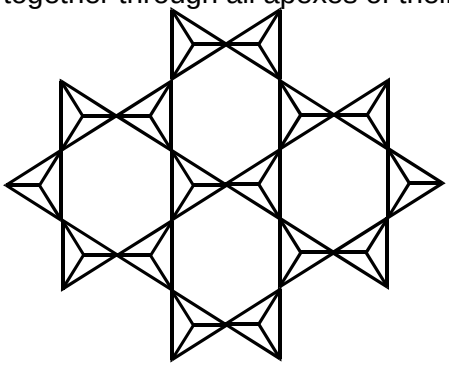
6.2.3



6.2.4

m=4 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

$Si_4O_{10} \equiv 4[SiO_4] - 6O$, i.e. the formula of the tetrahedron is now $SiO_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution =3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.3.1

$Cu(H_2O)_4^{2+} + H_2O \longrightarrow Cu(OH)(H_2O)_3^{+} + H_3O^{+}$,

$[H^+] \approx (c\ K_a^I)^{1/2} \longrightarrow 1 \cdot 10^{-4}$ M, pH = -log$[H^+]$ = 4 pH = 4

6.3.2

$CuSO_4 + Na_2SiO_3 + 2H_2O \longrightarrow Cu(OH)_2\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

or $2CuSO_4 + Na_2SiO_3 + 2H_2O \longrightarrow (CuOH)_2SO_4\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.3.1**).

Solution to problem 7

7.1.1 E2-E4

catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is

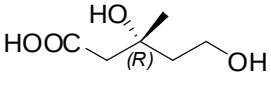
introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β-oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

E1 ~~*4, 5*~~

E3 ~~*6*~~

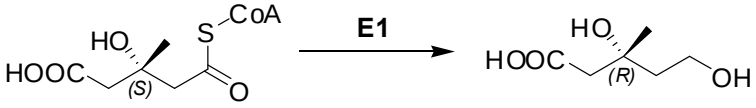
7.1.2

Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:

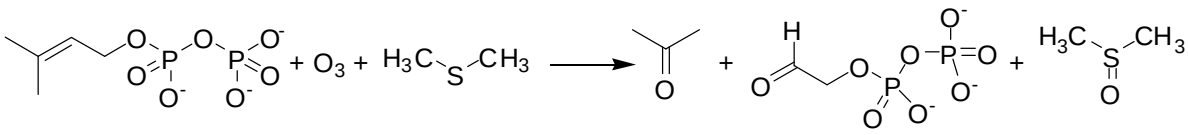


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



7.2.1



7.2.2

DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in **7.2.1**). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(C)= 2*n_{Y1}(C)+4* n_{Y2}(C)+ n_{Y3}(C)= 2*3 + 4*5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to

get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$n_Y(C)= 2*n_{Y1}(C)+4*n_{Y2}(C)+ n_{Y3}(C)= 2*3 + 4*5 + 4 =30$

$n(H)= 2*n_Y(C)+2–2*n_{c=c}=30*2 + 2 - 6*2 = 50$

Y (squalene) formula – $C_{30}H_{50}$.

7.2.3

IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

$$n(IPP\&DAP)= n_Y(C)/5=30/5=6$$

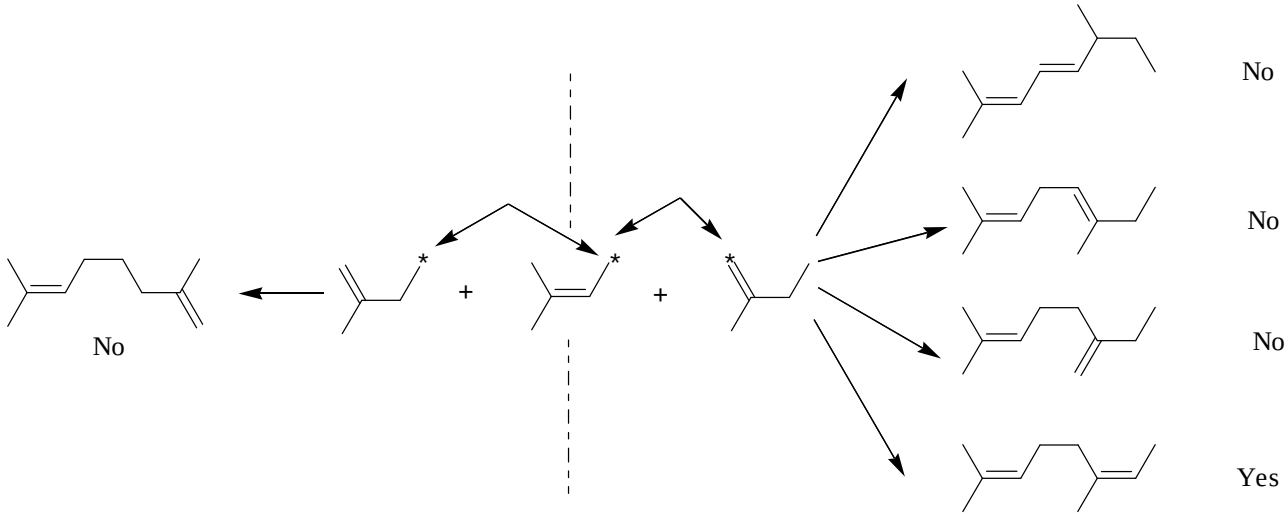
The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

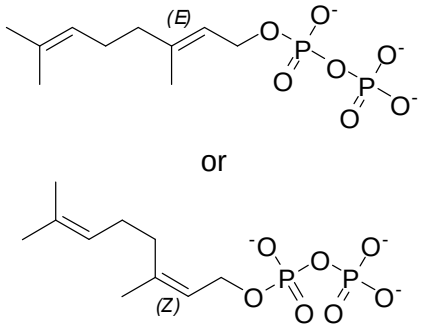
$n(IPP\&DAP)= n_Y(C)/5=30/5=6$

Number of DAP molecules 2 Number of IPP molecules 4

7.2.4

All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details



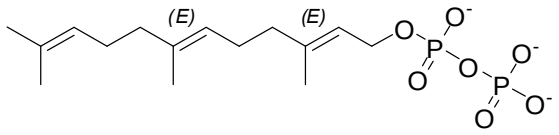


or

The upper isomer is geranyl pyrophosphate

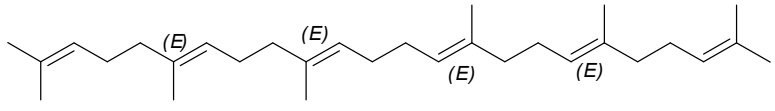
7.2.5

It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4,** since **Y3** is formed as a result of ozonolysis in a molar ratio of 1:1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in ***trans*** configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



Y4, farnesyl pyrophosphate

Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:



Y, squalene

Solution to problem 8

8.1.1

$v_{act} = k_{act} \cdot [R\text{-}Hal] \cdot [CuHal(Ligand)_k]$

$v_{deact} = k_{deact} \cdot [R^{\cdot}] \cdot [CuHal_2(Ligand)_k]$

$v_p = k_p \cdot [R^{\cdot}] \cdot [M]$

$v_t = 2k_t \cdot [R^{\cdot}]^2$

8.1.2

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination. So:

$$v_{deact} >> v_{act}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$v_{deact} >> v_p$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$v_{deact} >> v_t$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

8.2.1

<u>1st variant</u>

$[M] = [M]_0 \exp(-k_P[R\cdot]t)$ or $n(MMA) = n_0(MMA)\exp(-k_P[R\cdot]t)$

Quantity of MMA monomer remaining after polymerization during 1400 s is
$31.0 \cdot \exp(-1616 \cdot 1.76 \cdot 10^{-7} \cdot 1400) = 20.8$ mmol.

Quantity of monomer consumed during polymerization: 31-20.8=10.2 mmol

Mass of the obtained polymer is

$$m = \Delta n(MMA) \cdot M(MMA) = (10.2/1000) \cdot 100.1 = 1.03\,\text{g}$$

<u>2nd variant</u>

$[M] = [M]_0 \exp(-k_P[R\cdot]t)$ or $n(MMA) = n_0(MMA)\exp(-k_P[R\cdot]t)$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is
$\Delta n(MMA) = n_0(MMA)(1-\exp(-k_p \cdot [R^{\bullet}] \cdot t)) = 31.0 \cdot (1-1616 \cdot 1.76 \cdot 10^{-7} \cdot 1400) = 10.2\,\text{mmol}$

Mass of the obtained polymer is

$$m = \Delta n(MMA) \cdot M(MMA) = (10.2/1000) \cdot 100.1 = 1.03\,\text{g}$$ 1 mark

3rd variant

$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_P[R\cdot]t = -1616\cdot 1.76\cdot 10^{-7}\cdot 1400 = -0.398$$

$$\frac{[M]}{[M]_0} = e^{-0.398} = 0.672 \qquad \frac{[M]}{[M]_0} = \frac{n(MMA)}{n_0(MMA)}$$

$$n(MMA) = 0.672\cdot n_0(MMA) = 20.8 \text{ mmol}$$

Quantity of monomer consumed during polymerization is 31-20.8=10.2 mmol

Mass of the obtained polymer is

$$m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03\,\text{g}$$

m = 1.03 g

8.2.2

Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73/100.1).

The total quantity of monomers at the beginning of the 2nd stage is 23.7 + 23.7 = 47.4 mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$\Delta n = n_0(1-\exp(-k_P[R\cdot]t)) = 47.4(1-\exp(-1616\cdot 1.76\cdot 10^{-7}\cdot 1295)) = 14.6$ mmol.

Totally 7.3+14.6 = 21.9 mmol of monomers was polymerized during two stages.

DP = 21.9/0.12 = 182.5

DP = 182-183

8.2.3

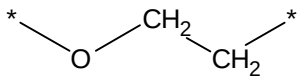
The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is 7.3/0.12 = 60.8 ≈ 61 monomer units.

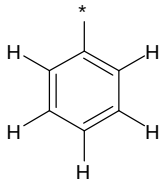
The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning of the 2nd stage were equal. The DP of the 2nd block is 183-61 = 122 monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A_{61}-block-(A-stat-B)$_{61}$-Cl or Ts-A_{61}-block-(A_{61}-stat-B_{61})-Cl

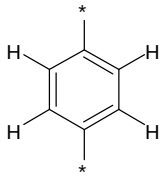
8.3.1.



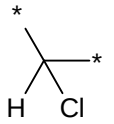
a, b, g



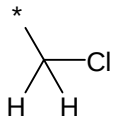
c



d



e



f

8.3.2

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is 40.2/4/58=0.173 for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to 13.0/0.173=75 protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is 75/5=**15.**

2 marks

Molar fraction of styrene units in P1 is 15/(15+58) = **20.5%**

Intensity of multiplet d is 10.4, which is equivalent to 10.4/0.173=60 protons. Since each monomer unit of *p*-chloromethylstyrene has 4 protons, DP of PCS is 60/4=15.

Molar fraction of D is 15/(15+58) = **20.5%**

M(P1) = 15.03+58x44.05+72.06+15x104.15+35.45 = **4240**

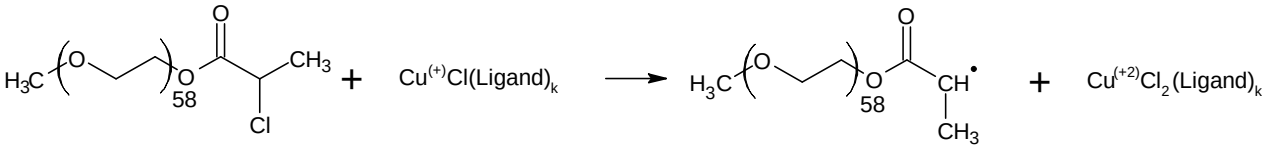
M(P2) = 15.03+58 x44.05+72.06+15x152.62+35.45 = **4967**

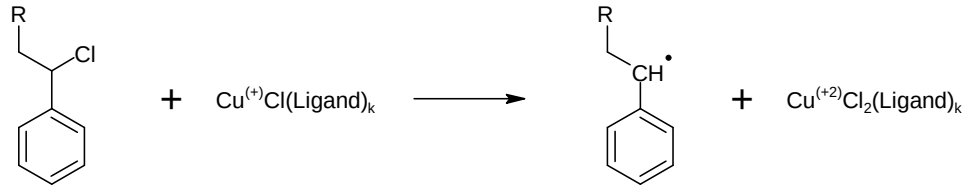
M(P1) = 4240 M(P2) = 4967

n(C) = 20.5% n(D) = 20.5%

8.3.3

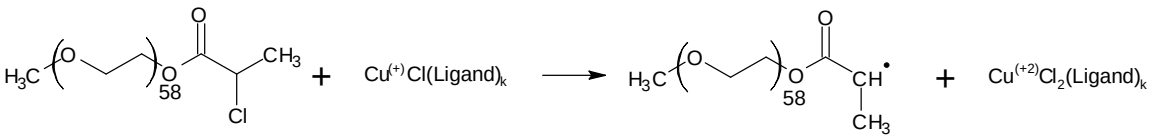
P1:

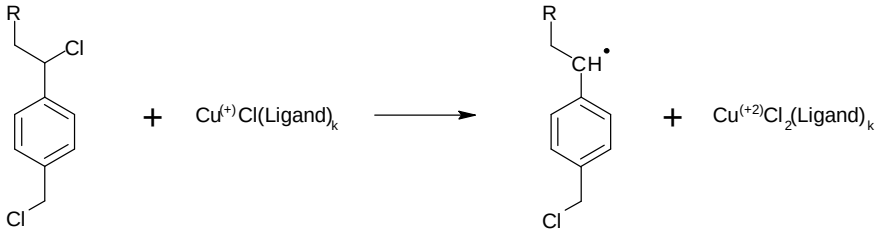


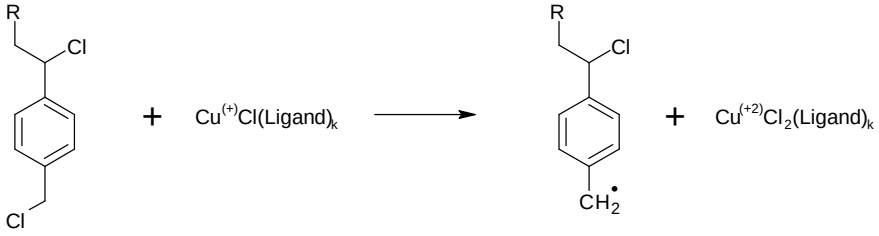


Here R is used for the macroinitiator fragment with one or several styrene units attached.

P2:







Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

8.3.4 *The structure of P1 and one of possible structures of P2*

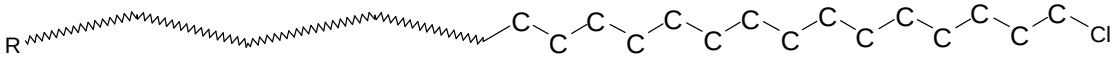
P1 is a block copolymer of PEO and PS. The PS block contains 15 units.

P2 is a block copolymer composed of PEO block and branched styrene block.

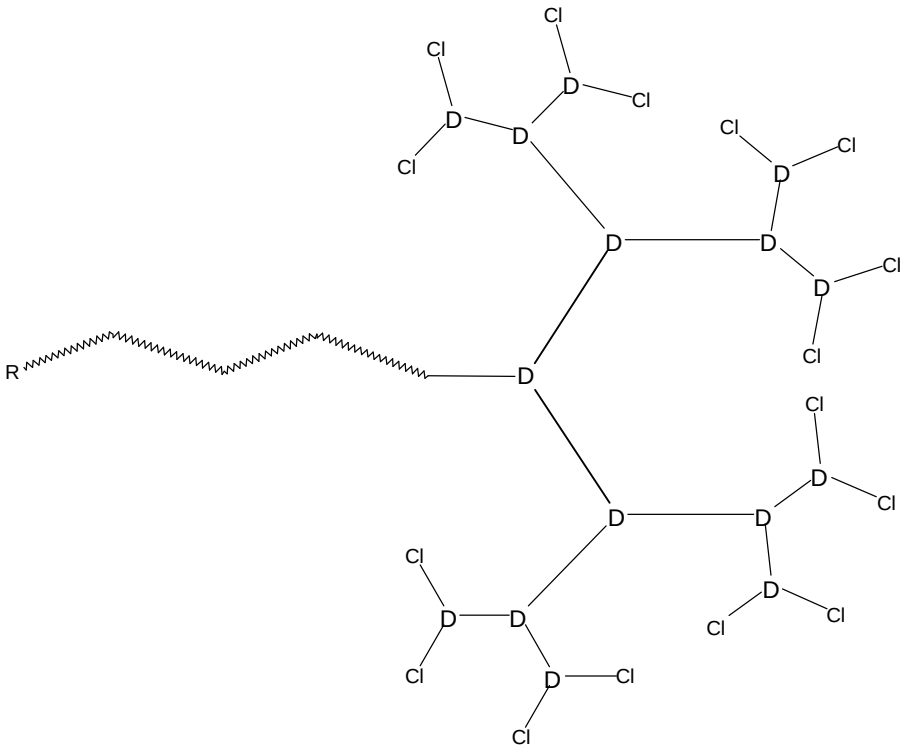
The integral intensity of multiplet f is 2.75, so 2.75/0.173=15.9, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P2, it would contain 15 choromethyl groups. Each branching reduces the number of such groups by 1. Thus P2 has 15-8 = 7 branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units

P1



P2

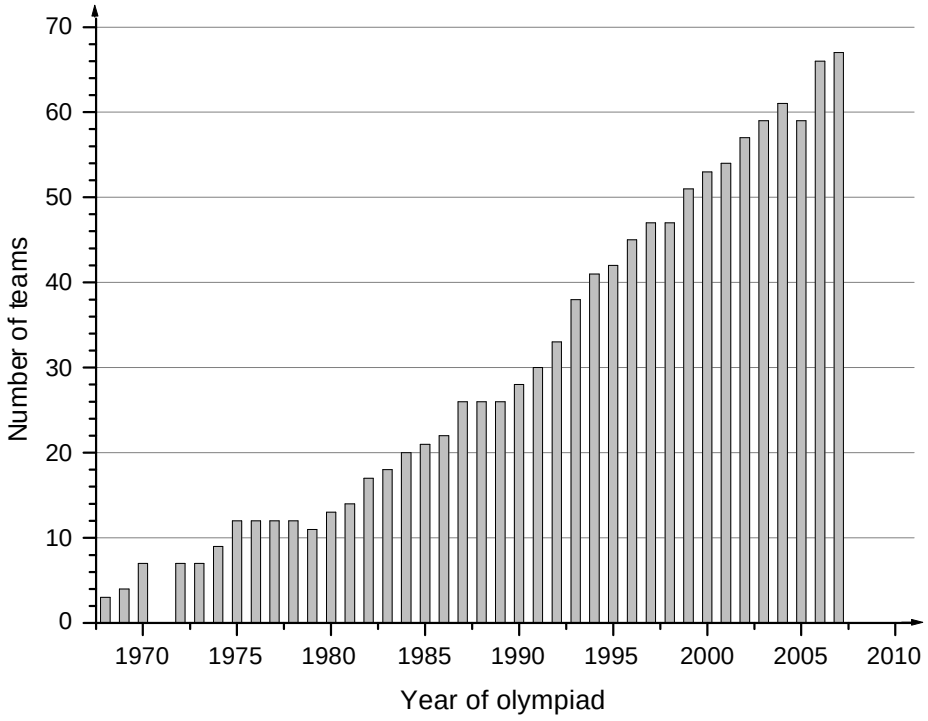


Part 4

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 attentding 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

in alphabetical order

+ = 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	00	01	02	03	04	05	06	07	08	09	10
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Armenia																																				o	o	+	+			
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Azerbaijan																												o	o		+	+	+	+	+	+	+	+			
Belarus																											+	+	+	+	+	+	+	+	+	+	+	+			
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Brasil																												o	o	+	+	+	+	+	+	+	+			
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Canada																	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+				
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Croatia																													o	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	00	01	02	03	04	05	06	07	08	09	10

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	00	01	02	03	04	05	06	07	08	09	10
Cuba																	+	o	+	+	+	+	+		+	+	+	+	+		+		+	+	+	+	+	+	+			
Cyprus																					o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Czech Rep.																									+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Czechoslovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+																		
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
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Iceland																																o	o	+	+	+	+	+				
India																													o	o	+	+	+	+	+	+	+	+			
Indonesia																												o	+	+	+	+	+	+	+	+	+	+			
Iran																									+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Ireland																												o	o	+	+	+	+	+	+	+	+	+			
Israel																																			o	o	+	+			
Italy												+	+	+	+	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Japan																																o	+	+	+	+	+	+			
Jugoslavia						+	+	+	+					+	+	+	+	+	+													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	00	01	02	03	04	05	06	07	08	09	10

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Kazakhstan																											o	o	+	+	+	+	+	+	+	+	+	+	+			
Kenia																												o				o										
Korea																							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Kuwait															o	o		+	+	+	+	+		+	+	+	+	+		+	+	+	+	+	+	+	+	+	+			
Kyrgyzstan																											o	o	+		+	+	+	+	+	+	+	+	+			
Latvia																							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
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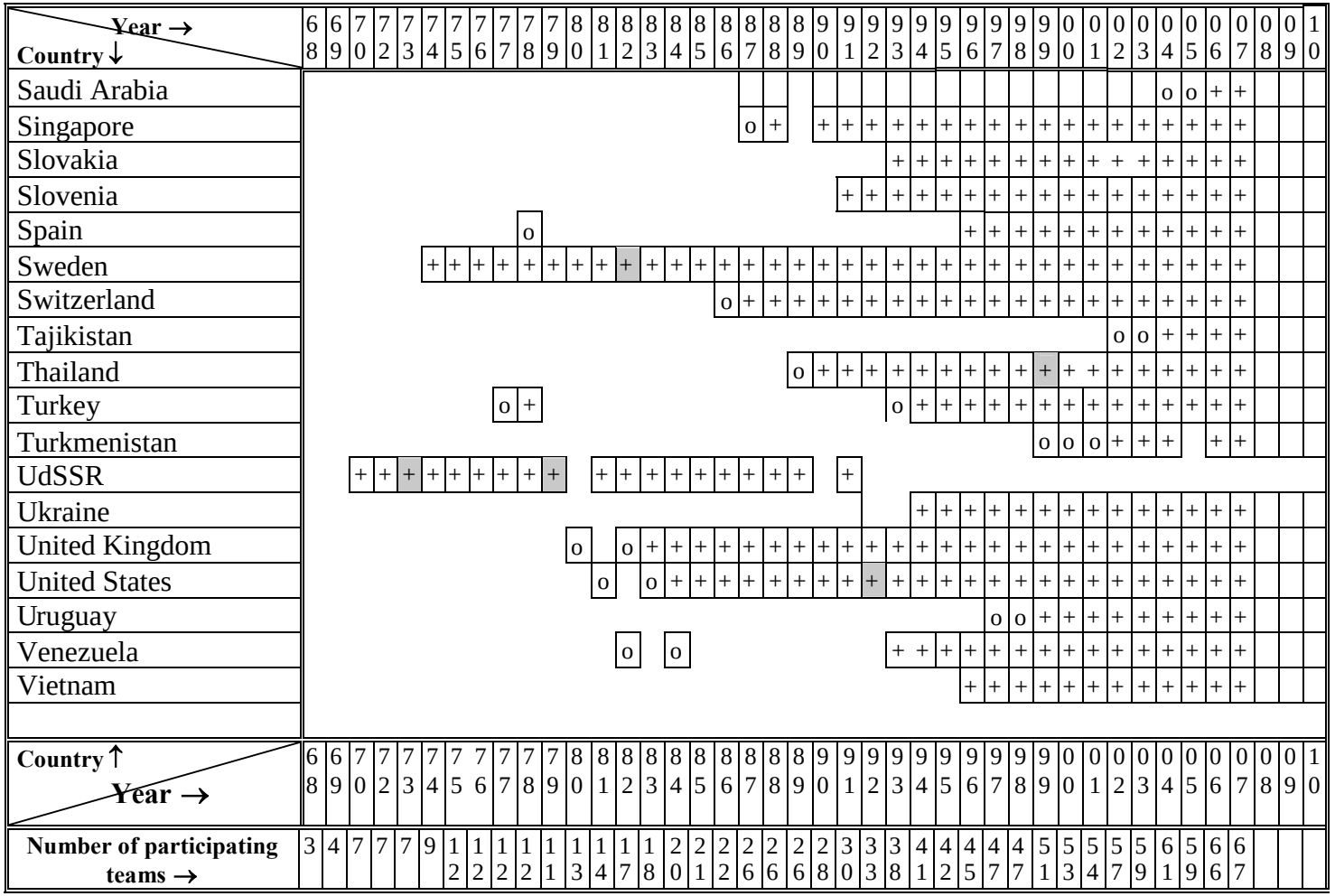
Moldova																																			o		o	+			
Mongolia																																o		o	o	+	+			
Netherlands													+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
New Zealand																							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Nigeria																																						+			
Norway													o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Pakistan																																			o	o	+	+			
Peru																																	o	o	+	+		+			
Philippines																														o											
Poland	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
Portugal																																	o	o	+	+	+	+			
Romania			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
GUS/Russ.Fed.																							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+			
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	00	01	02	03	04	05	06	07	08	09	10


Year →
Country ↓
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Saudi Arabia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Tajikistan
Thailand
Turkey
Turkmenistan
UdSSR
Ukraine
United Kingdom
United States
Uruguay
Venezuela
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 00 01 02 03 04 05 06 07 08 09 10
Number of participating teams →
3 4 7 7 7 9 12 12 12 12 11 13 14 17 18 20 21 22 26 26 26 28 30 33 38 41 42 45 47 47 51 53 54 57 59 61 59 66 67

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 concours						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

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	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

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	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**		
1	RC	RC	RC	RC	ROK	RC	RC					
.	ROK	T	IR	ROK	VN	TPE	RUS					
.	USA	TPE	ROK	RUS	IR	ROK	TPE					
.	RUS	ROK	T	UA	RUS	RUS	PL					
5	IR	A	BY	D	AZ	VN	ROK					
.	TR	UA	RUS	PL	TPE	T	**D**					
.	IND	USA	IND	TPE	T	J	T					
.	AUS	PL	SGP	H	RA	Pl	IND					
.	TPE	IND	D	TR	D	IND	H					
10	T	D	TPE	VN	IND	D	SK					
.	SGP	IR	UA	IND	A	SK	LT					
.	PL	H	PL	IR	CZ	DK	USA					
.	RO	RUS	CDN	RO	UA	SGP	VN					
.	F	CDN	CZ	LT	PL	BR	GB					
15	SK	TR	RO	CZ	AUS	CDN	BY					
.	H	AUS	KZ	USA	TR	AZ	EST					
.	VN	GB	VN	SGP	H	UA	UA					
.	CZ	SGP	EST	CDN	SK	USA	RI					
.	RA	E	GB	AZ	USA	H	IR					
20	BY	SK	AUS	AUS	GB	CZ	RO					
.	C	BY	H	KZ	RO	AUS	AUS					
.	D	VN	SK	GB	BY	IRL	A					
.	GB	FIN	USA	J	SGP	F	KZ					
.	UA	F	YV	A	J	IR	SGP					
25	A	LT	IND	BY	RI	A	NZ					
.	MEX	CZ	F	SK	LV	TR	CZ					
.	DK	KZ	A	T	BG	RI	F					
.	CDN	LV	I	RA	HR	GB	TR					
.	EST	NL	TR	EST	MEX	RO	J					
30	RI	RO	AZ	F	KZ	NL	ARM					
.	HR	RA	MEX	NZ	LT	HR	SLO					
.	I	EST	LT	SLO	F	LT	RA					
.	N	HR	NL	HR	EST	KZ	BR					
.	BG	BG	FIN	LV	CDN	SLO	CDN					
35	CY	NZ	HR	NL	I	EST	I					
.	KZ	I	J	I	DK	RA	MAL					
.	B	DK	DK	CH	SLO	BR	IL					
.	LT	SLO	RA	FIN	FIN	TJ	IRL					
.	NZ	N	GR	RI	NL	LV	NL					
40	CH	YV	LT	S	IRL	MAL	CH					
.	E	MEX	E	BG	GR	S	S					
.	FIN	BR	TM	KS	NZ	IRL	LV					
.	SLO	S	BR	E	KS	IL	DK					
.	NL	RI	BG	GR	S	FIN	MD					
45	LV	TM	CH	BR	B	IS	E					
.	BR	B	NZ	TM	BR	I	BG					
.	S	IRL	IS	CY	CH	CY	TM					
.	YV	CH	IRL	YVA	P	N	HR					
.	IRL	C	CY	IRL	IS	TM	PK					
50	GR	CY	KS	IS	N	CH	N					

(List of abbreviations see page 154)

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	Czechoslovacia
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 Indep. States
H	Hungary
HR	Croatia
I	Italy
IL	Israel
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgistan
KWT	Kuwait
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
MD	Moldova
MAL	Malaysia
MEX	Mexico
MGL	Mongolei
N	Norway
NL	Netherlands
NZ	New Zealand
P	Portugal
PE	Peru
PK	Pakistan
PL	Polen
RA	Argentina
RI	Indonesia
RC	China
RO	Romania
ROK	South Korea
ROU	Uruguay
RUS	Russian Federation
S	Sweden
SGP	Singapore
SK	Slovakia
SLO	Slowenia
SU	Sowjet Union
T	Thailand
TJ	Tadschikistan
TM	Turkmenistan
TPE	Chinese Taipei
TR	Turkey
UA	Ukraine
USA	United States of America
VN	Vietnam
WAN	Nigeria
YU	Yugoslavia
YV	Venezuela